THE THERMOMECHANICS OF NONLINEAR IRREVERSIBLE BEHAVIORS

An Introduction

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FOREWORD

During a meeting in Haïfa in 1992 Joseph Kestin from Brown approached me for a common project concerning a book on thermodynamics. Both Prof. Kestin's untimely death in the Spring 1993 and another reason made, or would have made, such an enterprise impossible. The second reason is that I wanted to remain in friendly terms with Joseph Kestin. Once Louis de Broglie, creator of *Wave Mechanics*, was asked why he had co-authored so few papers in his very long career (he died having reached the age of 96). His answer was that he did it once with Maurice de Broglie, his own elder brother, while he was in his twenties, and they almost went to the point of rupture in their brotherhood, so that, being a gentleman, he never tried such an experience again. If this adventure reflects well the situation with spectral analysis and atomic theory in the early 1920s, the situation would even be more touchy with *thermodynamics*, a field for which it is, as we all know, an extremely difficult, perhaps even insuperable task, to find two individuals who fully agree on all its basic aspects and the way it should be taught to students and researchers alike. In other words, therefore, this book had to be written by one author only, even though we cannot forget the immense debt that we owe to Joseph Kestin, Paul Germain and others, especially in France. My own pragmatic standpoint concerning thermodynamics, or as we prefer to say, *thermomechanics*, is expressed at length in Chapter 1 which has some historical and controversial flavor. Here, however, we simply want to point out a drastic change in the physical view of the World that took place during the last two or three decades, and which somewhat justifies, if there is any need for that, the existence of this book. We are all aware of the arrogant reductionism brought by elementary particle physics in the physical landscape after World

War II. But it is our view, shared by some prominent physicists (e.g. P. W. Anderson) that *condensed-matter physics*, through both its object and methods, have had a radical influence that, to some extent, has helped to counteract this type of intellectual imperialism. In particular, if many good fundamental equations are definitely known, it is the *solutions* to the equations, and not the equations themselves, that provide a mathematical description of the physical phenomena. Furthermore, although no one would be so ridiculous as to reject any attempt at looking for some ultimate building block of matter — a search which closely parallels the childish ambition to reach the *horizon line* — and we certainly gain a better understanding of our World, if not a higher spiritual status, through this quest, we must also recognize that the behavior of a *large* and *complex* aggregate of "elementary" entities is not to be understood "in terms of simple extrapolation of the properties of few particles" (P. W. Anderson). Parodying the French epistemologist Gaston Bachelard, physics at our scale seems to have become more a science of *effects* than of *facts.*[1] This was particularly well captured by L. D. Landau, John Bardeen, and P. G. de Gennes. Our conception of the *thermomechanics of complex irreversible behaviors* goes along this direction, being conceived from the start as a field of cross fertilization of many subdisciplines, accompanied by a deep experimental foundation and precise time and space scales of observations. This combines in a blend of P. Duhem (for his rigor), P. G. Bridgman (for his operationalism), and J. Kestin (for his inquisitiveness), and others. This may seem unbearable to either elementary-particle physicists who reject such developments in the darkness of macroscopic science, or to applied mathematicians who cannot stand the view of a thermometer and who presently have the tendency to mistake the proof of existence for a solution. We hope that this book (perhaps nothing more than a pamphlet), with all its defects and shortcomings, can bridge the gap between these two communities. But our natural naïveté is also bounded by our own pragmatism.

A paradox exists in the thermodynamic literature. Practically all the books and treatises dealing with irreversible thermodynamics simultaneously claim an unbounded generality and present a very restricted range of applications only. These are essentially linear irreversible thermodynamic processes limited to the phenomena of viscosity in Newtonian fluids, diffusion-like processes

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[1] But the joke works only in French (*"d'effets"* and *"de faits"*, practically with the same pronounciation). We could say that physics has become a science of *artifacts* more than of *facts.* This is what happened to chemistry in the recent past.

such as in mixture theory, and the traditional linear coupling between heat and electricity conductions. Sometimes an application to plasmas (another example of mixture) and a remark on electric relaxation are presented as ultimate examples. From this it would seem that only physico-chemists and chemical engineers may get some benefit from a thermodynamical framework. Our attitude is completely different as this book testifies and the title implies. Rich in our experience in several fields of physics and engineering science, we *do* present *irreversible thermodynamics* in its *realm* and *splendor.* The reader will find here the application of this inclusive science to both fluids and solids, to viscous as well as viscoelastic, viscoplastic or purely plastic continua, to solutions of polymers and polyelectrolytes, to liquid crystals, to the phenomena of damage and creep in solids, to the fracture of solids, to phase transitions, to complex phenomena in electromagnetic bodies (dielectric relaxation in ceramics, application to shock wave propagation, electric and magnetic hysteresis, dissipation in deformable superconductors, the fracture of electromagnetic solids) and, finally, reaction-diffusion systems such as those exhibited in models of nerve-pulse dynamics or the propagation of phase-transition fronts. This richness and wide vision are, we believe, unmatched by other books. Most of the time we have tried to give general theorems which find applications in several fields and we have not hesitated to have recourse to modern mathematical techniques such as *convex analysis* or the theory of *generalized functions.* This is the price we had to pay to reach a sufficient degree of generality. Vector and tensor analysis on flat manifolds, are used systematically.

The origins of this book are to be found in the lectures which I delivered at the *Institut Français du Pétrole* in Paris in 1987 in a seminar devoted to *irreversible thermodynamics.* I have had several opportunities to improve, polish, and elaborate upon those notes, especially through my yearly lectures on plasticity and fracture at the University of Paris (*Pierre et Marie Curie*), during the writing of a long review paper on *internal variables* together with Prof. Wolfgang Muschik of T. U. Berlin during my stay at the *Wissenschaftskolleg zu Berlin* in 1991–1992, during our research on *complex fluids* together with Prof. Raymonde Drouot in the years 1980–1988, during our research in the field of *material forces* with Prof. Marcelo Epstein (Calgary, Canada) and Prof. Carmine Trimarco (Pisa, Italy) in the years 1989–1994, during our research on the thermodynamics of nerve-pulse dynamics together with Prof. Jüri Engelbrecht (Tallinn, Estonia), while writing my lecture notes for a course in Udine (C.I.S.M., Italy, 1992) on the applications of thermodynamics to electromagnetic solids, during the preparation of my previous two books, respectively on the *Thermomechanics of Plasticity and Fracture* (C.U.P., 1992) and the *Theory of Material Inhomogeneities in Elasticity* (Chapman, 1993), and obviously in fruitful discussions with colleagues (in particular, D. Lhuillier) and students and co-workers (especially, M. Motogi, M. Sabir, E. Bassiouny and C. Dascalu, respectively from Japan, Morocco, Egypt, and Romania) at the *Laboratoire de Modélisation en Mécanique*, Université Pierre et Marie Curie, Paris, over the last two decades. My early experience with continuum thermodynamics was deeply influenced by Prof. A. C. Eringen at Princeton University. Private discussions with Joseph Kestin, wherever we could meet in the World, have enriched this view to an extent that the reader can hardly conceive. My heart felt thanks go to all the individuals mentioned and many whom I have unjustly forgotten. We wish an enjoyable time to our readers as pleasure should always accompany study . This is what I felt during the writing of this book.

Paris, January 1997. G.A.M.

CONTENTS

Laws of Thermodynamics:
1. You cannot win
2. You cannot break even
3. You cannot get out of the game

Anonymous.

A man viewed as a behaving system, is quite simple. The apparent complexity of his behaviour over time is largely a reflection of the complexity of the environment in which he finds himself.

H. A. Simon (*The Sciences of the Artificial*, MIT Press, Cambridge, Mass., 1969).

To the devil with those who published before us
(Pereant qui ante nos nostra dixerunt)

Attributed to Aelius Donatus (4th Century) by his pupil St. Jerome.

Chapter 1

INTRODUCTION: A POST-DUHEMIAN THERMODYNAMICS

> *The "irreversibility" of many processes arises because they are so complex that adequate description is impossible, for the practical attitude of thermodynamics toward such complicated processes will be merely to have anything to do with them, which is also its attitude towards irreversible processes.*
>
> **P. W. Bridgman**, *The Nature of Thermodynamics, 1943, p. 134.*

Perhaps, after all, the wise man's attitude towards thermodynamics should be to have *nothing to do with it.* To deal with thermodynamics is to look for trouble. This is not the citation of a famous scientist, but the result of a deep cogitation following mere observations. Why do we need to get involved in a field of knowledge which, within the last hundred years, has exhibited the largest number of schizophrenics and megalomaniacs, imbalanced scientists, paranoiacs, egocentrists, and probably insomniacs and sleepwalkers? Is there any other field of scientific activity such as this one where, apparently, each of the bricklayers has unhesitatingly revindicated an originality that, to our eyes, and looking through the mirror dear to St. Paul (but also to *Alice*), we may see but with confusion. The intimate relationship between psychoanalysis and the behavior of more than one thermodynamicist may be due to the fact that Ludwig Boltzman (1844–1906) — may his soul rest in peace — both studied and dramatically ended his life in a city that saw the birth and burgeoning of Freud's theory.

In introducing our subject we shall have to deal with hard-headed scientists and uncompromising characters, among them Pierre Duhem (1861–1916), Percy W. Bridgman (1882–1965), Joseph Kestin (1913–1993), and Clifford

A. Truesdell (born 1919), all kind and affable personalities but sharp, witty, and somewhat aggressive and vivacious critics of the scientific scene who, willingly or not, belong to the above-sketched out "medical" landscape and who, like the author, are not exempt from apriorisms and idiosyncrasies.

For some thermodynamicists and for their enemies as well, *thermodynamics* is the science of everything, so that for the second category of individuals, it is, by mere logic, the science of *nothing*, and thus not a science at all; and the *everything* is naturally seen as a sign of megalomania from which some have not escaped. Let us admit that *megalomonia* in a moderate dose is an admissible behavior (after all, sometimes it *does* help in science). What is then the purpose of such a "science"? Is it to *explain* or to *classify* phenomena? Here we touch on the whole problem of the significance of *physical theory.* Should we try to explain essentially through *models* or are we to be satisfied with a mere *natural* classification of phenomena, i.e. *saving the phenomena.* It is not by chance that one of those epistemologists who most impressively pondered this question in a remarkable book full of hindsight was indeed Pierre Duhem (*The Aim and Structure of Physical Theory*, 1906a) who was so active in defending the cause of *thermodynamics* and who produced the longest treatise so far published in *energetics* or, as he says, *general thermodynamics* (Duhem, 1911).[1]

Nobody can deny the urge to explain things, whether physical or belonging to other categories. That is, if it is true that a good classification, such as Carl Linnaeus' in natural history, helps one to describe the variety of life, it does not explain it, so that we easily imagine the relief first brought by the Holy scriptures, and then by a solidly documented theory of evolution. The same applies in physics to which *thermodynamics* belongs. A natural classification dear to P. Duhem[2] helps us in organizing our knowledge and presenting to our students a neat logico-deductive framework. But this does not disqualify

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[1] To the few who have read it in the original French, this imposing treatise sounds like an unfinished program of "rational thermomechanics", simultaneously a declaration of faith in a type of approach to field theory that was later to blossom, and a course on the pedagogy of logico-deductive science where "no hypotheses are framed". Some of it sounds prematurely Truesdellian in tune, and parts have obviously inspired B. D. Coleman and J. L. Ericksen in some of their approaches to the *stability of continua.*

[2] In a *secrete*, (at the time) document (report in my French Doctoral Thesis in Mathematics), a well-known French mathematician classified my approach to thermomechanics as *neo-Duhemian* (I had *not* yet read Duhem in those times). When I could read that document after a law was passed giving access to all such personal papers, I felt that this was intended to be derogatory by its author, who could not figure out how much I later became pleased with such a classification.

before hand the use of *ingenious models*[3] and, obviously, the call to microscopic descriptions. This is to specify our credo without ambiguity from the outset: we shall be *pragmatic*, and like Henri Poincaré and Percy Bridgman, somewhat *conventionalist* and *operationalist*. That is, like the Romans regarding religion, we would like to take the best out of each contribution while keeping a down-to-earth attitude. We shall accept objects and definitions which can be observed or realized through well-defined *operations*, but we shall not hesitate to have recourse to *pencil and paper* operations (versus *instrumental* operations), and to *gedanckenexperiment(s)*, often the deepest and certainly the least costly ones. This "mixed salad" is welcomed as it should avoid fanatism, dogmatism and sectarism, as a matter of fact, any spirit of chapel (so much religious wording which tells a lot!) and it should bring some tranquility of mind, some *felicità*.[4]

At this point it is customary to make a historical digression which should span some hundred and fifty years.[5] But we shall do this in gigantic (in Greek *megalo* — again!) steps, following in the footsteps of C. A. Truesdell (1984, "Historical Introit") but not advocating the entirety of his standpoint.[6] Apart from an *axiomatic foundation line* and kinetic-theoretical arguments and the recent "*extended*" thermodynamics to be discussed later on in this book, one easily recognizes two main lines, which concurred at some time and then coalesced to our modern view (see Fig. 1.1). On the one hand, we obviously have the line inaugurated by Sadi Carnot (1796–1832) and B. Clapeyron (1799–1864) which built on notions of *thermometry* and *calorimetry* and emphasized to start with the notion of *work*, and then took its most fruitful form with R. Clausius (1822–1888) and the statements of the *first law* (energy conservation) and the *second law* (*nondecrease* of entropy). Regarding the *second law*, one must recall that if energy is to be conserved at all [this is the *first law* whose

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[3] To Duhem, W. Thomson (Lord Kelvin) in England and J. Boussinesq (1842 1929) in France epitomize the class of those who cannot do without (mechanical) models. As to J. C. Maxwell, Duhem criticizes him not for his achievements, which nobody can deny, but for his *inconsistencies* and, finally, for his enlightened amateurism.

[4] We are indebted to Paul Germain for this wise and serene approach to the thermomechanics of continua.

[5] This attitude is exemplified by J. L. Lagrange who, in his classical "*Méchanique Analytique*" of 1788, indeed introduces each part with a long historical quest which, in his opinion, gives the essentials of a somewhat linear development. This is *not* "history of science" in this more mythological, fairy-tale-like *success story* — and not history — which has been fruitful and bears pedagogical value.

[6] "*Tradutore, traditore*".

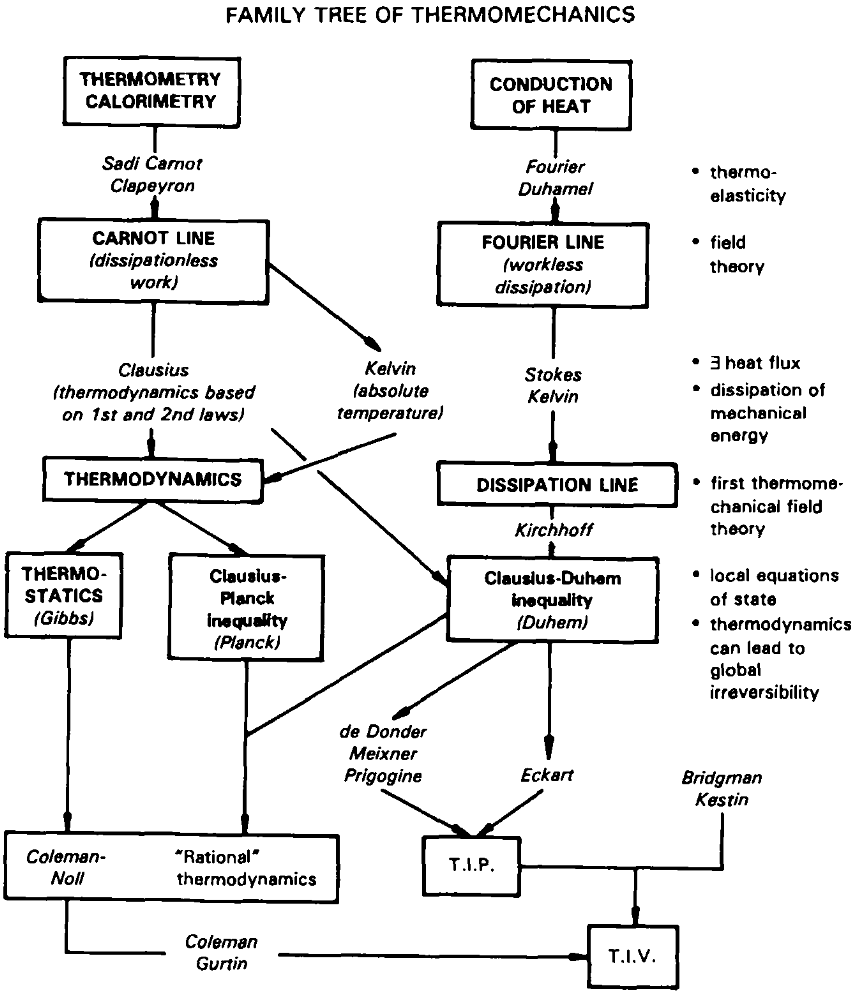

Fig. 1.1. Family tree of thermomechanics.

statement is due in essence to J. R. Mayer (1814–1878) and Kelvin (1824–1907)], energy in most physical situations *changes its nature*. This change of quality, according to Clausius, goes only in one way, either there is *no change* or energy is *degraded*. But this last word had no meaning in Clausius' time, the 1840s–1850s. By analogy with the word *en-ergy*, Clausius then invented a neologism, *en-tropy*, a word specially designed to qualify what changes when energy is conserved, a word which has a meaning only to physicists or this was what expected.[7] Thus a quantity other than energy evolves only in *one direction*, later called the *Arrow of time* — and is witness to the irresistible *degradation* of energy (see the book by Brunhes, 1909). In practice, heat is the ultimate form of energy, in some sense the *worst* one, the one that we feel when an intense electric current passes through a resistive wire or when friction occurs between two parts of materials in contact in relative motion. Two general *laws of Nature*, i.e. *principles*, have thus emerged, the *conservation of energy* and the *necessary non-decrease of entropy*, of which the first developed at length in the works in *thermostatics* of W. Gibbs (1839–1905) (book, 1928), while the second gave rise to the *Clausius-Planck inequality* in the expert hands of Max Planck (1858–1947).

On the other hand, J.-B. Fourier (1768–1830) and later J.-M.-C. Duhamel (1797–1872) are the founding fathers of the *Fourier line*, a true *mathematical physics*, which gave rise to a paragon of *field theory* (first, *thermal conduction* and then *thermoelasticity* in isotropic bodies and anisotropic crystals — see Bachelard, 1927) with its paraphernalia of partial differential equations and "mathematical methods for physics and engineering", among them the celebrated Fourier series and integrals. This line would emphasize the role of *dissipation* with the recognition of the existence of the *heat flux vector* by G. G. Stokes (1819-1903) and of the *dissipation of mechanical energy* by Kelvin. This line, via G. Kirchhoff (1824–1887) who completed the first *thermomechanical field theory*, would lead to the essential formulation of the *Clausius-Duhem inequality* by P. Duhem who also clearly introduced *local equations of state* while recognizing that thermo-*dynamics* can lead to *global irreversibility*. With Gibbs, Planck and Duhem we enter the twentieth century. The Belgian school of thermodynamics, under the leadership of Th. de Donder (1872–1957) was then to create the *standard* theory of thermodynamics, the *theory of irreversible processes*, referred to as *T.I.P.* for short. At this point we need to pause as some of the ingredients introduced become our daily bread and the main actors our contemporaries.

What is the situation with thermodynamics on the eve of World War I? Along the kinetic-theoretical line which was also inaugurated by Clausius and

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[7] "*τροπη*" (*tropé*) means change, transformation; "*tropism*" in fact relates to changes in orientation. But in modern Greek "entropy" means something like "pudeur" or "sense of decency", a virtue seldom exhibited by thermodynamicists!

much improved by J. C. Maxwell (1831–1879) with the introduction of his equilibrium distribution function, Ludwig Boltzmann (1844–1906), in breakthrough studies, has definitely shown that the notion of *entropy*, whether of Clausius' or Gibbs' origin,[8] coincides with his definition (essentially a number) that is attributed, via a statistical theory of time-asymmetric irreversible non-equilibrium behavior, to each *microscopic* state of a *macroscopic* system be it solid, liquid, gas or otherwise. But contrary to Gibbs' entropy which does not change in time even for ensembles describing isolated systems not in equilibrium, Boltzmann's entropy *increases* in a way that explains the evolution toward equilibrium of such systems. Unlike Gibbs' entropy, Boltzmann's one captures the separation between *microscopic* and *mesoscopic* scales (see Lebowitz, 1993). More practically, Lord Rayleigh (J. W. Strutt, 1842–1919) has already introduced his *dissipation function* to deal with some macroscopic systems — essentially Newtonian–Stockesian viscosity — (Rayleigh, 1945; originally 1877, 1894), and this has already been used by Maxwell in some problems of electrodynamics (electric conduction currents, Maxwell, 1873). But apart from this, researchers are stocked as far as phenomenology is concerned. This is illustrated by P. Duhem who, in a rather famous literary review of the state of the Art, entitled "*The Evolution of Mechanics*" (Duhem, 1903), identifies several branches of applied physics that seem to resist a thermodynamical unification and are therefore called *nonsensical.* These branches are *friction, hysteresis* (such as in the plasticity of metals, or magnetic hysteresis), and *electromagnetic fields.* This was very well explored by Manville (1927) who wrote a masterly review of Duhem's scientific achievements. Three essential ingredients which are still lacking at that moment (1910s) are: (i) the expression of a *balance law for entropy,* (ii) the formal expression of the *production of entropy as a bilinear form,* and (iii) the *nonquadratic nature* of the assumed dissipation potential (truly *nonlinear* dissipative processes). The first of these is clarified in Bridgman (1943, pp. 142, 143) who speaks (at the time) of the "not very much used"[9] equation of balance that, parodying Bridgman, we can state as:

> *"(net entropy leaving a close region) = (entropy created within the region) – (increase of entropy localized in this region)",*

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[8] In Clausius' case entropy is that of a system at equilibrium. In Gibbs' case, it is defined for a *statistical ensemble* (a collection of independent systems, all with the same Hamiltonian, distributed in different microscopic states consistent with some specified macroscopic constraints). This quantity does *not* change in time even for systems not in equilibrium.

[9] An exception seems to be in discussions by Paul Ehrenfest (Bridgman, 1943, p. 146).

or in mathematical modern terms, where S is the entropy per unit volume, $\mathbf{S}$ is the entropy flux (also called entropy flow vector), and C is the body source of entropy:

$$\operatorname{div} \mathbf{S} = -\frac{\partial S}{\partial t} + C. \tag{1.0.1}$$

The last quantity C is at first a pure convention. The problem resides in its expression. Bridgman shows in the case of pure heat conduction that for heat passing through a bridge between two reservoirs, one has

$$C = -\theta^{-2}\mathbf{q} \cdot \nabla\theta, \tag{1.0.2}$$

if $\mathbf{S} = \mathbf{q}/\theta$, where $\mathbf{q}$ is the heat current and θ is the absolute temperature, the introduction of which is due to Lord Kelvin. He shows by the same token that the "final location of *entropy change* may be different from the location of the irreversible processes which generates it ... There need be *no* irreversible process occurring at the place where the flow of entropy occurs". For pure thermal processes, the second law of thermodynamics results then in the non-negativeness of the C term in the form of a *dissipation inequality*:

$$C = \theta^{-1}\Phi_{\text{th}} = \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0, \tag{1.0.3}$$

where Φ_{th} is the *thermal dissipation* that we shall meet later on on several occasions.

The second ingredient (ii) was reached by Carl Eckart (1902–1980) who, in a beautiful series of papers (Eckart, 1940, 1948), laid out part of the mathematical framework for describing the phenomenon of *diffusion*, a fully thermo-*mechanical* phenomenon as it is associated not only with mass transport but also with thermal influences and flow of heat. In the same papers Eckart introduces a consistent formulation of relativistic continuum thermodynamics and, last but not least, he remarks that the density of production of entropy (the C term above) is a *bilinear form in certain variables*, all of which vanish in equilibrium. This *bilinearity* property was also noticed by Josef Meixner (1908–1994) who, in addition, brought the support of the kinetic theory (of monatomic gases) and of Lars Onsager's 1931 statistical treatment of small fluctuations about equilibrium (the celebrated *Onsager symmetry relations* between coefficients of the bilinear form in the presence of coupled dissipative phenomena). With this *T.I.P.* was born and it would take a definite, almost dogmatic, form in the famous treatise of S. R. de Groot and P. Mazur (1962), still probably the most reliable and best available on the market. This, however, did not fully give satisfactory answers to the questions raised by the third point (iii). One had to await for the 1970s–1980s for its fulfillment.

It is probably at this point that Bridgman's thorough analysis of the bases of thermodynamics — *its nature* — plays a most important role, the main question being: *What are the independent variables of thermo-mechanics?* (this is Truesdell's language, 1960, p. 100). In other words, what are the most relevant *variables of state* in a true thermo-*dynamical* description of irreversible phenomena, i.e. those that may make the entropy grow? The answer to this question is clearly related to matters of time and space *scales*, perhaps *frequencies* (for periodic processes), and a *threshold value* of some characteristic fields, a matter that shall be recurrent in the remainder of this book.

Bridgman first admits that thermodynamics (1943, p. 6) is "a subject not yet complete or at least,..., one whose ultimate possibilities have not yet been explored, so that perhaps there may still be further generalizations awaiting discovery..." (he writes in the early 1940s). Then he emphasizes the notion of thermodynamical *state* and that of parameters of state (p. 17). Classical thermodynamics — to fix ideas, at the human scale of experience, and *not* the *quantum* scale — presupposes *large-scale* instrumental operations (p. 135) and this, in turn, provides a framework for the relevant parameters of state (p. 152). These are the parameters which *completely* define a state, in the way we can present specific values to the properties of a body (if God knows what is meant by that).[10] In any case, this demonstrates the "macroscopic attack" of thermodynamics whose main function is *not* to explain (p. 222) in agreement with P. Duhem's vision of the physical theory. "Thermodynamics smells more of its human origin than other branches of physics" (p. 214).[11] Relating to characteristic scales Bridgman rightfully mentions that in some "situations the irreversible aspects could be made to vanish in comparison with the reversible aspects by a suitable choice of the *dimension* of the apparatus and the *time*[12] of the experiments, or of some other parameters" (p. 138). Along the same line he points out to the possibility of "measurements on systems which are not *too* inhomogeneous" (p. 75).

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[10] Bridgman will be very instrumental in the clear-cut selection of state variables in elastoplasticity (cf. Kestin, 1966, p. 369; Bridgman, 1950).

[11] This may explain the practically neurotic behavior of more than one thermodynamicist; see first paragraph of this chapter.

[12] The Deborah number will be introduced for that purpose.

Although simple cases of irreversible processes exist which include "heat conduction, Joulean heat, diffusion, laminar flow of a viscous fluid" (p. 134), there are also obvious complex cases of which *hysteresis* (one of Duhem's nonsensical examples) is paradigmatic. His feeling towards such cases is reflected by the difficulty in writing the functional dependence of the energy function (pp. 65, 66) — this is essential to write down the expression of the first law of thermodynamics or Gibbs' equation — and he already alludes to "one or more new parameters that would effect the desired reduction to states of these complex cases" (p. 64). Perhaps in those complicated cases "the expression of the flow vector of entropy has to be modified" (p. 146)[13] — remember that $\mathbf{S} = \mathbf{q}/\theta$ in Eq. (1.0.1) — and, in any case, "a more detailed study and classification of irreversible processes than any yet attempted would doubtless be rewarding" (p. 135). The present monograph is just about that, relying heavily on the notion of *internal variables of state.* This notion, some sharp observers believe to have spotted it in Bridgman's writings,[14] at least this is what the above quotation about additional parameters allowing for the definition of a "state" hints at. Other writers see the germ of this notion in some of Duhem's works (Truesdell, 1984, p. 39, citing Duhem's 1911 treatise). As it happened, this notion and presently no other one, allows one to construct a true *post-Duhemian* thermomechanics which does bring the nonsensical branches of mechanics of P. Duhem under the unifying, but also constraining, umbrella of *irreversible thermodynamics.* This has materialized through the works of many contributors, not the least among them, Kluitenberg (1962a, b; 1963), Coleman and Gurtin (1967a), Rice (1971), Sidoroff (1976), Nguyen Quoc Son (1973) and several others whom we shall discover as we proceed from one chapter to the next. Other developments such as the so-called "*rational*" thermodynamics of Coleman, Noll and Truesdell which may be considered an offspring of Gibbs'

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[13] This remark is of far reaching insight when we consider what happens in *diffusive systems involving gradients* (see below).

[14] J. Kestin (1992, p. 1830; also in Muschik and Maugin, 1992, p. 44, the last publication of the late Prof. Kestin) cites Bridgman (1943):

> *"I believe that in general the analysis of such systems will be furthered by the recognition of a new type of large-scale thermodynamic parameter of state, namely the parameter of state which can be measured but not controlled... These parameters are measurable, but they are not controllable, which means that they are coupled to no external force variable which might provide the means of control. And not being coupled to a force variable, they cannot take part in mechanical work."*

thermodynamics and Duhem's grand program, and "*extended*" thermodynamics whose bases are rooted in the kinetic-theoretical program, are part of the present study, and we shall deal with them in due course, although briefly.

The above-developed ideas, brief as they are, are just to preach to the already convinced the usefulness of a general thermodynamical view. But 80 years after Duhem's writings there are still groups of scientists working at the *human* scale of experience, who do not recognize this evidence. For instance, some very active rheologists still completely ignore thermodynamical constraints (e.g. Larson, 1988, in an otherwise well-documented work). The same holds true in elastoplasticity and its generalizations with the Russian and English engineering schools. If it is true that thermodynamics amounted only to the consideration of Rayleigh's dissipation function for the Newtonian–Stockesian fluids, and could thus be dispensed with, this is no longer a tenable position with more involved behaviors that, according to others (e.g. Sidoroff, 1976; Luillier and Ouibrahim, 1980; Maugin and Drouot, 1983a; Jou *et al.*, 1993; Grmela, 1990, 1995), clearly necessitate, and practically fit, a thermodynamical background. The wealth of theoretically *dissipative* constitutive behaviors certainly needs to be restrained by the second law which then does provide some information. Likewise in elastoplasticity, fracture, and their generalizations where first the American and French, and now the German and North-European (Denmark, Holland) schools of theoretical mechanics have shown that the strict thermomechanical framework was the one which also corresponds to the best numerical one in so far as implementation is concerned (treatment of mathematical systems of evolution, use of convexity properties, exhibition of good stability properties, problems analogous to those handled in nonlinear programming techniques such as in econometry). Thus the "national style"[15] in science, often originally propounded by only a few creative individuals, has some importance here because, like Newton's and Leibniz's notations for calculus, it may either hinder or foster a fruitful and rapid development. Furthermore, while the Art of cooking gains through the continuous aggregation of new recipes, the main purpose of Science — an economical one — is to *reduce* the number of *recipes*.[16] General thermodynamics or *energetics à la Duhem*, or *thermomechanics* as we shall say, is just such a scientific framework

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[15] No "nationalistic" connotation, obviously; pre-World War I Duhem's times are gone.

[16] Think of the endless collection of rheological models which discard *invariance* rules and thermodynamical constraints!

that gathers under the same umbrella so many phenomena while singularizing an evolution in a definite sense, the *Arrow of time.*

Now in attacking such a program we face the problem of the degree of abstractness and mathematical formalism that we should work with. Again, we shall stick to our pragmatic attitude. Is it reasonable, following thinkers like Auguste Comte, Nicolas Bourbaki (a famous collective author in mathematics), and some disciples of C. A. Truesdell, to assume previous knowledge of all of mathematics, to start studying a specialized, although vast, domain of physics? The answer is definitely *no*, because one should not expect so much from both our readers and ourselves. This would be both cheating and supererogatory pedantry. We shall rather be satisfied with a basic knowledge of college mathematics for physics and engineering.[17] If the message does not go through, then we, alone, shall be considered responsible for this failure.

The contents of this book:

Following the general arguments expanded in following sections, we shall spend some time on introducing the basic elements of thermodynamics, that is, thermo-*statics* and the various approaches to thermo-*dynamics*, i.e. outside (even-though just slightly outside) equilibrium. In order to introduce thermodynamics in its thermo-*static* background (this is our approach which contrasts with "rational" thermodynamics), we must, it is clear, carefully define the notions of *system, state*, and *variable of state.* This is done in Chapter 2, where the Born-Caratheodory formulation of the *second law* has been followed. This is where the trouble starts. While we practically all agree on the statement of the *first law of thermodynamics*, the second law can be formulated in different more or less mathematical, formal, or physical ways. The *Born-Caratheodory* formulation of the second law was proposed by C. Caratheodory (1873-1950) on a suggestion by Max Born (1882-1970). Achieving elegance and generality in exposition, this is the mathematical formulation which is based on a common characteristic of all irreversible processes, the *inaccessibility of states.* The question boils down to whether some states can be reached from other neighboring ones in an *adiabatic* process (no exchange of heat in the bulk or

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[17] We are referring to a good college where analysis and algebra are cultivated in a modern fashion, but without unnecessary symbolism. This does not exclude elements of topology, matrix algebra, vector analysis, tensor analysis, convex analysis, and functional analysis, all things which have become a necessity for a competitive engineer of high standard.

per unit area) taking place in a *closed* system (all terms are precisely defined in Chapter 2). This is a convincing formulation which supersedes the more classical ones derived from the Clausius and Kelvin–Planck statements found in classical college books (e.g. Kestin, 1966); Truesdell (1986, p. 114 on), however, strongly criticized the Born–Caratheodory formulation, claiming, with some controversial exaggeration, that in Caratheodory one finds "both mathematical gaps and errors". It was supposedly shown by Cooper (1967) that Caratheodory failed to prove that his "absolute temperature" deserves the name of temperature. But this was proved false by Walter (1976). According to Bernstein (1960), the problem with Caratheodory's absolute temperature is that its existence is established only *locally*, while the scale of such a temperature should be *global*. But then J. Serrin has also claimed (cf. Truesdell, 1986, p. 117) "that all 'flaws' [quotation marks mine, G.A.M.], whether mathematical or physical, can be overcome by a thorough reformulation and recasting". Walter (1978) has indeed provided some reconciliation of the classical method (Carnot, Gibbs) with that of Caratheodory. Walter's development, it is true, like Caratheodory's, makes the second law contingent on the first. We shall be satisfied with the "modest" formulation of Caratheodory while referring the reader to Truesdell's writing for a flavor of scandal and a touch of excitement. Whether Caratheodory distracted us from Carnot and Gibbs (cf. Truesdell and Bharatha, 1977; Pitteri, 1982) is somewhat peripheral and a disputable subject.

Chapter 3 has for declared purpose to present in a nutshell the essential *theories* of irreversible thermodynamics. We have already mentioned *T.I.P.* as the "successful" one. It indeed provides the core for further developments as we shall exploit a direct extension of it, leaving aside the *linearity* of constitutive equations while enlarging the set of *state variables*. "Rational thermodynamics", of which the credo and dogma are cognizably expanded in Truesdell (1969, 1984), offers the elegance and temptations of all formal logico-deductive approaches: *it is very attractive*! P. Germain (1975) has thoroughly analyzed its biases, shortcomings and audacity. "Extended thermodynamics", of much more recent extraction [although early works by R. E. Nettleton (e.g. 1960) should not be discarded], and well expanded in two monographs by its most ardent proponents (Müller and Ruggieri, 1993; Jou *et al.*, 1993), lends itself to few manageable applications and suffers from its intrinsic limitations to the set of fluxes considered. Thus the essential of our efforts will naturally be placed on the *thermodynamics with internal variables*, for short, *T.I.V.*, i.e. the thermodynamics which introduces additional *variables of state*, say along the timid but farsighted proposal of P. W. Bridgman, that are *not controllable.*

Thermodynamics with internal variables is formally examined in Chapter 4. The main problems there are the proper selection of such internal variables, the relationship of the resulting theory with other thermodynamics, the way entropy can be defined in spite of the lack of equilibrium, and how does one generalize the notion of dissipation potential initiallly introduced by Rayleigh. Furthermore, there exist some relationships between the notions of *internal variables* and *internal degrees of freedom*, as also with the *order parameter* of phase-transition theory. What are we to do when the bodies subject of our thermodynamical analysis are highly heterogeneous, i.e. when length-scales enter the stage? This is complemented in Chapter 5 by the statement of the general rules of application of *T.I.V.*

Chapter 6 outlines the numerous applications which will allow the reader to grasp the flexibility of the method and the profusion of applications in all domains of physical science, especially in *materials science*, in the sense granted nowadays to this term. Many of these successful applications have been developed by the author and co-workers during the last two decades. These applications are presented in order, following a somewhat traditional classification of the behavior of materials (recall Duhem's vision of the *physical theory*). Thus Chapter 6 discusses the problem of the representation of *viscosity* in fluids of all kinds, with an emphasis on dilute solutions of polymers, liquid crystals, and turbulence. This representation varies within a large spectrum, depending markedly on the *internal variables* introduced as new "Bridgmanian" variables of state. This provides a true *thermodynamically admissible* approach to *rheology* (the science of what flows).

T.I.V. applied to solid-like materials is probably the most successful of its application as its acceptance in this domain has practically become universal. Our previous (specialized) textbook on the *Thermomechanics of Plasticity and Fracture* (Maugin, 1992a) is witness of this trend. This also holds true of the book on the *Mechanics of Materials* by J. Lemaitre and J.-L. Chaboche (1990) which, in a different style, has been instrumental in spreading the gospel of *Thermomechanics. Viscoelasticity*, *Viscoplasticity*, at both small and large strains, together with *damage* and *creep* are obviously covered, although rather briefly in order to avoid duplication, in Chapter 7. *Mechanical hysteresis* and *friction* (two of the Duhem's *nonsensical* branches of mechanics) are thus incorporated in the thermodynamical framework, at the price, however, of some mathematical complication (use of convex analysis, potential which are homogeneous functions of degree one, and thus somewhat singular). The debt to the original views of Ziegler in Switzerland, to J. R. Rice and J. Kestin (in the USA) and to the French school of analysis and theoretical mechanics, especially with J. Mandel, P. Germain, J.-J. Moreau, Nguyen Quoc Son, and P. Suquet, in these developments need to be emphasized.

With *fracture*, we enter a different domain of application in Chapter 8. That is, the global thermodynamical behavior of a specimen may be *dissipative*, while the local constitutive equations in the bulk do not manifest any dissipation. This is the case in *brittle fracture* where the irreversibility clearly stems from the fact that we cannot solder back the faces of the growing crack; the latter progresses irreversibly, if it progresses at all. Here the expression of the laws of thermodynamics in global form plays a fundamental role. But the originality is that the *domain of integration of these laws evolves with the progress of the crack*. It is possible to construct the corresponding *global irreversible thermodynamics* and to devise thermodynamically based criteria of progress. This in fact is an example of thermodynamics of *material forces* (see our book on "*Material Inhomogeneities in Elasticity*", Maugin, 1993a) of which other examples are exhibited in further chapters. The role of Griffith (energy concept of fracture, 1920), Eshelby (force on an elastic singularity, 1951), Cherepanov (Γ-integral in many phenomena, 1967), Rice (path-independent integral of fracture, 1968), Freund (dynamical fracture, 1972, 1990), Bui (fracture of different types, 1978) and Nguyen Quoc Son (1980) must be recognized as decisive. In our own works with co-workers to be cited in due course we have placed the fracture of solids under the umbrella of the general *theory of material forces* on a material manifold and *not* in physical space, as the nonlinear deformation theory of material demands. Brittle, dynamic, and ductile fractures can be treated thus, as well as the fracture of electromagnetic solids (see below).

Electromagnetic theory was conceived by Duhem as the most difficult branch of continuum physics to incorporate into the thermodynamical framework. This is certainly true if one considers the full electrodynamics of continua, i.e. the theory of moving media which are magnetized, electrically polarized, and possibly conductors of current. The problem remains at first view inextricable even though we satisfy ourselves with an approximate Galilean invariant theory to start with (which is sufficient in all cases of engineering interest). For the general aspects of the electrodynamics of nonlinear continua, whether solids or fluids, for the time being we can find no better references in the existing literature than our own books (Maugin, 1988; Eringen and Maugin, 1990). Thus only a sketch of this theory is given in the first sections of Chapter 9. Rather than duplicating existing books, after a brief review we show how the simplest irreversible behaviors follow from a more or less standard use of *T.I.P.* once the appropriately invariant fields have been introduced. Of greater interest is the application of *T.I.V.* which answers Duhem's worries about this *nonsensical branch of mechanics.* Dielectric relaxation, electro- and magneto-hysteresis, and their coupling with temperature and mechanical effects can be incorporated in the thermodynamical framework which *does* provide rules and constraints to select the most comprehensive and satisfactory representations of these somewhat singular behaviors. As in the case of viscoplasticity, the identification of the relevant *internal variables* is the most formidable problem, requiring physical insight. A prime example from this viewpoint is the identification of the unexpected variable in the magnetic-hysteresis theory developed by Motogi and Maugin (1993a, b): the area of magnetic domains oriented at 90° to the direction of the magnetizing field. Other sensible applications concern *deformable superconductors* where the internal variable of interest is a function which intervenes at a lower degree of description (the complex-valued wave function of Cooper's pairs), polyelectrolyte solutions (Drouot and Maugin, 1985), ferrofluidic solutions, elastic semiconductors, and the mechanical fracture and electric breakdown of electromagnetic structures. Most of the examples presented have been devised by the author and co-workers in a long series of memoirs and collated here for the first time. Some of the aspects concerning *nonlinear dissipative electromechanical behaviors, per se*, have been examined in a different monograph (Maugin, Pouget *et al.*, 1992).

We have gathered in Chapter 10 problems relating to the *reaction-diffusion systems* which abound in physics and which have played historically an important role in the inception of *T.I.V.* (think of reaction advancement rates and the associated thermodynamics). Nowadays such systems are exemplary of some typical problems of *progress* of some signals (like in nerve-pulse dynamics) or some phase-transition fronts. The latter problem can also be viewed as one of *thermodynamic material forces* (see above) but which relates to moving jumps in properties of the material. Coherent phase-transition fronts in elastic crystals enter this framework. In this respect we must underline the contributions of Jü. Engelbrecht, C. Trimarco, M. E. Gurtin and coworkers (e.g., Gurtin, 1993a, b), M. Grinfeld (1991), and L. Truskinowski (1987, 1991), the first two in collaboration with the author (see bibliography).

> Notation. *As a rule we use the standard notation of* vector analysis *(with the nabla symbol* ∇*) without indices. For tensors the* intrinsic *(no index) notation is in general preferred over the indexed* Cartesian *tensor notation commonly used by engineers, but, in harmony with our opened declaration of pragmatism, indices may be called for in case of ambiguity. Because of the wealth of material expanded in this book, we may have to use several different types of fonts (including German Gothic ones!), but these are used in a consistent manner which the reader will identify as we proceed, especially when dealing with electromagnetic fields in various frameworks.*

Chapter 2

THERMOSTATICS AND THERMODYNAMICS

"Die Energie der Welt ist constant,
Die Entropie der Welt strebt einem
Maximum zu." (R. Clausius, 1863)

2.1. Thermodynamic Systems

The object of thermodynamics: As emphasized in Chapter 1, the object of thermodynamics is *everything*. This is certainly not a very convenient delineation. But thermodynamics, according to Bridgman, has to do with some *macroscopic* aspects of matter and fields. How does this *macro* versus *atomic* standpoint arise? To be more specific, we may follow Callen (1960, p. 7):

> *"Thermodynamics is the study of the macroscopic consequences of myriads of atomic coordinates, which by virtue of the statistical averaging, do not appear explicitly in a macroscopic description of a system".*

In agreement with Bridgman's view as recalled in Chapter 1, we must then specify what is a *macroscopic system* in terms of numbers, time and length scales. To that purpose we may remind the reader of the following orders of magnitude (which will be either underlying, or recurrent in, various subsequent chapters):[1]

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[1] All figures relevant to physics have been collected or evaluated and reported in Maugin (1988), de Gennes (1974) and Eringen and Maugin (1990).

Characteristic numbers of elements (in units):

10^{23} : Avogadro's number ($A = 6.024 \times 10^{23}$)

10^{15} : number of macromolecules in suspension in one cubic meter of dilute solution

10^{9} : World population

10^{7} : Greece's population

10^{6} : number of grains in a 0.5 cm^3 volume of piezoelectric powder (each grain is a continuum such as an elastic plate!)

10^{5}–10^{4} : typical number of students in a large state university

10^{3} : usual size of population sample in a Gallup test

10^{3} : Typical number of faculty members in a large university (note the ratio 1/10 to the above number of students in the optimist view; ratio at University of Pierre and Marie Curie: 1/9 — 1993 figure)

10^{3} : number of students in a selective private college

10^{1}–10^{0} : number of magnetic domains in a whisker

Characteristic times (in seconds):

10^{-15} : period of atomic motion

10^{-10} : reciprocal magnetoacoustic resonance frequency

reciprocal Larmor frequency in ferromagnets

10^{-9}–10^{-6} : relaxation time of macromolecule

10^{-8} : orientational relaxation of a grain in a piezoelectric powder

10^{-7} : acoustic relaxation time in liquids

10^{-6} : nuclear spin relaxation

dielectric relaxation in a ferroelectric

liquid-crystal relaxation time

10^{-5} : waiting time of dislocation between two obstables/ Barkhausen jumps

10^{-4}–10^{-3} : charge relaxation in a ferrofluidic suspension

10^{-3}–10^{-2} : speed of photo-camera shutter

Landau-Lifshitz damping of spin precession

10^{-1} : reaction time of average car driver

10^{1} : inverse strain-rate in viscoelasticity of solids

10^{2} : cooking time in a micro-oven

10^{4} : long fiction movie

creep-fatigue response

10^{5} : one day

10^{6} : a fortnight

10^{7} : a year/one and thousand nights

10^{8} : large-mammal life duration

10^{9} : sequoia's life duration

Chinese and Egyptian dynasties

Characteristic lengths (in meters):

10^{-15} : classical radius of the electron

10^{-13} : Compton wave length

10^{-10} : lattice spacing in an elastic crystal

10^{-10}–10^{-9} : molecular dimension in liquid crystals

10^{-9} : thickness of domain wall (twin boundary) in elastic crystals)

10^{-8} : range of interaction in nonlocal elasticity (coherence length in solids)

thickness of domain walls in ferroelectric of the displacement type

10^{-8}–10^{-7} : coiled-uncoiled size of a macromolecule of polyelectrolyte in solution

10^{-7} : magnetoacoustic resonance wavelength in a ferromagnet

10^{-7}–10^{-6} : wavelength of sodium light

10^{-6} : thickness of domain wall in a ferroelectric of the molecular-group type

typical range of variation of order parameter in ordered solutions (liquid crystals)

length of microcrack in a solid

10^{-6}–10^{-4} : typical scale of observation of orientational changes of magnetic spins in ferromagnets

accuracy of machine tooling

10^{-4}–10^{-3} : size of thermometer

10^{-2} : size of ferromagnetic domains

size of electronic chips

length of macrocrack in a solid

10^{-1} : width of a hand

10^{0} : shock-formation distance in an elastic crystal

Many of the above-mentioned figures having a scientific basis will herein after intervene at some point in various modelings. Now we can make Callen's delineation of the aim of thermodynamics more palpable. At the *microscopic* scale where, discarding quantum mechanical effects, Newton's equations of motion and potential forces of interaction govern the whole system (this is the scale of large numbers of elements, lengths of the order between the Compton length and a typical lattice spacing, and time intervals of the order of 10^{-15} sec), such systems are endowed with extremely large numbers of *degrees of freedom* which we also call *atomic coordinates*. Their number is in the range of the Avogadro number, say 10^{24}. It is no question to study such systems, even with the help of the fastest available computers. But the organized pattern of the motion of so many particles gives rise to so-called *normal modes*. The number of the latter is also of the same order, 10^{24}. However, on a *macroscopic* scale (say time scales of the order of 10^{-3} sec and length scales of the order of 10^{-6} meters) we can average out using some statistical averaging and in the process only a few surviving "coordinates" with unique symmetry properties will be extracted, some of them being *mechanical* in nature, e.g. the *specific volume* τ in a fluid (*strain* in a solid), some others of electric or magnetic nature, e.g. the *electric polarization* **P** and the *magnetization* **M**, per unit volume, etc. (notice that there are so-called *extensive* variables — see below for this notion). With each of these particular macroscopic modes we can associate an *elementary work* which is exemplified by expressions such as $p\ d\tau$ and $\mathbf{E}.d\mathbf{P}$, where p is the *pressure*, $\mathbf{E}$ is the *electric field*, etc. These expressions convey the transfer of energy in mechanical and electric form in a *schematic* manner. But it is equally possible to transfer energy to those modes of motion — the hidden atomic modes of motion — that we have mentioned, in passing to the macroscopic description: the energy transferred to the hidden modes is called *heat*. The existence of this additional term to those of *work* by mechanical, electric and magnetic means is, in fact, the outstanding consequence of the existence of those apparently neglected hidden atomic coordinates. Thermodynamics is very much concerned with the notion of *heat*. What is true in modern developments, however, is that we are taking into account more and more atomic coordinates by progressively reducing both space and time scales.[2] This appears to be the unveiled project of modern generalizations of thermodynamics such as extended thermodynamics or the present thermodynamics with internal variables. In some way we are going to improve the mechanical, electric and magnetic thermodynamical description while the role of heat is correlatively reduced (to some small extent only). In any case, the ultimate form of energy, the most degraded one, remains as *heat*, hence the important role of the second law of thermodynamics whose formulation is based on the heat concept and the notion of temperature. We shall first consider *classical* thermodynamics, i.e. in the absence of internal variables, for which we now recall the more inclusive definition of a *system*.

Closed systems, thermodynamic systems, isolated systems:

Following the remarks made above, we recognize as basic the fact that *mass*, *work*, and *heat* are those "things" which can be exchanged between systems. Thus we are led to introduce the following definitions within the framework of *nonrelativistic* physics (which is sufficient for our purpose):

We call a system S a part of the material universe, i.e. a topologically *open* region of three-dimensional Euclidean space $\mathbb{E}^3$. The complement of S in $\mathbb{E}^3$ is called the *exterior* of S, or S^{ext}. A system is said to be *closed* when there is no exchange of *matter* between it and its exterior. Limiting ourselves to thermomechanics only, we call a *thermodynamic system* a system whose energy

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[2] For example we consider length scales of the order of 10^{-8}–10^{-6} meters and time scales of the order of 10^{-6} sec.

exchange with its exterior is nothing but an exchange of *heat* and of *work* done by volume forces or by surface forces acting upon $\mathcal{S}$. A thermodynamic system in which there is no energy exchange with the exterior is said to be *isolated*.

The definitions just given bring into play three kinds of exchange: mass, work and heat. This obviously leads to the introduction of the notion of *membrane* and the specification of this notion for each type of exchange. A membrane is a geometrical delimitation (regular surface) of a system. We recognize thus three types of membranes:

1. *Impermeable membrane* (contrary: *permeable*): This is a membrane that does not permit mass exchange.
2. *Rigid membrane* (contrary: *deformable*): This is a membrane that does not permit work exchange.
3. *Adiabatic membrane* (contrary: *diathermal*): This is a membrane that does not permit heat exchange.

Now we need to describe the main properties of a system with the help of typical entities which can be given some quantitative content. These are *thermodynamic variables.*

Definition 2.1. A thermodynamic state variable is a macroscopic quantity, which is characteristic of a system $\mathcal{S}$, and which can be a scalar, a tensor, an n-vector, etc., such as temperature or a stress tensor.

A state variable is said to be *extensive* if, within a homogeneous system $\mathcal{S}$, it is proportional to the mass of the system. We remind the reader that a homogeneous system is one in which state variables are spatially uniform. Obviously, mass itself, but also electric polarization and magnetization are *extensive* variables. If a variable does not depend upon the mass of the system, then it is said to be *intensive*. All thermodynamic state variables are either extensive or intensive. We accept that with each extensive variable a *specific* intensive variable (i.e. defined per unit of mass) can be associated. Ultimately this is the fact that makes it possible to work with intensive variables alone. Among intensive variables of state we note *specific volume* τ (a scalar) and the electric polarization and magnetization per unit mass, respectively π and μ (a polar vector and an axial vector, respectively).

2.2. Thermodynamic States

The choice of the thermodynamic state variables is determined not only by the physical nature of the system $\mathcal{S}$ under study (e.g. do we include π or μ among the list of state variables if the system does not markedly exhibit electromagnetic properties?) and its transformations, but also by the scheme adopted and the hoped-for precision of the description; so the number of thermodynamic state variables may vary from one system and theory to another; they may, for instance, depend upon the number of secondary effects and couplings taken into consideration. For example, in a liquid suspension exhibiting a marked electric polarization, both τ and π should be considered as relevant state variables where we may expect a phenomenon of *electrostriction*. In any case, by the very notion of averaging when moving from atomic coordinates to state variables, the latter will be in small numbers (say of the order of 10^0–10^2, and this must be compared to 10^{24})

Definition 2.2. The set of values of the thermodynamic state variables that characterize a system $\mathcal{S}$ at a certain moment constitutes the *thermodynamic state* $\mathcal{E}(\mathcal{S}, t)$ of the system at that given moment t.

We say that a system is in *thermodynamic equilibrium* if this system does not evolve with time. But, in general, thermodynamic systems *do* evolve with time, under the action of various external *stimuli*. The transition from one thermodynamic state to another is called a *thermodynamic process*. A thermodynamic process is said to be *reversible* if the inverse evolution of the system in time — i.e. the succession of thermodynamic states that the system has gone through — implies the reversal in time of the action of the external stimuli. This can be pleasantly visualized by picturing a movie that we project backwards by rewinding the film. Otherwise the thermodynamic process is said to be *irreversible*.

Definition 2.3. *Thermostatics* is the science that compares systems in thermodynamic *equilibrium*.

For example, thermostatics describes the transition from a state of equilibrium $\mathcal{E}_1(\mathcal{S})$ to another state $\mathcal{E}_2(\mathcal{S})$. *Thermodynamics*, in its main sense, then is the study of phenomena relating to systems *out of equilibrium*, but are actually not far from equilibrium (see below for that limitation). Everybody of course agrees that in the years 1890 to 1920 thermostatics was developed to an unsurpassed persuasive and elegant mathematical form by Clausius, Gibbs, Duhem and Caratheodory (see Chapter 1) in full harmony with the experiments. Unfortunately, we cannot say the same about thermodynamics outside equilibrium. This is one more reason why thermostatics deserves some careful study.

2.3. Thermostatics (Born–Caratheodory)

A. Axioms of thermostatics

The exclusive object of thermostatics is systems $\mathcal{S}$ which are in thermodynamic equilibrium. Above we gave some kind of "experimental" definition of equilibrium. The exact mathematical definition is the following.

Definition 2.4. The state $\mathcal{E}(\mathcal{S})$ of a system $\mathcal{S}$ in *thermodynamic equilibrium* is the set of the quantities proper to this equilibrium, whether of geometric, mechanical, or physicochemical, etc., nature, expressed by real numbers that remain invariable in time.

The system $\mathcal{S}$ is said to be *finite* if $n+1$ of these characteristics, (denoted by $\chi_0, \chi_1, \ldots, \chi_n$, i.e. $\chi_\alpha, \alpha = 0, 1, \ldots, n$) constitute a system of *independent variables*, so that any other characteristic quantity becomes a well-defined function, called a *function of state* of the χ_α, in this way forming a complete system of variables of state of the state $\mathcal{E}(\mathcal{S})$. In geometrical terms, *the set of all possible states $\mathcal{E}$ of a system forms a simply connected differentiable manifold* which is denoted by $\mathcal{V}(\mathcal{S}) = \mathcal{V}$.

This definition inevitably leads us to an *axiomatic* formulation of thermostatics as given by C. Caratheodory (1909, 1925) — a German analyst well known for his work on the calculus of variations — following the guidance and advice of M. Born, the physicist of quantum-mechanical fame (among other things; see Born, 1921) — see also Landé (1926) and Falk and Jung (1959).

The *transformation*, denoted by $\mathcal{F}(\mathcal{E}_1, \mathcal{E}_2)$, is the transition of a system $\mathcal{S}$, from one state of equilibrium $\mathcal{E}_1$ to another state of equilibrium $\mathcal{E}_2$. Let $\{\mathcal{F}\}$ be the set of these transformations. During a transformation there is the possibility of *exchange*. According to the notion of *membrane* mentioned above, we can state that a system is *closed* if all membranes (external of internal) are

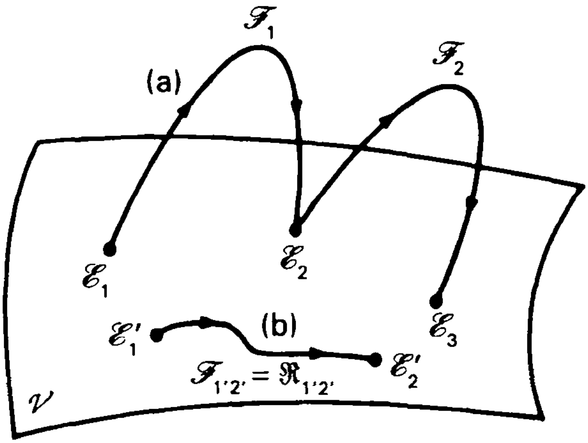

Fig. 2.1. (a) Composition of general transformations between equilibrium states (Caratheodory's formulation); (b) reversible transformation (the path $\mathcal{F}_{1',2'}$ is entirely in $\mathcal{V}$).

impermeable. A system will be called *simple* if there is no internal membrane, while all the parts of the system are *homogeneous* in any state of equilibrium $\mathcal{E}$.[3]

When a transformation $\mathcal{F}(\mathcal{E}_2, \mathcal{E}_2)$ is such that $\mathcal{E}_2$ is identical to $\mathcal{E}_1$, it is then called *cyclic*. The composition of transformations is defined in an obvious way by Fig. 2.1

$$\mathcal{F}(\mathcal{E}_1, \mathcal{E}_2) = \mathcal{F}_2(\mathcal{E}_2, \mathcal{E}_3) \circ \mathcal{F}_1(\mathcal{E}_1, \mathcal{E}_2)\,, \tag{2.3.1}$$

so that the final state of the first transformation $\mathcal{F}_1$ becomes the initial state of the second $\mathcal{F}_2$. We can then state the following.

First law of thermodynamics in axiomatic form: *To any transformation* $\mathcal{F}(\mathcal{E}_1, \mathcal{E}_2)$ *of a system* S *two numbers* $\mathcal{T}_{\mathcal{F}}$ *and* $\mathcal{Q}_{\mathcal{F}}$ *can be associated, called respectively work received and heat received by* S *during the transformation. The thermodynamic function called internal energy* $\mathbb{E}(\chi_\alpha)$, *defined up to an additive constant, is defined such that*

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[3] Note that other authors define *simple systems* (e.g., Callen, 1960, p. 8) as "systems that are macroscopically homogeneous, isotropic, uncharged, and chemically inert, that are sufficiently large that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields" (in other words, these are *not complex* systems as opposed to those that will provide the essential subject for our study, *G.A.M.*). We are faithful to our definition in the body of the text.

$$\mathbb{E}(\mathcal{E}_2) - \mathbb{E}(\mathcal{E}_1) = \mathcal{T}_{\mathcal{F}} + \mathcal{Q}_{\mathcal{F}} . \tag{2.3.2}$$

Although the notion of *work* is the same as in pure mechanics, the notion of *heat* is not specified; which means that within an axiomatic system (2.3.2) may be considered as a *definition* of $\mathcal{Q}_{\mathcal{F}}$. If $\mathcal{F}$ is defined by a composition similar to (2.3.1) then

$$\mathcal{T}_{\mathcal{F}} = \mathcal{T}_{\mathcal{F}_1} + \mathcal{T}_{\mathcal{F}_2} , \qquad \mathcal{Q}_{\mathcal{F}} = \mathcal{Q}_{\mathcal{F}_1} + \mathcal{Q}_{\mathcal{F}_2} . \tag{2.3.3}$$

And this leads us to consider the existence of two particular classes of transformations.

Adiabatic transformations. These are the transformations belonging to the subset $\{\mathcal{A}\}$ of $\{\mathcal{F}\}$ that take place without *heat exchange* with the exterior (consequently within the limits of an adiabatic membrane); so

$$\mathcal{Q}_{\mathcal{F}\in\{\mathcal{A}\}} = 0 . \tag{2.3.4}$$

We then have the following axiom.

Axiom of adiabatic transformations. *If $\mathcal{E}_0$ is a state of the system $\mathcal{S}$ and $\mathcal{N}(\mathcal{E}_0)$ is the set of the states, in such a way that each one of them will be the final state of an adiabatic transformation of which $\mathcal{E}_0$ is the initial state, i.e.,*

$$\mathcal{N}(\mathcal{E}_0) = \{\mathcal{E} | \exists \mathcal{A}(\mathcal{E}_0, \mathcal{E})\} , \tag{2.3.5}$$

and $\mathcal{I}(\mathcal{E}_0)$ is the set of states where each state is the initial state of an adiabatic transformation of which $\mathcal{E}_0$ is the final state, i.e.,

$$\mathcal{I}(\mathcal{E}_0) = \{\mathcal{E} | \exists \mathcal{A}(\mathcal{E}, \mathcal{E}_0)\} , \tag{2.3.6}$$

then

$$\mathcal{N}(\mathcal{E}_0) \cup \mathcal{I}(\mathcal{E}_0) \supset \mathcal{V}(\mathcal{S}) . \tag{2.3.7}$$

This means that two states of $\mathcal{V}$ can always be connected by an adiabatic transformation, but in general we cannot arbitrarily select which one of these two states will be the initial state of the transformation. In so far as notation is concerned, $\mathcal{N}$ clearly refers to "natural" evolutions and $\mathcal{I}$ to "impossible" evolutions.

Reversible transformations. These are the transformations that belong to the subset $\{\mathcal{R}\}$ of $\{\mathcal{S}\}$, where the path from $\mathcal{E}_1$ to $\mathcal{E}_2$ takes place *entirely* inside $\mathcal{V}$ (which is *not* the case for any $\mathcal{F}$!) If $\mathcal{L}$ is the transition path from $\mathcal{E}_1$ to $\mathcal{E}_2$ in $\mathcal{V}$, then we have

$$\mathcal{T}_{\mathcal{F}\in\{\mathcal{R}\}} = \int_{\mathcal{L}} \omega\,, \qquad \mathcal{Q}_{\mathcal{F}\in\{\mathcal{R}\}} = \int_{\mathcal{L}} \phi\,, \tag{2.3.8}$$

where ω and ϕ are *two differential forms of the first order*,[4] which are not identically zero and not proportional to one another, defined on $\mathcal{V}$. We say then that the system is in *reversible evolution* between the states $\mathcal{E}_1$ and $\mathcal{E}_2$, and that ω and ϕ are, respectively, the *elementary work received* and the *elementary heat received* in this reversible evolution. For example, we can write explicitly

$$\omega = \sum_{\alpha=0}^{n} A_\alpha d\chi_\alpha\,, \qquad \phi = \sum_{\alpha=0}^{n} B_\alpha d\chi_\alpha\,, \tag{2.3.9}$$

and the first law (2.3.2), in the case of reversible transformations, is written here in an elementary form as

$$d\mathbb{E} = \omega + \phi\,. \tag{2.3.10}$$

What is then the statement of the *second law of thermodynamics* according to Caratheodory?

Second law for a simple closed system (Caratheodory). *Given that $\mathcal{E}_0 \in \mathcal{V}$, then $\mathcal{E}_0 \notin \overset{\circ}{\mathcal{N}}(\mathcal{E}_0)$* — the interior of $\mathcal{N}$, i.e. *$\mathcal{E}_0$ belongs to the boundary of $\mathcal{N}(\mathcal{E}_0)$.*

In less esoteric language, this means that there are neighboring states of $\mathcal{E}_0$ that cannot be reached through an adiabatic transformation starting from $\mathcal{E}_0$ so that, as announced, Caratheodory's formulation of the second law is an *axiom of inaccessibility of states.* We have then the following.

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[4] See any book on exterior calculus and differential forms, e.g. Lovelock and Rund, 1975.

Caratheodory's theorem. *If the axiom above is true, then there exist two functions of state* $\theta(\chi_\alpha)$ and $S(\chi_\alpha)$, which are not unique, such that

$$\phi = \theta dS\,. \tag{2.3.11}$$

That the two functions are not unique is obvious from the fact that we can introduce a once differentiable function ψ such that

$$\theta' = \theta(d\psi/dS)^{-1}\,, \qquad S' = \psi(S)\,, \tag{2.3.12}$$

so that (2.3.11) is still satisfied for θ' and S' if it holds true for θ and S.

Proof of Caratheodory's theorem.[5] As the form ϕ is not identically zero let us assume that in a neighborhood $\mathcal{U}(\mathcal{E}_0)$ of $\mathcal{E}_0$ where, without loss in generality we can set all χ_α equal to zero, the equality $\phi = 0$ can also be written as

$$\psi = d\chi_0 - \sum_{\beta=1}^{n} C_\beta d\chi_\beta = 0\,. \tag{a}$$

A curve along which $\phi = \psi = 0$ defines a reversible and adiabatic transformation and is, in the neighborhood of $\mathcal{E}_0$, an integral curve of the differential equation

$$\frac{d\chi_0}{dt} = \sum_{\beta=1}^{n} C_\beta(\chi_0, \chi_1, \ldots, \chi_n)\frac{d\chi_\beta}{dt}\,. \tag{b}$$

Now let us try to construct integral curves that pass through $\mathcal{E}_0$ (where $\chi_0 = c$, $\chi_1 = \cdots = \chi_n = 0$); t is a parameter such as time which we can suppose equal to zero at $\mathcal{E}_0$. Such curves C will be obtained as

$$\chi_1 = a_1 t, \ldots, \chi_n = a_n t\,, \tag{c}$$

where the a_β are arbitrary constants, by selecting $\chi_0(t)$ as the unique solution $\chi_0 = F(t, a_1, \ldots, a_n, c)$ of the differential equation

$$\frac{d\chi_0}{dt} = \sum_{\beta=1}^{n} C_\beta(\chi_0, a_1 t, \ldots, a_n t) a_\beta\,, \tag{d}$$

with initial condition

$$F(0, a_1, \ldots, a_n, c) = c\,. \tag{e}$$

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[5] This proof can be skipped by readers not keen on mathematics.

Let k be a non-vanishing positive real constant. Then we also have

$$\chi_0 = F(k^{-1}t, ka_1, \ldots, ka_n, c) = F(t, a_1, \ldots, a_n, c) .$$

This identity for F shows, when we make $k = t$, that

$$\chi_0 = F(1, a_1 t, \ldots, a_n t, c) .$$

But from the continuity of F with respect to t, when t goes to zero we also have that

$$F(0, a_1, \ldots, a_n, c) = c = F(1, 0, \ldots, 0, c) .$$

At this point it is convenient to simplify the geometric representation of the neighborhood $\mathcal{U}(\mathcal{E}_0)$ by effecting a change of variables which transforms the curves $\mathcal{C}$ above into so-called "horizontal straight lines". That is, we replace $\{\chi_\alpha\}$ by new variables $(S, \{\xi_\beta\})$ such that

$$\begin{aligned} \xi_\beta &= \chi_\beta , \qquad \beta = 1, 2, \ldots, n , \\ \chi_0 &= F(1, \xi_1, \ldots, \xi_n, S) . \end{aligned} \tag{f}$$

As $\partial F / \partial S = 1$ at point $(1, 0, \ldots, 0, 0)$, the transformation is regular, and, in particular, *invertible*, in a neighborhood of $\mathcal{E}_0$. The result of this is that ϕ can now be written as

$$\phi = \theta dS - \sum_{\beta=1}^{n} D_\beta(S, \xi_1, \ldots, \xi_n) d\xi_\beta , \tag{g}$$

together with

$$\theta(0, 0, \ldots, 0) = 1 .$$

In this representation the set of curves $\mathcal{C}$ becomes a set of straight lines $\mathcal{D}$ of the $\{\xi_\beta\}$ space, which are all parallel to $S = 0$ and intersect the S-axis. Furthermore, two points $\mathcal{E}_3$ and $\mathcal{E}_2$ of a hyperplane $S = c$ can be connected by a reversible adiabatic path. To see this it suffices to consider segments of $\mathcal{D}$'s which join $\mathcal{E}_3$ to $\mathcal{E}_c$ and $\mathcal{E}_c$ to $\mathcal{E}_2$, and these are particular curves $\mathcal{C}$. It remains to prove that in a neighborhood of $\mathcal{E}_0$, all D_β in (g) are identically zero. With this in mind we shall use a *reductio at absurdum* proof and suppose, to start with, that there exists a point $\mathcal{E}_1(S^{(1)}, \xi_1^{(1)}, \ldots, \xi_n^{(1)})$ of $\mathcal{U}(\mathcal{E}_0)$ where at least one of the D_β is *not* zero. Then the second law would be violated. This is shown by proving that there exists a reversible adiabatic path Δ, passing through $\mathcal{E}_1$ and along which S is strictly increasing, $\gamma < S < \delta$, where γ and δ are such that $\gamma < S^{(1)} < \delta$. Then if $\mathcal{E}_2$ is a point in a neighborhood of $\mathcal{E}_1$ formed by the points of $\mathcal{U}(\mathcal{E}_0)$ such that $\gamma < S < \delta$, it is possible to connect $\mathcal{E}_1$ and $\mathcal{E}_2$ via a reversible adiabatic path. To do this it suffices to take the path $\mathcal{E}_1\mathcal{E}_3$ of Δ, with $\mathcal{E}_3$ a point of Δ such that $S(\mathcal{E}_3) = S(\mathcal{E}_2)$, and then to apply the foregoing remark that $\mathcal{E}_3$ and $\mathcal{E}_2$ can always be connected by two "straight segments". Indeed, set $d_\beta = D_\beta(\mathcal{E}_1) \not\equiv 0$, β fixed. Let an integral path of $\phi = 0$ be given in parametric representation by

$$\begin{aligned} &\xi_\beta = \xi_\beta^{(1)} + d_\beta t\,, \qquad \beta = 1, 2, \ldots, n\,, \\ &S = f(t)\,, \qquad f(0) = S^{(1)}\,. \end{aligned} \tag{h}$$

Then $f(t)$ must be a solution of the differential equation

$$\bar{\theta}(t)\frac{df}{dt} = \sum_{\beta=1}^{n} d_\beta \bar{D}_\beta(t)\,, \qquad f(0) = S^{(1)}\,, \tag{i}$$

wherein

$$\begin{aligned} \bar{\theta}(t) &= \theta(f(t), \xi_1^{(1)} + d_1 t, \ldots, \xi_n^{(1)} + d_n t)\,, \\ \bar{D}_\beta(t) &= D_\beta(f(t), \xi_1^{(1)} + d_1 t, \ldots, \xi_n^{(1)} + d_n t)\,. \end{aligned} \tag{j}$$

As $\theta(\mathcal{E}_0) = 1$, we may suppose that $\theta(\mathcal{E}) > O$ for state points in $\mathcal{U}(\mathcal{E}_0)$ even though we may have to limit the neighborhood of $\mathcal{E}_0$ so that this holds true. As a consequence $\bar{\theta}(0) > 0$ strictly. The classical existence and uniqueness theorem for solutions of a differential equation of the type (i) then yields that $f(t)$ exists and its derivative at the origin is strictly positive since

$$\bar{\theta}(0)\frac{df}{dt}(0) = \sum_{\beta=1}^{n} d_\beta^2 \tag{k}$$

if, as was assumed, all d_β do not vanish simultaneously. The df/dt is also strictly positive in an interval $(-t_1, t_1)$ so that there exists a path Δ along which S increases and this is contrary to the second law as stated by Caratheodory for simple closed systems. Therefore, all D_β must vanish simultaneously, and the theorem is proved. This is essentially the proof given by Buchdahl (1960, 1966) of Caratheodory's (1925) theorem (see also Germain, 1973, pp. 340–342). The proof is mathematically satisfactory but it does *not* shed any light on the physical significance of the variables θ and S. To reach this "physical" hindsight we must introduce the notion of temperature.

B. Scaling of temperature, Carnot's theorem

Notion of temperature

We shall say that two *simple closed systems*, S_1 and S_2, are in *thermal equilibrium* when, although they are initially separated by an adiabatic membrane, the equilibrium is left unchanged if this membrane is replaced by a diathermal membrane. This refers to the definitions mentioned previously. It follows that if two systems are in thermal equilibrium with a third one, then they are in thermal equilibrium between them. This statement defines, in terms of mathematics, an *equivalence relation.* The *classes of equivalence* of V through this equivalence relation are isomorphic to the real line $\mathbb{R}$. The states of equilibrium of a well-defined system in thermal equilibrium defines then a *submanifold* of dimension n of V, called *isothermal*, which we consider to be sufficiently regular. This submanifold is a hypersurface of equation

$$T = g(\chi_\alpha) = \text{const.}, \tag{2.3.13}$$

so that T is a *function of state* by this very relation. We say then that (2.3.13) defines a *scaling of temperature* and that T is the temperature of the system in the state $\{\chi_\alpha\}$. We can also say that a *complex* closed system S is *thermally simple* if all the simple subsystems S_β that compose it are at the same temperature. *The second law applies to thermally simple systems.* The above-given introduction of temperature is sometimes referred to as the "*zero principle*" of thermodynamics. We then have the following.

Carnot's theorem. *There is a universal scaling of temperature θ, called* thermodynamic temperature *or* absolute temperature *and a function of state $S(\chi_\alpha)$ called* entropy of the system, *such that*

$$\phi = \theta dS, \qquad S = S(\chi_\alpha), \qquad \theta > 0, \qquad \inf \theta = 0, \tag{2.3.14}$$

and the entropy of a combination of thermally simple systems is the sum of the entropy of each one of these systems. S is defined up to an additive constant (often considered as equal to zero in the limit as θ goes to zero).

This theorem attributed to Sadi Carnot and often called the *zero principle* of thermodynamics in fact reflects the introduction of the notion of *absolute* *temperature by* W. Thomson (Lord Kelvin). It provides the physical significance of Caratheodory's theorem in which absolute temperature appears as the reciprocal of an *integrating factor* for heat as we can write $dS = \theta^{-1}\phi$, where ϕ is the elementary heat received by the system. We shall call *isentropic* those transformations that are both *reversible* and *adiabatic.*

Proof of Carnot's theorem: By the "zero principle" θ can never be zero, so we can always arrange to have $\theta > 0$ strictly while entropy remains defined up to an additive constant. This ensures that absolute temperature and entropy differences are well determined and present a universal character. A sketchy proof of Carnot's theorem, which amounts to an exercise on exact differentials, is as follows.

Let Σ be a thermally simple system made of two subsystems Σ_1 and Σ_2. These are defined by the following state variables:

$$\begin{aligned} &\Sigma : \xi_0, T, \xi_2, \ldots, \xi_p \\ &\Sigma_1 : \chi_0\,, T\,, \chi_2, \ldots, \chi_n \\ &\Sigma_2 : \eta_0\,, T\,, \eta_2, \ldots, \eta_m \\ &p = n + m + 1\,, \end{aligned} \tag{a}$$

where T is the common scaling of temperature. According to Caratheodory's theorem we can write

$$\begin{aligned} \phi &= M(\xi_0, T, \ldots, \xi_p)d\xi_0\,, \\ \phi_1 &= M_1(\chi_0, T, \ldots, \chi_n)d\chi_0\,, \\ \phi_2 &= M_2(\eta_0, T, \ldots, \eta_m)d\eta_0\,, \end{aligned} \tag{b}$$

which are the elementary amounts of heat received by the various systems. As internal energy is additive, we have $\phi = \phi_1 + \phi_2$, i.e.

$$Md\xi_0 = M_1 d\chi_0 + M_2 d\eta_0\,, \tag{c}$$

or setting $\mu = M^{-1}$ as $M \not\equiv 0$ necessarily, we can extract from this

$$d\xi_0 = \mu M_1 d\chi_0 + \mu M_2 d\eta_0\,. \tag{d}$$

From this it follows first that μM_1 and μM_2 depend only on χ_0 and η_0. The same is also true of the ratio M_1/M_2, so that we have the relation

$$M_1(\chi_0, T, \ldots, \chi_n) = M_2(\eta_0, T, \ldots, \eta_m) a(\chi_0, \eta_0) \,. \tag{e}$$

But the variables of state $\chi_2, \ldots, \chi_n$ and $\eta_2, \ldots, \eta_m$ are independent so that M_1 can at most be a function of χ_0 and T while M_2 can at most be a function of η_0 and T. Let $M_1(\chi_0, T)$ and $M_2(\eta_0, T)$ those functions. Let further $T = T_f$ be a fixed value of T. Accounting for (e) above we then have that

$$\frac{M_1(\chi_0, T)}{M_2(\eta_0, T)} = \frac{M_1(\chi_0, T_f)}{M_2(\eta_0, T_f)} \,. \tag{f}$$

Consequently we can also write

$$\frac{M_1(\chi_0, T)}{M_1(\eta_0, T_f)} = \frac{M_2(\chi_0, T)}{M_2(\eta_0, T_f)} \,. \tag{g}$$

But χ_0 and η_0 are also independent variables so that each of the ratios in (g) is independent of χ_0 and η_0. We call $m(T)$ the value of this ratio (as T_f is a fixed constant). Therefore

$$M_1 = m(T) a_1(\chi_0) \,, \qquad M_2 = m(T) a_2(\eta_0) \,, \tag{h}$$

and thus from (c)

$$\frac{M}{m(T)} d\xi_0 = a_1(\chi_0) d\chi_0 + a_2(\eta_0) d\eta_0 \,. \tag{i}$$

The right-hand side of this equation is an *exact differential* (as a_1 and a_2 do not depend on η_0 and χ_0, respectively). This must also be the case of the left-hand side of (i), so that we can write

$$\frac{M}{m(T)} = a(\xi_0) \tag{j}$$

only. Now define $S_1(\chi_0)$ and $S_2(\eta_0)$ as the primitive functions of $a_1(\chi_0)$ and $a_2(\eta_0)$, respectively. It follows then from (j) that

$$a(\xi_0) d\xi_0 = dS_1 + dS_2 \,. \tag{k}$$

Whence there exists a primitive function of $a(\xi_0)$, say $S(\xi_0)$, such that

$$S = S_1 + S_2 \,.$$

Selecting then S, S_1 and S_2 as new variables replacing ξ_0, χ_0 and η_0, respectively, and noting $\theta = m(T)$ the new scaling of temperature introduced in the course of the derivation, we have shown that

$$\phi = \phi_1 + \phi_2 = \theta dS \,, \qquad \phi_1 = \theta dS_1 \,, \qquad \phi_2 = \theta dS_2 \,. \tag{Q.E.D.}$$

This is essentially the proof reported in Germain (1973, pp. 344–345).

As a corollary of the previous theorem we have the following.

Corollary of Carnot's theorem. *We can always describe a thermodynamic system by the state variables called* normal, $\{\chi_\alpha\} = \{\chi_0 = S, \chi_1, \ldots, \chi_n\}$ *in such a way that*

$$\phi = \theta dS \,, \qquad \omega = \sum_{\beta=1}^{n} \tau_\beta d\chi_\beta \,, \tag{2.3.15}$$

where there is no dS in ω.

The introduction of *normal* state variables is due to P. Duhem (1911).

C. Thermodynamic potentials

We should point out that both $\mathbb{E}$ (internal energy) and S (entropy) are *extensive variables* (i.e. they are proportional to the mass of the system). The χ_β's are also extensive variables. Furthermore, $\mathbb{E}$ is a positively homogeneous function of degree *one* with respect to the variables χ_β. We note that (2.3.15), in an obvious way, gives

$$\theta = \frac{\partial \mathbb{E}}{\partial S} \,, \qquad \tau_\beta = \frac{\partial \mathbb{E}}{\partial \chi_\beta} \,, \qquad \beta = 1, \ldots, n \,, \tag{2.3.16}$$

in such a manner that θ and the τ_β's are positively *homogeneous* functions of degree *zero*. They are *intensive* variables of state. We say then that $\mathbb{E}(\chi_0 = S, \chi_1, \ldots, \chi_n)$ is a *thermodynamic potential* from which both θ and the τ_β's are derived through (2.3.16). Generally speaking, we have the following broader definition: we call thermodynamic potentials those variables from which we can deduce the variables characterizing *all* the thermodynamic properties of the system. There exists a large *class* of thermodynamic potentials which are all introduced through the notion of *Legendre transformation* (or *contact transformation*).

Associated thermodynamic potentials

Let $Z = Z(\chi_\alpha) = Z(\chi_0, \chi_1, \ldots, \chi_n)$ be a given thermodynamic potential. We then have

$$dZ = \sum_{\alpha=0}^{n} \mu_\alpha d\chi_\alpha = \mu \cdot d\chi\,, \qquad \mu_\alpha = \frac{\partial Z}{\partial \chi_\alpha}\,, \tag{2.3.17}$$

where the dot indicates the scalar product of $(n+1)$-vectors. We define an *associated* thermodynamic potential $g(\mu_0, \mu_1, \ldots, \mu_p, \chi_{p+1}, \ldots, \chi_n)$ through the *partial Legendre transformation* on the first $p+1$ variables of state, by

$$\begin{aligned} &g(\underline{\mu}^{(1)}, \underline{\chi}^{(2)}) = Z(\underline{\chi}) - \underline{\mu}^{(1)} \cdot \underline{\chi}^{(1)}\,, \\ &\qquad \underline{\chi}^{(1)} = (\chi_0, \chi_1, \ldots, \chi_p)\,, \qquad \underline{\mu}^{(1)} = (\mu_0, \mu_1, \ldots, \mu_p)^T\,, \\ &\qquad \underline{\chi}^{(2)} = (\chi_{p+1}, \chi_1, \ldots, \chi_n)\,, \qquad \underline{\chi}^{(2)} = (\mu_{p+1}, \ldots, \mu_n)^T\,, \end{aligned} \tag{2.3.18}$$

in such a way that

$$\begin{aligned} \chi_\alpha &= -\frac{\partial g}{\partial \mu_\alpha}\,, \qquad \alpha = 0, 1, \ldots, p \\ \mu_\beta &= \frac{\partial Z}{\partial \chi_\beta}\,, \qquad \beta = p+1, \ldots, n\,. \end{aligned} \tag{2.3.19}$$

The Legendre transformation (after the French mathematician A. M. Legendre, 1752–1833) is called *partial* as it affects only the first $p+1$ variables and corresponding functions. For example, we may consider thermodynamic potentials which are associated with the *internal energy* in agreement with the foregoing transformation. Remember that $\chi_0 = S$. The *Helmholtz free energy* F can be defined by

$$F = \mathbb{E} - \theta S\,, \tag{2.3.20}$$

so that

$$F = F(\theta, \chi_1, \ldots, \chi_n)\,, \qquad S = -\frac{\partial F}{\partial \theta}\,. \tag{2.3.21}$$

This clearly is the appropriate thermodynamic potential to study *isothermal processes* ($\theta =$ const.) whereas internal energy is adapted to the treatment of *isentropic processes* ($S =$ const.). Now, if among the remaining χ_α, $\alpha \geq 1$, we find the *volume* V, e.g. $\chi_1 = V$, then the dual function τ_1 is minus the *pressure* p, and we can define the *enthalpy* H by

$$H = \mathbb{E} + pV\,, \tag{2.3.22}$$

so that

$$H = H(S, p, \chi_2, \ldots, \chi_n)\,, \qquad V = \frac{\partial H}{\partial p}\,. \tag{2.3.23}$$

As to the *Gibbs* potential, this is obtained by combining (2.3.20) and (2.3.22), that is

$$\begin{gathered} G = G(\theta, p, \chi_2, \ldots, \chi_n) = \mathbb{E} - \theta S + pV\,, \\ S = -\frac{\partial G}{\partial \theta}\,, \qquad V = \frac{\partial G}{\partial p}\,. \end{gathered} \tag{2.3.24}$$

It is thus well adapted to the treatment of processes which are simultaneously *isothermal* and *isopressure* (at constant pressure). In a general way the potentials associated with S through Legendre transformations are called *Massieu functions* of the system (after F. Massieu, 1832–1896, a French geologist and mineralogist). Different potentials present different properties of *convexity* with respect to the different choices of independent state variables. For example, $\mathbb{E}$ is convex in S and in the strain components in an elastic solid. It follows that F is *concave* in θ (in particular it has a negative second derivative with respect to θ) but it is still convex in the strain components. Actually, the properties of convexity (and homogeneity) are preserved by the Legendre transformation (or the more general Legendre–Fenchel transformation). For a gas, S is concave in $\mathbb{E}$ and the volume V. Convexity is a property which is necessarily involved when *stability* matters are discussed (see, for instance, Germain, 1973, pp. 352–362, for this question concerning thermodynamic potentials). In any case, as $\theta > 0$ strictly, the potential $\mathbb{E}$ must be an *increasing* function of S — cf. Eqs. (2.3.16).

D. The evolution of real systems; continua

We call *real systems* those systems which are subject to all types of thermodynamic transformations, including *irreversible ones.* That is, we now want to apply the second law to all transformations $\{\mathcal{F}\}$ including the last class. Starting from *any* state $\mathcal{E}_0$ we can show that the set $\mathcal{N}(\mathcal{E}_0)$ may be defined by the inequality (whose sign is prescribed by experiments)

$$S \geq S_0\,, \tag{2.3.25}$$

the equality sign holding good for reversible transformations only. The inequality (2.3.25) is a characteristic of the *entire set* of adiabatic transformations, whereas the reversible adiabatic transformations were used in order to introduce the universal concepts of temperature and entropy. We recognize in (2.3.25) the second part of the celebrated statement of R. Clausius (see heading citation of the chapter) according to which *entropy of an isolated system cannot decrease.*

As temperature plays a crucial role, we must first specify further the notion of *isothermal transformations* and *thermal irreversibilities.*

Isothermal transformations. During such a transformation of the system the temperature remains constant. If, in addition, this transformation is *reversible*, then the evolution of the system between the initial state $\mathcal{E}_0$ and the actual state $\mathcal{E}$ is described by a succession of *equilibrium states*, and the quantity of heat received Q_r during this transformation is given by

$$S(\mathcal{E}) - S(\mathcal{E}_0) - \frac{Q_r}{\theta} = 0\,. \tag{2.3.26}$$

If the transformation is *irreversible* we may suppose that (2.3.26) is replaced by

$$S(\mathcal{E}) - S(\mathcal{E}_0) - \frac{Q}{\theta} \geq 0\,, \tag{2.3.27}$$

in such a way that, for a given Q, the final entropy will be greater than the one we would have observed in a reversible transformation. We can also say that the quantity of heat received during the transition from $\mathcal{E}_0$ to $\mathcal{E}$ is *smaller* in the case of irreversible transformations, and that the resulting *loss* of received energy is due to the intrinsic irreversibilities of the system. According to (2.3.27), these losses caused by *intrinsic irreversibilities* are defined by

$$\mathcal{P}(\mathcal{F}_{\text{isoth}}(\mathcal{E}_0,\mathcal{E})) = S(\mathcal{E}) - S(\mathcal{E}_0) - \theta^{-1}Q(\mathcal{F}_{\text{isoth}}(\mathcal{E}_0,\mathcal{E})) \geq 0\,. \tag{2.3.28}$$

We can define in the same manner the losses due to *thermal irreversibilities*:

$$\mathcal{P}(\mathcal{F}_{\text{monoth}}(\mathcal{E}_0,\mathcal{E})) = S(\mathcal{E}) - S(\mathcal{E}_0) - \theta_0^{-1}Q(\mathcal{F}_{\text{monoth}}(\mathcal{E}_0,\mathcal{E})) \geq 0\,, \tag{2.3.29}$$

where $\mathcal{F}_{\text{monoth}}(\mathcal{E}_0,\mathcal{E})$ is a *monothermal* transformation which corresponds to an exchange of heat with a source at *constant* temperature θ_0.

For a *continuous medium* we shall use the form

$$S_2 - S_1 \geq \int_1^2 \frac{dQ}{\theta} \tag{2.3.30}$$

of Eq. (2.3.27), where 1 and 2 denote the initial and final states of the continuum. More precisely, for a material body occupying the volume Ω of Euclidean physical space $\mathbb{E}^3$ at time t, with a regular boundary $\partial\Omega$, and evolving between two instants t_1 and t_2, we shall write (2.3.30) in the more expressive form

$$S(t_1) - S(t_2) \geq \int_{t_1}^{t_2} \left\{ \int_{\partial\Omega} \frac{q}{\theta} da + \int_{\Omega} \rho \frac{h}{\theta} d\Omega \right\} dt \,, \tag{2.3.31}$$

where q and h are, respectively, a flux and a source (per unit mass) of heat. The inequality (2.3.31) is known as the *inequality of Clausius* (who, in 1854, postulated its existence for an isolated system with $h = 0$ and $q = 0$). In fact, at moment t, this fundamental inequality can be written in a differential form as

$$\frac{dS}{dt} \geq \int_{\Omega} \rho \frac{h}{\theta} d\Omega - \int_{\partial\Omega} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} da \,, \tag{2.3.32}$$

where $\mathbf{q}$ is the *heat flux vector* (directed conventionally towards the interior of Ω, hence the minus sign) and $\mathbf{n}$ is the unit outward normal to $\partial\Omega$. Since entropy is en *extensive* quantity, at time t we can write

$$S(\Omega) = \int_{\Omega} \rho\eta d\Omega \,, \tag{2.3.33}$$

where η is the *specific entropy* at event point $(\mathbf{x}, t)$, $\mathbf{x} \in \Omega$. Then the time derivative present in (2.3.32), d/dt, is the *material time derivative* of continuum mechanics (see below).

The above given formulation brings about a few remarks. First, the above statements and results apply to transformations linking between them states in *equilibrium*. What can we say about the states *outside equilibrium*, i.e., for *thermodynamics* in the full sense of the term? This is the problem to be examined in Chapter 3. As we shall see entropy is still attributed its equilibrium values and the inequality (2.3.32) is to be applied at nearby instants. Equation (2.3.32) is nowadays called the global expression of the *Clausius–Duhem inequality*, so that Duhem, who added the flux term, is associated to Clausius. The volume source term was later added by Truesdell and Toupin (1960). Finally, it must be noted that the *entropy flux*, that we shall denote by $\mathbf{S}$, a vector field, is above assumed to be the ratio of heat flux to temperature, i.e.,

$$\mathbf{S} = \frac{\mathbf{q}}{\theta} \,. \tag{2.3.34}$$

This is *not true* for all theories of continua, in particular in presence of diffusion-like phenomena (when the gradient of state variables is involved in the thermodynamic formulation). Thus it may be wise *not* to suppose (2.3.34) to start with. Such an approach was advocated by I. Müller (1967, 1973), although (2.3.34) may hold in numerous cases indeed. To proceed further we need to introduce a few elements of *continuum mechanics.* That is, in addition to the statements of the first and second laws for a system formed by a material body Ω, we need to postulate the mechanical balance laws and the equation of conservation of mass. For the time being we consider a so-called *simple material body* in the absence of electromagnetic and chemicophysical effects, which is made of just one constituent (all material "points" are made of the *same material*).

Material body: In what follows, a *nondefective material body is a simply connected region B of an Euclidean three-dimensional manifold $\mathcal{M}$, called the* material *manifold. The elements of this manifold are* material points, denoted X. In a system of (possibly but not necessarily) curvilinear coordinates X^K, $K = 1, 2, 3$, this point is simply represented by $\mathbf{X}$.

If the said region of $\mathcal{M}$ is not simply connected, then we say that the material body is *defective* (e.g., it presents voids, inclusions, cracks). It may be that we can replace in thought this multiply-connected Euclidean manifold by a simply connected but then *non-Euclidean* (and sometimes not even *Riemannian*) one as is done in some theories of continuous distributions of structural defects (dislocations, disclinations, see Maugin, 1993a). In what follows we shall stick to the above definition as we shall *not* consider microscopic defects. To each point $\mathbf{X}$ on $\mathcal{M}$ there is attached a density, the *matter density* $\rho_0(\mathbf{X})$ which is the density of matter at the *reference configuration* $\mathcal{K}_R$. This scalar quantity is at most a function of $\mathbf{X}$, when the body is *materially inhomogeneous*, i.e. with material properties (here mass) varying from point to point. For a *homogeneous* body, ρ_0 is a mere constant expressing the *quantity of matter* in Newton's sense. In these conditions, as we all know, density is defined by the limit procedure:

$$\rho = \lim_{\Delta V \to 0} \frac{\Delta m}{\Delta V} \geq 0 , \qquad (2.3.35)$$

where Δm is the total mass contained in a small volume ΔV of B. For *homogeneous* materials, one finds that the limit quantity defined by (2.3.35) is nearly constant when we select ΔV at random in B, under the condition that

ΔV be large enough to erase the ultimate discrete nature of matter. This defines some kind of *critical length* L which delineates in a rather imprecise manner the *macroscopic world* (to which we shall apply *thermomechanics*) and the microscopic world of true particles, lattices and quantum physics.

Then the motion (or deformation) of the material body B of $\mathcal{M}$ is the *time sequence* of the positions (also called *placements*) occupied by the point $\mathbf{X}$ in *Euclidean physical space* $\mathbb{E}^3$, the arena of classical phenomenologic physics. That is, t representing Newtonian absolute time ($t \in \mathbb{R}$), we can write

$$\mathbf{x} = \chi(\mathbf{X}, t) . \tag{2.3.36}$$

The placement $\mathbf{x}$ is usually reported to a Cartesian system of coordinates x^i, $i = 1, 2, 3$.[6] The set of geometrical points $\mathbf{x}(B, t$ fixed) constitutes the *actual* or *current configuration* $\mathcal{K}_t$ of the body B at time t. For a certain time t_0, usually preceding t in the time sequence, we can write

$$\mathbf{x}_0 = \chi(\mathbf{X}, t_0) . \tag{2.3.37}$$

If the functions involved in (2.3.36) and (2.3.37) are sufficiently smooth and, in particular, invertible, then we can rewrite (2.3.36) as

$$\mathbf{x} = \chi(\chi^{-1}(\mathbf{x}_0, t_0), t) = \bar{\chi}(\mathbf{x}_0, t; t_0) = \bar{\bar{\chi}}(\mathbf{x}_0, t) \tag{2.3.38}$$

as t_0 may conventionally be taken as 0. The configuration $\mathcal{K}_{t_0} = \mathcal{K}_0$ of the body $\mathcal{B}$ defined by (2.3.37), and which *does* belong to the sequence of actual configurations, is often referred to as *Lagrangian* after its introduction by J. L. Lagrange (1736–1813) in *fluid mechanics* while $\mathbf{x}$ given by (2.3.38) refers to the *Eulerian representation* (after L. Euler, 1707–1783). From the above we see that the *reference configuration* on the material manifold $\mathcal{M}$ is a somewhat more abstract notion than that of Lagrangian configuration. It was introduced by G. Piola (1848) in a paper of far reaching insight,[7] as this configuration, which corresponds to an ideally unstrained and unloaded configuration, is needed in *solid mechanics* to define the *material symmetry* of the body (it also has to correspond to a minimizer of the energy) while in fluid

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[6] Or, for that matter, any other system of coordinates which fits better the shape of the body and is better suited to the analytical solution of a boundary-value problem than a rectangular one.

[7] The abstract nature of $\mathcal{K}_R$ in Piola is enhanced by the fact that Piola takes it as a configuration of *a priori* uniform matter density conventionally normalized to unity.

mechanics, for *ideal* fluids (those which present neither *deformable* nor *rigid but orientable microstructure*), any configuration, including the current one, is as good as another for an inclusive description of the material properties of the continuum. Thus the x_0^i, $i = 1, 2, 3$, are referred to as *Lagrangian* coordinates, and the X^k as *material* coordinates. We shall use only the latter (see Fig. 2.2). More detailed elements of continuum kinematics and of deformation theory will be introduced when the need arises.[8]

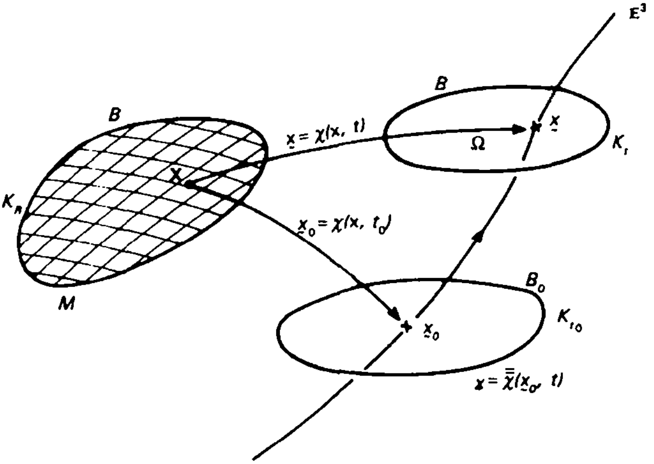

Fig. 2.2. General kinematics of a continuum

Let $\mathcal{B} = \Omega$ the image of B at time t in physical space. Then we have the following balance laws in the absence of electromagnetic and physico-chemical couplings:

(i) Conservation of mass:

$$\frac{d}{dt} m(\mathcal{B}) = 0\,, \qquad m(\mathcal{B}) = \int_\Omega dm\,, \qquad dm = \rho d\Omega\,, \tag{2.3.39}$$

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[8] This book is *not* a textbook on continuum mechanics for which there exist many valuable introductions and treatises; in the first class, see e.g., Eringen (1980), Germain (1973), Maugin (1988, Chapter 3), and in the second class, Eringen and Maugin (1990), Truesdell and Toupin (1960), Truesdell and Noll (1965).

where dm is a *mass measure* and ρ is the image by (2.3.36) of the matter density ρ_0, i.e.

$$\rho(\mathbf{x},t) = \rho_0(\mathbf{X})J_F^{-1}\,, \tag{2.3.40}$$

where

$$J_F = \det F \geq 0\,, \qquad \mathbf{F} := \nabla_R \chi \equiv \frac{\partial \chi}{\partial \mathbf{X}}\,. \tag{2.3.41}$$

Here $\mathbf{F}$ is the so-called *motion gradient* (a denomination that we prefer over that of "deformation gradient"). The *direct motion* $\chi(\mathbf{X},t)$ has been assumed smooth enough for the definition of $\mathbf{F}$ to make sense and the fact that J_F keeps in one sign (say +) during motion. Thus χ is invertible (this was already used for writing (2.3.39)) and we call *inverse motion* the mapping of $\mathbb{E}^3$ onto $\mathcal{M}$ at fixed t given by

$$\mathbf{X} = \chi^{-1}(\mathbf{x},t)\,, \tag{2.3.42}$$

so that the inverse-motion gradient $\mathbf{F}^{-1}$ given by

$$\mathbf{F}^{-1} := \nabla\chi^{-1} \equiv \frac{\partial \chi^{-1}}{\partial \mathbf{x}}\,. \tag{2.3.43}$$

is well defined. It is readily checked that $\mathbf{F}^{-1}$ indeed is the inverse of $\mathbf{F}$ at fixed t, so that we have the identities

$$\mathbf{F}.\mathbf{F}^{-1} = \mathbf{1}\,, \qquad \mathbf{F}^{-1}.\mathbf{F} = \mathbf{1}_R\,, \tag{2.3.44}$$

where the symbols $\mathbf{1}$ and $\mathbf{1}_R$ represent the unit dyadics in $\mathbb{E}^3$ and on $\mathcal{M}$, respectively. It must be emphasized that both $\mathbf{F}$ and $\mathbf{F}^{-1}$ are *not* tensors *per se*, as they are geometric objects defined on *two manifolds* simultaneously (i.e. in a picturesque language, they have one foot in $\mathcal{K}_t$ and one foot in $\mathcal{K}_R$; their components are F_K^{-1} and $(\mathbf{F}^{-1})_i^K$, respectively; such objects are *two-point fields*). Speaking of their symmetry, for instance, has no meaning. Equation (2.3.40) is none other than the *integral* of the local form of (2.3.39).

(ii) Balance of linear momentum (physical momentum):

$$\frac{d}{dt}\int_\Omega \mathbf{v}dm = \int_\Omega \mathbf{f}\,dm + \int_{\partial\Omega} \mathbf{T}^d da\,, \tag{2.3.45}$$

where $\mathbf{f}$ is a *physical* force acting per unit mass of the body and $\mathbf{T}^d$ is a *physical* force, called *traction*, acting per unit area of the boundary $\partial\Omega$. The field $\mathbf{v}$ is the *physical velocity* defined from the direct motion mapping (2.3.36) by

$$\mathbf{v} := \left.\frac{\partial \chi}{\partial t}\right|_{\mathbf{X}} . \tag{2.3.46}$$

The formulation (2.3.45) of the balance of physical momentum — the vector $\rho\mathbf{v}$, per unit volume of Ω, in E^3 — emphasizes the physical nature (action of gravity or electromagnetic fields) of the force $\mathbf{f}$. Equation (2.3.45) is complemented by the

(iii) Balance of angular (or moment of) momentum:

$$\frac{d}{dt}\int_\Omega \mathbf{x}\times\mathbf{v}dm = \int_\Omega \mathbf{x}\times\mathbf{f}dm + \int_{\partial\Omega} \mathbf{x}\times\mathbf{T}^d da\,, \tag{2.3.47}$$

where × denotes the vector product. Equation (2.3.47) which accounts for Newton's third law (that of action and reaction) does not bring any new concept into the picture in the absence of *body couples*, which is the case in the present situation (see further developments below).

As we know from continuum mechanics, the application of (2.3.45) to an infinitesimal tetrahedron following a celebrated argument of A.-L. Cauchy (1789–1857) which marked in 1828 the very beginnings of continuum physics (independently of any microscopic *discrete* model), leads to the introduction of the notion of *Cauchy's stress tensor*, i.e. the fact that the *natural boundary condition* at $\partial\Omega$ reads

$$\sigma\cdot\mathbf{n} = \mathbf{T}^d \qquad \text{or} \qquad \sigma_{ij}n_j = T_i^d\,, \tag{2.3.48}$$

where the last form has been expressed in Cartesian tensor components on account of Einstein's summation rule on dummy indices. The *material time derivative* present in Eqs. (2.3.45) and (2.3.47) is such that

$$\frac{d}{dt}\int_\Omega A\,dm = \int_\Omega \frac{dA}{dt}dm\,. \tag{2.3.49}$$

This is a direct consequence of the conservation of mass (2.3.39). It must be understood that the symbolism dA/dt here means

$$\frac{dA}{dt} = \left.\frac{\partial A}{\partial t}\right|_{\mathbf{X}} = \left.\frac{\partial \bar{A}}{\partial t}\right|_{x} + (\mathbf{v}\cdot\nabla)\bar{A}\,, \tag{2.3.50}$$

depending on whether A is expressed as a function of $(\mathbf{X}, t)$ or $(\mathbf{x}, t)$, i.e. $A(\mathbf{X}, t) = A(\chi^{-1}(\mathbf{x}, t), t) = \bar{A}(\mathbf{x}, t)$. Using then a classical *localization argument* *based on the* assumed continuity of all fields, (2.3.45) and (2.3.47) yields the following local field equations on account of the introduction of σ:

Local balance of physical momentum:

$$\rho\frac{d\mathbf{v}}{dt} = \operatorname{div}\sigma + \rho\mathbf{f} \qquad \text{or} \qquad \rho\dot{v}_i = \sigma_{ij,j} + \rho f_i \tag{2.3.51}$$

at all points $\mathbf{x}$ in Ω, and

Local balance law of angular momentum:

$$\sigma = \sigma^T \qquad \text{or} \qquad \sigma_{ij} = \sigma_{ji}\,, \tag{2.3.52}$$

which expresses the symmetry of Cauchy's stress tensor in the absence of body couples. The superscript T indicates *transposition* as explained in the second of (2.3.52).

For completeness we must formulate the *first law of thermodynamics* for a continuous body B. This reads:

$$\frac{d}{dt}(K(B) + E(B)) = \mathcal{P}_{\text{ext}}(B) + \dot{Q}(\bar{B})\,, \tag{2.3.53}$$

where K is the total kinetic energy, E is the total internal energy, $\mathcal{P}_{\text{ext}}$ is the mechanical power expanded by *applied forces* both in the bulk and at the bounding surface, and $\dot{Q}$ is the total heat received by radiation or conduction by the body. As kinetic energy and internal energy are extensive, we have

$$K(B) = \int_\Omega \frac{1}{2}\mathbf{v}^2 dm\,, \qquad E(B) = \int_\Omega e dm\,, \tag{2.3.54}$$

where e is the *internal energy per unit mass* of the body. Finally, according to (2.3.45) on the one hand and in agreement with (2.3.42) on the other hand, we have the following expressions for the source terms in (2.3.53):

$$\mathcal{P}_{\text{ext}}(B) = \int_\Omega \mathbf{f}.\mathbf{v} dm + \int_{\partial\Omega} \mathbf{T}^d.\mathbf{v} da\,, \tag{2.3.55}$$

and

$$\dot{Q}(\bar{B}) = \int_\Omega h dm - \int_{\partial\Omega} \mathbf{q}.\mathbf{n} da\,. \tag{2.3.56}$$

With Eqs. (2.3.39), (2.3.45), (2.3.47), (2.3.53) and (2.3.32) we have at hand all the global balance or inequality equations governing the thermomechanics of *continuous bodies* made of *simple materials.*

Principle of virtual power: The following *variational* or *weak* formulation of mechanical balance laws is equivalent to Eqs. (2.3.45) and (2.3.47) when $\mathbf{v}^*$ is an arbitrary continuous virtual velocity field defined on Ω and $\partial\Omega$:

$$\mathcal{P}^*_{(a)} = \mathcal{P}^*_{(i)} + \mathcal{P}^*_{(b)} + \mathcal{P}^*_{(c)}, \tag{2.3.57}$$

where

$$\mathcal{P}^*_{(a)} = \int_\Omega \frac{d\mathbf{v}}{dt}.\mathbf{v}^* dm, \tag{2.3.58}$$

$$\mathcal{P}^*_{(i)} = -\int_\Omega \rho^{-1}\sigma : \mathbf{D}^* dm, \tag{2.3.59}$$

$$\mathcal{P}^*_{(b)} = \int_\Omega \mathbf{f}.\mathbf{v}^* dm, \tag{2.3.60}$$

and

$$\mathcal{P}^*_{(c)} = \int_{\partial\Omega} \mathbf{T}^d.\mathbf{v}^* da, \tag{2.3.61}$$

where (tr = trace)

$$\sigma : \mathbf{D}^* = \mathrm{tr}(\sigma D^*) = \sigma_{ij} D^*_{ji} \tag{2.3.62}$$

with

$$\mathbf{D}^* := (\nabla \mathbf{v}^*)_s, \qquad \text{i.e.} \qquad D^*_{ij} = \frac{1}{2}(v^*_{i,j} + v^*_{j,i}) = D^*_{ji}. \tag{2.3.63}$$

The equivalence between *d'Alembert's formulation* (2.3.57) and *Newton's formulation* (2.3.45) and (2.3.47) follows from the fact that (2.3.57) in particular holds true for $\mathbf{v}^*$ fields which correspond to a *rigid-body motion* for which $\mathbf{D}^* = 0$ at t for all $\mathbf{x}$s. (see Maugin, 1980, 1988, pp. 78–79). The *d'alembert formulation* is closer to the spirit of modern applied mathematics, distribution theory, and numerical analysis (e.g. finite-element method). Verbally, however, (2.3.57) reads: *the virtual power of acceleration* (or inertial) *forces in a continuous body is balanced by the sum total of the virtual powers of all types of external and internal forces impressed on the body either at distance* (body forces) *or by contact* (tractions), *and internally* (stresses). In particular, for a *real velocity field* v (no asterisk), i.e. that field which corresponds to the actual solution of the dynamical problem, the statement (2.3.57) produces the global equation:

$$\frac{d}{dt}K(B) = \mathcal{P}_{(i)} + \mathcal{P}_{\text{ext}}\,, \tag{2.3.64}$$

where the quantity $\mathcal{P}_{\text{ext}}$ has already been defined in (2.3.55).

A straightforward combination of (2.3.53) and (2.3.64) then yields the so-called *theorem of energy*:

$$\frac{d}{dt}E(B) + \mathcal{P}_{(i)} = \dot{Q}(\bar{B})\,. \tag{2.3.65}$$

The *thermodynamics* of continuous bodies made of a simple material is encapsulated in the global formula (2.3.65), a statement of the first law on account of the mechanical balance laws, and (2.3.32), the statement of the second law. For sure, in the presence of motion (2.3.36) or (2.3.42), we need a true *thermodynamics* as the time evolution, unless it takes place at a sufficiently slow pace, is a true *dynamic process*. Thermodynamics *per se*, in various guises, is the subject matter of Chapter 3.

Chapter 3

VARIOUS THERMODYNAMICS

"So many thermodynamicists,
so many thermodynamics !"
(a faked true common citation)

3.1. Preliminary Remarks

Thermo-*dynamics* has a wealth of applications and several presentations. Applications shall be dealt with in Chapters 6 to 10. Here we focus on its various representations. Among these presentations, some are more "traditional" and others more adventurous. Some are based on microscopic insight, others discard any "atomic" basis. Some exploit the experience acquired in thermo-*statics*, others simply ignore it. Some specify how little far-from-equilibrium their validity stands, others claim a general validity truly *outside equilibrium*. Some use a classical balance-law postulational approach, others claim a variational basis. By combining all these possibilities we see that the variety of presentations and justifications has a natural tendency to become isomorphic to the number of thermodynamicists. We shall restrict ourselves to giving limited information on the most adventurous presentation, that of *rational thermodynamics* which ignores altogether the acquired experience of thermostatics and claims the largest validity outside equilibrium (Sec. 3.3), and on the recent approach known as *extended thermodynamics* on account of its (in our opinion) lack of versatility (at least for the moment — see Sec. 3.4), to concentrate on the accepted formulation known as the *theory of irreversible processes* (*T.I.P.*). The latter builds on the experience gained in thermostatics and modestly envisages only slight deviations from equilibrium (Sec 3.2). We shall also pay extensive attention to its modern generalization to which most of the book is in fact devoted, the *thermodynamics with* *internal variables* (for short *T.I.V.*). This one cautiously builds on the previous knowledge of thermostatics while enlarging the theory of irreversible processes so as to include a large variety of phenomena as well as *nonlinear* irreversible processes (Sec. 3.5 and further chapters). In doing so we follow the advice of Duhem, Bridgman and Kestin while bringing an efficiency, both physical and mathematical, to the thermodynamical description of physical phenomena that no other approach has so far attained.

3.2. Theory of Irreversible Processes (*T.I.P.*)

A. Axiom of local state

This approach is the most standard, and most widely accepted by physicists and physico-chemists alike. It is exemplified by the now classical treatise of de Groot and Mazur (1962).[1] Relating to small deviations from equilibrium, it is supported by a microscopic analysis which was achieved in celebrated works by Onsager (1931) and Casimir (1945). For our present purpose it suffices to emphasize the role played in *T.I.P.* by the *axiom of local* (equilibrium) state that we can state thus:

Axiom of local (equilibrium) state. *Each part Ω of a material system S can be approximately considered, at each time t, as being in thermal equilibrium.*

In other words, a thermo-*dynamic* process *close* to equilibrium can be viewed as a sequence of thermostatic equilibria and this allows us to grant to *entropy*

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[1] There exists a wealth of books presenting *T.I.P.* in various degrees of rigor and generality, among these, in alphabetic order: Fitts (1962), de Groot (1951), de Groot and Mazur (1962, reprint 1986), Haase (1968), Katchalsky and Curran (1965), Lavenda (1978), Meixner and Reik (1959), Prigogine (1947), Stueckelberg and Scheurer (1974), Sychev (1981, 1983), Wisniewski *et al.* (1976), Woods (1975). The most persuasive presentation remains that of de Groot and Mazur. The most critical and rigorous is that of Woods. Papers such as those of Eckart (1940, 1948) and Eringen (1960) were instrumental in reconciliating *T.I.P.* and continuum mechanics. Rather original in its presentation based on some variational formulation is the book of Gyarmati (1970), an author who founded a true Hungarian school of thermodynamics. Classical *T.I.P.* was much publicized by many publications in the journal *Physica* published in the Netherlands by Elsevier. Both *T.I.P.* and its generalizations have received the forum of the *Journal of Non-Equilibrium Thermodynamics* (de Gruyter, Berlin). The series of books on *Non-Equilibrium Thermodynamics* edited by P. Salamon and S. Sieniutycz at Taylor and Francis, Washington (1991), is also a fruitful source of expositions by various active contributors.

and *temperature* their usual thermostatic definitions. That is, at each moment t there exists a set of *normal* extensive state variables χ_α, $\alpha = 0, 1, \ldots, n$, $\chi_0 = \eta$ the *specific entropy*, and a specific *internal energy* $e(\chi_\alpha)$ such that the temperature θ and the *laws of state* for τ_β, $\beta = 1, \ldots, n$ are given by

$$\theta = \frac{\partial e}{\partial \eta} > 0, \qquad \tau_\beta = \frac{\partial e}{\partial \chi_\beta}\,. \tag{3.2.1}$$

One must naturally make the notion of *closeness to equilibrium* more precise. This is achieved by introducing *time scales* and *length scales*. In effect, first the *closeness to equilibrium* may be measured at each spatial location by the ratio of the characteristic response time τ_R which allows the thermostatic system to recover a new state of thermostatic equilibrium to the characteristic duration τ_M of the kinematic and dynamic evolution of the material medium. Inspired by rheology (Reiner, 1964) we may call *Deborah number* $\mathcal{D}e$[2] this ratio which, for *T.I.P.* to apply must be very small. That is,

$$(\mathcal{D}e)_{\text{TIP}} = \tau_R/\tau_M \ll 1\,. \tag{3.2.2a}$$

This will prove impracticable each time that the evolution of the system is *too fast* (e.g. in a shock-like evolution). The listing of characteristic times in Sec 2.1 is a useful guide to decide on the validity of the application of *T.I.P. in* many rather complex situations. In many cases the smallness of $\mathcal{D}e$ indicates that the response time inherent in *perturbations* of a thermal equilibrium is such that the relevant subsystem will recur to a new equilibrium state in a much shorter time than the typical duration of kinematical (e.g. flow rate) or dynamical (inverse frequency) evolutions so that one can indeed attribute to the entropy its equilibrium value and apply the inequality (2.3.31) at nearby instants, i.e. the expression (2.3.32) of the *global Clausius-Duhem inequality*.

In the beginning of the reasoning made on time scales we indicated the local spatial validity of the present argument if we remember that thermostatics is also based on the notion of *spatially uniform systems*. Thus closeness to equilibrium should ideally be defined in *space-time* as it also imposes some condition on the *gradient* of variables of state during a true thermo-*dynamic* evolution (remember that heat conduction itself involves the *gradient* of temperature, but there will be many other processes in the same class). We expect that all gradients involved will be such that

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[2] Remember the biblical saying: "*and Deborah saw the mountain flowing before her...*" (free translation, G.A.M.). Deborah's time scale is the geological one if we admit with Heraclitus (circa 544–483 B.C.), that everything, including mountains, can flow: παντα ρει.

$$\lambda := \frac{\chi/L}{|\nabla\chi|} \gg 1\,, \tag{3.2.2b}$$

where χ is a typical variable of state, $\nabla\chi$ is its "microscopic" gradient, and L is a macroscopic length scale — hence macroscopic gradients are much less "stiff" than microscopic ones. As a matter of fact, adopting Bridgman's point of view of pencil and paper experiments, we note that instruments (e.g. a thermometer) used in measuring thermodynamic features measure gross quantities and disregard the small length scale strong gradients to capture only those gradients that are significant over a relatively large length scale.[3] The list of characteristic length scales given in Sec 2.1 will be useful in assessing whether a physical dissipative phenomenon involving spatial *dis*-uniformities is amenable through the methodology of *T.I.P.*

Equations (3.2.1) are *state laws*: the expression and validity of these laws are justified by the corresponding relations valid in thermostatics — where the internal energy plays the role of a potential — and also by the axiom of local (equilibrium) state. Here

$$e = e(\eta, \chi_\beta)\,. \tag{3.2.3}$$

The *first law* can be locally rewritten as

$$\dot{e} = \theta\dot{\eta} + \omega, \qquad \omega = \sum_{\beta=1}^{n} \tau_\beta \dot{\chi}_\beta = \underline{\tau}\cdot\underline{\chi}\,\cdot \tag{3.2.4}$$

We may also refer to this as *Gibbs' equation.* A *dual formulation* makes use of the partial Legendre transformation

$$\psi := e - \eta\theta, \quad \eta = -\frac{\partial\psi}{\partial\theta}, \quad \tau_\beta = \frac{\partial\psi}{\partial\chi_\beta}\,, \tag{3.2.5}$$

where ψ is the *Helmholtz free energy* per unit mass. Simultaneously, the *second law* (2.3.32), under appropriate continuity conditions for the integrands, reads in local (in time and position) form:

$$\rho\dot{\eta} \geq \rho(h/\theta) - \nabla\cdot(\mathrm{q}/\theta)\,, \tag{3.2.6}$$

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[3] According to Bachelard (1927): "...*C'est l'ordre de grandeur qui, à lui seul, crée le phénoméne. Si la longueur d'onde* λ *n'était pas assez grande pour enjamber en quelque sorte les discontinuités de la distribution punctiforme, la confusion s'établirait... La grandeur de la quantité* λ *relativement aux distances interatomiques, détermine une solidarité qui calque la continuité...*" (This was written apropos heat conduction; "distances interatomiques" could be replaced by "*mean free path*", or "*lattice spacing*" depending on the application envisaged).

where ρ is the matter density at time t, $\mathbf{q}$ is the heat-flux vector, and h is the heat source per unit mass. The *dissipation* Φ *per unit volume* is then obtained by combining (3.2.4) and (3.2.6). That is,

$$\Phi = \rho(\dot{e} - h + \rho^{-1}\nabla \cdot \mathbf{q} - \omega) + \theta\mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0 \,. \tag{3.2.7}$$

B. Application to deformable material continua:

In this case the localization of Eq. (2.3.65) immediately gives:

$$\rho\dot{e} = \sigma : \mathbf{D} - \nabla \cdot \mathbf{q} + \rho h \,, \tag{3.2.8}$$

with the notation of (2.3.62), whence (3.2.7) takes on the reduced form:

$$\Phi = \Phi_{\mathrm{intr}} + \Phi_{\mathrm{th}} \geq 0 \,, \tag{3.2.9}$$

where the *intrinsic* and *thermal dissipation* have been defined in general by

$$\Phi_{\mathrm{intr}} := \sigma : \mathbf{D} - \rho\omega, \qquad \Phi_{\mathrm{th}} = \theta\mathbf{q} \cdot \nabla(\theta^{-1}) \,. \tag{3.2.10}$$

Sometimes stronger conditions than (3.2.9) are imposed, e.g.,

$$\Phi_{\mathrm{intr}} \geq 0, \qquad \phi_{\mathrm{th}} \geq 0 \,, \tag{3.2.11}$$

separately. The first of these is known as the *Clausius-Planck inequality*. The second one expresses the intuitive condition that heat flows in the direction of negative gradients of temperature. According to the weaker condition (3.2.9), the second of conditions (3.2.11) may no longer hold true when there is intrinsic dissipation. In the present case, Φ_{intr} takes on the following simple form that results solely from deformation processes:

$$\Phi_{\mathrm{intr}} = \sigma : \mathbf{D} - \rho\omega = -(p_{(i)} + \rho\omega) \,, \tag{3.2.12}$$

where, compared to (2.3.52), $p_{(i)}$ is the power developed by internal forces per unit volume in the current configuration $\mathcal{K}_t$. We can also work per unit volume of the *reference configuration* $\mathcal{K}_R$. In that case it is fitting to introduce the *first Piola-Kirchhoff stress* $\mathbf{T}$ *and the material heat flux vector* $\mathbf{Q}$ *by the convection* formulas:

$$\mathbf{T} = J_F\mathbf{F}^{-1} \cdot \sigma, \qquad \mathbf{Q} = J_F\mathbf{F}^{-1} \cdot \mathbf{q} \,, \tag{3.2.13}$$

so that by taking note of the demonstrable identities

$$\nabla \cdot (J_F^{-1}\mathbf{F}) = \mathbf{0}, \qquad \nabla_R \cdot (J_F \mathbf{F}^{-1}) = 0\,, \tag{3.2.14}$$

and accounting for (2.3.40), we find that (2.3.51) and (2.3.52) are replaced by

$$\rho_0 \left.\frac{\partial \mathbf{v}}{\partial t}\right|_{\mathbf{X}} = \mathrm{div}_R \mathbf{T} + \rho_0 \mathbf{f} \quad \text{or} \quad \rho_0 \frac{\partial \mathbf{v}^i}{\partial t} = T^i_{\cdot K,K} + \rho_0 \mathbf{f}^i\,, \tag{3.2.15}$$

and

$$\mathbf{T} \cdot \mathbf{F}^T = \mathbf{F} \cdot \mathbf{T}^T \quad \text{or} \quad \mathbf{T}^i_{\cdot K} F^j_{\cdot L} \delta^{KL} = T^j_{\cdot K} F^i_{\cdot L} \delta^{KL}\,, \tag{3.2.16}$$

while (3.2.9) takes on the form

$$\Phi_R = J_F \Phi = \mathrm{tr}\,(\dot{\mathbf{T}}\mathbf{F}) - \rho_0 \omega + \theta \mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0\,. \tag{3.2.17}$$

The *convection operation* (on *one* index) defined in (3.2.13) is called the *Piola transformation* (after Piola, 1848). The relationship between $\mathbf{D}$ and $\dot{\mathbf{F}}$ is as follows:

$$\dot{\mathbf{F}} = \mathbf{L} \cdot \mathbf{F}, \qquad \dot{\mathbf{F}} = \left.\frac{\partial}{\partial t}\mathbf{F}\right|_{\mathbf{X}} = \nabla_R \left(\frac{\partial \chi}{\partial t}\right) = \nabla_R \mathbf{v}\,, \tag{3.2.18}$$

and

$$\mathbf{L} = \nabla \mathbf{v} = \dot{\mathbf{F}} \cdot \mathbf{F}^{-1}, \qquad \mathbf{D} = \mathbf{L}_s = \mathrm{sym}\,\mathbf{L}\,, \tag{3.2.19}$$

where sym denotes the action of taking the symmetric part.

For *small strains*, we introduce the *displacement vector* $\mathbf{u}$ and the *infinitesimal strain* ε by

$$\mathbf{F} = \mathbf{1} + \nabla_R \mathbf{u}(\mathbf{X}, t), \qquad \mathbf{v} = \dot{\mathbf{u}}(\mathbf{X}, t)\,, \tag{3.2.20}$$

and

$$\nabla \mathbf{u} = (\mathbf{F}^{-1})^T \cdot \nabla_R \mathbf{u} \cong \nabla_R \mathbf{u}, \qquad \varepsilon = \mathrm{sym}\nabla \mathbf{u} \equiv (\nabla \mathbf{u})_s\,, \tag{3.2.21}$$

where we no longer distinguish between the reference and the current configurations. In these conditions we obtain the dissipation inequality in the form:

$$\Phi_R \cong \Phi = \sigma : \dot{\varepsilon} - \rho\omega + \theta \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0\,, \tag{3.2.22}$$

i.e.

$$\Phi_{\text{intr}} = \sigma : \dot{\varepsilon} - \rho\omega\,. \tag{3.2.23}$$

We are now in a position to illustrate the exploitation of *T.I.P.* in some simple paradigmatic cases.

C. The compressible Newtonian fluid

In that case we take $e = \hat{e}(\eta, \tau)$, where τ is the specific volume ($\tau = \rho^{-1}$). Equations (3.2.1) read:

$$\theta = \frac{\partial \hat{e}}{\partial \eta}, \qquad p = -\frac{\partial \hat{e}}{\partial \tau}, \tag{3.2.24}$$

and on account of the *continuity equation* (2.3.40) that we can rewrite in any of the following two forms:

$$\dot{\rho} + \rho \operatorname{tr} \mathbf{D} = 0 \quad \text{or} \quad \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \tag{3.2.25}$$

we note that the dissipation inequality (3.2.10) takes on the form

$$\Phi = \sigma^D : \mathbf{D} + \theta \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0, \tag{3.2.26}$$

with

$$\sigma^D := \sigma + p\mathbf{1} \quad \text{since} \quad \rho\omega = -p \operatorname{tr} \mathbf{D} = -(p\mathbf{1}) : \mathbf{D}. \tag{3.2.27}$$

The simplifcation of *T.I.P.* now consists of rewriting (3.2.26) as

$$\Phi = \sigma^D : \mathbf{D} - \theta_0^{-1} \mathbf{q} \cdot \nabla \theta \geq 0, \tag{3.2.28}$$

where θ_0 is the ambient temperature (spatially uniform reference temperature about which θ varies only slightly) and considering *linear relationships* between the so-called *dissipative fluxes* σ^D and $\mathbf{q}$ and their "causes", referred to as *forces* in general (although $\nabla\theta$ does not appear as such at a macroscopic scale). We shall return to this practice in due time. For the time being we simply note that a **Newtonian fluid** is often considered as a *viscous*, i.e. dissipative, fluid, which is *incompressible* (or practically so). If this is indeed the case then we have to enforce the mathematical constraint of *incompressibility* in the form (this also refers to *isochoric* flows)

$$\nabla \cdot \mathbf{v} = \operatorname{tr} \mathbf{D} = 0. \tag{3.2.29}$$

As a consequence both ρ and τ are constants, and (3.2.29) is taken into account through the introduction of a Lagrange multiplier, called the *mechanical pressure* π (an unknown scalar field to be determined upon solving a well-posed boundary-value problem). The Cauchy stress tensor σ now is defined up to the isotropic stress field $-\pi\mathbf{1}$, while, clearly, only the *deviatoric part of* $\mathbf{D}$ *is involved*, since

$$\sigma = \sigma^d + \frac{1}{3}\,\mathrm{tr}\,\sigma\mathbf{1}\,, \tag{3.2.30}$$

in general, where σ^d denotes the *deviator* of σ. The resulting *residual dissipation inequality* reads

$$\Phi = \sigma^D : \mathbf{D}^d - \theta_0^{-1}\mathbf{q}\cdot\nabla\theta \geq 0\,, \qquad \sigma^D := \sigma^d + \pi\mathbf{1}\,, \tag{3.2.31}$$

where $\mathbf{D}^d$ is the deviator of $\mathbf{D}$. Classically (*T.I.P.*) one assumes that σ^D and $\mathbf{q}$ have expressions given by

$$\sigma^D = 2\eta_v\mathbf{D}^d, \qquad \mathbf{q} = -\chi\nabla\theta\,, \tag{3.2.32}$$

with $\eta_v(\theta_0) \geq 0$ and $\chi(\theta_0) \geq 0$, so that the inequality (3.2.30) is identically satisfied. This is a naive application of *T.I.P.* (see below). The second of (3.2.32) is known as *Fourier's law of heat conduction* for isotropic bodies (although the notion of heat vector was introduced only later by W. Thomson so that Fourier did not have a clear idea of a *constitutive equation*). Now back to the compressible case. Had we not assumed incompressibility, the whole of $\mathbf{D}$ would have remained involved in the dissipation inequality (3.2.26). In that case, still for *isotropy*, the first of (3.2.32) would be replaced by the more general formula:

$$\sigma^D = \eta_{v1}(\theta_0)(\mathrm{tr}\,\mathbf{D})\mathbf{1} + 2\eta_{v2}(\theta_0)\mathbf{D}\,, \tag{3.2.33}$$

with the constitutive inequalities

$$3\eta_{v1} + 2\eta_{v2} \geq 0\,, \qquad \eta_{v2} \geq 0\,, \tag{3.2.34}$$

which we ask the reader to establish by himself, by substituting (3.2.33) and the second of (3.2.32) — still valid — into (3.2.26). We have indicated a possible dependence of the coefficients on the ambient temperature; a dependence on τ or ρ is not ruled out by the second law of thermodynamics, but is not indicated here. A fluid is said to be *Stockesian* when the viscosity coefficients η_{v1} and η_{v2} jointly satisfy the condition of *vanishing bulk viscosity*:

$$3\eta_{v1} + 2\eta_{v2} = 0\,. \tag{3.2.35}$$

The expression in the left-hand side of this expression stems from the fact that, on account of the general decomposition (3.2.30) for a second-order symmetric tensor, (3.2.33) can also be written as

$$\sigma^D = 2\eta_{v2}\mathbf{D}^d + \frac{3\eta_{v1} + 2\eta_{v2}}{3}(\operatorname{tr}\mathbf{D})1\,, \tag{3.2.36}$$

thus separately emphasizing the pure shear (term in $\mathbf{D}^d$) and bulk behaviors of the fluid's response.

D. The linear viscoelastic solid

In this case we start with $e = \hat{e}(\varepsilon, \eta)$, so that Eqs. (3.2.1) read

$$\theta = \frac{\partial \hat{e}}{\partial \eta}\,, \qquad \sigma^e = \rho\frac{\partial \hat{e}}{\partial \varepsilon}\,. \tag{3.2.37}$$

The dissipation inequality (3.2.22) takes on the following form.

$$\Phi = \sigma^D : \dot{\varepsilon} - \theta_0^{-1}\mathbf{q}\cdot\nabla\theta \geq 0\,, \qquad \sigma^D = \sigma - \sigma^e\,, \tag{3.2.38}$$

where σ^e may legitimately be referred to as the *elastic* (*thermodynamic*) *stress* and σ^D the *viscous stress* (this by analogy with the fluid case). Here we have a better application of *T.I.P.*, especially for *anisotropic media* such as *crystals* which are solids in small strains (typically strains of the order of 10^{-4} in ultrasonic experiments). So-called *complementary laws* (constitutive equations) for the dissipative fields σ^D and $\mathbf{q}$ can be looked for as linear combinations of $\dot{\varepsilon}$ and $\nabla\theta$. That is, one will *a priori* write

$$\begin{aligned} \sigma^D &= \mathbf{N}[\mathbf{D}] + \mathbf{A}[\mathbf{g}]\,, \\ \mathbf{q} &= \mathbf{B}[\mathbf{D}] - \chi_0[\mathbf{g}]\,, \end{aligned} \tag{3.2.39}$$

where we set $\mathbf{g} = \nabla\theta$ and $\mathbf{N}$, $\mathbf{A}$, $\mathbf{B}$ and χ_0 are linear operators. Thus they are represented by Cartesian tensors of fourth, third, third, and second order, respectively. On substituting from (3.2.39) into (3.2.38) we see that *it is sufficient* to consider $\mathbf{N}$ as a *symmetric application* of the set of second-order tensors onto itself, χ_0 as a *symmetric application* of the set of polar vectors onto itself and that $\mathbf{A}$ and $\mathbf{B}$ may, without loss in generality, satisfy the following symmetries:

$$A_{jik} = A_{ijk}\,, \qquad B_{ijk} = B_{ikj}\,. \tag{3.2.40}$$

For *materials having a center of symmetry*, the tensors $\mathbf{A}$ and $\mathbf{B}$ have identically vanishing components. In *this case* from (3.2.39) there remains the linear relationships:

$$\sigma_{ij}^D = \mathbf{N}_{ijkl}\dot{\varepsilon}_{kl}\,, \qquad \mathbf{q}_i = -\chi_{oij}\theta_{,j}\,. \tag{3.2.41}$$

If we further specify $\hat{e}(\varepsilon, \eta)$, for instance in the form of an expansion limited to the second order in the components of ε and the small deviation $\bar{\eta} = \eta - \eta_0$, from a spatially uniform equilibrium value η_0, then Eqs. (3.2.37) and (3.2.41) provide a complete set of constitutive equations for the *thermoelasticity of viscous, heat conducting anisotropic (but homogeneous) solids* in small strains, e.g. a *crystal that presents a center of symmetry.* For an *isotropic material* (very special case of the above where full isotropy includes invariance under the *full orthogonal* group and under reflection of axes of Eqs. (3.2.37) and (3.2.41), then $\hat{e}$ can depend on ε only through its elementary invariants, and according to a well-known irreducible representation due to Racah (1933), the surviving linear operators $\mathbf{N}$ and χ_0 takes on the following form:

$$\begin{aligned} N_{ijkl} &= \eta_{vl}\delta_{ji}\delta_{kl} + \eta_{v2}(\delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik})\,, \\ \chi_{0ij} &= \chi_0\delta_{ij}\,, \end{aligned} \tag{3.2.42}$$

where δ_{ij} is Kronecker's symbol. As a consequence, σ^D and $\mathbf{q}$ acquires practically the same form as for a compressible viscous fluid. That is,

$$\begin{aligned} \sigma_{ij}^D &= \eta_{v1}(\theta_0)(\operatorname{tr}\dot{\varepsilon})\delta_{ij} + 2\eta_{v2}(\theta_0)\dot{\varepsilon}_{ij}\,, \\ \mathbf{q} &= -\chi(\theta_0)\nabla\theta\,, \end{aligned} \tag{3.2.43}$$

whose coefficients satisfy the same inequalities as (3.2.33) and $\chi \geq 0$. The dissipation inequality does *not* rule out a dependency of these coefficients on the principal invariants of ε, but this is not indicated here in the equations as this dependency is seldom considered. A solid that exhibits *linear elasticity* (derived from an energy $\hat{e}$ quadratic in the components of the strain ε) *additively* combined to a *viscous* behavior described by $(3.2.41)_1$ or $(3.2.43)_1$ is called a *Kelvin–Voigt linear viscoelastic solid,* after the theoretical representation introduced by W. Voigt (1850–1919) in 1891 and the original idea of W. Thomson (Lord Kelvin).

We see in passing from (3.2.39) to (3.2.41) that Nature here refuses a coupling of dissipative processes between effects which are represented by tensorial objects of differing orders. This has often been considered as another manifestation of the principle of *symmetry* attributed to P. Curie. It also seems to be a tenet of many applications of *T.I.P.* in the form of the so-called *symmetry relations* of Onsager and Casimir. But the application of this restriction must be considered much more precautiously than this simple remark indicates (see the general presentation below).

E. Finite-strain behavior of a solid

On account on the remark on admissible length scales the motion gradient must still remain small in some sense. Here we consider $\hat{e}(\mathbf{F}, \eta)$ and have to exploit the dissipation inequality (3.2.17). Here Eqs. (3.2.1) read

$$\theta = \frac{\partial \hat{e}}{\partial \eta}, \qquad \mathbf{T}^e = \rho_0 \left(\frac{\partial \hat{e}}{\partial \mathbf{F}} \right)^T , \tag{3.2.44}$$

from which it follows by using the reciprocal of (3.2.13) that the Cauchy stress tensor is given by

$$\sigma = \rho \mathbf{F} \cdot \left(\frac{\partial \hat{e}}{\partial \mathbf{F}} \right)^T + J_F^{-1} \mathbf{F}^{-T} \cdot \mathbf{T}^d , \tag{3.2.45}$$

in which the dissipative contribution $\mathbf{T}^d$, if any, still satisfies the following residual dissipation inequality jointly with the material heat-flux vector:

$$\Phi_R = \operatorname{tr}(\mathbf{T}^d \dot{\mathbf{F}}) - \theta_0^{-1} \mathbf{Q} \cdot \nabla_R \theta \geq 0 . \tag{3.2.46}$$

We shall not pursue further this case which will receive more attention in the framework of *rational thermodynamics*. We simply note first that a partial Legendre transformation can be performed on the energy density so as to introduce the Helmholtz free energy ψ per unit mass in the current configuration $\mathcal{K}_t$, i.e. $\psi(\mathbf{F}, \theta) = \hat{e}(\mathbf{F}, \eta) - \eta\theta$ so that we obtain also the *laws of state* as

$$\eta = -\frac{\partial \psi}{\partial \theta}, \qquad \sigma^e = \rho \mathbf{F} \cdot \left(\frac{\partial \psi}{\partial \mathbf{F}} \right)^T . \tag{3.2.47}$$

The second of these is the Cauchy-stress constitutive equation for a *thermoelastic solid.* In particular, if the said solid is *isotropic*, then the scalar-valued function $\psi(\mathbf{F}, \theta)$ must be form invariant under the full orthogonal group on $\mathcal{M}$. Let (cf. Truesdell and Noll, 1965; Maugin, 1988, p. 70)

$$\mathbf{F} = \mathbf{R} \cdot \mathbf{U}, \quad \mathbf{U} = \mathbf{U}^T, \quad \mathbf{R} \cdot \mathbf{R}^T = \mathbf{R}^T \cdot \mathbf{R} = \mathbf{1}, \quad \det \mathbf{R} = \pm 1 , \tag{3.2.48}$$

$$\mathbf{F} = \mathbf{V} \cdot \mathbf{R}, \qquad \mathbf{V} = \mathbf{V}^T , \tag{3.2.49}$$

be the so-called right and left polar decompositions of $\mathbf{F}$, where $\mathbf{U}$ and $\mathbf{V}$ are positive-definite symmetric tensors (on $\mathcal{M}$ and $\mathbf{E}^3$, respectively), and $\mathbf{R}$ is an orthogonal transformation. It is a simple matter to show that

$$\mathbf{U} = \mathbf{C}^{1/2}, \qquad \mathbf{V} = \mathbf{B}^{1/2} , \tag{3.2.50}$$

where $\mathbf{C}$ and $\mathbf{B}$ are defined by

$$\mathbf{C} = \mathbf{F}^T \cdot \mathbf{F}, \quad \mathbf{B} = \mathbf{F} \cdot \mathbf{F}^T . \tag{3.2.51}$$

These are the Green and Finger finite-strain tensors, respectively (the first is defined on $\mathcal{M}$ while the second one is defined in $\mathbb{E}^3$ at $\mathcal{K}_t$).

For ψ to be form-invariant under the full orthogonal group on $\mathcal{M}$ we have to verify the condition

$$\psi(\mathbf{F}, \theta) = \psi(\mathbf{F}\mathbf{P}^{-1}, \theta) , \tag{3.2.52}$$

where $\mathbf{P}^{-1}$ belongs to $O(3)$. We can make it to coincide with $\mathbf{R}^T$. But $\mathbf{V} = \mathbf{F} \cdot \mathbf{R}^T$, so that, in agreement with (3.2.50), $\mathbf{V}^2 = \mathbf{B}$, it follows that a necessary and sufficient condition for ψ to be the *free energy of an isotropic* body is that

$$\psi = \bar{\psi}(\mathbf{B}, \theta) . \tag{3.2.53}$$

But constitutive equations have to be independent of the observer. That is, they must be frame-indifferent under the time-dependent orthogonal group in $\mathbb{E}^3$ in $\mathcal{K}_t$. Let $\mathbf{Q}(t)$ such an orthogonal transformation belonging to this group. The function ψ must satisfy the following invariance:

$$\bar{\psi}(\mathbf{B}, \theta) = \bar{\psi}(\mathbf{Q}\mathbf{B}\mathbf{Q}^T, \theta) . \tag{3.2.54}$$

This in turn means that $\bar{\psi}$ must be *an isotropic scalar-valued function* of the tensor $\mathbf{B}$, or, in orther words, after a well-known result due to Cauchy (later, Weyl), it may depend on $\mathbf{B}$ only through its three principal invariants I_α, $\alpha = 1, 2, 3$ defined by

$$\begin{aligned} I_1 &= \operatorname{tr} \mathbf{B} \\ I_2 &= \text{sum of the principal minors of } \mathbf{B} \\ I_3 &= \det \mathbf{B} . \end{aligned} \tag{3.2.55}$$

Thus $\psi = \hat{\psi}(I_\alpha, \theta)$, from which it follows through an elementary computation that σ^e has the following expression for *elastic isotropic bodies*:

$$\sigma^e = 2\rho \left(I_3 \left(\frac{\partial \hat{\psi}}{\partial I_3} \right) \mathbf{1} + \left[\left(\frac{\partial \bar{\psi}}{\partial I_1} \right) + I_1 \left(\frac{\partial \bar{\psi}}{\partial I_2} \right) \right] \mathbf{B} - \left(\frac{\partial \bar{\psi}}{\partial I_2} \right) \mathbf{B}^2 \right) . \tag{3.2.56}$$

A further use of the Cayley–Hamilton theorem according to which the invariants satisfy the characteristic equation

$$\mathbf{B}^3 - I_1 \mathbf{B}^2 + I_2 \mathbf{B} - I_3 \mathbf{1} = \mathbf{0} , \tag{3.2.57}$$

allows one to transform the expression (3.2.56) into the one obtained by F. Murnaghan (1951) in his original work on elastic solids in finite strains:

$$\sigma^e = 2\rho\left(\left(\frac{\partial\psi}{\partial I_1}\right)\mathbf{B} + \left[I_3\left(\frac{\partial\psi}{\partial I_3}\right) + I_2\left(\frac{\partial\psi}{\partial I_2}\right)\right]\mathbf{1} - I_3\left(\frac{\partial\psi}{\partial I_2}\right)\mathbf{B}^{-1}\right). \tag{3.2.58}$$

Equations (3.2.56) and (3.2.57) are in general, *exact*, equations.

F. Rubber-like materials

These are elastic materials which are essentially incompressible while being subject to finite strains. Incompressibility now requires the satisfaction of the mathematical constraint: $\det\mathbf{B} = \text{const.} = 1$. Like in the case of fluids the stress tensor of rubber-like materials will be defined up to an isotropic pressure tensor while the energy reduces to $\rho\psi = \rho_0\psi = \Psi(I_1, I_2, \theta)$. *Mooney materials* correspond to a simple expression of ψ in terms of I_1 and I_2 with no dependence on θ:

$$\Psi(I_1, I_2) = A_1(I_1 - 3) + A_2(I_2 - 3), \qquad A_{1,2} \geq 0. \tag{3.2.59}$$

And this appears to be in fair agreement with experiments for a wide range of strains.

G. Anisotropic elastic materials

In that case we must remain with a material measure of strain so as to be able to express the *material symmetry* of the material on the material manifold $\mathcal{M}$. A basic relative material measure of strain is provided by the *Lagrange strain tensor*

$$\mathbb{E} := \frac{1}{2}(\mathbf{C} - \mathbf{1}_R) = \mathbb{E}^T. \tag{3.2.60}$$

Then we can consider a free energy of the type $\psi = \psi(\mathbb{E}, \theta)$ which is automatically *objective* or frame-indifferent as this expression is a first integral of the functional equation:

$$\psi(\mathbf{F}, \theta) = \psi(\mathbf{QF}, \theta), \tag{3.2.61}$$

as is immediately realized since we may take $\mathbf{Q}(t) = \mathbf{R}^{-1} = \mathbf{R}^T$ while accounting for (3.2.50) and (3.2.60). It follows then that σ^e takes on the following form:

$$\sigma^e = \rho\mathbf{F}\left(\frac{\partial\psi}{\partial\mathbb{E}}\right)\mathbf{F}^T = (\sigma^e)^T. \tag{3.2.62}$$

This is the form to be used when dealing with *anisotropic homogeneous crystals* subject to infinitesimal deformations superimposed on finite strains, as is often the case in the acoustics of crystals (cf. Maugin, 1985, 1988). Then the additional *dissipative* contribution of the viscous type will be governed by the remaining dissipation inequality (3.2.46). We do not elaborate further along this line. Rather, the few examples treated help us to draw a more general picture of the methodology of *T.I.P.*

H. Onsager–Casimir symmetry relations

Once laws of state — that part of the constitutive equations which does not "dissipate" — are given by Gibbs' equation or, in a simple way, by the derivatives of the energy with respect to the various variables of state, the remaining dissipation inequality, e.g. (3.2.28), $(3.2.38)_1$ or (3.2.46), may in fact be written in a symbolic form, whether in $\mathcal{K}_t$ or $\mathcal{K}_R$, as the celebrated *bilinear* form of the thermodynamics of irreversible processes:

$$\Phi = \mathbf{Y} \cdot \dot{\mathbf{X}} = \sum_{\gamma=1}^{m} Y_\gamma \dot{X}_\gamma \geq 0\,, \tag{3.2.63}$$

where the Y_γ are referred to as the *thermodynamic forces* (typically σ or $\nabla\theta^{-1}$) and the $\dot{\mathbf{X}}_\gamma$ are *thermodynamic velocities* (typically $\mathbf{D}$ or $\dot{\varepsilon}$ and $\theta\mathbf{q}$). One class is placed in *thermodynamic duality* to the other through the bilinear expression (3.2.63), the duality being induced by the usual scalar product in $\mathbb{R}^m$. The term *velocity* may be ill-chosen for the heat-flux vector unless we remember from kinetic theory that the heat flux is also a flux of energy related to the fluctuation velocity (but this argument relying on another level of description is more than suspicious to several authors, e.g. Truesdell, 1969).

The bilinear form (3.2.63) does *not* presuppose that the m-vector $\mathbf{Y}$ is linear affine in $\dot{\mathbf{X}}$ and vice versa. It is *T.I.P.* that relates to slight deviations from equilibrium — for which we emphasize that *both* $\mathbf{Y}$ and $\dot{\mathbf{X}}$ vanish:

$$\mathbf{Y}|_{\text{eq}} = \mathbf{0}, \qquad \dot{\mathbf{X}}|_{\text{eq}} = \mathbf{0}-\,, \tag{3.2.64}$$

which simply proposes to write *linear affine* relationships between the $\mathbf{Y}$s and $\dot{\mathbf{X}}$s, e.g. in the form of *evolution equations* (typical of kinetics)

$$\dot{X}_\gamma = \sum_{\gamma=1}^{m} L_{\gamma\nu} Y_\nu\,, \tag{3.2.65}$$

or, assuming that **L** is *not* singular (det **L** always in one sign, say +), in the *dual* form

$$Y_\nu = \sum_{\gamma=1}^{m} L^{-1}_{\nu\gamma} \dot{X}_\gamma . \tag{3.2.66}$$

There are two fundamental questions raised in writing (3.2.65) or (3.2.66). One is how do we identify thermodynamic *forces* and *velocities*? A hint of answer to this was given above. Velocities are those quantities which, in a general way, can be expressed as time-rates of change of *state variables*. If this is not clearly the case, as seen above for **q**, then we need a *microscopic definition* which provides us with the *time parity* of the quantity labeled $\dot{\mathbf{X}}$. Such quantities should reverse sign with *time reversal*. Thus we can say that a good exploitation of *T.I.P.* in fact borrows some ingredients to microscopic considerations. But this is not all. Equations (3.2.65)-(3.2.66), together with the *symmetry relations*,

$$\mathbf{L} = \mathbf{L}^T , \tag{3.2.67}$$

receive microscopic support in terms of the theory of fluctuations in statistical mechanics as shown by L. Onsager (1931) and H. G. B. Casimir (1945).[4] Macroscopically, the Onsager-Casimir relations (3.2.67) simply mean that the skew part of the linear application **L** is irrelevant as, by virtue of (3.2.65) or (3.2.66), only the *symmetric part* of **L** is involved in the final dissipation

$$\Phi = \mathbf{Y} \cdot \mathbf{L} \cdot \mathbf{Y} = \dot{\mathbf{X}} \cdot \mathbf{L}^{-1} \cdot \dot{\mathbf{X}} \geq 0 . \tag{3.2.68}$$

We should in fact note that the vanishing property (3.2.64) and the fundamental linearity of *T.I.P.* ensures that the clear distinction between *forces* and *fluxes* or *velocities* becomes peripheral, so that any suitable combination of the components of **Y** and $\dot{\mathbf{X}}$ will do. What remains important is the *time parity* of the various quantities. That is, while (3.2.67) strictly applies to the case where both **Y** and **X** (*not* $\dot{\mathbf{X}}$) behave like polar vectors, a more general expression of the Onsager-Casimir relations reads

$$L_{\gamma\nu} = \varepsilon_\gamma \varepsilon_\nu L_{\nu\gamma} , \tag{3.2.69}$$

where ε_γ and ε_ν are *indicators of time-parity* such that they equal +1 and −1 depending on whether the corresponding state variables (i.e. X_γ and X_ν)

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[4] The experimental validity of the Onsager-Casimir relations is established beyond any doubt (cf. Miller, 1973).

are even or odd under time reversal. If, furthermore, **L** depends linearly on a magnetic induction **B** and/or an angular velocity (spin) ω — both quantities are *axial vectors* — then (3.2.69) must be further amended to read

$$L_{\gamma\nu}(\mathbf{B},\omega) = \varepsilon_\gamma \varepsilon_\nu L_{\nu\gamma}(-\mathbf{B},-\omega)\,, \tag{3.2.70}$$

which includes most of the possibilities. Finally, *material symmetry* may also rule out certain linear couplings in (3.2.65) and (3.2.66), i.e. some components of the applications **L** and $\mathbf{L}^{-1}$ may be identically zero to start with. This was exemplified by the vanishing of the coefficients (3.2.40) in a material exhibiting a center of symmetry. Such complications show up especially when dealing with electromagnetic dissipative couplings involving the Hall effect, spin-precession phenomena, etc. (see Maugin, 1988; Eringen and Maugin, 1990, Vol. I; also Chapter 9 below).

I. Dissipation potential

To end this section we note, following an early proposal by Lord Rayleigh (1945) to study the dissipation through Newtonian viscosity in acoustics, by J. C. Maxwell (1873) to deal with electric conduction effects in circuits, that if we assume the existence of a *dissipation function* $\mathcal{D}(\mathbf{Y})$ and its Legendre transform $\mathcal{D}^*(\dot{\mathbf{X}})$, which are twice differentiable and, in fact, non-negative and homogeneous functions of degree *two* in their arguments, and if we can write

$$\begin{aligned} \dot{X}_\gamma &= \frac{\partial \mathcal{D}(\mathbf{Y})}{\partial Y_\gamma}\,, \qquad \mathcal{D} = \mathcal{D}(\mathbf{Y})\,, \\ Y_\gamma &= \frac{\partial \mathcal{D}^*(\dot{\mathbf{X}})}{\partial \dot{X}_\gamma}\,, \qquad \mathcal{D}^*(\dot{\mathbf{X}}) = \mathbf{Y}\cdot\dot{\mathbf{X}} - \mathcal{D}(\mathbf{Y})\,, \end{aligned} \tag{3.2.71}$$

then

$$\begin{aligned} \partial \dot{X}_\gamma/\partial Y_\nu &= \partial \dot{X}_\nu/\partial Y_\gamma = L_{\gamma\nu} = L_{\nu\gamma}\,, \\ \partial Y_\gamma/\partial \dot{X}_\nu &= \partial Y_\nu/\partial \dot{X}_\gamma = L^{-1}_{\gamma\nu} = L^{-1}_{\nu\gamma}\,, \end{aligned} \tag{3.2.72}$$

so that the Onsager–Casimir symmetry relations are automatically fulfilled while, with Euler's identity for homogeneous functions

$$\sum_{\gamma=1}^{m} \frac{\partial \mathcal{D}(\mathbf{Y})}{\partial Y_\gamma} Y_\gamma = 2\mathcal{D}(\mathbf{Y}) = \Phi \geq 0\,, \tag{3.2.73}$$

the dissipation inequality is also satisfied. A modern *nonlinear* generalization of Onsager–Casimir relations relies on the consideration of nonquadratic dissipation potentials and the use of Maxwell's differentiation rules such as (3.2.72), cf. Edelen (1972).

3.3. Rational Thermodynamics

A. General features

Rational thermodynamics (for short *R.T.*) is the phenomenological thermodynamics developed essentially by B. D. Coleman, W. Noll, C. A. Truesdell and their co-workers in the 1960s,[5] which takes as a model the rational mechanics of the mathematicians of the eighteenth and nineteenth centuries (especially the French mathematicians Lagrange and Cauchy) and the embryonic thermomechanics of Duhem (1911). It openly ignores, or bypass, the experience acquired in thermostatics. Caratheodory (1909, 1925) and Born (1921) become thus the Great Satanic figures (cf. Truesdell, 1986) of this school of thought that also belongs to the *axiomatic trend of* thermodynamics. Its basic postulates (this is *our* interpretation) seem to be that those notions which precisely could be defined only at equilibrium in thermostatics, exist *a priori* for any thermodynamical state whatever, even largely outside equilibrium. Again, a certain measure (distance in the appropriate space) of departure from equilibrium should be defined in order to clarify that matter. Thus the notions of *temperature* and *entropy* are *a priori* granted to any state, so that the formal bases of this thermodynamics are the *a priori* statement of the second law (assuming the existence fo the functions θ and η) such as in (2.3.32) and the usual first law — say (2.3.53) — on which, fortunately, everybody agrees. In localized form these equations yield, on account of the equation of motion:

$$\rho \dot{e} = \sigma : \mathbf{D} + \rho h - \nabla \cdot \mathbf{q} \,, \tag{3.3.74}$$

and

$$\rho \dot{\eta} \geq \rho (h/\theta) - \nabla \cdot (\mathbf{q}/\theta) \tag{3.3.75}$$

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[5] The foundation paper is Coleman (1964). The standard exposition is given in Truesdell (1969, 1984) — see also Truesdell (1966), Müller (1967, 1973, 1985). The thermodynamics considered by Eringen (1980) is of a similar type. The axiomatic trend in thermodynamics was also developed in Boyling (1972), Buchdahl (1966), Giles (1964), Landsberg (1964, 1970), Muschik (1990), Tisza (1966), Turner (1961), but without special attention to the thermomechanics of continua, except for the paper by Muschik.

at all regular placements $\mathbf{x}$ in the material body in $\mathcal{K}_t$. Introducing then the free energy density ψ by $(3.2.5)_1$ and combining (3.3.74) and (3.3.75) leads to the celebrated *Clausius–Duhem inequality* in local form as:

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \sigma : \mathbf{D} + \theta\mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0 . \tag{3.3.76}$$

In *finite-strains* this can also be cast in the form

$$-(\dot{W} + S\dot{\theta}) + \operatorname{tr}(\dot{\mathbf{T}}\mathbf{F}) + \theta\mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0 , \tag{3.3.77}$$

where we defined the free energy and entropy per unit volume in $\mathcal{K}_R$ by

$$W := \rho_0\psi , \qquad S = \rho_0\eta . \tag{3.3.78}$$

These expressions are valid whether the material body is homogeneous or not. Dynamics then enters the framework through the fact that, in theory, the whole *past history* must be taken into account; for example, in the case of (3.3.76) or (3.3.77), as only temperature and *motion* appears as *dynamical quantities*, their whole past hisory, i.e. the collection of all values taken by these fields at a point $\mathbf{x}$ for all past times and the present time is thought to determine the thermo-mechanical behavior of the material at the current time t. And this should apply to all types of behavior, the only constraint being that (3.3.76), (3.3.77) must be respected. One is then naturally led to the consideration of the *constitutive equations* in a *functional form* on the temporal line, the *instantaneous behavior* being formally the same as the one described by the laws of state of *T.I.P.* The Clausius–Duhem inequality (3.3.76), (3.3.77) plays the role of a mathematical constraint that must be satisfied by the functional constitutive equations, written down for η, σ, ψ and θ as, e.g. for σ

$$\sigma(t) = \mathop{\mathcal{G}}_{s=0}^{\infty} [\varepsilon(t-s), \theta(t-s)] \tag{3.3.79}$$

for any so-called *thermodynamically admissible* process. We shall not dwell further on this functional approach which, in practice, can only be useful for behaviors with *memory* [such as so-called Boltzmann's (1874) viscoelastic solids and the *hereditary media* introduced by the Italian mathematician V. Volterra early in this century] as we saw in certain types of *viscoelastic media* with a *non-Newtonian viscous* behavior and of *electromagnetic media* (see Eringen and Maugin, 1990, Vol. 2, Chapter 13). This type of approach that radiates a wonderful elegance was seriously criticized by "classical" thermodynamicists for its lack of touch with the experimental definition of concepts such as temperature. Its application to a relatively simple case, that of *thermoelastic materials*, is nonetheless particularly enlightening.

B. Thermoelastic materials[6]

According to Coleman (1964), such materials are *defined* by a set of four constitutive equations which describe the specific free energy ψ, the stress tensor σ, the specific entropy η, and the heat-flux vector $\mathbf{q}$ as *a priori* functions (here no functionals over time as we discard any *viscoelastic component* in the behavior of the material) of the motion gradient $\mathbf{F}$, the absolute temperature θ, and the material temperature gradient $\mathbf{G} = \nabla_R\theta$. That is, writing the expression for one quantity only,

$$\psi = \hat{\psi}(\mathbf{F}, \theta, \mathbf{G}) . \tag{3.3.80}$$

The fact that all four dependent variables are *a priori* supposed to be functions of the *same* set of arguments may be referred to as the *working hypothesis of equipresence*. This simply is a precautionary measure to avoid missing any significant dependence or coupling.[7] Of course, the scalar-, vector-, or tensor-valued functions $\hat{\psi}$, $\hat{\eta}$, $\hat{\mathbf{q}}$ and $\hat{\sigma}$ are assumed to be sufficiently differentiable on their domain of definition. Then a set of seven functions $(\mathbf{F}, \theta, \mathbf{G}, \psi, \sigma, \eta, \mathbf{q})$ that satisfies constitutive equations of the type (3.3.80), the local balance laws, and the second law of thermodynamics in its form (3.3.76) or (3.3.77), is said to define an *admissible thermoelastic process*. Such a process is specified as soon as one knows the solution

$$\mathbf{x} = \chi(\mathbf{X}, t), \qquad \theta = \theta(\mathbf{X}, t) , \tag{3.3.81}$$

since one can then compute $\mathbf{F}$ and $\mathbf{G}$, while the fields ψ, θ, η and $\mathbf{q}$ are computed through the constitutive equations (3.3.80). The remaining quantities $\mathbf{f}$ and h that still appear in the field equations (motion and first law) are finally evaluated from these equations. Clearly, this procedure constitute a *thought*

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[6] With very insignificant changes we follow here the exposition that we previously gave in pp. 111–115 in Maugin (1988).

[7] To call this the *principle of equipresence*, as was originally done by the school of *R.T.* would be to deny any profound meaning to the word *principle* (a principle is usually never contradicted, e.g. the *first principle* — first law — *of thermodynamics*. *Equipresence* is *always negated* as ψ cannot depend on G, except in *extended thermodynamics*, but that is another story (see Sec 3.4).

experiment since, in general, it is $\mathbf{f}$ and h that are prescribed. What is then the reduced form of the constitutive equations? We must exploit the inequality (3.3.76) in order to reduce the generality of expressions (3.3.80). There holds the following.

Lemma 3.1. *There exists at least one admissible thermoelastic process such that the fields* $\mathbf{F}$, $\dot{\mathbf{F}}$, θ, $\dot{\theta}$, $\mathbf{G}$ *and* $\dot{\mathbf{G}}$, *for each given material point* $\bar{\mathbf{X}}$ *and at each given time* $\bar{t} \in (t_0, t_M)$, *may take arbitrary prescribed values, respectively,* $\bar{\mathbf{F}}$, $\mathbf{A}$, $\bar{\theta}$, α, $\bar{\mathbf{G}}$, *and* $\mathbf{a}$, *with* $\bar{\mathbf{F}}$, $\bar{\theta}$ *and* $\bar{\mathbf{G}}$ *defined on the domain of definition of* $\mathbf{F}$, θ *and* $\mathbf{G}$, *respectively.*

The proof of this lemma goes as follows. It is sufficient to consider fields of the type (3.3.81) in the following special form:

$$\begin{aligned} \chi(\mathbf{X}, t) &= [\bar{\mathbf{F}} + (t - \bar{t})\mathbf{A}] \cdot (\mathbf{X} - \bar{\mathbf{X}}) , \\ \theta(\mathbf{X}, t) &= \bar{\theta} + \bar{\alpha}(t - \bar{t}) + [\bar{\mathbf{G}} + (t - \bar{t})\mathbf{a}] \cdot (\mathbf{X} - \bar{\mathbf{X}}) . \end{aligned} \tag{3.3.82}$$

Indeed, from these equations and the definition of $\mathbf{F}$ and $\mathbf{G}$, we obtain $\mathbf{F}(\mathbf{X}, t) = \bar{\mathbf{F}} + (t - \bar{t})\mathbf{A}$ and $\mathbf{G}(\mathbf{X}, t) = \bar{\mathbf{G}} + (t - \bar{t})\mathbf{a}$; from which it follows that $\mathbf{F}(\bar{\mathbf{X}}, \bar{t}) = \bar{\mathbf{F}}$, $\theta(\bar{\mathbf{X}}, \bar{t}) = \bar{\theta}$, $\mathbf{G}(\bar{\mathbf{X}}, \bar{t}) = \bar{\mathbf{G}}$, $\dot{\mathbf{F}}(\bar{\mathbf{X}}, t) = \mathbf{A}$, $\dot{\theta}(\bar{\mathbf{X}}, \bar{t}) = \alpha$, and $\dot{\mathbf{G}}(\bar{\mathbf{X}}, \bar{t}) = \mathbf{a}$ (Q.E.D.). Then we can state the following.

Theorem 3.1. *In order that the Clausius-Duhem inequality (3.3.76) be satisfied for thermoelastic solids, it is necessary and sufficient that the constitutive equations of the type of (3.3.80) fulfill the following three conditions:*

(i) the functions $\hat{\psi}$, σ *and* η *do not depend on* $\mathbf{G}$:

$$\psi = \hat{\psi}(\mathbf{F}, \theta), \quad \sigma = \hat{\sigma}(\mathbf{F}, \theta), \quad \eta = \hat{\eta}(\mathbf{F}, \theta) ; \tag{3.3.83}$$

(ii) $\hat{\sigma}$ *and* $\hat{\eta}$ *are related to* $\hat{\psi}$ *by*

$$\sigma = \rho \mathbf{F} \left(\frac{\partial \hat{\psi}}{\partial \mathbf{F}} \right)^T , \qquad \hat{\eta} = - \frac{\partial \hat{\psi}}{\partial \theta} ; \tag{3.3.84}$$

(iii) $\hat{\mathbf{q}}$ *satisfies the thermal conduction inequality:*

$$\hat{\mathbf{q}}(\mathbf{F}, \theta, \mathbf{G}) \cdot \nabla \theta \leq 0 . \tag{3.3.85}$$

This is proved as follows. First, as a consequence of (3.3.80), we have

$$\dot{\psi} = \operatorname{tr}\left[\left(\frac{\partial\hat{\psi}}{\partial\mathbf{F}}\right)^T \dot{\mathbf{F}}\right] + \frac{\partial\hat{\psi}}{\partial\theta}\dot{\theta} + \frac{\partial\hat{\psi}}{\partial\mathbf{G}}\cdot\dot{\mathbf{G}}\,.$$

Substituting from this into (3.3.76), we obtain

$$\operatorname{tr}\left\{\left[\mathbf{F}^{-T}\sigma - \rho\left(\frac{\partial\hat{\psi}}{\partial\mathbf{F}}\right)^T\right]\dot{\mathbf{F}}\right\} - \rho\left(\hat{\eta} + \frac{\partial\hat{\psi}}{\partial\theta}\right)\dot{\theta} - \rho\frac{\partial\hat{\psi}}{\partial\mathbf{G}}\cdot\hat{\mathbf{G}} - \theta^{-1}\hat{\mathbf{q}}\cdot\nabla\theta \geq 0\,,$$

where the dependence of $\hat{\psi}$, $\hat{\sigma}$, $\hat{\eta}$ and $\hat{\mathbf{q}}$ is understood. The conditions (3.3.84) through (3.3.86) are obviously sufficient. The necessary conditions are thus established. Let us apply the last inequality to the special processes introduced in (3.3.82) with $x^i = \delta^i_K \bar{X}^K$ and $t = \bar{t}$. From the inequality we obtain

$$\operatorname{tr}\left\{\left[\mathbf{F}^{-T}\sigma - \rho\left(\frac{\partial\hat{\psi}}{\partial\mathbf{F}}\right)^T\right]\mathbf{A}\right\} - \rho\left(\hat{\eta} + \frac{\partial\hat{\psi}}{\partial\theta}\right)\alpha - \rho\frac{\partial\hat{\psi}}{\partial\mathbf{G}}\cdot\mathbf{a} - \theta^{-1}\hat{\mathbf{q}}\cdot\nabla\theta \geq 0\,,$$

from which it follows the necessary character of (3.3.83)–(3.3.85) since $\bar{\mathbf{X}}$, $\bar{t}$, $\mathbf{A}$, α, and $\mathbf{a}$ are arbitrary (*Q.E.D.*).

On account of the above results we immediately transform (3.3.74) into the equation (the future equation of heat propagation)

$$\rho\theta\dot{\eta} = \rho h - \nabla\cdot\mathbf{q}\,. \tag{3.3.86}$$

This is a very special form (no *intrinsic dissipation*) of the heat equation. For this particular case we see that an admissible thermoelastic process which is adiabatic, i.e. $\rho h - \nabla\cdot\mathbf{q} = 0$, is also *isentropic* ($\dot{\eta} = 0$); this is a necessary and sufficient condition.

Applying now the condition of frame-indifference to the scalar function ψ we can show that it reduces, for instance, to a function

$$\psi = \bar{\psi}(\mathbf{E},\theta)\,. \tag{3.3.87}$$

From this there follow the constitutive equations (laws of state in *T.I.P.*) for *nonlinear thermoelasticity*:

$$\sigma = \rho\mathbf{F}\left(\frac{\partial\bar{\psi}}{\partial\mathbf{E}}\right)_\theta \mathbf{F}^T, \qquad \eta = -\left(\frac{\partial\bar{\psi}}{\partial\theta}\right)_{\mathbf{E}_{\text{fixed}}}\,. \tag{3.3.88}$$

In like manner we show that $\mathbf{q}$ takes on the form

$$\mathbf{q} = \mathbf{F}\bar{\mathbf{Q}}(\mathbb{E}, \theta, \mathbf{G}) \quad \text{with} \quad \bar{\mathbf{Q}} \cdot \mathbf{G} \leq 0\,, \tag{3.3.89}$$

where $\bar{\mathbf{Q}}$ is assumed to be sufficiently continuous (say C^1) with respect to the components of $\mathbf{G}$ (here $\mathbb{E}$ and θ play the role of parameters). As a matter of fact, let

$$\mathbf{K}(\mathbb{E}, \theta) := -\frac{\partial \bar{\mathbf{Q}}(\mathbb{E}, \theta, \mathbf{G})}{\partial \mathbf{G}}\bigg|_{\mathbf{G}=\mathbf{0}} \tag{3.3.90}$$

be the *conduction tensor* in the reference configuration $\mathcal{K}_R$. Fixing $\mathbb{E}$ and θ and assuming $\bar{\mathbf{Q}}$ to be smooth enough in the neighborhood of $\mathbf{G} = \mathbf{O}$, we can expand $\bar{\mathbf{Q}}$ as

$$\bar{\mathbf{Q}}(\mathbf{G}) = \bar{\mathbf{Q}}(0) - \mathbf{K} \cdot \mathbf{G} + o(|\mathbf{G}|) \tag{3.3.91}$$

for $|\mathbf{G}|$ tending toward zero. Carrying this truncated expansion in the second of (3.3.89) yields

$$\bar{\mathbf{Q}}(\mathbf{0}) \cdot \mathbf{G} - \mathbf{G} \cdot \mathbf{K} \cdot \mathbf{G} + o(|\mathbf{G}|^2) \leq 0 \tag{3.3.92}$$

for $|\mathbf{G}| \to 0$. This last equation must be checked for all $\mathbf{G}s$ in their domain of definition Ω. This is true only if $\bar{\mathbf{Q}}(\mathbf{0}) = \mathbf{0}$ and $\mathbf{G} \cdot \mathbf{K} \cdot \mathbf{G} \geq 0$. Hence we can state: *In an admissible thermoelastic process which satisfies the Clausius–Duhem inequality, the heat flux vanishes whenever the temperature gradient vanishes and the heat conduction tensor* $\mathbf{K}(\mathbb{E}, \theta)$ *is non-negative definite.* Thus

$$\bar{\mathbf{Q}}(\mathbb{E}, \theta, \mathbf{G})|_{\mathbf{G}=\mathbf{0}} = \mathbf{0}\,, \tag{3.3.93}$$

and

$$\bar{\mathbf{Q}}(\mathbb{E}, \theta, \mathbf{G}) = -\mathbf{K}(\mathbb{E}, \theta) \cdot \mathbf{G} + o(|\mathbf{G}|), \qquad \mathbf{K} = \mathbf{K}^T\,, \tag{3.3.94}$$

where the last property can be considered without loss in generality. Equations (3.3.93) and (3.3.94) show that in a thermoelastic body it is not possible to produce a heat flux by a pure deformation and a uniform temperature field only. In other words, the *piezocaloric effect* is not possible in thermoelastic bodies. Equation $(3.3.94)_1$ is an anisotropic generalization of Fourier's law in which the coefficients of conduction may depend on the state of strain and temperature. We would like to believe that the reader will be convinced of the elegance of the methodology of *rational thermodynamics* by this simple example which offers the best presentation of *thermoelasticity.* The linear thermoelaticity theory is straightforwardly deduced from the above with due account of simplifying assumptions [for this, see Sec 2.11 in Maugin (1988)]. We simply quote the final constitutive relations and most relevant field equations for *linear anisotropic homogeneous thermoelastic bodies*:

Constitutive equations:

$$\begin{aligned}\sigma_{ij} &= C_{ijkl}e_{kl} + (\theta - \theta_0)M_{ij}\,,\\ \eta &= \eta_0 + \theta_0^{-1}C(\theta - \theta_0) - \rho_0^{-1}M_{ij}e_{ij}\,,\\ q_i &= -K_{ij}^0(\theta_0)\theta_{,j}\,.\end{aligned} \tag{3.3.95}$$

Field equations inside the body:

$$\begin{aligned}\sigma_{ij,j} + \rho_0 f_i &= \rho_0 \ddot{u}_i\,,\\ \rho_0 C\dot{\theta} - \theta_0 M_{ij}\dot{e}_{ij} &= (K_{ij}^0\theta_{,j})_{,i} + \rho_0 h\,,\end{aligned} \tag{3.3.96}$$

in which the *isothermal elasticity-coefficient tensor of components* C_{ijkl}, the *thermoelastic-coupling tensor* of components M_{ij}, and the specific heat at constant strain, C, are defined by

$$C_{ijkl}(\theta_0) := \rho_0 \left.\frac{\partial^2\psi(\mathbb{E},\theta)}{\partial E_{IJ}\partial E_{KL}}\right|_{\substack{\mathbb{E}=0\\ \theta=\theta_0}} \delta_i^I\delta_j^J\delta_k^K\delta_l^L\,, \tag{3.3.97a}$$

$$M_{ij}(\theta_0) := \rho_0 \left.\frac{\partial^2\psi(\mathbb{E},\theta)}{\partial E_{IJ}\partial\theta}\right|_{\substack{\mathbb{E}=0\\ \theta=\theta_0}} \delta_i^I\delta_j^J\,, \tag{3.3.97b}$$

$$C(\theta_0) := \theta_0 \left.\frac{\partial\eta(\mathbb{E},\theta)}{\partial\theta}\right|_{\substack{\mathbb{E}=0\\ \theta=\theta_0}}\,. \tag{3.3.97c}$$

They satisfy the following obvious tensorial symmetry relations.

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{klij}\,, \quad M_{ij} = M_{ji}\,. \tag{3.3.98}$$

The scalars θ_0 and η_0 are spatially uniform, reference values, and e_{ij} are the components of the infinitesimal-strain tensor:

$$e_{ij} = E_{KL}\delta_i^K\delta_j^L \cong u_{(i,j)} \equiv \frac{1}{2}(u_{i,j} + u_{j,i})\,, \tag{3.3.99}$$

if u_i are the Cartesian components of the elastic displacement. We recognize in Eqs. (3.3.96) the linearized equation of motion and the equation of *heat propagation*, where the superimposed dot now denotes the partial time derivative.

For *isotropic thermoelastic solids* we have the following reduction:

$$\begin{aligned} C_{ijkl} &= \lambda(\theta_0)\delta_{ij}\delta_{kl} + \mu(\theta_0)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\,, \\ M_{ij} &= m(\theta_0)\delta_{ij}, \quad K^0_{ij} = \kappa(\theta_0)\delta_{ij}\,, \end{aligned} \tag{3.3.100}$$

with

$$3\lambda + 2\mu \geq 0, \quad \mu \geq 0, \quad \kappa \geq 0, \quad m \gtrless 0\,,$$

from which it follows that (3.3.95) and $(3.3.96)_2$ takes on the reduced form

$$\begin{aligned} \sigma_{ij} &= [\lambda e_{kk} + m(\theta - \theta_0)]\delta_{ij} + 2\mu e_{ij}\,, \\ \eta &= \eta_0 + \theta_0^{-1}C(\theta - \theta_0) - \rho_0^{-1} m e_{kk}, \quad q_i = -\chi\theta_{,i}\,, \end{aligned} \tag{3.3.101}$$

and

$$\rho_0 C\dot{\theta} - m\theta_0\dot{e}_{kk} = \kappa\nabla^2\theta + \rho_0 h\,; \tag{3.3.102}$$

the scalar coefficients λ and μ are the celebrated *Lamé coefficients of linear isotropic elasticity*, while

$$\alpha = -\frac{m}{(3\lambda + 2\mu)} \tag{3.3.103}$$

is the *dilatation coefficient.* The first of (3.3.101) reduces to *Hooke's law for isothermal processes* for $\theta = \theta_0$. For *isentropic processes*, the situation is quite different as $\dot{\eta} = 0$, hence $\eta = \eta_0$ is the prevailing condition. From $(3.3.95)_2$ it follows then that θ is given by

$$\theta = \theta_0 + \frac{\theta_0}{\rho_0 C} M_{ij} e_{ij}\,, \tag{3.3.104}$$

so that $(3.3.95)_1$ takes on the form:

$$\sigma_{ij} = C^{\eta}_{ijkl} e_{kl}, \quad C^{\eta}_{ijkl} = C_{ijkl} + \frac{\theta_0}{\rho_0 C} M_{ij} M_{kl}\,. \tag{3.3.105}$$

From this we immediately conclude that *isentropic elasticity coefficients are never less than the corresponding isothermal ones.* Isothermal elasticity coefficients can be measured using a *quasi-static* method as during very slow deformation in a thermostat. Isentropic ones can be measured by means of *dynamical* methods such as *ultrasonic waves* so as to respect the *adiabaticity* condition which follows from (3.3.86). For the solutions of problems in linear thermoelasticity on the basis of (3.3.96) and the accompanying boundary conditions, we refer to Nowacki (1975).

C. Comparison with *T.I.P.*

First we note that Eq. (3.2.8) of *T.I.P.* can also be rewritten as

$$\rho\dot{\theta}\eta = \Phi_{\text{intr}} + (\rho h - \nabla \cdot \mathbf{q}) \,, \tag{3.3.106}$$

wherein

$$\Phi_{\text{intr}} = -\rho(\dot{\psi} + \eta\dot{\theta}) + \sigma : \mathbf{D} \,. \tag{3.3.107}$$

This is indeed identical to (3.2.12) whenever the basic consequence of the axiom of local state holds true, i.e. entropy has its *thermostatic definition*

$$\eta = -\frac{\partial\psi}{\partial\theta} \,. \tag{3.3.108}$$

Therefore, we see that, in practice, assuming that θ coincides instantaneously with the absolute temperature of thermostatics and that the definition (3.3.108) applies, make it such that (3.2.9) is equivalent to the statement of the Clausius–Duhem inequality of *R.T.* This is usually what the present writer applied in practical cases without having to repeat all the detailed working assumptions of both theories. However, the application of both theories is quite different if one sticks with the original *R.T. approach* that considers *functional* constitutive equations. In this latter framework several authors have tried to encompass all types of thermomechanical behaviors, including *rate-independent plasticity* (see works by D. R. Owen and Lucchesi) but, in our opinion and in spite of rather interesting developments, they have failed to produce a manageable and directly applicable theory such as the one based on *T.I.V.* (see Chapter 7 below). The same holds true for electromagnetic behaviors involving hysteresis (cf. Chapter 9).

D. Further improvements

Further justifications of *R.T.* are to be found in the works of I. Müller (1967, 1973, 1985) and a remarkable paper by I.-Shih Liu (1972). First, it was observed that the general notion of *coldness* as an integrating factor for entropy is essential. With an appropriate scaling of temperature this indeed reduces to the reciprocal of *thermodynamical temperature*. Second, as a deviation from the strict orthodoxy of *R.T.* some freedom is given to the expression of the *entropy flux* present in (2.3.32) by letting it differ *a priori* from the ratio of the heat flux to the temperature. That is, we can rewrite (2.3.32) as

$$\frac{dS}{dt} \geq \int_{\Omega} \rho \frac{h}{\theta} d\Omega - \int_{\partial\Omega} \mathbf{S} \cdot \mathbf{n} da \,, \tag{3.3.109}$$

with

$$\mathbf{S} = \theta^{-1}\mathbf{q} + \mathbf{k} \,, \tag{3.3.110}$$

where the *extra entropy flux* **k** has to be determined by a *constitutive equation.* Thus it theoretically varies in form from one material to another. In practice, however, after some tedious and cumbersome algebra it is often found that $k \equiv 0$, except for systems exhibiting a diffusion-like behavior (i.e. thermodynamic systems that account for the spatial gradient of state variables). We shall see a few applications of these in later chapters. Finally, Liu introduced the beautiful idea that in applying thermodynamical admissibility (i.e. the necessary and sufficient condition of satisfying the Clausius–Duhem), it is generally necessary to consider the field equations (in pure thermomechanics, the conservation of mass, the balance of momentum, and the energy equation) as mathematical constraints in that procedure. That is, they are each multiplied by the appropriate *Lagrange multiplier* and the resulting vanishing quantities are added to the left-hand side of the Clausius–Duhem inequality; again, for many cases, this astute but cumbersome manipulation results in very little change, if any at all. Notice for later use that with account of the general formula (3.3.110) for **S**, the local Clausius–Duhem inequality takes on the general form:

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \sigma : \mathbf{D} + \nabla \cdot (\theta \mathbf{k}) - \mathbf{S} \cdot \nabla\theta \geq 0 \,. \tag{3.3.111}$$

This form exhibits a rather annoying divergence term (that one is tempted to formally discard altogether by setting $\mathbf{k} = 0$; we shall see later that in more involved cases, this yields a particular nonzero expression for **k**), while it also shows that the thermodynamical dual of $\nabla\theta$ is $(-\mathbf{S})$.

3.4. Extended Thermodynamics

It may be an insuperable challenge to draw a sketch of *extended thermodynamics* (for short *E.T.*, a "thermodynamics of the third type" as humorously emphasized by G. Lebon, 1992).[8] In order to go beyond the classical

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[8] In addition to sketchy presentations in Casas–Vasquez *et al.* (1984) and Lebon (1989) and the contributions in the book on *Extended Thermodynamics* edited by Salamon, Sieniutycz, Taylor Francis and Washington, 1991), the most comprehensive and articulate expositions of *E.T.* are given in Jou *et al.* (1988, 1993), Müller (1985) and Müller and Ruggeri (1993). A lengthy bibliography including many items up to 1992 is given in Jou *et al.* (1992).

description, *E.T.* envisages the consideration of the usual *dissipative fluxes* (e.g. viscous stress, heat flux, electric conduction current) as *additional independent variables.* As a consequence the entropy itself, in agreement with an early proposal of Machlup and Onsager (1953), becomes a function of these *fluxes.* The same generally holds true of the extra entropy flux introduced in (3.3.110). In addition to their contribution in classical field equations (Euler–Cauchy equations of motion, energy equation, equation of conservation of charge in electricity), the fluxes satisfy *evolution-diffusion equations* inspired by higher-order kinetic-theory developments that we shall not touch upon here. As a matter of fact, the print left by kinetic theory is so strong with some authors that often one cannot see how to accommodate the case of truly *deformable solids* in *E.T.* Putting aside some of the reasons at the basis of this approach (e.g. causality and hyperbolicity; see Müller and Ruggeri, 1993), we simply note a few examples which will help us to shed light in a comparison with the theory with internal variables (*T.I.V.*). Possible outcomes of *E.T.* are (i) the so-called *Maxwell-Cattaneo-Vernotte* law of heat conduction (see Cattaneo, 1948) that we intentionally rewrite in the form

$$\dot{\mathbf{q}} = -\frac{1}{\tau_q}(\mathbf{q} - \mathbf{q}_F), \quad \mathbf{q}_F \equiv -\kappa \nabla \theta \,, \tag{3.4.112}$$

for *isotropic rigid bodies*, and (ii) an evolution-diffusion generalization of *Ohm's law* (the celebrated $U = Ri$ of our gymnasium/lycée/public-school years) as (Jou *et al.*, 1988; p. 1161)

$$\dot{\mathbf{J}} = -\frac{1}{\tau_J}(\mathbf{J} - \mathbf{J}_0) + (l^2/\tau_J)\nabla^2 \mathbf{J}, \qquad \mathbf{J}_0 \equiv \Sigma \mathbf{E} \,, \tag{3.4.113}$$

in an isotropic electric rigid conductor, where $\mathbf{E}$ is the electric field, $\mathbf{J}$ is the electric current (jointly they produce the *Joulean dissipation* $\Phi_J = \mathbf{J} \cdot \mathbf{E}$, *see Chapter 8*), and τ_q and τ_J are two (positive) relaxation times and l is a characteristic length. We recognize in $(3.4.112)_2$ and $(3.4.113)_2$ the classical Fourier and Ohm laws of heat and electricity conduction in rigid conductors. Let σ^D be the dissipative part of the stress tensor, which is also governed by such an evolution-diffusion equation. Then the free energy density ψ, entropy density η and entropy flux $\mathbf{S}$, in a deformable body, will be given by general expressions:

$$\psi = \psi(\theta, -; \sigma^D, \mathbf{q}, \mathbf{J}) \,,$$

$$\eta = \eta_s + \mathcal{N}(\sigma^D, \mathbf{q}, \mathbf{J}) \,,$$

$$\mathbf{S} = \theta^{-1}\mathbf{q} + \mathbf{k}(\sigma^D, \mathbf{q}, \mathbf{J}), \tag{3.4.114}$$

where we expect η_s and θ to coincide with thermostatic values when all dissipative fluxes vanish. Because of the tensorial orders involved, the deviations from thermostatic definitions in $(3.4.114)_{1,2}$ are usually at least *quadratic* in the dissipative fluxes, i.e. in an isotropic body ψ and η will certainly contain terms proportional to $\mathbf{q} \cdot \mathbf{q}$ and $\mathbf{J} \cdot \mathbf{J}$, while $\mathbf{k}$ may in fact contain a term linear in $\mathbf{q}$ or $\mathbf{J}$, or perhaps a term jointly quadratic in σ^D and $\mathbf{q}$!

The first example (3.4.112) intentionally discards a diffusion phenomenon in order to increase the resemblance with equations of a similar form to be developed in *T.I.V.*, but for other variables. For the time being we simply note that in equations of the type of (3.4.112) — or (3.4.113) for nearly spatially uniform fluxes — relaxation occurs towards a quantity, e.g. $\mathbf{q}_F$ or $\mathbf{J}_0$, which is not at thermodynamic equilibrium. As matter of fact, *thermodynamic equilibrium* corresponds to *all* three contributions in (3.4.112) going to zero *simultaneously*. In the case of (3.4.113) all four terms, with $\mathbf{E} = -\nabla\phi$ (where ϕ is the electrostatic potential) must go to zero simultaneously as thermodynamic equilibrium also includes spatial uniformity in its definition. The problem with the formulation above is that the number of possible additional variables represented by the fluxes is limited to those already introduced above in the framework of the thermomechanics of electromagnetic bodies. This is too poor to allow for the phenomenological description of the wide classes of phenomena that we have in mind. As remarked by some authors (e.g. Jou *et al.*, 1988, p. 1171), these variables cannot cope with many other dissipative processes involving the hidden complexity of, say, a microstructure. It is only with the introduction of *internal variables of state* that we can proceed to a larger generality. This is the object of the final section of this chapter.

3.5. Thermodynamics With Internal Variables

The detailed structure, advantages, and shortcomings of the *thermodynamics with internal variables* (for short, *T.I.V.*) will be dealt with at some length in Chapter 4. Here we simply note a few general facts about *T.I.V.* It is a thermodynamic theory which stands somewhat between *T.I.P.* and *R.T.* but, in fact is the simplest generalization of *T.I.P.* P. Germain (1975) qualified of *cautious* those who favor this approach as they succeed in describing a rich variety of material responses without invoking a drastic revision of the basic concepts of thermodynamic laws. The origin of this *improved T.I.P.* may first be traced back in the kinetic description of *physico-chemical processes of evolution*, e.g. while considering the advancement rate of chemical reactions; see Müller (1985, Chapter 12). But its spectacular development is related to *rheological* models and the *elasto-visco-plasticity* of deformable materials of the metallic type (alloys, polycrystals) — see Maugin (1992a), Lemaitre and Chaboche (1990), and Chapter 7 below. In particular, if we consier all *rheological behaviors* described, for instance, in the early book of Reiner (1960 - the original version goes back to 1943) or the more recent book of Vyalov (1986), *T.I.V.* offers a nice thermodynamic framework to all behaviors formally described in these books. The same holds true for fluid-like behaviors in *rheology* that gently come under the umbrella of *T.I.V.*

As already mentioned, *T.I.V.* is adopting a somewhat intermediary line between *T.I.P.* and *R.T.* Essentially, it provides a new characterization of the behavior of continuous media which, in order to define the thermodynamic state $\mathcal{E}(S,t)$ of a system S, introduces in addition to the usual *observable* variables of state (heretofore collectively noted $\underset{\sim}{\chi}$, e.g. temperature and elastic strain), a certain number of *internal variables* of state, collectively denoted by α. These are supposed to describe the internal structure that is *hidden* to the eye of the (untrained) external observer who can only see a *black box* — hence they are also called *hidden variables.*[9] It follows at this state of generality that the value, at time t, of the dependent variables (e.g. the stress) becomes simultaneously a *function* of the values of *both* the independent observable variables and the internal variables. This constitutive equation, for example the *mechanical one* $\sigma(\chi,\alpha)$ where χ represents as before the *controllable* variables of state (those on which we can act per unit mass or else by the intermediate of surface actions, e.g. imposed tractions), must be complemented by an *evolution equation* law which describes the temporal evolution of the variable α, essentially the way in which it returns to its equilibrium value. For instance, we can write the following:

$$\sigma = \bar{\sigma}(\chi,\alpha) : \quad \text{law of state (mechanical here)} \tag{3.5.115}$$

and

$$\dot{\alpha} = f(\chi,\alpha) + g(\chi,\alpha)\dot{\chi} : \quad \text{evolution equation}\,. \tag{3.5.116}$$

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[9] This last naming will be avoided as it sometimes creates confusion with variables so christened in certain causal re-interpretations of quantum mechanics — for this last point see Sec 4.1.

In fact, we may suppose that we have been able to select the α's in such a way that $g(\chi, \alpha)$ might be identically zero and that an instantaneous variation of χ does not cause any instantaneous variation in the α's. In the present mechanical case, if χ is a strain, then the hypothesis $g(\chi, \alpha) = 0$ corresponds to the fact that instantaneous strains are elastic or zero).

The freedom in the choice of α makes it such that a framework can accommodate an incredibly wide range of dissipative behaviors, including those that P. Duhem early in this century could only consider as nonsensical from a thermodynamic point of view. Obviously, the internal variables are those gross "microscopic" variables of state of which P. Bridgman was dreaming before the full development of *T.I.P.* The latter must in fact be revisited so as to encompass these new variables, especially in so far as the *axiom of local* (equilibrium) *state* is concerned. Equations such as (3.5.116) will not have to contradict the second law. Methodologically, it in fact is this mathematical constraint that produces the sought evolution equations. The necessary appearance of *evolution* equations simultaneously indicates the important role that *time scales* will play. Length scales are not to be ignored altogether as, although there appear no *diffusion* term in (3.5.116) to start with, one must theoretically account for the size of the microstructure which gives rise to the dissipative processes that *T.I.V.* has to model in the most efficient manner. In particular, some materials may be *micro-heterogeneous* and this, indeed, causes dissipation on the macroscopic scale as shown in the case of composite materials (cf. Maugin, 1992a, Chapter 8). Last but not least, we should be able to *identify* the *internal variables of state* in terms of the underlying microscopic mechanisms which are responsible for the sensible dissipation. This is needed if we want to build a theory that is not physically empty. All these peculiar aspects of *T.I.V.* in comparison with other thermodynamics are specified in the forthcoming chapter.

Chapter 4

THERMODYNAMICS WITH INTERNAL VARIABLES[1]

"Hide and seek"
(The motto of internal
variables, G.A.M.)

4.1. Nature and Choice of Internal Variables

According to our historical disquisition of Chapter One the idea of *internal variables* in thermodynamics seems to have germinated in the mind of our grand predecessors, P. Duhem (1911) and P. Bridgman (1943). To start with, we have to provide a list, the length and detail of which depend on our own inclinations, of the parameters that we think will completely (this means to our own satisfaction) define a thermodynamic state. The question arises then of the *one or more new parameters that would affect the desired reduction of states of these complex cases* to a manageable list.[2]

The above-mentioned manageability is fostered by an astute choice of a new type of large-scale thermodynamic parameters of state... which can be measured but not controlled (Bridgman, 1943). By this we more precisely mean *internal variables* of state which can be *identified* and *measured*; but they are *not* coupled to any external-force variable which, like a body force or an applied traction, might provide the means of control. As a consequence these new *variables of state* do not appear beforehand in the *mechanical* work

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[1] This chapter depends heavily on the contents of Sections 3 to 6 of our review paper (Maugin and Muschik, 1994a).

[2] Recent works in physico-mechanico-metallurgical models involve up to 150 such variables with the accompanying evolution equations and a plethora of phenomenological coefficients to be determined by all means.

present in the statement (2.3.53) of the first law of thermodynamics. This is what gives them this special status of being *internal* or *hidden*. In spite of this, however, the tensorial nature of the internal variable α (scalar, vector, tensor, n-vector) as well as its "physical" nature must in general be specified. Does it represent the average of some microscopic effect or is it the measure of some local structural rearrangement? This identification is the most difficult part of phenomenological analysis. One must also point out at that stage that the notion of being "internal" for a variable of state depends on the level of observation. We can very easily think of a variable that might be considered as *internal* from the macroscopic observation point of view, say, at the usual macro-scale of continuum mechanics — in which a strong nonlocality is not taken into account (see below for this) — or as *observable* from a point of view of *mesoscopic* observation which, while already outside the usual scope of phenomenological physics, might still be understood in an enlarged (in length and time scales) phenomenological framework. Therefore, along with J. Mandel (1980) we can always say that a "clever physicist will always manage to detect the 'internal' variables and measure them". Controlling them may be outside his power, so that they are indeed *internal variables*. Thus in practice, these variables are *measurable* but not *controllable*, i.e. they cannot *a priori* be adjusted to a prescribed value through a direct action via a surface or body (volume) stimulus. We shall return to this critical point later (Sec. 4.7).

Is the idea of *internal variable* proper to thermomechanics or is it an old and recurring idea in physics? This question deserves a short digression if we are to believe M. Jammer (1974) in his discussion of a related idea in quantum mechanics. In that branch of physics it was thought in the 1950–1960s that one could introduce hypothetical quantities in order to "define" or "modify" the theory which was considered by some researchers, including Einstein and de Broglie, to give an incomplete, and therefore unsatisfactory, description of physical reality at the microscopic (atomic) scale. Such quantities were usually called "hidden variables" and the refinement or modification were called hidden-variable interpretations of the theory. The conceptual problem was, and remains, to find a generally accepted definition. David Bohm (1962) — one of the most active and penetrating exponents of this approach — characterized such variables as a "further set of variables, describing the state of new kinds of entities existing in a deeper subquantum mechanical level and obeying qualitatively new types of individual laws". According to other authors (quoted in Jammer, 1974, pp. 255–256), "hidden variables characterize a theory in the formulation of which one dispenses with a pervasive realizability of the theory". Such hidden variables are, in the quantum mechanical jargon, *unobservable*. Thus we see that although we come close to a similarity between "hidden" and "internal" variables, up to a drift in scale, in so far as the definition of state is concerned, the definitions clearly differ where *observability* is concerned. Still, this difference may only be conjunctural in the sense that the sub-quantum level was unobservable at the time, but it may later become decipherable through the use of to-be-discovered techniques, while on the other hand in *T.I.V.* we also use the qualitative "internal" in order to complement the "*incomplete*" description of thermodynamic states given by standard *observable* variables of state. To Max Jammer (1974, Chapter 7), a recognized observer of the quantum-mechanical scene, the idea of hidden variables and the accompanying two levels of description of physical reality are as old as physical thought, the continuum-versus-discreteness struggle being a clear illustration of this accompanying duality and complementarity, but most often antagonism. This idea was "applied in man's early attempts to explain the world in terms of a postulated *invisible* world" (p. 257). In modern but pre-quantum times, *atomic quantities* formed the basis of a not clearly advocated theory of *hidden variables*. Along this historical view, Ernst Mach (1838–1916) and P. Duhem seem to have been those who most forcefully opposed Ludwig Boltzmann's mechanical kinetic interpretation of phenomenological thermodynamics, a *hidden-variable theory* in its own right. Mach's arguments, similar to those of opponents to *hidden variables in causal re-interpretations of quantum mechanics* or opponents to *internal-variable theory* in modern thermodynamics, were the metaphysical print and scientific futility of such variables. It is the irony of the history of science that modern physicists almost unanimously follow Boltzmann and not Mach, while some authors find in P. Duhem's writing the very bases of a theory that was to become that of *internal variables* in thermomechanics.

4.2. Internal Variables and Functional Constitutive Equations

It is easily understood that the elimination of the variable α between, for example, Eqs. (3.5.115) and (3.5.116) by integration of the second on account of appropriate initial conditions will lead in theory to a *time-functional* law for σ with respect to the observable variables alone, i.e. a relationship of the type of (3.3.76) in thermomechanics. This interplay between *T.I.V.* and functional constitutive equations in the manner of *R.T.* was obviously noticed by some of the initiators of *T.I.V.* [Meixner,(1961); Coleman and Gurtin (1967a), Lubliner (1969, 1972, 1973)]. But from a practical point of view, what may look like an *approximation*, Eqs. (3.5.115) and (3.5.116), of a functional constitutive equation through the notion of internal variables, offers two main advantages: (i) it only requires a *finite number* of variables (the space of state remains of *finite dimension*). We may say that the past history has been condensed into the present values of a finite number of internal variables. But this number either may increase with the size of the sample if the structural rearrangements under study are local, or is relatively small if the internal variables represent averaged effects; and (ii) it enables us to use all the lessons learnt from *T.I.P.* (see below). In this manner we combine the two apparently markedly different approaches to thermodynamics, *T.I.P.* and *R.T.*, and at the same time we are automatically led to a *differential* mathematical problem of the *evolution type*, which *a priori* seems quite reasonable on account of known theoretical results concerning such systems and their rather simple numerical implementation. In conclusion, we note that introducing *internal variables* allows one to work with a *large* state space while material properties defined by maps of process histories, as in Eq. (3.3.79), make use of a *small* state space (cf. Muschik, 1990). However, it is clear that the state space of internal-variable theory, although larger than that of rational thermodynamics, should be as small as possible, whereas for the best validity of the forthcoming analysis it should be as large as possible.[3] As usual this contradiction is resolved in a compromise.

4.3. Non-Equilibrium and Equilibrium States

Equation (3.5.116) shows that we are placed within a *dynamic* framework. What are we to do then with those notions, like temperature and entropy, that are well defined only in thermostatics? It is obvious that we must formulate some axiom of the *local-state* type and that we must pay attention that the characteristic times that eventually enter (3.5.116)[4] remain relatively small as against the macroscopic evolution. If this is possible, we can then actually use

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[3] Parodying a saying attributed to Einstein, this state space should be "as small as possible, but not smaller!".

[4] This is *not* always the case; see elastoplasticity which has *no* time scale (Chapters 5 and 7)

the theory of irreversible processes, *enlarged so as to encompass the internal variables of state*. And in this case *T.I.V.* will remain a thermodynamic theory in the vicinity of equilibrium. In the process we expect that the looked-for evolution equation for α, being constrained to satisfy the local statement of dissipation, will indeed follow from this very statement, for instance through the appropriately generalized notion of *dissipation potential*. Incorporating internal variables in such a framework is the object of this section.

We consider a *discrete system* S in the sense of W. Schottky (1886–1976). This is a system which can suffer the three types of exchange mentioned in Sec. 2.1. while the power expanded by the usual *normal* (in the sense of Duhem) variables of state χ_β $\beta = 1, \ldots, n$, reads (cf. Muschik, 1990):

$$p_{(i)} = -\sum_{\beta=1}^{n} \rho\tau_\beta \dot{\chi}_\beta \,. \tag{4.3.1}$$

We shall not consider exchanges of mass. Thus, in a general manner the thermodynamic state $\mathcal{E}(S,t)$ at each time t is characterized by a set of *independent* and *dependent state variables*. For instance, outside equilibrium, which is our concern, and accounting for a set α of *internal variables*, the *state space at non-equilibrium* is defined by

$$\mathcal{Z} = (e, \chi_\beta, \alpha, \theta_c; \theta_s^*, \tau_\beta^*) \,, \tag{4.3.2}$$

where e is the internal energy, χ_β are the *observable* variables of state, θ_s is the *thermostatic* temperature — defined from e — (cf. Eq. (3.2.1)) — and θ_c is the *so-called contact temperature* which is independent of e in non-equilibrium (cf. Muschik, 1977, 1979, 1981, 1990a, b). The latter notion which we shall not elaborate upon, receives a statistical-mechanics justification (Muschik and Fang, 1989). The superscript asterisk $*$ denotes the quantities defined in the equilibrium state $\mathcal{E}^*(S)$ in the vicinity of $\mathcal{E}(S,t$ fixed). The equilibrium subspace of $\mathcal{Z}$ is generated by

$$\mathcal{Z}_{\mathrm{eq}} = (e, \chi_\beta, \alpha(e, \chi_\beta)) \,, \tag{4.3.3}$$

according to which the equilibrium values of internal variables α are expressible in terms of energy and the observable variables alone at *equilibrium*. Whether this determination is *unique* or not depends on the type of phenomenon considered. The solution $\alpha_{\mathrm{eq}} = \bar{\alpha}(e, \chi_\beta)$ may present a *multiplicity* of order m of determinations as is the case in plasticity (Muschik, 1990a). If we remember that the *equations of state* relate variables in the equilibrium state, then with the identification of θ_c and θ_s at equilibrium and the fact that θ_s and τ_β then derive from e, the reduction from (4.3.2) to (4.3.3) is easily understood.

At this point we recall that the α's have been introduced to compensate for our lack of a precise description of underlying microscopic instablities [e.g. the growth of Frank–Read sources in dislocated (plastic) bodies, the jerky motion of domain walls in ferromagnets, etc.] which manifest themselves as *irreversibility* at the macroscopic scale. Along a trajectory $\mathcal{T}$ of a process joining two states in non-equilibrium state space, the time evolution of *non-equilibrium entropy* η has the form [cf. (3.2.4)]

$$\rho\theta_c\dot{\eta} = \rho(\dot{e} - \omega) + \mathcal{A}\dot{\alpha} + \Sigma\,, \tag{4.3.4}$$

where $\mathcal{A}$ is the force (affinity) conjugate to α and Σ is the entropy production per unit volume through heat processes. The additional power term $\mathcal{A}\dot{\alpha}$ represents an *internal* power which, in the case of a real (i.e. irreversible) evolution is entirely *dissipated* inside the system instead of being developed against the exterior (this is a definition of *internal variables*). As a consequence of this characteristic manifestation of the *internal* nature of α, this power does not appear in the following statement, which therefore remains unchanged compared to classical thermodynamics. That is, for a thermodeformable continuum the local *first law reads the same as in the energy equation* (3.2.8)

$$\rho\dot{e} = \sigma : \mathbf{D} + \dot{q}, \qquad \dot{q} := \rho h - \nabla\cdot\mathbf{q}\,. \tag{4.3.5}$$

On combining (4.3.4) and (4.3.5) we obtain

$$\rho\theta_s\dot{\eta} = \Phi_{\text{intr}} + \dot{q} + \Sigma\,, \tag{4.3.6}$$

where we have now

$$\Phi_{\text{intr}} = \sigma : \mathbf{D} + \mathcal{A}\dot{\alpha} - \rho\omega\,. \tag{4.3.7}$$

At *equilibrium*, Eqs. (4.3.4) and (4.3.6) reduce to

$$\rho\theta_s\dot{\eta}_{\text{eq}} = \rho(\dot{e} - \omega_{\text{eq}}), \quad \mathcal{A}_{\text{eq}} = \mathbf{0}, \quad \Sigma_{\text{eq}} = 0\,, \tag{4.3.8}$$

and

$$\rho\theta_s\dot{\eta}_{\text{eq}} = \dot{q}_{\text{eq}}\,, \tag{4.3.9}$$

respectively. Equation $(4.3.8)_1$ is none other than Eq. (3.2.3) up to the factor ρ.

The constitutive quantities present in (4.3.4) form a set $M = (\eta, \tau_\beta, \mathcal{A}, \Sigma)$ which can be defined either on a large state space (theory with internal variables) or a small state space (theory with time functionals). The former choice is preferred here. According to Muschik (1990), an *isolation* of the system S from its vicinity does not influence internal variables. This isolation is defined by $\dot{e} = 0$, $\dot{q} = 0$ (adiabaticity), so that the *second law of thermodynamics* is given by the *dissipation inequality*

$$\rho\theta_c\dot{\eta}_{\mathrm{isol}} = \mathcal{A}\dot{\alpha} + \Sigma \geq 0 . \tag{4.3.10}$$

Equilibrium can now be defined in a more precise maner. We, in fact, give *two* definitions. First, *unconstrained equilibrium* is defined by

$$\begin{gathered} \theta_c(e) = \theta_s, \quad \Sigma = 0 , \\ \mathcal{A} = 0 \longrightarrow \dot{\alpha} = 0 . \end{gathered} \tag{4.3.11}$$

That is, contact temperature at equilibrium takes on the thermostatic value. The third of (4.3.11) follows from the assumed continuity of $\mathcal{A}$ with respect to $\dot{\alpha}$ in the neighborhood of vanishing forces $\mathcal{A}$. In contrast, *constrained equilibrium* imposes a vanishing time evolution of α but not necessarily vanishing conjugate forces, so that (4.3.11) is then replaced by the conditions:

$$\begin{gathered} \theta_c(e) = \theta_s, \quad \Sigma = 0 , \\ \dot{\alpha} = 0 \longrightarrow \mathcal{A} = 0 \text{ possibly} , \end{gathered} \tag{4.3.12}$$

In such constrained equilibria the internal variables are *frozen* in; they do not evolve with time. This definition proves to be useful in associating an equilibrium state to a non-equilibrium one following along the works of Bataille and Kestin (1975, 1979) — see next section.

4.4. Accompanying Processes and States

Now we associate points of non-equilibrium state space with points of equilibrium state space by means of a *projection*. This procedure has a long history which is mainly due to by Meixner (1972), Bataille and Kestin (1975, 1979), Kestin (1990, 1992), and Muschik (1990). It is the most commonly accepted point of view which consists of replacing the axiom of the *local equilibrium* state of classical irreversible thermodynamics with a somewhat straightforward generalization known under the name of the axiom of *local accompanying state* (for short, $L.A.S$). We first deal with this in a nontechnical manner.

A. Verbal statement of the $L.A.S$

According to Bataille and Kestin (1975, 1979), the *axiom of* $L.A.S$ can be enunciated thus: To each "particle" of the continuum we may associate at time t a *thermostatic system* (of unit mass) characterized by the set of variables (e, χ_β, α) for which Gibbs' equation can be written as

$$d\eta_\alpha = \theta_\alpha^{-1}\left(de - \sum_{\beta=1}^{n} \tau_\beta^\alpha d\chi_\beta + \rho^{-1} \mathcal{A}_\alpha d\alpha\right), \tag{4.4.13}$$

where θ_α and η_α are an absolute temperature and an entropy density to be used for the thermo-*dynamic* description of the "particle". Note the labeling "α" of θ, τ_β and $\mathcal{A}$ related to the fact that this particular set α has been selected. The association (4.4.13) is effected at each instant of time t of the evolution of the said particle which is generally thermodynamically irreversible. In agreement with a previous remark, Gibbs' equation (4.4.13) provides us with the *equations of state*, here either

$$\theta_\alpha^{-1} = \frac{\partial \eta_\alpha}{\partial e}, \quad \tau_\beta^\alpha = -\theta_\alpha \frac{\partial \eta_\alpha}{\partial \alpha_\beta}, \quad \mathcal{A}_\alpha = \rho\theta_\alpha \frac{\partial \eta_\alpha}{\partial \alpha}, \tag{4.4.14}$$

or else, after partial Legendre transformation of the type of (3.5),

$$\eta_\alpha = -\frac{\partial \psi}{\partial \theta_\alpha}, \quad \tau_\beta^\alpha = \frac{\partial \psi}{\partial \chi_\beta}, \quad \mathcal{A}_\alpha = -\rho \frac{\partial \psi}{\partial \alpha}. \tag{4.4.15}$$

The thermostatic system thus introduced is called the *local accompanying system* ($L.A.S$). The introduction of this $L.A.S$ raises several questions concerning its physical significance, applicability, and the selection of significant internal variables. To shed some light on the first point, let us consider the simple case where χ is the strain tensor ε of the small-strain theory of deformable solids, and the system presents no anelastic stress. Thus $\tau = \sigma/\rho$ and $\sigma^{\text{anel}} = 0$. Then the $L.A.S$ method in fact assumes that the "particle" or "cell" in question in fact represents itself a continuum at a finer level of description (cf. Germain *et al.*, 1983).[5] The local value of the internal energy e can be looked upon as the *global* internal energy of the particle or cell. In like manner, ε may be viewed as the global geometrical description of the cell. Then keeping both

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[5] This is not without recalling the subquantum level for *hidden variables in quantum mechanics*.

e and ε constant means, from a thermodynamical viewpoint, that the cell is *isolated.* But this "macroscopic" cell may be highly heterogeneous and the various dissipative mechanisms at work in it are then described by *internal variables* α which indeed appear as the *new type of large-scale thermodynamic parameters* to which Bridgman (1943) hinted at in order to fulfil J. W. Gibbs' wishes. We obviously would like to have the number of such variables relatively small, and there must exist some criterion to decide on how to retain or discard any physically interpretable internal variables from the description.

It is at this point that *characteristic time scales* enter the picture, c.f. (3.2.2a). The macroscopic time that one related to the cell as a whole is $\tau_M = \varepsilon/\dot{\varepsilon}$. Let further σ_M be a possible bound on macroscopic stresses acting on this cell. Some internal dissipative mechanisms are characterized by a *relaxation time* $\tau_\alpha = \alpha/\dot{\alpha}$, e.g. in viscoelasticity. If $(\mathcal{D}e)_{\mathrm{relax}} = \tau_\alpha/\tau_M = 0(1)$, then the corresponding mechanism can be discarded. If, however, $(\mathcal{D}e)_{\mathrm{relax}} \ll 1$, then the corresponding internal variables take their *equilibrium value* that they have reached once the whole sytem has been considered isolated (with e, ε and the *other internal* variables frozen), while if $(\mathcal{D}e)_{\mathrm{relax}} \gg 1$, then the corresponding internal variable appears to be *frozen in* on the time scale of strain evolution. For dissipative mechanisms such as *rate-independent plasticity* which, by definition, do not involve a characteristic time (cf. Maugin, 1992a), it is the *yield limit* which plays a determining role. If that yield limit — in microscopic terms, the activation level of dislocation glide — is below σ_M, the corresponding α must be kept while for a yield limit much larger than σ_M, again the corresponding α may be considered as frozen, and this plays no role in the *L.A.S.*

A simple example due to J. Mandel (1973) illustrates particularly well the above emphasized point in relation to the choice of the pertinent internal variable. Consider the simple rheological model known as *Maxwell's model* (Fig. 4.1) where a dash-pot (viscous or Newton element) and a spring are placed in series. Clearly, the *observable variable* β — the relative displacement of the two ends of the model — is not sufficient for the determination of the *state* of the model. As internal variables we have the choice between the abscissa α of the piston in the dash-pot and the elongation $x = \beta - \alpha$ of the spring. But if a *fast* change is imposed on β via the force σ (stress) x clearly changes accordingly while α remains practically unchanged. Thus we must discard x and select α as the pertinent internal variable in so far as time scales and the application of the *L.A.S* are concerned. The hierarchy of such time scales

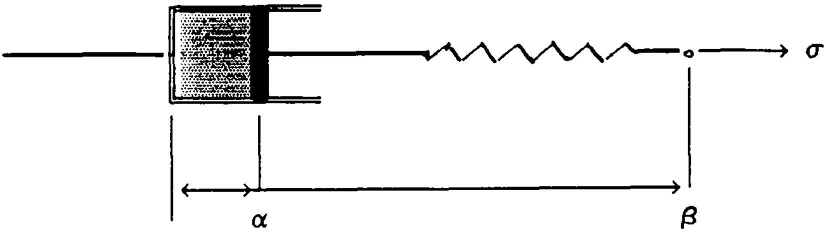

Fig. 4.1. The Maxwell model and the choice of internal variable.

was heavily emphasized by Bataille and Kestin (1979, pp. 242–243) in their interesting *gedanken experiment* involving a sequence of less and less admissible accompanying equilibrium states — corresponding to progressively fewer constrained deformation variables. The same idea was again used in a model of plasticity (Ponter *et al.*, 1979; see also Muschik, 1990a, b) where different *projections* onto equilibrium subspaces relate to very dissimilar time scales.

The variety of behaviors which results from the above sketched out method makes it such that the definition of a system associated with a particle depends on the degree of refinement which seems suitable to the description, both spatially and timewise. This decides on the choice and number of internal variables to be kept in the description. In turn, entropy density and absolute temperature are very much associated with a definite level of description. Therefore, *they have a relative significance.* This points to an inherent weakness of the method. This lack of uniqueness in the concept of entropy of a non-equilibrium state was first discovered by J. Meixner (1973a).But once the selection of internal variables is achieved, the nature of microscopic mechanisms of interest delineated, and the relevant time scales and stress levels (or of other fields in a different branch of physics) well established, then this definition of entropy $\eta = \eta_\alpha$ and temperature $\theta = \theta_\alpha$ becomes unambiguous to a trained scientist who masters the *art of material modeling.* However, we must still notice, together with Meixner (1973b) that it is still possible to assume that η differs from η_α and θ from θ_α, and these differences will generate additional terms in the final dissipation inquality. As a matter of fact, the entropy η_α of the *L.A.S* is always larger than that of the original non-equilibrium state because the former is produced from the latter by an *adiabatic, no-work* process (Kestin, 1992; Bataille and Kestin, 1979). But this complication can often be discarded (see Bataille and Kestin, 1975, pp. 376–377).

B. Formal statement of the *L.A.S.*

The above statement can now be formally summarized as follows (Muschik, 1990a): *call* α_f *the subset of internal variables which may be considered as frozen in on the time scale* τ_M, α_e *that subset which, having fast relaxation, reaches their equilibrium values, and* α_m *the final subset such that* $\tau_{\alpha m}/\tau_M = 0(1)$. *Then to each point in state space* (4.3.2) *we associate a general* **local accompanying state** (*L.A.S*) *by*

$$\mathcal{Z}^{\alpha}_{\mathrm{eq}} = (e, \chi_\beta, \alpha_e(e, \chi_\beta), \alpha_m, \alpha_f \text{frozen}) , \tag{4.4.16}$$

so that Eqs. (4.3.4) *through* (4.3.11) *hold true and, by isolation, we obtain the dissipation inequality* (4.3.10) *while* $\theta_c(e) = \theta_s$ *at equilibrium.*

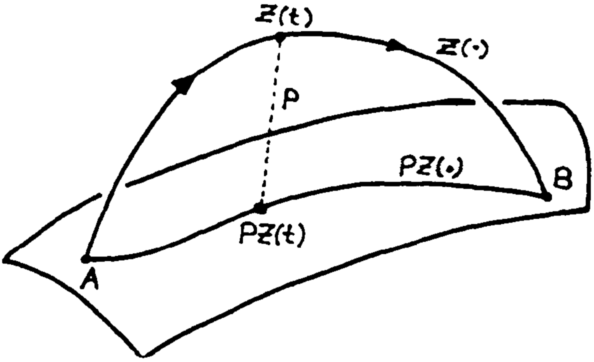

Fig. 4.2. Projection of the process $\mathcal{Z}(t)$ point by point onto the equilibrium subspace represented as a hypersurface in state space (after Muschik, 1990).

Equation (4.4.16) is viewed as a *projection* $P\mathcal{Z}$ onto equilibrium state space (Fig. 4.2). Several different projections exist, e.g.

$$P_0\mathcal{Z}(t) = (e, \chi_\beta, \alpha_f) , \tag{4.4.17}$$

or

$$P_{\mathrm{relax}}\mathcal{Z}(t) = (e, \chi_\beta, \alpha_e(e, \chi_\beta)) , \tag{4.4.18}$$

or else

$$P\mathcal{Z}(t) = (e, \chi_\beta, \alpha_e(e, \chi_\beta), \alpha_f) . \tag{4.4.19}$$

These possibilities are well illustrated by the Ponter–Bataille–Kestin model of plasticity (1979) where internal variables are supposed to account for modes of operation of Frank–Read sources of dislocations (see also Muschik, 1990a, for a formal presentation in the above formalism).

The time parameter that appears in Eqs. (4.4.17)–(4.4.19) is fixed. But in thermo-*dynamics* a *process* is a time sequence of states. The reversible process obtained as the sequence of projections of points of non-equilibrium state space onto equilibrium state space may be called the *accompanying reversible process* so that, in theory, "process" and "state" cannot be misunderstood for one another. However, the qualitative "accompanying" has an unavoidable dynamical connotation and this favors that misunderstanding. The accompanying reversible process is *enslaved* to the time evolution of the real (irreversible) process, i.e. the time sequence of points in non-equilibrium state space; in truth, the time solution of the general problem of evolution on account of initial conditions and boundary conditions. This slaving is due to the fact that according to (4.4.17) through (4.4.19) the time is left untouched by the projection. As recently noted by Kestin (1992), this gives a picture of a "reversible process as one which occurs at a finite rate in contrast with the historic prescription that a reversible process must occur *infinitely slowly* or must be the result of the convergence from a real process when its rate is reduced to zero".[6]

In the practice of many worked out examples the present author has often followed the *pragmatic* point of view of J. Mandel (1971, 1973) in that the starting point has often been the Clausius–Duhem inequality — say Eq. (3.3.76) — in the form favored by rational thermodynamics, but with η and θ defined by the $L.A.S$ method. Thus,

$$\eta = \eta_\alpha = -\left.\frac{\partial \psi}{\partial \theta}\right|_{\theta=\theta_\alpha}, \qquad \psi = \psi(\chi_\beta, \theta, \alpha), \tag{4.4.20}$$

in agreement with (4.4.15), so that the remaining dissipation inequality will read [cf. (4.3.6)]

$$\Phi = \Phi_{\text{intr}} + \theta_\alpha \mathbf{q} \cdot \nabla(\theta_\alpha^{-1}) \geq 0, \tag{4.4.21}$$

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[6] Kestin (1992) continues by noting that readers not persuaded by this apparent paradox "can imagine that, departing from equilibrium at any state $\mathcal{Z}_{\text{eq}}$, the system keeps continuously reverting to it (say by coaxing of Maxwell's demon) with a negligibly short relaxation time ($\mathcal{D}e \cong 0$)."

where, obviously, it has been assumed in general that the entropy flux $\mathbf{S}$ is the heat flux $\mathbf{q}$ divided by θ_α. This last constraint can eventually be relaxed (see below). This pragmatism is also demonstrated by Sidoroff (1976). Furthermore, some extensive works (e.g. Lemaitre and Chaboche, 1990) that make constant use of *T.I.V.* do not even bother with the subtleties touched upon in this section.

In conclusion, as pointed out by Germain *et al.* (1985), the flexibility of the *L.A.S* method thus exhibited and its simplicity in formulating constitutive equations (by following *T.I.P.* — see below) are two assets which other approaches can hardly compete with.

4.5. Applying *T.I.P.* to *T.I.V.*

Here we introduce the viewpoint expressed in Eqs. (4.4.20) and (4.4.21) according to which the starting point is the Clausius–Duhem inequality given by Eq. (3.3.76), it being understood that $\theta = \theta_c = \theta_s = \theta_\alpha$ when (4.4.20) is valid. Here, for the sake of illustration we consider only *thermomechanical processes*; more general cases will be examined in the application part (Chapters 6 to 10). More precisely, we look at *solids in small strains*, but there are no difficulties in rewriting the same expressions in *material formalism* in order to accommodate large (finite) strains — see Chapter 7. That is, we consider that strain ε decomposes *additively* into *elastic* (ε^e) and *anelastic* (ε^p) contributions, none of which being a gradient. The latter, ε^p, always causes *dissipation*, i.e. it has a fully *dissipative* nature. With the *laws of state*

$$\begin{gathered}\eta = \eta_\alpha \equiv -\rho_0^{-1} \frac{\partial \bar{W}}{\partial \theta}\bigg|_{\theta=\theta_\alpha}, \qquad \sigma^e = \sigma^e_\alpha \equiv \frac{\partial \bar{W}}{\partial \varepsilon^e}, \\ \mathcal{A} = -\frac{\partial \bar{W}}{\partial \alpha}, \qquad W := \rho_0 \psi = \bar{W}(\varepsilon^e, \alpha, \theta),\end{gathered} \tag{4.5.22}$$

we deduce the *dissipation inequality* in the form

$$\Phi = \Phi_{\mathsf{intr}} + \Phi_{\mathsf{th}} \geq 0, \tag{4.5.23}$$

wherein

$$\begin{gathered}\phi_{\mathsf{intr}} = \sigma^v : \dot{\varepsilon}^e + \sigma : \dot{\varepsilon}^p + \mathcal{A}\dot{\alpha}, \qquad \sigma^v := \sigma - \sigma^e = \sigma^v_\alpha, \\ \phi_{\mathsf{th}} = \theta_\alpha \mathbf{q} \cdot \nabla(\theta_\alpha^{-1}),\end{gathered} \tag{4.5.24}$$

where subscripts α emphasize the choice of the phenomenological description with the set of α internal variables. Equations (4.5.24) are rich enough to accommodate very many material behaviors via the presence or absence of ε^p, and whether σ^v exists at all. Again Φ is in the *canonical bilinear form* (3.63) which encourages the application of *T.I.P.* in the most straightforward manner. The interesting points at this state of generality are the following. First, one often assumes separate non-negativeness conditions for *intrinsic* and *thermal* dissipations, i.e.

$$\Phi_{\text{intr}} \geq 0, \qquad \phi_{\text{th}} \geq 0 . \tag{4.5.25}$$

although this is *not* a general rule. Second, according to (4.5.24), while σ — the *total* stress — remains the thermodynamic conjugate of the *anelastic* (in most cases *plastic*) strain, the *viscous stress* σ^v has for thermodynamic conjugate the *elastic strain* only. Whenever $\varepsilon^p = 0$, σ^v is none other than the dissipative stress introduced in (3.2.26). Third, one could be tempted to apply *T.I.P.* — Eq. (4.5.22) or the *dissipation-function* framework, Eqs. (3.2.71)-(3.2.73) — directly to (4.5.24). But, on the one hand, this cannot be so blindly applied without precisely knowing the time parity and tensorial nature of the internal variables α. On the other hand the very naming of ε^e, ε^p and σ^v suggests that markedly different behaviors are expected from the first two contributions in $(4.5.24)_1$. As a matter of fact, σ^v is to denote *viscous-stress* processes which typically exhibit a characteristic time and are therefore of the *relaxation* type, whereas we expect the second contribution (and perhaps the third as well) to represent typically rate-independent (plastic-like) effects, thus exhibiting no characteristic time but rather a yield stress level in agreement with a foregoing discussion. Whether the third contribution in $(4.5.24)_1$ is of the former type or the latter depends on the type of microscopic phenomenon accounted for through α. Such distinct behaviors cannot be accommodated simultaneously in the *classical framework of T.I.P.* — Eq. (3.2.65) and (3.2.66) — which, certainly, was not initially built to account for plasticity and rate-independent hysteresis.[7] The solution to this problem is provided (see Chapter 5) by an *ad hoc* generalization of the second point of view, resulting in the introduction of a non-negative convex *dissipation potential* with the appropriate degree

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[7] Thus Duhem's hope (1903) — see also Manville (1927) — to incorporate friction and hysteresis in a harmonious thermodynamic framework was far from being realized with classical *T.I.P.* But J. J. Moreau's paper (1971), short as it is, indeed fulfills this dream concerning two of the *nonsensical* branches of thermodynamics.

of (mathematical) homogeneity with respect to its arguments. This had to await the proposal by Ziegler (1963, among other works by this author) and Moreau (1971) of the consideration of such a *pseudo*-potential of dissipation. The same method, applied to the internal variable α, enabled other authors to incorporate *hardening* (Nguyen Quoc Son, 1973; Halphen and Nguyen Quoc Son, 1975) in the same thermodynamical framework. Magnetic (Chernyi, 1983; Maugin, Sabir and Chambon, 1987) and electric (Bassiouny *et al.*, 1988; Maugin and Bassiouny, 1989) hysteretic responses would then find their right place in this framework by also combining the notion of internal variables and rate-independent, plastic-like, response, and the existence of a pseudopotential of dissipation. These belong to a class of *singular* behaviors as *all* other dissipative behaviors that we shall consider in this book are of the more *regular*, *relaxation* type. Such relaxation behaviors are exemplified by evolution equations of the type

$$\dot{\alpha}(t) = -\frac{1}{\tau_\alpha(\chi_\beta, \theta_\alpha)}\{\alpha(t) - \alpha_e(\chi_\beta(t), \theta_\alpha(t))\} \tag{4.5.26}$$

where $\tau_\alpha > 0$ is the relaxation time and α_e is the "equilibrium" functional form of α, and

$$\dot{\alpha}(t) = \gamma(\chi_\beta, \theta_\alpha)\{1 - \exp[-\mu(t)\mathcal{A}_\alpha(\chi_\beta(t), \theta_\alpha(t))]\}\,. \tag{4.5.27}$$

The latter is typical of *reaction kinetics* ($\gamma > 0$, $\mu > 0$) and satisfies the condition that $\mathcal{A}_\alpha = 0$ implies $\dot{\alpha} = 0$; Typically, (4.5.26) is obtained from Eqs. (4.5.24) and (3.2.71) through

$$\begin{aligned} \bar{W} &= \frac{1}{2}\lambda(\chi_\beta, \theta)[\alpha - \alpha_e(\chi_\beta, \theta)]^2 + f(\chi_\beta, \theta)\,, \\ \mathcal{D} &= \frac{1}{2}\nu(\chi_\beta, \theta)\mathcal{A}^2 + g\,, \end{aligned} \tag{4.5.28}$$

where g is *not* a function of $\mathcal{A}$. Thus,

$$\tau_\alpha^{-1}(\chi_\beta \theta) = \lambda(\chi_\beta, \theta)\nu(\chi_\beta, \theta)|_{\theta=\theta_\alpha}\,. \tag{4.5.29}$$

Clearly, the case of Eq. (4.5.27) is more involved and does not lend itself to this simple formalism because a potential $\mathcal{D}$ from which (4.5.27) would be derivable, is *not* homogeneous, at any degree, in $\mathcal{A}$ so that no guarantee of non-negativeness of dissipation Φ exists!

The final point concerns the rich *couplings* that may exist between σ^v and α on the one hand, and the time evolution of α and the state variables χ_β

essentially through the energy density W. That is, in most cases where such couplings are allowed by the time parity and tensorial nature of both χ_β and α, the application of *T.I.P.* or of the pseudopotential of dissipation imposes rather definite couplings between the additional (complementary) constitutive equations, e.g. for σ^v or σ^D, and the right-hand side of evolution equations for internal variables. This is particularly true when α is a second-order tensor (for instance, in solutions of polymers and liquid crystals — see Sec. 6.4 below) or α is a polar vector such as in suspensions of fibers and some liquid crystals (see Chapter 6 below).

4.6. Potentials of Dissipation

In many cases the introduction of a dissipation potential along the above-indicated lines is practically automatic. We illustrate this by essentially following Kestin and Rice (1970), Rice (1971), and Germain *et al.* (1985).[8] We wish here to account for an *anelastic* behavior as a result, for example, of the *microscale structural rearrangements* of the constitutive elements of the examined sample. This type of behavior may well be the result of a plastic deformation due to a dislocation movement, e.g. the slip of crystallographic planes in a metal, to the *twinning* of crystals, to the slip of grain boundaries, or to a stress-induced phase transition, etc. Then the internal variables are represented collectively by an n-vector α, of which each component characterizes a *local* structural rearrangement at a *given* point in the sample. Obviously, the number of this type of internal variables increases in relation to the size of the sample under consideration, and this is *not* what we would like most. Perhaps more usual and more interesting for the applicability of the method is the case of internal variables of the *average* type. They then represent the *mean measures* of the structural rearrangements that take place at *several* points. As a consequence the number n then is independent of the size of the sample and we expect it to be small, in any case. Examples of such internal variables are the different *statistical moments* of the distribution of dislocations as proposed by Kröner (1963).

Let us suppose that the internal variable α may be kept at a prescribed value by the imposition of an appropriate stress σ. Note that we can only act via classical mechanical forces but not through a *force* directly conjugated to

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[8] See also Maugin (1992a, pp. 278–281) to whom we borrow much of the final form of this section.

α. The sample will then tend towards a state of thermodynamic *equilibrium* characterized by a stress (response) σ, a strain ε, and a temperature θ. Let us further assume following Kestin and Rice (1970) that if different states of equilibrium between the variables of state (σ or ε, θ, α) are possible for the *same* values of α, then the neighboring states are connected by the laws of ordinary *thermoelasticity* (which are established in thermostatics, in the absence of heat conduction), i.e. in small strains (see Sec. 3.4):

$$\begin{aligned} \sigma &= \frac{\partial \bar{W}}{\partial \varepsilon}, \qquad \eta = -\rho_0^{-1}\frac{\partial \bar{W}}{\partial \theta}, \\ \mathcal{A} &= -\frac{\partial \bar{W}}{\partial \alpha}, \qquad W = \rho_0 \psi = \bar{W}(\varepsilon, \theta, \alpha), \end{aligned} \tag{4.6.30}$$

where $\bar{W}$ is concave in θ and convex and lower semicontinuous in ε and α. We can thus introduce a partial Legendre–Fenchel transform of $\bar{W}$ by

$$W^*(\sigma, \theta, \alpha) = \sup_{\varepsilon}(\sigma : \varepsilon - \bar{W}), \tag{4.6.31}$$

so that

$$\begin{aligned} \varepsilon &= \frac{\partial W^*}{\partial \sigma}, \qquad \eta = \rho_0^{-1}\frac{\partial W^*}{\partial \alpha}, \\ \mathcal{A} &= \frac{\partial W^*}{\partial \alpha}, \qquad W^* = \bar{W}^*(\sigma, \theta, \alpha). \end{aligned} \tag{4.6.32}$$

The infinitesimal *anelastic* strain will be the contribution resulting from a variation of internal variables when both stress and temperature are kept fixed. That is,

$$(\delta\varepsilon)^p = \frac{\partial \varepsilon}{\partial \alpha} \cdot \delta\alpha = \frac{\partial^2 W^*}{\partial \sigma \partial \alpha} \cdot \delta\alpha = \frac{\partial \mathcal{A}}{\partial \sigma} \cdot \delta\alpha \tag{4.6.33}$$

according to Maxwell's relation between second order partial derivatives of W^*. As to the *thermoelastic* strain, it is that one which results from a variation of θ and σ alone, so that

$$(\delta\varepsilon)^e = \frac{\partial^2 W^*}{\partial \sigma \partial \sigma} : \delta\sigma + \frac{\partial^2 W^*}{\partial \sigma \partial \theta}\delta\theta, \tag{4.6.34}$$

where the two factors of variations introduced in the right-hand side are the so-called *elastic compliances* and *thermal dilatations*, respectively. Then we can apply *T.I.P.* as a process of homogeneous macroscopic strains may be approached by a true sequence of *constrained* (controlled) states of equilibrium

$(L.A.S)$. Furthermore, the above development shows that a potential of dissipation can be introduced which will provide, by differentiation, a *kinetic relation* for the internal variables α. A natural way to proceed is, following Kestin and Rice (1970) to suppose that: "the rate at which any structural rearrangement (α) happens is entirely determined by the force ($\mathcal{A}$) associated with this rearrangement". This is some kind of common-sense *causality* proposal (which does not in general imply a linear relationship) according to which we should write:

$$\dot{\alpha} = \bar{\alpha}(\mathcal{A}, \theta, \alpha) , \tag{4.6.35}$$

where $\mathcal{A}$ depends on σ as shown by (4.6.32) and (4.6.33). This formalism is particularly well suited to the *viscoplasticity* of metals, in which case the above supposition translates to: "the force on a segment of dislocation line governs its movement".

From (4.6.35) we can write in an identical way, by evaluating the integral at θ and α fixed,

$$\dot{\alpha} = \frac{\partial}{\partial \mathcal{A}} \int_0^{\mathcal{A}} \bar{\alpha}(\mathcal{A}, \theta, \alpha) d\mathcal{A} . \tag{4.6.36}$$

Setting

$$\mathcal{D}^*(\sigma, \theta, \alpha) := \int_0^{\mathcal{A}(\sigma,\theta,\alpha)} \bar{\alpha}(\mathcal{A}, \theta, \alpha) d\mathcal{A} , \tag{4.6.37}$$

we check that

$$\frac{\partial \mathcal{D}^*}{\partial \sigma} = \frac{\partial \mathcal{D}^*}{\partial \mathcal{A}} \cdot \frac{\partial \mathcal{A}}{\partial \sigma} = \dot{\alpha} \cdot \frac{\partial \varepsilon}{\partial \alpha} = \dot{\varepsilon}^p \tag{4.6.38}$$

through the use of (4.6.33). Thus we have the proof of the existence of a *flow potential* $\mathcal{D}^*$ such that

$$\dot{\varepsilon}^p = \frac{\partial \mathcal{D}^*(\sigma, \theta, \alpha)}{\partial \sigma} . \tag{4.6.39}$$

This also expresses the fact that the increment $\dot{\varepsilon}^p$ is *normal* to a constant flow potential in *stress space*. This situation is met within the *elastoviscoplasticity of metals*, where a time scale (viscosity) plays an important role. This is illustrated by a continuous model of *slip* in metal viscoplasticity (Zarka, 1973) where (4.6.39) is written as

$$\dot{\gamma}^{(\alpha)} = \bar{\gamma}^{(\alpha)}(\tau^{(\alpha)}, \theta, \gamma) = \frac{\partial \mathcal{D}^*}{\partial \tau^{(\alpha)}} , \tag{4.6.40}$$

in which $\gamma^{(\alpha)}$ is the slip in the α-simple-slip system in the crystal — it is a variable of the "structural rearrangement type — and

$$\tau^{(\alpha)} = \frac{\partial W^*}{\partial \gamma^{(\alpha)}} \tag{4.6.41}$$

is the so-called *resolved-shear stress* related to the α system of slip.

We also note that Eq. (4.6.35) can be written as

$$\dot{\alpha} = \frac{\partial \mathcal{D}^*(\mathcal{A}, \theta, \alpha)}{\partial \mathcal{A}} . \tag{4.6.42}$$

If $\mathcal{D}^*$ is associated to a non-negative dissipation (pseudo) potential which is homogeneous of degree m in the force $\mathcal{A}$, then $\mathcal{A}\dot{\alpha}$ is also non-negative and homogeneous of degree m by virtue of Euler's identity. The intrinsic dissipation thus satisfies, in the condition where (4.5.25) applies, the second law of thermodynamics

$$\Phi = \mathcal{A}\dot{\alpha} \geq 0 . \tag{4.6.43}$$

We shall return to this framework in Chapter 5 in general and in Chapter 7 for the case of solids.

4.7. Internal Variables and Microstructure

A. Highly heterogeneous bodies

Through the procedure known as *homogenization*, a material body which presents a high degree of heterogeneity at a microscopic scale (characteristic length L_m) is, in some asymptotic sense, replaced by a conveniently *homogeneous* body at a larger (macroscopic) scale (characteristic scale L_M) endowed with *effective* material properties. Then $\lambda = L_m/L_M$ is a small parameter. This is exemplified by *periodic structures*, bodies which are made up of *cells* (so-called Representative Volume Element, *R.E.V*), polycrystalline media, etc. In commenting upon the *L.A.S* we have already hinted at the fact that global state variables for a cell could be viewed as (local) internal variables of state for the homogenized body. This was masterly dealt with by Suquet (1982) — also in Germain *et al.* (1985) and in Maugin (1992a, Chapter 9). Special attention must be paid to systems in equilibrium and non-equilibrium evolutions. In the first case (thermo-*statics*) one may assume that the temperature fields θ_M and θ_m at the macroscopic and microscopic scales may be practically equal. But

$\nabla\theta_M$ and $\nabla\theta_m$ may be markedly different because θ_m may exhibit very high (stiff) spatial variations due to heterogeneities. However, it is possible to show that the *usual laws of state* are valid at the level of the macroscopic description, while the generalized Fourier law of heat conduction — including a relaxation effect such as in Eq. $(3.4.112)_1$ — follows for the homogenized material. Next, when the thermo*dynamic* evolution is very close to equilibrium, the working hypothesis now is that τ_M is large compared to any time τ_m of propagation of information inside the cell. Thus

$$(\mathcal{D}e)_{\text{cell}} = \tau_m/\tau_M \ll 1\,. \tag{4.7.44}$$

If we admit the first and second laws in their classical form — Eqs. (4.3.5) and (3.2.6) — at the microscopic level, then it is possible to prove that, at each time, similar laws hold true among averaged variables of state at the macroscopic level so that the thermostatic description and Gibbs' equation are indeed valid at the macroscopic scale if they were assumed to hold for each constituent at the microscopic one.

More interesting perhaps is the case of true *non-equilibrium* evolutions. Then the previous analysis fails, as inertia effects can no longer be neglected at the microscopic scale as they manifest themselves as *small-wavelength effects*. One has then to apply the artificial process described above in Sec. 4.4. In particular, one has to study a *dynamical evolution* toward equilibrium in order to obtain the set of characteristic microscopic parameters. For instance, as remarked by Germain *et al.* (1985), if α, the set of internal variables such that

$$(\mathcal{D}e)_\alpha = \tau_\alpha/\tau_M \ll 1\,, \tag{4.7.45}$$

is empty, then one has to study a dynamical *thermoelastic evolution toward equilibrium*. A most spectacular feature of this procedure is obtained when some of the constitutents of the structured material are elastic-perfectly plastic (*no* hardening) — see Suquet, 1982, 1987 — but the homogenized medium *does* present hardening (i.e. the property that the yield point evolves with the loading history). This results from the fact that some energy is stored in the form of *residual stresses* at the microscopic level, and the *internal variables of the macroscopic picture* are defined from this. The fact that the *backstress* (residual stresses embedded in a polycrystalline structure) may be considered as an *internal* (tensor) *variable* giving rise to *kinematic hardening* is also an established result of polycrystalline plasticity. We shall return to these two phenomena in Chapter 7. Relating more closely to *dislocation concepts*, we also recall that two internal variables may be introduced in that spirit, a *scalar* one which is associated with the stress field arising from forest dislocations, point-defect clusters or fine precipitates and yielding *isotropic hardening*, and a second-order tensor one which is related to the stress field due to cell walls or piles of dislocations and giving rise to *kinematic hardening* (see, e.g. Bamman, 1985).

B. Internal variables or internal degrees of freedom

Having disposed of the qualitative of "hidden" variables, we now focus on the differences or resemblances between thermodynamic *internal variables* of state and so-called *internal degrees of freedom*. The confusion between the two notions arises even among the best specialists (for instance, in the title of papers: Parry, 1987; Kluitenberg, 1977), although a clear distinction between these two classes can be precisely drawn (see Maugin, 1990a). To be more general and pave the way for the discussion, we shall consider now that the entropy flux deviates from its usual definition and, therefore, Eqs. (3.3.110) and (3.2.11) hold true. That is,

$$\mathbf{S} = \theta^{-1}\mathbf{q} + \mathbf{k}\,, \tag{4.7.46}$$

and

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + p_{(i)} + \nabla \cdot (\theta\mathbf{k}) - \mathbf{S} \cdot \nabla\theta \geq 0\,, \tag{4.7.47}$$

where $\mathbf{S}$ is the entropy flux, *per se*, the excess $\mathbf{k}$ is called the *extra entropy flux*, and $p_{(i)}$ is the power developed by *internal forces*, e.g. classical stresses in small strains yield $p_{(i)} = \sigma : \dot{\varepsilon}$. We generally need *constitutive equations* for these internal forces. The latter, as emphasized above, are quite different from the thermodynamic forces conjugate to α, because they contribute to the power (4.3.1) while the $\mathcal{A}$'s *do not* by virtue of their very nature of being *internal*. It is at this crucial point that the whole difference between internal variables of state and additional degrees of freedom becomes the most forceful.

First, if α were an additional *observable variable* which serves to describe the *dynamics* (in the full sense of that word) of a *microstructure* attached to each point in the continuum (as is the case in the mechanics of *micropolar*, *micromorphic*, and *Cosserat* continua — see Maugin, 1980, for an introduction of these models along the present line) then, according to general principles of rational mechanics (e.g. the principle of virtual power recalled in Sec. 2.3), α is to be governed by a true *field* equation of the canonical form:

$$\frac{\delta \mathcal{L}}{\delta \alpha} - \mathbf{f}_d^\alpha = \mathbf{0}, \tag{4.7.48}$$

where $\mathbf{f}_d^\alpha$ is a *dissipative* force acting on the α-microstructure and $\delta/\delta\alpha$ denotes the Euler–Lagrange functional derivative defined by

$$\frac{\delta}{\delta \alpha} = \frac{\partial}{\partial \alpha} - \frac{\partial}{\partial t}\left(\frac{\partial}{\partial \dot{\alpha}}\right) - \nabla \cdot \left(\frac{\partial}{\partial(\nabla \alpha)}\right) + \dots . \tag{4.7.49}$$

In usual situations the Lagrangian $\mathcal{L}$ depends at most on $\nabla\alpha$, so that there are no terms further than the third in the definition (4.7.49). This Lagrangian typically has the general expression

$$\mathcal{L} = \mathcal{K}(\mathbf{v}, \dot{\alpha}) - \rho\psi(-, \alpha, \nabla\alpha, \theta), \tag{4.7.50}$$

where $\mathbf{v}$ is the classical velocity field of the continuum and the "-" in ψ stands for the relevant observable variable (e.g. the density in a fluid, or the infinitesimal strain in some solids). Equation (4.48) complements the classical equations of motion of Euler and Cauchy that we do not rewrite here (note that the stress tensor may no longer be symmetric if there exists a mechanical torque associated with the variable α, as is the case in liquid crystals and some electromagnetic continua). It is valid at each regular point in the body and it must itself be supplemented by a *boundary condition* whose "natural" form at the boundary $\delta\Omega$ of the body at time t is [cf. (2.3.48)]

$$-\mathbf{n} \cdot \frac{\partial \mathcal{L}}{\partial(\nabla \alpha)} = \mathbf{T}^\alpha, \tag{4.7.51}$$

where $\mathbf{T}^\alpha$ is the surface "force" (traction) acting on the α-field. This follows from the general structure of a "*first-order gradient*" theory — an easily understood name if we remember that $\mathcal{L}$ depends at most on the *first* gradient of α — see Maugin (1980) for this concept in continuum physics. A *dual* boundary condition involving either α or $\dot{\alpha}$ is also admissible (in the same way a displacement or velocity field — or some components of them — may be imposed at a boundary in classical continuum mechanics).

For instance, if the overall material is considered as a *solid* in small strains, then it is easily shown that (4.7.47) will formally yield the following *dissipation* *inequality* on account of the *classical* axiom of local equilibrium state (here α is *not* an internal variable):

$$\phi = \sigma^D : \dot{\varepsilon} + \mathbf{f}_d^\alpha \cdot \dot{\alpha} + \nabla \cdot (\theta_s \mathbf{k}) - \mathbf{S} \cdot \nabla \theta_s \geq 0 , \tag{4.7.52}$$

where θ takes locally its thermostatic value (here *not* indexed by α). The extra entropy flux $\mathbf{k}$ may be taken to be equal to zero without loss in generality so that (4.7.52) reverts to its classical form [cf. (3.2.26)]:

$$\Phi = \sigma^D : \dot{\varepsilon} + \mathbf{f}_d^\alpha \cdot \dot{\alpha} + \theta_s \mathbf{q} \cdot \nabla(\theta_s^{-1}) \geq 0 . \tag{4.7.53}$$

The second contribution may be studied by means of *T.I.P.* or by introducing a dissipation potential. If the latter, say $\mathcal{D}$, is positive, homogeneous of degree two in $\dot{\alpha}$, it will yield a *relaxation effect*, together with the general expression $\mathbf{f}^\alpha = \partial \mathcal{D} / \partial \dot{\alpha}$. The resulting field equation (4.7.48) will be of the form

$$\frac{\delta \mathcal{L}}{\delta \alpha} - \frac{\partial \mathcal{D}}{\partial \dot{\alpha}} = \mathbf{0} , \tag{4.7.54}$$

together with the boundary condition (4.7.51) or its kinematic dual. In summary, α here is an additional observable variable which we assume to be related to a *microstructure*. It represents an *internal degree of freedom* as compared to the classical description of a continuum. It is *controllable* through boundary conditions and possibly also *body forces* which we did not introduce in (4.7.48). The reader will find complete examples of continuum theories with such internal degrees of freedom of *electric* or *magnetic nature* in Maugin (1988) with a special interest in *coupled dynamical effects* (as α *does* present an inertia).

On the other hand, had we considered α as an *internal variable of state*, we would not have assumed any equation such as (4.7.48) to start with and, therefore, no accompanying boundary condition of the form (4.7.51) would show up! Following the method of internal-variable theory we would simply have computed $\dot{\psi}$ and used the trick to select $\mathbf{k}$ in such a form as to eliminate any true divergence term in the dissipation inequality (Maugin, 1990a). Thus instead of (4.52), we would have obtained

$$\phi = \sigma^D : \dot{\varepsilon} + \mathcal{A}\dot{\alpha} - (\mathbf{S}_\alpha \cdot \nabla)\theta_\alpha \geq 0 , \tag{4.7.55}$$

wherein we have set

$$\begin{gathered} \sigma^D = \sigma - (\partial \bar{W} / \partial \varepsilon)_\alpha , \qquad \mathbf{S}_\alpha = \theta_\alpha^{-1} \mathbf{q} + \mathbf{k} , \\ \mathcal{A} = -\delta \bar{W} / \delta \alpha \equiv - \left(\frac{\partial \bar{W}}{\partial \alpha} \right) + \nabla \cdot \left(\frac{\partial \bar{W}}{\partial (\nabla \alpha)} \right) , \end{gathered} \tag{4.7.56}$$

with

$$\begin{gathered}\mathbf{k} = -\theta_\alpha^{-1}[\partial \bar{W}/\partial(\nabla\alpha)] \cdot \dot{\alpha}, \qquad \eta_\alpha = -\rho_0^{-1}\partial\bar{W}/\partial\theta|_{\theta=\theta_\alpha}, \\ W = \rho_0\psi = \bar{W}(\varepsilon, \alpha, \nabla\alpha, \theta).\end{gathered} \tag{4.7.57}$$

The classical theory of internal variables is recovered by ignoring the dependence of $\bar{W}$ on $\nabla\alpha$. If we now assume the existence of a dissipation potential $\mathcal{D}$ such that (this is only an example to fix ideas):

$$\sigma^D = \frac{\partial \mathcal{D}}{\partial \dot{\varepsilon}}, \qquad \mathcal{A} = \frac{\partial \mathcal{D}}{\partial \dot{\alpha}}, \tag{4.7.58}$$

then in particular $(4.7.56)_3$ and $(4.7.58)_2$ combine to give

$$\frac{\delta \bar{W}}{\delta \alpha} + \frac{\partial \mathcal{D}}{\partial \dot{\alpha}} = 0, \tag{4.7.59}$$

with apparently no accompanying boundary conditions. However, if the last equation is assumed to be valid at any regular point in the body, then at the crossing of a discontinuity surface one can deduce a related *jump relation* by using a local method such as the so-called "pill-box" method, or else more sophisticated mathematics such as the theory of *generalized functions* (distributions). This indicates that if one side of this "discontinuity surface" is occupied by a foreign body, and the surface becomes a *material one*, then the method will yield a local *boundary condition* of the same type as (4.7.51). This subtlety disappears when $\bar{W}$ does not depend on $\nabla\alpha$. Nonetheless, Eqs. (4.7.54) and (4.7.59) encapsulate the essential differences and resemblances between the basic equations that govern *internal degrees of freedom* in a first-order gradient theory and *internal variables* for which we account for *spatial gradients*. Both consider a *weak nonlocality* likely to give rise to *transition layers* and *surface effects*. We rewrite (4.7.54) as

$$\frac{\delta \bar{W}}{\delta \alpha} + \mu\frac{\partial \mathcal{D}}{\partial \dot{\alpha}} + \epsilon\frac{\partial}{\partial t}\left(\frac{\partial \mathcal{K}}{\partial \dot{\alpha}}\right) = 0, \tag{4.7.60}$$

where μ and ε are so-called *ordering parameters* (i.e. nondimensional parameters that provide an appreciation of the "size" of the terms in which they appear) to become eventually small. For example, Eq. (4.7.54), on account of its rewriting as (4.7.60), for small μ's but ε's which are 0(1), is a typical *field equation* with a *weak* dissipation. At the other end of the spectrum, for

$\mu = 0(1)$ and vanishingly small ε (**Caution:** this, in general, is a *mathematically singular* procedure), (4.7.60) takes on the form (4.7.59). Internal-variable theory would then principally be characterized by the neglect of *inertial effects* and its very classical form by the further neglect of any *nonlocality*, how weak the latter may be. A weak nonlocality, as is happens, describes a very short range of interactions in the α-field or small *coherence* or *correlation* length in the language of *organized structures*.

Indeed, the above dichotomy probably reflects again the fact that whether some variables are to be considered as internal variables or internal degrees of freedom is a matter of scale of *space-time observations*. If one is able to comprehend both the time and length scales on which the variables vary, then it is possible to view these variables as true internal degrees of freedom which enrich the dynamical description of the medium by requiring additional *field* equations on an equal footing with the old ones. For example, the continuum theory of *nematic liquid crystals* of Leslie and Ericksen (cf. Leslie, 1968), where the additional variable is a vector field $\mathbf{n}$ of constant amplitude representing the mean orientation of a bunch of elongated "particles", was originally conceived by its authors as a field theory with an internal degree of freedom $\mathbf{n}$ (with only two independent components). But the corresponding inertia is most often neglected (cf. de Gennes, 1974) and the above internal-variable theory applies (cf. Maugin, 1990a) with an extra entropy flux $(4.7.57)_1$ which indeed coincides with some proposals (Kats and Lebedev, 1988, p. 23).

The idea of introducing *spatial gradients* of internal variables recently appeared in the description of some physical properties coupled to mechanics, e.g. magnetic spin in magnetically ordered bodies (Maugin, 1979a,b), and of some other mechanical properties, among them the *localization of damage* and the problem of *shear-band evolution* related to the *localization of plastic strains* (cf. Maugin, 1990a; Zbib and Aifantis, 1989). The problem, however, is that α may be *controlled* through an external force such as the "traction" $\mathbf{T}^{\alpha}$ of Eq. (4.7.51). It is only when the length scale $L_m = 0(\alpha/|\nabla\alpha|)$ is small compared to the macroscopic scale L_M or when one is far away from boundaries and transition layers that the true "*Bridgmanian*" character of internal variables is recovered. If external excitations (wave length of dynamical processes, spatial variations of external fields affecting the α-field such as a nonuniform magnetic or electric field) are of the same order as L_m, then the internal-degree-of-freedom interpretation and equations should be enforced. Whether one should consider a *weak nonlocality* (using gradients) or a *strong* *nonlocality*, with constitutive equations that then become *functionals over space*, is debatable (in this respect, see Maugin, 1979c).

To conclude this section with a note on dynamics, we remark that, in general, the internal-degree-of-freedom approach accounting for the *inertia* of additional degrees of freedom and the allied *nonlinearity* and *weak nonlocality* provide physical systems which are prone to exhibiting the dynamic phenomenon of *solitary waves*, and sometimes of *solitons*, if the systems in question are *exactly integrable.* The internal-variable formalism, on its side, neglects the inertia of α and fosters mathematical systems of equations of the *evolution type.* With the *ad hoc* amount of *nonlinearity* (with respect to α — to that purpose it is sufficient to have a dissipation potential homogeneous of degree two in $\dot{\alpha}$ and an energy function W highly *nonquadratic in* $\mathcal{A}$) and *diffusion*, such model equations may give rise to *dissipative structures* and *autowave phenomena* (cf. Vasilev *et al.*, 1987), two other basic tenets of *nonlinear science* (cf. Maugin, 1990a). This viewpoint will be expanded in Chapter 10. Some characteristics of the theory are also very close to those met in *phase transition theory.* Therefore, it is salient to spend some time on the relationship between internal-variable theory and phase-transition theory.

4.8. Internal Variables and Phase Transitions

If $\mathcal{A}$ vanishes in Eq. $(4.7.58)_2$, then (4.7.59) takes the form

$$\delta\bar{W}/\delta\alpha = 0\,, \tag{4.8.61}$$

which is reminiscent of the equation that defines *static structures* as elementary solutions for the *order parameter* in the Landau–Ginzburg theory of phase transition (cf. Kittel, 1971).

We remind the reader that an *order parameter* is a variable of state which is essentially zero above the temperature of the phase transition and nonzero below (e.g. the magnetization vector in ferromagnetism, the polarization vector in ferroelectricity, a certain characteristic combination of components of the strain tensor e in ferroelasticity, etc.). In many cases, then, it seems that the theory of internal variables including gradients is the *same* as the corresponding continuum (mean field) theory of *phase transitions* if α is assimilated to an *order parameter* which, indeed, vanishes in the high-temperature *disordered phase* and is *nonzero* in the low-temperature *ordered phase.* We have already cited magnetization and polarization as appropriate *vectorial* order parameters. The second moment — a *second-order symmetric tensor* – of the director **n** of unit length in nematic liquid crystals, and the conformation tensor in polymeric solutions (see Chapter 6 below) may be considered as order parameters. Perhaps more subtle is the fact that the complex-valued wave function ψ (not to be mistaken for the free energy) of Cooper's superconducting pairs is the relevant order parameter of *superconductivity* (see de Gennes, 1966, reprint 1989). Landau's phase-transition theory is then reflected in the *nonlinearity* of $\partial\bar{W}/\partial\alpha$ with respect to α — it may be a polynomial up to a certain order different from one and the resulting multi-valued solutions of (4.8.61) for spatially uniform fields, $\nabla\alpha = 0$ everywhere in the body.

The incorporation of spatial gradients in the tradition of the original work of Landau and Lishitz on ferromagnets (1935) and Ginzburg's general idea concerning these gradients, allow one to study smooth transition zones with steep gradients but not true discontinuities in α (considered as a field). If some relaxation toward these equilibrium solutions exists, then the formalism (4.7.59) applies and, with $\mathcal{D}$ quadratic in $\dot{\alpha}$, yields the relaxation equation of the Ginzburg–Landau theory of phase transitions as

$$\dot{\alpha} = -\frac{1}{\tau_\alpha}\frac{\delta\bar{W}}{\delta\alpha} \tag{4.8.62}$$

in the appropriate units for $\bar{W}$. This equation, here a direct consequence of the internal-variable formalism, is typical of the *kinetics of phase transitions* and also of *reaction-diffusion* processes (see, e.g. Ebeling *et al.*, 1990, pp. 99–100; also Chapter 10 below). An example of such an equation with a quartic potential $\bar{W}(\alpha, \nabla\alpha, \theta)$ in the real-valued scalar parameter α, reads

$$\tau_\alpha\dot{\alpha} = -(a\alpha + b\alpha^3) + c\nabla^2\alpha\,, \tag{4.8.63}$$

where the coefficient a vanishes at a critical temperature $\theta = \theta_\alpha = \theta_{\mathrm{cr}}$. If α is a *complex-valued scalar* (such as a wave function in quantum mechanics), then typically (4.8.62) will read

$$\tau_\alpha\dot{\alpha} = -(a\alpha + b|\alpha|^2\alpha) + c\nabla^2\alpha\,. \tag{4.8.64}$$

The addition of a *random* force in the right-hand side in Eqs. (4.8.63) and (4.8.64) transforms them into so-called *Langevin* equations (compare Haken, 1982, pp. 201–204). An equation such as (4.8.64), coupled to strains and temperature, indeed obtains in the internal-variable theory of elastic superconductors (Maugin, 1992b, also Sec. 9.8 below) in which τ_α is the finite relaxation time of superconducting electrons. Equations of the type of (4.8.62) also occur in the kinetics of non-equilibrium phase transformations in many materials (see Chvoj, 1993). Whenever $\bar{W}$ may have several extrema, at $\nabla\alpha = 0$, by factorization (4.8.62) may also be written as

$$\tau_\alpha \dot{\alpha} = -k_\alpha \Pi_j (\alpha - \alpha_j)\,, \tag{4.8.65}$$

where the α_j's are the indexed local extrema. It is not clear to which one of the α_j's, i.e. to what metastable state corresponding to a minimum of $\bar{W}$, would the system relax with characteristic time τ_α. As a rule relaxation time and growth rate play an important role. In phase transitions driven by temperature these should always be compared to the time rate of change of temperature

$$\tau_\theta = |\theta - \theta_0| / |\dot{\theta}|\,, \tag{4.8.66}$$

where θ_0 is some reference temperature.

In the case of polymer and polyelectrolyte solutions (see Chapter 6), where α is a second-order tensor called the *conformation*, an equation such as (4.8.62) also involves the fluid motion and electric fields. Then it allows one to study flow-induced and polarization-induced conformational *phase transitions* (Drouot and Maugin, 1988). A similar scheme can apply to liquid crystals in their transition between isotropic and nematic phases (de Gennes, 1971).

4.9. Comparison with Extended Thermodynamics

In briefly sketching out the approach of *extended thermodynamics* (*E.T.*) in Sec. 3.4, we have seen that the additional state variables in *E.T.* are none other than the *dissipative fluxes* of classical *T.I.P.*, with the added possibility that these fluxes satisfy themselves new equations which are of the *evolution-diffusion* type. Equation (3.4.113) for electric conduction is an example of these additional governing equations. But the fluxes in question are *still controllable*, essentially through the usual boundary conditions dealing with stress, heat and electric currents. Thus from this point of view at least, these fluxes *cannot* be considered as internal variables. But it is true that when we take into account the spatial gradient of α in the above presentation, the two approaches are brought into close contact. However, as mentioned above, the variety of phenomena to be described by *T.I.V.* is practically *unlimited*, save for the imagination of the scientist. In a case such as the heat-conduction *relaxation equation* (3.4.112) where this problem with gradients no longer exists, it is still true that the heat flux is *controllable* through the boundary as it is still involved in the boundary conditions accompanying the energy equation. Furthermore, the *three* terms in (3.4.112) go simultaneously to zero in the limit of equilibrium. In *T.I.V.* with relaxation, the internal variable relaxes toward an equilibrium value which is then entirely determined by the values of the observable variables. It is true, however, than with a certain normalization, such variables may be made to relax to a zero value. In any case the clear delineation between the two thermodynamics makes the frequent misunderstandings and assimilations between these two all the more surprising. On the one hand some true *T.I.V.* are presented as *extended thermodynamics* (e.g. in Jou *et al.*, 1988, p. 1170). On the other hand, some examples that belong to *E.T.* are sometimes presented as examples of *T.I.V.* in the guise of the *hidden-variable theory* (Bampi and Morro, 1980; 1981a,b; 1984).

We hope that we have been sufficiently clear in unveiling the true and fascinating nature of *T.I.V.* compared to other approaches to thermodynamics so that any shadow of a doubt has been *dissipated* (an appropriate word, obviously). We can now enunciate the working rules of *T.I.V.* in a somewhat abstract framework.

Chapter 5

APPLICATIONS: GENERAL FRAMEWORK

> *So hidden in his hocus-pocus*
> *There lies the gift of double focus*
> *(W.H. Auden, New Year Letter)*

5.1. Summary

Once *thermodynamics with internal variables* (*T.I.V.*) has been distinguished from rational and extended thermodynamics, we can work with confidence within its clearly delineated framework. As it happens, with a clear insight in the time and space scales of the dissipative mechanisms that we want to take into account (this is based on each individual's experience) and with the *axiom of local accompanying state* (*L.A.S.*) enforced, we are then left with an exploitation of the *dissipation inequality* in a manner that reminds us of the *classical theory of irreversible processes* (*T.I.P.*). The essential difference, however, is that with progress in the understanding of exemplary behaviors (e.g. plasticity) and advances in some techniques of analysis (e.g. convex analysis), we can now incorporate within a proper thermodynamical framework all *nonsensical branches of thermomechanics* of Pierre Duhem. All we need to note is the general form taken by the thermodynamic theory that we sum up as follows:

Clausius–Duhem inequality:

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + p_{(i)} + \Phi_{\mathrm{th}} \geq 0\,, \tag{5.1.1}$$

where η is the entropy per unit volume in the actual configuration $\mathcal{K}_t$ of a continuous body at time t, ρ is the matter density at $\mathcal{K}_t$, θ is the absolute temperature, and the density of Helmholtz free energy ψ, the power of internal forces $p_{(i)}$ and the thermal dissipation Φ_{th} are given by

$$\psi = \bar{\psi}(\chi_\beta, \alpha, \theta)\,, \tag{5.1.2}$$

$$p_{(i)} = \rho \sum_{\beta=1}^{n} \tau_\beta \dot{\chi}_\beta\,, \tag{5.1.3}$$

and

$$\Phi_{\text{th}} = \theta \mathbf{q} \cdot \nabla(\theta^{-1})\,, \tag{5.1.4}$$

where χ_β, $\beta = 1, \ldots, n$ are the n independent components of the set of *observable variables of state*, τ_β is the corresponding set of thermodynamic *forces*, and $\mathbf{q}$ is the heat flux per unit area in $\mathcal{K}_t$. The set of *internal variables of state* α is supposed to contribute to the energy density only through its own values and not its gradients. Then the $L.A.S$ allows one to write the following *constitutive equation* for the entropy density:

$$\eta = -\frac{\partial \bar{\psi}}{\partial \theta}\bigg|_{\theta=\theta\alpha} = \bar{\eta}(\chi_\beta, \alpha, \theta)\,. \tag{5.1.5}$$

It is commonly admitted that the function $\bar{\psi}$ is *concave* in the variable θ, so that

$$\partial^2 \bar{\psi}/\partial \theta^2 \leq 0 \quad \text{for all} \quad \theta\,. \tag{5.1.6}$$

From the illustrative examples already introduced in previous chapters we gather that essentially two different cases present themselves. The first one corresponds to the case where we can write the *dissipation inequality* as

$$\Phi = \Phi_{\text{intr}} + \Phi_{\text{th}} \geq 0\,, \tag{5.1.7}$$

with an *intrinsic dissipation* given by (the summation convention is used)

$$\Phi_{\text{intr}} = \rho \tau_\beta^d \dot{\chi}_\beta + \mathcal{A}\dot{\alpha}\,, \tag{5.1.8}$$

together with the *laws of state*

$$\tau_\beta^r = \frac{\partial \bar{\psi}}{\partial \chi_\beta}, \qquad \mathcal{A} = -\rho \frac{\partial \bar{\psi}}{\partial \alpha}, \qquad \tau_\beta^d := \tau_\beta - \tau_\beta^r\,. \tag{5.1.9}$$

In the second exemplary case, (5.1.7) is obviously still valid, but the *intrinsic dissipation* is given by

$$\Phi_{\text{intr}} = \rho \tau_\beta \dot{\chi}_\beta^d + \mathcal{A}\dot{\alpha}\,, \tag{5.1.10}$$

together with the *laws of state*

$$\tau_\beta = \frac{\partial \bar{\psi}}{\partial \chi_\beta}, \qquad \mathcal{A} = -\rho \frac{\partial \bar{\psi}}{\partial \alpha}, \tag{5.1.11}$$

and the decomposition

$$\chi_\beta = \chi_\beta^r + \chi_\beta^d. \tag{5.1.12}$$

The example of solid mechanics in small strains of Eq. (4.5.24) partakes of the two cases in gathering them in a single expression for dissipation. But similar situations occur, for instance in magnetism or for electric polarization, if a different physical meaning is granted to the state variable χ_β. Thus Eqs. (5.1.8) and (5.1.10) are generic. For all practical purposes we can even rewrite any of the two intrinsic dissipations in the simple form (i.e. retaining only the *internal variables* as we are mostly interested in them)

$$\Phi_{\text{intr}} = \mathcal{A}\dot{\alpha}, \tag{5.1.13}$$

and this will satisfy the *intrinsic dissipation inequality*

$$\Phi_{\text{intr}} = \mathcal{A}\dot{\alpha} \geq 0, \tag{5.1.14}$$

if we admit the separate non-negativeness of the thermal dissipation as in (3.2.11). In all cases the *heat propagation equation* will be given by [cf. Eq. (3.3.106)]

$$\rho\theta\dot{\eta} = \Phi_{\text{intr}} + (\rho h - \nabla \cdot \mathbf{q}), \tag{5.1.14}$$

where η is given by (5.1.5), hence the importance of the inequality (5.1.6) in order to define a non-negative heat capacity [cf. Eq. (3.3.97c) as an example].

Relaxation of the *L.A.S.*

As a curiosity we note that we could relax the *L.A.S* by assuming that the entropy *outside equilibrium* is *not* equal to the value given by Eq. (5.1.5). Let η^d denote that deviation from $\bar{\eta}$, so that we have

$$\eta = \bar{\eta} + \eta^d, \qquad \bar{\eta} = -\partial\bar{\psi}/\partial\theta. \tag{5.1.15}$$

Nothing in principle forbids this generalization where a *constitutive equation* must be formulated for η^d whose thermodynamic conjugate remains the observable variable of state θ. This formal generalization results in an additional term

$$\Phi_\eta := -\rho\eta^d\dot{\theta} \tag{5.1.16}$$

in any of the above dissipation inequalities. This additional term, although strange to many of our readers, enters the general frame that we wish to apply. As η^d will principally be determined by $\dot{\theta}$, if η^d is taken linear affine in $\dot{\theta}$ as is the case in a straightforward application of the rules of *T.I.P.*, then we see that the heat-propagation equation (5.1.14) will then result in an equation with a second order time derivative in θ, hence, with the appropriate sign, a propagation of heat at *finite speed*. This is a simple but still very interesting result if we consider the marked interest of many scientists in formulating a heat-propagation equation that does not violate the relativistic causality principle (we remind the reader that *extended thermodynamics* was designed in part to remedy this violation by Fourier's law in classical *T.I.P.* — see Müller and Ruggeri, 1993). The above approach — Eqs. (5.1.15)–(5.1.16) has been exploited by A. F. Ghaleb (1986). As our interest is not focused on this aspect of causality since there are many other interesting problems which, in our opinion, are more important from the experimental viewpoint, we shall not pursue the above farther. Consequently, for subsequent use we only note the generic formulas (5.1.13) and (5.1.14).

5.2. Convexity of the Energy

Now we make all our reasonings on (5.1.14) *independently* of whether α is an *observable* or an *internal* variable. Thus $\psi = \bar{\psi}(\alpha, \theta)$. As we know $\bar{\psi}$ is *concave* in the scalar variable θ, whence the useful inequality (5.1.6). What about the dependence on α? The latter is, in general an n-dimensional Cartesian vector in $\mathbb{R}^m$, or it can be represented as such after indexing the various independent components of the multiple tensorial objects of various orders that make up α. Let α_j the m indexed components of α. Is $\bar{\psi}$ to be *convex* in the α_j's and is there a physical necessity for this requirement? The answer to the last question is definitely *no*! As a matter of fact, it is possible in many cases of interest that the convexity properties of $\bar{\psi}$ vary in a more or less continuous manner with a change in a characteristic parameter, say θ itself. This is the case in so far as mechanical, electric, and magnetic, and probably other, properties are concerned.

Generally speaking we say that a scalar-valued function ψ is convex in the α_j's if and only if, for λ any positive number between zero and one, we have the inequality

$$\bar{\psi}(\lambda\alpha_j + (1-\lambda)\bar{\alpha}_j) \leq \lambda\bar{\psi}(\alpha_j) + (1-\lambda)\bar{\psi}(\bar{\alpha}_j)\,, \tag{5.2.17}$$

where α_j and $\bar{\alpha}_j$ denote any two values of the components of the variable α. $\bar{\psi}$ is said to be *strictly convex* if the strict inequality sign holds in (5.2.17). A *convex set* K in α space is such that any two points of its closure (boundary) satisfy the inequality (5.2.17). It is then said in a *vivid* language that all cords are entirely inside K. An equivalent statement is that all *tangent hyperplanes* lie entirely outside K except the contact point. The strange function I_k defined by

$$I_K = \begin{cases} 0 & \text{if} \quad \alpha \in K\,, \\ \infty & \text{if} \quad \alpha \in \dot{K} \text{ (exterior of } K)\,, \end{cases} \tag{5.2.18}$$

is called the *indicator function of K*. An essential property of convex functions already illustratred in (5.1.6) for $-\psi$ which is *convex in θ*, is the property of non-negativeness of the second-order derivative of ψ, i.e. the fact that

$$\sum_{i,j=1}^{m} \beta_i \frac{\partial^2\bar{\psi}}{\partial\alpha_i\partial\alpha_j}\beta_j \geq 0\,, \tag{5.2.19}$$

for all β belonging to the α-space. This has particularly important consequences in all approximate theories which involve a quadratic energy in α or any situations, such as in a *linearization* or in the study of *stability properties*, which will involve the second-order derivatives of ψ with respect to α. For instance, consider the case where α is none other than the infinitesimal strain and $\psi = \bar{\psi}(\varepsilon, \theta)$, a form familiar to us in *thermoelasticity*. With the law of state $\sigma = \rho_0 \partial\bar{\psi}/\partial\varepsilon$, we look at the linearized form about a state of zero initial stress. The resulting "small stress" is obviously given by the straightforward variation:

$$\delta\sigma = \rho_0 \frac{\partial^2\bar{\psi}}{\partial\varepsilon\partial\varepsilon} : \delta\varepsilon + \rho_0 \frac{\partial^2\bar{\psi}}{\partial\varepsilon\partial\theta}\delta\theta\,. \tag{5.2.20}$$

The tensorial coefficients, respectively of the fourth order and of the second order, defined by

$$\begin{aligned} C_{ijkl} &= \rho_0 \frac{\partial^2\bar{\psi}}{\partial\varepsilon_{ij}\partial\varepsilon_{kl}}\bigg|_{\substack{\varepsilon=0\\ \theta}}\,, \\ M_{ij} &= \rho_0 \frac{\partial^2\bar{\psi}}{\partial\varepsilon_{ij}\partial\theta}\bigg|_{\substack{\varepsilon=0\\ \theta}}\,, \end{aligned} \tag{5.2.21}$$

obviously are the tensors of elasticity and thermoelasticity coefficients. The assumed convexity of $\bar{\psi}$ with respect to ε_{ij}, but concavity with respect to

θ, together with (5.2.19), make it such that C_{ijkl} is not only symmetric but also *non-negative definite* while nothing can be concluded, as we know, for M_{ij} which is simply symmetric. The essentially *positive character of* C_{ijkl} has for immediate consequence the proof of the existence of three nonzero positive squared velocities of propagation of small elastic isothermal disturbances (see, e.g. Maugin, 1988, Chapter 2). The same will hold true for isentropic disturbances according to (3.3.105).

Now we notice that what is important qualitatively is not so much the *quadratic* nature of the approximation (5.2.20) and (5.2.21), but the *convexity* of the energy ψ, which obviously includes much more than the case of quadratic energies. The convexity without quadratic nature is of prime importance for the existence of phenomena such as the propagation of *shock waves*, whether in solids or in fluids, or for electromagnetic shock waves (see, e.g. Eringen and Maugin, 1990a, Chapter 6).

But the problem may be that within a certain range of temperature, $\bar{\psi}$ is no longer a *convex function* of α, in the deformable solid case, of ε. For instance, in the latter case this occurs in *ferroelasticity* (e.g. in shape-memory alloys), while for electric and magnetic bodies this occurs in ferroelectricity and ferromagnetism, respectively (in all three cases, α plays the role of an *order parameter* — see Sec. 4.8). Then contrary to a quadratic function in particular, and a convex one in general, the function $\bar{\psi}$ may present a multiplicity of minima. As a result the associated *law of state* may give a multiple determination in terms of α. As a simple example one can think of a *double-well* energy in one-dimension where α is a scalar. That is,

$$\psi = \frac{1}{4}(a/\alpha_0^2)(\alpha^2 - \alpha_0^2)^2 \,. \tag{5.2.22}$$

Here a and α_0 are two positive constants. The minima are at $\pm\alpha_0$ while $\alpha = 0$ corresponds to a so-called metastable state of nonzero energy. In ferroelasticity one may have to envisage ψ functions which are of the sixth order in the strain, thus with the possibility of presenting *three minima*. One is naturally tempted to *convexify* those energies (by taking the convex *hull*), but then one misses essential physical critical properties of the bodies of interest (see Maugin, Pouget *et al.*, 1992, pp. 44–45 and Appendices I and II). In general, for "small" α_j's one can envisage an expansion of the type

$$\psi = \psi_0(\theta) + \frac{1}{2}C_{ij}(\theta)\alpha_i\alpha_j + \frac{1}{6}C_{ijk}(\theta)\alpha_i\alpha_j\alpha_k + \frac{1}{24}C_{ijkl}(\theta)\alpha_i\alpha_j\alpha_k\alpha_l + h.o.t., \tag{5.2.23}$$

where we recognize in successive tensorial coefficients the successive derivatives of ψ with respect to the α_j's. No obvious conditions of sign apply *a priori* to the components of these tensors in a general case. Examples of expansions in continuum mechanics, electricity and magnetism , and electromagneto-mechanical interactions are to be found in previous books such as in Maugin (1985, 1988), Eringen and Maugin (1990a,b), Maugin, Pouget *et al.* (1992).

5.3. General Properties of Dissipation Potentials

As in *T.I.P.*, it is tempting in *T.I.V.* to have recourse to the notion of *dissipation potential*, according to which, if (5.1.14) holds true, then the existence of a *dissipation potential* $\mathcal{D}$ which is *positive* and *homogeneous* of degree n in $\dot{\alpha}$, conduces to the *dissipative constitutive equation*

$$\mathcal{A} = \partial\mathcal{D}/\partial\dot{\alpha}, \tag{5.3.24}$$

and

$$\Phi = \mathcal{A}\dot{\alpha} = \dot{\alpha}\cdot\frac{\partial\mathcal{D}}{\partial\dot{\alpha}} = n\mathcal{D} \geq 0 \tag{5.3.25}$$

by virtue of Euler's identity for homogeneous functions of degree n. Now *two essential* cases can be recognized. The first one is that of *classical T.I.P.* where $\mathcal{D}$ is taken as homogenous of *degree two* in $\dot{\alpha}$, so that $\mathcal{A}$ is homogenous of degree one in $\dot{\alpha}$. Consequently, the constitutive equation for $\mathcal{A}$ involves a characteristic time. This is even more visible on the dual expression obtained after Legendre transformation to a *dissipation potential* $\mathcal{D}^*$ such that

$$\begin{aligned}\mathcal{D}^*(\mathcal{A}) &:= \mathcal{A}\dot{\alpha} - \mathcal{D}(\dot{\alpha}) \\ &= \mathcal{A}\dot{\alpha} - \frac{1}{2}\mathcal{A}\dot{\alpha} = \frac{1}{2}\mathcal{A}\dot{\alpha} = \mathcal{D}(\dot{\alpha}),\end{aligned} \tag{5.3.26}$$

from which it follows that

$$\dot{\alpha} = \frac{\partial\mathcal{D}^*}{\partial\mathcal{A}} = \mathcal{L}(\mathcal{A}), \tag{5.3.27}$$

where $\mathcal{L}$ is a linear affine operator. But $\mathcal{A}$ derives from $\bar{\psi}$ via the equation of state $\mathcal{A} = -\partial\bar{\psi}/\partial\alpha$. For $\bar{\psi}$ quadratic in α we have thus $\mathcal{A} = -k_\alpha(\alpha - \alpha_0)$, where α_0 is the equilibrium value of α, and k_α is another linear affine operator, and (5.3.27) yields an *evolution equation* of the relaxation type:

$$\dot{\alpha} = -\tau_\alpha^{-1}(\alpha - \alpha_0)\,, \tag{5.3.28}$$

where τ_α^{-1} is a linear operator obtained by composition of $\mathcal{L}$ and k_α. This operator has components which are reciprocal *relaxation times*, hence its form. Its components in general still depend on the *observable variables* of state, including θ. The formalism presented practically encompasses all applications which exhibit *relaxation effects* and are thus, in the spirit of the discussion of Sec. 4.7, endowed with a characteristic time and a corresponding *Deborah number* whose relative value indicates if we need to account for the corresponding internal variable or not.

But there also exist *dissipative processes* which are not characterized by a characteristic time but by a certain critical level of "force" $\mathcal{A}$ (e.g. the stress level). This is the case in the most current theory of plasticity which practically exhibits no sensitivity to the rate of change of α (i.e. the resulting response is not markedly affected by the *velocity* at which α evolves), but dissipation occurs only when a certain threshold $\mathcal{A}$ is reached. *Behaviors of this type are referred to as plastic.* For a wide range of frequencies in the magnetizing field magnetic hysteresis belongs to this class. This "plastic" case is more difficult to deal with and deserves more attention than the "relaxation" case.

5.4. Convex Pseudo-Potential of Dissipation

Using as a basis the exemplary case of strain-rate insensitive plasticity (see the brief description in Maugin, 1992a, Chapter 1), we consider the case where the thermodynamic force $\mathcal{A}$ (an m-dimensional Cartesian vector in general) is constrained to a closed convex set K in $\mathbb{R}^m$. No dissipation occurs when $\mathcal{A}$ is *inside* K. Dissipation may occur when $\mathcal{A}$ corresponds to one point of the boundary of K. As a consequence, we can formally rewrite the dissipation inequality (5.1.14) as

$$\Phi = \sup_{\mathcal{A}\in K} \mathcal{A}\dot{\alpha} \geq 0\,, \tag{5.4.29}$$

which is a more precise form of the dissipation inequality than (5.1.14) in the present case as its means that there is *possible* dissipation only if $\mathcal{A}$ has reached a border point of K. But this can also be expressed in the following *variational-inequality* form

$$(\mathcal{A} - \mathcal{A}^*) \cdot \dot{\alpha} \geq 0 , \tag{5.4.30}$$

for all $\mathcal{A}^* \in K$. It is immediately verified that (5.4.29) and (5.4.30) are fully equivalent statements. Equation (5.4.30) with the appropriate choice of variables is referred to as the *principle of maximal dissipation of Hill and Mandel* in elasto-plasticity (cf. Hill, 1948; Mandel, 1971). This looks as a rather reasonable principle to start with. What is less clear is that if we enforce (5.4.29) or (5.4.30) simultaneously with the mathematical constraint that the dissipative mechanism considered exhibits *no time scale* (if it is to be insensitive to the rate $\dot{\alpha}$), so that $\mathcal{A}$ must be *homogeneous of degree zero* in $\dot{\alpha}$ and therefore Φ will simply be homogeneous of *degree one in* $\dot{\alpha}$, then Eqs. (5.4.29) and (5.4.30) are also expressions of a *normality law* according to which the *evolution* of α, *if any*, satisfies the condition that

$$\dot{\alpha} = \dot{\lambda} \frac{\partial f}{\partial \mathcal{A}} , \tag{5.4.31}$$

where $\dot{\lambda}$ is a positive scalar [the dot is put intentionally to show that although (5.4.31) is paradoxically expressed by means of $\dot{\alpha}$, it presents no time scale — there is a "time derivative" on each side of (5.4.30)] and $f = 0$ is the equation of the hypersurface in $\mathcal{A}$-space which describes the *convex boundary* of the convex set K. Equation (5.4.31) means that $\dot{\alpha}$, if nonzero (i.e. when $\dot{\lambda}$ is nonzero) is parallel to the unit outward normal to $f = 0$ in $\mathcal{A}$-space. The *multiplier* $\dot{\lambda}$ belongs to the solution of the *evolution problem.* It must also be emphasized that the convex K, although convex alright, may have angular points such as vertices or appices, or edges. Thus the notion of normal to $f = 0$ may not be uniquely defined. One in general needs a mathematical apparatus which accounts for these complexities in a natural way. *Convex analysis* is the appropriate tool for this. So let us briefly prove the above statement (5.4.31) on the basis of this technique of advanced calculus requiring some abstractness from the part of the reader. The proof is based on the following.

Theorem 5.2. *If* $\varphi^* = I_K$ *is the indicator function of* K, *and* $\varphi = \sup_{\mathcal{A} \in K} \mathcal{A}\dot{\alpha}$ *is the Legendre–Fenchel transform of* φ, *then* φ *is a positively homogenous function of degree one, and this property is characteristic in that if* φ^* *is a lower semi-continuous convex function on the* $\mathcal{A}$*-space, then there exists a closed convex set* K *such that* $\varphi = (I_K)^*$.

The proof of this can be found in Suquet (1982) and in Appendix 2 in (Maugin, 1992a) to which we refer the reader. Here we simply analyze the consequences of the theorem for the thermodynamic application. We need the following few elements of convex analysis (see, e.g. Germain, 1973):

(i) Let $\mathcal{D}(\dot{\alpha})$ be a positive *convex function* of $\dot{\alpha}$. Then the Legendre–Fenchel transform (generalization of the classical Legendre transformation) of $\mathcal{D}(\dot{\alpha})$ is given by

$$\mathcal{D}^*(\mathcal{A}) = \sup_{\mathcal{A}}[\mathcal{A}\dot{\alpha} - \mathcal{D}(\dot{\alpha})]\,, \tag{5.4.32}$$

where, in our case, $\mathcal{A}$ is restrained to the convex set K in $\mathcal{A}$-space. Furthermore, this transform preserves both *homogeneity* and *convexity* properties. It is noted that the *conjugate* $\mathcal{D}^*$ obtained from $\mathcal{D}$ by the Legendre–Fenchel transform is such that

$$(\mathcal{D}^*)^* \equiv \mathcal{D}\,. \tag{5.4.33}$$

(ii) We call *subdifferential* $\partial\mathcal{D}^*$ *of* $\mathcal{D}^*$ the set of points $\mathcal{A}$ of $\mathcal{A}$-space such that

$$\mathcal{D}^*(\bar{\mathcal{A}}) - \mathcal{D}^*(\mathcal{A}) \geq \dot{\alpha}\cdot(\bar{\mathcal{A}} - \mathcal{A}) \tag{5.4.34}$$

for all $\bar{\mathcal{A}}$. For a smooth set K this is the usual differential. But the remarkable result of convex analysis is that if $\mathcal{D}^*(\mathcal{A})$ is none other than I_K, then

$$\partial\mathcal{D}^* \equiv \partial I_K = N_K(\mathcal{A})\,, \tag{5.4.35}$$

where $N_K(\mathcal{A})$ denotes the *cone of outward normals of K at its boundary*. In particular, at any regular point of this boundary $f = 0, N_K(\mathcal{A})$ reduces to the unique outward normal to $f = 0$ at that point, i.e. $\partial\mathcal{D}^*$ is proportional to $\partial f/\partial\mathcal{A}$.

(iii) It is noted that if $\mathcal{D}$ and $\mathcal{D}^*$ are conjugate through Legendre–Fenchel transform, then

$$\partial\mathcal{D}^* = (\partial\mathcal{D})^{-1}\,. \tag{5.4.36}$$

Let us apply these definitions and results to our thermodynamical considerations. Assume that there exists a dissipation potential $\mathcal{D}(\dot{\alpha})$ which is positive and only *homogeneous of degree one* in $\dot{\alpha}$, so that $\mathcal{A}$ is given by $\mathcal{A} = \partial\mathcal{D}/\partial\dot{\alpha}$, and Φ is necessarily homogeneous of degree one in $\dot{\alpha}$ also, and the dissipative mechanism studied is not rate-sensitive. Let $\mathcal{D}^*(\mathcal{A})$ be the conjugate of $\mathcal{D}$ via the Legendre–Fenchel transform in agreement with (5.4.31). But our $\mathcal{A}$ here is restrained to the convex set K in $\mathcal{A}$-space. Equation (5.4.29) must hold and its left-hand side is precisely $\mathcal{D} = \mathcal{D}^* = \Phi$. As the result stated in the theorem is characteristic, it means that $\mathcal{D}^*$ according to (5.4.33) is none other than the indicator I_K of K, whose subdifferential in turn is none other than $N_K(\mathcal{A})$ so that, in an abstract way, we have the *evolution equation*

$$\dot{\alpha} \in \partial I_K \equiv N_K(\mathcal{A}), \tag{5.4.37}$$

or Eq. (5.4.31) at regular points of the boundary $f = 0$ of the convex set K in $\mathcal{A}$-space. In conclusion of this point, we can say that the *variational inequality* (5.4.30) for $\mathcal{A} \in K$ is completely equivalent to the *normality law* (5.4.37) or (5.4.31). These are but two different expressions of the same result. To distinguish it from a quadratic dissipation potential *à la* Rayleigh as prevails for relaxation effects, the above potential for "plastic" effects is sometimes referred to as *pseudo*-potential of dissipation.

The remarkable result above finds its roots in the early proposals of Ziegler (1957, 1958, 1961, 1963, 1970) — see also Ziegler (1977) and Ziegler and Wehrli (1987). But the neat mathematics exploiting powerful results of convex analysis belong to J.-J. Moreau (1971) and Germain (1973). These were polished by Nguyen Quoc Son (1973) and Suquet (1982) in the framework of plasticity, but they also apply to other fields of physics such as magnetic hysteresis (see Chapter 9 below). We shall elaborate further on the mechanical case in Chapter 7.

Notion of generalized standard material:

Remembering that $\mathcal{A}$ is still given by a *law of state* as $\mathcal{A} = -\rho \partial \bar{\psi} / \partial \alpha$, in many applications (elastoplasticity, fracture) we may find it convenient to consider that $\bar{\psi}$ is *convex* in α. This, together with the specifications given above for rate-insensitive phenomena involving a "plastic" threshold, was identified by Halphen and Nguyen Quoc Son (1975) as a general model for many responses of materials as the model of *generalized standard materials*. For such behaviors we have:

(i) $\psi = \bar{\psi}(\alpha, \theta)$ ($\bar{\psi}$ convex in α, concave in θ);

(ii) $\eta = -\partial \bar{\psi} / \partial \theta$ ($L.A.S.$);

(iii) $\mathcal{A} = -\rho \partial \bar{\psi} / \partial \alpha$ (law of state);

(iv) $\Phi = \mathcal{A}\dot{\alpha} \geq 0$ (intrinsic dissipation);

(v) $\mathcal{A} \in K$ (existence of a closed convex set K in $\mathcal{A}$-space);

(vi) $\dot{\alpha} \in N_K(\mathcal{A})$ (normality law).

Equivalently to (vi) we have:

(vi)′ $(\mathcal{A} - \mathcal{A}^*) \cdot \dot{\alpha} \geq 0$ (principle of maximal dissipation, where $\mathcal{A}^* \in K$ is at our disposal).

Models of response which enter this framework enjoy *local* and *global stability properties* that we shall evoke while examining the particular cases of elastoplasticity in Chapter 7 and electromagnetic hysteresis in Chapter 9. These properties result essentially from the assumed *convexity* of both the energy density and the pseudo-dissipation potential, thus resulting in nice properties for the *mathematical evolution systems* at hand.

"Viscoplastic" behavior:

By considering the mechanical case, we note that in general even "plastic" strains are *not instantaneous.* In other words, contrary to what was assumed above, a characteristic time, even though very small, hence *viscosity*, might be involved in the description. We call "*viscoplastic*" those behaviors which simultaneously exhibit a threshold in the generalized force $\mathcal{A}$ and a characteristic time akin to relaxation. Such behaviors are amenable in the present general framework by assuming that while for pure "plastic" behaviors $\mathcal{A}$ is restrained to the convex set K, for "viscoplastic" ones the representative point in $\mathcal{A}$-space may possibly lie outside the convex set K, but it is *restored* to the convex set with a characteristic time. Mathematically, this can be represented thus. In a simple case we can assume that $\dot{\alpha}$ is proportional to the distance between the representative point $\mathcal{A}$ in $\mathcal{A}$-space and the convex K. For example, with η_v a *viscosity coefficient*, we could write the *evolution equation* replacing (5.31) for a "viscoplastic" response as

$$\dot{\alpha} = (2\eta_v)^{-1}(\mathcal{A} - \Pi_K \mathcal{A}), \tag{5.4.38}$$

where Π_K is an operator of projection onto K. By the very definition of a *projector*, if $\mathcal{A}$ is already inside K, the right-hand side of (5.4.38) is zero as $\mathcal{A} \equiv \Pi_K \mathcal{A}$ in such a case. It is clear that (5.4.38) represents a rather *regular* behavior which contrasts with the *singular* one of pure "plasticity". It can also

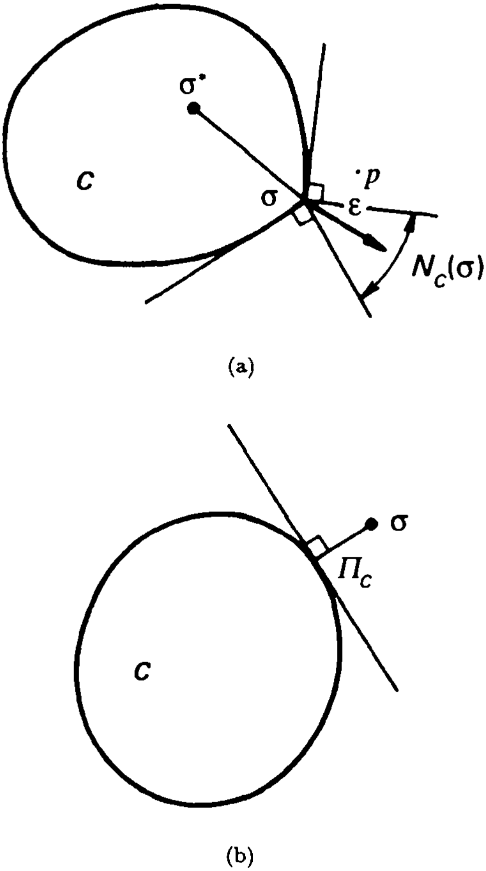


Fig. 5.1. Difference between "plastic" and "viscoplastic" behaviors in $\mathcal{A}(=\sigma)$-space; (a) plasticity, (b) visco-plasticity (the actual σ state can be outside the convex).

be derived from a dissipation potential by noting that

$$\dot{\alpha} = \partial\mathcal{D}^*/\partial\mathcal{A}, \qquad \mathcal{D}^* = \frac{1}{4\eta_v}||\mathcal{A} - \Pi_K\mathcal{A}||^2. \tag{5.4.39}$$

Such a dissipation potential was proposed by P. Perzyna (1966) in the viscoplasticity of solids where $\mathcal{A}$ is none other than the stress tensor σ. Figure 5.1 formally illustrates the difference in behavior for "plastic" and "viscoplastic" bodies in $\mathcal{A}$-space. It can be shown that with η_v going to zero, the *regular* behavior described by (5.4.39) coalesces in the *singular* one of rate-insensitive plasticity where $\mathcal{D}^*$ transforms into the *indicator* I_K of the convex set K. Following Kestin and Rice (1971), we may say that the plasticity pseudo-potential of dissipation may be considered as a *singular sequential limit* of surfaces of equipotentials of the viscoplastic type. The viscoplastic-like behavior has the mathematical advantage to *smooth out* the singularity of the plastic case. Thus many mathematical proofs can be first constructed within a "viscoplastic" framework and then a limit procedure of vanishing *viscosity* will yield, if correctly effected, the sought result for the plastic case (see Do, 1978).

General remark:

It is remarkable that when viscosity or relaxation is involved as an irreversible process, the corresponding dissipation potential is homogeneous of degree *two* (and thus convex) in $\dot{\alpha}$ or $\mathcal{A}$, while for "plastic" behavior the potential is only convex and homogeneous of degree *one* thus yielding a truly *nonlinear irreversible process.* But the common idea of *nonlinearity* would rather be to envisage a potential of *higher degree of* homogeneity, or at least of higher order than two in $\dot{\alpha}$. This possibility is not physically excluded and some physical processes seem indeed to fit this view. This is illustrated below by an example of *nonconvex* dissipation potential.

5.5. Nonconvex Dissipation Potential

For the sake of illustration we deviate from general features to present here a particular case that manifests itself in the study of the phenomena of *stick-slip* and *relaxation oscillations.* We, in fact, look at the intriguing problem of the adhesive tape that we try to unwind. It is remarked by the less gifted experimentalists like us that if we try to unwind the tape at a constant speed (a difficult task indeed), we cannot practically achieve this and we record a *jerky rate* of advancement of the unwinding tape with an accompanying characteristic "crack-crack-crack" noise, which, as it appears, is related to an *instability.* The problem is simply modeled as follows. We neglect *inertial effects*, so that the length α of unwound tape is a variable which will at most be described by some kind of *evolution equation.* Its equilibrium is governed by a balance between an elastic restoring force, say $\mathcal{A} = -k\alpha$, where k is a spring constant — this is the *law of state* — and a force which depends on the characteristics of *adhesion.* The modeling of the later is a difficult problem,

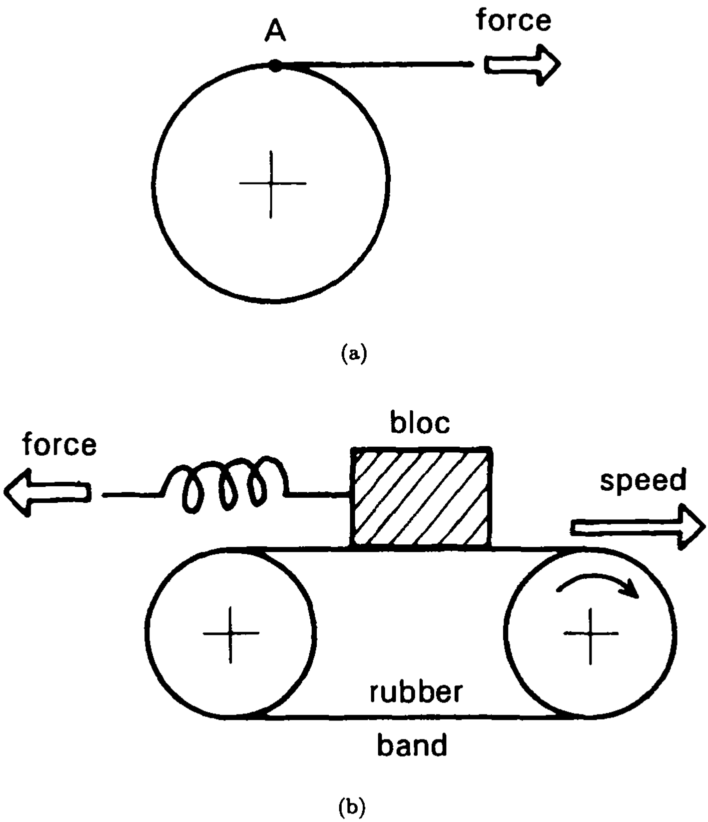


Fig. 5.2. Unwinding an adhesive tape.

although we know that such a force, which will therefore balance $\mathcal{A}$ in the absence of inertia, depends on $\dot{\alpha}$. We assume that this force is derivable from a potential of dissipation which is positive, but *not convex in* $\dot{\alpha}$. Thus, the equation governing α, reads

$$\mathcal{A} = -k\alpha = \partial\mathcal{D}/\partial\dot{\alpha}\,, \tag{5.5.40}$$

and this seems to enter quite well into our general framework (5.1.14) and (5.3.25) as we expect *dissipation in the form* $\Phi = \mathcal{A}\dot{\alpha} \geq 0$. For $\mathcal{D}$ we consider a *double-well potential* [compare to (5.2.22)] in the form

$$\mathcal{D}(\dot{\alpha}) = \frac{1}{4}(a/\dot{\alpha}_0^2)(\dot{\alpha}^2 - \dot{\alpha}_0^2)^2\,, \tag{5.5.41}$$

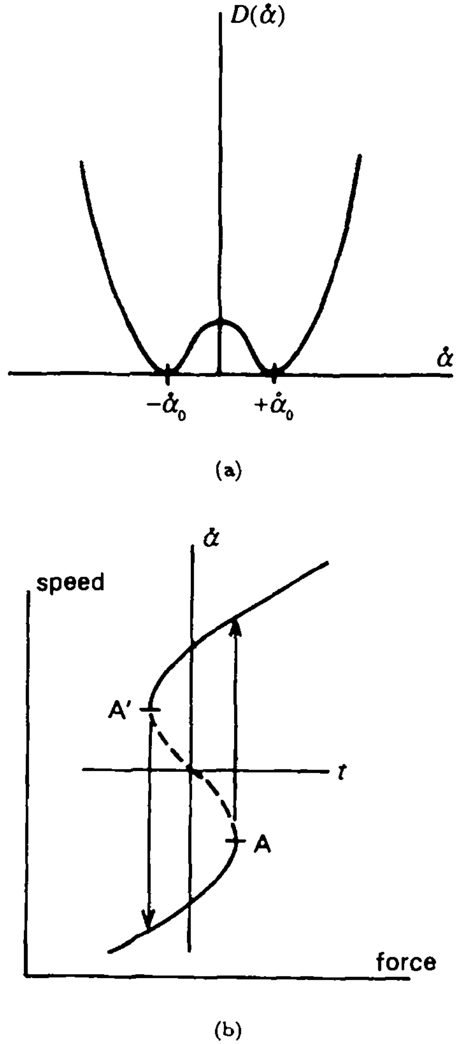


Fig. 5.3. Dissipation potential (a) and phase-plane picture (b) for stick-slip.

where a is a positive constant and $\dot\alpha_0$ is a critical value of the rate $\dot\alpha$. We obtain for $\mathcal{D}(\dot\alpha)$ and $\mathcal{A} = -k\alpha$ versus $\dot\alpha$, the curves shown in Figure 5.3, which obviously resemble similar curves for some phase-transition phenomena in condensed-matter physics (see, e.g. Fig. 1.25, p. 44 in Maugin, Pouget *et al.*, 1992). But up to the factor $(-k)$, part (b) in Figure 5.3 is none other than a picture of the *phase plane* as we are essentially representing α versus $\dot{\alpha}$. Thus $\mathcal{A}$ versus $\dot{\alpha}$ is the typical S-shaped curve with a maximum at $\dot{\alpha} = -\dot{\alpha}_0/\sqrt{3}$ and a minimum at $\dot{\alpha} = \dot{\alpha}_0/\sqrt{3}$. Unfortunately, if we compute the elementary dissipation,

$$\Phi = \mathcal{A}\dot{\alpha} = a\left(\frac{\dot{\alpha}^2}{\dot{\alpha}_0^2} - 1\right)\dot{\alpha}^2 , \tag{5.5.42}$$

we see that the interval $|\dot{\alpha}| < \dot{\alpha}_0$ should theoretically be forbidden as it would correspond to a negative dissipation. This corresponds to a *loss of uniqueness* in the determination of the velocity $\dot{\alpha}$ in terms of $(-\alpha)$. One way to resolve this problem would simply be to *convexify the dissipation potential* $\mathcal{D}$ by replacing the central part by an horizontal segment joining the two minima (in mathematical terms, this consists in taking the *convex hull* of $\mathcal{D}$). Then the resulting phase-plane curve would present a *Maxwell line* at $\mathcal{A} = 0$; but this regime would correspond to vanishing dissipation which is *not the case* as dissipation *does take place*. The only possibility to reconcile the model with irreversible thermodynamics is therefore to ignore the intermediate descending part of the S-shaped curve in the center of the diagram and to envisage *jump-like* vertical segments starting at A and going to the right on the top part and starting at A′ and going to the left on the bottom part, so that we recover a typical *hysteretic* curve or *limit cycle* in phase space. The remaining curved parts of the resulting cycle are covered in a finite time interval whereas the two vertical segments are covered in a practically zero time interval. These two segments correspond to a dissipation which is *homogeneous of order one* in the velocity (as $\mathcal{A}$ has reached a fixed constant level along these segments), just as in plasticity. It is the alternation of the two regimes which gives rise to the characterisic "crack-crack-crack" noise of the adhesive tape that we try to unwind. Typically, the above phenomenon refers to so-called *relaxation oscillations* and *stick-slip* (an expression that speaks for itself in the case of the adhesive tape) which occur when *dynamic losses* have a tendency to *decrease with increasing velocity* [see Eq. (5.5.42)]. *Crack propagation* in some materials such as glasses, ceramics, glassy polymers, and some metals and alloys, and the *peeling of viscoelastic solids* (this is the example of the tape) belong to this type of *dissipative phenomena*. For these we refer to Kubin and Poirier (1988) and Maugis (1985).

5.6. Reminder of Basic Equations

Here we gather in one place the basic equations that we shall need in subsequent chapters for establishing the essential classes of dissipative behaviors of continuous media. In the absence of (i) electromagnetic effects and some diffusion effects, which will be brought into the picture especially in Chapter 9, of (ii) any *internal degrees of freedom* (cf. Sec. 4.7 above), and (iii) any diffusion for internal variables, i.e. strictly for so-called *simple thermodeformable media*, the basic equation is the Clausius–Duhem inequality (3.3.76),

$$-\rho(\dot{\psi}+\eta\dot{\theta})+\sigma:\mathbf{D}+\theta\mathbf{q}\cdot\nabla(\theta^{-1})\geq 0\,, \tag{5.6.43}$$

together with the statement (4.4.20) of the so-called *L.A.S.* We further need to specify whether the medium under consideration is *incompressible* or not, and whether it is essentially *solid* in small or large strains, or *fluid*, although this distinction between solids and fluids is somewhat unjustified (especially in the presence of viscosity and, more generally, in *rheology*).

A. The case of solids

In the case of *small strains*, we have the expressions given in Eqs. (4.5.22)–(4.5.24). That is,

- *decomposition of strains:*

$$\varepsilon=\varepsilon^e+\varepsilon^p=(\nabla\mathbf{u})_s\,, \tag{5.6.44}$$

- *laws of state:*

$$\begin{aligned} W &:= \rho_0\psi=\bar{W}(\varepsilon^e,\alpha,\theta)\,,\\ \eta &= \eta_\alpha=-\rho_0^{-1}\partial\bar{W}/\partial\theta|_{\theta=\theta_\alpha}\,,\\ \sigma^e &= \sigma^e_\alpha=\partial\bar{W}/\partial\varepsilon^e, \qquad \mathcal{A}=-\partial\bar{W}/\partial\alpha\,, \end{aligned} \tag{5.6.45}$$

- *dissipation inequality:*

$$\begin{aligned} \Phi &= \Phi_{\text{intr}}+\Phi_{\text{th}}\geq 0\,,\\ \Phi_{\text{intr}} &= \sigma^v:\dot{\varepsilon}^e+\sigma:\dot{\varepsilon}^p+\mathcal{A}\dot{\alpha}, \qquad \Phi_{\text{th}}=\theta_\alpha\mathbf{q}\cdot\nabla(\theta_\alpha^{-1})\,,\\ \sigma^v &:= \sigma-\sigma^e\,, \end{aligned} \tag{5.6.46}$$

where σ is the *total stress*, σ^e is the *elastic stress*, and σ^v is the *viscous stress.*

For solids in *finite strains*, we better work per unit volume of the reference configuration $\mathcal{K}_R$ for which the Clausius-Duhem inequality (5.6.53) transforms to [cf. (3.2.46)]

$$-(\dot{W} + S\dot{\theta}) + \mathrm{tr}(\mathbf{T}\dot{\mathbf{F}}) + \theta\mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0\,, \tag{5.6.48}$$

where $\mathbf{T}$ is the first *Piola-Kirchhoff*, $\mathbf{F}$ is the *direct-motion gradient*, $\mathbf{Q}$ is the *heat flux referred to the unit area in* $\mathcal{K}_R$, and W and S are defined per unit volume in $\mathcal{K}_R$, i.e.

$$W = \rho_0\psi, \qquad S = \rho_0\eta\,. \tag{5.6.49}$$

In the presence of *anelastic finite strains*, the reasoning must be a little more subtle than in the case of small strains where the decomposition (5.6.44) holds. It is sufficient to remark that, in general, *deformation* is characterized by the tangent map $\mathbf{F}$ between the *reference configuration* K_R and the *current configuration* K_t. Such gradients compose in a multiplicative way. Thus, if there exists any *elastic* and *anelastic* finite strains, they should compose the total, and only true, gradient $\mathbf{F}$ in a multiplicative way, e.g.

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^p\,, \tag{5.6.50}$$

where none of the elements $\mathbf{F}^e$ and $\mathbf{F}^p$ of the multiplicative decomposition is a true gradient. In *geometrical differential* terms, they are only *Pfaffian forms.* The decomposition (5.6.50) was originally proposed by Lee (1969) and his co-workers. A simple picturesque interpretation of this is given in Figure 5.4 where the first step, i.e. $\mathbf{F}^p$, defines from $\mathcal{K}_R$ a so-called **intermediate configuration** $\mathcal{K}_{\mathcal{G}}$, which is also called *elastically released configuration* (hence the notation) as it is also obtained from $\mathcal{K}_t$ by applying $(\mathbf{F}^e)^{-1}$, and the name follows if $\mathbf{F}^e$ is indeed interpreted as the *elastic* finite strain. Let $\mathbb{Q}$ represent an orthogonal transformation of E^3 onto itself. Then it is clear that the decomposition (5.6.50) is invariant by rotation of $\mathcal{K}_{\mathcal{G}}$ as we can write

$$\begin{gathered}\mathbf{F}^e\mathbf{F}^p = \hat{\mathbf{F}}^e\hat{\mathbf{F}}^p, \quad \hat{\mathbf{F}}^e = \mathbf{F}^e\mathbb{Q}, \quad \hat{\mathbf{F}}^p = \mathbb{Q}^T\mathbf{F}^p\,, \\ \mathbb{Q}\mathbb{Q}^T = \mathbb{Q}^T\mathbb{Q} = \mathbf{1}, \quad \mathbb{Q}^T = \mathbb{Q}^{-1}, \quad \det\mathbb{Q} = \pm 1\,.\end{gathered} \tag{5.6.51}$$

In practice a definite orientation can be granted to $\mathcal{K}_{\mathcal{G}}$ through a particular crystal lattice (cf. Mandel, 1971). Concerning constitutive equations all we need to note for the moment is that we may rewrite the inequality (5.6.48) in a specific form by introducing the following elements of kinematics and kinetics. Let, by analogy with (5.6.45), the

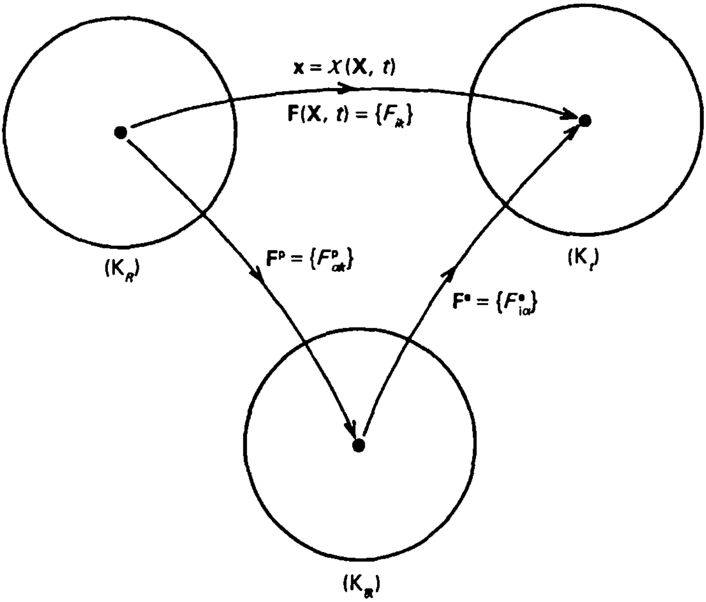


Fig. 5.4. Total deformation with intermediate configuration.

- *laws of state:*

$$
\begin{aligned}
W &= \bar{W}(\mathbf{F}^e, \alpha, \theta)\,, \\
S &= -\partial \bar{W}/\partial\theta|_{\theta=\theta_\alpha}\,, \\
\bar{\mathbf{T}}^e &:= \mathbf{T}^e_\alpha = (\partial \bar{W}/\partial \mathbf{F}^e)^T, \quad \mathcal{A} = -\partial \bar{W}/\partial \alpha\,.
\end{aligned}
\tag{5.6.52}
$$

Then we look for a convenient and suggestive expression of the residual *dissipation inequality*. To achieve this we first note that

$$
\dot{\mathbf{F}}^e = \dot{\mathbf{F}} \cdot (\mathbf{F}^p)^{-1} - \mathbf{F}^e \cdot \dot{\mathbf{F}}^p \cdot (\mathbf{F}^p)^{-1}\,. \tag{5.6.53}
$$

This is obtained by computing $\dot{\mathbf{F}}$ on the basis of (5.6.50) and applying $(\mathbf{F}^p)^{-1}$ to the left to the result. Furthermore, we set

$$
\bar{\mathbf{T}}^v := \mathbf{F}^p \cdot \mathbf{T} - \bar{\mathbf{T}}^e, \quad \bar{\mathbf{T}} := \mathbf{T} \cdot \mathbf{F}\,. \tag{5.6.54}
$$

Then it is readily checked on account of (5.6.52) that (5.6.48) provides the following

- *dissipation inequality:*

$$\begin{gathered}\Phi = \Phi_{\mathrm{intr}} + \Phi_{\mathrm{th}} \geq 0\,, \\ \Phi_{\mathrm{intr}} = \mathrm{tr}\{\bar{\mathbf{T}}^{v}\dot{\mathbf{F}}^{e} + \bar{\mathbf{T}}\dot{\mathbf{F}}^{p}\} + \mathcal{A}\dot{\alpha}, \quad \Phi_{\mathrm{th}} = \theta_{\alpha}\mathbf{Q}\cdot\nabla_{R}(\theta_{\alpha}^{-1})\,.\end{gathered} \tag{5.6.55}$$

Then the Piola–Kirchhoff stress is recovered by computing

$$\mathbf{T} = (\mathbf{F}^{p})^{-1}\cdot(\bar{\mathbf{T}}^{e} + \bar{\mathbf{T}}^{v}) = \mathbf{T}^{e} + \mathbf{T}^{v}\,, \tag{5.6.56}$$

wherein

$$\mathbf{T}^{e} = (\mathbf{F}^{p})^{-1}\cdot(\partial\bar{W}/\partial\mathbf{F}^{e}), \quad \mathbf{T}^{v} = (\mathbf{F}^{p})^{-1}\cdot\bar{\mathbf{T}}^{v}\,. \tag{5.6.57}$$

We remark that Φ has exactly the same structure as in the small-strain theory — compare $(5.6.55)_2$ and $(5.6.46)_2$. This convenient presentation was given by the author (1994a).

B. The case of fluids

Fluids, with their "flowing" behavior, are naturally subjected to large strains and displacements, although these notions are practically never used in fluids, except if some *markers*, such as suspended debris or deformable particles (e.g. polymers) make these clearly visible.

Discarding the case of *gases*, we shall mostly be concerned with *liquids* and *incompressible fluids*. Then we know that the Cauchy stress tensor σ is defined up to an *isotropic* pressure term, and only the *deviatoric* (or *shear*) part of σ contributes to the statements of irreversible thermodynamics. That is, we shall have the

- *laws of state:*

$$\begin{gathered}W = \rho_0\psi = \bar{W}(\rho_0 \text{ fixed, } \alpha, \theta)\,, \\ \mathcal{A} = -\partial\bar{W}/\partial\alpha, \quad \mathcal{S} = \rho_0\eta = -\partial\bar{W}/\partial\theta\,,\end{gathered} \tag{5.6.58}$$

and the

- *dissipation inequality:*

$$\begin{gathered}\Phi = \Phi_{\mathrm{intr}} + \Phi_{\mathrm{th}} \geq 0\,, \\ \Phi_{\mathrm{tr}} = \mathrm{tr}(\sigma^{D}\mathbf{D}) + \mathcal{A}\dot{\alpha}, \quad \Phi_{\mathrm{th}} = \theta\mathbf{q}\cdot\nabla(\theta^{-1})\,,\end{gathered} \tag{5.6.59}$$

where

$$\sigma^D := \sigma + p\mathbf{1}, \quad \mathrm{tr}\sigma^D \equiv 0\,. \tag{5.6.60}$$

It may be (see Chapter 3) that Φ_{intr} is somewhat more sophisticated than the above, especially when $\bar{W}$ involves an *elastic strain* as is the case in certain *elastic liquids*.

Conclusion: Although this may sound a bit presumptuous, we can say that we now have at our disposal all the ingredients to study a wealth of applications of *T.I.V* to solids and fluids, as a matter of fact, the richest collection of irreversible behaviors so far put under the same umbrella. This is developed in some detail in the following five chapters.

Chapter 6

VISCOSITY IN COMPLEX FLUIDS

I began my investigations because progress in physiology demands a knowledge of the laws of motion of the blood... in small-diameter pipes. (J. L. M. Poiseuille, Le mouvement des liquides dans les tubes de petits diamètres, Paris, 1844)

6.1. Introductory Remarks

Viscosity is the most ubiquitous dissipative mechanical behavior. Its essential feature is the manifestation of a *time scale.* It is, therefore, akin to *relaxation.* In practice this time behavior is experienced by a continuously evolving view of the pattern of the medium at a fixed placement in time. This is called a *flow.* If it is true, in agreement with Heraclitus' citation that "everything can flow", including the mountains of Prophetess Deborah and even the glass of our windows (we would be allowed to observe this if the sustaining structure could resist the passing of time), we limit ourselves here to those flows which are clearly observable at our human scale, say with significant changes in the pattern within a fraction of a second to a few minutes.

Both *solids* and *fluids* are capable of exhibiting *viscosity.* But the former do not correspond to the time scale just roughly introduced so that their viscosity — such as the one accounted for through the Kelvin–Voigt model of Sec. 3.2 — has manifestations that do not catch the eye, but are more subtle such as the slight *attenuation* of *ultrasonic waves.* Here we concentrate on the second class, so-called *fluids* for which the proper time scale, expressed through the reciprocal of a gradient of a velocity or, equivalently, a strain rate, is of the order of 10–10^3 seconds. This *capability* of relatively easy *flow, fluidity,* is captured by the fact that *fluids* have a tendency to occupy their actual container more or less rapidly. In terms of continuum mechanics (see Paragraph

2.3D), we may say that, in contradistinction to solids, fluids do not exhibit any privileged (reference) configuration, or rather, their reference configuration is constantly re-actualized with a certain characteristic time related to *viscosity*. A consequence of this is that one seldom refers to the notions of *displacements* and *deformations* in fluids, although this would be perfectly admissible. In turn, only an *Eulerian representation* is used where the physical velocity, and all other fields for that matter, are considered as function of the actual position and time. But markers introduced in a fluid, such as particles or long deformable fibers (in the ocean, shipwrecks) plainly exhibit those elements of kinematics such as displacement, rotation and stretch. This remark will prove essential in some of the developments below. Indeed, the classical incompressible viscous fluid behavior is that of *Newtonian fluids* for which classical *T.I.P.* is more than sufficient (Sec. 3.2 in which we already noted the possible introduction of Rayleigh's *dissipation function*). That is, those very simple fluids for which we have the celebrated Newtonian–Stockesian constitutive equations:

$$\sigma^D = 2\eta_v \mathbf{D}, \qquad \mathrm{tr}\,\mathbf{D} = 0, \qquad \eta_v \geq 0\,, \tag{6.1.1}$$

where η_v is the *shear viscosity* coefficient. The latter may depend on temperature θ in a way that we do not need to specify. From the point of view of *material symmetry*, fluids described by (6.1.1) are *isotropic*: their mechanical response at a point is direction-independent. Any fluid whose constitutive equation deviates from (6.1.1) is called a *non-Newtonian fluid*. The modern science of *rheology* is essentially concerned with the construction of models, and the subsequent study of the flows, of these fluids. The latter includes all types of materials such as paints, varnishes (strongly viscous materials), suspensions of macromolecules (very fluid but with anomalous viscosity properties), fluids with directional properties (e.g., suspensions of fibers, liquid crystals), etc. Mere *T.I.P.* is not sufficient to capture these generalizations, if we agree on the basis that *thermodynamics*, as a somewhat *general science* that points to the *Arrow of time*, should have something to do with this. Although this may seem obvious to the reader who is already convinced, it is fair to say that many rheologists do not feel the need to place *rheology* under the umbrella of thermodynamics. This is illustated by monographs (e.g. Reiner, 1960; Schowalter, 1976; Larson, 1988; Vyalov, 1986) that do not say a word concerning *thermodynamical constraints* on rheological models. Here, however, we do enforce thermodynamics and we are necessarily led to envisage a generalization of *T.I.P.* in order to accommodate *complex behaviors* where underlying complicated mechanisms are at the root of an additional irreversibility. The *thermodynamics with internal variables* (*T.I.V.*), as described in Chapters 4 and 5, proves to be an adequate tool to achieve this most inclusive view. This necessity is demonstrated in the next two sections.

6.2. The Notion of Simple (Non-Newtonian) Fluid

Here we expand the point of view which, following Coleman and Noll (1961) and others, prevailed with theoreticians of the continuum in the 1960s and 1970s, essentially because of (i) its conceptual simplicity, (ii) its aesthetically pleasing formulation and (iii) its relatively good efficiency in the interpretation of certain typical behaviors in so-called *viscometric flows* (Coleman, Markovitz and Noll, 1966). In some intuitive and anthropomorphic way, a viscous material of the fluid type has a rather *long memory* of its passed kinematical experience. Therefore, its stress should be determined by a *functional* of the *history* (we recognize the spirit of *rational thermodynamics*) of a "relative" strain tensor, an *observable* variable of state. Referring to Figure 2.2, we can introduce this *relative strain measure* by

$$\mathbf{C}(t,t') = \left(\frac{\partial\chi}{\partial\xi}\right)^T \cdot \frac{\partial\chi}{\partial\xi}, \quad \mathbf{x} = \chi(\mathbf{X},t), \qquad \xi = \chi(\mathbf{X},t'), \quad t' \le t. \tag{6.2.2}$$

Equivalently, we can write $\mathbf{C}(t,t') = \mathbf{C}_t(s)$, $s = t - t'$. Then for so-called *simple* fluids (that are simple only in name!) one has the following constitutive equation [cf. (3.3.79)]

$$\sigma(t) = \underset{S\in[0,\infty)}{\mathcal{G}} [\mathbf{C}_t(s)]. \tag{6.2.3}$$

With appropriate continuity assumptions concerning the functional, various approximations of (6.2.3) provide *hereditary* (time-integral) constitutive equations (see Coleman and Noll, 1961, for this procedure). Among these one must single out the Bernstein–Kearsley–Zapas (1963) model — the so-called *BKZ fluid* — for which (6.2.3) takes on the following explicit form:

$$\sigma(t) = \int_0^\infty \{\phi_1(s,I_1,I_2)\mathbf{B} - \phi_2(s,I_1,I_2)\mathbf{C}\}ds, \tag{6.2.4}$$

where **B** is the Finger measure of finite strains already introduced in (3.2.51), and the ϕ_i, $i = 1, 2$, are derived from a potential $\mathcal{W}$ by

$$\phi_i = 2\partial\mathcal{W}/\partial I_i \, . \tag{6.2.5}$$

The potential $\mathcal{W}$ is said to be separable if and only if

$$\mathcal{W}(s, I_1, I_2) = m(s)\mathcal{U}(I_1, I_2) \, , \tag{6.2.6}$$

where the function m can be represented by a linear combination of *memory functions* of the exponential decreasing type. The model (6.2.3)–(6.2.6) can be justified on a thermodynamical basis. But the reader has understood by now that we are now here doing the apology of rational thermodynamics. The interesting point for subsequent developments is that, following Larson (1983a), if $\mathcal{W}$ is separable then it is shown that B satisfies an objective (i.e. form-invariant by time-dependent rotations at time t) differential equation of the general form

$$\overset{\square}{\mathbf{B}} := \frac{\partial \mathbf{B}}{\partial t} + \mathbf{f}_c(\mathbf{B}, \nabla\mathbf{v}) = 0 \, , \tag{6.2.7}$$

where

$$\mathbf{L} = (\nabla\mathbf{v})^T = \dot{\mathbf{F}}\mathbf{F}^T \, , \tag{6.2.8}$$

is the velocity-gradient tensor, whose symmetric and skewsymmetric parts, respectively **D** and Ω, are referred to as the rate-of-strain tensor and vorticity or spin tensor:

$$\mathbf{D} = \mathbf{L}_s := \frac{1}{2}(\mathbf{L} + \mathbf{L}^T), \quad \Omega = \mathbf{L}_A := \frac{1}{2}(\mathbf{L} - \mathbf{L}^T) \, . \tag{6.2.9}$$

In (6.2.7) the $\square$ denotes an *objective* time derivative (e.g. a *convected-time derivative*), and $\mathbf{f}_c$ is linear affine in its two arguments. It follows from "separability" (6.2.6) that the stress satisfies a number of rheological evolution equations of the Maxwell type (see Chapter 7; also Proslier, 1979). For the sake of simplicity we call *differential rheological models* (for short *D.R.M.*) such evolution equations. Thus we stand at the left and bottom parts in the "flow" diagram of Fig. 6.1. Remark that no microstructure, no image relating to any physical vision, intervene in this formal construction. The situation is just the opposite with so-called *molecular models* to which we now briefly turn our attention with a particular interest in solutions of polymers.

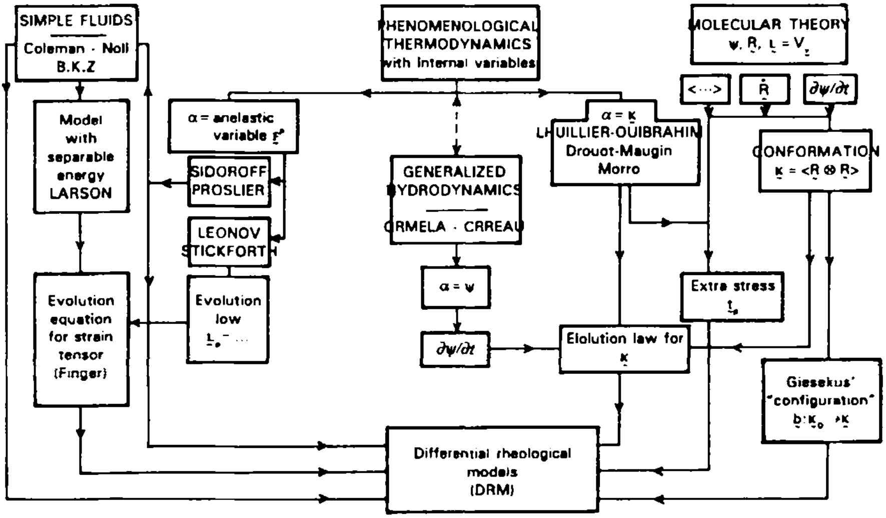


Fig. 6.1. Thermodynamical modeling of polymers in solution.

6.3. Statistical Theory of Polymeric Fluids

A. Molecular models[1]

Two models are at our disposal, the model of *dumbbells*, generalized to Rouse Chains if necessary, and that of *networks* with strands and entanglements. These two are schematically represented in Fig. 6.2. But the statistical philosophy is the same one for the two models, being based on the assumed existence of: (i) a distribution function f, (ii) a vector characterizing the *microstructure*, e.g. $\mathbf{R}$ or $\mathbf{R}'$ in Fig. 6.2, (iii) the velocity field of the solvent, hence by space differentiation, $\mathbf{L} = (\nabla \mathbf{v})^T$; (iv) an averaging procedure of the ensemble type noted $\langle \ldots \rangle$, and (v) a conservation law for f such as

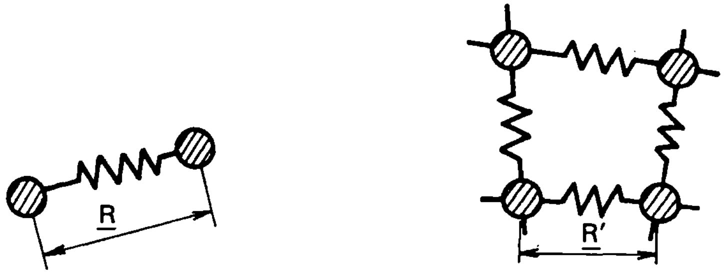
$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \mathbf{R}} \cdot (\dot{\mathbf{R}} f) = 0\,, \tag{6.3.10}$$

for dumbbells, and

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \mathbf{R}'} \cdot (\dot{\mathbf{R}}' f) = \hat{\mathbf{R}} \tag{6.3.11}$$

---

[1] This point of view is expressed at length in Bird *et al.* (1977). Here we follow the synthetic presentation of Maugin and Drouot (1988).



(a) dumbbell

R: oriented distance between extreme beads
ψ: distribution fuction
n: number of dumbbells per unit volume

$$\int_{\underline{R}} \psi(\underline{R}, t)\, d^3R = n = \text{const.}$$

(b) elastic network

R': oriented distance of a segment between two strands
ψ: distribution fuction
n': number of segments per unit volume

$$\int_{\underline{R}'} \psi(\underline{R}', t)\, d^3R' = n'(t)$$

Fig. 6.2. Molecular models.

for networks, where $\hat{\mathbf{R}}$ is a source term which accounts for creation and annihilation of strands in the elastic network. The essential problem here is to determine **R** or **R**′ in the form

$$\dot{\mathbf{R}} = \mathcal{R}_c(\mathbf{R}, \nabla \mathbf{v}) + \mathcal{R}_d(\mathbf{R}, f), \tag{6.3.12}$$

and also $\hat{\mathbf{R}}$ in the case (6.3.11). In (6.3.12) the subscripts c and d stand for "convection" and "diffusion", respectively, in the following mathematical sense. Once (6.3.12) has been carried in (6.3.10), the $\mathcal{R}_c$ term alone provides a *hyperbolic* equation (hence the justification for "convection") while the $\mathcal{R}_d$ term alone leads to a *parabolic* equation (hence "diffusion") if $\mathcal{R}_d$, as many force fields, is derivable from a potential W, i.e. $\mathcal{R}_d = -\partial W/\partial \mathbf{R}$. Clearly, (6.3.12) is nothing but an equation that governs the relative motion of the two beads in the dumbbell model, an equation in which inertia has been discarded compared to relaxation (*time scales again*!). This reduced "equation of motion" can contain other terms, i.e. *forces*, such as, for instance, a term $\mathcal{R}_e(\mathcal{R}, q)$ of the electrostatic type — if q is an electric charge — which will reinforce the diffusive nature of Eq. (6.3.10), — cf. e.g. Dunlap and Leal (1984). The scheme in Figure 6.2(a) where the interactions between neighboring dumbbells are neglected, applies to *dilute* or *semi-dilute* solutions of *macromolecules* while that in Figure 6.2(b) corresponds better to a dense solution or an elastomer (for this last case, see Treloar, 1955; Weiner, 1983). Equation (6.3.10) or (6.3.11) can also be looked upon as an *evolution equation* that we symbolically rewrite as

$$\frac{\partial f}{\partial t} = \mathcal{F}(f, \mathbf{R}, \dot{\mathbf{R}}, \nabla \mathbf{v}) , \tag{6.3.13}$$

for the "microscopic" variable f, which, usually, does not appear in the *hydrodynamical description* (see, however, Grmela, 1990, Grmela and Carreau, 1982, 1984).

The second statistical *moment* of R, i.e. classically,

$$\mathbf{K} := \langle \mathbf{R} \otimes \mathbf{R} \rangle = \int_{\mathbf{R}} \mathbf{R} \otimes \mathbf{R} f d^3 R = \mathbf{K}^T \tag{6.3.14}$$

defines a symmetric second-order tensor in the current configuration $\mathcal{K}_t$ of the fluid, that we shall call the *conformation* (cf. the pioneering works of Kuhn and Huhn, 1945, and Cerf, 1957). But, knowing in principle (6.3.12), one can, in theory at least, obtain an *evolution equation* for $\mathbf{K}$ in the symbolic form

$$\frac{\partial \mathbf{K}}{\partial t} = \mathcal{K}(\mathbf{K}, \nabla \mathbf{v}) . \tag{6.3.15}$$

We are therefore brought back to the essential problem which is obtaining (6.3.12) or a similar equation for $\mathbf{R}'$. One can rewrite (6.3.12) as

$$\dot{\mathbf{R}} = \mathcal{R}_c + \frac{2}{\zeta}\mathcal{F} , \tag{6.3.16}$$

where $\mathcal{R}_c$ is defined in terms of the hydrodynamical motion, $\nabla \mathbf{v}$, $\mathcal{F}$ is the *spring force* extertéd on the beads of the dumbbell, and ζ is the viscosity of the solvent — Stokes' flow may be assumed around dumbbells — with $\mathcal{F} = -\partial W/\partial \mathbf{R}$ and, for instance (see below),

$$W = \frac{H}{2}\mathbf{R}^2 + D \ln f . \tag{6.3.17}$$

The convection term $\mathcal{R}_c$ can be more or less involved depending on the degree of refinement considered for the interactions between the beads and the surrounding fluid solvent. Three examples can be quoted for the sake of illustration. In increasing order of complexity:

(a) *affine motion*:

$$\mathcal{R}_c = \mathbf{L} \cdot \mathbf{R}\,; \tag{6.3.18a}$$

(b) *motion with slip* (Gordon and Schowalter, 1972):

$$\mathcal{R}_c = (\mathbf{L} - \xi \mathbf{D}) \cdot \mathbf{R}\,, \tag{6.3.18b}$$

where ξ is a slip coefficient $(0 \leq \xi \leq 1)$, and

(c) *model of hydrodynamical interactions* (Ottinger, 1986):

$$\mathcal{R}_c = (1 - \zeta \bar{\Omega}) \cdot \left(\mathcal{R}_d^B + \frac{2}{\zeta} \mathcal{F} \right)\,, \tag{6.3.18c}$$

where

$$\bar{\Omega} = (8\pi\zeta |\mathbf{R}|^{-1})(\mathbf{1} + R^{-2} \mathbf{R} \otimes \mathbf{R})\,, \tag{6.3.19}$$

is *Oseen's tensor*, and $\mathcal{R}_d^B$ is given below. In this case $\mathcal{R}_c$ itself contains an average $\langle \ldots \rangle$ so that there arises a problem of consistency in the averaging procedure for which one must envisage a solution in the form of an asymptotic expansion (in terms of the *retarded motion* — see Ottinger, 1986).

For the *diffusion term* $\mathcal{R}_d$ the simplest expressions are given by $(D = k_B \theta$, where k_B is Boltzmann's constant and θ is the temperature):

(d) *Brownian motion*:

$$\mathcal{R}_d^B = -D \frac{\partial}{\partial \mathbf{R}} (\ln f) \tag{6.3.20a}$$

and

(e) *anisotropic diffusion* (Green and Tobolsky, 1946):

$$\mathcal{R}_d = -\mathcal{B} \cdot \frac{\partial}{\partial \mathbf{R}} (\ln f)\,, \tag{6.3.20b}$$

where the tensor $\mathcal{B} = D\underline{\zeta}^{-1}$ is the *anisotropic diffusivity tensor* of Giesekus (if $\underline{\zeta}$ is the *mobility tensor*) which, if it depends only on the mean orientation, can be shown to depend on $\mathbf{K}$ (cf. Giesekus, 1986).

The elastic term of diffusive nature can result from a quadratic or Hookean energy such as $W = H\mathbf{R}^2/2$ (linear spring) or can be more realistic (so-called *FENE* (*finite-extension*) model with a nonlinear spring of finite extensibility).

Finally, assuming that the rates of creation and annihilation of strands in the network are equal at equilibrium, the $\hat{\mathbf{R}}$ term in (6.3.11) can be characterized by a single coefficient τ' — the mean life time of a strand — and be written thus (Green and Tobolsky, 1946):

$$\hat{\mathbf{R}} = -\frac{1}{\tau'}(f - f_0). \tag{6.3.21}$$

It is then said that one has an *impulsive diffusion* (cf. Larson, 1983a).

B. Evolution equation for the conformation

Many authors have examined the influence of terms of the type of (6.3.18a) through (6.3.21) in the basic equation (6.3.10), hence the evolution equation (6.3.15). For instance, accounting for (6.3.18a) and (6.3.20a) and for *Hookean elasticity*, one obtains the *relaxation equation*

$$\overset{\nabla}{\mathbf{K}} = -\frac{1}{\tau_K}(\mathbf{K} - \mathbf{K}_0), \tag{6.3.22}$$

where we have set

$$\mathbf{K}_0 = (D/H)\mathbf{1}, \qquad \tau_K = \zeta/4H, \tag{6.3.23}$$

and

$$\overset{\nabla}{\mathbf{K}} := \dot{\mathbf{K}} - (\mathbf{L}\mathbf{K} + \mathbf{K}\mathbf{L}^T). \tag{6.3.24}$$

The latter is a well-known *convected time derivative* (in differential geometry, a so-called *Lie derivative* — see Maugin, 1988, Chapter 2), so that *both* sides on Eq. (6.3.22) are *objective*. If one takes account (6.3.18b) instead (6.3.18a), all other things being left unchanged, then one obtains an evolution equation which is also *objective* but with the derivative $\overset{\nabla}{\mathbf{K}}$ replaced by a *Gordon-Schowalter* derivative defined by

$$\overset{\square}{\mathbf{K}}_{GS} := D_J\mathbf{K} - a(\mathbf{K}\mathbf{D} + \mathbf{D}\mathbf{K}) = \overset{\nabla}{\mathbf{K}} + \xi(\mathbf{K}\mathbf{D} + \mathbf{D}\mathbf{K}), \tag{6.3.25}$$

where $a = 1 - \xi$, $0 \le a \le 1$, and D_J denotes the so-called *Jaumann* (*co-rotational*) derivative of continuum mechanics, such that (cf. Maugin, 1988, Chapter 2)

$$D_J\mathbf{K} := \dot{\mathbf{K}} - \Omega\mathbf{K} + \mathbf{K}\Omega, \tag{6.3.26}$$

when applied to a second-order symmetric tensor. At this point it can be remarked that any temporal derivative of the objective tensor field **K**, defined by

$$\mathcal{D}\mathbf{K} := D_J\mathbf{K} + \mathbf{f}(\mathbf{K},\mathbf{D}), \tag{6.3.27}$$

where **f** is a linear affine and isotropic tensor-valued function of **K** and **D** jointly, is also objective. Equation (6.3.27) holds for $\overset{\nabla}{\mathbf{K}}$ and $\overset{\Box}{\mathbf{K}}_{GS}$. This is also the case of the other convected time derivative defined by

$$\begin{aligned}\overset{\Delta}{\mathbf{K}} := \dot{\mathbf{K}} + (\mathbf{L}^T\mathbf{K} + \mathbf{K}\mathbf{L}) &= D_J\mathbf{K} + (\mathbf{K}\mathbf{D} + \mathbf{D}\mathbf{K}) \\ &= \overset{\nabla}{\mathbf{K}} + 2(\mathbf{K}\mathbf{D} + \mathbf{D}\mathbf{K}),\end{aligned} \tag{6.3.28}$$

which is much less used in *DRMs* than the "∇" derivative.

Instead of using **K**, Giesekus has suggested the use of a tensor **b** such that it effects the transformation of $\mathbf{K}_0$ into **K**, i.e.

$$\mathbf{K} = \mathbf{b} \cdot \mathbf{K}_0, \tag{6.3.29}$$

where $\mathbf{K}_0$ is an isotropic equilibrium value. He calls this tensor **b** the *configuration*. This name is rather confusing as "configuration" already has a precise meaning in continuum mechanics. Notice that since $\mathbf{K}_0$ is isotropic, **b** is in fact proportional to **K**, such that

$$\mathbf{b} = (H/D)\mathbf{K}; \tag{6.3.30}$$

and **b** appears to be nothing but a *normalization* of **K** to unity at equilibrium (for which $\mathbf{b}_0 = \mathbf{1}$).

C. Stress tensor

The above developments show how a statistical basis provides a plausible *evolution equation* for a tensor which seems to relate in some way to a *microstructure*. Within this framework this microstructure evolves under the action of the surrounding fluid. But this is not all, as the deformation of the microstructure should in some way influence the flow to some extent. We should, therefore, exhibit the contribution of the statistical variables **K** or **b** to the *stress tensor* of the overall fluid medium. This will manifest itself by the addition of a contribution σ_p to the Newtonian expression of Eq. (6.1.1). Classically in a statistical approach (cf. Bird *et al.*, 1977), this additional stress is determined by computing the first moment of forces acting on the microstructure. That is

$$\sigma_p = n\langle \mathcal{F} \otimes \mathbf{R} \rangle \,, \tag{6.3.31}$$

where, for example, $\mathcal{F}$ is the force present in expression (6.3.16). In the simple case where (6.3.22) holds good, one directly obtained (with $G = nk_B\theta$)

$$\sigma_p = G(\mathbf{b} - \mathbf{1}) = k(\mathbf{K} - \mathbf{K}_0) \,, \tag{6.3.32}$$

which obviously vanishes at equilibrium. As **b** or **K** satisfies an evolution equation of the relaxation type (6.3.22), the stress σ will satisfy a *DRM* with a time derivative $\overset{\nabla}{\sigma}$. This can be generalized to the case of a *Rouse chain* and this demonstrates the possibility of bringing into contact statistical molecular models and *DRMs*, while the latter can be equivalent to *simple fluids*, in particular to *BKZ* fluids. This is indeed the case if the notion of anisotropic diffusivity is introduced and it depends on the actual "configuration" of Giesekus **b**. This holds true in the *reptation theory* of Doi and Edwards (1978). Larson (1983a) has shown what are the models which, like the *BKZ fluids* subjected to the restriction of separability, lead to "separable" constitutive equations. He has also given the expression of objective derivatives and differential stress constitutive equations that emerge at the macroscopic scale when convection and diffusion models are considered at the microscopic (molecular) scale.

The essential problem that we now consider is: as both the equation for **K** and the constitutive equation of σ (i.e. *both* relaxation of the microstructure and the viscosity of the macroscopic flow) contribute to *dissipation*, what is the macroscopic thermodynamic scheme that allows one to account for these two effects which are coupled and co-operate in the entropy growth? The answer is to be found in *T.I.V.* for which the long excursion just made in the molecular landscape provides a *physical* background and a striking interpretation.

6.4. Thermodynamics with Internal Variables

A. General view

We consider now a purely phenomenological approach constrained by the second law of thermodynamics. We assume that ρ and $\mathbf{v}$ are the mass density and physical velocity field of the *macroscopic fluid* under consideration, i.e. the final product composed of a solvent (carrier fluid) and the solute (here macromolecules). Let ρ_p and ρ_s be the mass densities of polymer molecules and of the solvent, respectively. The *concentration* in macromolecules is defined by

$$c = \rho_p/\rho, \qquad \rho_p = \rho - \rho_s . \tag{6.4.33}$$

Then the local field and thermodynamical equations which govern the macroscopic fluid considered as a mixture with prevalent solvent mass are as follows at each point $\mathbf{x}$ in the domain occupied by the fluid at time t (configuration $\mathcal{K}_t$):

- *Balance of mass* (no chemical reactions occur in the solution):

$$\dot{\rho} + \rho\nabla \cdot \mathbf{v} = 0 , \tag{6.4.34}$$

and

$$\rho\dot{c} + \nabla \cdot \mathbf{J} = 0 ; \tag{6.4.35}$$

- *Balance of linear and angular momenta* (no externally applied couple):

$$\rho\dot{\mathbf{v}} = \mathrm{div}\sigma + \rho\mathbf{f} , \tag{6.4.36}$$

and (T =transpose)

$$\sigma = \sigma^T , \tag{6.4.37}$$

- *Balance of energy* (tr=trace)

$$\rho\dot{e} = \mathrm{tr}\,(\sigma\mathbf{D}) - \nabla \cdot \mathbf{q} + \rho h ; \tag{6.4.38}$$

- *Entropy inequality* [Clausius–Duhem form when the entropy flux has the general form (3.3.110)]

$$-(\dot{\psi} + \eta\dot{\theta}) + \mathrm{tr}(\sigma\mathbf{D}) + \nabla \cdot (\theta\mathbf{k}) - \mathbf{S} \cdot \nabla\theta \geq 0 . \tag{6.4.39}$$

In these equations a superimposed dot denotes the material time derivative, $\mathbf{J}$ is the *diffusion-flux* vector, σ is Cauchy's symmetric stress tensor. All other notations were introduced in previous chapters.

The system (6.4.34)–(6.4.38) — which must be accompanied by initial and boundary conditions in problem solving — will be closed if constitutive equations are given for the following set of fields:

$$\{\sigma, \mathbf{J}, \mathbf{q}, \mathbf{S}, e, \Psi, \eta\} , \tag{6.4.40}$$

the fields h and f being prescribed as functions of $(\mathbf{x}, t)$. The volumetric behavior of the macroscopic fluid is assumed to be the same as that of the solvent. Since the latter is usually *incompressible* (very often the solvent is just *water*), we also have

$$\operatorname{tr}\mathbf{D} = \nabla \cdot \mathbf{v} = \mathbf{0}. \tag{6.4.41}$$

For *dilute* solutions we have the condition

$$c \ll 1. \tag{6.4.42}$$

The internal structure of the macroscopic fluid, hence the microstructure or changes in shape and orientation of molecules, is phenomenologically described by the introduction of an *internal variable* α (of which the tensorial character will be chosen later on). This variable is such that it does not modify before hand the above-stated balance equations since, globally, the macroscopic fluid appears to us as a classical fluid, albeit perhaps not Newtonian. But the dependent variables of the set (6.4.40) will depend on α, and α itself is supposed to satisfy an *evolution equation*[2] of the form

$$\mathcal{D}\alpha = \mathbf{g}(\theta, \nabla\mathbf{v}, \ldots; \alpha), \tag{6.4.43}$$

where $\mathcal{D}$ is some appropriate time-like derivative. This is complemented by *equilibrium conditions* $\alpha = \alpha_0$ with $\nabla\alpha = 0$, such that at equilibrium

$$\mathbf{g}(\theta_0, \nabla\mathbf{v} = \mathbf{0}, \ldots; \alpha = \alpha_0) = \mathbf{0} \tag{6.4.44}$$

In the present case, due to the presence of α the stress tensor of our macroscopic fluid will deviate from Newton's incompressible fluid law by an additional contribution σ_p in such a way that if $\eta_v(c, \theta)$ is the usual viscosity coefficient

$$\sigma = 2\eta_v\mathbf{D} + \sigma_p(\theta, \nabla\mathbf{v}, \ldots, \alpha). \tag{6.4.45}$$

The simple equations (6.4.43) and (6.4.45) reveal at the outset the crucial interdependence between the way in which the fluid strain-rate induces the molecular deformation (changes in α) and the way in which the molecular deformability enters the stress tensor through the contribution σ_p. The requirement that (6.4.39) be satisfied for all admissible thermodynamic processes will

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[2] As a matter of fact, this, later on, is no longer a supposition but a consequence of the applications of the rules of *T.I.P.*

show that, in general, the functions $\mathbf{g}$ and σ_p are not independent. Our concern is obviously the determination or construction, on some rational basis, up to a few material constants to be determined experimentally, of these functions $\mathbf{g}$ and σ_p, once the *internal variable* has been selected. Note that only the deviatoric part of $\mathbf{D}$ is involved by virtue of (6.4.41) but no special symbol will be introduced for that matter. Now we face the problem of selecting the most relevant internal variable.

B. The internal variable is an anelastic strain

A strain, whether elastic or not, is represented by a second-order *tensor* as it should play the same role as a *metric* from the point of view of differential geometry (measure of distance between two infinitesimally close points). Several authors, among whom Buevich (1968), Gorodtsov and Leonov (1968) and Capriz (1968) must be credited with the original idea of introducing a *tensor* as an internal variable in *viscoelastic materials.* And we owe to Green and Naghdi (1967) and Perzyna (1974) the introduction of an *intermediate configuration* $\mathcal{K}_i$ and the idea of relating the *tensorial* internal variable to one of the elements of the kinematical decomposition thus introduced (at least in viscoplasticity). In the case of the viscoelasticity of complex fluids, Leonov (1976) has exploited the above ideas by considering the multiplicative decomposition (5.6.50) of Lee which we shall note here $\mathbf{F} = \mathbf{F}_e\mathbf{F}_a$, where $\mathbf{F}_a$ is the *anelastic* "gradient" (not a gradient *per se*). Now from the very definition of $\mathbf{B}$, Eq. $(3.2.51)_2$ and the definition (6.3.24) applied to $\mathbf{B}$, we let the reader check for himself that $\mathbf{B}$ satisfies the following kinematical identity:

$$\overset{\nabla}{\mathbf{B}} := D_J\mathbf{B} - (\mathbf{BD} + \mathbf{DB}) \equiv \mathbf{0}\,. \tag{6.4.46}$$

Now let

$$\begin{aligned} \mathbf{B}_e &= \mathbf{F}_e\mathbf{F}_e^T, & \mathbf{L} &= \mathbf{L}_e + \mathbf{L}_a\,, \\ \mathbf{L}_e &= \dot{\mathbf{F}}_e\mathbf{F}_e^{-1}, & \mathbf{L}_a &= \mathbf{F}_e \cdot (\dot{\mathbf{F}}_a\mathbf{F}_a^{-1})\mathbf{F}_e^{-1}\,. \end{aligned} \tag{6.4.47}$$

Then one shows that $\mathbf{B}_e$ satisfies the following differential equation:

$$\overset{\nabla}{\mathbf{B}}_e + (\mathbf{L} - \mathbf{L}_a)\mathbf{B}_e + \mathbf{B}_e(\mathbf{L} - \mathbf{L}_a)^T = \mathbf{0}\,. \tag{6.4.48}$$

One can view Eqs. (6.4.46) and (6.4.48) as *evolution equations.* In particular, following Leonov (1976), if we consider that for an incompressible fluid behavior the free energy function W per unit volume cannot depend on $\mathbf{B}$ (see Truesdell and Noll, 1965), we can only take W as a function of $\mathbf{B}_e$ and θ, and the procedure sketched in Chapter 5 for internal variables apply. In particular, the *intrinsic dissipation* takes on the form

$$\Phi_{\text{intr}} = \operatorname{tr}(\sigma^{ir}\mathbf{D} + \mathcal{A}\overset{\nabla}{\mathbf{B}}_e)\,, \tag{6.4.49}$$

where (d =deviatoric part)

$$\sigma^{ir} = \sigma^d - \sigma^R, \quad \sigma^R = 2\left(\frac{\partial W}{\partial \mathbf{B}_e}\mathbf{B}_e\right)^d, \quad \mathcal{A} = -\frac{\partial W}{\partial \mathbf{B}_e}, \tag{6.4.50}$$

where the last two equations constitute the *laws of state*. On assuming then the existence of a potential of dissipation $\mathcal{D}^*(\mathbf{D}, \mathcal{A})$, we obtain thermodynamically compatible *complementary* laws for mechanical dissipative processes in the form

$$\sigma^{ir} = \frac{\partial \mathcal{D}^*}{\partial \mathbf{D}}, \qquad \overset{\nabla}{\mathbf{B}}_e + \frac{\partial \mathcal{D}^*}{\partial(\partial W/\partial \mathbf{B}_e)} = \mathbf{0}\,. \tag{6.4.51}$$

This straighforward derivation was introduced by Maugin and Drouot (1988). Leonov (1976) does not follow this line of reasoning. Noticing that in order to know the evolution equation (6.4.48) in full we need to known an expression for the difference $(\mathbf{L} - \mathbf{L}_a)$ in terms of $\mathbf{B}_e$, he invokes an analogy with $(6.4.50)_2$ and write that the anelastic strain rate $\mathbf{L}_a$ is derivable from a "dissipation" potential $\mathcal{D}$ of the *same form* as W so that [cf. to $(6.4.50)_2$]

$$(\mathbf{L}_a)_s = 2\left(\frac{\partial \mathcal{D}}{\partial \mathbf{B}_e}\mathbf{B}_e\right)^d, \tag{6.4.52}$$

while for W he considers a Mooney–Rivlin type of incompressible free energy for an *elastomer* (justified by rubber elasticity — see Paragraphs 3.2E,F; also Treloar, 1955) and thus [cf. of (3.2.58)]

$$\sigma^R = 2\left\{\frac{\partial W}{\partial I_1}\left(\mathbf{B}_e - \frac{1}{3}I_1\mathbf{1}\right) - \frac{\partial W}{\partial I_2}\left(\mathbf{B}_e^{-1} - \frac{1}{3}I_2\mathbf{1}\right)\right\}, \tag{6.4.53}$$

the expression of $(\mathbf{L}_a)_s$ being formally the same but with $\mathcal{D}(I_1, I_2)$ replacing W. Equations (6.4.48), (6.4.52) and (6.4.53) are the bases of Leonov's theory. The elegance of the direct approach (6.4.51) for W and $\mathcal{D}^*$ both isotropic functions of $\mathbf{B}_e$ as a result of the objectivity requirement, hence depending only on the invariants I_1 and I_2 of $\mathbf{B}_e$ in the "Mooney" approximation, is to be emphasized as it is inescapable. Following a remarkable classification of all viscoelastic fluid behaviors by Sidoroff (1975a,b) on the basis on internal-variable theory, this more rational approach was used by Proslier (1979), independently of Leonov's work, to show that a viscoelastic model based on a tensorial internal variable and an intermediate "elastically released" configuration $\mathcal{K}_{\mathcal{R}} = \mathcal{K}_i$ — see Fig. 5.4 — could be equivalent to a class of *BKZ fluids* with separable energy. Stickforth (1981) and Dasher and Van Ardale (1981) have proposed theories which are quite comparable with Leonov's. Relationships between the latter and *DRMs* have been studied by Leonov (1982) and Larson (1983b). We however find no apparent relationship with the statistical presentation of Sec. 6.3 because $\mathbf{B}_e$ is on the same footing as $\mathbf{F}$ and is, therefore, not more "microscopic" than the usual deformation. To reach a close contact with the contents of Sec. 6.3 we need to consider another type of internal variable, although still a second order tensor.

C. The internal variable is a conformation

The "conformation" tensor introduced in Sec. 6.3 is an obvious candidate for a good tensorial internal variable in the theory of dilute or semi-dilute solutions of polymers and macromolecules. Being entangled in an intricate manner (Fig. 6.3) long polymeric chains in their equilibrium configuration $\mathcal{K}_0$ under the influence of Brownian agitation may be assumed to roughly have the shape of spherical balls (so-called spherically *coiled* conformation) of radius R_0. The "spheres" will be slightly deformed but will keep an essentially *three-dimensional* shape (spheroid, ellipsoid) in the presence of a weakly elongational flow of the surrounding fluid in a configuration $\mathcal{K}_t$, while they will more or less take a *one-dimensional* (rodlike) structure in strongly elongational flows. In the case of polymeric fluids such as *polyelectrolytes* which have electrical properties (Fig. 6.4), the overall shape of the molecules depends on the charge of the fluid, low charges yielding spherically coiled conformations and an increase in charge causing eventually a stretched rodlike or cylindrical conformation, ellipsoidal conformations comprehending the whole range of such conformations. Let $\mathbf{R}$ be the directed distance between extreme monomers in a molecule chain in $\mathcal{K}_t$. In the first case a *second-order* moment (lowest harmonic departure from sphericity), hence a symmetric second-order tensor, must be introduced to describe the three-dimensional deformability of the molecules.

In the second case, it is possible that a vector field indicating a *direction* be sufficient to obtain a satisfactory kinematic description. We shall return to this second case later on. For the time being, the tensor of interest, in fact akin to an *inertia* per unit mass, is defined as in the first of (6.3.14). That is,

$$\mathbf{K} := \langle \mathbf{R} \otimes \mathbf{R} \rangle\,, \tag{6.4.54}$$

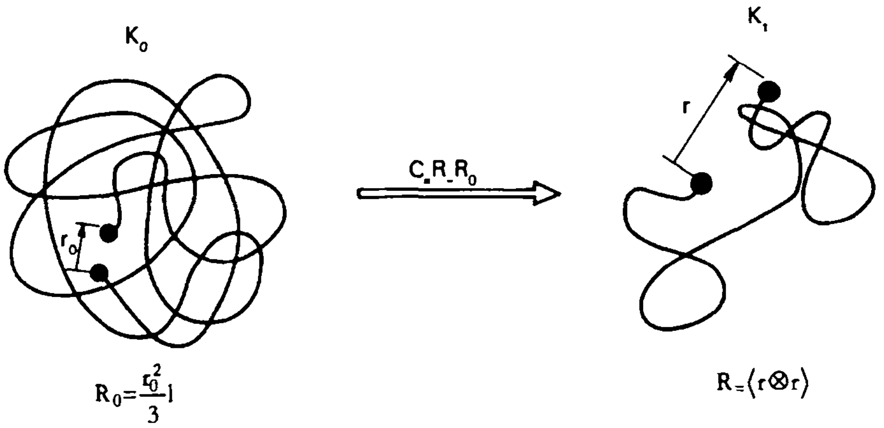

Fig. 6.3. Macromolecular deformation for spherically coiled conformations.

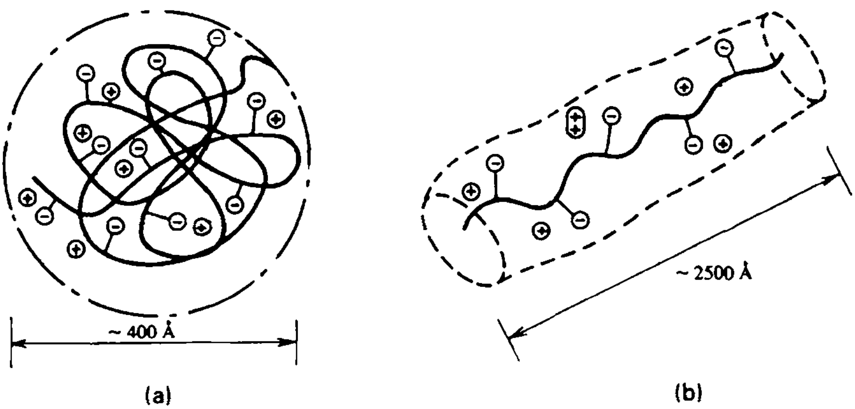

Fig. 6.4. Conformation of polyelectrolytes in solution (a) low pH; (b) high pH (after Drouot and Maugin, 1985).

so that this remains a *statistical concept*, and should not be interpreted as pertaining to any macromolecule in a specific configuration in particular. The average $\langle \ldots \rangle$ is over all possible realizations. We have tr $\mathbf{K} = \langle \mathbf{R}^2 \rangle$, and we can also write

$$\mathbf{K} = \mathbf{K}^d + \frac{1}{3}(\mathrm{tr}\mathbf{K})\mathbf{1}\,, \qquad (6.4.55)$$

where $\mathbf{K}^d$, the deviatoric part of $\mathbf{K}$, is the extensibility-free or shear part of $\mathbf{K}$. Obviously at $\mathcal{K}_0$

$$\langle \mathbf{R}_0 \rangle = \mathbf{0},\ \mathbf{K}_0 = \frac{R_0^2}{3}\mathbf{1}\,. \qquad (6.4.56)$$

The tensor $\bar{\mathbf{K}}$ defined by

$$\bar{\mathbf{K}} = \mathbf{K} - \mathbf{K}_0,\ \mathrm{tr}\,\bar{\mathbf{K}} = \langle R^2 \rangle - R_0^2,\ \bar{\mathbf{K}} \equiv \mathbf{0}\,, \qquad (6.4.57)$$

is a good *relative measure* of the conformation. A *volume-preserving* conformation of macromolecules is such that

$$\mathrm{tr}\,\bar{\mathbf{K}} = 0\,, \qquad (6.4.58)$$

so that only the deviatoric part, $\bar{\mathbf{K}}^d$, of $\bar{\mathbf{K}}$ needs be considered in this case.

For *strongly elongational flows* one is tempted to discard the lateral (with respect to the flow direction) behavior of elongated polymer molecules and to describe its "conformation" by a single vector $\mathbf{n}$ of variable magnitude. This situation appears to be somewhat limiting, considering the above-described situation where we neglect the components of $\mathbf{K}$ orthogonal to $\mathbf{n}$ and thus reduce it to the form

$$\mathbf{K} \cong K_n \mathbf{n} \otimes \mathbf{n}/|\mathbf{n}|^2\,, \qquad (6.4.59)$$

so that, indeed, $\mathbf{K}$ reduces to the knowledge of a direction $\mathbf{n}$ and a magnitude $K_n = \langle (\mathbf{R}\cdot\mathbf{n})^2 \rangle / |\mathbf{n}|^2$. Another way to view this is to consider that in a strongly elongational flow the unit vector $\lambda = \mathbf{n}/|\mathbf{n}|$ is an eigenvector of $\mathbf{K}$ with a corresponding eigenvalue which is much larger than the remaining two ones.

In both cases (i.e. the choice of $\mathbf{K}$ or $\mathbf{n}$), if $L = na$ is the total developed length of the polymeric chain, where n is the number of monomers in the chain and a is the length of a monomer, then $R_0 \cong \sqrt{n}a$. In polyelectrolytes R_0 is of the order of hundreds of angströms at neutral pH, whereas an extended length is rather in the order of 2500 angströms (Fig. 6.4b).

Having identified the *relevant internal variable*, we now pursue the thermodynamic approach independently of any statistical viewpoint (although we are strongly influenced by it). Lhuilier and Ouibrahim (1980) seem to be the first to have considered such an approach which was cast in *T.I.V.* by Maugin and Drouot (1983a). In agreement with the formal developments of Chapter 5, we start with an energy per unit volume $W(\theta, c, \mathbf{K})$, where $\mathbf{K}$ is traceless. We consider a volume-preserving conformation and an incompressible fluid carrier. The *laws of state are given by*

$$S = -\frac{\partial W}{\partial \theta}, \quad \mu = \frac{\partial W}{\partial c}, \quad \mathcal{F} = -\frac{\partial W}{\partial \mathbf{K}}, \tag{6.4.59}$$

where μ is the *chemical potential* of the polymer component and $\mathcal{F}$ is the *microstress*, i.e. the generalized thermodynamic force associated to the internal variable $\alpha = \mathbf{K}$. On the one hand, the scalar-valued function W is rotational invariant (or *objective*), i.e.

$$W(\theta, c, \mathbf{K}) = W(\theta, c, \mathbf{Q}\mathbf{K}\mathbf{Q}^T), \tag{6.4.60}$$

where $\mathbf{Q}$ is an orthogonal transformation. Equivalently, W satisfies the differential constraint (prove this by considering the case of an infinitesimal rotation $\mathbf{Q} = 1 + \epsilon\omega$, where ω is skewsymmetric and ε is an infinitesimally small parameter)

$$\frac{\partial W}{\partial K_{ik}} K_{kj} - \frac{\partial W}{\partial K_{jk}} K_{ki} = 0. \tag{6.4.61}$$

This, or (6.4.60), means that W depends on $\mathbf{K}$ only through its principal invariants. Simultaneously, we must enforce the Clausius–Duhem inequality (6.4.39) on account of (6.4.59), (6.4.61), and (6.4.35). This results in the dissipation inequality

$$\mathrm{tr}\,(\sigma^{ir}\mathbf{D} + \mathcal{F} D_J \mathbf{K}) + \nabla \cdot (\theta \mathbf{k} + \mu \mathbf{J}) - \mathbf{S} \cdot \nabla \theta \geq 0, \tag{6.4.62}$$

where we used the definition (6.3.26) and (6.4.61) while computing the time derivative of W. It is reasonable to select $\mathbf{k}$ in such a way that the divergence term in (6.4.62) disappears altogether. That is,

$$\mathbf{k} = -(\mu/\theta)\mathbf{J}. \tag{6.4.63}$$

We see that the extra-entropy flux is defined in terms of the laws of state and the diffusion flux. This agrees with simple theories of two-component mixtures (e.g. de Groot and Mazur, 1962, p. 24). Consequently, the residual dissipation inequality takes on the form

$$\Phi = \Phi_{\mathrm{intr}} + \Phi_{td} \geq 0, \tag{6.4.64}$$

where the intrinsic and *thermodiffusive* dissipations are given by

$$\begin{aligned}\Phi_{\text{int}} &= \text{tr}\,(\sigma^{ir}\mathbf{D} + \mathcal{F}D_J\mathbf{K})\,,\\ \Phi_{td} &= -(\mathbf{J}\cdot\nabla\mu + \mathbf{S}\cdot\nabla\theta)\,.\end{aligned} \tag{6.4.65}$$

The groupings in these two contributions are physically obvious. The working rules of *T.I.P.* enunciated in Chapter 2 can be applied at once. For instance, on noting that **K** is even while **D** is odd under time reversal, the *a priori* admissible linear isotropic dissipative contributions are given by

$$\begin{aligned}\sigma^{ir} = 2\eta_v\mathbf{D}\,, &\quad D_J\mathbf{K} = k\mathcal{F}\,,\\ \mathbf{J} = -(D\nabla\mu + A\nabla\theta), &\quad \mathbf{S} = -(\chi\nabla\theta + A\nabla\mu)\,,\end{aligned} \tag{6.4.66}$$

with

$$\eta_v \geq 0,\ k \geq 0,\ A^2 \leq \kappa D,\ \kappa \geq 0,\ D \geq 0\,. \tag{6.4.67}$$

Equivalently, we can envisage the existence of a *dissipation potential* $\mathcal{D}(\mathbf{D},\mathcal{F})$ such that

$$\sigma^{ir} = \frac{\partial\mathcal{D}}{\partial\mathbf{D}},\quad D_J\mathbf{K} = \frac{\partial\mathcal{D}}{\partial\mathcal{F}} \text{ or } D_J\mathbf{K} + \frac{\partial\mathcal{D}}{\partial(\partial W/\partial\mathbf{K})} = \mathbf{0}\,. \tag{6.4.68}$$

But there is more than that in (6.4.64), because this inequality does not rule out the occurrence of couplings between σ^{ir} and $D_J\mathbf{K}$, which do not contribute to the dissipation and are obviously no longer derivable from the energy density. These coupling terms that we call σ^G and $\mathcal{K}^G$ may be labeled *gyroscopic* as they correspond to "forces" and "velocities" which are *orthogonal* in the sense that they jointly satisfy the *orthogonality relation*:

$$\Phi_G := \text{tr}(\sigma^G\mathbf{D} + \mathcal{F}\mathcal{K}^G) = 0\,, \tag{6.4.69}$$

where

$$\sigma^G = \bar{\sigma}(\mathbf{D},\mathcal{F};\mathbf{K},\theta,c), \quad \mathcal{K}^G = \bar{\mathcal{K}}(\mathbf{D},\mathcal{F};\mathbf{K},\theta,c) \tag{6.4.70}$$

where the last three arguments — *which in fact define the laws of state* — are *parameters*. It is the presence of **K** in these last three arguments which allows for the existence of interesting couplings between σ and $D_J\mathbf{K}$. Globally then

$$\begin{aligned}\sigma &= -p\mathbf{1} + (\partial\mathcal{D}/\partial\mathbf{D}) + \bar{\sigma}(\mathbf{D},\mathcal{F};\mathbf{K},\theta,c)\,,\\ D_J\mathbf{K} &= (\partial\mathcal{D}/\partial\mathcal{F}) + \bar{\mathcal{K}}(\mathbf{D},\mathcal{F};\mathbf{K},\theta,c)\,.\end{aligned} \tag{6.4.71}$$

Examples of simple contributions (6.4.70), which must necessarily be linear affine jointly in D and $\mathcal{F}$, are given by (Lhuillier and Ouibrahim, 1980)

$$\begin{aligned} \sigma^G &= \lambda\mathcal{F} - \beta(\mathbf{K}\mathcal{F} + \mathcal{F}\mathbf{K}), \\ \mathcal{K}^G &= -\lambda\mathbf{D} + \beta(\mathbf{KD} + \mathbf{DK}), \end{aligned} \tag{6.4.72}$$

where λ and β are scalars which depend at most on θ, c, and the nonvanishing elementary invariants of $\mathbf{K}$. Their sign is not constrained by any thermodynamical inequality such as in (6.4.67), but they are the same coefficients in both contributions, otherwise they would not be consistent with the orthogonality condition (6.4.69).

With $\mathcal{D}$ quadratic in $\mathbf{D}$, we recover the Newtonian contribution $(6.4.66)_1$ to σ, while $(6.4.72)_1$ provides the looked for *non-Newtonian* contribution of which the expression is, as we have seen, intimately related to that of the contribution $\mathcal{K}^G$ to the evolution equation of $\mathbf{K}$. This is a characteristic feature of *T.I.V.* If W is now quadratic in $\mathbf{K}$, i.e. we have some kind of Hookean elasticity, $\mathbf{F}$ will be linear in $\mathbf{K}$ and thus, with $\mathcal{D}$ also quadratic in $\mathcal{F}$, we shall arrive at a first contribution in the right-hand side of $(6.4.71)_2$ of the relaxation type (i.e. linear in $\mathbf{K}$) and a second contribution in the right-hand side of $(6.4.71)_1$ quadratic in $\mathbf{K}$. In this case we will have the following final constitutive quations:

$$\begin{aligned} \sigma &= -p\mathbf{1} + 2\eta_v\mathbf{D} + 2\beta H\mathbf{K}\otimes\mathbf{K}, \\ D_J\mathbf{K} &= -\frac{1}{\tau_K}\mathbf{K} + \beta(K\mathbf{D} + \mathbf{DK}) - \lambda\mathbf{D}, \end{aligned} \tag{6.4.73}$$

which clearly exhibit the dependence of the non-Newtonian stress on the Hookean elasticity H of the polymer solute. The coefficient λ is related to the osmotic pressure of the solution. But the second equation of (6.4.73) can also be rewritten as

$$\mathcal{D}\mathbf{K} = -\frac{1}{\tau_K}\mathbf{K} - \lambda\mathbf{D}, \tag{6.4.74}$$

where $\mathcal{D}$ indicates one of these *objective* time derivatives introduced by (6.3.27), and the unknown coefficient β then plays the same role as the *slip* coefficient in the Gordon–Schowalter derivative (6.3.25). Only experiments or some conditions of existence and stability of solutions can reduce the generality of the coefficient β. It was in fact shown by Lhuillier (1981) that β must lie in the (0,1) interval so that the Taylor stability of such fluids is guaranteed.

The present theory can be made more complex by considering more lengthy expressions instead of (6.4.72) while respecting all stated principles, and considering additional internal variables (of the scalar type to represent an electric charge, a pH, or a strand density in a network). For these we refer the reader to the discussions in Maugin and Drouot (1983a, 1988, 1991). In particular, comparison with Hinch's (1977) model and Eringen's micromorphic fluids (Eringen, 1964), the Kramers–Giesekus stress tensor (cf. Bird *et al.*, 1977), models by Barthes–Biesel and Acrivos (1973), and Hinch and Leal (1976), and the pioneering work of Hand (1962) are found in those review papers. What is particularly striking is the resemblance between (6.4.74) and $(6.4.73)_1$ and the equations obtained by totally different means for a kinematical quantity **F** introduced in the description of emulsions of spherical-like drops, and the corresponding additional (non-Newtonian) stress, as

$$D_J\mathbf{F} = -\frac{1}{\tau}\mathbf{F} + \alpha_1\mathbf{D}, \qquad \sigma_p = 3ns\mathbf{F}^2, \tag{6.4.75}$$

where n is the number of drops per unit volume and τ is related to the surface tension s (cf. Frankel and Acrivos, 1970). Here **F** is a second-order tensor which describes the small deviations of viscous drops from sphericity. Surprisingly enough, the *two* expressions (6.4.75) check our thermodynamic presentation with the appropriate identification. This was noticed by D. Lhuillier. And this probably gave him the idea (Lhuillier, 1988) of approaching the theory of *suspensions* of deformable particles with spherical equilibrium shape along a similar line. A two-phase averaging then imposes a definite relation between critical material coefficients. His final results agree with those of Goddard and Miller (1967) and Barthes-Biesel and Acrivos (1977) from hydrodynamics for dilute suspensions. For concentrated ones, it is shown that a *Maxwell-like* constitutive equation follows for the stress.

D. The internal variable is a vector

If we formally introduce a single vector field **n** to account for the irreversibilities resulting from the inner structure of the fluid, we are tempted to introduce, along with **n**, its spatial gradient $\nabla\mathbf{n}$, because a kind of prevailing directional order may emerge (the tendency of all elongated macromolecules to align parallel in the same direction). This behavior is called *nematogen* after its characteristic appearance in *nematic liquid crystals* (see Sec. 6.7 below). Assume that this ordering is negligible, so that we may consider a free-energy density such as

$$W = W(\theta, c, \mathbf{n}) \text{ or } W = \bar{W}(\theta, c, \mathbf{n}^2 = |\mathbf{n}|^2), \tag{6.4.76}$$

where the last expression follows from the rotational invariance of W. Thus W depends only on the *magnitude* of $\mathbf{n}$. This in turn means that $\mathbf{n}$ plays an essential role in the description of *thermodynamically irreversible processes* by introducing a preferred direction and hence a markedly *anisotropic* behavior which contrasts with Euler's and Newton's fluids. Indeed, with the *laws of state*

$$S = -\frac{\partial \bar{W}}{\partial \theta}, \quad \mathbf{b} = -\frac{\partial \bar{W}}{\partial \mathbf{n}}, \quad \mu = \frac{\partial \bar{W}}{\partial c}, \tag{6.4.77}$$

and (6.4.63) still valid, the first of (6.4.65) is replaced by

$$\Phi_{\text{int}} = \operatorname{tr}\,(\sigma^{ir}\mathbf{D}) + \mathbf{b} \cdot D_J\mathbf{n}, \tag{6.4.78}$$

as is readily checked as

$$(D_J\mathbf{n})_i := \dot{n}_i - \omega_{ij}n_j, \quad \frac{\partial W}{\partial n_i}n_j - \frac{\partial W}{\partial n_j}n_i \equiv 0. \tag{6.4.79}$$

Although $\mathbf{D}$ and $\mathbf{n}$ behave differently under time reversal, there now exists a possible coupling of the dissipative type between σ^{ir} and $D_J\mathbf{n}$ by in reason of $\mathbf{n}$ being a vector field. Neglecting the coupling with heat conduction and diffusion which is now theoretically possible, and assuming that $\mathbf{n}$ and $-\mathbf{n}$ are equivalent (e.g. the two ends of a dumbbell are undistinguishable), the following reduced expressions emerge from the application of *T.I.P.* to the residual dissipation inequality ($\mathbf{d} = \mathbf{n}/|\mathbf{n}|$):

$$\sigma^{ir} = 2\eta_v\mathbf{D} + (\lambda_1 + \lambda_2\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d})\mathbf{n}\otimes\mathbf{n} + 2\lambda_4(\mathbf{d}\cdot\mathbf{D}\otimes\mathbf{n} + \mathbf{n}\otimes\mathbf{D}\cdot\mathbf{d}) \tag{6.4.80}$$

and

$$D_J\mathbf{n} = -(\mu_1 + \mu_2\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d})\mathbf{n} - \mu_3(\mathbf{D}\cdot\mathbf{n}), \tag{6.4.81}$$

where the coefficients λ_1, μ_2 and μ_3 are *not independent.* Note that

$$\tau = \mu_1^{-1}, \qquad \tau' = (\mu_1 + \mu_2\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d})^{-1}, \tag{6.4.82}$$

may be considered as a *relaxation time* (depending on θ and c) and a strain-rate dependent relaxation time. Equations (6.4.80) and (6.4.81) are formally identical with those of an *Ericksen anisotropic fluid* with a *director* $\mathbf{n}$ of variable length as considered by Abhiraman and George (1980) and much earlier by Kaloni (1965) *outside any thermodynamic framework*, so that these authors do not exhibit any relationship between the coefficients intervening in the two equations (6.4.80) and (6.4.81) and their coefficients were not constrained by any thermodynamic inequality. Improvements on these models are described in Maugin and Drouot (1983a). Piau and Doremus (1984) and Cartalos and Piau (1985) practically use such a model for polymeric solutions in strongly elongational regimes. It must be emphasized that kinetic theory may also yield an *evolution equation* of the type (6.4.81) for $\mathbf{n}$ (cf. Olbricht *et al.*, 1982), which can be rewritten in the form

$$D_J\mathbf{n} = G\left(\mathbf{D}\cdot\mathbf{n} - \frac{F}{1+F}(\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d})\mathbf{n}\right) - \frac{\alpha}{1+\alpha}\mathbf{n}, \tag{6.4.83}$$

through an appropriate redefinition of the coefficients. A general equation of the type (6.4.83) where the coefficients G, F and α depend on the properties of the molecules and of the carrier fluid, was obtained for particular axisymmetric models of microstructure (*rigid particles* in Bretherton, 1962; *elastic ellipsoids* in Hinch, 1977; *linear elastic dumbbell* with $G = 1$, $F = 0$ and $\alpha =$ const., in Kuhn and Kuhn, 1945; *linear elastic dumbbell* with F nonzero in Bird *et al.*, 1977). In general $0 < F < \infty$, and practically $G < 1$. (see further remarks in Maugin and Drouot, 1983a, p. 719). In a simple model of fluids carrying *fibers* (Hinch), we have the simple equations [compare to (6.4.80) and (6.4.81)]

$$\begin{aligned}\overset{\nabla}{\mathbf{n}} &:= \dot{\mathbf{n}} - (\mathbf{n}\cdot\nabla)\mathbf{v} - \mathbf{n}(\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d}),\\ \sigma &= -p\mathbf{1} + 2\eta_{\text{sh}}\mathbf{D} + 2\eta_{\text{ext}}\mathbf{d}\otimes\mathbf{d}(\mathbf{d}\cdot\mathbf{D}\cdot\mathbf{d}),\end{aligned} \tag{6.4.84}$$

where η_{sh} and η_{ext} are the viscosities in shear and extension, respectively, the former being typically ten times smaller than the latter. The *aligned* flow solution corresponds to $\mathbf{d} = \mathbf{v}/|\mathbf{v}|$. More on a closely related model below in Sec. 6.7.

E. The internal variable is a scalar

(a) By progressively reducing the tensorial order of our internal variable but still on the basis of the statistical view, it seems that we impoverish the description. For instance, if we consider the scalar product of Eq. (6.4.81) by $\mathbf{n}$ we shall obtain an *equation of evolution* for the squared magnitude of $\mathbf{n}$, i.e.

$$\frac{d}{dt}\mathbf{n}^2 = -\frac{1}{\tau'}\mathbf{n}^2 - 2(\mu_2+\mu_3)(\mathbf{n}\cdot\mathbf{D}\cdot\mathbf{n}), \quad \tau' = 1/2\mu_1. \tag{6.4.85}$$

This equation for the *scalar internal variable* $\mathbf{n}^2$ discards the entangled structure of polymer molecules in the solvent, retaining only the change in length.

Since entanglements play an important role as they would certainly hinder segmental motions, it can be expected that both relaxation time and modulus for a polymer will increase with increasing density of entanglement. If $\langle \mathbf{n}^2 \rangle$ denotes the average overall possible entanglements and $\mathbf{n}$ now represents the directional vector between two successive entanglements in a molecule within a fluid element, then the following simple equation of evolution can be proposed for the structural parameter $\langle \mathbf{n}^2 \rangle$

$$\frac{d}{dt}\langle \mathbf{n}^2 \rangle = \mathcal{H}(\theta, c, D_{II}, \langle \mathbf{n}^2 \rangle)\,, \tag{6.4.86}$$

where $D_{II} = \mathrm{tr}\, \mathbf{D}^2$. A linear approximation to (6.4.86) yields

$$\frac{d}{dt}\langle \mathbf{n}^2 \rangle = \alpha + \beta \langle \mathbf{n}^2 \rangle + \gamma D_{II}\,. \tag{6.4.87}$$

For a fluid at rest $\langle \mathbf{n}^2 \rangle_0 = -\alpha/\beta$ gives the equilibrium entanglement parameter and the quantity $H = \langle \mathbf{n}^2 \rangle - \langle \mathbf{n}^2 \rangle_0$ which measures the deviation from equilibrium value, could obviously be used as a *scalar internal variable*. Ideas similar to those underlying (6.4.86) are contained in several works (e.g. Southern and Porter (1970) — *relaxation time depending on* D_{II} — or Acierno *et al.* (1976, 1977) — *smooth evolution of an equilibrium network density*).

(b) To avoid the above-mentioned impoverishment we may follow the quite remarkable point of view of Grmela and Carreau (1984) by considering the scalar distribution function f of the statistical description as an *internal variable* compared to the hydrodynamical description. This is some kind of *generalized hydrodynamics* which couples two levels of description of physical reality, the sub-level, that of f, being required to satisfy the contraint imposed at the higher level, e.g. the non-negativeness of dissipation, so that a strong feedback is established between the two levels. Indeed, consider that in addition to the classical set of hydrodynamical fields $\{\rho, \mathbf{v}, e\}$ we need the extra field α which should be governed by an *evolution equation*

$$\frac{\partial \alpha}{\partial t} = g\,. \tag{6.4.88}$$

Now paying special attention to the parity of the variables we suppose that: (i) the function g is linear in $\mathbf{L} = (\nabla \mathbf{v})^T$; (ii) α does not depend explicitly on $\mathbf{x}$, (iii) one part of the energy depends only on α, and (iv) α depends on time and an *internal coordinate* $\mathbf{R}$ (e.g. the $\mathbf{R}$ already introduced in the statistical description). At equilibrium the entropy equation has also the form of an evolution equation (no source of entropy) symbolically as

$$\frac{\partial S}{\partial t} = \mathcal{S}. \tag{6.4.89}$$

One then shows that in order that (6.4.89) be a consequence of the field equations (balance of mass, momentum, and energy) and of (6.4.88), it is necessary and sufficient that the stress σ be given by

$$\sigma = \int_{\mathbf{R}} \frac{\delta \Psi}{\delta \alpha} \cdot \frac{\partial g}{\partial \mathbf{L}} d^3R, \tag{6.4.90}$$

where $\delta/\delta\alpha$ denotes Volterra's functional derivative and ψ is the free-energy functional. Obviously, the formalism (6.4.88) reminds us of the *internal-variable* approach. Indeed, consider that α is none other than the *distribution function* f of the statistical approach to polymeric solutions, and $\mathbf{R}$ is the vectorial distance introduced in Fig. 6.2. On account of an affine convection such as (6.18a), Eq. (6.4.88) reads

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{R}} \cdot (\mathbf{L} \cdot \mathbf{R} f), \qquad \int_{\mathbf{R}} f(\mathbf{R}, t) d^3R = n. \tag{6.4.91}$$

Then (6.4.90) delivers the usual formula for stress in the kinetic theory [see Eq. (6.3.31)] with

$$\mathcal{F} = -\frac{\partial W}{\partial \mathbf{R}}, \quad W = \frac{\delta \Psi}{\delta f}, \quad \langle \ldots \rangle = \int_{\mathbf{R}} (\ldots) f d^3R. \tag{6.4.92}$$

One still has to specify the functional form of Ψ. Suppose that Ψ depends on f only through the conformation tensor $\mathbf{K}$. It follows that

$$\frac{\delta \Psi}{\delta f} = -\mathcal{F}_{ij} R_i R_j, \qquad \mathcal{F}_{ij} = -\frac{\partial \Psi}{\partial K_{ij}}. \tag{6.4.93}$$

Multiplying then $(6.4.91)_1$ by $\mathbf{R} \otimes \mathbf{R}$ and taking the average of the result yields

$$\overset{\nabla}{\mathbf{K}} := D_J \mathbf{K} - (\mathbf{K}\mathbf{D} + \mathbf{D}\mathbf{K}) \equiv \mathbf{0}. \tag{6.4.94}$$

That is, *at equilibrium* $\mathbf{K}$ *evolves only by convection with the surrounding fluid.* Carrying then (6.4.93) into (6.4.90) one obtains σ as

$$\sigma = -(\mathcal{F}\mathbf{K} + \mathbf{K}\mathcal{F}), \tag{6.4.95}$$

which is none other than the second contribution (which does not "dissipate") in $(6.4.72)_1$ with $\beta = 1$, in the same way as (6.4.94) is none other than the form taken by (6.4.73) in the *absence* of dissipative processes and gyroscopic coupling with $\mathbf{D}(\lambda = 0)$ but with $\beta = 1$. Thus we have coincidence of the two approaches *at equilibrium*. For related dissipative processes we refer to subsequent works by Grmela and co-workers (in particular, Grmela, 1986, Grmela and Carreau, 1982, 1987).

The last approach mentioned presents the challenge of closing a theory with ingredients of microscopic origin by imposing a thermodynamic compatibility (at equilibrium in the above-illustrated case). This extremely promising aspect is discussed at length by Grmela (1990, 1995) who is the most active contributor to this trend.

F. Forced thermodynamic systems

The flow of the fluid surrounding macromolecules in a solution of polymer belongs to the global thermodynamic system and this is reflected in the expression of the intrinsic dissipation, e.g. $(6.65)_1$, where both $\mathbf{D}$ and $\mathcal{F}$ contribute to an equal extent to the dissipation. However, while studying the evolution of conformation and the stability of the conformations which are allowed by the expression of the energy W, one is led to envision this flow (or some other field such an an electric one) as some *forcing* on a system built of deformable macromolecules only. In particular, if the *dissipation potential* $\mathcal{D}$ in (6.4.71) is homogeneous of degree two while $\bar{\mathcal{K}}$ in $(6.4.71)_2$ is necessarily homogeneous of degree *one* in both $\mathbf{D}$ and $\mathcal{F}$, then Eqs. $(6.4.71)_2$ can formally be rewritten as

$$D_J\mathbf{K} = \frac{\partial \hat{\mathcal{D}}}{\partial \mathcal{F}}, \quad \hat{\mathcal{D}} := \mathcal{D}(\mathbf{D}, \mathcal{F}) - \mathrm{tr}(\mathbf{M}\mathcal{F}), \tag{6.4.96}$$

where $\mathbf{M}(\mathbf{D})$ is a tensor to be determined. In the case of pure shear of conformations and on account of the special expression (6.4.72) and with $\partial\mathcal{D}/\partial\mathcal{F} = -\zeta\mathcal{F}$ (quadratic approximation), Eq. $(6.4.96)_1$ can be rewritten as

$$D_J\mathbf{K} = \zeta\frac{\partial \hat{W}}{\partial \mathbf{K}}, \tag{6.4.97}$$

where $\hat{W}$ is the following *modified* free energy

$$\hat{W}(\theta, c, \mathbf{K}; \mathbf{D}) = W(\theta, c, \mathbf{K}) - \mathrm{tr}\,[\mathbf{Z}\cdot(\tau\mathbf{D})], \tag{6.4.98}$$

where τ is a characteristic time, and the *stress tensor* $\mathbf{Z}$ depends essentially on $\mathbf{K}$. With W quadratic in $\mathbf{K}$, $\mathbf{Z}$ is itself of second degree in $\mathbf{K}$. Equation (6.4.97) allows one to study the *isotropic-anisotropic conformational transtion induced by a flow* and the modified energy (6.4.98) plays the same role as the modified free energy of Landau in phase-transition theory where, for a ferroelastic solid,

$$\hat{W}(\theta, \varepsilon; \sigma) = W(\theta, \varepsilon) - \operatorname{tr}\,(\sigma\varepsilon)\,, \tag{6.4.99}$$

where σ is an *applied* stress (see Drouot and Maugin, 1988b).

6.5. Diffusion and Migration

The phenomenon of *diffusion* describes the relative translational motion between two species in a mixture. In the case of polymer solutions this is represented by the diffusion-flux vector

$$\mathbf{J} = \rho c(\mathbf{v}_p - \mathbf{v})\,, \tag{6.5.100}$$

where $\mathbf{v}_p$ is the velocity field of the center of mass of the polymer molecule. In a phenomenological theory a constitutive equation is given for $\mathbf{J}$, i.e. for the left-hand side of Eq. (6.5.100) — see, for instance, $(6.4.66)_2$. Apart from a possible anisotropic generalization, $(6.4.66)_2$ simply describes diffusion in terms of the gradient of the chemical potential and no fluid kinematics or macromolecule deformability is involved in such a simple equation. There is, however, strong interest in specific diffusion phenomena in non-homogeneous velocity gradient fields, and these phenomena have been put forward to explain a wall effect in laminar flows of polymeric fluids (Tirrell and Malone, 1977; Drouot and Maugin, 1983). Interest has also focused on the *molecular migration* in such velocity fields. It seems that macromolecules in a nonhomogeneous flow tend to minimize their configurational entropy by migrating toward less nonhomogeneous flow regions, thus escaping the more highly oriented configurations induced by higher velocity gradients. Aubert and Tirrell (1980) have shown that the bead-spring theory (see Bird *et al.*, 1977) for dilute solutions of polymers predicts a diffusion of macromolecules for nonhomogeneous flows. At the bottom of their mathematical model is a force — and then a diffusion flux — proportional to the second gradient $\nabla\nabla\mathbf{v}_L$ of the velocity $\mathbf{v}_L$ of the liquid solvent. Subsequent refinements were presented by Brunn (1983) by modeling macromolecules as nonlinear elastic dumbbells. But here also, while microscopic theories are fruitful for pointing out new mechanisms or more detailed mimics, macroscopic theories have the advantage of a simpler and more compact scheme. Furthermore, as a recurrent theme, a macroscopic theory allows the framing of the scheme within a *thermodynamic context*, which results in a selection of physically admissible phenomena.

A macroscopic thermodynamic investigation of *polymer diffusion* in nonhomogeneous flows was developed by Drouot and Maugin (1983) by modeling the polymer solution with a *vectorial* internal variable (see Paragraph 6.4D). They also allowed the constitutive properties of the solution to be described by second-order velocity gradients (a second-order gradient theory in the sense of Chapter 2). They deduced a *cross-streamline* migration effect. They showed that, accordingly, a second-gradient model deprived of the internal variable is inadequate for a satisfactory account of polymer diffusion. More recently, Morro *et al.* (1990) have set up a more refined scheme where the polymer solution is modeled as a *binary mixture.* Essentially, the macromolecules constitute the dispersed phase (with properties indexed by d) while the solvent is a classical liquid (index L). Then the internal variable, a tensor $\mathbf{K}$ such as a *conformation*, is ascribed to the dispersed phase and the second-order velocity gradient to the liquid. Without entering into details, it is worth mentioning the main thermodynamical equations of this modeling. The mixture is assumed to consist of *non*-reacting constituents, each one assumed incompressible for simplicity (but the mixture as a whole is compressible). Then neglecting heat conduction, the reduced *dissipation inequality* is shown to read

$$\Phi = \operatorname{tr}\,(\sigma_L \mathbf{D}_L + \mathcal{F} D_J \mathbf{K}) + \mathbf{m}\cdot(\mathbf{v}_L - \mathbf{v}_d) + \mathbf{c}_L \cdot (\Omega_L - \Omega_d) \geq 0\,, \quad (6.5.101)$$

where Ω_L and Ω_d are vorticity vectors related to liquid and dispersed phases, and $\mathbf{m}$ and $\mathbf{c}_L$ are the exchanges of linear and angular momenta between phases. In this modeling the extra flux of entropy $\mathbf{k}$ is given by [compare to (6.4.63)]

$$\mathbf{k} = \Lambda(\mathbf{v}_d - \mathbf{v}_L)\,, \quad (6.5.102)$$

where Λ is an arbitrary function of time which contributes terms $\Lambda\theta$ and $-\Lambda\theta$ to the partial pressures p_d and p_L of the constituents. In (6.5.101) the dissipative mechanisms are described by the fields $\mathbf{m}$, $\mathbf{c}_L$, $\mathbf{D}_L$ and $\mathcal{F}$ (as these vanish at thermodynamic equilibrium). Then thermodynamic schemes for modeling diffusion fluxes proportional to $(\mathbf{K} : \nabla\nabla)\mathbf{v}_L$ can be elaborated, which satisfy the dissipation inequality (6.5.101). The exploitation of the latter shows that a $\nabla\nabla\mathbf{v}_L$-depedent model can produce coupled dissipative constitutive equations of the following type (Morro *et al.*, 1990; the energy is assumed to be quadratic in $\mathbf{K}$)

$$\begin{aligned} D_J\mathbf{K} &= \kappa_1\bar{\delta}\mathbf{K} + \kappa_2\mathbf{D}_L - \alpha(\nabla\nabla\mathbf{v}_L)\cdot\mathbf{m} + \cdots \\ \mathbf{v}_L - \mathbf{v}_d &= \nu_1\mathbf{m} + \alpha\bar{\delta}(\mathbf{K} : \nabla\nabla)\mathbf{v}_L + \tau(\mathbf{D}_L : \nabla\nabla)\mathbf{v}_L + \cdots \\ \sigma_L &= 2\eta_v\mathbf{D}_L - \kappa_2\bar{\delta}\mathbf{K} - \tau(\nabla\nabla\mathbf{v}_L)\cdot\mathbf{m} + \cdots , \end{aligned} \tag{6.5.103}$$

where κ_1, κ_2, ν_1, η_v, τ, α, and $\bar{\delta}$ are macroscopic material coefficients constrained by thermodynamical inequalities. The second of Eqs. (6.5.103) contains the looked for phenomenon. This must be compared to the results of other works. For instance Lhuillier (1983), by using a classical theory of mixtures, arrives at an expression for the relative acceleration containing terms which, in the present notation, read $\mathrm{div}(\mathcal{F}\mathbf{K} + \mathbf{K}\mathcal{F})$ and $\mathrm{div}\,\sigma_L$. So he provides an expression for the force that causes migration via the divergence of the stress, and then through a scheme conceptually akin to the one above, but without introducing a $\nabla\nabla\mathbf{v}_L$-dependence. An analogous procedure was developed by Sehkon *et al.* (1982). The procedure of Tirrell and Malone (1977), although essentially microscopic in character and without thermodynamic analysis, resembles more closely the above presented $\nabla\nabla\mathbf{v}_L$-dependent model.

6.6. Vorticity and Conformation

With their generally entangled conformations macromolecules should be prone to being strongly influenced by *vortices*, if the latter are of a length-scale that matches the macromolecules. With this coupling phenomenon in view, we may ask for the thermodynamical admissibility of such couplings, if any. To that purpose it is convenient (Maugin and Drouot, 1991) to imagine that the field of vortices is described *a priori* by a field of axial vector $\bar{\omega}$, an *intrinsic spin*, which is not related to the rate-of-rotation or vorticity tensor Ω, of the $\mathbf{v}$-flow. Through rotational invariance, one is led to introduce a *relative spin density* $\omega = \bar{\omega} - \Omega$, where $\Omega = (\nabla \times \mathbf{v})/2$. This relative spin measures the deviation of intrinsic spin from the local vorticity. With neglect of heat conduction and with an energy-density $W = \bar{W}(\theta, \mathbf{K}, \mathbf{D}, \omega)$, one can deduce a *reduced dissipation inequality* in the following form:

$$\Phi = \mathrm{tr}\,(\bar{\sigma}\mathbf{A}^{(1)} + \mathbf{B}\mathbf{A}^{(2)} + \mathcal{F}D_c\mathbf{K}) + \mathbf{A}\cdot D_c\omega \geq 0\,, \tag{6.6.104}$$

where we have set

$$\bar{\sigma} := \sigma + (\mathbf{A} \otimes \omega)_s + (\mathcal{F}\mathbf{K} + \mathbf{K}\mathcal{F}) + (\mathbf{BD} + \mathbf{DB}), \tag{6.6.105}$$

and

$$\begin{aligned} \mathbf{A}^{(1)} &\equiv \mathbf{D}, \\ \mathbf{A}^{(2)} &:= \dot{D} - (\nabla\mathbf{v} \cdot \mathbf{D} + \mathbf{D} \cdot \nabla\mathbf{v}), \\ D_c\omega &:= \dot{\omega} - (\nabla\mathbf{v}) \cdot \omega, \\ D_c\mathbf{K} &:= \dot{\mathbf{K}} - (\nabla\mathbf{v} \cdot \mathbf{K} + \mathbf{K} \cdot \nabla\mathbf{v}) \equiv \overset{\nabla}{\mathbf{K}}, \end{aligned} \tag{6.6.106}$$

and

$$\mathcal{F} = -\frac{\partial W}{\partial \mathbf{K}}, \qquad \mathbf{A} = -\frac{\partial W}{\partial \omega}, \qquad \mathbf{B} = -\frac{\partial W}{\partial \mathbf{D}}. \tag{6.6.107}$$

Here, convected-time derivatives — cf. (6.3.24) — naturally appear instead of Jaumann derivatives. The kinematic tensors $\mathbf{A}^{(i)}$, $i = 1, 2$, are the first two Rivlin–Ericksen tensors. The introduction of the new stress tensor $\bar{\sigma}$ shows that the stress will in general contain *non-Newtonian* contributions involving both the elasticity of polymeric chains through $\mathcal{F}$ and $\mathbf{B}$ and also a contribution due to the intrinsic spin which is not ruled out by time-symmetry conditions. At *thermodynamic equilibrium*, among other constraints we shall have

$$D_c\omega = \mathbf{0}. \tag{6.6.108}$$

If $\bar{\omega} = \Omega$ initially, then this property is conserved by convection according to (6.6.108). This is the essence of *Helmholtz's theorem* in perfect fluids. *Outside equilibrium*, the dissipation inequality (6.6.104), which still is of the classical *bilinear* form although containing a significant number of terms, can be exploited as in previous cases. In particular, *evolution* equations can be obtained for both $\mathbf{K}$ and ω. These two will couple, resulting for instance in *dissipative constitutive equations* of the general type (Maugin and Drouot, 1991):

$$\begin{aligned} \sigma &= \mathcal{N}(\mathbf{K}, \omega) \cdot \mathbf{D} + \hat{\sigma}(\mathbf{K}, \omega), \\ D_c\omega &= -\mathbf{T}_\omega^{-1}(\mathbf{D}, \mathbf{K}, \mathbf{w}) \cdot \omega, \\ D_c\mathbf{K} &= -\mathbf{T}_K^{-1}(\mathbf{D}, \mathbf{K}, \omega) : \mathbf{K} + \kappa_2\mathbf{D} + \hat{\mathcal{K}}(\mathbf{D}, \omega), \end{aligned} \tag{6.6.109}$$

where $\mathcal{N}$ and $\mathbf{T}_K^{-1}$ are fourth-order tensors and $\hat{\sigma}$, $\mathbf{T}_\omega^{-1}$, and $\hat{\mathbf{K}}$ are second-order tensors of which the last one is homogeneous of degree two in ω. The latter dependence and that of $\mathbf{T}_{\omega}^{-1}$ on $\mathbf{K}$ are the sought couplings between conformational behavior and the intrinsic spin evolution. Satisfaction of (6.6.104) imposes the restriction that the coefficients present in Eqs. (6.6.109) cannot all be independent. The modeling sketched out above can be further refined by introducing a *weakly nonlocal* behavior assuming that the energy density depends on the additional gradients $\nabla\nabla\mathbf{v}$, $\nabla\mathbf{K}$ and $\nabla\omega$. We shall not pursue further the arcanes of these technicalities.

6.7. Liquid Crystals

Liquid crystals are obviously *complex fluids* as (i) according to their very name they are similar to fluids as they can flow, and to crystals as they show a tendency towards some *ordering*, and (ii) *physically* they are solutions of macromolecules in a solvent. Concerning the last aspect, there seem to be three large classes of *liquid crystals* known as *nematic, smectic* and *cholesteric* liquid crystals (we refer the reader to de Gennes, 1974 for the essential properties of such materials; see Fig. 6.5). We shall focus particularly on *nematics* because the latter admit a thermodynamic description which closely resembles that already given for polymeric solutions. The natural tendency of a bunch of "particles" in liquid crystals is to agglomerate in more or less aligned groupings so as to minimize energy. Thus these materials present a prevailing order which may be described adequately by a vector field of *directions*, called *director*, $\mathbf{n}$.

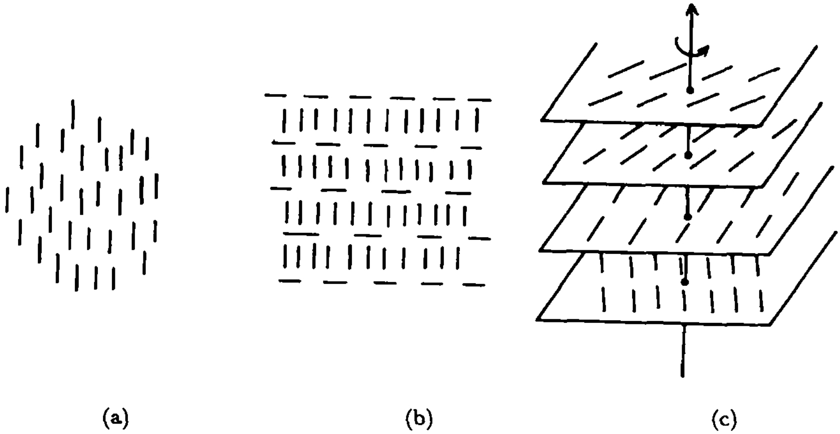

Fig. 6.5. The three large classes of liquid crystals: (a) nematic, (b) smectic, (c) cholesteric.

This type of description goes back to F. C. Frank, Oseen and J. L. Ericksen, and was further developed by Leslie (1968) using a standard thermodynamic formalism, that is, assuming that **n** is a new *vectorial degree of freedom*, requiring thus an additional *balance equation*. If the inertia is negligible in that equation (this is usually the case), then **n** can be considered as an *internal variable*. But the ordering already mentioned requires accounting for the gradient, $\nabla\mathbf{n}$, of **n**, as the "*elasticity*" of the liquid crystal can in fact be measured only by this quantity (as usually $|\mathbf{n}|^2 = \text{const.} = 1$ by normalization). Thus we are in the framework delineated in Paragraph 4.7B that we can apply directly (Maugin, 1990). That is, the dissipation is given by (this has to be exploited following *T.I.P.*)

$$\Phi = \operatorname{tr}(\bar{\sigma}\mathbf{D}) + \mathcal{A}\cdot D_J\mathbf{n} - (\mathbf{S}\cdot\nabla)\theta \geq 0\,, \tag{6.7.110}$$

where

$$\begin{aligned} \bar{\sigma}_{ij} &:= \sigma_{ij} + p\delta_{ij} + B_{(ik}n_{k,j)}\,, \\ k_i &= \theta^{-1}B_{iq}(D_J\mathbf{n})_q\,, \end{aligned} \tag{6.7.111}$$

and

$$\begin{gathered} W = W(\theta, \mathbf{n}, \nabla\mathbf{n}), \qquad S = -\frac{\partial W}{\partial\theta}\,, \\ \mathcal{A}_i = -\frac{\delta W}{\delta n_i} = -\left(\frac{\partial W}{\partial n_i} - \frac{\partial}{\partial x_j}\left(\frac{\partial W}{\partial(n_{i,j})}\right)\right), \qquad B_{ij} = -\frac{\partial W}{\partial n_{i,j}}\,, \end{gathered} \tag{6.7.112}$$

and the energy W satisfies the rotational invariance:

$$\frac{\partial W}{\partial n_{[i}}n_{j]} + \frac{\partial W}{\partial n_{p,k}}\delta_{p[i}n_{j],k} + \frac{\partial W}{\partial n_{k,[i}}\delta_{j]p}n_{k,p} = 0\,. \tag{6.7.113}$$

This last property has been used in computing the time derivative of W and introducing the Jaumann derivative $D_J\mathbf{n}$. The first of (6.7.111) means that liquid crystals do not obey *Euler's hydrodynamics* at rest unless the distribution of **n**'s is spatially uniform. As a matter of fact it is not difficult to recognize in the above-formulated set the equations that govern the thermodynamics of *nematic liquid crystals* (e.g. Müller, 1985, de Gennes, 1974, Kats and Lebedev, 1988), where W is Frank's energy density, the director's inertia is neglected, and $D_J\mathbf{n}$ is written as a linear affine function of $\mathcal{A}$ [by application of *T.I.P.* to the inequality (6.7.110)], thus providing an evolution-diffusion equation for the internal variable **n**. The evolution-diffusion equation (equation of motion) for the fluid velocity $\mathbf{v}$ will be highly nonlinear in $\mathbf{n}$ as $\bar{\sigma}$ depends on $\mathcal{A}$. The extra entropy flux $\mathbf{k}$ in $(6.7.111)_2$ agrees with that obtained by Kats and Lebedev [1988, p. 23, Eq. (16)] once $D_J\mathbf{n}$ is taken linear in $\mathbf{n}$.

The many analogies between the continuum thermodynamic theory of nematics and that of strongly anisotropic fluids and fluid suspensions of fibers as sketched in Paragraph 6.4D above are obvious.

But this is not all, as liquid crystals are also subjected to *phase transitions*, in particular from a high-temperature *isotropic phase* to a *nematic phase* (there are other types of transition and other phases which are not our concern here). The relevant *order parameter* is the second moment of $\mathbf{n}$ or, rather, its deviatoric part:

$$\mathbb{Q} := \left\langle \mathbf{n} \otimes \mathbf{n} - \frac{1}{3}\mathbf{1} \right\rangle, \qquad \operatorname{tr} \mathbb{Q} \equiv 0 . \tag{6.7.114}$$

Then the phase-transition theory of such liquid crystals is to be based on a free-energy density $W = W(\theta, \mathbb{Q}, \nabla\mathbb{Q})$ and this looks very much like a *T.I.V.*, with spatial gradients of the tensorial internal variable $\mathbb{Q}$ for which we have the general framework of Paragraph 4.7B on account of the additional remarks made in Sec. 4.8. In particular, a relaxation equation of the type (4.8.62) will follow, but as $\mathbb{Q}$ is essentially of the same nature as a trace-free conformation $\mathbf{K}$, we may also have gyroscopic couplings of the type mentioned in Paragraph 6.3B. Pioneering works along that line are found in de Gennes (1971). Anisotropic optical properties, e.g. the Kerr effect (cf. Maugin, 1988, p. 46), of these nematic solutions are governed essentially by $\mathbb{Q}$ since $\mathbb{Q}$ and the optical tensors are proportional. This has direct applications in optical investigations of liquid crystals, e.g. optical-field induced ordering (Prost and Lalannes, 1973; Drouot and Maugin, 1985). The theory of liquid crystals presented by H. Hess, W. Muschik and their co-workers in a series of work in the 1990s (e.g. Blenk and Muschik, 1991; Blenk *et al.*, 1991) makes use of an *alignment tensor* which belongs to the same class as $\mathbb{Q}$ or $\mathbf{K}$. But the typically *nematogen* behavior can also be reproduced by considering directly the *distribution function* f as a *scalar internal variable* and then accounting for the Lifshitz or Onsager entropy term (see Grmela and Chlon Ly, 1987). In general, with or without additional gradient, liquid crystals easily enter the thermodynamic framework of *T.I.V.* by a careful selection of a meaningful variable which may be either a scalar, a vector, or a second-order tensor.

6.8. Structurally Complex Flows

We should not, obviously, mistake a structurally complex fluid, whose complexity results from the multicomponent feature of the fluid and *structurally complex flows* such as those which arises in *turbulence* in more or less definite conditions of velocity, velocity gradient, and "size" of the flow (in fact depending on the value of a nondimensional number called the *Reynolds* number which compares the viscous and kinetic energies). We acknowledge that the manisfestations of turbulence are related to combined effects of *nonlinearity* (through convection) and *dissipation* in an apparently *noncomplex fluid*, although additives in a fluid may have a strong influence on turbulence, e.g. drag reduction effects by polymeric additives. These manifestations of turbulence are sometimes modeled by the (relatively) simple *Burgers* equation (*convection* and *simple shear viscosity*). However, even fruitful contributors to the theory of statistical turbulence such as Rotta (1951) or Lumley (1979) presented some views on turbulence that amount to trying to characterize some aspects of turbulence (e.g. return to isotropy) by means of *constitutive equations.* This is an original view which does not receive general agreement in the "turbulence" community. The author (Maugin, 1981c) has made a proposal in that direction by noting that a working regime which, experimentally, exhibits *time* and *space* scales, may be described by thermodynamically constrained generalized constitutive equations that rely on the consideration of *internal variables.* Indeed, far from boundaries, the development of *Reynolds'* stresses in homogeneous flows may be described by *tensorial* internal variables. *Two* of these are necessary in order to account simultaneously for a characteristic time τ and a characteristic length λ (or a characteristic velocity $q = \lambda/\tau$). For instance, if $\mathbf{u}$ is the fluctuation velocity about the mean flow velocity $\mathbf{v}$, we may introduce a "deformation measure" of Reynolds stresses, $\mathbf{R}$ (this is a second-order tensor which measures velocity correlations), and a "deformation measure" of the energy related to fluctuation-velocity gradients by ($\langle\ldots\rangle$ indicates an ensemble average)

$$\begin{aligned} \mathbf{R} &= q^{-2}\langle \mathbf{u} \otimes \mathbf{u} \rangle = \mathbf{R}^T , \\ \mathbf{U} &= (\lambda/q)^2 \langle \nabla\mathbf{u} \otimes (\nabla\mathbf{u})^T \rangle = \mathbf{U}^T . \end{aligned} \qquad (6.8.115)$$

In the spirit of *T.I.V.* the free energy per unit volume volume of the incompressible fluid defines new thermodynamic forces (tensors) $\mathbf{H}$ and $\mathbf{M}$ by

$$\mathbf{H} = -\frac{\partial W}{\partial \mathbf{R}} = \mathbf{H}^T, \qquad \mathbf{M} = -\frac{\partial W}{\partial \mathbf{U}} = \mathbf{M}^T, \tag{6.8.116}$$

and the evolution equations for **R** and **U** are to be looked for in the form ($\mathcal{D}$ here stands for an *objective* time derivative)

$$\mathcal{D}\mathbf{R} = \mathcal{R}(\mathbf{R}, \mathbf{U}; \mathbf{D}), \qquad \mathcal{D}\mathbf{U} = \mathcal{U}(\mathbf{R}, \mathbf{U}; \mathbf{D}), \tag{6.8.117}$$

where **D** is the strain-rate tensor of the mean flow, and there remains the dissipation inequality

$$\Phi_{\text{int}} = \text{tr}\ (\sigma^D \mathbf{D} + \mathbf{H}\mathcal{R} + \mathcal{M}\mathcal{U}) \geq 0\,. \tag{6.8.118}$$

Possible expressions for σ^D and $\mathcal{D}\mathbf{R}$ are (many couplings may be envisaged)

$$\begin{aligned} \sigma^D &= 2\eta_V \mathbf{D} + \gamma \mathbf{R} + \delta \mathbf{U} + \cdots\,, \qquad \gamma = q^2 > 0\,, \\ \mathcal{D}\mathbf{R} &= -\frac{1}{\tau}(\mathbf{R} - \mathbf{R}_0) + \zeta(\text{tr}\mathbf{U})\mathbf{1} + \cdots\,, \qquad \mathbf{R}_0 = \frac{1}{3}\mathbf{1}\,, \end{aligned} \tag{6.8.119}$$

where τ is the time constant associated with return to isotropy. Here no problem of *closure* — *the* problem of turbulence — arises as the closure is given by a constitutive assumption (see, e.g. Favre *et al.*, 1979, for such closures). The above, however, is worth only as a sketchy example.

6.9. Conclusions

To conclude this chapter on *fluid viscosity*, we should also mention that in a spirit combining the idea of *internal variables* (e.g. the conformation **K** of polymeric solutions or the order parameter **Q** of liquid crystals), avoiding the introduction of gradients, but applying a reasoning close to that of *extended thermodynamics* (i.e. assuming that the so-called internal variable has to satisfy an *evolution*-diffusion *equation*, which requires a closure hypothesis to formulate the flux present in that equation), we refer to the works of Hess and Pardowitz (1981), Hess (1986), Hess and Koo (1989), and Drouot and Berrajaa (1993). We refer the reader to these authors for this fruitful line of approach which allows one to consider anew the effect of "apparent slip" at a solid boundary, but also presents the difficulty of having to solve spatially partial differential equations for the components of **K**, which can be achieved only in very simple situations and with stationariness of the flow (e.g., steady shear flow).

More complicated schemes introducing several internal variables find their justification in some fluid solutions such as so-called *magnetic fluids* which in fact are colloidal suspensions of magnetic particles.[3] Rather than forming ellipsoidal *blobs*, the magnetic particles suspended in the magnetic fluid may show a tendency to form *chains* and *needle-like aggregates* in a magnetic field. Such a situation can be tackled by making an astute choice of *internal variables*. Following Kiriushin (1983), we consider the *average relative* stretch of forming chains

$$\varepsilon = \frac{l - l_0}{l_0}, \tag{6.9.120}$$

and a *unit orientation* vector $\mathbf{n}$ in the direction of microscopic chains of equilibrium length l_0 as internal variables. This locally defined direction $\mathbf{n}$ plays an important role by endowing the fluid with *directional properties*, not unlike the director field in liquid crystals. We note that $1 + \varepsilon = (l/l_0)$. Thus we consider an energy $W = \bar{W}(\theta, \varepsilon, \mathbf{n})$ and define the following *objective* (convected) time derivatives:

$$\begin{aligned} \overset{*}{\mathbf{n}} &:= \dot{\mathbf{n}} - (\mathbf{n} \cdot \nabla)\mathbf{v} + \mathbf{n}(\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{n}) = \overset{\nabla}{\mathbf{n}} + \mathbf{n}(\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{n}), \\ \overset{*}{\varepsilon} &= \dot{\varepsilon} - (l/l_0)(\mathbf{n} \cdot \mathbf{D} \cdot \mathbf{n}). \end{aligned} \tag{6.9.121}$$

The *intrinsic dissipation* will read

$$\Phi_{\text{intr}} = \operatorname{tr}(\bar{\sigma}\mathbf{D}) + \mathcal{T} \cdot \overset{*}{\mathbf{n}} + \mathcal{E}\overset{*}{\varepsilon}, \tag{6.9.122}$$

wherein

$$\begin{aligned} \bar{\sigma}_{ij} &= \sigma^D_{ij} + \mathcal{T}_{(i}n_{j)} + [\mathcal{E}(1 + \varepsilon) - \mathcal{T} \cdot \mathbf{n}]n_i n_j, \\ \mathcal{T}_i &= -\partial\bar{W}/\partial n_i, \qquad \mathcal{E} = -\partial\bar{W}/\partial\varepsilon. \end{aligned} \tag{6.9.123}$$

As in previous examples, application of *T.I.P.* to the separate dissipation inequality $\Phi_{\text{intr}} \geq 0$ will yield a constitutive equation for $\bar{\sigma}$, and hence also for σ^D through the first part of (6.9.123) once $\bar{W}$ is prescribed, and relaxation equations for $\mathbf{n}$ and ε. The present model is a formalization (Maugin, 1993b) of the one briefly sketched out by Kiriushin (1983).

The study *of fluid viscosity* would not be complete without mentioning the phenomenon of *superfluidity* which manifests itself through a complete lack of viscosity in certain circumstances. This has also been approached in a

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[3] Sometimes these fluids are also called "ferrofluids" but this is also a trademark (Ferrofluidic Corporation, USA).

continuum framework which is none other than *T.I.V.* In that case the relevant internal variable is a *kinetic quantity*, in fact an *internal linear momentum* which relates to the relative motion of normal and superfluid components in the two-fluid description of superfluidity. Its evolution equation, coupled to the usual flow equation and the stress constitutive equation, is an internal equation of *motion*; but it is still constrained by the second law of thermodynamics. This appears to be one of the most satisfactory continuum theories of superfluid helium (see Lhuillier *et al.*, 1975).

Chapter 7

VISCOPLASTICITY AND PLASTICITY

7.1. Introductory Remarks

Thermodynamics of *solids* began with George Green (1793–1841)[1] when he introduced the *conservative* behavior of finite-strain elasticity through an *energy function* or *potential*. This line of thought was taken over by some scientists such as G. Piola in Italy, W. Thomson (Lord Kelvin) in England, Kirchhoff and later Voigt in Germany, and Boussinesq and the Cosserat brothers in France, but we had to wait for P. Duhem's *Hydrodynamics, Elasticity and Acoustics* (1891) and the last part of his *Treatise on Energetics* (1911) before we were able to see these thermodynamic notions, including that of free energy, taken into account in discussions on *stability*.[2] The subject seems to have more or less laid dormant until a revival of thermodynamics in *solids*, essentially through Eckart's (1940, 1948) works and some of P. G. Bridgman's (1943, 1950, 1953) deeply thought remarks, brought *irreversibility* into the picture. P. Duhem has thought about this, but often in vain (see Manville, 1927). Then A. C. Eringen (1960), G. A. Kluitenberg (1962a,b; 1963), and

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[1] G. Green is an interesting scientific figure who, in addition to being one of the creators of potential theory and vectorial analysis, presents two original traits. Firstly, practically self-educated in mathematics and a miller by profession, he first did *creative research* and then went to Cambridge as a *student* only to practically leave that world just after graduating; Second, he had seven children (whom he recognized in his will) from the same woman whom he never officially married, being apparently a confirmed bachelor. But these were pre-Victorian times! (information provided by L. J. Challis and A. J. M. Spencer, Nottingham). Whether these anecdotal facts have any bearing on thermodynamics is left to the reader's judgment.

[2] This was revisited by modern authors (see Ericksen, 1991).

Kestin (1966) were instrumental in bringing the complex behaviors of solids into contact with thermodynamics. To proceed further, however, more mathematics was needed, especially in the province of *convex analysis*. This was achieved rather recently with the works of H. Ziegler (1957 to 1970), the mathematical analysis of J.-J. Moreau (1971), and the more physical insight mixed with applied mathematics of J. Mandel (1965), P. Perzyna (1966, 1971, 1974, 1978), Nguyen Quoc Son (1973), and others (P. Germain 1973; P. Suquet, 1984; Germain *et al.*, 1983).

This chapter will present only a few essential elements on the thermomechanics of *solid-like* behavior. The reason for this is that recent textbooks and treatises develop that theme at length in a spirit that fits the present book, so we leave it out to avoid duplication.[3]

7.2. Viscoelasticity of Solids

Apart from the *rational-thermodynamics* approach due to Coleman and Noll (1961), the thermodynamics of the *viscoelasticity* of solids finds its roots in works by Eckart, Kluitenberg, and others. Rheological models, exemplified in Fig. 4.1, have played a crucial role in this development, see, e.g. Reiner (1960) and Vyalov (1986) for an extensive use of these models without thermodynamic framework, and Mandel (1965) for one of the first clear relationships with thermodynamics. The most elementary models are those of Kelvin–Voigt (viscous and elastic elements in parallel) and Maxwell (viscous and elastic elements in series — Fig. 4.1) for linear behaviors. Whereas the former is, like Newtonian viscosity in fluids, derivable in the classical *T.I.P.* framework without internal variables (see Paragraph 3.2D) and is *not* a very good model of solid viscoelasticity, the latter is a good one but is reputedly not amenable through a thermodynamical analysis. This last statement is *not* true as the *thermodynamic with internal variables* accommodates the formulation of Maxwell's model and, therefore, of the so-called *standard model of rheology* (cf. Maugin, 1992a, pp. 42, 43). To prove this we consider the framework of *small strains* and the intrinsic dissipation $(5.6.46)_2$ for which

$$\varepsilon^p = 0\,, \qquad \sigma^v = 0\,, \qquad \alpha = \{\varepsilon^v\}\,, \tag{7.2.1}$$

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[3] These books include Mandel (1971), Germain (1973), Ziegler (1977), Lemaitre and Chaboche (1990), Lubliner (1990), and Maugin (1992a).

where ε^v is an *infinitesimally small strain*, and we take an energy and dissipation potential of the form

$$W = \bar{W}(\varepsilon - \varepsilon^v, \theta), \qquad \mathcal{D}^* = \mathcal{D}^*(\sigma, \theta), \tag{7.2.2}$$

from which it follows that

$$S = -\frac{\partial \bar{W}}{\partial \theta}, \quad \sigma = \sigma^e = \mathcal{A} = \frac{\partial \bar{W}}{\partial(\varepsilon - \varepsilon^v)}, \quad \Phi_{\text{intr}} = \sigma : \dot{\varepsilon}^v. \tag{7.2.3}$$

The second of these equations indeed means that it is the *same stress* which acts on both elastic (σ^e) and viscous ($\mathcal{A}$) elements, hence the setting in series in Fig. 4.1. In agreement with Mandel's remark as alluded to in Sec. 4.4, it is indeed the strain related to the viscous element (ε^v) which provides a good choice as internal variable. Now if we let W depend quadratically (linear elasticity) on ($\varepsilon - \varepsilon^v$) and $\mathcal{D}^*$ depend quadratically (linear viscoelasticity) on σ — in agreement with *T.I.P.* — it is readily shown by elimination of ε^v by taking the time derivative of ε, that σ and ε are finally related through a *DRM* of the type

$$\dot{\sigma} + \tau^{-1} \cdot \sigma = \mathbf{E} \cdot \dot{\varepsilon}, \tag{7.2.4}$$

where $\mathbf{E}$ and τ^{-1} are linear operators with components representing elasticity coefficients and reciprocal relaxation times, respectively. With $\mathbf{E}$ and τ^{-1} reduced to scalars, we have the behavior of the model of Fig. 4.1, i.e. the *Maxwell model* that, supposedly, could not be placed under the umbrella of *thermodynamics*.

A combination of the model of Kelvin–Voigt and Maxwell's modeling will yield the so-called *standard model* of the rheology of solids in small strains as

$$\tau_\sigma^{-1} \cdot \sigma + \dot{\sigma} = (\tau_\varepsilon^{-1}\mathbf{E}) \cdot \varepsilon + \mathbf{E} \cdot \dot{\varepsilon}, \tag{7.2.5}$$

where τ_σ^{-1}, $\mathbf{E}$ and $\tau_\varepsilon^{-1}\mathbf{E}$ are three linear operators (fourth-order tensors in the fully *anisotropic* case), whose components may still depend on temperature. When these operators are *isotropic*, so that proportionality factors replace the operators in (7.2.5), we have the mathematical expression of the rheological model in Fig. 7.1. Let H, N, M, and KV denotes the Hookean (linear spring), Newtonian, Maxwell and Kelvin–Voigt rheological models, and the symbols — and || denotes the setting in parallel and series, respectively. Then we have:

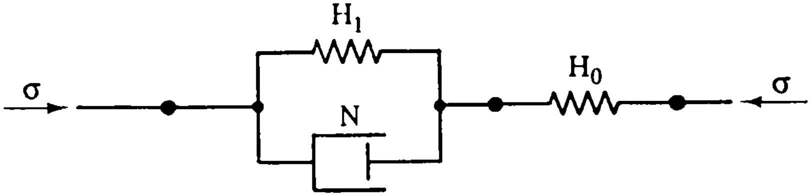

Fig. 7.1. Standard model of solid viscoelasticity.

- Kelvin–Voigt model: KV = H || N;
- Maxwell model: M = H – N;
- Standard model: S = KV – H$_0$ = (H$_1$ || N) – H$_0$;
- Poynting–Thomson model: PT = H || M;
- Lethersich model: L = N – KV;
- Jeffrey model: J = N || L;
- Burgers model: Bu = M – KV; etc.

For example, the *J*-model introduced by the geophysicist H. Jeffrey, often used to model the Earth's crust has formula:

$$\dot{\sigma} + \tau_\sigma^{-1}\sigma = 2\eta_v(\overset{\prime\prime}{\varepsilon} + \tau_J^{-1}\dot{\varepsilon}), \tag{7.2.6}$$

where τ_σ and τ_J are two relaxation times.

In a general manner multi-element models built from H and N elements yield *stres-strain* relations of the following general *time-rate* type:

$$\begin{aligned} & a_0\sigma + \sigma_1\dot{\sigma} + a_2\overset{\prime\prime}{\sigma} + \cdots + a_n\sigma^{(n)} \\ & \quad = b_0\varepsilon + b_1\dot{\varepsilon} + b_2\overset{\prime\prime}{\varepsilon} + \cdots + b_m\varepsilon^{(m)}, \end{aligned} \tag{7.2.7}$$

where (n) denotes the nth order time derivative, and it is to be noted that (m) is not necessarily equal to (n). This is illustrated by the *J*-model. A problem of *causality* (initial conditions) will naturally arise given the possibly high degree in the time derivatives involved (this problem starts with the second derivative!).

All the above models are *viscoelastic* ones as they present characteristic times but no threshold. Their *thermodynamic realization* requires in general decomposing the total strain ε and the Cauchy stress σ in as many elements as necessary with the corresponding interpretation as *internal variables* (see

Kluitenberg, 1984, for these laborious generalizations). The natural question which arises then is whether this procedure can be generalized to *finite strains*? For *viscoelasticity* this has been examined in detail by Sidoroff (1976) by considering the notion of internal variables and the existence of *one* or *several* intermediate configurations (cf. Fig. 5.4 in the case of *one* such configuration) following along the path paved by Perzyna (1971a,b). These multiple intermediate configurations in fact serve as nonlinear generalizations of rheological models. The Maxwell model in *finite strains* was thus obtained by Gorodzov and Leonov (1968) and Buevich (1968). In his masterly constructed classification Sidoroff (1976) has shown, after linearization, how important the *model* of *Biot* (1954) was in this general background. Characteristic of *T.I.V.*, this model in all generality involves n observable variables a and p internal variables α and two *quadratic* forms, an energy $W(a,\alpha)$ and a dissipation $\mathcal{D}(\dot{a},\dot{\alpha})$ — this will typically result in a *DRM* such as that described by (7.2.7).

In conclusion, we note the two main characteristics of the models studied heretofore: (i) there is no apparent limit to the value of stresses involved, and (ii) there exists at least one characteristic time, which is typical of viscosity. In *viscoplasticity*, the first characteristic is lost as there appears to exist, at each time, a *threshold in stress*, while the second characteristic remains. This is classically illustrated by *Bingham fluids*, i.e. those highly viscous toothpaste-like materials which flow like fluids until the stress involved has reached such a level that the material moves *en bloc* as if it were rigid (we have all experienced this with toothpaste). This enters a thermodynamic framework by considering the following model:

$$\alpha = \{\varepsilon^{vp}\}, \qquad W = \bar{W}(\varepsilon - \varepsilon^{vp}),$$

$$\Phi_{\text{intr}} = \sigma^D : \dot{\varepsilon}^{vp} = \mathcal{A}\dot{\alpha} \geq 0, \tag{7.2.8a}$$

$$\sigma = \frac{\partial W}{\partial \varepsilon}, \qquad \mathcal{A} = -\frac{\partial W}{\partial \alpha} = \sigma = \sigma^D,$$

and there exists a pseudo-potential $\mathcal{D}^*$ such that

$$\mathcal{D}^* = \frac{1}{4\eta_v}\langle \| \sigma^D \| - \sigma_0 \rangle^2, \qquad \dot{\alpha} = \dot{\varepsilon}^{vp} = \frac{\partial \mathcal{D}^*}{\partial \sigma^D}, \tag{7.2.8b}$$

where $\langle \cdots \rangle$ denotes the *positive part*, i.e. $\langle a \rangle = 0$ if $a < 0$ and $\langle a \rangle = a$ if $a \geq 0$, and $\| \sigma^D \|$ must be understood as the *norm of the deviatoric part of the dissipative stress*, i.e.

$$\| \sigma^D \| = (\mathrm{tr}\,[(\sigma^D)^d]^2)^{1/2} .$$

With $\varepsilon = \varepsilon^e + \varepsilon^{vp}$, and $\bar{W}$ quadratic in ε^e, we obtain an *evolution equation* for ε in the form

$$\dot{\varepsilon} = \mathbf{E}^{-1} \cdot \dot{\sigma} + \frac{1}{2\eta_v} \frac{\langle \| \sigma^D \| - \sigma_0 \rangle}{\| \sigma^D \|} (\sigma^D)^d , \tag{7.2.9}$$

where $\mathbf{E}^{-1}$ is the tensor of elastic compliances. In the absence of elasticity, the first term in the right-hand side is not present, and we have an incompressible *Bingham fluid, per se.* If, furthermore, the yield stress σ_0 vanishes, then this further reduces to an incompressible Newtonian fluid, while if it is η_v which tends to zero, then we recover the behavior of an elasto-plastic body with a Mises type of flow rule (see below). In one dimension the model (7.2.9) reduces to the rheological model

$$\dot{\varepsilon} = \mathbf{E}^{-1} \dot{\sigma} + \frac{1}{2\eta_v} \langle \sigma - \sigma_0 \rangle .$$

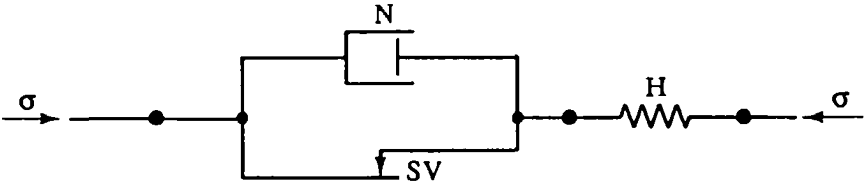

Fig. 7.2. Bingham visco-plastic rheological model.

This corresponds to the *rheological model* sketched out in Fig. 7.2 with *rheological recipe*: Bi = (N ‖ SV) − H, where SV designates a Saint–Venant friction element (perfect plasticity). Indeed, in this rheological model we have

$$\varepsilon = \varepsilon^e + \varepsilon^{vp} , \qquad \varepsilon_N = \varepsilon_{SV} = \varepsilon^{vp} ,$$

$$\sigma = \sigma_N + \sigma_{SV} , \qquad \sigma = \mathbf{E} \varepsilon^e , \qquad \sigma_N = 2\eta_v \dot{\varepsilon}_N = 2\eta_v \dot{\varepsilon}^{vp} ,$$

$$\dot{\varepsilon}_{SV} = (\mathrm{sign}\, \sigma_{SV}) |\dot{\varepsilon}_{SV}| \qquad \text{for } |\sigma_{SV}| \geq \sigma_0 ,$$

from which there follows the above equation after elimination of $\dot{\varepsilon}^e$ and $\dot{\varepsilon}^{vp}$. Remarkably enough, this behavior (in the absence of elasticity) results from a dissipative mechanism which is the *sum* of two *normal* dissipative mechanisms, viscosity and plasticity (cf. Germain, 1973, p. 200). *Normal* mechanisms are those for which we can write an evolution equation of the form $(5.4.39)_1$. This can be seen if we note that the first of $(7.2.8\mathrm{a})_3$ can be rewritten as

$$\Phi_{\text{intr}} = \sigma^v : \dot{\varepsilon}^{vp} + \sigma^p : \dot{\varepsilon}^{vp} , \qquad \sigma = \sigma^v + \sigma^p ,$$

where σ^v is of the viscous type in that it produces a power that is homogeneous of degree *two* in $\dot{\varepsilon}^{vp}$, while σ^p is of the plastic type developing a power which is homogeneous only of degree *one* in $\dot{\varepsilon}^{vp}$. Obviously, the pseudo-dissipation potential introduced here is of the same type as the Perzyna potential $(5.4.39)_2$. Out of curiosity we note in Brun (1984) the case of a dissipative mechanism which involves two dissipative mechanisms, but only one of these is *normal*.

In plasticity, the second characteristic above is also lost in most cases: *no time scale* is apparent in the phenomenon, and this should correspond to some *singular* behavior as the dissipated power *a priori* involves time rates. This is examined at some length in the next section.

7.3. Plasticity and Viscoplasticity in Small Strains

We are placed in the framework of Eqs. (5.6.44)–(5.6.46) for which we may discard the index α once we have recorded its meaning and we assume that no *viscous* phenomena are present. Thus Eqs. (5.6.44) through (5.6.46) reduce to the following:

$$\varepsilon = \varepsilon^e + \varepsilon^p = (\nabla \mathbf{u})_s , \tag{7.3.10}$$

$$W = \bar{W}(\varepsilon^e, \alpha) , \qquad \text{convex in } \varepsilon^e \text{ and } \alpha , \tag{7.3.11}$$

$$S = -\frac{\partial \bar{W}}{\partial \theta} , \qquad \sigma = \frac{\partial \bar{W}}{\partial \varepsilon^e} , \qquad \mathcal{A} = -\frac{\partial \bar{W}}{\partial \alpha} , \tag{7.3.12}$$

$$\Phi = \Phi_{\text{intr}} + \Phi_{\text{th}} \geq 0 , \tag{7.3.13}$$

$$\Phi_{\text{intr}} = \sigma : \dot{\varepsilon}^p + \mathcal{A}\dot{\alpha} , \qquad \Phi_{\text{th}} = \theta \mathbf{q} \cdot \nabla(\theta^{-1}) . \tag{7.3.14}$$

Here it is emphasized that ε^e, the *elastic strain*, is an observable variable, while α contains all *internal variables*. This follows the following essential remark of Bridgman (1950). During isothermal plastic straining, i.e. when the material is yielding, there is no change in the state of the system, so that the strain ε does not in this view constitutes a good parameter of state. The reason for this is that *plastic deformation appears to be a process of energy dissipation* (that is essential) *but at constant state*! The proper strain parameter is identified by letting the system *unload* and *relax* so that only the *reversible strain* ε^e *can enter the thermal equation of state or the expression for energy*, W (cf. Kestin, 1966, pp. 369, 370). This is what is expressed by (7.3.11) to which *convexity conditions* are added for stability reasons (see below).

Plasticity is characterized then by the fact that stress is constrained to remain in a closed *convex set* C *of stress space* and that it is essentially strain-rate independent, so that the dissipation Φ_{intr} can only be homogeneous of degree *one* in the fluxes (generalized thermodynamic forces) σ and $\mathcal{A}$. According to the fundamental theorem of convex analysis outlined in Sec. 5.4, we thus have (applying a stronger version of the second law)

$$\Phi_{\text{intr}} = \mathbf{Y} \cdot \dot{\mathbf{X}} = \Phi(\dot{\mathbf{X}}) \geq 0 \,, \tag{7.3.15}$$

$$\mathbf{Y} = (\sigma, \mathcal{A}) \,, \qquad \mathbf{X} = (\varepsilon^p, \alpha) \,, \tag{7.3.16}$$

and the equivalent statements:

(i) *principle of maximal dissipation*:

$$\Phi(\dot{\mathbf{X}}) = \sup_{\mathbf{Y}^* \in C} \mathbf{Y}^* \cdot \dot{\mathbf{X}} \geq 0 \,, \tag{7.3.17a}$$

or

$$(\mathbf{Y} - \mathbf{Y}^*) \cdot \dot{\mathbf{X}} \geq 0 \,, \qquad \forall \mathbf{Y}^* \in C \,; \tag{7.3.17b}$$

(ii) *normality law*:

$$\dot{\mathbf{X}} = \dot{\lambda} \frac{\partial f}{\partial \mathbf{Y}} \,, \tag{7.3.18a}$$

at all regular points of the *yield surface* $\partial C : f(\mathbf{Y}) = 0$ in generalized stress space, where $\dot{\lambda} \geq 0$ is the so-called *plastic multiplier* to be determined later on, and more generally and in an abstract way

$$\dot{\mathbf{X}} \in N_C(\mathbf{Y}) \,, \tag{7.3.18b}$$

where N_C denotes the cone of outward normals to C at $\mathbf{Y}$. Equation (7.3.18a) or (7.3.18b) is an *evolution equation* of somewhat singular character in that $\dot{\mathbf{X}} = 0$ if $\mathbf{Y}$ lies *inside* C.

In the present thermodynamic approach the *pseudo-dissipation potential* $\mathcal{D}^*$ is none other than the *flow surface* $f = 0$. We say that we are dealing with *associated plasticity* as dissipation is associated to the flow rule. Historically, flow rules were found outside any thermodynamic setting, and the knowledge of the fundamental equation $f = 0$ remains an *experimental datum* (except in some polycrystals where a sensible $f = 0$ can be justified on some microscopic basis; cf. Maugin, 1992a, p. 196). We refer the reader to specialized books on elastoplasticity (Maugin, already cited, Lubliner, 1990) for a list of experimentally discovered *flow rules* or *yield surfaces*, or *plasticity criteria*, $f = 0$ or, for that matter, *pseudo-dissipation potentials*. *All surfaces* $f = 0$ observed so far are indeed *convex*, but some of them are *not* closed (e.g. in geophysical materials). Typically, however, the mathematical expression of such *flow rules* relates to a criterion which involves either a *pure stress level or* some *stress energy*: for instance, the celebrated *Tresca criterion* observed experimentally by H. E. Tresca in 1872 relates to a *maximum shear* whereas the ubiquitous *Hubber-Mises criterion* (often referred to as Mises criterion, and which was proposed only for its mathematical simplicity by its two proponents — in 1904 by Hubber and in 1913 by von Mises) in fact relates to a *maximum-distortion energy* (i.e. excluding dilatation effects). The *Rankine* and *Beltrami* criteria, now essentially of historical interest, relate to a *maximum stress*, and a *maximum strain energy*, respectively. The *Coulomb criterion* involves an *internal friction* (hence its validity for powder-like materials; this one involves a *non-closed* convex set) and the von Schleicher (1926), and Gurson (1977) criteria try to accommodate the influence of the *mean stress* and *porosity*. Whenever the surface $f = 0$ is a fixed experimental datum which depends only on the material, we say that we have *perfect plasticity*. When this surface evolves with loading, we say that we have *plasticity* with *hardening*.

We make more explicit some of the above outlined points with the aid of a simple example involving *hardening*. Assume that $f = 0$ is regular enough so that we can unambiguously use the formulation (7.3.18a) which reads in full

$$\dot{\varepsilon}^p = \dot{\lambda}\frac{\partial f}{\partial \sigma}, \qquad \dot{\alpha} = \dot{\lambda}\frac{\partial f}{\partial A}, \tag{7.3.19}$$

where, for the time being, $\dot{\lambda} \geq 0$ if $f = 0$ (we are sitting on the yield surface) and $\dot{\lambda} = 0$ if $f < 0$. Now sitting on the yield surface is not enough to guarantee that there is any evolution of ε^p. But a simple reasoning based on the exploitation of the *variational inequality* (7.3.17b) — and considering Y at instant $t + h$ and $t - h$, and Y^* at instant t with h infinitesimally small and taking the limit of vanishingly small h — leads to the following *orthogonality* *condition* between "velocities":

$$\dot{\mathbf{Y}} \cdot \dot{\mathbf{X}} = 0 . \tag{7.3.20}$$

Using the definition of $\mathbf{Y} = (\sigma, \mathcal{A})$ and the condition of convexity of W (so that our material is *generalized standard* in the sense of Halphen and Nguyen Quoc Son, 1975), Eq. (7.3.20) shows that in the absence of hardening (no α in the formulation), $W = \bar{W}(\varepsilon - \varepsilon^p)$, we have the strict *orthogonality relation*

$$\dot{\sigma} : \dot{\varepsilon}^p = 0 ; \tag{7.3.21}$$

while in the presence of hardening, $W = \bar{W}(\varepsilon - \varepsilon^p, \alpha)$, we have the *inequality*

$$\dot{\sigma} : \dot{\varepsilon}^p \geq 0 . \tag{7.3.22}$$

The latter condition, which results from both the *principle of maximal dissipation* and the *convexity of* W, is a *local stability condition* which is none other than the celebrated *Drucker's inequality.* For one-dimensional effects, this means that increments in stress and plastic strain can only be in the same sign. As a consequence of (7.3.21) by expressing the *consistency condition,* $\dot{f} = 0$, we can find an expression for the *plastic multiplier* $\dot{\lambda}$ in terms of $\dot{\sigma}$ or $\dot{\varepsilon}$, and also prove the more accurate conditions:

$$\begin{aligned} &\dot{\lambda} \geq 0 \text{ if } f = 0 \text{ and } \dot{f} = 0 , \\ &\dot{\lambda} = 0 \text{ if } f < 0 \text{ or } f = 0 \text{ and } \dot{f} < 0 . \end{aligned} \tag{7.3.23}$$

This clearly distinguishes *loading* and *unloading* from one another. This is also what makes *elastoplasticity with hardening* essentially different from *nonlinear elasticity.* Indeed, if only loading is considered then there is no way to distinguish *plasticity* from a special type of *nonlinear elasticity* (*with appropriate convexity conditions on the "elastic" potential* — see Maugin, 1992a). Theories of elastoplasticity, such as the Hencky–Nadaï–Ilyushin one, which only envisage loading, are *not theories of elastoplasticity per se.*

To be more specific, consider the case where α is made of ε^p itself (not only this is *not* forbidden, but this is very meaningful indeed) and a scalar β, i.e. we note

$$\alpha = (\varepsilon^p, \beta) , \tag{7.3.24}$$

together with the energy and convex stress set

$$\begin{aligned} W &= \frac{1}{2}(\varepsilon - \varepsilon^p) \cdot \mathbf{E} \cdot (\varepsilon - \varepsilon^p) + \bar{W}(\beta) , \\ C &= \{(\sigma, B) | \{\operatorname{tr} (\sigma^d)^2\}^{1/2} + B - \sigma_0 \leq 0 , \sigma_0 > 0\} , \end{aligned} \tag{7.3.25}$$

where $\mathbf{E}$ is the (fourth-order) tensor of elasticity moduli. The laws of state are given by

$$\sigma = \frac{\partial W}{\partial \varepsilon^e} = \frac{\partial W}{\partial \varepsilon}\,, \quad \mathcal{A} = -\frac{\partial W}{\partial \varepsilon^p} = \sigma\,, \quad B = -\frac{\partial W}{\partial \beta} = -\frac{d\bar{W}}{d\beta}\,, \tag{7.3.26}$$

with $\bar{W}$ convex in β. The presence of *the distortion-energy norm* in $(7.3.25)_2$ means that we are building on a criterion of the Hubber–Mises type, in which the thermodynamical force B — also homogeneous to a stress — associated to β has for effect to modify the yield limit σ_0. A straightforward elimination of $\dot{\lambda}$ between the two equations (7.3.19) leads to the scalar internal variable β in the form

$$\beta(t) = \int_0^t \{\dot{\varepsilon}^p(t') : \dot{\varepsilon}^p(t')\}^{1/2} dt' =: \overline{\varepsilon^p}\,, \tag{7.3.27}$$

where only the deviatoric part of ε^p has to be considered. The quantity defined by (7.3.27) is the so-called *cumulative* or *accumulated* plastic strain. This shows that, indeed, the internal variable β accounts for the *whole history* of the plastic deformation up to the present time, although *no time scale* is involved in the formulation. This variable is none other than the *hardening parameter* proposed by F. K. G. Odqvist in 1933 to account for the experimental fact of *isotropic hardening*, i.e. the uniform expansion of the flow surface in stress space. This surface may also be displaced by a translation of its origin by introducing a *tensorial internal variable* which is none other than the so-called *backstress* — in the first approximation linear in ε^p — that is responsible for *kinematic hardening* (see Maugin, 1992a, Chapter 5).

The above presentation, essentially built by Nguyen Quoc Son (1973) on the basis of preliminary works by Ziegler (1963) and Moreau (1971), is a beautiful application of *T.I.V.* to a nontrivial case. It shows that contrary to persisting rumors plasticity can be incorporated in the framework of *irreversible thermodynamics* (see the interesting remarks in Ziegler, 1970). This elegant thermodynamic formulation within the frame of *generalized standard materials* not only includes the local stability "postulate" of Drucker (7.3.22) — so-called *positive hardening* — but also *Ilyushin*'s celebrated *global stability criterion* according to which:

> *Ilyushin's* "postulate": For any strain cycle $\varepsilon(t)$, $t \in [0,1]$, $\varepsilon(0) = \varepsilon(1)$, the *strain power* is positive or zero:

$$\int_0^1 \sigma : \dot{\varepsilon} dt = \int_0^1 \sigma : d\varepsilon \geq 0 . \tag{7.3.28}$$

This was presented as a postulate by the Russian scientist A. A. Ilyushin in 1948. Here we can *prove* that the result (7.3.28) follows from the satisfaction of the *principle of maximal dissipation* (convexity of the yield surface and homogeneity of degree one of the dissipation) and the convexity of the energy function.

Proof. For generalized standard materials, we have (see Chapter 5)

$$W = W(\varepsilon, \alpha) , \qquad \sigma = \frac{\partial W}{\partial \varepsilon} , \qquad \mathcal{A} = -\frac{\partial W}{\partial \alpha} , \qquad \mathcal{A} \in C , \tag{7.3.29}$$

and

$$(\mathcal{A} - \mathcal{A}^*) \cdot \dot{\alpha} \geq 0 , \qquad \forall \mathcal{A}^* \in C . \tag{7.3.30}$$

From (7.3.29) we have

$$\dot{W} = \sigma : \dot{\varepsilon} - \mathcal{A} \cdot \dot{\alpha} . \tag{a}$$

Integrating this over the time interval [0,1] (this has been normalized to the *unit* interval as there is *no time scale*] we have

$$\int_0^1 \sigma : \dot{\varepsilon} dt = \int_0^1 \dot{W} dt + \int_0^1 \mathcal{A} \cdot \dot{\alpha} dt . \tag{b}$$

The first integral in the right-hand side is estimated as

$$\begin{aligned} & W(\varepsilon(1), \alpha(1)) - W(\varepsilon(0), \alpha(0)) \\ & \quad = W(\varepsilon(0), \alpha(1)) - W(\varepsilon(0), \alpha(0)) \geq \left(\frac{\partial W}{\partial \alpha}\right)_0 [\alpha(1) - \alpha(0)] \\ & \quad = -\mathcal{A}(0)[\alpha(1) - \alpha(0)] , \end{aligned} \tag{c}$$

by virtue of the periodicity of ε, the convexity of W in α, and the law of state $(7.3.29)_3$. Substituting now from (c) into the right-hand side of (b) and considering the integral of (7.3.30) between $t = 0$ and $t = 1$ by selecting $\mathcal{A}(0)$ as $\mathcal{A}^*$, we deduce (7.3.28). *Q.E.D.*

This result means (classical interpretation of integrals as areas below the curve) that the *hysteresis loops*, in the plane (ε, σ) in the one-dimensional case, can only be followed *clockwise*. This is a global stability result. If, in addition,

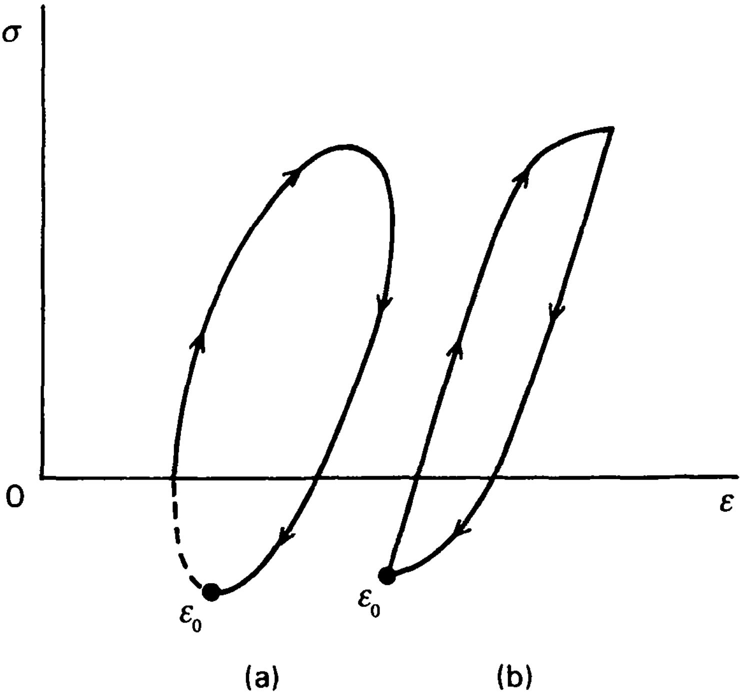

Fig. 7.3. *Hysteresis loop in elastoplasticity with positive hardening* (Ilyushin's "postulate" combined to Drucker's inequality makes that only the right-hand figure is admissible.

we account for Drucker's inequality (7.3.22) at all points of these loops, in particular at the maximal and minimal stress points, we see that these hysteresis loops cannot present any rounded corners: they must exhibit sharp corners (included in an accute angle) at upper and lower extrema of the loop (see Fig. 7.3). This is a characteristic sign of the periodic response of elastoplastic materials with positive hardening admitting a convex energy potential. Any experimentally observed markedly rounded extremum on such a hysteresis loop is an indicator that either *viscosity* is present or the material considered exhibits some softening (negative "hardening"). Remarkably enough, in his studies of what he called, at the time, *theory of permanent strains*, P. Duhem was led to propose a theory of *hysteretic phenomena* which clearly anticipated the exposed results, in particular in so far as the existence of state laws and convex dissipation are concerned, and also the resulting hysteresis diagram with sharp corners (in this respect see Manville, 1927, pp. 307–316).[4]

Viscoplasticity in small strain was already exemplified by the *Bingham model* which enters the rigorous "viscoplastic" framework given in Sec. 5.4. In the case of solids, however, viscoplasticity is of utmost interest in the plasticity of the monocrystal and polycrystals, in which case a *finite-strain* background is usually requested (see next section).

7.4. Plasticity and Viscoplasticity in Finite Strains

Plasticity and viscoplasticity in finite strains are the realm of *single crystals* for which the finiteness of strain is essential (see Havner, 1992). The main problems from the methodological viewpoint are the finite-strain generalization of the decomposition (7.3.10) and the formulation of an evolution equation for the plastic strain and the accompanying internal variables which should now possess a good form-invariance as requested in all nonlinear theories of continua. This includes the identification of a meaningful "plastic rate" and the solution of the problem related to "plastic spin". An enormous amount of literature has appeared which testifies of the interest for such extensions. But the subject matter becomes rapidly highly technical. For an extensive approach to this we refer the reader to original works with special attention to those that emphasize the role of *internal variables* of state, in particular, Mandel (1971, 1973), Rice (1972), Zarka (1973), Bamman (1985), Dillon (1967), Kratochvil and Dillon (1969), Stolz (1982, 1987), Teodosiu (1975), Teodosiu and Sidoroff (1976), Sidoroff (1975, 1976), Ting (1971), Lehmann (1988), Haupt (1984), Haupt and Tsakmakis (1988), van der Giessen (1989), Critescu and Suliciu (1980) — and many others that we cannot list — the most recent review works by Cleja-Tigoiu and Soos (1990), and the books of Mandel (1978), Lubliner (1990) and Maugin (1992a), and the original contributions of Kluitenberg (1984) and Valanis (1972). Here we shall content ourselves with simply illustrating the model sketched out in Sec. 5.6.

We tentatively answer the first query by considering the *multiplicative decomposition* (5.6.50) of the motion gradient as an exact replacement of the

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[4] In particular, Eqs. (9) in p. 310 and the (un-numbered) third equation in p. 313 in Manville (1927), who is supposed to faithfully reproduce Duhem's thought, are equivalent to Drucker's and Ilyushin's proposals, respectively. By some chance, the symbols employed are practically those of our approach (A, a) replacing $(\mathcal{A}, \alpha)$. The crucial paper of P. Duhem is Duhem (1901).

approximate *additive decomposition* (7.3.10). Consequently, if $\mathbf{F}^e$, the *elastic "gradient"* is considered as the mechanical observable variable of state, we may envisage the laws of state given by Eqs. (5.6.52) and we shall inevitably be led to the *dissipation inequality* (5.6.55). It is at this crucial point that an answer to the second query is sought. Obviously the *structure* of the remaining *intrinsic dissipation* $(5.6.55)_2$ is the *same* as in the small strain theory. So we could try to follow along the same path, but most of the geometric objects present in $(5.6.55)_2$ are not *true tensors*. They are still *two-point tensor fields* with "two feet in different systems". It is tempting, if not the only clear-cut solution, to refer all fields to the intermediate configuration $\mathcal{K}_{\mathcal{R}}$ as it is the one with respect to which *elasticity* is defined, unfortunately up to the rotation of $\mathcal{K}_{\mathcal{R}}$ as indicated by (5.6.51). But we can take the stand of Mandel (1971, 1973) that it is possible to fix reference directions in $\mathcal{K}_{\mathcal{R}}$, in particular through a *director frame* $\{\mathbf{d}^{(\alpha)};\ \alpha = 1,2,3\}$ that specifies the crystalline lattice in its elastically released configuration, and such that there is no ambiguity in the definition of $\mathcal{K}_{\mathcal{R}}$, at least at each point $\mathbf{X}$ in the material. Thus $\mathcal{K}_{\mathcal{R}}$ is *local* rather than global, i.e. it cannot be integrated in space to yield a global reference configuration for the whole body. This is the price we have to pay for this definition which concurs with that admitted in the elasticity of bodies endowed with a continuous distribution of defects (such as dislocations, cf. Kröner, 1962). With this in mind we can define the following *finite-strain* tensors, *deformation rates*, and *stress tensors*:

- Strain tensors relative to $\mathcal{K}_{\mathcal{R}}$:

$$\mathbf{C}^e := (\mathbf{F}^e)^T\mathbf{F}^e\,, \qquad \mathbb{E}^e_{\mathcal{R}} := \frac{1}{2}(\mathbf{C}^e - \mathbf{1}_{\mathcal{R}})\,, \tag{7.4.31}$$

- Plastic strain rates:

$$\mathbb{D}^p := \{\mathbf{F}^e\mathbf{L}^p(\mathbf{F}^e)^{-T}\}_S = (\mathbb{D}^p)^T\,, \qquad \text{in } \mathcal{K}_t \tag{7.4.32}$$

and

$$\mathbb{D}^p_{\mathcal{R}} := \{\mathbf{C}^e \cdot \mathbf{L}^p\}_S = (\mathbb{D}^p_{\mathcal{R}})^T\,, \qquad \text{in } \mathcal{K}_{\mathcal{R}}\,; \tag{7.4.33}$$

- Second–Piola Kirchhoff stress relative to $\mathcal{K}_{\mathcal{R}}$:

$$\mathbb{S}_{\mathcal{R}} = \mathrm{J}^e(\mathbf{F}^e)^{-1} \cdot \sigma \cdot (\mathbf{F}^e)^{-T} = (\mathbb{S}_{\mathcal{R}})^T\,, \tag{7.4.34}$$

where

$$\mathrm{J}^e = \det \mathbf{F}^e\,, \qquad \mathrm{J}^p = \det \mathbf{F}^p\,, \qquad \mathrm{J}_F = \mathrm{J}^e\mathrm{J}^p > 0\,. \tag{7.4.35}$$

We assume for the case of *elastoplasticity* that there are no *viscous stresses*. Then the *intrinsic dissipation* (5.6.55)$_2$ is shown to read

- per unit volume in $\mathcal{K}_t$:

$$\Phi_{\text{intr}} = \sigma : \mathbb{D}^p + \mathrm{J}_F^{-1} A\dot{\alpha}\,; \tag{7.4.36}$$

- per unit volume in $\mathcal{K}_{\mathcal{R}}$:

$$(\Phi_{\text{intr}})_{\mathcal{R}} = \operatorname{tr}(\mathbb{S}_{\mathcal{R}}\mathbb{D}^p_{\mathcal{R}}) + \mathcal{A}\dot{\alpha}\,, \tag{7.4.37}$$

together with the energy (per unit volume in $\mathcal{K}_{\mathcal{R}}$) and the laws of state:

$$\mathcal{W} = \bar{\mathcal{W}}(\mathbb{E}^e_{\mathcal{R}}, \alpha, \theta)\,, \tag{7.4.38}$$

and

$$\mathbb{S}_{\mathcal{R}} = \frac{\partial\bar{\mathcal{W}}}{\partial\mathbb{E}^e_{\mathcal{R}}}, \qquad \mathcal{A} = -\frac{\partial\bar{\mathcal{W}}}{\partial\alpha}, \qquad \mathcal{S}_{\mathcal{R}} = -\frac{\partial\bar{\mathcal{W}}}{\partial\theta}\,. \tag{7.4.39}$$

It is assumed here that $\mathbb{E}^e_{\mathcal{R}}$ is the mechanical *observable* variable of state. This is a symmetric tensor in $\mathcal{K}_{\mathcal{R}}$. Its thermodynamic dual or *conjugate* is $\mathbb{S}_{\mathcal{R}}$. Apart from the tensorial order of α which is not yet specified, we have thus reduced the elastoplasticity in finite strain to a thermodynamic formulation which is strictly identical to that of the small-strain case. We shall assume that the energy $\mathcal{W}$ is convex in its first two arguments and concave in the temperature, and that there exists a *pseudo-potential of dissipation* $\mathcal{D}^*$ from which the remaining *evolution equations* derive. That is, for a rate-independent *plastic* behavior:

$$\mathcal{D}^* = \mathcal{D}^*(\mathbb{S}_{\mathcal{R}}, \mathcal{A}) \tag{7.4.40}$$

convex and homogeneous of degree one in both $\mathbb{S}_{\mathcal{R}}$ and $\mathcal{A}$, so that

$$\mathbb{D}^p_{\mathcal{R}} = \dot{\lambda}\frac{\partial f_{\mathcal{R}}}{\partial\mathbb{S}_{\mathcal{R}}}, \qquad \dot{\alpha} = \dot{\lambda}\frac{\partial f_{\mathcal{R}}}{\partial\mathcal{A}}, \qquad \dot{\lambda} \geq 0\,, \tag{7.4.41}$$

with a yield surface $f_{\mathcal{R}}(\mathbb{S}_{\mathcal{R}}, \mathcal{A}) = 0$ bounding a convex C in $(\mathbb{S}_{\mathcal{R}}, \mathcal{A})$-space.

The above formulation is strictly correct and appropriately form-invariant only when α is a pure *scalar*. In this case we see that no problem appears with any "plastic spin" as this notion does not show up since the first of (7.4.41)$_1$ involves only symmetric *true* tensors while (7.4.41)$_2$ involves only a classical material time derivative.

If α is a *tensorial internal variable*, then we should specify its tensorial order and in what "space" (configuration) it is represented. This is essential in order to write $(7.4.41)_2$ in proper invariant form. For instance, if α is a symmetric-tensor-valued function in $\mathcal{K}_{\mathcal{R}}$, then in writing a form-invariant Eq. $(7.4.41)_2$ we may introduce an *objective time derivative* with respect to $\mathcal{K}_{\mathcal{R}}$, e.g. a *co-rotational derivative* $D_\omega \alpha$, such that

$$D_\omega \alpha := \dot{\alpha} - \omega_d \cdot \alpha + \alpha \cdot \omega_d \,, \qquad (\omega_d)_{\beta\gamma} := \sum_\alpha \dot{d}^{(\alpha)}_{.\beta} d^{(\alpha)}_{.\gamma} \,, \tag{7.4.42}$$

where ω_d is the *spin tensor* associated with the *director* lattice triad of Mandel. Note that $D_\omega \alpha$ is defined just like a Jaumann derivative with ω_d replacing the usual spin tensor. But then the right-hand side of $(7.4.41)_2$ has also to be form-invariant under the rotations (orthogonal transformations) $\mathbf{Q}$ in $\mathcal{K}_{\mathcal{R}}$. This imposes, through a well-known representation theorem, that f be an *isotropic* scalar-valued function of both $\mathbb{S}_R$ and $\mathcal{A}$, where $\mathcal{A}$ itself, being the thermodynamic conjugate of α, is also a symmetric second-order tensor in $\mathcal{K}_{\mathcal{R}}$, for instance, a *backstress* responsible for some kinematic hardening. It is fair to say that the developments along such lines are still in their infancy and the subject of sometimes *frantic scientific* discussions. For these and the case of *viscoplasticity* in finite strain we refer to the excellent review of Cleja-Tigoiu and Soos (1990) which rightly emphasizes the role of intermediate configurations and internal state variable in the spirit of the present book. For simple models of viscoplasticity, we also refer to Lemaitre and Chaboche (1990)'s book (Chapter 6) which offers a rich discussion.

7.5. Damage, Cyclic Plasticity and Creep

In contrast to *fracture*, which is due to the progress of *macro-cracks* and which we shall examine in Chapter 8, we agree to call *damage* the decrease in elasticity caused by the reduction in area likely to transmit stresses (contact actions) through the body. This is a consequence of the progress of *micro*-cracks and of the expansion of *micro*-cavities. A rather naive but simple way to describe this phenomenon is to introduce, under certain hypotheses of isotropy, a scalar variable D (for damage) such that $0 \leq D \leq 1$, where $D = 0$ corresponds to the virgin element of matter (no microcracks nor microcavity) and $D = 1$ corresponds to fracture (cf. Fig. 7.4). In reality the element is out of order before the last limit is reached as atomic decohesion takes place before D reaches the value one. In fact, then, D is limited to a *convex* set smaller than the closed segment $[0,1]$, but a closed convex indeed, so that the idea to use the formulation of generalized standard materials for damage phenomena emerges

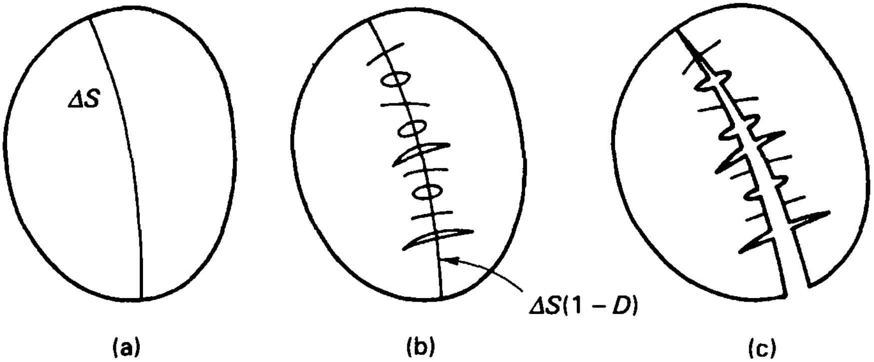

Fig. 7.4. Three stages of damage: (a) virgin element, (b) partially damaged, (c) fully damaged element ($D = 1$).

naturally. One can thus envisage a *damage criterion* or criterion of initiation of macroscopic fracture when the upper limit is reached (this can correspond to, say, a value of $D = 0.8$, but it is an experimental datum). The convex set in question is

$$C_D = \{D \,|\, 0 \leq D \leq D_C < 1\}. \tag{7.5.43}$$

This is essentially the idea of Kachanov (1958) and Rabotnov (1963), although the thermodynamical framework was to come only with the works of Chaboche (1974, 1978, 1989) and Lemaitre and Chaboche (1990), which would develop into a true *Continuum Damage Mechanics* (for short *C.D.M.*). It is obvious that D may be considered as an *internal variable* of state. The elementary power developed in an *isotropic* damage process thus reads

$$\Phi_D = Y\dot{D}, \qquad Y = -\partial W/\partial D, \tag{7.5.44}$$

where Y is the scalar thermodynamic force associated to D. This is much documented in Lemaitre and Chaboche (1990), Lemaitre (1992), and Maugin (1992a, Chapter 10). In the case of *anisotropic damage*, which is most often the case, an internal variable of higher order should be introduced.

Physical and experimental realities are much more complex than the simple picture just recalled. In particular, it is observed that *plastic hardening* decreases with increasing damage (it may even become *negative*) and the increase in plastic strain during so-called *tertiary creep* is also due to damage. *Tertiary creep* is that regime of creep observed where under relatively small stresses, strain grows rapidly in time. In an analysis which goes all the way to the neighborhood of fracture, one must then necessarily envisage a coupling between damage and elastoplasticity (Lemaitre, 1985). For the sake of example, we shall give in full the model of *ductile* damage (i.e. damage in the plastic regime) of Cordebois (1983) in which the notion of generalized standard materials is exploited (normality law in a plastic-like manner) along with *associated* plasticity (i.e. the plasticity criterion *is* the plastic potential). In this model constructed for small strains, α and β are the plasticity internal variables and we have:

- *laws of state*:

$$
\begin{gathered}
W = \bar{W}(\varepsilon^e, \theta, \alpha, \beta, D)\,, \qquad S = -\frac{\partial \bar{W}}{\partial \theta} \\
\sigma = \frac{\partial \bar{W}}{\partial \varepsilon^e}\,, \qquad A = -\frac{\partial \bar{W}}{\partial \alpha}\,, \qquad B = -\frac{\partial \bar{W}}{\partial \beta}\,, \qquad (7.5.45) \\
Y = -\frac{\partial \bar{W}}{\partial D}\,;
\end{gathered}
$$

- *intrinsic dissipation*:

$$
\Phi = \sigma : \dot{\varepsilon}^p + A \cdot \dot{\alpha} + B\dot{\beta} + Y\dot{D} \geq 0\,; \qquad (7.5.46)
$$

- *Convex of plasticity*:

$$
C_{\text{plastic}} = \{\sigma, A, B, Y \mid f(\alpha, A, B, Y) \leq 0\}\,. \qquad (7.5.47)
$$

More precisely, for an *isotropic* material in small strains we can take:

- *Laws of isotropic elasticity with damage*:

$$
\dot{\varepsilon}^e = (1-D)^{-1}\left\{\frac{1+\nu}{E}\dot{\sigma} - \frac{\nu}{E}(\operatorname{tr}\dot{\sigma})\mathbf{1}\right\}\,, \qquad (7.5.48)
$$

where E is Young's modulus and ν is Poisson's ratio of the virgin elastic material;

- *Plasticity evolution equation* (after determination of the plastic multiplier $\dot{\lambda}$):

$$
\dot{\varepsilon}^p = \frac{3}{2}H(f)\langle\dot{\sigma}_{\text{eq}}\rangle\left\{(K/M)^{(1-M)/M} - k_0\frac{D_c R_\nu}{\varepsilon_c - \varepsilon_D}\right\}^{-1} \cdot \frac{\sigma^d}{\sigma_{\text{eq}}}\,, \qquad (7.5.49)
$$

where β is the *cumulative plastic strain*, $\beta < \varepsilon_D$ entails $D = 0$, $D = D_c$ at the initiation (start) of macro-cracking, $\varepsilon = \varepsilon_R$ is the strain at fracture, and σ_{eq} is von Mises equivalent stress: $\sigma_{\text{eq}} = \| \sigma^d \| \cdot K$ and M are coefficients which can be measured in hardening tests in traction. The function $H(f)$ is such that for $f < 0$, $H = 0$, while $H = 1$ for $f = 0$. The criterion $f = 0$ is a straightforward generalization of Mises' criterion with hardening in which the stress σ has been replaced by an effective stress

$$\bar{\sigma} = \frac{\sigma}{(1 - D)}, \tag{7.5.50}$$

that accounts for elasticity weakening through damage. Finally,

$$R_c = \frac{2}{3}(1 + \nu) + 3(1 - 2\nu)(\sigma_m / \sigma_{\text{eq}}), \tag{7.5.51}$$

where σ_m is the mean stress;

- *Evolution equation for D* (once $\dot{\lambda}$ has been eliminated):

$$\dot{D} = \frac{D_c}{\varepsilon_R - \varepsilon_D} R_\nu \dot{\beta}. \tag{7.5.52}$$

The above modeling is complete, thermodynamically admissible, and all its coefficients $(E, \nu, k_0, K, M, \varepsilon_D, \varepsilon_R, D_c)$ have been experimentally determined for steel 35 NCD 16 (French standards).

The following remarks are in order:

(i) From Eqs. (7.5.48) and $(7.5.45)_6$ it is easily seen that the thermodynamic conjugate force of the scalar damage parameter D is none other than the *elastic energy* of the *undamaged* material;

(ii) For loading at high temperature one should generalize the above model by coupling damage with elasto-*visco*-plasticity;

(iii) Damage progresses essentially during *periodic* loading. There is thus a special interest in *cyclic plasticity* (and *creep*) and its coupling with damage. For this we refer to the original work of Chaboche (1978) — also Dafalias and Popov (1976) — which makes extensive use of the concept of internal variable;

(iv) Clearly, *porosity* is a parameter akin to damage and can also be viewed as an internal variable in a thermodynamic modeling. A degree of *humidity* or *moisture* could also be introduced in a similar way to assess the deterioration of some materials under these effects;

(v) In recent works it has been envisaged that *damage* could present a marked *nonlocal* feature. If this *nonlocality* is nonetheless weak, then it can be accounted for by introducing the spatial gradient of the variable D, i.e. ∇D, in the energy density. For instance (Maugin, 1990a), in the case of damage coupled *only* to elasticity, we could consider the following energy density in small strains:

$$W = \bar{W}(\varepsilon, \theta, D, \nabla D) , \tag{7.5.53}$$

and thereafter apply the formulation of Paragraph 4.7B. For example, with

$$W = (1 - D)W_e(\varepsilon, \theta) + \frac{1}{2}\nu_D(\nabla D)^2 , \tag{7.5.54}$$

where W_e is the thermoelastic energy of the virgin sample (at $D = 0$) and the material coefficient $\nu_D > 0$ accounts for *damage localization*, we have from Eqs. (4.7.55)–(4.7.59)

$$\begin{aligned} \sigma &= \frac{\partial W}{\partial \varepsilon} = (1 - d)\frac{\partial W_e}{\partial \varepsilon} , & \mathcal{A} &= W_e(\varepsilon, \theta) + \nu_D \nabla^2 D , \\ \mathbf{k} &= \theta^{-1}(\nabla D)\dot{D} , & \Phi &= \mathcal{A}\dot{D} - (\mathbf{S} \cdot \nabla)\theta \geq 0 . \end{aligned} \tag{7.5.55}$$

This provides a system of *evolution* for the *whole thermomechanical* problem in the following form:

$$\begin{aligned} &\dot{\mathbf{u}} = \mathbf{v} , \qquad \dot{\varepsilon} = (\nabla \dot{\mathbf{u}})_S , \qquad \rho_0 \dot{\mathbf{v}} = \operatorname{div} \sigma , \\ &\dot{\sigma} = -\bar{\sigma}\dot{D} + (1 - D)(\mathbf{E} \cdot \dot{\varepsilon} - \tau\dot{\theta}) , \\ &\tau_D \dot{D} = (W_e/W_0) + l_D^2 \nabla^2 D , \\ &C\dot{\theta} + \nabla \cdot (\theta \mathbf{S}) = \Phi_{\text{intr}} + \Phi_{te} , \end{aligned} \tag{7.5.56}$$

where

$$\mathbf{E} = \frac{\partial^2 W_e}{\partial \varepsilon \otimes \partial \varepsilon} , \qquad \tau = -\frac{\partial^2 W_e}{\partial \varepsilon \partial \theta} , \qquad \mathbf{S} = -\kappa \nabla \theta , \tag{7.5.57}$$

where W_0 is a reference energy, τ_D is a characteristic time, $\Phi_{\text{intr}} = \mathcal{A}\dot{D}$, Φ_{te} is the thermoelastic dissipation, l_D is a characteristic length of damage localization, and $\bar{\sigma}$ is defined in (7.5.50). For the coupling with *plasticity*, we refer the reader to Maugin (1990a). Another approach where ∇D is involved but D is considered as an *observable variable* of state (this matter can be discussed) is due to Frémond and Nedjar (1993). If the *nonlocality* is more pronounced (i.e. larger range of l_D), then one may be obliged to have recourse to a constitutive equation of the *functional* type over space but nevertheless with a sufficiently fast decreasing kernel (cf. Pijaudier-Cabot and Bazant, 1987). Our general view on this problem of nonlocality is given in Maugin (1979c).

7.6. Relationship with Microscopic Theory

Plasticity and viscoplasticity are known to be intimately related to the irreversible motion of defects such as dislocations while damage is related to microcracking and the growth of microcavities. Establishing a bridge between these two levels of descriptions is an active and fruitful scientific activity, especially as it concerns the detection of what should be *good* internal variables for the macroscopic thermodynamic description. While dislocation densities defined in different manners (total length of dislocation lines in a volume, number of dislocation lines intersecting a unit area, etc.) are obvious candidates for the "nomination" as internal variables bridging the two scales, we have also seen in Sec. 4.6 that slips in single slip systems [see the evolution Eq. (4.6.40)] could be appropriate internal variables in *metal plasticity*. Among the most original proposals, however, we must single out the Ponter–Bataille–Kestin (1979) model of *viscoplastic deformation* for it shows that, at sufficiently low temperatures and strain rates, and following the careful analysis of Lambermont (1974), a meaningful internal variable can be the *area swept by the loops of Frank–Read sources.* As these expand and contract repeatedly (see Fig. 7.5), a microscopic instability is exhibited along the mechanical loading curve, reflecting thus the real process that takes place at the microscale. More precisely, according to this picture, a *good* internal variable α is given by

$$\alpha = \frac{SNb}{L^3}, \tag{7.6.58}$$

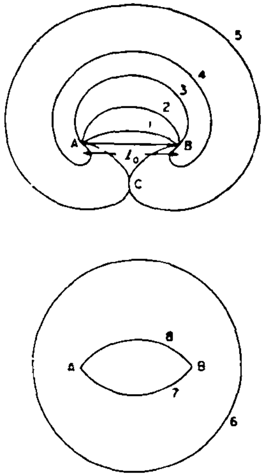

Fig. 7.5. Mode of operation of Frank–Read source (eight different phases).

where b is Burgers' vector, N is the uniform distribution of noninteracting identical Frank–Read sources in the volume L^3, and S is the total area swept out by the dislocation lines. In the linear case, Ponter *et al.* (1979) have determined an explicit model which provides the energy $W = W(\varepsilon, \alpha, \theta)$, where ε is an averaged strain (over volume L^3) and α is given by (7.6.58). The average plastic strain is then given by

$$\varepsilon^p = \frac{\alpha}{2}(\mathbf{n} \otimes \mathbf{m} + \mathbf{m} \otimes \mathbf{n}), \tag{7.6.59}$$

where $\mathbf{m}$ is a unit vector perpendicular to the initial position of the dislocation line and $\mathbf{n}$ is the normal unit vector to parallel slip planes. The model is *not* generalized standard as the energy may be *nonconvex* in the above α variable. The micro-instabilities *cannot be controlled* by external forces; we recognize here one of the characteristic features of phenomena amenable by *T.I.V.* Furthermore, as these micro-instabilities are of small extent, they are not always clearly observable on the macroscopic loading curve which exhibits at a gross scale only a rather regular hardening (cf. Fig. 7.6). But these instabilities are known to manifest themselves collectively through the phenomenon of *acoustic emission* (compare to the Barkhausen jumps in Sec. 9.7). Further research along this line is reported in Grolig (1985). This, in our opinion, is one of the most fertile models devised in the spirit of *T.I.V.* According to the analysis of

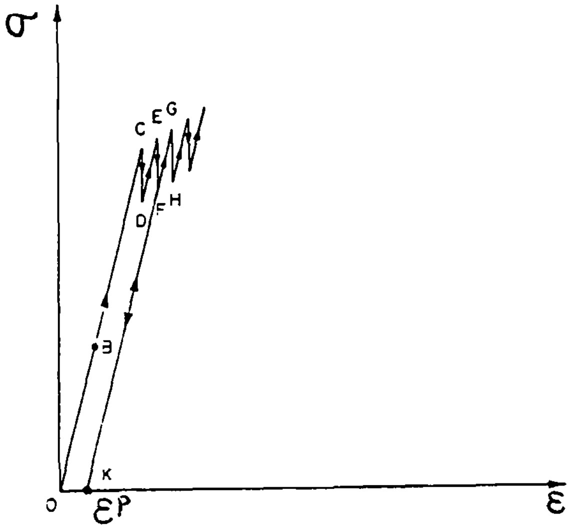

Fig. 7.6. Stress-strain behavior of plasticity model exaggeratingly showing the microinstabilities along the hardening curve.

Muschik (1990a,b), this model fits perfectly well with the framework given in Chapter 5.

Other mechanical models exhibiting a marked *hysteresis* are those related to *shape-memory alloys.* In a thermodynamical description using the concept of internal variables, these are then the *phase fractions* of martensite and austenite components; They are thus directly related to measurable metallurgical quantities (cf. Frémond, 1987, Wilmanski, 1992). The observed effects, however, may be *pseudo-elastic* in that they result from the *nonconvexity* of the strain energy function. This is called "*reversible plasticity*" of crystals by some authors (Boiko "*et al.*, 1991). Still an essentially *internal-variable* thermodynamic description is feasible (Wilmanski, 1993).

7.7. Remark on Elastoplastic Composites

Although we do not return to the intimate microscopic level, it is of interest to see if a description at a *mesoscale* has an influence on one at the macroscopic scale and how does the notion of internal variable emerge in the transition

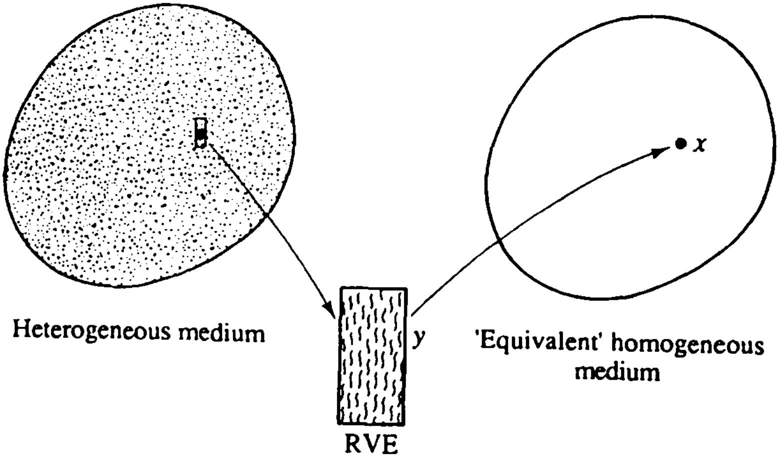

Fig. 7.7. Representative volume element and the two scales y (micro) and x (macro).

between the two scales. This influence is illuminating in the case of the elastoplastic *composites* to which we alluded in Paragraph 4.7A. Composite materials may be thought of as *highly heterogeneous* materials exhibiting two spatial scales. One, y, is that of the strong inhomogeneities which may be averaged out over a so-called *representative volume element* (*R. V.E.*) — see Fig. 7.7 — and thus allowing the passing to the second scale, the macroscopic one, x. Let $\langle\cdots\rangle$ denote the average operation over an *R. V.E.*, so that macroscopic stress and strain, Σ and $\mathcal{E}$, are defined by

$$\begin{aligned}\Sigma(x) &= \langle\sigma\rangle = \frac{1}{V}\int_{RVE}\sigma(x,y)d^3y\,,\\ \mathcal{E}(x) &= \langle\varepsilon\rangle = \frac{1}{V}\int_{RVE}\varepsilon(x,y)d^3y\,.\end{aligned}\tag{7.7.60}$$

where V is the volume of the *R.V.E.* The local strain $\varepsilon(\mathbf{u})$ of the problem is naturally rewritten as

$$\varepsilon(\mathbf{u}) = \mathcal{E} + \varepsilon(\mathbf{u}^*)\,, \qquad \langle\varepsilon(\mathbf{u}^*)\rangle = \mathbf{0}\,, \tag{7.7.61}$$

where $\mathbf{u}^*$ represents the *fluctuation* part.

In most *homogenization techniques* the following "*principle of macrohomogeneitity*" applies. Let $\bar{\sigma}$ and $\bar{\mathbf{u}}$ be so-called *statically admissible* (i.e. compatible with the data in *forces*) and *kinematically admissible* (i.e. compatible with the data in displacement) *fields*, respectively. Then we have the following remarkable equality concerning *mechanical works*:

$$\langle \bar{\sigma} : \varepsilon(\bar{\mathbf{u}}) \rangle = \bar{\Sigma} : \bar{\mathcal{E}} \,. \tag{7.7.62}$$

This was formulated by R. Hill (1965) and J. Mandel (1971). In *statistical theories* (e.g. Kröner, 1972), (7.7.62) is viewed as an *ergodic hypothesis*. Now the important results are as follows.

(i) Any quantity which is an *additive* function, i.e. *extensive* in the thermodynamical language, is averaged in the *micro-macro transition*. That is, for example (the bar here denotes the result of the averaging)

$$\begin{aligned} \bar{\rho} &= \langle \rho \rangle \,, && \text{density} \\ \bar{\rho} E &= \langle \rho e \rangle \,, && \text{internal energy} \\ \bar{S} &= \bar{\rho} N = \langle \rho \eta \rangle \,, && \text{entropy} \\ \bar{\Phi} &= \langle \Phi \rangle \,, && \text{dissipation}\,. \end{aligned} \tag{7.7.63}$$

(ii) In elastoplastic components, the elastoplastic solution can be formulated as the *sum* of an *elastic solution* (with superscript E) with identical data and loading, and a *residual field* (with a superscript r), the latter being self-equilibrated, i.e. corresponding to vanishing data in the body and at the boundary (cf. Maugin, 1992a, p. 78). This is independent of scale and here it is applied at the *microscale* y. We can write thus

$$\begin{aligned} \sigma(t) &= \sigma^{E}(t) + \sigma^{r}(t) \\ \mathbf{u}(t) &= \mathbf{u}^{E}(t) + \mathbf{u}^{r}(t)\,, \end{aligned} \tag{7.7.64}$$

where the presence of the residual solution is what distinguishes an *essentially elasto*-plastic *solution* from a purely elastic one.

For the sake of simplicity and because it helps one to emphasize a characteristic property of homogenization, we assume that the elastoplastic constituent are *linear elastic-perfectly plastic* (no hardening) at the microscale. Then the strict orthogonality condition (7.3.21) holds at the microscale. What about the homogenized elastoplastic material at the x scale? By an average of the elastic strain energy it was shown that (Suquet, 1982)

$$\rho E = \frac{1}{2}\Sigma : \mathbf{S}^{\text{hom}} : \Sigma + \frac{1}{2}\langle \sigma^{r} : \mathbf{S} : \sigma^{r} \rangle \,, \tag{7.7.65}$$

where $\mathbf{S}$ is the tensor of microscopic elastic compliances, and $\mathbf{S}^{\text{hom}}$ is that of the homogenized elastoplastic material. The latter is deduced from the former by

$$\mathbf{S}^{\text{hom}} = \langle \mathcal{C}^T : \mathbf{S} : \mathcal{C} \rangle , \tag{7.7.66}$$

where $\mathcal{C}$ is the so-called tensor of *stress localization* defined by $\sigma = \mathcal{C} : \Sigma$, (an application of $\mathbb{R}^6$ onto $\mathbb{R}^6$). The expression (7.7.65) is tantamount to granting to σ^r the status of *thermodynamic internal variable* of state although it is a field (cf. Suquet, 1987). The important result, however, is that on averaging the orthogonality condition (7.3.21) one arrives at the *inequality*

$$\dot{\Sigma} : \dot{\mathcal{E}}^p = \langle \dot{\sigma}^r : \mathbf{S} : \dot{\sigma}^r \rangle \geq 0 , \tag{7.7.67}$$

where

$$\mathcal{E}^p = \mathcal{E} - \mathcal{E}^e , \qquad \mathcal{E}^e = \mathbf{S}^{\text{hom}} : \Sigma . \tag{7.7.68}$$

In other words the homogenized elastoplastic material satisfies *Drucker's inequality* for a material with *positive hardening*. This hardening finds its origin in the residual stresses of the microscale. We may say that the homogenization transition "stabilizes" the elastoplastic material. By selecting the *local flow rule* as the *microscopic elastic energy* itself, i.e.

$$f(y, \sigma) = \frac{1}{2} \sigma : \mathbf{S} : \sigma - k_0 , \tag{7.7.69}$$

Michel (1984) has provided a striking example where the homogenized medium exhibits the behavior of a *generalized standard material*. Indeed, in his formulation we have:

- *laws of state*:

$$\begin{gathered} \bar{\rho} E(\mathcal{E}, \mathcal{E}^p, \alpha) = \frac{1}{2} (\mathcal{E} - \mathcal{E}^p) : \mathbf{E}^{\text{hom}} : (\mathcal{E} - \mathcal{E}^p) + \frac{1}{2} h \alpha^2 , \quad h \geq 0 , \\ \Sigma = \bar{\rho} \frac{\partial E}{\partial \mathcal{E}} = -\bar{\rho} \frac{\partial E}{\partial \mathcal{E}^p} , \qquad \mathcal{A} = -\bar{\rho} \frac{\partial E}{\partial \alpha} = -h \alpha ; \end{gathered} \tag{7.7.70}$$

- *evolution equations*:

$$\begin{aligned} \dot{\mathcal{E}}^p &= \dot{\lambda} \mathbf{S}^{\text{hom}} : \Sigma = \dot{\lambda} \frac{\partial \mathcal{F}}{\partial \Sigma} (\Sigma, \mathcal{A}) , \\ \dot{\alpha} &= \dot{\lambda} \frac{\partial \mathcal{F}}{\partial \mathcal{A}} (\Sigma, \mathcal{A}) \end{aligned} \tag{7.7.71}$$

with the *macroscopic flow rule*

$$\mathcal{F}(\Sigma, \mathcal{A}) = \langle f \rangle = \frac{1}{2}\Sigma : \mathbf{S}^{\mathrm{hom}} : \Sigma + \frac{1}{2h}\mathcal{A}^2 - \langle k_0 \rangle , \tag{7.7.72}$$

while the following relations exist with the microscopic scale:

$$\begin{aligned} h &= \langle \sigma^r(0) : \mathbf{S} : \sigma^r(0) \rangle , \\ \sigma^r(t) &= \sigma^r(0) \exp\{-[\lambda(t) - \lambda_0]\} = \sigma^r(0)\alpha(t) . \end{aligned} \tag{7.7.73}$$

That is, only one parameter $\alpha(t)$ allows one to determine the whole field of residual stresses once the initial distribution $\sigma^r(0)$ is known (this may be a difficult but not insuperable task). The latter, through its energy, determines the hardening modulus h. It is checked that the macroscopic dissipation $(7.7.63)_4$ is given by

$$\bar{\Phi} = \langle \Phi \rangle = \langle \sigma : \dot{\varepsilon}^p \rangle = \dot{\lambda} \langle \sigma : \mathbf{S} : \sigma \rangle = \dot{\lambda} \langle k_0 \rangle . \tag{7.7.74}$$

We refer to Michel (1984), Suquet (1987) and Maugin (1992a, Chapter 9) for more detail on this *micro-macro* transition in which the flow surface $\mathcal{F} = 0$ expands until its reaches $\langle k_0 \rangle$.

7.8. Remark on the Heat Equation

In most of the above presented developments, couplings with thermal effects were ignored or, at the very least, considered secondary. Obviously, temperature plays a fundamental role in temperature-driven phase transitions concerning mechanical properties, and thermal fields, in general, influence the mechanical response. But what is perhaps more essential in concluding this chapter is to note that both dissipative and nondissipative phenomena (thermoelasticity belong to the last class) also influence the distribution of temperature, and this influence may serve as an experimental means of detection, or even *measurement*, of dissipation due to both *macro* and *semi-micro-* (through internal variables) irreversibilities . This is particularly true with the experimental technique known as *infrared thermography*. The latter consists in reconstructing the spatial distribution of temperature, hence also its second-order space derivatives and its Laplacian from point-like thermal measurements — as in a finite-difference numerical scheme or in the same way as a lattice with nearest neighbors reconstructs the continuum with second-order derivative — via a scanning infrared camera. By the same token this reconstructs the spatial distribution of *intrinsic* or *thermoelastic dissipation*.[5] The possibility in

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[5] Although thermoelasticity is not a dissipative phenomenon, *per se*, it contributes a term in the heat equation (this term often is neglected because it is quadratic jointly in thermal and strain fields).

fact exists in dynamics to discriminate between dissipations of *viscoelastic* and *plastic* types by considering the in-phase and out-of-phase parts of the temperature signal (as the corresponding dissipations are homogeneous either of degree two or of degree one in strain rates). As explained in greater detail in Maugin (1992a, Chapter 12), the main theoretical and practical ingredient here is the *heat equation.* Examples of such equations were already given in Eqs. (3.3.96) and the last of (7.5.56). In all generality, this equation is none other than a transformed form of the energy equation, i.e. in a sufficiently general case (no body heat source):

$$C\dot{\theta} + \nabla \cdot (\theta \mathbf{S}) = \Phi_{\text{intr}} + \Phi_{te}\,, \tag{7.8.75}$$

with

$$\begin{aligned} C &= -\theta \frac{\partial^2 W}{\partial \theta^2} > 0\,, \\ \Phi_{te} &= \theta \sum_{\beta} \frac{\partial^2 W}{\partial \theta \partial \varepsilon^e} : \dot{\varepsilon}^e + \theta \frac{\partial^2 W}{\partial \theta \partial \alpha} \cdot \dot{\alpha}\,, \end{aligned} \tag{7.8.76}$$

and Φ_{intr} in general includes both "viscous" and "plastic" contributions, depending on the dissipative model considered. The heat equation (7.8.75) is completed by the constitutive equation for $\mathbf{S}$ directly in terms of $\nabla\theta$, e.g. in the simple isotropic case of Fourier, $\mathbf{S} = -\kappa(\theta)\nabla\theta$, with $\kappa > 0$. A reconstruction of the left-hand side of Eq. (7.8.75) by the above method will therefore provide a reconstruction of the spatial map of the right-hand side, i.e. the dissipation. The practical exploitation of Eq. (7.8.75) still requires some kind of linearization in θ about the ambient temperature θ_0 and a so-called *natural state.* It should be written in the material framework in the case of finite strains. We refer the reader to our book on plasticity and fracture (1992a, Chapter 12) for specific applications of (7.8.75) to these two behaviors.

Chapter 8

THERMODYNAMICS OF FRACTURE

If only I could break my leg, what
a lot of scientific work I could do.
Thomas H. Huxley (1825–1895)

8.1. Preliminary Remark

Although one may have recourse to *glue*, i.e. some expense of energy, it is clear that the *fracture of solids* belongs to the class of *thermodynamically irreversible phenomena.* Obviously, even a perspicacious physicist/thermodynamicist such as Duhem could not envisage that fracture would one day be incorporated in the framework of *irreversible thermodynamics.* That energy concepts had to be present and played an important role in fracture became evident with the pioneering work of A. A. Griffith in the 1920s, when this scientist related fracture to the notion of *surface energy* — the energy we need to suppress the atomic bonds along the fractured surface. It is only in the period 1970–1990 that a sound thermodynamical framework was to develop with the exploitation of the first and second laws, and the working out of a sensical expression of the *dissipation* accompanying fracture. The differences and resemblances with other typically irreversible behaviors, viscoelasticity and plasticity in particular, were also to be emphasized but rather belatedly.

The essential fact to be recognized in the phenomenon of fracture is that dissipation, in any, is manifested first through the irreversible change in the domain occupied in a continuous (say, simply connected) way by the material. Fracture resembles other phenomena such as the expansion of cavities or the motion of dislocations, all in fact *defects* in the material body. That is, the local behavior described by constitutive equations and the local dissipation inequality as a mathematical constraint, is not so relevant at first. This is why the most fruitful analysis of fracture, that one which captures the essential features while remaining relatively simple, is to be conducted in the frame of *brittle fracture*, i.e. when the material at hand allows for crack propagation while it still has an *elastic* response locally. Accounting for more complicated local behaviors comes next in order of complexity, but it is not so rewarding from the point of view of understanding.

Using as a basis this important remark, we present here the thermodynamics of fracture, essentially *brittle fracture*, in two guises: one of these is naturally based on the exploitation of the *global energy equation* and the computation of the *global dissipation* occurring during fracture. The other is perhaps more difficult to comprehend but it is based on the recognition that fracture indeed takes place in *the material* and may be represented in an abstract way as if a *fictitious force* (of a non-Newtonian nature)[1] was trying to pull — "to suck" — the crack in the material. This is visually manifested by the extension of the crack. This is the point of view that we advocated recently as a general approach, not only to fracture, but to several problems of mechanics and physics that *do* consider a material manifold, e.g. a crystal lattice, as the arena of interesting effects, and mostly *defects* (see Maugin, 1993a). This has dictated the logic of the succession of sections. The most traditional energy aspects of brittle fracture are presented in Secs. 8.2 and 8.3 both with neglect and account of thermal couplings. This is the viewpoint of Cherepanov (1967 to 1985), Rice (1968), Bui (1978), Nguyen Quoc Son (1980), and Freund (1990). The point of view of *material forces*, that was strongly influenced by the original work of J. D. Eshelby (1951), is given in the long Sec. 8.4 and further commented upon for the cases of thermoelasticity and elastoplasticity in Sec. 8.6. Section 8.5 presents the view that the total system "material plus elastic defects (e.g. crack)" is a *conservative one*, although written in local form, when the formalism of *generalized functions* is dutifully exploited. The "energy of defects" goes all in dissipation, obviously, as it is only a *truly potential energy* that is no longer available in any form except heat, once the defects have irreversibly progressed.

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[1] This fictitious force, later called *material force*, acts not on elements of mass like a Newtonian force (e.g. gravity) nor on elements of charge like the Lorentz force, but on *defects* (cracks, cavities, dislocations, disclinations, solitons...) which are localized singular solutions of partial differential equations.

8.2. Energy Aspects of Brittle Fracture (No Thermal Fields)

In a general way, the first law of thermodynamics for a material body occupying the regular domain Ω of $\mathbb{E}^3$ in its current configuration K_t is given by Eq. (2.3.53), i.e. in the absence of body forces and heat sources,

$$\frac{d}{dt}\int_{\Omega}\rho\left(\frac{1}{2}\mathbf{v}^2+e\right)d\Omega=\int_{\partial\Omega}(\mathbf{T}^d\cdot\mathbf{v}-\mathbf{q}\cdot\mathbf{n})da\,, \tag{8.2.1}$$

where $\partial\Omega$ is the regular boundary of Ω equipped with unit outward normal $\mathbf{n}$.

The problem of fracture: We are interested in the following problem. Although we shall consider that the material itself is *not dissipative*, for instance, it is a *linear elastic* material and we can neglect heat conduction (quasi-adiabaticity), so that there is no *local dissipation* at all regular points in Ω, we look at the problem in Fig. 8.1 where the material region Ω may evolve *irreversibly* (in quasi-statics) through the progress of a *macroscopic crack* called Σ. Its two

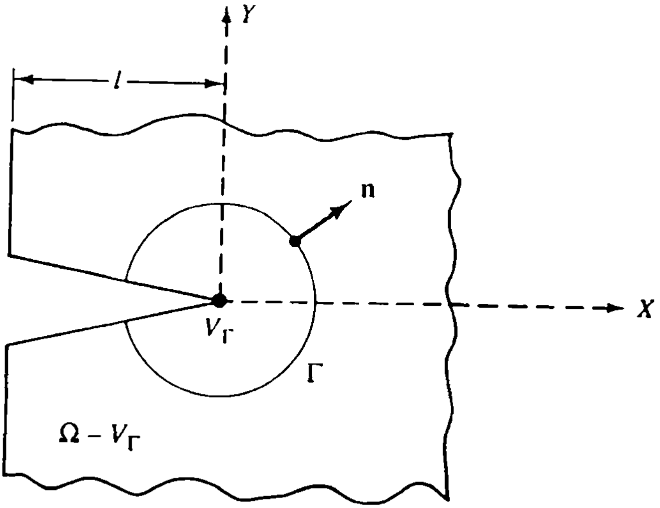

Fig. 8.1. Straight-through crack (frame moving with the tip of the crack).

stress-free faces Σ^+ and Σ^-, although remaining geometrically in contact, cannot solder back once separated by rectilinear fracture (Fig. 8.1). This is where the *global irreversibility* of the problem resides. On a closer look it appears that the irreversibility, from the thermodynamic point of view (see below), is the combined result of this geometric fact (the irreversible separation) and the fact that the tip of the crack (that line perpendicular to the figure passing through the end point of the crack) carries with it a singularity in the fields that causes *dissipation.* This dissipation should correspond to the energy spent in loading the body from which is subtracted the energy consumed from the body. Thus, *when* Σ *progresses*, (8.2.1) without kinetic energy and heat-flux term, should be replaced by the expression of the total dissipation

$$\Phi(\Omega(l)) = \int_{\partial\Omega(l)} \mathbf{T}^d \cdot \mathbf{v} da - \frac{d}{dt} \int_{\Omega(l)} \rho e d\Omega . \tag{8.2.2}$$

Here Ω is naturally parametrized by the actual length of the crack. If the crack does not progress, i.e. Ω does not evolve, then $\Phi(\Omega(l)) = 0$. In small strains we can replace $\mathbf{v}$ by $\dot{\mathbf{u}}$, $\mathbf{T}^d$ by $\sigma \cdot \mathbf{n}$ and ρe by W, and for elasticity, $W = W(\varepsilon)$ where $\varepsilon = (\nabla \mathbf{u})_s$. We adopt the notation in Fig. 8.2.

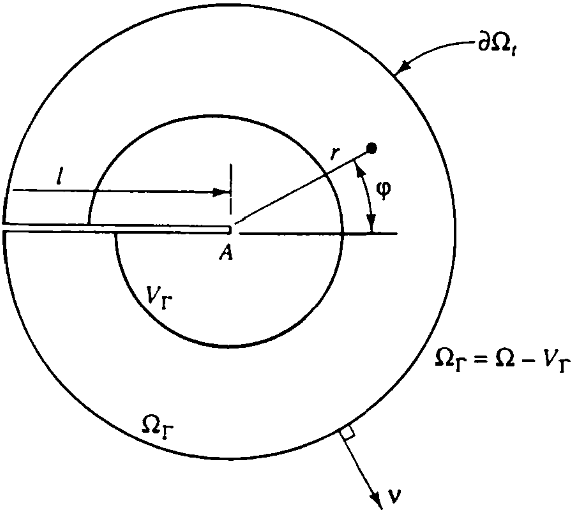

Fig. 8.2. Isolating the singularity.

In the absence of propagation of the crack, $\dot{l} = 0$, there is no difficulty in evaluating the second contribution in the right-hand side of (8.2.2) as Ω is fixed, so that

$$\frac{d}{dt}\int_{\Omega} W d\Omega = \int_{\Omega} \frac{dW}{dt} d\Omega = \int_{\Omega} \sigma : \dot{\varepsilon} d\Omega . \tag{8.2.3}$$

But this is simply *wrong* when the crack progresses. The reason for this follows from a short reasoning concerning the *mechanical problem* (determination of the displacement and stress field in the vicinity of the tip) around the crack. Although the exact solution of this problem depends on the shape of the body and the loads, an idea of the behavior of the solution may be found heuristically (cf. Maugin, 1993a). In *linear elasticity*, it is found that up to an irrelevant angular factor the *displacement field* for the *plane problem* of elasticity behaves like $\sqrt{r}$ as r goes to zero, if r is the radius from the tip. Thus the relevant strain components ε behaves like $1/\sqrt{r}$ and similarly for the stress components σ. These evaluations are valid in a frame (X, Y) attached to the tip. Obviously $X = x - l(t)$. Computing the time derivative of ε, we will thus obtain

$$\dot{\varepsilon} = \dot{\varepsilon}_t(X, Y) = \dot{l}\frac{\partial}{\partial X}\varepsilon_t(X, Y) , \tag{8.2.4}$$

where we used the formula of time differentiation in a moving frame. We see that $\partial\varepsilon_t(X, Y)/\partial x$ will behave like $r^{-3/2}$ as r goes to zero. Whence the last integral in (8.2.3) will diverge, so that some more precautions must be taken. To perform the computation of the second contribution in (8.2.2) when the crack progresses, we must *isolate* the singularity. For this we follow the notation in Fig. 8.2 and call Γ a contour starting on one lip Σ^- of the crack and ending at the other lip, Σ^+, and delimiting the volume V_Γ. The outside is noted $\Omega - V_\Gamma$. We write in an obvious manner

$$\frac{d}{dt}\int_{\Omega} W d\Omega = \frac{d}{dt}\int_{V_\Gamma} W d\Omega + \frac{d}{dt}\int_{\Omega - V_\Gamma} W d\Omega . \tag{8.2.5}$$

As Γ is fixed in the moving (X, Y)-frame, we have trivially

$$\frac{d}{dt}\int_{V_\Gamma} W d\Omega = \int_{V_\Gamma} \sigma : \dot{\varepsilon}_t(X, Y) d\Omega , \qquad (X, Y) \text{ fixed} , \tag{8.2.6}$$

where $\dot{\varepsilon}_t$ behaves like r^{-1} hence the integrability in (8.2.6). Besides, by using the formula for the material time derivative of a nonmaterial volume integral, we have

$$\frac{d}{dt}\int_{\Omega - V_\Gamma} W d\Omega = \int_{\Omega - V_\Gamma} \sigma : \dot{\varepsilon} d\Omega - \int_\Gamma W\dot{l}(\mathbf{e}_1 \cdot \mathbf{n}) d\Gamma\,, \tag{8.2.7}$$

since the volume V_Γ moves as a whole with speed $\dot{l}$ in the direction of unit vector $\mathbf{e}_1$. We shall note $n_1 = \mathbf{e}_1 \cdot \mathbf{n}$ where $\mathbf{n}$ is the unit outward pointing normal to Γ.

Now we write the *energy balance* for the region $\Omega - V_\Gamma$ in which *neither dissipation nor singularities* occur, keeping in mind that $\mathbf{n}(\Gamma) = -\mathbf{n}(\partial\bar{\Omega})$. We have

$$\begin{aligned}\int_{\Omega - V_\Gamma} \sigma : \dot{\varepsilon} d\Omega &= \int_{\partial\bar{\Omega}} \dot{\mathbf{u}} \cdot \sigma \cdot \mathbf{n} ds \\ &= \int_{\partial\Omega} \dot{\mathbf{u}} \cdot \sigma \cdot n ds - \int_\Gamma \dot{\mathbf{u}} \cdot \sigma \cdot \mathbf{n} d\Gamma\,,\end{aligned} \tag{8.2.8}$$

at time t. With this given, as well as (8.2.7), (8.2.2) may be expressed as

$$\Phi(\Omega(l)) = \int_\Gamma (W\dot{l}n_1 + \dot{\mathbf{u}} \cdot \sigma \cdot \mathbf{n}) d\Gamma + \int_{V_\Gamma} \sigma : \dot{\varepsilon}_t(X,Y) d\Omega\,, \tag{8.2.9}$$

where the integrand of the last contribution is integrable. If we now take the limit where we make the contour Γ tend towards the crack tip ($\Gamma \to 0$) and if we account for this integrability, there remains

$$\Phi(\Omega(l), \dot{l}) = \lim_{\Gamma \to 0} \int_\Gamma (W\dot{l}n_1 + \dot{\mathbf{u}} \cdot \sigma \cdot \mathbf{n}) d\Gamma\,, \tag{8.2.10}$$

since the second contribution tends towards zero. This shows the *localization* of dissipation at the tip of the crack.

At this point it is appropriate to note that, for any physical quantity f attached to the tip of the crack, $\dot{f}$ has the *same* singularity as — $(\partial f/\partial \mathbf{x})\dot{l}$. This, in particular, applies to $\dot{\mathbf{u}}$, so that when Γ goes to zero, $\dot{\mathbf{u}}$ behaves like $-(\partial \mathbf{u}/\partial \mathbf{x})\dot{l}$. Taking $\dot{l}$ outside the integral and the limit, we can rewrite (8.2.10) as

$$\Phi = \Phi(G, \dot{l}) = G(\Sigma)\dot{l}\,, \tag{8.2.11}$$

where we have set

$$G(\Sigma) = \lim_{\Gamma \to 0} \int_\Gamma \left(W n_1 - \mathbf{n} \cdot \sigma \cdot \frac{\partial \mathbf{u}}{\partial x} \right) d\Gamma\,. \tag{8.2.12}$$

Because of the way it was introduced [Eq. (8.2.2)], and the fact that (8.2.11) is defined as a dissipation or a *power*, G is called the *energy-release rate*: It is the energy released to the crack per unit extension length and unit time during the progress of the crack. The expressions (8.2.11) and (8.2.12) merit three important comments:

(i) the first one brings us back to *irreversible thermodynamics*. It is clear that the *global dissipation* (8.2.11) is exactly written in the traditional *bilinear form of T.I.P.*, where G is the thermodynamic force conjugate to the velocity $\dot{l}$. Thus we can apply *T.I.P.*, just like in plasticity, viscoplasticity or damage, and envisage several types of thermodynamic behaviors for the "force" G. Close to physical reality is a *plastic-like* behavior for which G is constrained to a *closed convex set* (belonging to $\mathbb{R}$). This is nothing but a *criterion of progress of the crack* in the form:

Griffith's criterion: There exists a threshold value G_c of the energy-release rate G such that:

$$\begin{aligned} & G \in C_F = \{G \leq G_c\} \\ & \dot{l} = 0 \text{ (no progress) if } G < G_c\,, \\ & \dot{l} \geq 0 \text{ (possible progress) if } G = G_c\,. \end{aligned} \tag{8.2.13}$$

As G is dimensionally a *surface energy*, we see that the criterion (8.2.13) is none other than the criterion proposed in the 1920s by A. A. Griffith, one of the creators of the theory of fracture. Just like plasticity, the above can also be formulated in a more abstract form, e.g.

$$\dot{l} \in \partial\varphi(G)\,, \tag{8.2.14}$$

where ∂ indicates the subdifferential and $\varphi(G)$ is a *pseudo-potential of dissipation*. For Griffith's criterion $\varphi(G)$ is none other than the *indicator function of the convex* $\{G \leq G_c\}$, i.e.

$$\varphi(G) = 0 \text{ if } G \leq G_c\,, \qquad \varphi(G) = +\infty \text{ if } G > 0\,. \tag{8.2.15}$$

We can then also write a *principle of maximal dissipation* in the form

$$(G - G^*)\dot{l} \geq 0\,, \qquad \forall G^* \in C_F\,. \tag{8.2.16}$$

This fracture behavior describes well the situation for *brittle fracture*, i.e. in those materials where fracture occurs in the *elastic* mechanical regime. For material such as polymers or rubber, fracture would be of the *viscoelastic* type. Accordingly, we can use (8.2.14) with, for example,

$$\varphi(G) = \frac{1}{2\eta_F} G^2 , \tag{8.2.17}$$

yielding an evolution law for l as $G = 2\eta_F \dot{l}$, which looks just like a Newtonian model. A law of the *viscoplastic* type may be even more appropriate. We let the reader construct such a law by analogy with the case of Bingham fluids.

(ii) We can set

$$G = \lim_{\Gamma\to 0} J_\Gamma , \qquad J_\Gamma := \int_\Gamma \left(W n_1 - \mathbf{n} \cdot \sigma \cdot \frac{\partial \mathbf{u}}{\partial x} \right) d\Gamma . \tag{8.2.18}$$

It happens that the left-hand side of the definition $(8.2.18)_2$ is independent of the choice of Γ in the case of an *elastic (linear or not) and homogeneous material*. This was discovered by J. R. Rice (1968); (also Cherepanov, 1967). The contour-independent integral J (no more Γ) defined in (8.2.18) is called the Rice–Eshelby–Cherepanov integral. This property of independence of the contour is essential in practical applications that deliver an estimate of G.

(iii) With a dead loading at $\partial\Omega$, we notice that (8.2.2) can also be written as

$$\Phi = -\frac{\partial P}{\partial l} \dot{l} , \qquad \text{i.e.} \qquad G = -\frac{\partial P}{\partial l} , \tag{8.2.19}$$

if P denotes the total *potential energy of the body* $\Omega(l)$. Notice that P is a *functional of* l, as l intervenes through the change in time of the volume of integration (cf. Maugin, 1992a, pp. 149–152).

8.3. On Account of Thermal Fields

The localization of dissipation at the tip of a crack progressing in a glassy material is experimentally observed by a concentration of heat at the tip via infrared thermography. There is thus need for a fully *thermomechanical analysis* of brittle fracture. To proceed along this line one must consider the full energy balance (8.2.1) with $\Omega = \Omega(l(t))$, $\dot{l}$ nonzero. We must adjoin to this the global statement of the second law. That is,

$$\frac{d}{dt} \int_\Omega \rho\eta \, d\Omega \geq - \int_{\partial\Omega} \theta^{-1} \mathbf{q} \cdot \mathbf{n} \, da . \tag{8.3.20}$$

Here it is Eq. (8.2.1) as such which provides the transformation of mechanical energy into *heat*, while Eq. (8.3.20) will provide an indication on the "direction" of heat production. This is indeed the case. The corresponding analysis is due to Nguyen Quoc Son (1980). We follow the same reasoning as in the first paragraph but we no longer are in quasi-statics. We obviously have

$$\frac{d}{dt}\int_{V_\Gamma} \rho\left(\frac{1}{2}\mathbf{v}^2 + e\right) d\Omega = \int_{V_\Gamma} \rho\left(\frac{1}{2}\mathbf{v}^2 + e\right)^{*} d\Omega\,, \tag{8.3.21}$$

where the notation g^* means

$$g^* = \frac{\partial g}{\partial t}(x + l(t), y, t) = \dot{g} + \dot{l}\frac{\partial g}{\partial x}\,. \tag{8.3.22}$$

Then the integrand in the right-hand side of (8.3.21) is an *integrable function* for the asymptotic behavior assumed in elasticity so that, indeed, the limit of expression (8.3.21) when Γ shrinks to zero is zero. There remains thus the quantity [cf. (8.2.7)]

$$\begin{aligned}\frac{d}{dt}\int_{\Omega - V_\Gamma} \rho\left(\frac{1}{2}\mathbf{v}^2 + e\right) d\Omega &= \int_{\Omega - V_\Gamma} \rho\frac{d}{dt}\left(\frac{1}{2}\mathbf{v}^2 + e\right) d\Omega \\ &\quad - \int_\Gamma \rho\left(\frac{1}{2}\mathbf{v}^2 + e\right)\dot{l} n_1 d\Gamma\,.\end{aligned} \tag{8.3.23}$$

Now we assume that the *system Ω is thermally isolated.* Hence $\mathbf{q} = 0$ at the outer boundary of Ω. On account of the above obtained results the first law (8.2.2) therefore reduces to

$$\begin{aligned}\lim_{\Gamma\to 0}\Bigg\{\int_{\partial\Omega} \mathbf{T}^d \cdot \dot{\mathbf{u}} da &- \int_{\Omega - V_\Gamma} \rho\frac{d}{dt}\left(\frac{1}{2}\dot{\mathbf{u}}^2 + e\right) d\Omega \\ &+ \int_\Gamma \rho\left(\frac{1}{2}\dot{\mathbf{u}}^2 + e\right)\dot{l} n_1 d\Gamma\Bigg\} = 0\,,\end{aligned} \tag{8.3.24}$$

in the limit as Γ tends towards zero.

We can also apply the first law of thermodynamics (8.2.1) to the system $\Omega_\Gamma = \Omega - V_\Gamma$ which is *not thermally isolated* as it can exchange heat with V_Γ

by conduction through Γ. For any Γ we have

$$\begin{aligned}\int_{\Gamma}(\mathbf{q}\cdot\mathbf{n}-\mathbf{n}\cdot\sigma\cdot\dot{\mathbf{u}})d\Gamma+\int_{\partial\Omega}\mathbf{n}\cdot\sigma\cdot\dot{\mathbf{u}}da \\ =\int_{\Omega_\Gamma}\rho\frac{d}{dt}\left(\frac{1}{2}\dot{\mathbf{u}}^2+e\right)d\Omega\,.\end{aligned} \tag{8.3.25}$$

Eliminating the boundary term at $\partial\Omega$ between (8.3.24) and (8.3.25) while taking the limit as Γ shrinks to zero, we obtain that

$$H=\lim_{\Gamma\to 0}\int_{\Gamma}\left\{\rho\left(\frac{1}{2}\dot{\mathbf{u}}^2+e\right)\dot{l}n_1+\mathbf{n}\cdot\sigma\cdot\dot{\mathbf{u}}\right\}d\Gamma\,, \tag{8.3.26}$$

where the quantity H, which represents a *heat source concentrated at the crack tip*, is defined by

$$H=\lim_{\Gamma\to 0}\int_{\Gamma}\mathbf{q}\cdot\mathbf{n}d\Gamma\,. \tag{8.3.27}$$

Equation (8.3.26) tells us that the dissipation created during the progress of the rectilinear crack in the material goes entirely into heat at the crack tip. This is indeed observed as a high temperature almost pointlike source (of an extent of, say, 20 angströms) in *fast* fracture of glass and steel. It is the second law of thermodynamics which decides on the sign of this "source". This law can be applied to three different systems, (a) the whole system Ω which is *isolated*, so that (8.3.20) reduces to

$$\frac{d}{dt}\int_{\Omega}\rho\eta d\Omega\geq 0\,; \tag{8.3.28}$$

(b) the system $\Omega_\Gamma=\Omega-V_\Gamma$ which is *not isolated* and for which the second law takes the form

$$\frac{d}{dt}\int_{\Omega_\Gamma}\rho\eta d\Omega=\int_{\Omega_\Gamma}\rho\dot{\eta}d\Omega\geq\int_{\Gamma}\theta^{-1}\mathbf{q}\cdot\mathbf{n}d\Gamma\,, \tag{8.3.29}$$

and (c) the system V_Γ itself which is not isolated either and for which (8.3.29) is replaced by

$$\int_{V_\Gamma}\rho\dot{\eta}d\Omega+\int_{\Gamma}\theta^{-1}\mathbf{q}\cdot\mathbf{n}d\Gamma\geq 0\,. \tag{8.3.30}$$

An evaluation of the same type as in (8.3.23) for (8.3.28) yields

$$\lim_{\Gamma\to 0}\left(\int_{\Omega_\Gamma}\rho\dot{\eta}d\Omega-\int_{\Gamma}\rho\eta\dot{l}n_1d\Gamma\right)\geq 0\,. \tag{8.3.31}$$

For (8.3.29), calling θ_A (nonzero) the temperature at the crack tip, we obtain

$$\lim_{\Gamma\to 0}\left(\int_{\Omega_\Gamma}\rho\dot{\eta}\,d\Omega\right)-\frac{H}{\theta_A}\geq 0\,, \tag{8.3.32}$$

where H is none other than the quantity defined by (8.3.27). As is easily shown, we also have

$$\int_{\Omega}\rho\dot{\eta}\,d\Omega=\lim_{\Omega_\Gamma\to 0}\int_{\Omega_\Gamma}\rho\dot{\eta}\,d\Omega\geq 0\,, \tag{8.3.33a}$$

$$\lim_{\Gamma\to 0}\int_{\Gamma}\rho\eta\dot{l}n_1\,d\Gamma=0\,,\qquad \lim_{\Gamma\to 0}\int_{V_\Gamma}\rho\dot{\eta}\,d\Omega=0\,. \tag{8.3.33b}$$

On combining the above results we finally obtain

$$\lim_{\Gamma\to 0}\int_{\Gamma}\theta^{-1}\mathbf{q}\cdot\mathbf{n}\,d\Gamma=\frac{H}{\theta_A}\geq 0\,,\qquad \text{i.e. } H\geq 0\,. \tag{8.3.34}$$

This means that the pointlike heat source at the crack tip necessarily is a *warm source*: the whole of the intrinsic power concentrated at the crack tip is transformed into heat.

Note that (8.3.26) can be rewritten in terms of the *free energy* ψ, i.e. equivalently to (8.3.26),

$$H=\lim_{\Gamma\to 0}\int_{\Gamma}\left\{\rho\left(\psi+\frac{1}{2}\dot{\mathbf{u}}^2\right)\dot{l}n_1+\mathbf{n}\cdot\sigma\cdot\dot{\mathbf{u}}\right\}d\Gamma\,, \tag{8.3.35}$$

because $\theta\eta$ is such that

$$\lim_{\Gamma\to 0}\int_{\Gamma}\rho\theta\dot{l}n_1\,d\Gamma=0\,. \tag{8.3.36}$$

Moreover, using the fact that $\dot{\mathbf{u}}$ behaves essentially like $-\dot{l}\partial\mathbf{u}/\partial x$, we can also rewrite (8.3.35) as

$$H=G_{\mathrm{dyn}}\dot{l}\geq 0\,, \tag{8.3.37}$$

where G_{dyn} is a kind of *dynamic energy-release rate* given by

$$G_{\mathrm{dyn}}:=\lim_{\Gamma\to 0}\int_{\Gamma}\left\{\rho\left(\psi+\frac{1}{2}\dot{\mathbf{u}}^2\right)n_1-\mathbf{n}\cdot\sigma\cdot\frac{\partial\mathbf{u}}{\partial x}\right\}d\Gamma\,. \tag{8.3.38}$$

Again H is in the canonical *bilinear* form of a dissipation and a criterion of crack progression can be proposed on a true thermodynamic basis, e.g. there exists G_c such that $G_{\mathrm{dyn}} = G_c$ when propagation occurs and $G_{\mathrm{dyn}} \leq G_c$ otherwise. For the temperature and heat-flux behavior in the vicinity of the crack tip, we refer the reader to Bui *et al.* (1987) who give a rather comprehensive discussion depending on the heat-flux law assumed and the type of local dissipation (plasticity, viscosity) which may exist *in* the material surrounding the crack tip. This requires considering the solution of the heat equation with a concentrated heat source at the crack tip.

8.4. Material Forces in Fracture

A. General features

Here we look at brittle fracture in a different way which considers operations, not in physical space, but on the *material* manifold $\mathcal{M}$ introduced in Chapter 2 (Fig. 2.2) for the description of the finite deformation of a solid. To illustrate our point we consider the equation of motion (3.2.15) in the absence of body forces, $\mathbf{f} = \mathbf{0}$, and also the energy equation (3.2.8) for adiabatic processes. These two, at all *regular* points in the body B (i.e. at points where the fields do not take any infinite value), can be rewritten as

$$\left.\frac{\partial}{\partial t}\mathbf{p}\right|_{\mathbf{X}} - \mathrm{div}_R\, \mathbf{T} = \mathbf{0}\,, \tag{8.4.39}$$

and

$$\left.\frac{\partial}{\partial t}\mathcal{H}\right|_{\mathbf{X}} - \mathrm{div}_R\, \mathbf{Q} = 0\,, \tag{8.4.40}$$

where

$$\mathbf{p} = \rho_0(\mathbf{X})\mathbf{v}\,, \qquad \mathcal{H} = \rho_0\left(\frac{1}{2}\mathbf{v}^2 + e\right), \qquad \mathbf{Q} = \mathbf{T}\cdot\mathbf{v}\,. \tag{8.4.41}$$

Equations (8.4.39) and (8.4.40) are written in the form of *strict balance/conservation laws* with space-time derivatives with respect to independent space-time variables $(\mathbf{X}, t)$. While (8.4.40) is a scalar equation, (8.4.39) has vectorial components in physical space $\mathbb{E}^3$ at the current configuration $\mathcal{K}_t$. For a nonlinear, in general anisotropic and inhomogeneous body, we have

$$\mathbf{T} = \left(\frac{\partial W}{\partial \mathbf{F}}\right)^T, \qquad \mathbf{T}\mathbf{F}^T = \mathbf{F}\mathbf{T}^T, \qquad W = \rho_0(\mathbf{X})e(\mathbf{F}, \mathbf{X}) = \bar{W}(\mathbf{F}; \mathbf{X})\,, \tag{8.4.42}$$

and (8.4.40) appears to be none other than the result of (8.4.39) multiplied scalarly by $\mathbf{v}$ and integrated by parts. We have let e depend, not only on $\mathbf{F}$, but also explicitly on $\mathbf{X}$ to account for a possible material *elastic* inhomogeneity (i.e. the fact that *elasticity properties* depend on the *material* point considered). Similarly, ρ_0 may depend on $\mathbf{X}$, thus accounting for possible material inhomogeneities in *inertial* properties. By left multiplication by $\mathbf{F}^T$ and integration by parts, we immediately check that Eq. (8.4.39) also provides an equation with components on $\mathcal{M}$, that is

$$\left.\frac{\partial}{\partial t}\mathcal{P}\right|_{\mathbf{X}} - \mathrm{div}_R\,\mathbf{b} = \mathbf{f}^{\mathrm{inh}}\,, \tag{8.4.43}$$

where we have defined the following four quantities:

$$\mathcal{P} := -\rho_0(\mathbf{X})\mathbf{F}^T \cdot \mathbf{v}\,, \tag{8.4.44}$$

$$\mathbf{b} = -(\mathcal{L}\mathbf{1}_R + \mathbf{F}^T \cdot \mathbf{T})\,, \tag{8.4.45}$$

$$\mathcal{L} := \frac{1}{2}\rho_0(\mathbf{X})\mathbf{v}^2 - \bar{W}(\mathbf{F};\mathbf{X})\,, \tag{8.4.46}$$

and

$$\mathbf{f}^{\mathrm{inh}} := \left(\frac{\partial \mathcal{L}}{\partial \mathbf{X}}\right)_{\mathrm{expl}} = \left(\frac{1}{2}\mathbf{v}^2\right)\nabla_R\rho_0 - \left(\frac{\partial \bar{W}}{\partial \mathbf{X}}\right)_{\mathrm{expl}}\,, \tag{8.4.47}$$

where $(\ )_{\mathrm{expl}}$ denotes the *explicit* derivative with respect to $\mathbf{X}$, keeping the other arguments of the function fixed. The four fields defined by (8.4.43)–(8.4.47) are called, respectively, the *pseudomomentum* (a material covariant vector on $\mathcal{M}$), the *Eshelby stress tensor* (a mixed material second-order tensor on $\mathcal{M}$), the *Lagrangian* density per unit volume of $\mathcal{K}_R$, and the *inhomogeneity material force* (a material covariant vector on $\mathcal{M}$) — cf. Maugin and Trimarco (1992), Maugin (1993a).[2] From (2.3.42), we can also define the *material velocity field* by

$$\mathbf{V} := \left.\frac{\partial \chi^{-1}}{\partial t}\right|_{x}\,. \tag{8.4.48}$$

Then one verifies by using the chain rule of differentiation that $\mathbf{v}$ and $\mathbf{V}$ are related by

$$\mathbf{v} + \mathbf{F}\cdot\mathbf{V} = 0 \qquad \text{or} \qquad \mathbf{V} = -\mathbf{F}^{-1}\cdot\mathbf{v}\,, \tag{8.4.49}$$

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[2] The fact that both *Lagrangian* and *Hamiltonian* densities appear in the formulation is not fortuitous as there is a strong interrelation with the *analytical mechanics of continua* (for these developments see Maugin, 1993a, Chapter 5).

so that $\mathcal{P}$ also reads

$$\mathcal{P} = \rho_0(\mathbf{X})\mathbf{C} \cdot \mathbf{V}\,, \tag{8.4.50}$$

The latter shows that $\mathcal{P}$ is indeed a *covector on* $\mathcal{M}$ as $\rho_0\mathbf{V}$ is a contravector and the finite-strain $\mathbf{C}$ plays the role of *a deformed metric* to produce from it the covector $\mathcal{P}$ (see any book on *tensors* on manifolds). We let the reader check that if he takes the scalar product of (8.4.43) by $\mathbf{V}$, then he recovers (8.4.40), since this is the same as multiplying (8.4.39) by $\mathbf{V} \cdot \mathbf{F}^T$ or $-\mathbf{v}$. Thus there is only *one local energy equation*, (8.4.40), whereas (8.4.39) and (8.4.43) are but two *equivalent* local expressions of the balance of linear momentum on two different manifolds, $\mathbb{E}^3$ and $\mathcal{M}$, respectively. The second form (8.4.43) extracts in a clear manner the *material inhomogeneities* via the material force $\mathbf{f}^{\mathrm{inh}}$. We also note that $(8.4.42)_2$ is equivalent to

$$\mathbf{b}\mathbf{C} = \mathbf{C}\mathbf{b}^T\,. \tag{8.4.51}$$

The question now is what is the relation between the material description given here and the problem of fracture? One obvious answer is, following J. D. Eshelby (1951, 1970, 1975), that *macrocracks are material inhomogeneities* in their own right, albeit rather abrupt ones. Consequently Eq. (8.4.43) is *the form* of the balance of linear momentum that should be used when dealing with fracture. We illustrate this point in Paragraph B below by a direct calculation of the *dissipation* developed during a quasi-static progression of a crack in material space $\mathcal{M}$. A second point (Paragraph C below) is that, so far, the problem of fracture has been approached only on a pure *energetic* basis, while Eq. (8.4.43) is an equation of *motion* (or *equilibrium*, in quasi-statics). It is obvious that the components of tensor $\mathbf{b}$ are none other than *energies*: they are quadratic in the basic fields of the theory. Thus they have, in a way, the same order of singularity as energetic quantities, and this should agree with the energy approach.

B. Evaluation of elementary dissipation

We consider again Fig. 8.1 for quasi-statics but *finite strains*. Let $\mathcal{D}$ be the defect, i.e. the crack is Σ. In an elementary progress of the crack we have an elementary dissipation given by [cf. (8.2.2)]

$$\delta\Phi(\mathcal{D}) = \int_{\partial\Omega-\mathcal{D}} (\mathbf{N} \cdot \mathbf{T}) \cdot \delta_{\mathbf{X}}\chi\, dA - \delta_{\mathbf{X}} \int_{\Omega} W dV\,, \tag{8.4.52}$$

where all reasoning is now performed on the *material manifold* (elements dV and dA, unit normal $\mathbf{N}$ to Ω). The variation $\delta_{\mathbf{X}}$ introduced is a so-called *Lagrangian variation* strictly defined by

$$\delta_{\mathbf{X}}\chi(\mathbf{X},t,\varepsilon)=\left.\frac{\partial\chi}{\partial\varepsilon}\right|_{\mathbf{X}}\text{fixed}\,,\qquad \varepsilon=0\,. \tag{8.4.53}$$

It is noted that $\delta_{\mathbf{X}}$ commutes with ∇_R. As in (8.2.2), one must pay special attention to the computation of the second contribution in (8.4.52) as the domain of integration evolves with the quasi-static extension of the crack. That is, isolating the region V_Γ around the crack tip, taking into account the fact that no tractions are acting along the lips of the crack and that we are working in the reference configuration, we have

$$\delta_{\mathbf{X}}\int_\Omega W dV=\delta_{\mathbf{X}}\int_{\Omega-V_\Gamma}W dV+\int_\Gamma W(\mathbf{N}\cdot\delta_x\mathbf{X})d\Gamma\,, \tag{8.4.54a}$$

$$\delta_{\mathbf{X}}\int_{\Omega-V_\Gamma}W dV=\int_{\Omega-V_\Gamma}(\delta_{\mathbf{X}}W)dV\,,\qquad \delta_{\mathbf{X}}(dV)\equiv 0\,, \tag{8.4.54b}$$

$$\delta_{\mathbf{X}}W=(\partial\mathbf{W}/\partial\mathbf{F})\cdot\delta_{\mathbf{X}}(\nabla_R\chi)=T\cdot\nabla_R(\delta_{\mathbf{X}}\chi)\,, \tag{8.4.54c}$$

where the *Eulerian variation* $\delta_x\mathbf{X}=\delta_x\chi^{-1}$ is defined by

$$\delta_x\chi\;^{1}(x,t,\varepsilon)=\left.\frac{\partial\chi^{-1}}{\partial\varepsilon}\right|_x\quad\text{fixed}\,,\qquad \varepsilon=0\,, \tag{8.4.55}$$

and is related to $\delta_{\mathbf{X}}\chi$ by [cf. (8.4.49)]

$$\delta_{\mathbf{X}}\chi+\mathbf{F}\cdot\delta_x\chi^{-1}=\mathbf{0}\,. \tag{8.4.56}$$

The final result of the computation (8.4.52) is

$$\delta\Phi=\int_\Gamma(\delta_x\chi^{-1}\cdot\mathbf{b}\cdot\mathbf{N})d\Gamma\,, \tag{8.4.57}$$

which directly involves the *Eshelby stress* in its quasi-static form and a variation of the *material points* themselves. For an "*en bloc*" virtual (inverse) motion of the region Γ around the crack tip, e.g.

$$\delta_x\chi^{-1}=\mathbf{E}_I\delta l\,, \tag{8.4.58}$$

where $\mathbf{E}_I$ is a unit material vector along the crack direction (here X), the elementary dissipation (8.4.57) takes on the form

$$\delta\Phi = G\delta l\,, \qquad G = \mathcal{F}_{(I)}\,, \qquad \mathcal{F}_{(I)} := \int_\Gamma \mathbf{E}_I \cdot \mathbf{b} \cdot \mathbf{N} d\Gamma\,. \tag{8.4.59}$$

This result shows that the energy-release rate G is none other than the component along $\mathbf{E}_I$ of the *global material force*

$$\mathcal{F} = \int_\Gamma \mathbf{b} \cdot \mathbf{N} d\Gamma\,, \tag{8.4.60}$$

which is the *flux* of the Eshelby stress across Γ. There is *no* disagreement between (8.4.60) and (8.2.12) although the latter is written for small strain. The reason for this is that the Γ-integral is independent of the contour so that we do not need to take the limit, and that for the degree of singularity observed for σ in linear elasticity, we have

$$\lim_{\Gamma \to 0} \int_\Gamma \mathbf{n} \cdot \sigma \cdot \mathbf{e}_1 d\Gamma = 0\,, \tag{8.4.61}$$

so that with the appropriate change in notation in (8.2.12) and accounting for (3.2.20), the latter can be rewritten as

$$G = \int_\Gamma (W\mathbf{N} \cdot \mathbf{E}_I - \mathbf{E}_I \cdot \mathbf{F}^T \cdot \mathbf{T} \cdot \mathbf{N}) d\Gamma \equiv \mathcal{F}_{(I)}\,. \tag{8.4.62}$$

The above reasoning generalizes to the *dynamical case* (Maugin, 1994a) for which a term involving the flux of the pseudomomentum across Γ in the $\mathbf{E}_I$-direction allows one to introduce the Hamiltonian $\mathcal{H}$ in the final result of G via a Legendre transformation of the Lagrangian density. But this equivalence or nonequivalence between the two approaches deserves more attention (see Dascalu and Maugin, 1993).

C. Global balances of momentum

Consider for the sake of simplicity the two expressions of the balance of linear momentum in quasi-statics in the absence of material inhomogeneities and body forces. They read

$$\mathrm{div}_R \mathbf{T} = 0\,, \qquad \mathrm{div}_R\, \mathbf{b} = 0\,. \tag{8.4.63}$$

At any *regular* point $\mathbf{x} = \chi(\mathbf{X})$ or $\mathbf{X} = \chi^{-1}(\mathbf{x})$, these two are *strictly equivalent.* The second is none other than the first multiplied by $\mathbf{F}^T$, and reciprocally, the first is the second multiplied by $(\mathbf{F}^{-1})^T$. If we take a small region V_Γ encircling a *singular point* (by this we mean a point where the *elasticity solution* of the boundary value problem *diverges*, say like $\sqrt{r}$ for the displacement). Then as we saw in (8.4.61), the global form of $(8.4.63)_1$ yields nothing as we shrink V_Γ to the singular point, whereas the global form of $(8.4.63)_2$, that is (8.4.60), captures the *singularity* as the resulting expression does not yield zero as the integrand is no longer integrable! Thus the equivalence between the two expressions (8.4.63) has been lost in passing from the *local* to the *global.* This lack of equivalence at the global level is what makes the reasoning on the *material manifold* particularly relevant in the presence of *material defects,* i.e. *elastic singularities,* of which a macrocrack is a simple example. To see this in an even clearer manner we follow Dascalu and Maugin (1993) in their consideration of the fully dynamical case. The integral of (8.4.39) over a material volume $\mathcal{B}$, i.e.

$$\frac{d}{dt}\int_{\mathcal{B}} \mathbf{p} dV = \int_{\partial\mathcal{B}} \mathbf{N}\cdot\mathbf{T} dA\,, \tag{8.4.64}$$

is to be considered as being the *set of three components* on the vectorial basis $\{\mathbf{e}_i\}$, $i = 1, 2, 3$, on $\chi(\mathcal{B}, t)$ at $\mathcal{K}_t$. For the global form of (8.4.43) to be viewed as a *tensorial* relation, it must be considered *by component* on a basis $\{\mathbf{E}_I\}$,

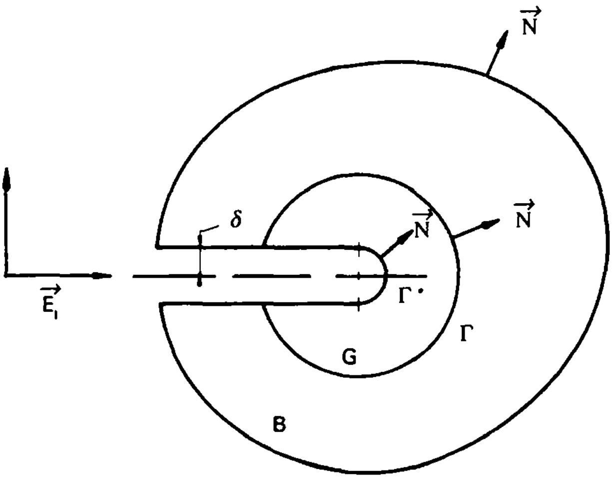

Fig. 8.3. Notch δ in a nonlinear elastic solid body $\mathcal{B}$.

$I = 1, 2, 3$. Then while the local equations are placed in correspondence *via convection*, this is no longer the case between the corresponding *global balance laws*. Now we use this, following Dascalu and Maugin (1993), in dealing with the situation where the material body $\mathcal{B}$ presents a *notch* (Fig. 8.3) whose front Γ^* propagates with *material* velocity $\bar{V}(\mathbf{X}, t)$ in the $\mathbf{E}_I$-direction (I fixed, in fact equal to one). Integrating the balance of pseudomomentum over $\mathcal{B}$ while exploiting the transport theorem for an *evolutive domain* in the material framework, we obtain

$$\frac{d}{dt}\int_{\mathcal{B}} \mathcal{P}_I dV + \mathcal{F}_{(I)} = \int_{\partial\mathcal{B}} (\mathrm{b}\cdot\mathbf{N})_I dA\,, \qquad I = 1, 2, 3\,, \tag{8.4.65}$$

where we used the fact that the notch is supposed to be free of tractions and we emphasize the *component* character of (8.4.65). The quantity

$$\mathcal{F}_{(I)} = -\int_{\Gamma^*} \{\mathcal{L}N_I - \mathcal{P}_I(\bar{\mathbf{V}}\cdot\mathbf{N})\} dA \tag{8.4.66}$$

is the Ith (material) component of the *global material force acting on the notch*. In order to deduce an equivalent statement for a straight-through crack Σ (Fig. 8.4) we consider a family of notches indexed by the parameter δ such

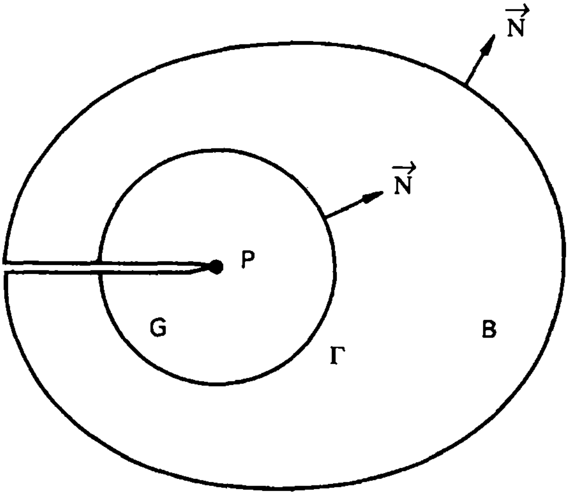

Fig. 8.4. The straight-through crack as a limit case of a notch.

that for δ going to zero the notches converge toward the crack while the limit of the family of solutions of the boundary-value problems for each δ converges toward the solution of the same problem with the crack. If the first term in (8.4.65) converges in such a procedure, then in the limit as δ tends towards zero we obtain for the relevant material force the expression

$$\mathcal{F}_{(I)} = - \lim_{\delta \to 0} \int_{\Gamma^\bullet(\delta)} \{\mathcal{L}\mathbf{N}_I - \mathcal{P}_I(\bar{\mathbf{V}} \cdot \mathbf{N})\} dA \,. \tag{8.4.67}$$

This is the *material force* which acts on the crack when the latter progresses in the direction $\mathbf{E}_I$, I fixed. In linear elasticity, the singularity of the solution and the relation (8.4.49) show that the convergence hypothesis assumed for the first term in (8.4.65) is verified. In a different manner, using the balance of pseudomomentum over the region V_Γ in the case of a notch and using (8.4.66), in the limit $\delta \to 0$ we have the following equivalent expression for the crack:

$$\mathcal{F}_{(I)} = \int_\Gamma \{(\mathbf{b} \cdot \mathbf{N})_I + \mathcal{P}_I(\bar{\mathbf{V}} \cdot \mathbf{N})\} dA - \frac{d}{dt} \int_{V_\Gamma} \mathcal{P}_I dV \,. \tag{8.4.68}$$

For a straight-through crack this expression is independent of the domain V_Γ that encircles the tip of the crack and moves rigidly with it. An expression such as (8.4.68) does not involve any *energy* argument beforehand. Nonetheless there should be a deep relationship between the result (8.4.68) and more classical arguments such as the ones we use above. This is elucidated next.

D. Energy argument

In the *dynamical case based on the energy equation*, we shall obtain in the case of the notch of Fig. 8.3, the following *global energy balance* with a source term $\mathcal{G}$:

$$\frac{d}{dt} \int_\mathcal{B} \mathcal{H} dV + \mathcal{G} = \int_{\partial\mathcal{B}} \mathbf{N} \cdot \mathbf{Q} dA \,, \qquad \mathbf{Q} \equiv \mathbf{T} \cdot \mathbf{v} \,, \tag{8.4.69}$$

together with

$$\mathcal{G} = \int_{\Gamma^\bullet} \mathcal{H}(\bar{\mathbf{V}} \cdot \mathbf{N}) dA \,. \tag{8.4.70}$$

This, according to the very form of Eq. (8.4.69), is the *rate of energy released* during the propagation of the notch, expressed in a somewhat unconventional way. Considering now the "crack limit" of the δ-indexed family of notches we shall arrive at (8.4.69) but with $\mathcal{G}$ defined by

$$\mathcal{G} = \lim_{\delta \to 0} \int_{\Gamma^*} \mathcal{H}(\bar{\mathbf{V}} \cdot \mathbf{N}) dA \, . \tag{8.4.71}$$

But considering a contour Γ as in Fig. 8.4, a computation of the same type as the one performed for $\mathcal{F}_{(I)}$ will yield the *classical* expression of $\mathcal{G}$ in *dynamics* (compare Freund, 1990)

$$\mathcal{G} = \int_{\Gamma} \{\mathcal{H}(\bar{\mathbf{V}} \cdot \mathbf{N}) + \mathbf{N} \cdot \mathbf{T} \cdot \mathbf{v}\} dA - \frac{d}{dt} \int_{V_\Gamma} \mathcal{H} dV \, . \tag{8.4.72}$$

We are now in a position to unequivocally relate the notion of material force and that of energy-release rate for the rather general case of the *elastodynamics in finite strains.* To that purpose let P be a point of Γ^* for the case of a notch (Fig. 8.3). Let $\mathbf{r}$ denote the position vector from P. We can write $\chi(\mathbf{X}, t) = \chi(\mathbf{X}_P + \mathbf{r}, t)$, from which it follows by differentiation that

$$\mathbf{v} = -\mathbf{F} \cdot \bar{\mathbf{V}} + \frac{\partial \bar{\chi}}{\partial t} \, , \qquad \bar{\mathbf{V}} = \frac{\partial \mathbf{X}_P}{\partial t} \, , \tag{8.4.73}$$

where $\chi(\mathbf{X}, t) = \bar{\chi}(\mathbf{r}, t)$ and $\bar{\mathbf{V}}$ is none other than the *material* velocity of P. Convection of (8.4.73) by $\mathbf{F}^{-1}$ leads to

$$\mathbf{V} = \bar{\mathbf{V}} - \mathbf{F}^{-1} \cdot \frac{\partial \bar{\chi}}{\partial t} \, , \qquad \bar{\mathbf{V}} = \bar{V}_I \mathbf{E}_I \, . \tag{8.4.74}$$

Let us assume now that the points P of Γ^* have a uniform motion, $\bar{\mathbf{V}} = \bar{\mathbf{V}}(t)$ only. In this case it is reasonable to assume that the deformation shall be the same at all points along Γ^* and that $\partial \bar{\chi} / \partial t = 0$. As the only nonzero component of $\bar{\mathbf{V}}$ is $\bar{V}_I$, multiplying (8.4.67) — or (8.4.68) — by $\bar{V}_I$ and considering the identity

$$\mathbf{V} \cdot \mathbf{C} \cdot \mathbf{V} = \mathbf{v}^2 \, , \tag{8.4.75}$$

we obtain that

$$\mathcal{G} = \bar{V}_I \mathcal{F}_{(I)} \, , \tag{8.4.76}$$

as the reader can check by himself. We have thus obtained that the material force acting on Γ^* coïncides with the rate of energy released per unit length of progress of the notch. The reasoning used emphasizes the fact that *global material forces* are intimately related to the "*en bloc*" motion of defects on the material manifold. Indeed, had points P had different velocities the second term in (8.4.74) would have not vanished. Nor could multiplication by $\bar{V}_I$ any longer commute with integration over Γ^* in (8.4.67). A relation such as (8.4.76) is meaningful only whenever $\bar{\mathbf{V}}$ does not depend on P. For a crack, however, P reduces to *one point* in the limit (obviously a mathematical abstraction), the tip of the crack. In this limit case, by repeating the above argument and taking the appropriate limit we shall arrive at an expression such as (8.4.76) for the crack. Combined with (8.4.68), the latter expression will take the classical form involving the energy-release rate of a crack in elasto-*dynamics* [see Eq. (8.3.38)]. In the process we have passed from the Lagrangian density $\mathcal{L}$ present in $\mathbf{b}$, hence in $\mathcal{F}_{(I)}$, to the Hamiltonian density $\mathcal{H}$ — total energy density — in $\mathcal{G}$ thanks to the contribution of the flux of pseudomomentum in the $\mathbf{E}_I$-direction which allows for the *Legendre transformation* between these two quantities:

$$\mathcal{H} = \frac{\partial \mathcal{L}}{\partial \mathbf{V}} \cdot \mathbf{V} - \mathcal{L}, \qquad \mathcal{P} = \frac{\partial \mathcal{L}}{\partial \mathbf{V}}, \qquad \mathbf{V} = \frac{\partial \mathcal{H}}{\partial \mathcal{P}}. \tag{8.4.77}$$

From here on we enter the domain of *analytic continuum mechanics* (see Maugin, 1993a, Chapter 5). A result essentially equivalent to (8.4.76) was obtained by Ehrlacher (1981) in small-strain elasticity.

8.5. The Use of Generalized Functions in the Energy Equation

Generalized functions or *distributions* were introduced in the 1940s by Laurent Schwartz following pre-World War II pioneering works by J. Leray and L. Sobolev. By transferring operations of differentiation on sufficiently smooth *test functions* after integration by part over a compact support, they allow for a *weak formulation* of solutions of partial differential equations which admits singular behaviors at points or jump discontinuities across surfaces (see Gelfand and Shilov, 1964). The principle of virtual power in continuum mechanics, e.g. Eq. (2.3.57), may itself be considered as an exemplary use of a *distributional formulation* in which the role of test functions is played by virtual fields of displacements or velocities (see Maugin, 1980). The theory of cracks in particular and, more generally, of *elastic defects* should have the theory of *distributions* for natural mathematical background. But few authors have worked along this line, with the noticeable exceptions of Dascalu and the author (1994a). Before discussing their approach, it is necessary to recall that *generalized functions* may be viewed as *linear continuous functionals* on a set of very smooth functions with bounded, compact support. The paragon of generalized functions is the celebrated and ubiquitous *delta function* of P. A. M. Dirac which may be considered as a "unit" (for the *convolution product*) and which extracts the value of a function at a point (for the delta function with punctual support) or at a hypersurface (for the delta function having this hypersurface for support). For instance, in $\mathbb{R}$, $\langle \ldots \rangle$ indicating the duality product between *distributions* and the set of smooth test functions:

$$f(a) = \langle \delta(a), f \rangle = \int_{\mathbb{R}} \delta(x-a) f(x) dx \,, \tag{8.5.78}$$

so that δ has the strange property of vanishing almost everywhere, except at point a where it diverges to infinity; still it is normalized to one over $\mathbb{R}$, i.e.

$$\int_{\mathbb{R}} \delta dx = 1 \,. \tag{8.5.79}$$

Such a "function" can be defined as the limit of several sequences of functions which yield properties (8.5.78) and (8.5.79). The *operational* definition (8.5.78) extends to the case where the support of δ is a surface or a line in $\mathbb{E}^3$ or on the material manifold $\mathcal{M}$. Let us apply this to the continuum mechanics of *elastic bodies* presenting "defects" such as cracks. The argument of Dascalu and Maugin (1994a) is that the very structure of elasticity theory and the singularity order of elastic solutions dictates (i) the expression of the energy balance law in the presence of cracks and (ii) that a Griffith-like surface-energy distribution follows by necessity. Without repeating the mathematical detail of their proof which is outside the scope of this book, it seems necessary to emphasize the following results as they bear direct relationship to the thermodynamic results exposed in previous sections.

First of all, assuming *quasi-statics* and the absence of any body and inhomogeneity forces, the local balance of physical momentum, angular momentum, energy, and pseudomomentum for an elastic body in finite strain are written as

$$\begin{gathered} \operatorname{div}_R \mathbf{T} = 0 \,, \qquad \operatorname{div}_R (\mathbf{x} \times \mathbf{T}) = \mathbf{0} \,, \\ \frac{\partial W}{\partial t} - \operatorname{div}_R (\mathbf{T} \cdot \dot{\mathbf{x}}) = 0 \,, \qquad \operatorname{div}_R \mathbf{b} = \mathbf{0} \,, \end{gathered} \tag{8.5.80}$$

at all *regular points in the body* $\mathcal{B}$. In the absence of *defects*, the first three parts of Eqs. (8.5.80) take on the following *distributional form* (over the whole of $\mathbb{R}^3$)

$$\begin{aligned}
&\mathrm{Div}_R\,\mathbf{T} + \mathbf{T}^d\delta(\partial\mathcal{B}) = \mathbf{0}\,, \\
&\mathrm{Div}_R\,(\mathbf{x}\times\mathbf{T}) + (\mathbf{x}\times\mathbf{T}^d)\delta(\partial\mathcal{B}) = \mathbf{0}\,, \qquad (8.5.81)\\
&D_t W - \mathrm{Div}_R\,(\mathbf{T}\cdot\dot{\mathbf{x}}) - (\mathbf{T}^d\cdot\dot{\mathbf{x}})\delta(\partial\mathcal{B}) = 0\,,
\end{aligned}$$

where Div_R and D_t are distributional operators (i.e. classical derivatives where this notion applies), $\mathbf{T}^d$ is the mechanical traction at $\partial\mathcal{B}$, and $\delta(\partial\mathcal{B})$ is the delta generalized function with support $\partial\mathcal{B}$. That is, writing (8.5.81) allows one to work on the whole of $\mathbb{R}^3$ while the natural boundary conditions are directly incorporated in the local *field* equations. Under the present conditions (no defects) this writing is elegant but does not provide anything new, as it is simply of a *synthetic* nature. In the *presence of elastic defects* (e.g. crack, cavity, dislocation), the first two parts of Eqs. (8.5.81) are shown to be left unchanged while the third takes on the following generalized form (this exceptional status of this third equation is due to the essentially quadratic nature of energy in the basic fields — this, therefore, would also apply to the fourth part of (8.5.80); but we have already emphasized the equivalence between reasonings on energy and pseudomomentum):

$$D_t W + VG\delta(\mathcal{S}) = \mathrm{Div}_R(\mathbf{T}\cdot\dot{\mathbf{x}}) + (\mathbf{T}^d\cdot\dot{\mathbf{x}})\delta(\partial\mathcal{B})\,. \qquad (8.5.82)$$

Here C is the *set of defect points*, $\mathcal{B}/C$ is the homogeneous elastic body, $\mathcal{S}$ is the *set of extension points of the defect* (this reduces to a point, the crack tip, in the case of a crack), G is the energy absorbed per unit area (or length) extension of the said defect, and V is the propagation speed. Equation (8.5.82) is valid at *all points* of $\mathcal{B}$, $\partial\mathcal{B}$, and in fact $\mathbb{R}^3$. If, furthermore, there exists a steady-state propagation criterion of the type (8.2.13), i.e. $G = G_c$ yields a possible progress, then (8.5.82) becomes a *true* distributional *conservation law* in the form

$$D_t(W + G_c H(C)) = \mathrm{Div}_R(\mathbf{T}\cdot\dot{\mathbf{x}}) + (\mathbf{T}^d\cdot\dot{\mathbf{x}})\delta(\partial\mathcal{B})\,, \qquad (8.5.83)$$

where $H(C)$ is a Heaviside function and the quantity $G_c H(C)$ may truly be called the *energy of the defect.* This last quantity depends on time through the time rate of change of the defect's size. Equation (8.5.83) was proved for a straight crack, and both screw and edge dislocations (cf. Dascalu and Maugin, 1994a) by introducing regularizations of *nonintegrable* quantities (this is the case of $\dot{W}$ in the case of a crack) and principal values in the Cauchy–Hadamard–Schwartz sense.

The results (8.5.82) and (8.5.83) are interesting from the energy point of view as they show that we can alternately consider that either the crack's extension causes a global dissipation (while there is no *local dissipation* at all regular points in the *elastic body*) — this is the point of view developed in previous sections — or that, within a globally *conservative system* (conservation expressed by Eq. (8.5.83) in the case of a crack), there is an exchange of energy between the *defect* and the evolving nondefective material, because we have granted *energy* to the defect. This is of particular interest when the set of extension points has the same dimension as the body (case of cavities where the set of extension points becomes a surface — cf. Dascalu and Maugin, 1994a).

8.6. Remark on Cases Exhibiting Local Dissipation

Until now we have addressed the problem of fracture only in bodies that do not exhibit any local dissipation, whether intrinsic or thermal, at all regular points. It is true indeed that the essential characteristic of the "fracture problem" is dissipation due to the progress of the crack. But it is also evident that *dissipative* materials are also subjected to the phenomenon of fracture. This is the case of *elastic conductors* in which the local dissipation is only of thermal origin, and also of materials such as *viscoelastic*, *viscoplastic* and *elastoplastic ones* that exhibit *intrinsic dissipation*. In contrast to *brittle fracture*, fracture is called *ductile* when it occurs during the *plastic* response of the material.

Thermoelastic conductors. This case was already touched upon in Sec. 8.3. But it can also be examined in the light of the theory of *material forces* (Epstein and Maugin, 1994). The basic equations for *nonlinear thermoelastic conductors* have been established in Paragraph 3.4B. Transcribed in the formalism of Sec. 8.4, these equations read, in the absence of body forces and heat sources, but for a possibly anisotropic and materially inhomogeneous material,

$$\left.\frac{\partial}{\partial t}\mathbf{p}\right|_{\mathbf{X}} - \mathrm{div}_R\,\mathbf{T} = \mathbf{0} \qquad \text{(equation of motion)}, \qquad (8.6.84)$$

$$\theta\left.\frac{\partial S}{\partial t}\right|_{\mathbf{X}} + \nabla_R \cdot \mathbf{Q} = 0 \qquad \text{(equation of energy)}, \qquad (8.6.85)$$

$$\mathbf{T} = \left(\frac{\partial \bar{W}}{\partial \mathbf{F}}\right)^T, \; S = -\frac{\partial \bar{W}}{\partial \theta}, \; W = \bar{W}(\mathbf{F}, \theta; \mathbf{X}) \qquad \text{(laws of state)}, \qquad (8.6.86)$$

$$\mathbf{Q}\cdot\nabla_R(\ln\theta)\leq 0\,,\ \lim_{\nabla_R\theta\to 0}\mathbf{Q}=\mathbf{0}\qquad\text{(residual dissipation)}\,,\tag{8.6.87}$$

where $\mathbf{Q}$ is the (material) heat flux vector and W is the *free energy* per unit volume in $\mathcal{K}_R$. These are the bare essentials of the theory as the heat-flux law still needs to be specified, verifying (8.6.87). Proceeding as in Sec. 8.4, i.e. multiplying (8.6.84) to the left by $\mathbf{F}^T$ integrating by parts, and using (8.6.86), we arrive at the *balance of pseudomomentum* in the form

$$\left.\frac{\partial}{\partial t}\mathcal{P}\right|_{\mathbf{X}}-\mathrm{div}_R\,\mathbf{b}=\mathbf{f}^{\mathrm{inh}}+\mathbf{f}^{\mathrm{th}}\,,\tag{8.6.88}$$

where $\mathcal{P}$, $\mathbf{b}$, $\mathcal{L}$ and $\mathbf{f}^{\mathrm{inh}}$ are formally defined just as in Eqs. (8.4.44)–(8.4.47), but we emphasize that W here is the *free energy* (i.e. the thermodynamic potential that depends on *temperature*), and the *material force* $\mathbf{f}^{\mathrm{th}}$ is given by the remarkably simple expression

$$\mathbf{f}^{\mathrm{th}}:=S\nabla_R\theta\,,\qquad\text{i.e.}\qquad\lim_{\nabla_R\theta\to 0}\mathbf{f}^{\mathrm{th}}=\mathbf{0}\,.\tag{8.6.89}$$

This may be called the *material thermal force*. It acts exactly like a true material inhomogeneity ($\mathbf{f}^{\mathrm{inh}}$) on the material manifold $\mathcal{M}$. As a matter of fact, the property that thermoelastic strains are *internal strains* is already well known in small strain elasticity. Here we have the same result but in finite strains. This line can be pursued to treat the problem of *thermoelastic fracture* on the basis on (8.6.88) by integrating this equation in a small region around the tip of a crack. But this requires also exploiting (8.6.85) and having the knowledge of the conduction law and of the behaviors of thermomechanical fields in the vicinity of the crack. The left-hand side of (8.6.88) will necessarily yield the expression (8.3.38) for a straight-through crack. It remains to show that the right-hand side (with $\mathbf{f}^{\mathrm{inh}}=\mathbf{0}$) will integrate to give (8.3.27).

Elastoplastic case. One can theoretically treat the case of a straight-through crack progressing in an elastoplastic material in finite strains by using (8.6.84) jointly with the results of the constitutive and evolution equations of Sec. 7.4 and constructing the corresponding equation of balance of *pseudomomentum* in which the elastoplastic behavior materializes in two facts: (i) in the Eshelby stress tensor, the energy density W is replaced by

$$W+\int_t\Phi_{\mathrm{intr}}\,dt\,,\tag{8.6.90}$$

and (ii) there exists an extra *material force* $\mathbf{f}^p$ due to elastoplastic effects as an additional source term. This shows that elastoplastic strains can also be interpreted as creating a *material inhomogeneity.* We refer to Maugin (1993c, 1994b) for more precise developments along this line where a J-integral is obtained for this case. The usual argument in small strains is more traditionally based on exploiting the energy balance only (cf. Freund, 1990).

In both *thermoelastic* and *elastoplastic cases* the *material* formalism shows the intricacies of the mixed problem of *local* dissipation — due to the behavior of the material — and of *global* dissipation — due to the irreversible progress of the defect *into* the material. We conclude this chapter with this warning.

Chapter 9

NON-EQUILIBRIUM THERMODYNAMICS OF ELECTROMAGNETIC MATERIALS

He who controls magnetism
controls the Universe
(attributed to) Dick Tracy

He who understands the thermodynamics of magnetism,
controls Dick Tracy
(attributed to) G.A.M.

9.1. Introductory Remarks

The thermomechanics of *electromagnetic continua* is a branch of energetics which deals with the unification of continuum mechanics and electrodynamics of material media under the umbrella of general thermodynamics. This ambitious, somewhat Aristotelian-like scheme adds one difficulty to another. In effect, in addition to the cumbersome and rather heavy framework of nonlinear continuum mechanics (as exposed in preceding chapters), one has to consider *electromagnetism* (e.g. Jackson, 1962), and then combine them within the harmonious frame of thermodynamics. But this combination is generally *nonlinear*, i.e. we cannot proceed to a simple and naive linear superposition. Some of the difficulties met have to do with the electrodynamics of *moving* bodies (e.g. writing fields and equations in appropriate frames), while others relate to the introduction of a general deformation field ("material" writing of the fields). Last but not least, there are difficulties connected with the inherent complexity of some of the behaviors (e.g. hysteresis and *ferro*-properties).

In spite of the many obstacles mentioned above which one has to overcome to achieve as clean and rigorous an approach as possible, the most courageous and entrepreneurial among us did not hesitate to attack such a formidable problem.[1] The principal purpose of this chapter is to present in a synthetic manner those developments that relate to *thermodynamically irreversible effects* in electrodeformable continua, whether solids or fluids. That is, after recalling the more or less classical thermodynamical background for electromagnetic continua and the simplest irreversible behaviors (relaxation and classical conduction), the chapter is devoted to an organized description of more complex behaviors (as announced in the book's title) which necessitate the implementation of a richer thermomechanical background, e.g. *thermodynamics with internal variables* and/or the introduction of *internal degrees of freedom of electromagnetic origin*. The applications presented are multifaceted, exhibiting an interest in all types of *electromagnetic* behaviors either in *solids* or in *fluids*.

In the course of this chapter many analogies are drawn upon with the thermomechanics of solids exhibiting mechanical irreversible behaviors. As a rule we remain in the engineering context so that only nonrelativistic concepts are used. But many of the results obtained can be generalized to a fully (special or general) relativistic background as shown in Maugin (1978a) — also Eringen and Maugin (1990, Chapter 16). The background (modern continuum approach to electromagnetic bodies) is essentially found in the following books: Truesdell and Toupin (1960), Eringen (1980, Chapter 10), Nelson (1979), Maugin (1985, 1988), Eringen and Maugin (1990), Maugin, Pouget *et al.* (1992). Readers who do not feel sufficiently comfortable with the pure, albeit simpler, electromagnetic background should consult Jackson (1962) or Landau and Lifshitz (1984).[2]

9.2. Reminder on Electromagnetism

Electromagnetic fields are of a different nature than mechanical and thermal fields dealt with in other chapters. They are governed by a set of equations known as *Maxwell's equations*. As a matter of fact, after pioneering works

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[1] Here a special tribute must be paid to the pioneers, R. A. Toupin, A. C. Eringen, H. F. Tiersten, and D. F. Nelson who, in the Western World, have been so instrumental in organizing the general background. We have had the chance to be closely associated to these most recent advances during the last twenty five years.

[2] The present chapter leans heavily on our Udine lecture notes (Maugin, 1993d).

by Coulomb, Gauss, Poisson, Oersted, Ampère, Faraday, Weber and others, Maxwell (1873) succeeded in formulating a coherent set of *dynamical* equations valid in a continuous material. At each regular point $\mathbf{x}$ in a material volume Ω at time t, this set reads[3]

$$\begin{aligned} \nabla \times \mathbf{E} + \frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} &= \mathbf{0}, & \nabla \cdot \mathbf{B} &= 0, \\ \nabla \times \mathbf{H} - \frac{1}{c}\frac{\partial \mathbf{D}}{\partial t} &= \frac{1}{c}\mathbf{J}, & \nabla \cdot \mathbf{D} &= q_f, \end{aligned} \tag{9.2.1}$$

together with

$$\mathbf{H} = \mathbf{B} - \mathbf{M}, \qquad \mathbf{D} = \mathbf{E} + \mathbf{P}. \tag{9.2.2}$$

In these equations the various symbols introduced bear the following significance: c is the speed of light *in vacuo*, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic induction, $\mathbf{H}$ is the magnetic field, $\mathbf{D}$ is the electric displacement, $\mathbf{J}$ is the electric current, q_f is the volume density of free electric charges, and $\mathbf{M}$ and $\mathbf{P}$ are the magnetization and electric polarization per unit volume. Here, $\mathbf{E}$, $\mathbf{D}$ and $\mathbf{P}$ are *polar vectors*, while $\mathbf{H}$, $\mathbf{B}$ and $\mathbf{M}$ are *axial vectors* which reverse sign in time reversal. The fields $\mathbf{H}$ and $\mathbf{D}$ differ from $\mathbf{B}$ and $\mathbf{E}$, respectively, *only in matter.* Thus the first two parts of Eqs. (9.2.1) — Faraday's law and the equation indicating the nonexistence of magnetic monopoles — are valid everywhere, even in a vacuum. The fields $\mathbf{M}$, $\mathbf{P}$, $\mathbf{J}$ and q_f relate to the presence of *ponderable matter.* Equations (9.2.1) can be deduced from a statistical average of microscopic Maxwell's equations with point-like sources of charge and current (this is the point of view of H. A. Lorentz in his celebrated "theory of electrons" which has *not* been superseded so far). In that case $\mathbf{M}$, $\mathbf{P}$, $\mathbf{J}$ and q_f are given expressions in terms of the elementary charges and the motion (position and velocity or linear momentum) of these charges. The "microscopic" definitions may be helpful in establishing the invariance properties of these "material" fields, especially in so far as *objectivity* (invariance under time-dependent rotations of the actual frame). However, in a *phenomenological* framework which is the one adopted here, q_f is a datum or the result of a computation while $\mathbf{M}$, $\mathbf{P}$ and $\mathbf{J}$ have to be given *constitutive equations*, e.g. to

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[3] This is written here using so-called *Lorentz-Heaviside units* where neither factor 4π nor vacuum permeability μ_0 and dielectric constant ϵ_0 are involved. This is the most convenient system in theoretical considerations, especially in so far as *dynamical effects* are concerned. See Maugin (1988, p. 56) for other systems which may be more or less *rational*.

give an idea to the readers, *functional relations* of the type

$$\mathbf{M} = \bar{\mathbf{M}}(\mathbf{H},.)\,, \qquad \mathbf{P} = \bar{\mathbf{P}}(\mathbf{E},.)\,, \qquad \mathbf{J} = \bar{\mathbf{J}}(\mathbf{E},.)\,, \tag{9.2.3}$$

where the dot stands for some other variables such as temperature, the strain in a deformable solid, or the density in a compressible fluid, etc. Note that the inverse relations, e.g. $\mathbf{E} = \bar{\mathbf{E}}(\mathbf{P},.)$ or $\mathbf{D} = \bar{\mathbf{D}}(\mathbf{E},.)$, $\mathbf{H} = \bar{\mathbf{H}}(\mathbf{B},.)$, $\mathbf{E} = \hat{\mathbf{E}}(\mathbf{J},.)$ may be preferable depending on what we want to put the emphasis. Thus Ohm's law of our secondary-school years is usually written in the last form, $U = RI$ where U is the difference of potential (electric field), I the intensity of the current, and R is the resistance which is the proportionality coefficient that may depend on the stretching of the wire (so-called *elasto-resistance*) and temperature.

It must be emphasized that Eqs. (9.2.1) are expressed in a fixed frame $\mathcal{R}_L$ traditionally called the *laboratory frame*. It is known since Lorentz, Heaviside, Larmor, Poincaré and Einstein that Maxwell's equation *in a vacuum* are form-invariant by the special-relativistic group of space-time transformations (so-called Lorentz Poincaré group). For Maxwell's equations *in matter* the results depend on what one assumes for the transformation of the "material" fields $\mathbf{M}$, $\mathbf{P}$, $\mathbf{J}$ and q_f. Being interested in material velocities much smaller, and dynamical processes much slower, than c, we may *impose* on Eqs. (9.2.1) a restricted invariance which will be the same as the one already verified by the mechanical equations, namely, the *Galilean invariance* of classical Newtonian mechanics (cf. de Groot and Suttorp, 1972; Maugin and Eringen, 1977, Maugin, 1988, Chapter 3). Bearing this in mind, it is found that Eqs. (9.2.1) can be rewritten in a frame $\mathcal{R}_c(\mathbf{x}, t)$ *co-moving* with the infinitesimal element of deformable matter at velocity $\mathbf{v}$ in physical space $\mathbb{E}^3$ as

$$\begin{aligned} &\nabla \times \mathcal{E} + \frac{1}{c}\overset{*}{\mathbf{B}} = \mathbf{0}\,, \qquad && \nabla \cdot \mathbf{B} = 0\,, \\ &\nabla \times \mathcal{H} - \frac{1}{c}\overset{*}{\mathbf{D}} = \frac{1}{c}\mathcal{J}\,, \qquad && \nabla \cdot \mathbf{D} = q_f\,, \end{aligned} \tag{9.2.4}$$

where a superimposed $*$ denotes the convected time derivative such that [cf. (6.3.24) and (6.9.121)]

$$\begin{aligned} \overset{*}{\mathbf{P}} &:= \dot{\mathbf{P}} - (\mathbf{P} \cdot \nabla)\mathbf{v} + \mathbf{P}(\nabla \cdot \mathbf{v})\,, \\ &= \frac{\partial \mathbf{P}}{\partial t} + \nabla \times (\mathbf{P} \times \mathbf{v}) + \mathbf{v}(\nabla \cdot \mathbf{P})\,, \end{aligned} \tag{9.2.5}$$

and the "script upper case" fields are given by the following "Galilean transformation laws" between $\mathcal{R}_L$ and $\mathcal{R}_c(\mathbf{x}, t)$:

$$\begin{aligned}
\mathcal{E} &= \mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{B}\,, & \mathcal{H} &= \mathbf{H} - \frac{1}{c}\mathbf{v} \times \mathbf{D}\,, \\
\mathcal{B} &= \mathbf{B} - \frac{1}{c}\mathbf{v} \times \mathbf{E}\,, & \mathcal{H} &= \mathcal{B} - \mathcal{M}\,, \\
\mathcal{M} &= \mathbf{M} + \frac{1}{c}\mathbf{v} \times \mathbf{P}\,, & \mathcal{P} &= \mathbf{P}\,, \\
\mathcal{J} &= \mathbf{J} - q_f\mathbf{v}\,, & \mathcal{D} &\neq \mathcal{E} + \mathcal{P}\,.
\end{aligned} \tag{9.2.6}$$

Clearly, in such transformations the symmetry between magnetization and polarization processes is lost (but this is fully justified by the microscopic definitions of such fields; cf. Maugin, 1988). The field $\mathcal{E}$, electric field in $\mathcal{R}_c$, is usually referred to as the *electromotive intensity.* The field $\mathcal{J}$, current in $\mathcal{R}_c$, is called the *conduction current,* since $q_f\mathbf{v}$ is the *convection current*; q_f and $\mathbf{v}$ will be known through the solution of a boundary-value problem; only $\mathcal{J}$ requires a constitutive equation.

Large classes of electromagnetic materials. We shall say that a material is *nonmagnetizable* and *nonpolarizable* if and only if (exact definition, independent of whether a Galilean or Lorentzian framework is assumed):

$$\mathcal{M}(\mathbf{x}, t) = \mathbf{0},\ \forall\mathbf{x}, \forall t\,, \tag{9.2.7}$$

and

$$\mathcal{P}(\mathbf{x}, t) = \mathbf{0},\ \forall\mathbf{x}, \forall t\,; \tag{9.2.8}$$

These give the *approximate "Galilean"* conditions

$$\mathbf{M} = \frac{1}{c}\mathbf{P} \times \mathbf{v}\,, \qquad \text{and} \qquad \mathbf{P} = \mathbf{0}, \forall\mathbf{x}, \forall t\,. \tag{9.2.9}$$

The material is said to be a *conductor of electricity* if and only if $\mathcal{J}$ is nonzero; otherwise it is called an *insulator.* The material is said to be *electrically charged if* $q_f \neq 0$ at all points in the material. A material is called a *dielectric* when it is an insulator and $q_f = 0$. Most of electrically polarizable media (solids) are either dielectrics or semiconductors. Strongly magnetizable media may be insulators or conductors. Weakly magnetizable media may be extremely good conductors (in the limit which is a mathematical idealization, *perfect conductors*).

In metals, heat conduction usually accompanies electricity conduction. This is why *magneto-thermo-elasticity* is a fashionable subject of research. Some electrically polarized materials may present a permanent electric polarization in the absence of electric fields. These are called *ferroelectric*, *antiferroelectic* or *ferrielectric* media depending on the circumstances. The equivalent behavior for magnetism refers to *ferromagnetism*, *antiferromagnetism*, and *ferrimagnetism.* Some materials may conduct electricity without apparent resistance and no dissipation; these are called *superconductors.* The last three classes of materials present the noted critical behavior only below a certain temperature at which a *change of phase* has occured. In all we see that the range of possible behaviors is very wide.

Direct consequences of Eqs. (9.2.1) are:

(i) the *law of conservation of electric charge* [this is obtained by taking the divergence of $(9.2.1)_3$ and accounting for $(9.2.1)_4$]

$$\frac{\partial q_f}{\partial t} + \nabla \cdot \mathbf{J} = \mathbf{0}\,; \tag{9.2.10}$$

and

(ii) an *energy identity* called the "*Poynting theorem*" [this is obtained by multiplying scalarly $(9.2.1)_1$ by $\mathbf{H}$ and $(9.2.1)_3$ by $\mathbf{E}$ and making a combination of the two resulting expressions]

$$\mathbf{H} \cdot \frac{\partial \mathbf{B}}{\partial t} + \mathbf{E} \cdot \frac{\partial \mathbf{D}}{\partial t} = -\mathbf{J} \cdot \mathbf{E} - \nabla \cdot \mathbf{S}\,, \qquad \mathbf{S} \equiv c\mathbf{E} \times \mathbf{H}\,, \tag{9.2.11}$$

or, using the fields introduced by (9.2.6),

$$\mathcal{H} \cdot \overset{*}{\mathbf{B}} + \mathcal{E} \cdot \overset{*}{\mathbf{D}} = -\mathcal{J} \cdot \mathcal{E} - \nabla \cdot \mathcal{S}\,, \qquad \mathcal{S} \equiv c\mathcal{E} \times \mathcal{H}\,, \tag{9.2.12}$$

where nothing has been assumed concerning the behavior. These are mere *identities* and *not* statements of a law of thermodynamics. The vectors $\mathbf{S}$ and $\mathcal{S}$ are the so-called *Poynting vector* (flux of electromagnetic energy) in $\mathcal{R}_L$ and $\mathcal{R}_c$, respectively. Equation (9.2.11) is exact. The very structure of Eq. (9.2.12) reflects the "Galilean" approximation because, whereas all terms in the right-hand side are expressed in $\mathcal{R}_c$, terms in the left-hand side are typically composed of products of a field in $\mathcal{R}_c$ and the convected time derivative of a thermodynamically conjugate field, in $\mathcal{R}_L$. To proceed further we need to introduce the *interactions* between electromagnetic fields and deformable matter in the fundamental *balance laws of thermomechanics.*

9.3. Thermomechanics of Electromagnetic Materials

Now we consider a material body such as in Paragraph 2.3D. The body, just as before, is acted upon by mechanical tractions $\mathbf{T}^d$ at $\partial\Omega$ and physical forces (say, gravity) $\mathbf{f}$ per unit mass in Ω with a possible influx of heat $\mathbf{q}$ per unit area across $\partial\Omega$ and a supply of heat h per unit mass in Ω. If this body is a general electromagnetic body *without internal degrees of freedom* (of mechanical or electromagnetic origin) and it is acted upon by electromagnetic fields, then the general balance laws of thermomechanics for that body can be *a priori* written in the following general form (see Maugin, 1988, Chapter 3):

- *Balance of mass*:

$$\frac{d}{dt}\int_{\Omega} dm = 0\,; \tag{9.3.13}$$

- *Balance of linear (physical) momentum*:

$$\frac{d}{dt}\int_{\Omega} \mathbf{v}dm = \int_{\Omega}(\mathbf{f} + \rho^{-1}\mathbf{f}^{em}dm + \int_{\partial\Omega}(\mathbf{T}^d + \mathbf{T}^{em})da\,; \tag{9.3.14}$$

- *Balance of angular (physical) momentum*:

$$\frac{d}{dt}\int_{\Omega}(\mathbf{r}\times\mathbf{v})dm = \int_{\Omega}(\mathbf{r}\times\mathbf{f} + \rho^{-1}\bar{\mathbf{c}}^{em})dm + \int_{\partial\Omega}(r\times(\mathbf{T}^d + \mathbf{T}^{em}))da\,; \tag{9.3.15}$$

- *First law of thermodynamics*:

$$\frac{d}{dt}\int_{\Omega}\left(\frac{1}{2}\mathbf{v}^2 + e\right)dm = \int_{\Omega}(\mathbf{f}\cdot\mathbf{v} + h + \rho^{-1}\mathbf{w}^{em})dm + \int_{\partial\Omega}(\mathbf{T}^d\cdot\mathbf{v} - \mathbf{q}\cdot\mathbf{n})da\,; \tag{9.3.16}$$

- *Second law of thermodynamics*:

$$\frac{d}{dt}\int_{\Omega}\eta dm \geq \int_{\Omega} h\theta^{-1}dm - \int_{\partial\Omega}\theta^{-1}\mathbf{q}\cdot\mathbf{n}\,da\,. \tag{9.3.17}$$

In these equations we assume that the *entropy flux* has the classical form. The *interaction contributions* $\mathbf{f}^{em}$, $\mathbf{T}^{em}$, $\bar{\mathbf{c}}^{em}$, and $\mathbf{w}^{em}$ have to be determined by an analysis which is *foreign* to continuum thermomechanics, *per se.* There is *no* general agreement on their expressions as they depend either upon the taste of the scientist or on the quality and fineness of the model used to build them at a sub-macroscopic scale. A practical approach based on an averaging procedure was proposed by Maugin and Eringen (1977) in the tradition set forth by Lorentz in his theory of electrons and carried on by Nijboer, de Groot, Suttorp, etc. We shall use their expressions because these were exactly obtained within the above-introduced "Galilean" approximation. $\mathbf{T}^{em}$ here is irrelevant. For the other electromagnetic source terms we have (neglecting quadrupole contributions)

$$\mathbf{f}^{em} = q_f\mathcal{E} + \frac{1}{c}(\mathcal{J} + \overset{*}{\mathbf{P}}) \times \mathbf{B} + (\mathbf{P}\cdot\nabla)\mathcal{E} + (\nabla\mathbf{B})\cdot\mathcal{M}\,, \tag{9.3.18}$$

$$\bar{\mathbf{c}}^{em} = \mathbf{r} \times \mathbf{f}^{em} + \mathbf{c}^{em}\,, \tag{9.3.19}$$

$$\mathbf{w}^{em} = \mathbf{f}^{em}\cdot\mathbf{v} + \mathbf{c}^{em}\cdot\mathit{\Omega} + \rho h^{em}\,, \tag{9.3.20}$$

wherein

$$\begin{aligned} \mathcal{C}^{em} &= \mathbf{P}\times\mathcal{E} + \mathcal{M}\times\mathbf{B}\,, \\ \rho h^{em} &= \mathcal{J}\cdot\mathcal{E} + \mathcal{E}\cdot\overset{*}{\mathbf{P}} - \mathcal{M}\cdot\overset{*}{\mathbf{B}} + \mathrm{tr}\,(\bar{\sigma}^{em}\mathbf{D})\,, \end{aligned} \tag{9.3.21}$$

and

$$\bar{\sigma}^{em} = \mathbf{P}\otimes\mathcal{E} - \mathbf{B}\otimes\mathcal{M} + (\mathcal{M}\cdot\mathbf{B})\mathbf{1} \tag{9.3.22}$$

together with

$$\mathit{\Omega} := \frac{1}{2}\nabla\times\mathbf{v}\,, \tag{9.3.23}$$

where ⊗ indicates the tensor product.

The local form of Eqs. (9.3.14) through (9.3.17) is easily shown to be (the divergence of second-order tensors — which are no longer necessarily symmetric

— is taken on the first index)

$$\dot{\rho} + \rho\nabla\cdot\mathbf{v} = 0 \qquad \text{or} \qquad \rho_0 = \rho J_F \text{ in } \Omega\,, \tag{9.3.24}$$

$$\rho\dot{\mathbf{v}} = \operatorname{div}\sigma + \rho\mathbf{f} + \mathbf{f}^{em}\,, \qquad \text{in } \Omega \tag{9.3.25}$$

$$\mathbf{n}\cdot\sigma = \mathbf{T}^d + \mathbf{T}^{em} \qquad \text{at } \partial\Omega\,, \tag{9.3.26}$$

$$\sigma_A := \frac{1}{2}(\sigma - \sigma^T) = (\bar{\sigma}^{em})_A = (\mathbf{P}\otimes\mathcal{E} + \mathcal{M}\otimes\mathbf{B})_A\,, \tag{9.3.27}$$

$$\rho\dot{e} = \operatorname{tr}(\sigma\mathbf{L}) - \mathbf{f}^{em}\cdot\mathbf{v} + \mathbf{w}^{em} - \nabla\cdot\mathbf{q} + \rho h\,, \text{ in } \Omega\,, \tag{9.3.28}$$

and

$$\rho\dot{\eta} \geq \rho h\theta^{-1} - \nabla\cdot(\mathbf{q}\theta^{-1})\,, \tag{9.3.29}$$

where **L** is the velocity-gradient tensor and we note that the Cauchy stress tensor is no longer symmetric. Its antisymmetric part σ_A is given by a quantity called the *ponderomotive torque*. In this model which admits no internal degrees of freedom, this torque goes to zero with magnetization and electric polarization, or when the latter are aligned with electric and magnetic fields, respectively (in the magnetic case, this torque is responsible for the transient rotation of the compass' needle). Equation (9.3.25) has been used to transform the local form of (9.3.16).

Of special interest for further developments is the transformation of the local form of (9.3.28) and (9.3.29) of the first and second laws of thermodynamics. First we can transform the expression of w^{em} on account of the identity (9.2.11) or (9.2.12). Thus it can be shown that (prove this by the way of exercise)

$$\mathbf{w}^{em} = \mathbf{f}^{em}\cdot\mathbf{v} + \rho\mathcal{E}\cdot\dot{\pi} - \mathcal{M}\cdot\overset{*}{\mathbf{B}} + \mathcal{J}\cdot\mathcal{E} \tag{9.3.30}$$

or

$$\mathbf{w}^{em} = \mathbf{J}\cdot\mathbf{E} + \mathbf{E}\cdot\frac{\partial\mathbf{P}}{\partial t} - \mathbf{M}\cdot\frac{\partial\mathbf{B}}{\partial t} + \nabla\cdot[\mathbf{v}(\mathbf{E}\cdot\mathbf{P})]\,, \tag{9.3.31}$$

or else

$$\mathbf{w}^{em} = -\frac{\partial u^{em\cdot f}}{\partial t} - \nabla\cdot\{\mathbf{S} - \mathbf{v}(\mathbf{E}\cdot\mathbf{P})\}\,, \tag{9.3.32}$$

where

$$\pi = \mathbf{P}/\rho\,, \qquad \mu = \mathcal{M}/\rho\,, \qquad u^{em\cdot f} = \frac{1}{2}(\mathbf{E}^2 + \mathbf{B}^2)\,. \tag{9.3.33}$$

Accounting for the first of these in (9.3.28) yields the form

$$\rho\dot{e} = \operatorname{tr}(\sigma\mathbf{L}) - \nabla\cdot\mathbf{q} + \rho h + \mathcal{J}\cdot\mathcal{E} + \rho\mathcal{E}\cdot\dot{\pi} - \mathcal{M}\cdot\dot{\mathbf{B}}\,. \tag{9.3.34}$$

Introducing now the Helmholtz free energy density ψ by (Legendre transformation if $\theta = \partial e/\partial\eta$)

$$\begin{aligned} -\rho(\dot{\psi} + \eta\dot{\theta}) + \operatorname{tr}(\sigma\mathbf{L}) + \mathcal{J}\cdot\mathcal{E} + \rho\mathcal{E}\cdot\dot{\pi} \\ - \mathcal{M}\cdot\dot{\mathbf{B}} + \theta\mathbf{q}\cdot\nabla(\theta^{-1}) \geq 0\,. \end{aligned} \tag{9.3.34}$$

This, together with (9.3.34) can be further transformed by performing Legendre transformations and introducing various types of time derivatives. For instance, introducing

$$\hat{e} = e + \mu\cdot\mathbf{B}\,, \qquad \hat{\psi} = \Psi + \mu\cdot\mathbf{B}\,, \tag{9.3.35}$$

we can transform Eq. (9.3.34) to

$$\begin{aligned} -\rho(\dot{\hat{\psi}} + \eta\dot{\theta}) + \operatorname{tr}(\sigma\mathbf{L}) + \mathcal{J}\cdot\mathcal{E} \\ + \rho\mathcal{E}\cdot\dot{\pi} + \rho\mathbf{B}\cdot\dot{\mu} + \theta\mathbf{q}\cdot\nabla(\theta^{-1}) \geq 0\,. \end{aligned} \tag{9.3.36}$$

Alternately, defining $\bar{e}$ and $\bar{\psi}$ by

$$\begin{aligned} \bar{e} &= e - \pi\cdot\mathcal{E} = \hat{e} - \mu\cdot\mathbf{B} - \pi\cdot\mathcal{E}\,, \\ \bar{\psi} &= \bar{e} - \eta\theta = \hat{\psi} - \mu\cdot\mathbf{B} - \pi\cdot\mathcal{E}\,, \end{aligned} \tag{9.3.37}$$

we can write (9.3.34) or (9.3.36) in the form

$$\begin{aligned} -\rho(\dot{\bar{\psi}} + \eta\dot{\theta}) + \operatorname{tr}(\sigma\mathbf{L}) + \mathcal{J}\cdot\mathcal{E} \\ - \mathbf{P}\cdot\dot{\mathcal{E}} - \mathcal{M}\cdot\overset{*}{\mathbf{B}} + \theta\mathbf{q}\cdot\nabla(\theta^{-1}) \geq 0\,. \end{aligned} \tag{9.3.39}$$

The relevance of each of the inequalities (9.3.34) through (9.3.39) depends on the choice of independent variables to describe the interactions that take place between the Maxwellian electromagnetic fields $\mathcal{E}$ and $\mathbf{B}$ and the (material) polarization and magnetization fields. Furthermore, if we note that, e.g.

$$\rho\dot{\pi} = \overset{*}{\mathbf{P}} + (\mathbf{P}\cdot\nabla)\mathbf{v}\,, \tag{9.3.40}$$

and define the symmetric stress σ^E by

$$\sigma^E = (\sigma + \mathcal{E} \otimes \mathbf{P} + \mathbf{B} \otimes \mathcal{M})_S \,, \tag{9.3.41}$$

then, on account of (9.3.27),

$$\sigma_A^{em} = \mathbf{C}^{em} \,, \qquad \mathbf{C}^{em} = -\mathrm{dual}\, \mathbf{c}^{em} \,, \tag{9.3.42}$$

we can rewrite (9.3.36) as

$$\begin{aligned} &-\rho(\dot{\hat{\psi}} + \eta\dot{\theta}) + \mathrm{tr}\,(\sigma^E \mathbf{D}) + \mathcal{J} \cdot \mathcal{E} \\ &\qquad + \mathcal{E} \cdot \overset{*}{\mathbf{P}} + \mathfrak{B} \cdot \overset{*}{\mathcal{M}} + \theta \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0 \,. \end{aligned} \tag{9.3.43}$$

Another possibility is

$$\begin{aligned} &-\rho(\dot{\bar{\psi}} + \eta\dot{\theta}) + \mathrm{tr}\,(\sigma^E \mathbf{D}) + \mathcal{J} \cdot \mathcal{E} \\ &\qquad - \mathbf{P} \cdot \overset{*}{\mathcal{E}} - \mathcal{M} \cdot \overset{*}{\mathbf{B}} + \theta \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0 \,, \end{aligned} \tag{9.3.44}$$

where

$$\bar{\sigma}^E := \sigma^E - (\mathcal{E} \cdot \mathbf{P} + \mathcal{M} \cdot \mathbf{B})\mathbf{1} \,. \tag{9.3.45}$$

This is not all in the case of deformable solids in finite strains where one often prefers to introduce *material fields* for both mechanical and electromagnetic entities (at points in space where this is meaningful for the latter as we remind the reader that electromagnetic fields exist also outside the body, in vacuum). This is achieved in the following manner. We look for material expressions of electromagnetic fields which allow one to express equations formally as (9.2.1) or (9.2.4) but in terms of material fields which are functions of $\mathbf{X}$ and t only, and indeed *vectors* on the material manifold $\mathcal{M}^3$. Here, however — this was not the case for Euclidean physical space $\mathbb{E}^3$ — that manifold makes the distinction between *contravectors* and *covectors*. As a matter of fact, the following "Maxwellian" formulation of Maxwell's equations in matter:

$$\begin{aligned} &\nabla_R \times \mathfrak{E} + \frac{1}{c} \frac{\partial \mathfrak{B}}{\partial t}\bigg|_{\mathbf{X}} = \mathbf{0} \,, \qquad \nabla_R \cdot \mathfrak{B} = 0 \,, \\ &\nabla_R \times \mathfrak{H} - \frac{1}{c} \frac{\partial \mathfrak{D}}{\partial t}\bigg|_{\mathbf{X}} = \frac{1}{c}\mathfrak{J} \,, \qquad \nabla_R \cdot \mathfrak{D} = \mathfrak{Q}_f \,, \end{aligned} \tag{9.3.46}$$

is obtained if we introduce the fields noted with Gothic letters by the following *operations of convection* (so-called "pull back") to the reference configuration $\mathcal{K}_R$ (see, e.g. Nelson, 1979, or Maugin, 1988):

$$\begin{aligned} &\mathfrak{B} = J_F \mathbf{F}^{-1} \cdot \mathbf{B}\,, && \mathfrak{D} = J_F \mathbf{F}^{-1} \cdot \mathbf{D}\,, \\ &\mathfrak{E} = \bar{\mathfrak{E}} - \frac{1}{c}\mathbf{V} \times \mathfrak{B}\,, && \mathfrak{H} = \mathbf{H} \cdot \mathbf{F} + \frac{1}{c}\mathbf{V} \times \mathfrak{D}\,, \\ &\Pi = J_F \mathbf{F}^{-1} \cdot \mathbf{P}\,, && \mathbb{M} = \mathcal{M} \cdot \mathbf{F}\,, \\ &\mathfrak{J} = J_F \mathbf{F}^{-1} \cdot \mathcal{J}\,, && \mathfrak{Q}_f = J_F q_f\,, \end{aligned} \tag{9.3.47}$$

and

$$\bar{\mathfrak{E}} = \mathbf{E} \cdot \mathbf{F}\,, \qquad \bar{\mathfrak{B}} = \mathfrak{B} - \frac{1}{c}\mathbf{V} \times \bar{\mathfrak{E}} = J_F \mathbf{F}^{-1} \cdot \mathcal{B}\,. \tag{9.3.48}$$

We check that

$$\mathfrak{D} = J_F \mathbf{C}^{-1} \cdot \bar{\mathfrak{E}} + \Pi\,, \qquad \mathfrak{H} = J_F^{-1} \mathbf{C} \cdot \bar{\mathfrak{B}} - \mathbb{M}\,, \tag{9.3.49}$$

which replace the simple (spatial) relations (9.2.2).

Introducing now the so-called second Piola–Kirchhoff (or "thermodynamic") "elastic" stress $\mathbb{S}^E$ by

$$\mathbb{S}^E = J_F \mathbf{F}^{-1} \cdot \sigma^E \cdot \mathbf{F}^{-T}\,, \tag{9.3.50}$$

and the fields

$$\mathbf{Q} = J_F \mathbf{F}^{-1} \cdot \mathbf{q}\,, \qquad \nabla_R \mathcal{A} = (\nabla \mathcal{A}) \cdot \mathbf{F}\,, \tag{9.3.51}$$

by multiplication by J_F of equations such as (9.3.43) and noting that

$$\overset{*}{\mathbf{P}} = J_F^{-1} \mathbf{F} \cdot \left.\frac{\partial \Pi}{\partial t}\right|_{\mathbf{X}}\,, \qquad \overset{*}{\mathcal{M}} = J_F^{-1} \mathbf{F} \cdot \left.\frac{\partial \bar{\mathbb{M}}}{\partial t}\right|_{\mathbf{X}}\,, \tag{9.3.52}$$

we readily show that Eqs. (9.3.43) and (9.3.44) transform to

$$\begin{aligned} &-(\dot{\hat{W}} + S\dot{\theta}) + \mathrm{tr}\,(\mathbb{S}^E \dot{\mathbb{E}}) + \mathfrak{J} \cdot \mathfrak{E} \\ &\qquad + \mathfrak{E} \cdot \dot{\Pi} + \mathfrak{B} \cdot \dot{\mathbb{M}} + \theta \mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0 \end{aligned} \tag{9.3.53}$$

or

$$\begin{aligned} &-(\dot{\bar{W}} + S\dot{\theta}) + \mathrm{tr}\,(\bar{\mathbb{S}}^E \dot{\mathbb{E}}) + \mathfrak{J} \cdot \mathfrak{E} \\ &\qquad - \Pi \cdot \dot{\mathfrak{E}} - \bar{\mathbb{M}} \cdot \dot{\mathfrak{B}} + \theta \mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0\,, \end{aligned} \tag{9.3.54}$$

where we have set

$$\hat{W} = \rho_0 \hat{\psi}\,, \qquad \bar{W} = \rho_0 \bar{\psi}\,, \qquad S = \rho_0 \eta\,. \tag{9.3.55}$$

Any of the Clausius-Duhem inequalities obtained may be considered as a constraint imposed on the formulation of constitutive equations for the fields, e.g.

$$W, S, \bar{\mathbb{S}}^E, \mathfrak{J}, \Pi, \bar{\mathbb{M}}, \mathbf{Q}\,, \tag{9.3.56}$$

or any equivalent set defined, for instance, through partial Legendre transformations The following two remarks are in order:

(i) The above derivation does not pay attention to the *tensorial variance* of various geometrical objects, so that we have straightforwardly applied derivatives such as those marked * to objects which, in fact, do not have the same variance. One could think that those are irrelevant mathematical details as we work to start with in a Cartesian framework in $\mathcal{K}_t$. But, as mentioned before, this is *not* the case because the *material manifold* used to described the reference configuration *does make that difference* [e.g. between the elements of the pair (P, $\mathcal{M}$) or ($\mathcal{E}$, **B**)]. A correct derivation is to be found (in the absence of dissipative processes) in Maugin, 1993a, Chapter 8. The correct definition of materially convected fields is forced upon us by the rewriting of Maxwell's equations as (9.3.46), as the curl operator ($\nabla\times$) and the divergence operator ($\nabla\cdot$) distinguish between contravariant and covariant vectors [see the definitions (9.3.47)].

(ii) An important case where the previous remark becomes irrelevant is that of *rigid bodies* which are *not* in motion. Then the fundamental inequality (9.3.43) reduces to

$$-(\dot{W} + S\dot{\theta}) + \mathbf{J}\cdot\mathbf{E} + \mathbf{E}\cdot\dot{\mathbf{P}} + \mathbf{B}\cdot\dot{\mathbf{M}} + \theta\mathbf{q}\cdot\nabla(\theta^{-1}) \geq 0\,, \tag{9.3.57}$$

while the *energy equation* takes on the reduced form

$$\dot{E} = (\rho h - \nabla\cdot\mathbf{q}) + (\mathbf{J}\cdot\mathbf{E} + \mathbf{E}\cdot\dot{\mathbf{P}} + \mathbf{B}\cdot\dot{\mathbf{M}})\,, \tag{9.3.58}$$

where the contribution within parentheses is the *electromagnetic dissipation.* Indeed, the rigid-body motion is defined in differential form by the condition

$$\mathbf{D}(x,t) = \mathbf{0}\,, \forall \mathbf{x}, t\,, \tag{9.3.59}$$

where **D** is the rate-of-strain tensor. Furthermore, $\mathbf{v} = \mathbf{0}$ if the body does not move at all, even rigidly. From which there follows (9.3.57) and (9.3.58) with $E = \rho_0 e$.

9.4. Classical Irreversible Processes: Conduction and Relaxation

We call *classical* irreversible processes of electromagnetic bodies, those behaviors which can practically be "read" from the expression of the Clausius–Duhem inequality as their description does not necessitate the introduction of additional entities (e.g. either extra thermodynamical variable of states of the "internal" type or internal degrees of freedom). The corresponding formulation is none other than the classical theory of irreversible processes (*T.I.P.*).

A. Rigid bodies

It goes in the natural order of complexity to start with *rigid bodies* for which we have the inequality (9.3.57) and the energy equation (9.3.58). Here electromagnetic properties for which constitutive equations are needed in a macroscopic description amount to three: electric polarization, magnetization, and electric conduction. On the one hand we note that an electric dipole density **P** placed in an electric field **E** and a magnetic dipole density **M** placed in a magnetic induction $\mathbf{B}^4$ develop mechanical powers [see Eq. (9.3.57)]

$$p^E = \mathbf{E}\cdot\dot{\mathbf{P}}\,, \qquad p^M = \mathbf{B}\cdot\dot{\mathbf{M}}\,. \tag{9.4.60}$$

The obvious analogy between these formulas and the expression of the corresponding deformation power in small strain

$$p_{(i)} = \sigma : \dot{\varepsilon}\,, \tag{9.4.61}$$

up to the tensorial order of the objects involved, also means that there is a direct analogy between stress and electric and magnetic fields (the "causes") on the one hand, and between strain and electric polarization and magnetization (the "effects") on the other hand. In principle, therefore, all developments concerning the irreversible thermodynamics of deformation processes have analogs in dielectrics (electrically polarizable media) and in magnetism, accounting however for the differing tensorial character. *Electric conduction* both is of a different nature and shares something in common with mechanical processes. Indeed, the elementary power dissipated by the conduction current

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[4] We can replace **B** by **H**, on the condition to change the definition of energy, i.e. to introduce $\bar{W} = W(\mathbf{M},\mathbf{P},\theta) - (\mathbf{M}^2/2) = \bar{W}(\mathbf{M},\mathbf{P},\theta)$.

(here noted simply **J**) in an electric field **E**, is as we all know, given by *Joule's expression*

$$p^c = \mathbf{E} \cdot \mathbf{J} \,. \tag{9.4.62}$$

On the one hand, as **E** is given in statics by $-\nabla\phi$, where ϕ is the electrostatic potential, electric conduction, as recognized 150 years ago by W. Thomson, is very similar to heat conduction. In fact, *Joule's* contribution (9.4.62) then reads $-\mathbf{J} \cdot \nabla\phi$ in total analogy with the heat contribution $-S \cdot \nabla\theta$ or the diffusion term found before as $-\mathbf{J} \cdot \nabla\mu$, where **J** was the diffusion current. Thus, a vanishing potential difference belongs to the condition of application of the axiom of the local equilibrium state (the system must be spatially uniform at thermostatic equilibrium). Simultaneously, from the microscopic definition of current, we have the equivalence

$$p^c = \mathbf{E} \cdot \mathbf{J} = (q\mathbf{E}) \cdot (\mathbf{J}/q) = \mathbf{F} \cdot \hat{\mathbf{v}} \,, \tag{9.4.63}$$

where q is an electric charge density, **F** is a mechanical force and $\hat{\mathbf{v}}$ is a vector field akin to a velocity. This demonstrates the *current* nature of **J** — e.g. **J** has the same nature as $\dot{\mathbf{P}}$; compare (9.4.63) and $(9.4.60)_1$. These two visions of **J** reflect the duality of the concept of conduction. These two aspects materialize in the modeling of various regimes of conduction such as normal, semi- and super-conduction.

Joule and Hall effects. Here we just want to remark on normal conduction and the *Hall effect.* We examine only the contribution (9.4.62) to dissipation. According to *T.I.P.*, we can take E linear affine in **J**, i.e.

$$\mathbf{E} = \hat{\mathbf{E}}(\mathbf{J};\theta) \,, \qquad \hat{\mathbf{E}}(\mathbf{J} = \mathbf{0};\theta) = \mathbf{0} \,. \tag{9.4.64}$$

For an *isotropic body* this yields, in the *linear approximation*, the celebrated *Joule equation*:

$$\mathbf{E} = R(\theta)\mathbf{J} \,, \tag{9.4.65}$$

where $R(\theta)$ is a temperature-dependent *resistivity*.

Now imagine that, as the dependence on **B** is *not ruled out*, we consider a somewhat more general equation than (9.4.64):

$$\mathbf{E} = \hat{\mathbf{E}}(\mathbf{J};\mathbf{B},\theta) \,, \qquad \hat{\mathbf{E}}(\mathbf{J} = \mathbf{0};\mathbf{B},\theta) = \mathbf{0} \,, \tag{9.4.66}$$

where **B** and θ, which belong to the observable state variables, here play the role of simple parameters. But **B** is a *vectorial parameter having an axial* *nature.* Even for an *isotropic body*, using simple arguments of group theory and its representation theorems, we can write a linear affine relation between $\mathbf{E}$ and $\mathbf{J}$ as follows

$$\mathbf{E} = R_0(|\mathbf{B}|^2, \theta)\mathbf{J} + R_1(|\mathbf{B}|^2, \theta)\mathbf{B} \times \mathbf{J} \,. \tag{9.4.67}$$

The last contribution, *noted* $\mathbf{E}^G$, representing the so-called *Hall effect*, is a *gyroscopic effect* in the sense that it satisfies the following *orthogonality relation* [cf. (6.4.69)]

$$\mathbf{E}^G \cdot \mathbf{J} = 0 \,. \tag{9.4.68}$$

Typical of this type of contribution is the fact that they do not cause any dissipation while they are *not* given by a law of state. As a consequence, there are no thermodynamical restriction on the sign of the scalar coefficient R_1. Effects of the Hall type are important not only in rigid bodies but also in *plasmas* (fluid mixtures) and elastic *semi-conductors* (solid mixtures). But they remain *classical* effects in so far as we are concerned.

The inequality (9.3.57) also allows one to establish the constitutive equations of linear isotropic or anisotropic electrically polarized or magnetized rigid bodies — also see below, the case of fluids and deformable solids — as well as the coupling between the two effects in a *nonlinear theory*, and also the couplings between heat and electricity conductions in the absence or presence of a magnetic induction (effects known as the *thermoelectric* and *galvanomagnetic effects*: Thomson, Peltier, Nernst, Leduc-Righi, Ettingshausen and Hall effects). We refer the reader to more standard treatises for these e.g. de Groot and Mazur, 1962; Eringen and Maugin, 1990, Chapter 5.

B. Fluids

In this case we are satisfied with an Eulerian description and all fields are considered at time t in the actual configuration K_t. The basic thermodynamic inequality is provided by Eq. (9.3.43) or (9.3.44) depending on the set of independent variables chosen. On should consider to start with

$$\bar{\psi} = \bar{\psi}(\rho, \theta, \mathcal{E}, \mathbf{B}) \,, \tag{9.4.69}$$

limited to the case where dissipation is only of viscous, Joulean, and thermal origin. We refer the reader to Eringen and Maugin (1990, Chapter 5). As the fluids considered have no *preferred direction*, i.e. they are *isotropic*, it is consequently shown, even in the nonlinear theory, that **P** is linear in the vector $\mathcal{E}$ and M is linear in the vector **B** (they can also depend parametrically on the magnitude of these fields), so that the ponderomotive couple vanishes in such fluids, and the Cauchy stress tensor is symmetric (see Eringen and Maugin, 1990; p. 172). We do not duplicate these developments as we shall concentrate, on the case of solids, rigid or not, which admit more original dissipative behaviors.

C. Deformable solids

We are particularly concerned by the phenomena of *electric* and *magnetic relaxation.* We consider the Clausius–Duhem inequality in the form (9.3.54). The corresponding *Gibbs' equation* which serves to provide the *laws of state*, is naturally given:

$$\dot{\bar{\mathbf{W}}} = \operatorname{tr}(\bar{\mathbb{S}}^E \dot{\mathbb{E}}) - \Pi \cdot \dot{\mathfrak{E}} - \bar{\mathbb{M}} \cdot \dot{\mathfrak{B}} - S\dot{\theta} \,. \tag{9.4.70}$$

So that at thermodynamic equilibrium we have the following *laws of state*:

$$\begin{gathered} W = \bar{W}(\mathbb{E}, \mathfrak{E}, \mathfrak{B}, \theta)\,, \qquad S = -\partial \bar{W}/\partial \theta\,, \\ \mathbb{S}^E = \partial \bar{W}/\partial \mathbb{E}\,, \qquad \Pi = -\partial \bar{W}/\partial \bar{\mathfrak{E}}\,, \qquad \mathcal{M} = -\partial \bar{W}/\partial \mathfrak{B}\,. \end{gathered} \tag{9.4.71}$$

Slightly outside equilibrium, the temperature field θ and the electric potential ϕ may be spatially nonuniform, but we shall suppose that entropy still assumes its thermostatic definition $(9.4.71)_2$. We define the following quantities outside equilibrium, i.e. deviations from the definitions at equilibrium:

$$\begin{gathered} \mathbb{S}^v \equiv \bar{\mathbb{S}}^E - \partial \bar{W}/\partial \mathbb{E}\,, \\ \Pi^d \equiv \Pi + \partial \bar{W}/\partial \mathfrak{E}\,, \qquad \bar{\mathbb{M}}^d \equiv \bar{\mathbb{M}} + \partial \bar{W}/\partial \mathfrak{B}\,, \end{gathered} \tag{9.4.72}$$

so that the Clausius–Duhem inequality (9.3.54) provides the *dissipation inequality* in the form

$$\Phi = \operatorname{tr}(\mathbb{S}^v \dot{\mathbb{E}}) - \Pi^d \cdot \dot{\mathfrak{E}} - \bar{\mathbb{M}}^d \cdot \dot{\mathfrak{B}} + \mathfrak{J} \cdot \mathfrak{E} + \theta \mathbf{Q} \cdot \nabla_R(\theta^{-1}) \geq 0\,. \tag{9.4.73}$$

Again this inequality is in the canonical *bilinear* form favored by tenants of *T.I.P.*, with equilibrium defined by

$$\nabla_R \mathbf{v} = \mathbf{0}\,, \quad \Pi^d = \mathbf{0}\,; \quad \bar{\mathbb{M}}^d = \mathbf{0}\,, \quad \mathfrak{E} = \mathbf{0}\,, \quad \nabla_R \theta = \mathbf{0}\,. \tag{9.4.74}$$

The simplest idea, that of *T.I.P.*, on account of the smallness of deviations from equilibrium, is to consider the quantities dual to those appearing in (9.4.74) as *linear* in the respective fields. Thus

$$\begin{gathered}\mathbb{S}^v = \bar{\mathcal{L}}_S[\dot{\mathbb{E}}]\,, \qquad \dot{\mathfrak{E}} = -\bar{\mathcal{L}}_\pi[\Pi^d]\,, \qquad \dot{\mathfrak{B}} = -\bar{\mathcal{L}}_M[\bar{\mathbb{M}}^d]\,, \\ \mathfrak{J} = \bar{\mathcal{L}}_E[\mathfrak{E}] + \bar{\mathcal{L}}_{EQ}[\nabla_R\theta]\,, \qquad \mathbf{Q} = \bar{\mathcal{L}}_Q[\nabla_R\theta] + \bar{\mathcal{L}}_{QE}[\mathfrak{E}]\,,\end{gathered} \tag{9.4.75}$$

where the $\bar{\mathcal{L}}$'s are *linear operators* which are homogeneous of degree one. Equivalently, we could deduce Eqs. (9.4.75) from a *dissipation potential* homogeneous of degree *two* in the appropriate variables. It is clear that Eqs. $(9.4.75)_{4\text{-}5}$ describe coupled electricity and heat *conductions* while Eq. $(9.4.75)_1$ refers to *viscoelasticity* in the manner of Kelvin–Voigt, and $(9.4.75)_{2\text{-}3}$ describe one type of electric and magnetic *relaxations.* Once the relaxation is achieved, both polarization and magnetization recover their equilibrium definition given by Eqs. (9.4.71). *Onsager's relations* may be invoked to establish a necessary relationship between the operators $\bar{\mathcal{L}}_{EQ}$ and $\bar{\mathcal{L}}_{QE}$.

The approach given above is to be found in classical books so that we do not dwell in greater detail on it here. However, the expressions (9.4.75) deserve the following comments. First, in general the linear operators introduced in Eqs. (9.4.75) may still contain the thermodynamic variables of state on which W depended to start with, as this dependence is *not excluded* by any thermodynamical principle. Thus Eqs. (9.4.75) in fact contain a host of interesting coupled effects, of which *thermo-galvanomagnetic* ones have already been mentioned, but we may also have, for instance, dependence of relaxation times on the electric field and strain, and temperature, etc.

Second, typically, an equation such as $(9.4.75)_2$ will read (for *isotropy* to simplify the presentation)

$$\frac{\partial\mathfrak{E}}{\partial t} = -\frac{\alpha(\theta)}{\tau_E(\theta)}(\Pi - \Pi^r)\,, \qquad \Pi^r \equiv -\partial\bar{W}/\partial\mathfrak{E}\,, \tag{9.4.76}$$

where $\tau_E > 0$ is a relaxation time and $\alpha(\theta)$ will be chosen for convenience. For a *linear* nondissipative behavior, $\bar{W} \cong \mathfrak{E}^2$ and $\Pi^r = \chi_P(\theta)\mathfrak{E}$, where χ_P is the electric susceptibility. We can take $\alpha = \chi_P^{-1}(\theta)$. Then Eq. (9.4.76) in this case may also be written as

$$\Pi = \chi_P(\theta)\left(\mathfrak{E} - \tau_E\frac{\partial\mathfrak{E}}{\partial t}\right). \tag{9.4.77}$$

Similarly, for magnetic processes, working along the same line, we would obtain the "relaxation" equation

$$\bar{\mathbb{M}} = \gamma_M(\theta)\left(\mathfrak{B} - \tau_M \frac{\partial \mathfrak{B}}{\partial t}\right) . \tag{9.4.78}$$

Had we considered the formulation (9.3.53) to start with, Eqs. (9.4.75) would have been replaced by the set

$$\mathbb{S}^v = \hat{\mathcal{L}}_S[\dot{\mathbb{E}}] , \qquad \dot{\Pi} = \hat{\mathcal{L}}_\pi[\mathfrak{E}^d] , \qquad \dot{\mathbb{M}} = \hat{\mathcal{L}}_M[\mathfrak{B}^d] ,$$

$$\mathfrak{J} = \hat{\mathcal{L}}_E[\mathfrak{E}] + \hat{\mathcal{L}}_{EQ}[\nabla_R \theta] , \qquad \mathbf{Q} = \hat{\mathcal{L}}_Q[\nabla_R \theta] + \hat{\mathcal{L}}_{QE}[\mathfrak{E}] , \tag{9.4.79}$$

where the $\hat{\mathcal{L}}$'s are *a priori* different from the $\bar{\mathcal{L}}$'s in (9.4.75). Typically, the relaxation equation for Π would read

$$\frac{\partial \Pi}{\partial t} = \frac{\beta(\theta)}{\tau_M(\theta)}(\mathfrak{E} - \mathfrak{E}^r) , \qquad \mathfrak{E}^r \equiv \partial \hat{W}/\partial \Pi . \tag{9.4.80}$$

With $\hat{W} \cong \Pi^2$ and $\mathfrak{E}^r = \chi_P^{-1}(\theta)\Pi$, we can take $\beta(\theta) = \chi_P(\theta)$, and (9.4.80) will take on the typical form

$$\tau_\pi(\theta)\dot{\Pi} + \Pi = \chi_P(\theta)\mathfrak{E} . \tag{9.4.81}$$

Obviously, Eqs. (9.4.76) and (9.4.81) are different although they admit the same "equilibrium" limit, the truth, however, may be an admixture of the two formulas (9.4.76) and (9.4.81) involving two relaxation times. Such more complicated relaxation formulas, just like those for rheological models more involved than the pure Kelvin–Voigt and Maxwell models of viscoelasticity, require the consideration of *internal variables* to be justified on a thermodynamic basis. Similarly to (9.4.81), for *magnetization* we would obtain the *relaxation equation*

$$\tau_M(\theta)\dot{\bar{\mathbb{M}}} + \bar{\mathbb{M}} = \gamma_M(\theta)\mathfrak{B} , \tag{9.4.82}$$

or

$$\frac{\partial \bar{\mathbb{M}}}{\partial t} = -\frac{1}{\tau_M(\theta)}(\bar{\mathbb{M}} - \mathbb{M}_{eq}) , \tag{9.4.83}$$

where we have introduced the equilibrium value:

$$\mathbb{M}_{eq} = \tau_M(\theta)\gamma_M(\theta)\mathfrak{B} . \tag{9.4.84}$$

Equation (9.4.83) is of the standard *Bloch* type in nuclear magnetism. Generalizations for *deformable ferromagnets* and *magnetic fluids* will be derived in Secs. 9.10 and 9.11 below. To proceed further, we need to introduce either *internal variables* or *additional degrees of freedom.*

9.5. Thermodynamics with Internal Variables

The same way as for rheological models of solids, the thermodynamics with internal variables of electromagnetic bodies offers an unmatched variety of descriptions depending on the type of internal variables selected. The complication and confusion are increased by the combination with internal variables of mechanical origin, so that we may envisage fields of application such as the *magnetoplasticity* of solids in which *plastic* mechanical effects couple to magnetic *hysteresis* ones, a coupling that is fully justified on a microscopic basis. In order to remain within reasonable limits, we illustrate our *propos* with two separate, but still broad, examples, magnetic solids in small strains, and electrically polarized solids in large strains.

A. Magnetic solids in small strains

In that case we build on inequality (9.3.43) or (9.3.53) in which we discard electric and conduction effects so that with

$$\mathbf{H} = \mathbf{B} - \mathbf{M}\,, \qquad W = \hat{W}(\mathbb{E}, \theta, \mathbb{M}) - \frac{1}{2}\mathbb{M}^2 = W(\mathbb{E}, \theta, \mathbb{M})\,,$$

$$= W(\varepsilon, \theta, \mathbf{M}) \qquad (9.5.84)$$

and restoring a simple notation, we have the inequality

$$-(\dot{W} + S\dot{\theta}) + \sigma : \dot{\varepsilon} + \mathbf{H} \cdot \dot{\mathbf{M}} \geq 0\,, \qquad (9.5.85)$$

where $(\sigma, \mathbf{H})$ are the "forces" conjugate to the "velocities" $(\dot{\varepsilon}, \dot{\mathbf{M}})$. Thus $\mathbf{M}$ plays a role that parallels that of ε. Even more so, as $\mathbf{M}$ is indeed an *extensive variable* (it is proportional to the mass) and experimental evidence shows that magnetization, in total analogy with small strain, can be decomposed into a *reversible* part $\mathbf{M}^r$ and an *irreversible* contribution $\mathbf{M}^R$, also called *residual magnetization.* While in plasticity and viscoplasticity (Chapter 7) finding the evolution equation for the anelastic strain ε^p was the ultimate goal, the evolution equation for $\mathbf{M}^R$, eventually giving rise to magnetic hysteresis (see Sec. 9.7) should be the main concern of magneticians. The *axial* vector $\mathbf{M}^r$ is the *observable* magnetic thermodynamic variable of state. Obviously, we are aware that relaxation and hysteresis are complex phenomena and it would be surprising that only $\mathbf{M}^r$ and $\mathbf{M}^R$ are sufficient to describe them. Like in the mechanics of materials, to compensate for our relative ignorance of the underlying microscopic phenomena, we propose to introduce a set of *magnetic internal variables.* We shall assume that this set is composed of a traditional *axial* three-vector $\mathbf{M}^{\text{int}}$ and a scalar α, all four components thus introduced having the physical dimension of a magnetization (magnetic moment per unit volume). It seems that the idea of introducing *electromagnetic internal variables* such as $\mathbf{M}^{\text{int}}$ in particular (the scalar variable α is of more recent extract) goes back to Meixner (1961) where the internal variable is conceived as an *angular momentum* (*via the gyromagnetic ratio*, cf. Maugin, 1988, for these concepts). This was taken over by Maugin (1979a,b; 1981a,b) both in rigid and deformable ferromagnets, while in the meantime Kluitenberg (1973, 1977, 1981) presented a simple theory of Snoeck's formulation of magnetic relaxation based on the consideration of a magnetic internal vector variable.

For example, in *rigid bodies*, we are thus led to consider a free energy per unit volume as

$$W = \bar{W}(\mathbf{M}^r = \mathbf{M} - \mathbf{M}^R, \mathbf{M}^{\text{int}}, \alpha, \theta)\,. \tag{9.5.86}$$

Hence, the same way as for (5.6.44)–(5.6.46), we shall obtain the *dissipation inequality in the form*

$$\Phi_{\text{magn}} := \mathbf{H}^{\text{relax}} \cdot \dot{\mathbf{M}}^r + \mathbf{H} \cdot \dot{\mathbf{M}}^R + \mathbf{H}^{\text{int}} \cdot \dot{\mathbf{M}}^{\text{int}} + \mathcal{A}\dot{\alpha} \geq 0\,, \tag{9.5.87}$$

where we have set

$$\begin{aligned} \mathbf{H}^{\text{relax}} &= \mathbf{H} - \mathbf{H}^r\,, & \mathbf{H}^r &= \partial\bar{W}/\partial\mathbf{M}^r\,, \\ \mathbf{H}^{\text{int}} &= -\partial\bar{W}/\partial\mathbf{M}^{\text{int}}\,, & \mathcal{A} &= -\partial\bar{W}/\partial\alpha\,. \end{aligned} \tag{9.5.88}$$

The last three of these provide the *laws of state*, while *T.I.P.* can be applied to the four contributions present in the expression of the magnetic dissipation Φ_{magn}. Evidently, $\mathbf{H}^{\text{relax}}$ bears this name because it provides the usual *relaxation* contribution to the magnetic constitutive equation. The formalism (9.5.86)–(9.5.88) allows one to consider also a model of magnetic relaxation which is the magnetic analog of Maxwell's rheological model; it seems to be more satisfactory than (9.4.83) in macroscopic applications of *dynamical hysteresis loops* met in electrical engineering works (e.g. Chua and Stromsmoe, 1971; Saito *et al.*, 1988). To that purpose, parodying the mechanical Maxwell model, consider the case where $\alpha = 0$ and $\mathbf{M}^R = \mathbf{0}$, so that $\mathbf{H} = \mathbf{H}^r$, and further let W depend on $\mathbf{M}$ only through the difference $\mathbf{M} - \mathbf{M}^{\text{int}}$. It follows then that $\mathbf{H}^{\text{int}} = \mathbf{H}$, and (9.5.87) reduces to

$$\Phi_{\text{magn}} = \mathbf{H} \cdot \dot{\mathbf{M}}^{\text{int}} \geq 0\,. \tag{9.5.89}$$

For W quadratic in $\mathbf{M} - \mathbf{M}^{\text{int}}$ and $\dot{\mathbf{M}}^{\text{int}}$ linear in $\mathbf{H}$ in agreement with *T.I.P.*, by elimination of $\mathbf{M}^{\text{int}}$ we obtain a magnetic constitutive equation of the type (cf. Maugin, 1991a,b)

$$\mathbf{H} + \tau_H \cdot \dot{\mathbf{H}} = (\tau_H \cdot \chi_H^{-1}) \cdot \dot{\mathbf{M}}\,, \tag{9.5.90}$$

which is analogous to (7.2.4). This emphasizes the role of *magnetic-field relaxation* while (9.4.83) does the same for *magnetization relaxation.* It is clear that by weighting adequately the role of these two relaxations by an appropriate choice of internal variable, it is possible to generate *magnetic relaxation equations* of the general differential type (comparable to *RDM* in the beginning of Chapter 7):

$$\mathbf{M} + \tau_M \cdot \dot{\mathbf{M}} = \chi_M \cdot (\mathbf{H} + \tau_H \cdot \dot{\mathbf{H}})\,, \tag{9.5.91}$$

where χ_M is a tensor of magnetic susceptibilities and τ_M and τ_H are tensors of relaxation times. Equation (9.5.91) is the magnetic analog of (7.2.5). However, such laws, which are thermodynamically admissible so that they *do* represent some progress, will not reproduce an essential fact of hysteresis which is a markedly different response in loading and unloading. Furthermore, for relatively small magnetizing frequencies, it appears that magnetic hysteresis, just like plasticity, is practically rate-independent and, therefore, does not exhibit relaxation times in contrast to the laws (9.5.90) or (9.5.91). Appropriate laws must, in some way, involve the sign of the rate of loading, i.e. of $d\mathbf{H}/dt$, while being essentially independent of the time scale. This will be examined in Sec. 9.7 where, discarding any relaxation at all, we shall consider the following simplified version of (9.5.87):

$$\Phi_{\text{magn}} = \mathbf{H} \cdot \dot{\mathbf{M}}^r + \mathbf{H}^{\text{int}} \cdot \dot{\mathbf{M}}^{\text{int}} + \mathcal{A}\dot{\alpha} \geq 0\,. \tag{9.5.92}$$

B. Electrically polarized solids in finite strains

In the case of *nonmagnetizable dielectrics* the Clausius–Duhem equation (9.3.53) reduces to

$$-(\dot{W} + S\dot{\theta}) + \mathrm{tr}\,(\mathbb{S}^E\dot{\mathbb{E}}) + \mathfrak{E}\cdot\dot{\Pi} + \theta\mathbf{Q}\cdot\nabla_R(\theta^{-1}) \geq 0\,. \qquad (9.5.93)$$

To make the essentials of the theory clear to the reader we consider the following thermodynamic scheme which obviously draws on the modern formulation of *elastoplasticity with hardening* (Chapter 7 above). Assume that the total strain $\mathbb{E}$ is composed of an "elastic" part $\mathbb{E}^e$ and an "anelastic" part $\mathbb{E}^p$. In like manner, the electric polarization Π is built of two contributions, one Π^r called the *reversible* part (this will serve to define a *law of state* from the energy density) and the other Π^d called the *residual polarization*, i.e.

$$\mathbb{E} = \mathbb{E}^e + \mathbb{E}^p\,, \qquad \Pi = \Pi^r + \Pi^R\,. \qquad (9.5.94)$$

In addition, like in the magnetic case, we know that rather complicated microscopic mechanisms are at work (irreversible slip motions in the crystal lattice, dislocations, irreversible motions of ferroelectric domain walls, Barkhausen effect, etc.) which all imply a *dissipation* since they all have an irreversible nature. In the spirit of previous chapters we are thus led to the introduction of *internal variables*, say α and Π^{int}, respectively a set of variables accounting for mechanical hardening and a variable having the physical dimension of an electric polarization per unit volume. The observable variables are now the "elastic" strain $\mathbb{E}^e$, the reversible polarization Π^r and temperature θ. Accordingly, Gibbs' equation that replaces (9.4.70) reads

$$\dot{W} = -S\dot{\theta} + \mathrm{tr}\,(\mathbb{S}^E\dot{\mathbb{E}}) + \mathfrak{E}^r\cdot\dot{\Pi}^r - \mathcal{A}\cdot\dot{\alpha} - \mathfrak{E}^{\mathrm{int}}\cdot\dot{\Pi}^{\mathrm{int}}\,, \qquad (9.5.95)$$

and this yields the *laws of state* as

$$\begin{gathered} W = \hat{W}(\theta, \mathbb{E}^e, \Pi^r | \alpha, \Pi^{\mathrm{int}})\,, \\ S = -\partial\hat{W}/\partial\theta\,, \qquad \mathbb{S}^e = \partial\hat{W}/\partial\mathbb{E}^e\,, \qquad \mathfrak{E}^r = \partial\hat{W}/\partial\Pi^r\,, \\ \mathcal{A} = -\partial\hat{W}/\partial\alpha\,, \qquad \mathfrak{E}^{\mathrm{int}} = -\partial\hat{W}/\partial\Pi^{\mathrm{int}}\,. \end{gathered} \qquad (9.5.96)$$

On account of the axiom of local accompanying state ($L.A.S$), S is formally defined as in thermostatics, so that the Clausius–Duhem inequality (9.5.93) takes on the form of the following *dissipation inequality*:

$$\begin{aligned}\Phi &= \mathrm{tr}\,(\mathbb{S}^v\dot{\mathbb{E}}^e) + \mathrm{tr}\,(\mathbb{S}^E\dot{\mathbb{E}}^p) + \mathcal{A}\cdot\dot{\alpha} + \mathfrak{E}^{\mathrm{relax}}\cdot\dot{\Pi}^r \\ &\quad + \mathfrak{E}\cdot\dot{\Pi}^R + \mathfrak{E}^{\mathrm{int}}\cdot\dot{\Pi}^{\mathrm{int}} + \theta\mathbf{Q}\cdot\nabla_R(\theta^{-1}) \geq 0\,, \end{aligned} \qquad (9.5.97)$$

where we have set

$$\mathbb{S}^v := \mathbb{S}^E - \mathbb{S}^e\,, \qquad \mathfrak{E}^{\mathrm{relax}} := \mathfrak{E} - \mathfrak{E}^r\,. \qquad (9.5.98)$$

The inequality (9.5.97) is rewritten as

$$\Phi = \Phi_1 + \Phi_2\,, \qquad (9.5.99)$$

with

$$\begin{aligned}\Phi_2 &:= \mathrm{tr}\,(\mathbb{S}^v\dot{\mathbb{E}}^e) - \mathfrak{E}^{\mathrm{relax}}\cdot\dot{\Pi}^r + \theta\mathbf{Q}\cdot\nabla_R(\theta^{-1})\,, \\ \Phi_1 &:= \mathrm{tr}\,(\mathbb{S}^E\dot{\mathbb{E}}^p) + \mathcal{A}\cdot\dot{\alpha} + \mathfrak{E}\cdot\dot{\Pi}^R + \mathfrak{E}^{\mathrm{int}}\cdot\dot{\Pi}^{\mathrm{in}}\,. \end{aligned} \qquad (9.5.100)$$

Equations (9.5.97) through (9.5.100) deserve the following comments. First, we see by direct comparison with the general case that the roles of $\mathbb{E}$ and Π are now played by $\mathbb{E}^e$ and Π^r in the part Φ_2 of the dissipation. This means that the usual viscosity, electric relaxation, and electric conduction processes are expressed, according to *T.I.P.*, in terms of time rates of change of the reversible parts of strain and electric polarization, and the temperature gradient. In contradistinction, the *irreversible* parts of the strain and electric polarization ($\mathbb{E}^p$ and Π^R) produce a dissipation in the *total* mechanical symmetric stress $\mathbb{S}^E$ and the *total* electric field $\mathfrak{E}$. Finally, the split (9.5.99) is explained by the fact that the thermodynamic fluxes in Φ_2 are assumed to be derivable from a *dissipation potential* which is homogeneous of degree *two* in the corresponding forces (this is equivalent to *T.I.P.* — as the fluxes will then be linear, homogeneous of degree *one* in these forces) while the time rates in Φ_1 will be assumed to derive from a *pseudo-dissipation potential* which is homogeneous of degree *one* only in the corresponding thermodynamically conjugated quantities, providing thus the needed *evolution equations* for the internal variables as well as *plasticity* and *hysteresis* evolution equations (without time scale) for the irreversible parts of the strain and electric polarization. The first characterization of electromagnetic dissipative processes is rather similar to what was done in viscoelasticity. A critical illustration is given in the next section for *dielectric relaxation*. For the second class of dissipative processes, illustrations are given in Sec. 9.7 for both electric and magnetic cases.

9.6. Dielectric Relaxation in Ceramics

To illustrate the viewpoint developed in the preceding section for *dielectric relaxation* we shall consider the problem of the propagation of *transient plane nonlinear waves* in a one-dimensional model of ferroelectric ceramics. The problem was treated by Collet (1987) — see also Maugin, Pouget *et al.* (1992, Chapter 4). From the point of view of thermodynamics this problem is essentially of interest to show the importance of relative time scales (hence the Deborah number) in discussing a phenomenon in which both macro-scale and micro-scale are involved.

In this modeling we assume that

$$\alpha = 0\,, \qquad \mathbb{E}^p = \mathbf{0}\,, \qquad \Pi^R = \mathbf{0}\,. \tag{9.6.101}$$

Accordingly, $\mathbb{E}^e$ reduces to $\mathbb{E}$ and Π^r to Π, so that the free energy W reduces to

$$W = \hat{W}(\mathbb{E}, \Pi, \theta | \Pi^{\text{int}})\,. \tag{9.6.102}$$

The corresponding internal energy is obtained through a partial Legendre transformation as

$$\Sigma = \hat{W} + S\theta = \hat{\Sigma}(\mathbb{E}, \Pi, S | \Pi^{\text{int}})\,, \tag{9.6.103}$$

and the *laws of state* are

$$\begin{aligned} \theta &= \partial\hat{\Sigma}/\partial S\,, & \mathbb{S}^E &= \partial\hat{\Sigma}/\partial\mathbb{E}\,, \\ \mathfrak{E} &= \partial\hat{\Sigma}/\partial\Pi\,, & \mathfrak{E}^{\text{int}} &= -\partial\hat{\Sigma}/\partial\Pi^{\text{int}}\,, \end{aligned} \tag{9.6.104}$$

where the last one merely is a definition of $\mathfrak{E}^{\text{int}}$. We have assumed that $\mathfrak{E}^{\text{relax}} = \mathbf{0}$, and the quasi-electrostatic framework is sufficient (hence $\hat{\mathfrak{E}}$ reduces to $\mathfrak{E}$). Then the electric relaxation, if any, is taken care of via the dependence of energy on Π^{int} only. As there is no other dissipative process (remember that we have a *dielectric*, and we neglect heat conduction and mechanical dissipative effects), the *residual dissipation inequality* reads

$$\Phi_2 = \mathfrak{E}^{\text{int}} \cdot \dot{\Pi}^{\text{int}} \geq 0\,. \tag{9.6.105}$$

By way of example we may consider the *separable* case for which

$$\hat{\Sigma} = \Sigma_1(\mathbb{E}, \Pi, S) + \Sigma_2(\Pi, \Pi^{\text{int}})\,, \tag{9.6.106}$$

with

$$\Sigma_2(\Pi, \Pi^{\rm int}) = \frac{1}{2}\bar{a}\Pi^2 + \frac{1}{2}b(\Pi - \Pi^{\rm int})^2 . \tag{9.6.107}$$

Then

$$\mathfrak{E} = (\partial\Sigma_1/\partial\Pi) + (\bar{a} + b)\Pi - b\Pi^{\rm int} , \tag{9.6.108}$$

while, applying *T.I.P.* to the inequality (9.6.105) we obtain a *relaxation equation* (Collet, 1987)

$$\tau_d\dot{\Pi}^{\rm int} = \Pi - \Pi^{\rm int} , \qquad \tau_d \geq 0 , \tag{9.6.109}$$

where τ_d is called the dielectric (polarization) relaxation time. This shows that the equilibrium value of $\Pi^{\rm int}$ is none other than Π itself. The quantity τ_d is practically directly accessible to experiments in a study of shock-wave propagation in dielectrics (Yakuscov *et al.*, 1968). Obviously it intervenes in transient problems which themselves exhibit a characteristic time, or a characteristic length of propagation. In the present case, for a propagation process whose linear regime is characterized by the velocity c_0 (say, an acoustic speed), a characteristic length

$$L_a = c_0\tau_d \tag{9.6.110}$$

may be constructed and referred to as the *electric attenuation length.* It is clear that when the wavelengths associated with all dynamical disturbances (for small amplitude signals) are short compared to L_a, then the effect of electric relaxation is negligible and the material behaves locally as an elastic dielectric without losses. This is verified by establishing the expression that governs the behavior of an *acceleration wave* (i.e. a wavefront carrying a discontinuity in the acceleration) propagating through a material modelled by Eqs. (9.6.104)–(9.6.107) and considering the limit where the traveled distance L is much smaller than L_a (see McCarthy, 1984b). In this limit, one-dimensional motions admit *simple-wave* solutions (i.e. wavelike solutions which depend only on one space-time, or characteristic, coordinate). We refer the reader to McCarthy (1984a) and Collet (1985) for this problem. Here we prefer to deal in greater detail, but not exhaustively, with a problem which directly exhibits the role played by the Deborah number in nonlinear wave propagation. To that purpose we consider the effect of electric (polarization) relaxation on the transient nonlinear electroelastic motion inward a half-space $X > 0$ from the limiting plane $X = 0$. Third-order nonlinear elasticity and dielectric relaxation (9.6.109) are taken into account as we still need some *nonlinearity*, but the latter is purely *elastic.* Hence we are facing the *competition* between *nonlinearity* of elastic origin and a *dissipative mechanism* (related to another physical property, here electric polarization), the two being coupled via *piezoelectricity*, a very much classical *electroelastic coupling* (cf. Eringen and Maugin, 1990). We give only the broad lines of the derivation.

It is shown, in one space dimension and quasi-electrostatics, that the basic equations of the problem take on the following form:

$$
\begin{aligned}
0 &= \rho_0 \frac{\partial}{\partial t} v - \frac{\partial}{\partial X} T^t \,, \\
0 &= \frac{\partial}{\partial X} \mathfrak{D} \,, \\
\tau_d \frac{\partial}{\partial t} \Pi^{\text{int}} &= \Pi - \Pi^{\text{int}} \,,
\end{aligned}
\tag{9.6.111}
$$

along with the constitutive equations ($f = F - 1$, where F is the only surviving component of $\mathbf{F}$)

$$
\begin{aligned}
T^t &= Cf(1 + 2\gamma f) - e\Pi \,, \\
\mathfrak{D} &= ef + a\Pi - b\Pi^{\text{int}} \,.
\end{aligned}
\tag{9.6.112}
$$

Here C, γ, e, and a are, respectively, a second-order elasticity coefficient, a nondimensional third-order elasticity coefficient, a piezoelectric coefficient, and an electric constant.

The system (9.6.112)–(9.6.113) in a *quasi-linear* system which must be solved subject to *initial* conditions at $t = 0$, boundary conditions at $X = 0$, and *regularity* conditions as X tends towards infinity. These are given by

$$
\begin{aligned}
f &= 0, \Pi = 0, \Pi^{\text{int}} = 0 && \text{at } t = 0,\ X > 0 \,, \\
f &= K(t),\ \mathfrak{D} = 0, && \text{at } X = 0,\ t > 0 \,, \\
f &\to 0,\ \Pi \to 0,\ \Pi^{\text{int}} \to 0 && \text{as } X \to \infty,\ t \geq 0 \,.
\end{aligned}
\tag{9.6.113}
$$

An approximate (asymptotic) solution to this problem can be sought in two ways. One of them is to look at a *far-field* solution and the other one is to examine what occurs in the neighborhood of the traveling signal. These pertain to so-called *delayed* and *instantaneous* wave analyses, respectively.

A. Delayed-wave analysis

Let τ be a characteristic time scale. We call $\eta = \max|K(t)|$ the *small* parameter related to the amplitude of the input signal. Let

$$C_d = C - (e^2/\chi_{\mathrm{eq}}), \qquad \chi_{\mathrm{eq}} = (1+a) - b, \qquad V_d^2 = C_d/\rho_0, \tag{9.6.114}$$

a piezoelectrically altered elasticity coefficient, the thermodynamical equilibrium value of the electric susceptibility ($\Pi = \Pi^{\mathrm{int}}$ at equilibrium), and the squared *delayed* acoustic speed. We can introduce nondimensional variables (with superimposed bars) by

$$X = V_d\tau\bar{X}, \quad t = \tau\bar{t}, \quad f = \eta\bar{f}, \quad v = \gamma V_d\bar{v},$$

$$\Pi = \eta e\bar{\Pi}, \quad \Pi^{\mathrm{int}} = \eta e\bar{\Pi}^{\mathrm{int}}, \quad T = \eta V_d\bar{T}, \quad \mathfrak{D} = \eta e\bar{\mathfrak{D}}. \tag{9.6.115}$$

Furthermore,

$$\varepsilon_d = (\mathcal{D}e)_\pi := \tau_d/\tau \tag{9.6.116}$$

is a small parameter which is none other than the Deborah number related to polarization-relaxation processes [cf. (4.7.44) or (4.7.45)]. Equations (9.6.111) are rewritten using the new variables and then overbars are discarded in order to lighten the notation. We thus obtain the following system (where ∂_t and ∂_X denotes the partial derivatives)

$$\begin{gathered}\alpha_d\partial_X f + \eta\bar{\gamma}_d f\partial_X f + (e^2/C_d)\partial_X\Pi = \partial_t v,\\ \partial_X f + \chi\partial_X\Pi - \beta\partial_X\Pi^{\mathrm{int}} = 0,\\ \varepsilon_d\partial_t\Pi^{\mathrm{int}} = \Pi - \Pi^{\mathrm{int}},\end{gathered} \tag{9.6.117}$$

where $\alpha_d = C/C_d$, $\bar{\gamma}_d = 4\gamma\alpha_d$. Also, taking the X-derivative of $(9.6.117)_1$, we get the useful equation

$$\alpha_d\partial_X^2 f + \eta\bar{\gamma}_d\partial_X(f\partial_X f) + (e^2/C_d)\partial_X^2\Pi = \partial_t^2 f. \tag{9.6.118}$$

The appropriate time scale for the far-field study is $O(\eta^{-1})$ with $(\eta/\varepsilon_d) \to 0$ as $\varepsilon_d \to 0$. The system (9.6.117) is treated by introducing *multiple strained coordinates* $X_n = (\varepsilon_d)^n X$, $n \geq 0$. The zeroth- and first-order governing systems are then deduced from (9.6.117). The zeroth-order solution $S_0 = \{f_0, \Pi_0, \Pi_0^{\mathrm{int}}\}$ satisfies a linear wave equation, and this provides a solution $f_0 = \bar{f}_0(X_1, \zeta)$, where

$\zeta = t - X_0$ is a characteristic coordinate typical of simple-wave-propagation problems. The *secularity condition* for solving the first-order solution *uniformly* in space provides a constraint on the functional dependence of f_0 through the equation (here $\chi = 1 + a$; see details in Collet, 1987)

$$\frac{\partial f_0}{\partial X_1} + \hat{\gamma}_d f_0 \frac{\partial f_0}{\partial \zeta} = \frac{1}{2} d \frac{\partial^2 f_0}{\partial \zeta^2}\,, \tag{9.6.118}$$

where we have set

$$\hat{\gamma} = -\eta \bar{\gamma}_d / 2\varepsilon_d\,, \quad d = \frac{\chi}{\chi_{\text{eq}}} \frac{C_i - C_d}{C_d}\,, \quad C_i = C - (e^2/\chi) \geq 0\,, \tag{9.6.119}$$

where d is a *diffusivity coefficient* and C_i may be called the *instantaneous* (see below) effective second-order elasticity coefficient. Equation (9.6.118) is a paradigmatic equation of nonlinear wave theory known as the *Burgers' equation* (cf. Maugin, Pouget *et al.*, 1992) in which the roles of time and space are played by the variables X_1 and ζ, respectively, and that of the viscosity by the diffusion coefficient. Its solution is the *delayed wave* which is valid for

$$\begin{aligned} &\tau = 0(\eta^{-1}) \gg \tau_d\,, \qquad \text{i.e. } (\mathcal{D}e)_\pi \ll 1\,, \\ &(X, t) \in \mathcal{D}_d = \{X, t | X > L_d \gg V_d \tau_d\}\,, \\ &L_d \gg 0(V_i \tau_i) \end{aligned} \tag{9.6.120}$$

where V_i and τ_i are defined by

$$V_i^2 = C_i / \rho_0\,, \qquad \tau_i = \frac{\chi}{\chi_{\text{eq}}} \frac{C_i}{C_i - C_d} \tau_d\,. \tag{9.6.121}$$

The first equation of (9.6.120) is none other than a condition of very small electric Deborah number, which is characteristic of the local accompanying state hypothesis in internal-variable theory.

B. Instantaneous wave

The problem now consists of examining what occurs in the immediate neighborhood of the wave front as the latter travels inward the half-space $X > 0$. A solution is described in this neighborhood by considering an asymptotic procedure in which the perturbation parameter is none other than the distance from the wave front of the *linear* theory. That is, we introduce the parameter $\varepsilon_i = \tau/\tau_i$, with τ_i given by (9.6.121) and $\tau_i > \tau_d$. In this analysis the nondimensional form of Eq. $(9.6.111)_3$ is given by

$$\partial_t \Pi^{\text{int}} = \varepsilon_i(\tau_i/\tau_d)(\Pi - \Pi^{\text{int}}) . \tag{9.6.122}$$

A multiple strained-coordinate ($X_n = (\varepsilon_i)^n X$) analysis in which ε_i is the small parameter with $O(\eta/\varepsilon_i) = 1$ as ε_i goes to zero, yields a *secularity condition* on the zeroth-order solution $f_0(X_1, \zeta = t - X_0)$ in the form of a following *simple* nonlinear equation (Collet, 1987)

$$\frac{\partial f_0}{\partial X_1} + \hat{\gamma}_i f_0 \frac{\partial f_0}{\partial \zeta} + \frac{1}{2} f_0 = 0 , \tag{9.6.123}$$

with the boundary conditions

$$f_0(t, X_0 = 0, X_1 = 0) = f_0(\zeta = t, X_1 = 0) = K(t) . \tag{9.6.124}$$

This solution forms a *shock* at a *breaking distance* $(X_1)_B$ given by

$$(X_1)_B = -2\ln(1 - (2|\hat{\gamma}_i|K'_m)^{-1}) , \qquad K'_m = \max_{\xi} \left| \frac{dK(\xi)}{d\xi} \right| . \tag{9.6.125}$$

Here the electric losses, although small, have a *cumulative* effect on the attenuation of the wave. This is involved in (9.6.125) so as to prevent the formation of the shock. However, once the shock is formed, then it will evolve according to the rules of weak-shock theory. The instantaneous solution thus obtained is valid for

$$(X, t) \in \mathcal{D}_i = \{X, t \mid |V_i t - X| \ll L_i \ll V_i \tau_i\} . \tag{9.6.126}$$

For an input $K(t) = f(0, t)$ in the form of a ramp followed by a plateau, we obtain a space-time dynamical response as reproduced qualitatively in Fig. 9.1 (after Maugin, Pouget *et al.*, 1992). This response consists of an exponentially damped front and of the main wave which, at lowest order, is governed by the Burgers equation (9.6.118). We see that the influence of the internal variable is somewhat spectacular.

Other works of a more formal nature that consider electric internal variables and nonlinear waves in electroelasticity are those of Collet (1983, 1984, 1985) and McCarthy (1984a,b). The case of *semiconducting* electroelastic bodies may be even more interesting, but then the electric conduction certainly is the leading dissipative mechanism (see, e.g. Daher and Maugin, 1987, Maugin and Daher, 1986).

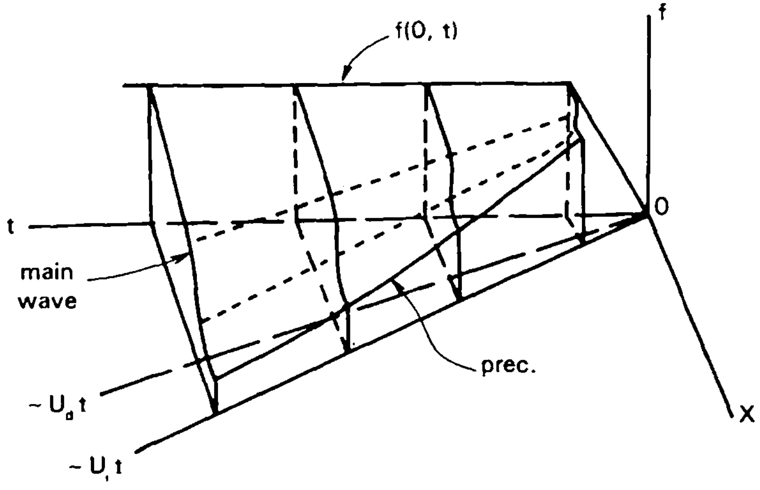

Fig. 9.1. Response of a half-space with electric relaxation to a ramp $f(0, t)$ in stress at the limiting plane $X = 0$ (after Maugin, Pouget *et al.*, 1992, p. 200).

9.7. Electro- and Magnetomechanical Hysteresis

A. Electric bodies

Here, basing on the equations of Sec. 9.5, we address the following problem: a polycrystalline multidomain dielectric material exhibits both *induced* electric polarization and *spontaneous* electric polarization. The former is *reversible* and may be modeled by Π^r while the latter is accompanied by dissipation and will be modeled by both Π^R and Π^{int}. We focus the attention on the last two fields, in particular on the first one and its relationship with the polarizing field and other stimuli such as temperature, stresses and bias electric fields. For a given temperature and fixed state of stresses and bias fields (usually zero or considered as such), the typical response $|\Pi^R|$ versus $|\mathfrak{E}|$ presents the shape of a *hysteresis* loop such as in Fig. 9.2 with a saturation such that $|\Pi^R| \to \Pi^R_S$ as $|\mathfrak{E}|$ goes to infinity (i.e. becomes large enough physically). This hysteresis loop is obtained in an alternating polarizing field of *low frequency*. As a matter of fact, we assume that this loop does *not* depend on that frequency. In other words, the electric hysteresis phenomenon is *rate-independent* and, as such, it does not involve any characteristic time (and is very much similar to *plasticity*

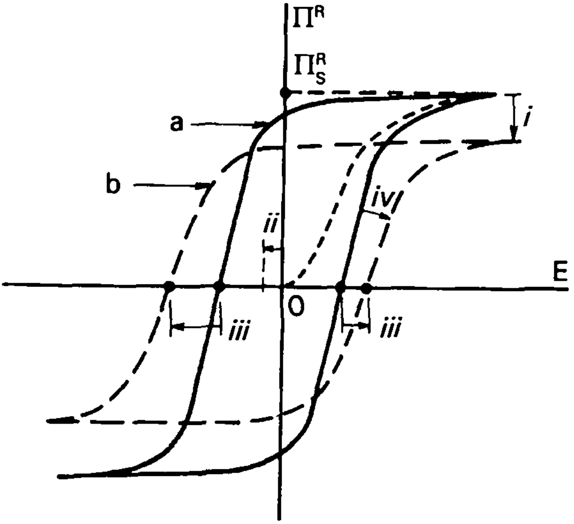

Fig. 9.2. Typical hysteresis behavior of ceramics: (a) in the absence of applied stress and bias electric field; (b) in the presence of such fields.

and locking — locking is the mechanical property that strains remain bounded although the level of stresses can be increased considerably such as in *biological materials*) in contradistinction, say, with viscosity or electric relaxation. This is probably not true for high frequencies of the polarizing field and for relatively high temperatures.

The hysteresis curve (*a*) in Fig. 9.2 is essentially characterized by: (i) the level of saturation Π^R_S; (ii) the value $E_c = \mathfrak{E}(\Pi^R = 0)$ of the so-called *coercive field*, and (iii) the "inclination" of the hysteresis loop on the Π^R-axis. We should remember that perfect hysteresis loops of one-domain crystals have vertical, jump-like, branches (cf. Maugin, Pouget *et al.*, 1992, Chapter 6). When this inclination is *not* zero — what appears the be the case for most industrial materials such as *ceramics* — then we say that the electric material exhibits *electric hardening*. This wording is granted by analogy to *mechanical hardening*. It simply means that it takes a greater value of the polarizing field to increase the polarization Π^R by a given amount.

Under the influence of a perturbation such as a bias (dc) electric field, an applied stress or irradiation, the loop (a) transforms into loop (b) in Fig. 9.2. In general, four essential effects are manifested in this transformation: (i) the saturation level is changed, (ii) the width of the hysteresis loop at zero polarization has been altered, (iii) the coercive field has evolved, presenting different values on loading and unloading (the loop is no longer symmetric with respect to the origin), and (iv) the electric hardening has been modified to some extent, all facts which are made more eloquent on the *derivative* curve (instantaneous electric susceptibility). All these recognized facts may be modeled in a necessarily *nonlinear* manner. This phenomenological theory was developed by Bassiouny *et al.* (1988a,b), Bassiouny and Maugin (1989), Maugin (1989), and Maugin and Bassiouny (1989).

The above brief description views electric hysteresis as a dissipative mechanism without time scale although the past history of the electric loading of the sample clearly plays a determining role at any instant. The first point is coped with by assuming that the power dissipated in the time evolution of Π^R is homogeneous of degree one in $\dot{\Pi}^R$, while the second point is taken care of by the presence of the electric internal variable Π^{int}. The latter will account for *electric hardening* and will also yield an entropy production which is homogeneous of degree *one* in its time evolution ($\dot{\Pi}^{\text{int}}$). Accordingly, focusing on electric processes, we only keep in the thermodynamic formulation the effects of Π^R and Π^{int}, so that the dissipation inequality (9.5.97) reduces, in quasi-electrostatics, to

$$\Phi_1 = \mathfrak{E} \cdot \dot{\Pi}^R + \mathfrak{E}^{\text{int}} \cdot \dot{\Pi}^{\text{int}} \geq 0 \,, \tag{9.7.127}$$

where Φ_1 is supposed to be positive, homogeneous of degree *one* in the elements of the set $V = \{\dot{\Pi}^R, \dot{\Pi}^{\text{int}}\}$ of generalized velocities or fluxes. The corresponding set of "forces" is $F = \{\mathfrak{E}, \mathfrak{E}^{\text{int}}\}$. Both homogeneity and non-negativeness properties of Φ_1 are satisfied, just like in elastoplasticity (Chapters 5 and 7), by the introduction of a *pseudo-dissipation potential*. Upon use of the basic theorem of Sec. 5.4, there exists a *closed convex set* C_E in the space of elements of F such that the said pseudo-dissipation potential is none other than the indicator function of that convex set. That is, we have

$$\mathcal{D}^*(F) = \operatorname{ind} C_E = \begin{cases} 0 & \text{if } f \leq 0 \\ +\infty & \text{if } f > 0 \end{cases} \,, \tag{9.7.128}$$

and

$$C_E = \{E = (\mathfrak{E}, \mathfrak{E}^{\text{int}}) \in F | f(E) < 0\} \,. \tag{9.7.129}$$

This physically means that dissipation occurs only when E belongs to the boundary of C_E. Then we necessarily have the following *normality laws* (equations of evolution)

$$\dot{\Pi}^R = \dot{\lambda}\frac{\partial f(E)}{\partial \mathfrak{E}}\,, \qquad \dot{\Pi}^{\mathrm{int}} = \dot{\lambda}\frac{\partial f(E)}{\partial \mathfrak{E}^{\mathrm{int}}}\,, \tag{9.7.130}$$

where the unknown multiplier $\dot{\lambda}$ is such that $\dot{\lambda} = 0$ if $f(E) < 0$ and $\dot{\lambda} \geq 0$ if $f(E) = 0$. The same as in elastoplasticity, this provides a very *singular* correspondence between elements of V and F spaces, which is proper to this type of rate-independent processes. Most of the following properties are derived just like in elastoplasticity to which we refer the reader for the analogies.

(i) *Principle of maximal dissipation for electric hysteresis*

Equivalently to the normality laws (9.7.129) we can state the following principle of maximal dissipation in perfect analogy with the Hill–Mandel principle of the plastic case:

$$(\mathfrak{E} - \mathfrak{E}^*) \cdot \dot{\Pi}^R + \{\mathfrak{E}^{\mathrm{int}} - (\mathfrak{E}^{\mathrm{int}})^*\} \cdot \dot{\Pi}^{\mathrm{int}} \geq 0\,. \tag{9.7.131}$$

This *variational inequality* holds true for any $E^* = \{\mathfrak{E}^*, (\mathfrak{E}^{\mathrm{int}})^*\} \in C_E(F)$;

(ii) *Orthogonality relation*:

The conditions pertaining to the multiplier $\dot{\lambda}$ can be made more precise, viz: $\dot{\lambda} \geq 0$ if $f = 0$ and $\dot{f} = 0$, and $\dot{\lambda} = 0$ if $f < 0$ or $f = 0$ and $\dot{f} < 0$. The proof of these is elementary once the following *orthogonality* property is proved:

$$\dot{\mathfrak{E}} \cdot \dot{\Pi}^R + \dot{\mathfrak{E}}^{\mathrm{int}} \cdot \dot{\Pi}^{\mathrm{int}} = 0\,. \tag{9.7.132}$$

Like in the plastic case the proof is based on the use of (9.7.131). The above model is mathematically neat. It corresponds to the case where the electric loading surface $f = 0$ is identified to a surface of *equi*-pseudo-potential $\mathcal{D}^*$. Several consequences and further specifications of this modeling are of particular interest.

(iii) *Local stability*:

Assume that

$$W = W^E(\Pi^r, \theta) + W^{(i)}(\Pi^{\mathrm{int}})\,, \tag{9.7.133}$$

where W^E is *convex* in Π^r and *concave* in θ, and $W^{(i)}$ is *convex in* Π^{int}. Then (9.7.132) yields

$$\dot{\mathfrak{E}} \cdot \dot{\Pi}^R = \dot{\Pi}^{\mathrm{int}} \cdot \frac{\partial^2 W^{(i)}}{\partial \Pi^{\mathrm{int}} \partial \Pi^{\mathrm{int}}} \dot{\Pi}^{\mathrm{int}} \geq 0\,. \tag{9.7.134}$$

Whence the vectorial increments in $\dot{\mathfrak{E}}$ and $\dot{\Pi}^R$ form an acute angle or, in a one-dimensional model, this translates to

$$\frac{\partial \mathfrak{E}}{\partial \Pi^R} \geq 0 \tag{9.7.135}$$

at all points of the hysteresis loop. Thus *electric hardening is always positive* in this model;

(iv) *Global stability*:

Another consequence of the formulation (9.7.131)—(9.7.133) is the following result

$$\oint_C \mathfrak{E} \cdot d\Pi \geq 0 \,, \tag{9.7.136}$$

for any closed (total) polarization cycle C. The proof follows the identical proof in plasticity with hardening in Chapter 7 where the roles of $\mathfrak{E}$ and Π were played by the stress and the total strain. Then (9.7.136) is the electric analog of *Ilyushin's postulate*. The result here means that electric hysteresis loops are always described in the *counterclockwise* direction (in a plane where $\mathfrak{E}$ is the abscissa and Π is the ordinate).

(v) Example of electric loading surface $f(E) = 0$.

Let Π^{int} be a *scalar* and $\mathcal{N}$ its thermodynamic conjugate such that $\mathcal{N} = \partial W / \partial \Pi^{\text{int}}$. Then $f = f(\mathfrak{E}, \mathcal{N})$. An example of such a function f is given by

$$f(E) = f(\mathfrak{E}, \mathcal{N}) = (||\mathfrak{E}|| + \mathcal{N})^2 - E_c^2 \,. \tag{9.7.137}$$

It is readily shown by using Eqs. (9.7.130) that

$$\Pi^{\text{int}}(t) = \int_0^t \{\dot{\Pi}^R(t') \cdot \mathbf{A}^{-1} \cdot \dot{\Pi}^R(t')\}^{1/2} dt' \equiv \overline{\Pi^R} \tag{9.7.138}$$

if $||\mathfrak{E}||^2 := \mathfrak{E} \cdot \mathbf{A} \cdot \mathfrak{E}$, where the real symmetric nonsingular $\mathbf{A}$ accounts for electric anisotropy (if any). In this case Π^{int} is none other than the *cumulative* or *accumulated* (in time) *residual polarization* at time t. It thus really accounts for the whole past history, up to the present, of the electric loading.

(vi) *First polarization curve*:

The above model is completed by the datum of a first polarization curve

$$\mathfrak{E} = \varphi(\Pi^R) \, \text{or} \, \Pi^R = \varphi^{-1}(\mathfrak{E}) \,, \tag{9.7.139}$$

such that

$$\begin{aligned} &\varphi(\Pi^R) = -\varphi(-\Pi^R)\,, \qquad \text{hence } \varphi(0) = 0\,, \\ &\partial\varphi/\partial\Pi^R > 0\,, \forall\mathfrak{E}\,, \\ &\varphi^{-1}(\mathfrak{E})|_{\mathfrak{E}=\pm\infty} = \pm\Pi^R_S\,. \end{aligned} \tag{9.7.140}$$

This allows one to construct the hysteresis curve from an alternating loading starting from a *virgin state*; expression (9.7.139) is foreign to the present theory in the sense that either it is given by experiments or it is obtained from a semi-microscopic theory of electric polarization relying on the effects of *domain-wall motions*. The construction of hysteresis curves on the basis of the above thermodynamically developed model is described in Bassiouny *et al.* (1988a,b).

(vii) A correct *parametrization* of the curve (9.7.139) and the loading surface (9.7.137) in terms of stresses and temperature allows one to reproduce (at least the tendency) of the alterations to the hysteresis loop due to such fields. Figure 9.3 reproduces the result of such a parametrization for the influence of *stress* for PLZT ceramics. The agreement with experimental data is not too bad in spite of the obvious complexity and strong nonlinearity of the phenomenon. It is also possible to describe the horizontal translation of the hysteresis loop under the action of a bias electric field or the nonsymmetric widening of the loop (see Bassiouny and Maugin, 1989).

In all, the above-given electric modeling, which somewhat parodies the elastoplasticity of metals, is thermodynamically sound while reproducing

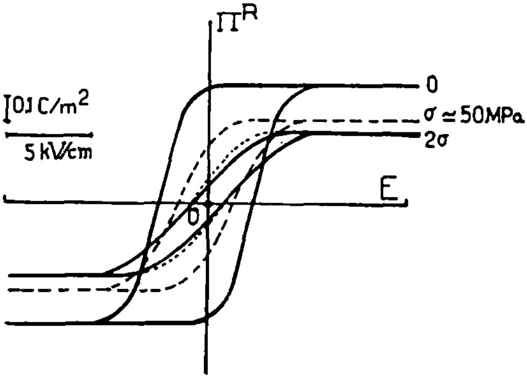

Fig. 9.3. Influence of compressive stresses on the electric hysteresis loop of PLZT ceramics (after Bassiouny and Maugin, 1989).

physical reality in a rather satisfactory manner. It is also "comprehensible" as it adheres well to the logic that we developed in previous sections. We obviously refer the reader to the original papers for the mathematical details and many graphic illustrations. It is fair to indicate that Chen (1980, 1984) — Chen and Peercy (1979) — has also attempted to construct a model of *electric hysteresis by domain switching* which in fact amounts to a theory with electric internal variables as shown by Bassiouny *et al.* (1988b). This theory reproduces well the general features of electric hysteresis and butterfly (strain versus field) loops in PZT ceramics although it had no thermodynamical basis to start with.

B. Magnetic bodies

The above-reported developments obviously admit of a magnetic analog in the description of *ferromagnetic hysteresis* and its couplings to mechanical effects. This is especially important in view of the potential applications to nondestructive testing (*NDT*) such as the measure of residual stresses via the Barkhausen effect [cf. Rudyak (1971), Karlajainen and Moilanen (1979), Ghaleb (1979), Chernyi (1983), Maugin (1989, 1991a,b), Maugin and Sabir (1990)].

Just for the sake of illustration we shall recall here the elements of a typical thermodynamically admissible modeling of magnetic hysteresis based on the exploitation of the inequality (9.5.87) when we discard any magnetic relaxation phenomenon. That is,

$$\Phi_{\mathrm{magn}} = \mathbf{H}\cdot\dot{\mathbf{M}}^{R} + \mathbf{H}^{\mathrm{int}}\cdot\dot{\mathbf{M}}^{\mathrm{int}} + \mathcal{A}\dot{\alpha} \geq 0\,, \qquad \mathbf{H} = \mathbf{H}^{r}\,. \tag{9.7.141}$$

This parodies plasticity in small strain and the electric behavior already examined in Paragraph A above. We have the following model (Maugin, Sabir and Chambon, 1987) for a *rigid* medium:

- *Free energy*:

$$W = W_m(\mathbf{M}^r,\theta) + \mathcal{W}(\alpha,\theta)\,; \tag{9.7.142}$$

- *Laws of state*:

$$S = -\frac{\partial W}{\partial \theta}\,, \qquad \mathbf{H} = \frac{\partial W_m}{\partial \mathbf{M}^r}\,, \qquad \mathcal{A} = -\frac{\partial \mathcal{W}}{\partial \alpha}\,; \tag{9.7.143}$$

- *Evolution laws*:

$$\dot{\mathbf{M}}^{R} = \dot{\lambda}\frac{\partial f}{\partial \mathbf{H}}\,, \qquad \dot{\alpha} = \dot{\lambda}\frac{\partial f}{\partial \mathcal{A}}\,, \tag{9.7.144}$$

where

$$\begin{aligned} &\dot{\lambda} \geq 0 \quad \text{if} \quad f = 0 \quad \text{and} \quad \dot{f} = 0\,, \\ &\dot{\lambda} = 0 \quad \text{if} \quad f < 0 \quad \text{or} \quad f = 0 \quad \text{and} \quad \dot{f} < 0\,, \end{aligned} \tag{9.7.145}$$

with the "convex" set of magnetism:

$$C_M = \{\mathbf{H}, \mathcal{A} | f(\mathbf{H}, \mathcal{A}) \leq 0\}\,. \tag{9.7.146}$$

For instance,

$$\begin{aligned} \mathbf{M}^r &= \mathfrak{X}^{-1}(\mathbf{H}) = \mathbf{M} - \mathbf{M}^R\,, \\ f(\mathbf{H}, \mathcal{A}) &= (||\mathbf{H}|| + \mathcal{A})^2 - H_c^2\,, \end{aligned} \tag{9.7.147}$$

where H_c, the *coercive field*, depends on the loading point, i.e. on $||\mathbf{H}||$, and $\mathfrak{X}^{-1}$ is obtained by inverting the second of (9.7.143). It has been assumed that magnetic hysteresis is *rate-independent*, hence the dissipation (9.7.141) is homogeneous of degree *one* only in the respective rates, and we have set $\mathbf{H}^{\text{int}} = 0$. By eliminating $\dot{\lambda}$ between the two equations (9.7.144), we obtain a result similar to (9.7.138) in the form

$$\alpha(t) = \overline{M^R} := \int_0^t ||\dot{\mathbf{M}}^R(t')||dt'\,, \tag{9.7.148}$$

i.e. the scalar internal variable is the *cumulative residual magnetization.* With the additional data of the *first magnetization curve* (which itself presents a saturation)

$$H = \varphi(M^R) \quad \text{or} \quad M^R = \varphi^{-1}(H)\,, \quad H \equiv ||\mathbf{H}|| \tag{9.7.149}$$

such that

$$\begin{aligned} &\varphi(M^R) = -\varphi(-M^R)\,, \qquad \partial\varphi/\partial M^R > 0\,, \qquad \forall H\,, \\ &\varphi^{-1}(H = \pm\infty) = \pm M_S^R\,, \end{aligned} \tag{9.7.150}$$

we check that the "convex" defined by (9.7.146) and (9.7.147) — a line segment — evolves with an alternating magnetizing field of growing amplitude until a maximum loop is formed [for which saturation corresponds to the last of (9.7.150)] of which the intersection with the H-axis corresponds to the usual definition of the *coercive field of the sample.* Such a "construction" of the final hysteresis curve is shown in Fig. 9.4. Figure 9.5 exhibits a hysteresis loop for steel with a comparison between the theoretical curve entering the above

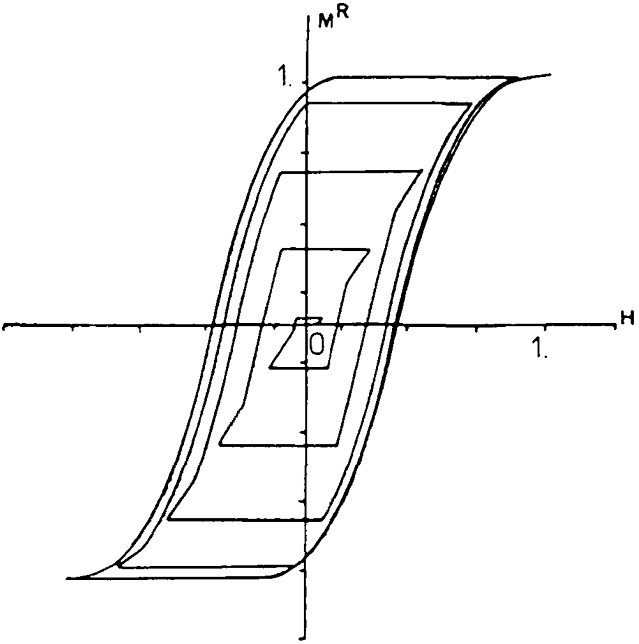

Fig. 9.4. Constructing the maximum magnetic hysteresis loop from a virgin state (after Maugin, Sabir and Chambon, 1987).

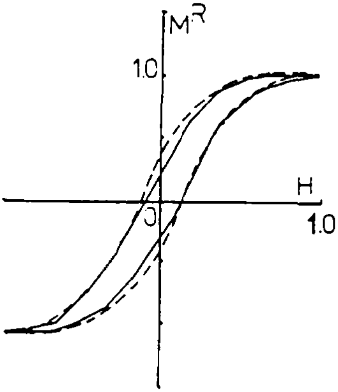

Fig. 9.5. Hysteresis loop for steel (in normalized units) at zero stress: --- experimental curve after Jiles and Athernon (J. Phys. D. App. Phys., 17, 1984, p. 1273) and — "good" theoretical fit (M. Sabir, Thesis, Paris, 1988).

scheme and some experimental data. A nonlinear parametrization of φ and the introduction of an effective magnetic field accounting for *magnetomechanical couplings* (e.g. magnetostriction) allow one to recover the essential features of the influence of mechanical stresses on magnetic hysteresis, at least in a one-dimensional model (Sabir, 1988). With the introduction of an internal axial variable $\mathbf{M}^{\text{int}}$ with companion "force"

$$\mathbf{H}^{\text{int}} = -\partial W/\partial \mathbf{M}^{\text{int}}, \tag{9.7.151}$$

it is possible, like in (mechanical) kinematic hardening, to mimic a *displacement* of the convex of magnetism, which will no longer be centered on the origin of the H-axis. In that case we may take, for example,

$$f(\mathbf{H}, \mathbf{H}^{\text{int}}) = ||\mathbf{H} + \mathbf{H}^{\text{int}}||^2 - H_c^2, \tag{9.7.152}$$

instead of $(9.7.147)_2$. It is found then that $\mathbf{M}^{\text{int}}$ is none other than $\mathbf{M}^R$ itself up to a constant vector (in the mechanical case the backstress is proportional to the plastic strain!).

C. Relation to microscopic descriptions

We briefly comment on the relationship between the above developed phenomenological models and microscopic or semimicroscopic descriptions. We illustrate this with the *magnetic case* which is better known from the microscopic viewpoint. At the scale of *magnetic domains* and *magnetic-domain walls* — which is a *mesoscopic* scale — the process of *magnetization* takes places *reversibly* through the reversible deformation (essentially bending) of magnetic domain walls or, when the input energy is sufficient enough, through the irreversible movement of the said domain walls. This occurs if the energy input is sufficient to overcome the *pinning energy of walls*, as the latter has a tendency to get pinned by lattice defects. This, in fact, explains the intimate relationship between "mechanical defects", and thus *plasticity*, and *magnetic hysteresis*, so that there is a need for a true *magneto-plasticity.*

The irreversible movement of magnetic domain walls is *jerky* and *takes some time to occur.* Thus, on the one hand the *jerky* movement of walls gives rise to *microinstabilities* along the magnetic-loading curve, and this is quite analogous to what we observed in mechanics in Fig. 7.6. The collective response of all magnetic domains is the resulting *magnetizing process*, and the usually observed M-H hysteresis is a smooth out version of this rather chaotic behavior. Nonetheless, this semi-microscopic behavior manifests through the so-called *Barkhausen noise* which, therefore, represents the magnetic analog of *acoustic emission*. It is of interest, following Sabir and Maugin (1988) to give a few elements of the semi-microscopic approach and to explain how it relates to the phenomenological one above.

For a magnetic *flow* equation such as $(9.7.147)_2$ we shall have a *macroscopic magnetic evolution equation* in the form

$$\dot{\mathbf{M}}^R = \pm 2\dot{\lambda}\frac{H_c}{\|\mathbf{H}\|}\mathbf{H}, \tag{9.7.153}$$

where H_c is defined at the loading and unloading branches. Sabir and Maugin (1988) have shown, by exploiting the ideas of L. Néel from the 1940s, that for *one* domain wall of area S, and across which the magnetic moment density $\mathbf{m}$ suffers a finite jump $[\mathbf{m}]$, with an applied magnetic field $\mathbf{H}$ and a mean free (or fly) path L_w between two successive stops of the wall on pinning points, we have the following *microscopic evolution*

$$\dot{\mathbf{m}}^R = (\text{const.}) \cdot \frac{2SL_m\|\mathbf{m}\|^2}{\tau_T}\langle 1 - \|\mathbf{H}_A\|/\|\mathbf{H}\|\rangle\, \mathfrak{A}\cdot\mathbf{H}, \tag{9.7.154}$$

where $\mathfrak{A}$ is a simple matrix whose numerical expression depends on the type of wall (e.g. so-called 180° and 90° walls); $\|\mathbf{H}_A\|$ is related to the pinning energy W_p of the wall by $\|\mathbf{H}_A\| = W_p/\|[\mathbf{m}]\|$, and τ_T is the mean *transit time* of the wall between two successive pinnings. The symbolism $\langle\ldots\rangle$ indicates the *positive part*. This microscopic law is not precisely of the same form as Eq. (9.7.153). It involves both a *threshold* (i.e. a sufficiently intense magnetic field needs to be applied to overcome the pinning energy) typical of plastic-like behaviors and also a *characteristic time* which is rather typical of viscous-like behaviors. We may say that (9.7.154) is the magnetic analog of a *viscoplasticity* evolution equation in solid mechanics. The essential properties of (9.7.154) are carried to the *macroscopic* level for a statistical distribution of domain walls. The final result is [cf. (5.4.39)]

$$\dot{\mathbf{M}}^R = \frac{\partial\mathcal{D}^*}{\partial\mathbf{H}}, \tag{9.7.155}$$

where it can be shown that (Sabir and Maugin, 1988)

$$\frac{\partial\mathcal{D}^*}{\partial\mathbf{H}} = (\text{const.}) \cdot \frac{S'L_w}{2\tau_T}M_S^2\langle 1 - \|\mathbf{H}_A\|/\|\mathbf{H}\|\rangle\mathbf{H}, \tag{9.7.156}$$

Table 9.1 State variables and dissipation in magnetism and solid mechanics (after Maugin, 1991a).

Magnetism		Solid mechanics in small strains	
magnetization (axial vector)	$\mathbf{M}$	small strain (tensor)	ε
power	$\mathbf{H}\cdot\dot{\mathbf{M}}$	power	$\sigma : \dot{\varepsilon}$
magnetic field (axial vector)	$\mathbf{H}$	stress (tensor)	σ
decomposition	$\mathbf{M} = \mathbf{M}^r + \mathbf{M}^R$	decomposition	$\varepsilon = \varepsilon^e + \varepsilon^p$
reversible magnetization	$\mathbf{M}^r$	elastic strain	ε^e
residual magnetization	$\mathbf{M}^R$	anelastic (plastic) strain	ε^p
dissipation	$\mathbf{H}\cdot\dot{\mathbf{M}}^R$	dissipation	$\sigma : \dot{\varepsilon}^p$
relaxation magnetic fied	$\mathbf{H}^{\text{relax}}$	viscous stress	σ^{visc}
dissipation	$\mathbf{H}^{\text{relax}}\cdot\dot{\mathbf{M}}^r$	dissipation	$\sigma^{\text{visc}} : \dot{\varepsilon}^e$
internal magnetization	$\mathbf{M}^{\text{int}}$	internal strain	ε^{int}
$(n-3)$ internal variable	α	$(n-6)$ internal variable	α
area of domain walls oriented perpendicular to a certain direction, per unit volume		densities of dislocations along different glide systems in the crystal	

where S' is the total area swept out by all walls in their motion and $\mathbf{H}_A$ is now an averaged pinning field. A complete analogy with the *viscoplastic behavior* of so-called *Bingham fluids* (see Sec. 7.2) can be drawn. This is reported in Table 9.2 after the analogies between magnetism and solid mechanics in general have been collected in Table 9.1. If the transit time τ_T tends to zero, then the expression (9.7.156) acquires a singular behavior which, in the limit, is none other than the one of Eq. (9.7.153). i.e., as in the mechanical case, the "plastic-like" behavior is a *singular* limit of the "viscoplastic-like" behavior.

In a different vein, by carefully examining the coupled magneto-mechanical unidirectional response of a magnetic specimen of unit thickness made of a few magnetic domains (a whisker), Motogi and Maugin (1993a,b) have been able to identify a *good magnetic internal variable of state* as being the area (volume) of (magnetically saturated) *magnetic domains* which are magnetized orthogonally to the direction of magnetization of the specimen or of the application of stress. In other words, these new internal variables take account of the *irreversible changes in the domain structure* in an unexpected way. The reason for this is that it is the deformation of walls which are *not* parallel

Table 9.2. Analogy between irreversible magnetization and viscoplasticity of crystals and Bingham fluids (after Maugin, 1991a).

Magnetism	Solid mechanics
Saturation in magnetization, magnetic loading surface, cumulative residual magnetization	locking, yield surface, cumulative plastic strain (Odqvist parameter)
Micromagnetism	Viscoplasticity of crystals
transition time of wall, Pinning pressure,	waiting time of dislocation,
Evolution equation:	Peierls-Nabarro force, Orowan's formula:
$\dot{\mathbf{m}}^R = -[\mathbf{m}]SV_{wn}$,	$\dot{\varepsilon}^p = \rho_m[u]\bar{v}$,
$[\mathbf{m}]$: jump in magnetic moment	$b = [u]$: Burgers vector
(a domain wall is a two-dimensional defect related to a discontinuity in magnetization)	(a dislocation is a one-dimensional defect related to a discontinuity in elastic displacement)
S: area of domain wall	ρ_m: density of mobile dislocations
V_{wn}: mean normal speed of the wall	$\bar{v}$: mean velocity of dislocation
$(\mathbf{H} - \mathbf{H}^*) \cdot \dot{\mathbf{m}}^R \geq 0$	Hill–Mandel maximal dissipation principle
Residual magnetization resulting from the motion of a distribution of domain walls	Evolution equation for Bingham fluids (rheology)
Magnetization rate: $\dot{\mathbf{M}}^R$	strain rate (tensor): $\mathbb{D}$
transition time: τ_R	viscosity: η
pinning field: $\Vert \mathbf{H}_A \Vert$	stress threshold: g
magnetic field: $\mathbf{H}$	deviator of stress tensor: σ^d
norm of magnetic field: $\Vert \mathbf{H} \Vert$	(second invariant of stress)$^{1/2}$: (σ_{II})

to the magnetizing field that contribute most to the resulting magnetization. This approach allows one to reproduce in a rather neat way the phenomenon of stress-induced magnetization (via magnetostriction) while fitting precisely with the above-presented phenomenological framework (see Motogi and Maugin, 1993a,b).

9.8. Elastic Superconductors

"Normal" electric conduction is probably one of the physical properties whose measurements vary within a largest interval (think of resistivities spanning the interval from 10^{-8} ohm × meter to 10^{+17} ohm × meter, i.e. an interval of

25 orders of magnitude) and which is characterized by so many well recognized regimes, i.e. average conduction, perfect conduction (as in astrophysics and magnetohydrodynamical studies), dielectrics (practically no conduction) and semi-conduction. While dielectrics request the condition $\mathfrak{J} = \mathbf{0}$ in the material framework, *perfect conduction* corresponds to a mathematical idealization of infinite conductivity which translates in the condition that the electric field in the co-moving frame must vanish in order to keep the Joule heating finite, i.e.

$$\mathcal{E} = \mathbf{0} \quad \text{or} \quad \mathfrak{E} = \mathbf{0} \quad \text{(perfect conductors)}.$$

The cases of normal and perfect conductions do not need any improved thermodynamics (see Sec. 9.4). Semi-conduction, as exhibited in certain piezoelectric crystals of technological interest is amenable through thermodynamics with internal variables as it exhibits *diffusion* of several charged species with possible dissociations and recombinations. The additional state variables then are *real scalars*. We do not dwell in this case for which we refer the reader to the original works (Maugin and Daher, 1986; Daher and Maugin, 1987).

Superconductivity, the property (not to be mistaken for perfect conduction) of certain materials to let electric current flow without opposing any resistance below a certain transition temperature, is of a totally different nature as a good treatment of it, if we discard *nonlocal* electrodynamics, necessarily involves the consideration of concepts which are foreign to phenomenological physics, *per se*, such as the *wave function* ψ of superconducting electrons (so-called Cooper's pairs — see de Gennes, 1966), obviously a *complex-valued scalar function*. That is, we are working in a framework where we couple the macroscopic vision with some arguments issued from a lower level of description, in fact the *quantum one*. The idea is to consider ψ itself as a *complex-valued internal variable* in an otherwise more or less classical background of deformable conductors. This type of approach should bear fruit with the current development of *high-temperature superconductors*, and with better knowledge of their coupled properties, such as those relating deformable and superconducting behaviors. Furthermore, as ψ is an order parameter from the point of view of *phase-transition theory*, the existence of a rather large correlation length imposes the consideration of the spatial gradients of ψ together with ψ. Thus we are right in the framework recalled in Secs. 4.7 and 4.8. In this we follow Maugin (1992b). We know now that in addition to the usual *material indifference* (objectivity) of continuum mechanics, the *gauge invariance* of superconductivity should be implemented. These two restrictions, together with the fulfilment of the second law of thermodynamics in its Clausius–Duhem form and where we know that entropy flux is no longer the ratio of heat flux to thermodynamical temperature (we have to account for the *gradients* of the *internal variable*, hence a diffusion-like phenomenon), make this approach superior to other attempts at a phenomenological formulation (e.g. Zhou and Miya, 1991; Zhou, 1991).

Calling $\mathbf{S}_R$ and $\mathbf{K}$ the *material vectors* associated with the entropy flux $\mathbf{S}$ and extra-entropy flux $\mathbf{k}$ by convection, i.e.

$$\mathbf{S}_R = J_F \mathbf{F}^{-1} \cdot \mathbf{S}\,, \qquad \mathbf{K} = J_F \mathbf{F}^{-1} \cdot \mathbf{k}\,, \tag{9.8.157}$$

it is trivial to show that (9.3.54) for a nonpolarizable body reads

$$\begin{aligned} &-(\dot{F} + S\dot{\theta}) + \mathrm{tr}\,(\bar{\mathbb{S}}^E \dot{\mathbb{E}}) + \mathfrak{J} \cdot \mathfrak{E} \\ &\qquad - \bar{\mathbb{M}} \cdot \dot{\mathfrak{B}} + \nabla_R \cdot (\theta \mathbf{K}) - \mathbf{S}_R \cdot \nabla_R \theta \geq 0\,. \end{aligned} \tag{9.8.158}$$

Here F designates the free energy per unit reference volume.

Obviously, Eqs. (9.3.46) show that there exist [*material*, i.e. functions of $(\mathbf{X}, t)$] *electromagnetic potentials* φ and $\mathfrak{A}$ such that

$$\mathfrak{E} = -\left(\nabla_R \varphi + \frac{1}{c} \frac{\partial \mathfrak{A}}{\partial t}\bigg|_X\right)\,, \qquad \mathfrak{B} = \nabla_R \times \mathfrak{A}\,. \tag{9.8.159}$$

But there is more than that in the *superconducting case* as the *gauge invariance of superconductivity* (de Gennes, 1969; Lynton, 1969) further imposes that $\mathfrak{E}$ and $\mathcal{B}$ remain form-invariant in the *space-time transformations* defined by ($\mathfrak{E} = \hat{\mathfrak{E}}$, $\mathfrak{B} = \hat{\mathfrak{B}}$)

$$\hat{\nabla}_R = \nabla_R - (ie^*/\hbar c)\mathfrak{A}\,, \qquad \frac{\hat{\partial}}{\partial t} = \frac{\partial}{\partial t} + (ie^*/\hbar)\varphi\,, \tag{9.8.160}$$

where $\hbar$ is Planck's reduced constant, i is the imaginary unit, and e^* is a characteristic electric charge (equal to $2e$ for Cooper's superconducting electrons, where e is the electronic charge). The constitutive equations for our deformable superconductors must satisfy the inequality (9.8.158) and the gauge invariance (9.8.160). For *elastic superconductors* (i.e. assuming no mechanical dissipation), we naturally assume that F, to start with, is a sufficiently regular function

$$F = F(\mathbf{F}, \mathcal{E}, \mathbf{B}, \theta, \psi, \nabla_R \psi)\,, \tag{9.8.161}$$

where ψ is a scalar-valued complex function, and we see that the first appearance of the gradient of this *internal* variable via $\nabla_R\psi$. That is, in the tradition of *T.I.V.*, we have no specific *field equation* for ψ.

The electric conduction current $\mathfrak{J}$ is composed of a *normal* contribution $\mathfrak{J}_n$ to be determined essentially by $\mathfrak{E}$ and that will *dissipate*, and a *superconducting* contribution $\mathfrak{J}_s$ determined by ψ and which does not contribute to the entropy growth, by definition of superconductivity. With this in mind we write, using (9.8.159),

$$\mathfrak{J}\cdot\mathfrak{E} = \mathfrak{J}_n\cdot\mathfrak{E} - \nabla_R\cdot(\mathfrak{J}_S\varphi) + (\nabla_R\cdot\mathfrak{J}_S)\varphi - \frac{1}{c}\mathfrak{J}_s\cdot\frac{\partial\mathfrak{A}}{\partial t}\,. \tag{9.8.162}$$

Applying first the requirement of material indifference to F, we easily show that the following F satisfies this invariance:

$$F = F(\mathbb{E},\mathfrak{E},\mathfrak{B},\theta,\psi,\nabla_R\psi)\,. \tag{9.8.163a}$$

Noting further that ψ is complex-valued while F is real valued, on account of the gauge invariance we consider the reduced form

$$F = \hat{F}(\mathbb{E},\mathfrak{E},\mathfrak{B},\theta,|\psi|,|\hat{\nabla}_R\psi|)\,. \tag{9.8.163b}$$

We now compute $\dot{F}$ while setting (ψ^* denotes the complex conjugate of ψ):

$$\begin{aligned} \mu^* &:= \partial\hat{F}/\partial(\hat{\nabla}_R\psi^*)\,,\\ \mathcal{A}_{\psi^*} &:= -\frac{\partial\hat{F}}{\partial\psi^*} + \hat{\nabla}_R\cdot\mu^* + (2ie^*/\hbar c)\mu^*\cdot\mathfrak{A}\,. \end{aligned} \tag{9.8.164}$$

On substituting the result of $\dot{F}$ into Eq. (9.8.158) while accounting for (9.8.162) and (9.8.164), and assuming that S, $\bar{\mathbb{S}}^E$, $\bar{\mathbb{M}}$ and $\mathfrak{J}_S$ do not depend on $\dot{\theta}$, $\dot{\mathbb{E}}$, $\dot{\mathfrak{B}}$ and $\dot{\mathfrak{A}}$, respectively, we obtain that the inequality (9.8.158) will keep in one sign if and only the following results hold true:

$$\begin{aligned} S &= -\frac{\partial\hat{F}}{\partial\theta}\,, & \bar{\mathbb{S}}^E &= \frac{\partial\hat{F}}{\partial\mathbb{E}}\,,\\ \frac{\partial\hat{F}}{\partial\mathfrak{E}} &= 0\,, & \bar{\mathbb{M}} &= -\frac{\partial\hat{F}}{\partial\mathfrak{B}}\,, \end{aligned} \tag{9.8.165}$$

and

$$\mathfrak{J}_S = \frac{ie^*}{2\hbar}(\mu^*\psi - \mu\psi^*)\,. \tag{9.8.166}$$

Furthermore, we select $\mathbf{K}$ in such a way as to avoid the appearance of a true divergence contribution in the second law of thermodynamics. Thus

$$\mathbf{K} = \frac{1}{\theta}\left\{\mathfrak{J}_S\varphi + \frac{1}{2}\left(\mu^*\frac{\hat{\partial}\psi}{\partial t} - \mu\frac{\hat{\partial}\psi^*}{\partial t}\right)\right\}. \tag{9.8.167}$$

as a consequence of (9.8.165) through (9.8.167), (9.8.158) reduces to the following dissipation inequality:

$$\Phi = \mathfrak{J}_n \cdot \mathfrak{E} - \mathbf{S}_R \cdot \nabla_R\theta + 2\mathrm{Re}\left(\mathcal{A}_\psi\frac{\hat{\partial}\psi^*}{\partial t}\right)$$

$$- \varphi\left[\nabla_R \cdot \mathcal{J}_S - 2\mathrm{Re}\left(\frac{ie^*}{\hbar}\mathcal{A}_\psi\psi^*\right)\right] \geq 0. \tag{9.8.168}$$

Proceeding now as in preceding sections, i.e. exploiting *T.I.P.* — or assuming the existence of a positive dissipation potential which is homogeneous of degree *two* in the fluxes — for the first three contributions in (9.8.168) we obtain (for instance, assuming *isotropy* for these effects, but there are no problems in considering an anisotropic case) the following *complementary laws*:

$$\mathbf{S}_R = -\frac{\kappa}{\theta}\nabla_R\theta + \nu_n\mathfrak{J}_n\,, \qquad \mathfrak{J}_n = \Sigma_n(\mathfrak{E} - \pi_0\nabla_R\theta)\,, \tag{9.8.169}$$

and

$$\mathcal{A}_\psi = \gamma_\psi\hbar\frac{\hat{\partial}\psi}{\partial t}\,, \tag{9.8.170}$$

while, on account of (9.8.170), (9.8.166) and (9.8.164), we check the following identity

$$\nabla_R \cdot \mathfrak{J}_S \equiv 2\mathrm{Re}\left(\frac{ie^*}{\hbar}\mathcal{A}_\psi\psi^*\right)\,, \tag{9.8.171}$$

so that the last term in the left-hand side of (9.8.168) just vanishes. The remaining dissipation is non-negative if and only if we have the following constraints on the coefficients:

$$\kappa \geq 0\,, \quad \Sigma_n \geq 0\,, \quad \nu_n = \theta\pi_0\,, \quad \gamma_\psi \geq 0\,. \tag{9.8.172}$$

Equations (9.8.169) are *thermoelectrically coupled Fourier's* and *Ohm's* laws (but note here that the former is given directly for the entropy flux). Equation (9.8.170) is the looked for gauge-invariant *evolution equation* for the internal variable ψ. The coefficient γ_ψ — which has to be positive according to the last of (9.8.172) — accounts for the *finite* relaxation time of superconducting electrons (however, this relaxation time must be sufficiently small compared to the characteristic time of external loads so as to justify the working hypothesis of *local accompanying state*). The constant $\hbar$ has been introduced for notational convenience. Both $\mathcal{J}_S$ and $\mathbf{K}$ are entirely expressible in terms of F and ψ because of Eq. (9.8.170).

If we consider as a particular case the following free energy — clearly some kind of truncated expansion — where $\hbar$ and the effective mass m^* are introduced for convenience:

$$F = F_n(\mathbb{E},\theta) + \alpha(\mathbb{E},\theta)|\psi|^2 + \beta(\mathbb{E},\theta)|\psi|^4 + \frac{\hbar^2}{2m^*}|\hat{\nabla}_R\psi|^2 \,, \tag{9.8.173}$$

then Eqs. (9.8.166) and (9.8.170) yield

$$\mathfrak{J}_S = \frac{ie^*\hbar}{2m^*}(\psi\nabla_R\psi^* - \psi^*\nabla_R\psi) - \frac{(e^*)^2}{m^*c}|\psi|^2\mathfrak{A} \tag{9.8.174}$$

and

$$\gamma_\psi\hbar\frac{\hat{\partial}\psi}{\partial t} + \alpha(\mathbb{E},\theta)\psi + \beta(\mathbb{E},\theta)|\psi|^2\psi - \frac{\hbar^2}{2m^*}\hat{\nabla}_R^2\psi = 0 \,, \tag{9.8.175}$$

respectively. Equation (9.8.174) is the accepted law for *supercurrent* (see, e.g. de Gennes, 1969). Equation (9.8.175) is obviously a straightforward *dynamical generalization* of the *Ginzburg–Landau* equation of superconductivity which accounts for the coupling with strains and for dissipation by *relaxing superconducting electrons* (cf. Tinkham, 1964). At this point, it remains to write down the *conservation-of-charge* equation deduced form $(9.3.46)_3$ by taking the divergence and accounting for $(9.3.46)_4$, (9.8.166) and $(9.8.169)_2$, and the *heat equation* which is obtained by expanding the intrinsic-dissipation equation which here reads

$$\theta\dot{S} = \Phi_{\text{intr}} + \nabla_R \cdot (\theta\mathbf{S}_R) \,, \tag{9.8.176}$$

with

$$\Phi_{\text{intr}} = \mathfrak{J}_n \cdot \mathfrak{E} + 2\mathrm{Re}\left(\mathcal{A}_\psi\frac{\hat{\partial}\psi^*}{\partial t}\right) . \tag{9.8.177}$$

This completes the essentials of the continuum thermomechanics of *thermoelastic superconductors* in the *Galilean* and *gauge-invariant* form which fits well in the general scheme for systems prone to exhibiting *dissipative structures* (see Maugin, 1990a, and Paragraph 4.7b). The coupling between typically superconducting features and strains will naturally come into the picture, e.g. through the functions α and β present in the energy (9.8.173), possibly with drastic behaviors at phase-transition points. Some of these are illustrated in the book of Zhou (1991).

9.9. Solutions of Polyelectrolytes[1]

We consider the case of *fluid solutions of polyelectrolytes* to illustrate simultaneously the *theory of mixtures* with *chemical reactions*, the presence of a *tensorial internal variable* (the conformation of Sec. 6.4), and the *interactions with electromagnetic fields*. Such solutions were schematically depicted in Fig. 6.4 with counter-ions forming a more or less tenuous cloud around the macro-ion.

A. Thermodynamical modeling

Polyelectrolyte solutions can be modeled as *mixtures*, the solvent being the carrier fluid, and the solute merely consisting of the polyelectrolyte molecules, or rather *macro-ions*. The different types of ions are dissolved into the fluid. For the sake of simplicity the solvent is supposed to undergo isochoric motions. The motion of the different types of ions gives rise to electric current densities which need not be conserved because of the possible ionization and recombination reactions. The volume charge density as a whole is assumed to vanish (*neutral fluid*). But the different types of ions are described through a set of charge densities q_α, $\alpha = 1, 2, \ldots$, one of them, q_m being the charge density of macro-ions. So the polyelectrolyte solution is modeled as a reacting mixture of several fluid components. However, in order to avoid the complexity inherent in the standard theory of fluid mixtures we introduce simplifying assumptions. Indeed, let ρ_c and ρ_m be the mass densities of the carrier fluid and the "macro-ion" fluid. Owing to the assumption of isochoric motions we have ρ_c, $\rho_m = \text{const.}$ and hence the total mass density $\rho = \rho_c + \rho_m$ is constant (the mass of counterions is discarded). The corresponding velocity fields $\mathbf{v}$ and $\mathbf{v}_m$ satisfy $\nabla \cdot \mathbf{v} = \nabla \cdot \mathbf{v}_m = 0$. Only the Eulerian description in the current configuration $\mathcal{K}_t$ is employed. We ascribe material properties to the carrier fluid and the macro-ions only. Thus ρ is the mass density of the mixture and we disregard the partial pressures of the different ions in the fluid. Finally, the local electric

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[1] We rely heavily on the review contribution of Maugin and Drouot (1991).

properties are taken care of through the *electric polarization* per unit volume (effective density of electric dipoles) $\mathbf{P}$, or unit mass, $\pi = \mathbf{P}/\rho$, and Maxwell's equations are considered within the framework of quasi-electrostatics (optics, however, requires the use of the full set of Maxwell's equations; see Drouot and Maugin, 1987, for these further developments). The carrier fluid itself is regarded as electrically neutral. All this being specified, we can now consider the basic equations.

The balances of electric charge for the ions α in the solution are written as

$$\frac{\partial q_\alpha}{\partial t} + \nabla \cdot (q_\alpha \mathbf{v}_\alpha) = \gamma_\alpha \,, \qquad \alpha = 1, 2, \dots \,, \tag{9.9.178}$$

γ_α being the charge supply (from the other ions) and $\mathbf{v}_\alpha$ is the velocity field of the αth type of ion. Conservation of charge implies by summation over α that

$$\sum_\alpha \gamma_\alpha = 0 \,. \tag{9.9.179}$$

Moreover, the charge supplies γ_α are not independent of one another since there can occur n distinct *chemical reactions* so that

$$\gamma_\alpha = \sum_{r=1}^{n} \nu_{\alpha r} \dot{\Lambda}_r \,, \tag{9.9.180}$$

where the $\nu_{\alpha r}$'s are *stochiometric coefficients* and $\dot{\Lambda}_r$ are *reaction progress rates.* Let $\mathcal{J}_\alpha = q_\alpha(\mathbf{v}_\alpha - \mathbf{v})$. In view of the condition $\nabla \cdot \mathbf{v} = 0$, we have

$$\nabla \cdot (q_\alpha \mathbf{v}_\alpha) = \nabla \cdot \mathcal{J}_\alpha + (\mathbf{v} \cdot \nabla) q_\alpha \,. \tag{9.9.181}$$

And Eq. (9.9.178) transforms to

$$\dot{q}_\alpha + \nabla \cdot \mathcal{J}_\alpha = \gamma_\alpha \,, \tag{9.9.182}$$

where the superimposed dot denotes the usual *material* time derivative (relative to the whole mixture). We emphasize that macro-ions are carried with the fluid and thus

$$\mathcal{J}_m = 0 \,, \qquad \dot{q}_m = \gamma_m \,. \tag{9.9.183}$$

B. Field equations

From the general theory of electromagnetic continua in interaction, which builds on a generalization of the *principle of virtual power* (cf. Maugin, 1980), it is shown that the local equations of physical linear and angular momenta for the whole solution are in the form

$$\rho\dot{\mathbf{v}} = \operatorname{div}\sigma + \rho\mathbf{f} + \mathbf{f}^{em}\,, \qquad \mathbf{f}^{em} \equiv (\mathbf{P}\cdot\nabla)\mathcal{E}\,, \tag{9.9.184}$$

and

$$\sigma = \bar{\sigma} + (\mathbf{P}\otimes\mathcal{E})_A\,, \qquad \text{i.e.} \qquad \sigma_A = (\mathbf{P}\otimes\mathcal{E})_A\,, \tag{9.9.185}$$

where the symmetric tensor $\bar{\sigma}$ is called the *intrinsic stress tensor*, and we see that the Cauchy stress becomes symmetric when $\mathbf{P}$ and $\mathcal{E}$ are aligned. Let

$$\mathcal{J} = \sum_{\alpha} \mathcal{J}_\alpha\,, \tag{9.9.186}$$

be the total current density, e the internal energy, $\mathbf{q}$ the heat flux, $\mathbf{S}$ the entropy flux, $\mathbf{k}$ the *extra* entropy flux (we have diffusion so that we expect a deviation from the classical formula of $\mathbf{S}$) and h the heat supply per unit mass. The local energy equation reads

$$\rho\dot{e} = \operatorname{tr}(\bar{\sigma}\mathbf{D}) + \mathcal{J}\cdot\mathcal{E} - \rho\mathcal{E}^L\cdot D_J\pi - \nabla\cdot\mathbf{q} + \rho h\,, \tag{9.9.187}$$

where $\mathcal{E}^L$ is the so-called *local electric field* which satisfies the "balance" equation

$$\mathcal{E}^L + \mathcal{E} = \mathbf{0}\,, \tag{9.9.188}$$

and $D_J\pi$ is the Jaumann derivative [cf. $(6.4.79)_1$] of the electric polarization π. Introducing the Helmholtz free energy $\psi = e - \eta\theta$, and combining (9.9.187) with the second law

$$\rho\dot{\eta} \geq (\rho h/\theta) - \nabla\cdot(\mathbf{S})\,, \qquad \mathbf{S} = \theta^{-1}\mathbf{Q} + \mathbf{k}\,, \tag{9.9.189}$$

we obtain the *Clausius-Duhem inequality* in the form

$$\begin{aligned} -\rho(\dot{\psi} + \eta\dot{\theta}) + \operatorname{tr}(\bar{\sigma}\mathbf{D}) + \mathcal{J}\cdot\mathcal{E} - \rho\mathcal{E}^L\cdot D_J\pi \\ + \nabla\cdot(\theta\mathbf{k}) - \mathbf{S}\cdot\nabla\theta \geq 0\,, \end{aligned} \tag{9.9.190}$$

where $\mathbf{D}$ is reduced to its deviatoric part in reason of the incompressibility of the mixture as a whole.

We call κ and $\mathbf{K}$ the volume and deviatoric parts of a general conformation tensor which accounts for the macro-ions deformability and is considered as an *internal variable* from the thermodynamical viewpoint. The function ψ thus has a general functional dependence

$$\psi = \psi(\theta, q_\alpha, \pi, k, \mathbf{K}) . \tag{9.9.191}$$

The *laws of state* read

$$\begin{gathered} \bar{\eta} = -\frac{\partial \psi}{\partial \theta} , \qquad \mu_\alpha = \frac{\partial \psi}{\partial q_\alpha} , \qquad \mathcal{E}^{Lr} = -\frac{\partial \psi}{\partial \pi} , \\ f = -\rho \frac{\partial \psi}{\partial \kappa} , \qquad \mathcal{F} = -\rho \frac{\partial \psi}{\partial \mathbf{K}} , \end{gathered} \tag{9.9.192}$$

where $\bar{\eta}$ is the entropy at local instantaneous equilibrium, μ_α are chemical potentials of the species α, f and $\mathcal{F}$ are generalized *forces*, and we also define $\mathcal{E}^R$ and $\mathbf{k}$ by

$$\mathcal{E}^R = \mathcal{E}^L - \mathcal{E}^{Lr} , \qquad \mathbf{k} = -\frac{\rho}{\theta} \sum_\alpha \mu_\alpha \mathcal{J}_\alpha , \tag{9.9.193}$$

and finally, for a spatially uniform state (i.e. $\nabla \mathbf{v} = \mathbf{0}$, $\mathcal{E} = -\nabla \phi = \mathbf{0}$, $\nabla \theta = \mathbf{0}$, where ϕ is the electrostatic potential) entropy has its *thermostatics definition*, i.e. $\eta = \bar{\eta}$, when all rates of internal variables $(\kappa, \mathbf{K}, \Lambda_r)$ are nil. Then after computing the time derivative of ψ, taking account of the invariance of ψ by *rotations*, expressed by (invariance under infinitesimal rotations of a scalar-valued function of a vector field π and a symmetric second order tensor $\mathbf{K}$)

$$2\left(\frac{\partial \psi}{\partial K_{ki}} K_{kj} - \frac{\partial \psi}{\partial K_{kj}} K_{ki}\right) + \left(\frac{\partial \psi}{\partial \pi_i} \pi_j - \frac{\partial \psi}{\partial \pi_j} \pi_i\right) = 0 , \tag{9.9.194}$$

and accounting for Eqs. (9.9.182), (9.9.189)$_2$, (9.9.192) and (9.9.193), we deduce from (9.9.190) the following *residual dissipation inequality*

$$\begin{aligned} \Phi = \operatorname{tr}(\bar{\sigma} \mathbf{D} + \mathcal{F} D_J \mathbf{K}) + f \dot{\kappa} - \mathcal{E}^R \cdot D_J \mathbf{P} & \\ + \sum_\alpha \mathcal{J}_\alpha \cdot \mathcal{E}_\alpha - \sum_{r=1}^{n} R_r \dot{\Lambda}_r - \mathbf{S} \cdot \nabla \theta \geq 0 , & \end{aligned} \tag{9.9.195}$$

where, on account of incompressibility, we have set

$$\begin{gathered}
\mathcal{E}_\alpha := \mathcal{E} - \nabla\bar{\mu}_\alpha\,, \qquad \bar{\mu}_\alpha = \frac{\partial\Psi}{\partial q_\alpha}\,, \qquad \mathbf{P} = \rho\pi\,, \\
\Psi = \rho\psi\,, \qquad S = \rho\eta = -\frac{\partial\Psi}{\partial\theta}\,, \qquad R_r = \sum_\alpha \bar{\mu}_\alpha \nu_{\alpha r}\,, \qquad (9.9.196) \\
\mathcal{E}^{Lr} = -\frac{\partial\Psi}{\partial\mathbf{P}}\,, \qquad f = -\frac{\partial\Psi}{\partial\kappa}\,, \qquad \mathcal{F} = -\frac{\partial\Psi}{\partial\mathbf{K}}\,.
\end{gathered}$$

All dissipative processes that contribute to (9.9.195) in the traditional *bilinear* form, can be studied on the basis of *T.I.P. Thermodynamical equilibrium* is defined by three groups of conditions:

$$S_{\mathrm{eq}} = -\left(\frac{\partial\Psi}{\partial\theta}\right)_{\mathrm{eq}}\,, \qquad (\bar{\mu}_\alpha)_{\mathrm{eq}} = \left(\frac{\partial\Psi}{\partial q_\alpha}\right)_{\mathrm{eq}}\,, \qquad (9.9.197)$$

$$\nabla\mathbf{v} = \mathbf{0}\,, \quad \nabla\phi = \mathbf{0}\,, \quad \nabla\bar{\mu}_\alpha = \mathbf{0}\,, \quad \nabla\theta = \mathbf{0}\,, \qquad (9.9.198)$$

and

$$f(\kappa_{\mathrm{eq}}) = 0\,, \quad \mathcal{F}(\mathbf{K}_{\mathrm{eq}}) = \mathbf{0}\,, \quad (\mathcal{E}^L)_{\mathrm{eq}} = (\mathcal{E}^{Lr})_{\mathrm{eq}}\,, \quad R_r = 0\,, \qquad (9.9.199)$$

of which the second corresponds to a spatially uniform state while Eqs. (9.9.199) define equilibrium values of κ, $\mathbf{K}$, $\mathbf{P}$ and Λ_r once the conditions (9.9.197) are fulfilled. A linear theory usually implies that $\mathbf{K}_{\mathrm{eq}} = \mathbf{0}$ and $(\Lambda_r)_{\mathrm{eq}} = 0$. But $\kappa_{\mathrm{eq}} \neq 0$ and $(9.9.198)_2$ and $(9.9.199)_3$ do not necessarily imply that $\mathbf{P}_{\mathrm{eq}} = \mathbf{0}$ since $(\mathcal{E}^{Lr})_{\mathrm{eq}}$ may be strongly nonlinear in $\mathbf{P}$ and the equation $(\mathcal{E}^{Lr})_{\mathrm{eq}} = 0$ could have non-zero $\mathbf{P}$ solutions (case of a *ferroelectric* behavior).

C. Dissipative processes

Equations (9.9.198) and (9.9.199) clearly single out two types of dissipative processes through their limit conditions corresponding to thermodynamical equilibrium. The former are the usual dissipative processes of *T.I.P.* (de Groot and Mazur, 1962) that correspond, at equilibrium, to spatially uniform states of the basic *observable* variables of *thermo-electro-mechanics*, while the latter represent *relaxation processes* governed by evolution equations and of which reaction kinetics have probably offered historically the first example. Electric and conformational relaxations belong to this class while shear viscosity, electric conduction and thermal conduction belong to the former. A third class, the "plasticity-like" one is not represented here, but was amply illustrated in previous chapters.

The various parities in time and tensorial orders of the *fluxes* and *forces* involved in the inequality (9.9.195) means that one can immediately envisage certain couplings, as well as decouplings, between various dissipative effects. Equivalently to the linear equations of *T.I.P.*, we can also assume the existence of a *dissipation potential* that is homogeneous of degree *two* in the fluxes. For instance,

$$\mathcal{D} = \frac{1}{2}\Bigg\{ 2\eta_v \operatorname{tr}\mathbf{D}^2 + \zeta \operatorname{tr}\mathcal{F}^2 + \xi f^2 + \sum_\alpha \mathcal{J}_\alpha \cdot \mathbf{R}_\alpha \cdot \mathcal{J}_\alpha$$

$$+ B(\nabla\theta)^2 + 2\sum_\alpha A_\alpha \mathcal{J}_\alpha \cdot \nabla\theta + \nu(\mathcal{E}^R)^2 + \sum_{1,r=1} R_1 \xi_{lr} R_r \Bigg\}, \qquad (9.9.200)$$

so that with this special choice we obtain the following *complementary "constitutive" equations*:

$$\mathbf{S} = -B\nabla\theta - \sum_\alpha A_\alpha \mathcal{J}_\alpha ,$$

$$\mathcal{E}_\alpha = \mathbf{R}_\alpha \cdot \mathcal{J}_\alpha + A_\alpha \nabla\theta , \qquad (9.9.201)$$

$$\bar{\sigma}^D = 2\eta_v \mathbf{D} , \qquad (9.9.202)$$

and

$$\begin{aligned} D_J\mathbf{K} &= -\zeta\frac{\partial\Psi}{\partial\mathbf{K}}, & \dot{\kappa} &= -\xi\frac{\partial\Psi}{\partial\kappa}, \\ D_J\mathbf{P} &= \nu\left(\mathcal{E} - \frac{\partial\Psi}{\partial\mathbf{P}}\right), & \dot{\Lambda}_r &= -\sum_{k=1}^{n}\sum_\alpha\left(\frac{\partial\Psi}{\partial q_\alpha}\nu_{\alpha k}\xi_{kr}\right). \end{aligned} \qquad (9.9.203)$$

The first two of these represent the coupled *Fourier–Ohm laws*. They can be rewritten in the following form:

$$\begin{aligned} \mathbf{q} &= -(\theta B)\nabla\theta - \sum_\alpha \left(\theta A_\alpha - \frac{\partial\Psi}{\partial q_\alpha}\right)\mathcal{J}_\alpha , \\ \mathcal{E} - \nabla\left(\frac{\partial\Psi}{\partial q_\alpha}\right) &= \mathbf{R}_\alpha \cdot \mathcal{J}_\alpha + A_\alpha\nabla\theta , \quad \alpha = 1, 2, \ldots . \end{aligned} \qquad (9.9.204)$$

The non-negativeness of Φ requires that the following inequalities be satisfied:

$$\begin{aligned} &\eta_v \geq 0\,, \quad \zeta \geq 0\,, \quad \xi \geq 0\,, \quad \nu \geq 0\,, \quad B \geq 0\,, \\ &A_\alpha^2 \leq B\bar{R}_\alpha\,, \qquad \xi_{kr} \qquad \text{a non-negative matrix}\,, \end{aligned} \tag{9.9.205}$$

where $\bar{R}_\alpha$ is the smallest eigenvalue of $\mathbf{R}_\alpha$.

Since dissipative entities can also depend on the *state variables* (e.g. θ and $\mathbf{K}$) it is clear that (9.9.200) is only to be considered as one of the simplest examples used for illustrative purposes. In particular, one can envisage conduction processes which involve $\mathbf{K}$ and will therefore be *anisotropic*. Also, *gyroscopic terms* such as those already exhibited in (6.4.69)–(6.4.72) are not excluded and can always be added to the equations for $D_J K$ and $\bar{\sigma}$. Just for the sake of example we specify a possible expression for the free energy Ψ:

$$\begin{aligned} \Psi = &-\frac{1}{2}(k_B\theta)\ln\left(\det\left(\mathbf{K}+\frac{1}{3}\kappa\mathbf{1}\right)\right) - q^{\text{eff}}(\kappa^{-1/2} - \nu_e I^{-1/2}) \\ &+ \frac{1}{2}e_1^*(E_{cr} - E)(\kappa-\kappa_0)^2 + \frac{1}{4}\gamma(\kappa-\kappa_0)^4 \\ &+ (\alpha_2 I_2 + \alpha_2' I_2^2 + \alpha_3' I_3^2 + \alpha_3'' I_3^3 \\ &+ \alpha_0 I_3 I_4 + \gamma_4 I_4 + \alpha_6 I_6 + \alpha_6' I_6^2) + \bar{\Psi}(\theta, \alpha)\,, \end{aligned} \tag{9.9.206}$$

where the first line represents *singular contributions*, the second line accounts for dilatational effects of the conformation with a coupling with an electric field E which may take a critical value E_{cr} (see below) and the long contribution within parentheses gathers *regular* contributions in the traceless tensor $\mathbf{K}$, the electric polarization $\mathbf{P}$, and the electroelastic couplings between these two. The α's, (α')'s and (α'')'s are coefficients and the invariants I_α are defined by

$$\begin{aligned} I_2 = \mathbf{P}^2\,, \quad I_3 = \operatorname{tr}\mathbf{K}^2\,, \quad I_4 = \mathbf{P}\cdot\mathbf{K}\cdot\mathbf{P}\,, \\ I_5 = \mathbf{P}\cdot\mathbf{K}^2\cdot\mathbf{P}\,, \quad I_6 = \operatorname{tr}\mathbf{K}^3\,. \end{aligned} \tag{9.9.207}$$

The first term in (9.9.206) accounts for the *Brownian agitation* which has a tendency to bring the conformation back to a spherical one (k_B is Boltzmann's constant), while q^{eff} being some effective electric charge, the contribution in $\kappa^{-1/2}$ accounts for *Coulombic electrostatic interactions*, that in $I_3^{-1/2}$ will account for the *mechano-chemical effect* with coefficient ν_e (see below), and the coefficient α_4 accounts for the *electrostriction effect*. Coulombic interactions were introduced by Dunleap and Leal (1984) in a dumbbell model. The other terms, together with the above-introduced dissipative contributions, were introduced by Drouot and Maugin (1985) and Morro, Drouot and Maugin (1985, 1987). The model thus built is extremely rich and only three remarkable effects are illustrated below.

D. Mechano-chemical effect

Consider the solvent (carrier fluid) at rest and a vanishing electric field. We look at deviations from a spherically coiled conformation (and thus $\kappa = \kappa_0 =$ fixed const. for all practical purposes). The effect of the charge $q_m < 0$ that we select for the q^{eff} in Eq. (9.9.206) is thought to be dominant over that of electric polarization. At the simplest level of approximation the free energy then is viewed as resulting from the deformation energy of macromolecules and the interaction between that deformation and electric charge. From (9.9.206) one therefore extracts the relevant contribution

$$\psi^{me} = \alpha_3 I_3 + q_m \nu_e I_3^{-1/2} . \tag{9.9.208}$$

Equation (9.9.203), in its *stationary* form yields (shear) conformations **K** which are not zero. They are given by

$$l^3 \equiv I_3^{3/2} = (\nu_e / 2\alpha_3) q_m . \tag{9.9.209}$$

Since $l > 0$ and $q_m < 0$, one must have $\nu_e < 0$. Let l_e the value of l given by Eq. (9.9.209). Then we can show in absence of flow that the *relaxation equation* for **K** gives, after tensorial contraction with **K** (cf. Morro *et al.*, 1985)

$$\dot{l} = -\frac{1}{\tau(l, l_e)}(l - l_e) , \tag{9.9.210}$$

where the conformation-dependent relaxation time is given by

$$\tau = l^2 / 2\zeta\alpha_3 (l^2 + l l_e + l_e^2) .$$

Thus l tends eventually toward l_e. Now the interaction between macro-ions and solvent is taken into account by observing that the number of dissociated groups in the polyanionic macro-ion increases (hence q_m decreases) with increasing the pH value p, of the solution; namely $dq_m/dp < 0$. In view of (9.9.209) one has $\partial I_3 / \partial q_m < 0$ and thus

$$\partial I_3 / \partial p > 0 \qquad \text{or} \qquad \partial l / \partial p > 0 . \tag{9.9.211}$$

This means that the polyanionic macroion elongates with increasing pH (and vice versa). This is the content of the *mechano-chemical effect* (Volkenshtein, 1983, pp. 91–94).

E. Electrically induced conformational phase transition

Without entering the detailed biophysical mechanism which allows for the occurrence of *sudden volume changes*, we set up a very simple scheme for describing these volume changes. We are thus concerned with the internal variable κ rather than $\mathbf{K}$. We concentrate on the second line of expression (9.9.206). There $e_1^* \geq 0$ is a pure constant (bulk elasticity of conformations) and E is the externally controllable parameter (magnitude of the electric field or induced electric polarization when the solution is placed between the plates of a condenser) which causes the transition. The corresponding elastic energy is minimum at $\kappa = \kappa_0$ for $E > E_{cr}$. After relaxation Eq. $(9.9.203)_2$ produces the equilibrium values via $\partial\Psi/\partial\kappa = 0$, i.e.

$$\kappa = \kappa_0 \qquad \text{or} \qquad \kappa - \kappa_0 = \gamma^{-1}(e_1^*(E_{cr} - E))^{1/2} . \tag{9.9.212}$$

This implies that $\gamma > 0$ if $E < E_{cr}$. It follows from the second of (9.9.212) that

$$\frac{d\kappa}{dE} = -\left[\frac{e_1^*}{\gamma(E_{cr} - E)}\right]^{1/2} , \tag{9.9.213}$$

which diverges to $-\infty$ for E tending to E_{cr}. This implies that although the transition is continuous, κ changes significantly near the critical value E_{cr} [for $E > E_{cr}$ we apply the first equation of (9.9.212)]. The phenomenon relates to the *collapse of polyelectrolytes* in certain circumstances (see, e.g. Tanaka *et al.*, 1982, where $E_{cr} \simeq 0.3$ volt/cm).

F. Kerr effect

We let the reader check for himself that on carrying the expression (9.9.206) into $(9.9.203)_1$ and accounting for the coupled gyroscopic effects between stress and conformation in the manner of Sec. 6.4, the evolution Eq. $(9.9.203)_1$ will give, up to irrelevant terms for our purpose, an equation such as (Drouot and Maugin, 1985, p. 485)

$$D_J\mathbf{K} + \frac{1}{\tau_K}\mathbf{K} = \hat{f}\left(\mathbf{E}\otimes\mathbf{E} - \frac{1}{3}E^2\mathbf{1}\right) - \lambda\mathbf{D} + \cdots \tag{9.9.214}$$

where we have defined the conformation-relaxation time τ_K, accounted for the fact that **P** has aligned with the electric field, and considered a quasi-static approach and the property that **K** is a deviator. The material coefficient $\hat{f}$ represents the *electrostrictive effect* combined to the elasticity of the conformation and the electric susceptibility; it may also be referred to as the *electro-optic coefficient* as Eq. (9.9.214) is none other than the evolution equation forming the basis of the analysis of the *laser-induced Kerr effect* — also called *optical-field induced ordering* — when applied to a *nematogen* in its isotropic phase (cf. Prost and Lalanne, 1973), the modeling of which was initially due to de Gennes (1971). The optical Kerr effect follows if we assume that **K** is directly proportional to a tensor that is representative of the *deviation from isotropy* of some electromagnetic property such as the magnetic susceptibility. The Kerr effect is then obtained by time integration of (9.9.214). A general study of optical effects for polyelectrolytes with the consideration of the effects of both intense bias fields and flows is due to Drouot and Maugin (1987) to whom we refer the reader, especially for a discussion of characteristic numbers including time scales and Deborah numbers.

To conclude this section which has simultaneously shown the complexity of physico-chemical processes involved and the relative simplicity with which these can be described in a fully thermodynamic framework, we note on the one hand *additional diffusion processes* can be incorporated along the lines of Eqs. (6.5.101)-(6.5.103) — cf. Morro, Maugin and Drouot (1989) — while on the other hand, with all the differences in mind, some part of the description introduced also applies to *elastic semiconductors* considered as mixtures of conducting electrons, holes, etc. In that case also, the effective electric field such as in the definition $(9.9.196)_1$ and the extra entropy flux $(9.9.193)_2$ play a fundamental role. **K** is then replaced by an *observable* state variable which is none other than the strain (see Maugin and Daher, 1986; Daher and Maugin, 1986b, 1987).

9.10. Ferroelectrics and Ferromagnets

There are two ways to look at electromagnetic materials such as *ferroelectrics* and *ferromagnets*, which exhibit a phase transition separating a high-temperature *disordered* phase from a low-temperature *ordered* phase. One way is to look, at a macroscopic scale, at multidomain specimens for which *irreversibility* is essentially meant as producing *hysteresis*. This was examined in Sec. 9.7

where *thermodynamic internal variables of state* appear to provide the most efficient tool in the description of irreversible phenomena. The other way (as seen in Sec. 4.7) which fits well the consideration of coupled *dynamical* processes in nondefective materials (i.e., without domain structure), consists of considering a *microstructure* of electric or magnetic origin as evidenced in condensed-matter physics and the theory of phase transitions. Indeed, whether in ferroelectrics or in ferromagnets, *electric polarization* or *magnetization density* have to be considered as an additional *degree of freedom* of vectorial nature endowed with some type of inertial properties, and for which spatial *gradients* have to be accounted for. It is thus surmised, if there is an obvious *dynamical* coupling between the mechanical fields of stress and displacement and either the electric fields of *electric polarization* and electric displacement, or the magnetic fields of *magnetization* and *magnetic induction*, that the most reasonable approach is the classical thermomechanics (*T.I.P.*) of a mechanically deformable medium equipped with a *microstructure* of electromagnetic origin. In this line of thought the kinematic and kinetic description increases in complexity while the thermodynamical frame becomes more standard, but for the larger number of *observable state variables.* This is the spirit of this section which briefly recalls some essential properties. Lengthy developments have previously been reported in other books (Maugin, 1988, Chapters 6 and 7; Eringen and Maugin, 1990, Chapter 9; Maugin, Pouget *et al.*, 1992, Chapters 2 and 5). Electric polarization in the ferroelectric case and magnetization in the ferromagnetic one provide the additional variables as both *order parameters* (and thus primary independent variables in the thermodynamic description) and *observable variables of state.* We start with the second case, which is more original.

A. Deformable ferromagnets[1]

We focus attention on the thermodynamic aspects. Let μ be an axial vector under time reversal, $\mathcal{K}_t$, the magnetization per unit mass in the current configuration and $\nabla_R\mu$, its material gradient. For *elastic materials*, we naturally

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[1] We refer to Maugin (1988, Chapter 6) for a rather exhaustive presentation and for numerous references to the early works of Landau and Lifshitz, Akhiezer *et al.*, Brown, Tiersten, Maugin and Eringen on the modeling of deformable ferromagnets and the corresponding dynamics.

consider a free energy density ψ in the functional form

$$\psi = \psi(\mathbf{F}, \theta, \mu, \nabla_R \mu), \tag{9.10.215}$$

where the gradient of μ takes care of the *magnetic ordering* typical of a *ferromagnetic phase*; $\nabla_R \mu = 0$ at all points in a *single* ferromagnetic domain, while μ varies rapidly with $\mathbf{X}$ through a transition zone such as a *magnetic domain wall*. In addition (dynamics), μ is related to a density of *intrinsic spin* $\mathbf{s}$ by the celebrated *gyromagnetic* relation:

$$\mathbf{s} = \gamma^{-1} \mu, \tag{9.10.216}$$

where γ is the so-called *gyromagnetic ratio.* At sufficiently low temperature $\theta \ll \theta_c$ (where θ_c is Curie's ferromagnetic transition temperature), it is assumed that μ is *saturated*, i.e. $|\mu| = \mu_S =$const. As μ is *not an internal variable*, but indeed an additional internal degree of freedom, it is governed by a field equation. This is the equation of *magnetic-spin* precession. Such an equation, together with the other field equations (balance of physical momentum and angular momentum) can be constructed by different means: postulate of global balance laws, application of a generalized form of the principle of virtual power (cf. Maugin, 1980), variational principle of the Hamiltonian type in the absence of dissipative processes. The last approach is insufficient here as we are mainly interested in dissipative processes. Whatever the method used, the fundamental local balance laws, in addition to that of mass, are found to read:

$$\rho \dot{\mathbf{v}} = \operatorname{div} \sigma + \rho \mathbf{f} + \mathbf{f}^{em}, \tag{9.10.217}$$

$$\sigma = \bar{\sigma} - (\rho \mathbf{B}^L \otimes \mu)_A \qquad \text{i.e.} \qquad \sigma_A = \rho(\mu \otimes \mathbf{b}^L)_A, \tag{9.10.218}$$

$$\dot{\mu} = -\gamma(\mathbf{B}^{\text{eff}} \times \mu), \qquad \mathbf{B}^{\text{eff}} := \mathbf{B} + \mathbf{B}^L + \rho^{-1} \operatorname{div} \mathcal{B}, \tag{9.10.219}$$

$$\nabla \times \mathbf{H} = \mathbf{0}, \qquad \nabla \cdot \mathbf{B} = 0,$$

and

$$\rho \dot{e} = \operatorname{tr}(\sigma \mathbf{L}) - \rho \mathbf{B}^L \cdot \dot{\mu} + \mathcal{B}_{ij} (\dot{\mu}_i)_{,j} - \nabla \cdot \mathbf{q} + \rho h. \tag{9.10.220}$$

Here we recognize in Eqs. (9.10.217) through (9.10.220), the balance of physical linear momentum, the balance of angular momentum (Cauchy's stress tensor σ is *not* symmetric), the balance of magnetic spin (or equation of spin precession), Maxwell's equations in their magnetostatic form for isolators, and the local balance of energy. In these equations, $\bar{\sigma}$ is an *intrinsic* symmetric stress, $\mathbf{f}^{em}$ is the reduced form of the electromagnetic force for the magnetostatics of nonpolarized isolators, $\mathbf{B}^L$ is called the *local* magnetic induction, and the second order (nonsymmetric) tensor of components $\mathcal{B}_{ij}$ accounts for Heisenberg exchange forces of quantum origin (cf. Kittel, 1971) through the gradient of μ. The above-given equation verifies the *condition of magnetic saturation*

$$\mathcal{B}_{k[i}\mu_{j],k} = 0\,. \tag{9.10.221}$$

Constitutive equations must be formulated for the set of fields $\{\bar{\sigma}, \mathbf{B}^L, \mathcal{B}, e$ or $\psi, \eta, \mathbf{q}\}$ subject to the standard form of the Clausius–Duhem inequality (3.3.75) — there is no need for an *extra entropy flux*. On introducing $\psi = e - \eta\theta$, and the *objective* time derivatives

$$\begin{aligned} \hat{m} &\equiv D_J\mu = \dot{\mu} - \Omega \times \mu\,, \\ \hat{\mathfrak{M}} &\equiv D_J(\nabla\mu) + (\nabla\mu)^T \cdot \mathbf{D}\,, \end{aligned} \tag{9.10.222}$$

we can express the Clausius–Duhem inequality in the form:

$$\begin{aligned} &-\rho(\dot{\psi} + \eta\dot{\theta}) + \mathrm{tr}\,(\bar{\sigma}\mathbf{D}) - \rho\mathbf{B}^L \cdot \hat{\mathbf{m}} + \mathrm{tr}\,(\mathfrak{B}\hat{\mathfrak{M}}^T) \\ &+ \theta\mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0\,, \end{aligned} \tag{9.10.223}$$

where we used (9.10.218). The whole reversible and irreversible thermodynamics of elastic ferromagnets is based on the exploitation of the inequality (9.10.223) by assuming the *axiom of local state* (η is given by its *thermostatic* expression) and applying *T.I.P.* to the residual *dissipation inequality* (Maugin, 1972, 1975). For instance, with the following functional dependence for *elastic ferromagnets*

$$\begin{aligned} &\psi = \bar{\psi}(E_{KL}, \theta, m_K, \mathcal{M}_{KL})\,, \\ &E_{KL} = \frac{1}{2}(C_{KL} - \delta_{KL})\,, \quad m_K = F_{iK}\mu_i\,, \quad \mathcal{M}_{KL} = \mu_{i,K}\mu_{i,L}\,, \end{aligned} \tag{9.10.224}$$

we have the *laws of state*:

$$\begin{aligned} &\eta = -\frac{\partial\bar{\psi}}{\partial\theta}\,, \qquad \sigma^E = \bar{\sigma}^r + \rho(\mathbf{B}^{Lr} \otimes \mu)_S = \rho\mathbf{F} \cdot \frac{\partial\bar{\psi}}{\partial\mathbb{E}} \cdot \mathbf{F}^T\,, \\ &\mathbf{B}^{Lr} = -\mathbf{F} \cdot \frac{\partial\bar{\psi}}{\partial m}\,, \qquad \mathcal{B} = 2\rho\mathbf{F} \cdot \frac{\partial\bar{\psi}}{\partial\mathcal{M}} \cdot (\nabla_R\mu)^T\,, \end{aligned} \tag{9.10.225}$$

while there remains the *dissipation inequality*

$$\Phi = \operatorname{tr}(\sigma^D \mathbf{D}) - \rho \mathbf{B}^{LD} \cdot \hat{\mathbf{m}} + \theta \mathbf{q} \cdot \nabla(\theta^{-1}) \geq 0 \,, \tag{9.10.226}$$

where we have set

$$\sigma^D := \bar{\sigma} - \bar{\sigma}^r \,, \qquad \mathbf{B}^{LD} := \mathbf{B}^L - \mathbf{B}^{Lr} \,, \tag{9.10.227}$$

and assumed that there are no dissipative processes associated with the exchange forces represented by the tensor $\mathcal{B}$. We recognize in Eq. (9.10.225) *magnetoelastic generalizations* of Eqs. (3.3.88). The *intrinsic-dissipation part* in Eq. (9.10.226) is in the traditional *bilinear form* and allows one to study *viscosity* and *magnetic-spin relaxation* via *T.I.P.* (Maugin, 1975). The simplest forms of corresponding complementary constitutive equations are obtained for *isotropy* as

$$\sigma^D = 2\eta_v \mathbf{D} + \lambda_v (\operatorname{tr} \mathbf{D}) \mathbf{1} \,, \qquad \mathbf{B}^{LD} = -\rho \tau_\mu \hat{\mathbf{m}} \,. \tag{9.10.228}$$

Because of the canonical decomposition of stress apparent in Eqs. (9.10.218) and $(9.10.225)_2$, we see that *magnetic-spin relaxation* will in fact contribute to the Cauchy stress, and consequently to the damping of essentially deformation waves. As a matter of fact, introducing the *relaxation term* **R** and the *viscous force* $\mathbf{f}^v$ by

$$\mathbf{R} := \rho \gamma \tau_\mu (\hat{\mathbf{m}} \times \mu) \,, \qquad \mathbf{f}^v = \operatorname{div} \sigma^D \,, \tag{9.10.229}$$

we can rewrite Eqs. (9.10.217) and (9.10.219) as

$$\begin{aligned} \rho \dot{\mathbf{v}} &= \operatorname{div} \sigma^r + \rho \mathbf{f} + \mathbf{f}^{em} + \mathbf{f}^v - (2\gamma)^{-1} (\nabla \times \rho \mathbf{R}) \,, \\ \dot{\mu} &= \gamma \mu \times \mathbf{B}_r^{\text{eff}} + \mathbf{R} \,, \end{aligned} \tag{9.10.230}$$

where σ^r and $\mathbf{B}_r^{\text{eff}}$ are defined solely in terms of the *thermodynamically reversible* contributions. If, in addition, the positive relaxation time τ_μ is small enough, then a naive perturbation scheme accounting for the definition of $\hat{\mathbf{m}}$ allows one to rewrite $(9.10.230)_2$ as

$$\dot{\mu} = \gamma \mu \times \mathbf{B}_r^{\text{eff}} + \bar{\mathbf{R}} \,, \tag{9.10.231}$$

where

$$\bar{\mathbf{R}} = -\frac{1}{2\tau_m \mu^2} \mu \times \left[\mu \times \left(\mathbf{B}_r^{\text{eff}} + \frac{\Omega}{\gamma} \right) \right] \,, \qquad \tau_m \equiv (\tau_\mu \gamma^2 \rho^2 \mu^2)^{-1} \,. \tag{9.10.232}$$

In the absence of deformation and vorticity, Eq. (9.10.231) is none other than the *damped-spin precession equation* proposed by Landau and Lifshitz in 1935, while Eq. $(9.10.230)_2$ with relaxation time τ_μ reduces to the more exact equation proposed by Gilbert in 1956. An attempt has been made to reformulate the same as (9.10.230) and (9.10.231) using only the concept of *internal variable* (by accounting for its gradient — following the view expressed in Sec. 4.7) in Maugin (1979a,b). It is also possible to complicate somewhat the mechanical description by accounting for eventual dissipative mechanisms such as *plasticity* or viscosplasticity, which may exist in *defective* ferromagnetic crystals. For this we refer the reader to Maugin and Fomèthe (1982). The magnetic structure can also be rendered more complex by considering μ to be a result of several magnetic *sublattices* as is the case in elastic *ferrimagnets* and *antiferromagnets*. For these developments we refer to Maugin (1976) and the few elements given in Eringen and Maugin (1990, Vol. 2, pp. 492–497).

B. Elastic ferroelectrics

The case of elastic ferroelectrics is treated by introducing a free energy density [cf. (9.10.215)]

$$\psi = \psi(\mathbf{F}, \theta, \pi, \nabla_R \pi)\,, \tag{9.10.233}$$

where π is the electric polarization per unit mass. The latter quantity serves as *order parameter* in the *ferroelectric phase* transition, and $\nabla_R \pi$ is naturally introduced to account for some "ferro" ordering. But this does not parallel further the ferromagnetic case because the *inertia* associated with π is quite different from that associated with μ. Indeed, (9.10.216) provided a *gyroscopic effect* in the sense that the time derivative of (9.10.216) is orthogonal to μ. But π has simply the nature of a displacement (multiplied by a charge) and thus its inertia will provide a term $d_E \partial^2 \pi / \partial t^2$ in the new equation that governs π, considered as an additional degree of freedom. The number d_E can be estimated from a microscopic analysis for each type of ferroelectric crystal (see Askar *et al.*, 1986). Furthermore, π, unlike μ, is *not* saturated. All these differences being borne in mind, it is shown that Eqs. (9.10.217)–(9.10.220) are replaced by

$$\rho \dot{\mathbf{v}} = \operatorname{div} \sigma + \rho \mathbf{f} + \mathbf{f}^{em}\,, \tag{9.10.234}$$

$$\sigma = \bar{\sigma} + \rho \mathbf{E}^L \otimes \pi - (\nabla \pi) \cdot \mathbf{E}^L \tag{9.10.235}$$

$$\text{i.e.}\quad \sigma_A = \rho(\mathbf{E}^L \otimes \pi)_A - [(\nabla\pi)\cdot\mathbb{E}^L]_A\,,$$

$$d_E\frac{\partial^2\pi}{\partial t^2} = \mathcal{E}^{\text{eff}}\,, \qquad \mathcal{E}^{\text{eff}} := \mathcal{E} + \mathbf{E}^L + \rho^{-1}\text{div}\,\mathbb{E}^L\,, \tag{9.10.236}$$

$$\nabla\times\mathbf{E} = \mathbf{0}\,, \qquad \nabla\cdot\mathbf{D} = 0\,, \qquad \mathbf{D} = \mathbf{E} + \rho\pi\,,$$

and

$$\rho\dot{e} = \text{tr}\,(\sigma^E\mathbf{D}) - \mathcal{E}^L\cdot\overset{*}{\mathbf{P}} - \mathbb{E}^L_{ij}\hat{\Pi}_{ji} - \nabla\cdot\mathbf{q} + \rho h\,, \tag{9.10.237}$$

where we have set

$$\sigma^E := \sigma - \rho(\mathcal{E}^L\otimes\pi)_S + [(\nabla\pi)\cdot\mathbb{E}^L]_S = (\sigma^E)^T\,,$$

$$\overset{*}{\mathbf{P}} = \dot{\mathbf{P}} - (\mathbf{v}\cdot\nabla)\mathbf{P} + \mathbf{P}(\nabla\cdot\mathbf{v})\,, \tag{9.10.238}$$

$$\hat{\Pi}_{ij} := \frac{d}{dt}(\pi_{i,j}) + \pi_{i,k}\mathbf{v}_{k,j} - \mathbf{v}_{i,k}\pi_{k,j}\,.$$

And the standard form of the second law yields the Clausius–Duhem inequality in the form:

$$-\rho(\dot{\psi} + \eta\dot{\theta}) + \text{tr}\,(\sigma^E\mathbf{D}) - \mathcal{E}^L\cdot\overset{*}{\mathbf{P}} + \text{tr}\,(\mathbb{E}^L\hat{\Pi})$$

$$+\,\theta\mathbf{q}\cdot\nabla(\theta^{-1}) \geq 0\,. \tag{9.10.239}$$

This inequality shows that we may have *dissipative* processes involving *viscosity*, *relaxation in electric polarization*, *heat conduction*, and possibly an additional process related to the gradient of polarization. Like in the ferromagnetic case, the general decompositions (9.10.235) and (9.10.238) show that electric relaxation will contribute to the Cauchy stress, hence to the damping of deformation waves. We do not further pursue this complicated case which is well documented in Maugin (1988, Chapter 7) and Maugin, Pouget *et al.* (1992, Chapter 2) and the original papers of Pouget and Maugin quoted in those two books. In any case, the thermodynamical formulation is somewhat standard in following *T.I.P.*

9.11. Solutions of Magnetic Fluids

Dilute solutions of solid strongly magnetizable particles are known under different names such as, magnetic fluids (not to be misunderstood for plasmas) and "ferrofluids". We have already alluded to these in Sec. 6.9, but we did not pay attention to the *magnetic properties.* It would appear that these could be treated in the same general framework as the ferromagnetic solids of Sec. 9.10. But simplifying assumptions can reasonably be envisaged. These are: (i) inertia of the gyromagnetic type does not show up at this larger scale of observation, and (ii) there is no apparent magnetic ordering, so that there is no need to introduce the gradient of magnetization. As the fluid as a whole is generally incompressible, this leaves as essential phenomena, *thermomagnetic couplings*, viscosity, *magnetic relaxation*, and *heat conduction.* Thus we consider a free energy such that, per unit volume,

$$\Psi = \Psi(\theta, \mathbf{M}) = \bar{\Psi}(\theta, M), \qquad M = |\mathbf{M}|, \mathbf{M} = \rho\mu . \tag{9.11.240}$$

The *laws of state* read

$$S = -\frac{\partial\Psi}{\partial\theta}, \qquad \mathbf{B}^{Lr} = -\frac{\partial\Psi}{\partial\mathbf{M}} = -2\frac{\partial\bar{\Psi}}{\partial M}\mathbf{M} . \tag{9.11.241}$$

Equation (9.10.219) provides the "balance" equation

$$\mathbf{H} = f(\theta, M)\mathbf{M} - \mathbf{B}^{LD} , \tag{9.11.242}$$

where

$$\mathbf{B}^{LD} = \mathbf{B}^{L} - \mathbf{B}^{Lr} , \qquad \mathbf{H} = \mathbf{B} - \mathbf{M} . \tag{9.11.243}$$

The field $\mathbf{B}^{LD}$, together with the viscous stress, contribute to the *intrinsic dissipation* [cf. (9.10.226)]

$$\Phi_{\mathrm{intr}} = \mathrm{tr}\,(\sigma^{D}\mathbf{D}) - \mathbf{B}^{LD} \cdot D_J\mathbf{M} . \tag{9.11.244}$$

In the *absence of magnetic relaxation*, Eq. (9.11.242) provides the *static nonlinear magnetization law* of the magnetic fluid, which can be rewritten in the scalar form $M = \bar{M}(\theta, H)$. Simple magneto-mechanical dissipative laws are taken as

$$\mathbf{B}^{LD} = -\tau_M D_J\mathbf{M} , \qquad \sigma^{D} = 2\eta_v\mathbf{D} , \tag{9.11.245}$$

where $\mathrm{tr}\,\mathbf{D} = 0$, $\tau_M \geq 0$, $\eta_v \geq 0$, in agreement with *T.I.P.* Then on setting

$$\begin{gathered} C = -\theta\left(\frac{\partial^2\Psi}{\partial\theta^2} + \frac{\partial^2\Psi}{\partial\theta\partial M}\frac{\partial\bar{M}}{\partial\theta}\right) , \\ \chi = \left(\frac{\partial\bar{M}}{\partial H}\right)_\theta , \qquad K := \chi\left|\frac{\partial^2\Psi}{\partial\theta\partial M}\right| , \end{gathered} \tag{9.11.246}$$

we obtain the following *dynamical magnetic equation* and *heat equation*:

$$C\dot{\theta} = \theta K \dot{H} + \Phi_{\text{intr}} + \rho h - \nabla \cdot \mathbf{q}\,, \tag{9.11.247}$$

and

$$\mathbf{H} = f(\theta, M)\mathbf{M} + \tau_M(\theta)(\dot{\mathbf{M}} - \Omega \times \mathbf{M})\,, \tag{9.11.248}$$

respectively, where we emphasized the *thermomagnetic couplings.* The rotation, even though *rigid*, of the medium, yields an interesting effect in the relaxation equation (9.11.248). This effect can be used in a special *ferrofluidic* viscometer. As for (9.11.247), it exhibits the phenomenon of *adiabatic magnetization* with material parameter K. We refer the reader to Eringen and Maugin, (1990, Vol. 2, Chapter 12) for applications of the above equations of which the thermodynamical description was given by Maugin and Drouot (1983b). More complex thermodynamical descriptions apply to *ferroliquids* in which the effects of *density* and *density gradients* can be relevant (Maugin, 1978b).

9.12. Electroelastic and Magnetoelastic Fracture

So far, we have only considered the effect of local dissipativity built in the electromagnetic material itself. To conclude this chapter, we may ask the question of how do the electromagnetic fields affect the *fracture* of the material. That is, we examine a *globally dissipative effect* due to the irreversible evolution of the material domain. We illustrate this with the *electroelastic* case (Maugin and Epstein, 1991; Dascalu and Maugin, 1994b).

We consider the problem of a straight-through crack in the *electroelasticity* of dielectrics in finite strains. The framework is that of *quasi-electrostatics.* The setting is that of Figs. 8.1 and 8.2. For the purpose of the derivation the problem may be considered as two-dimensional in space (variables x and y, or X and Y). But the elastic displacement may have a component along the axis perpendicular to the plane of the figure. As we know from Chapter 8, the energetic problem of fracture then consists of evaluating the *global expression* of the first law of thermodynamics or, in other words, the *source of dissipation* that shows up in this global balance law when a singular point such as the tip of the crack is progressing in the material. Special attention must first be paid to the *local energy balance* in the absence of bulk dissipation. With the notation of Sec. 9.3, by multiplication of Eq. (9.3.25) by J_F and integration by part, it can be shown (Maugin, 1988, Chapter 3) that the relevant field equations read as follows in *quasi-statics in dielectrics* [cf. Eq. (8.4.39)]

$$\begin{aligned} \mathrm{div}_R(\mathbf{T}^E + \mathbf{T}^F) &= \mathbf{0}\,, \\ \nabla_R \times \mathfrak{E} &= \mathbf{0}\,, \\ \nabla_R \cdot \mathfrak{D} &= 0\,, \end{aligned} \tag{9.12.249}$$

at any point $\chi(\mathbf{X}, t) \in \Omega$. Here $\mathbf{T}^E$ and $\mathbf{T}^F$ are first Piola–Kirchhoff tensors such that (we have rearranged terms)

$$\mathbf{T}^E = \mathbb{S}^E \mathbf{F}^T\,, \quad \mathbf{T}^F = \hat{\mathfrak{E}} \otimes \mathbf{E} - \frac{1}{2}\mathbf{F}^{-1}(\hat{\mathfrak{E}} \cdot \mathfrak{E})\,, \quad \hat{\mathfrak{E}} \equiv J_F \mathbf{C}^{-1} \bar{\mathfrak{E}}\,, \tag{9.12.250}$$

and

$$\mathbb{S}^E = \frac{\partial \Sigma}{\partial \mathbb{E}}\,, \qquad \Pi = -\frac{\partial \Sigma}{\partial \mathfrak{E}}\,, \qquad \Sigma = \bar{\Sigma}(\mathbb{E}, \mathfrak{E})\,. \tag{9.12.251}$$

The last of these means that the local energy balance reads [cf. (9.4.70)]

$$\dot{\Sigma} = \mathrm{tr}\,(\mathbb{S}^E \dot{E}) - \Pi \cdot \dot{\mathfrak{E}} = \mathrm{tr}\,(\mathbf{T}^E \dot{\mathbf{F}}) - \Pi \cdot \dot{\mathfrak{E}}\,. \tag{9.12.252}$$

But we can also use the *electric enthalpy*

$$W^E(\mathbb{E}, \mathfrak{E}) = \Sigma - \frac{1}{2}\hat{\mathfrak{E}} \cdot \mathfrak{E}\,, \qquad \mathbb{S}^E = \frac{\partial W^E}{\partial \mathbb{E}}\,, \qquad \mathfrak{D} = -\frac{\partial W^E}{\partial \mathfrak{E}}\,. \tag{9.12.253}$$

Furthermore, it is possible to prove the following identities (Dascalu and Maugin, 1994b)

$$\mathrm{tr}\,(\mathbf{T}^E \mathbf{L}) \;=\; \frac{1}{2}(\hat{\mathfrak{E}} \cdot \dot{\mathfrak{E}} - \dot{\hat{\mathfrak{E}}} \cdot \mathfrak{E})\,, \tag{9.12.254}$$

$$\mathrm{tr}\,(\mathbf{T}^E \mathbf{L}) \;=\; \nabla_R \cdot [(\mathbf{T}^E + \mathbf{T}^F) \cdot \mathbf{v}] - \mathrm{tr}\,(\mathbf{T}^F \mathbf{L})\,, \tag{9.12.255}$$

$$H := (\mathrm{div}_R \mathbf{T}^F) \cdot \mathbf{v} + (\nabla_R \cdot \hat{\mathfrak{E}})\dot{\varphi}_R = -(\nabla_R \cdot \Pi)\frac{\partial \varphi}{\partial t}\,, \tag{9.12.256}$$

where φ and φ_R are the electrostatic potentials in the current and reference configuration related by

$$\varphi(\mathbf{x}, t) = \varphi_R(\chi^{-1}(\mathbf{x}, t), t)\,, \qquad \mathfrak{E} = -\nabla_R \varphi_R\,. \tag{9.12.257}$$

On computing dW^E/dt and using the results (9.12.254) through (9.12.256) we arrive at the following useful equation which is in the form of a *true material conservation law*:

$$\left.\frac{\partial W^E}{\partial t}\right|_X - \nabla_R \cdot [(\mathbf{T}^E + \mathbf{T}^F) \cdot \mathbf{v} + \dot{\varphi}_R \mathfrak{D}] = 0\,. \tag{9.12.258}$$

By transforming (9.12.252) we also have the following *material balance law* with a *source term*:

$$\left.\frac{\partial \Sigma}{\partial t}\right|_X - \nabla_R \cdot [\mathbf{T}^E \cdot \mathbf{v} + \dot{\varphi}_R \Pi] = H\,, \tag{9.12.259}$$

where the source term H has been evaluated in (9.12.256).

Now the classical energy argument of fracture theory can be applied to either (9.12.258) or (9.12.259) which are entirely equivalent at all *regular* points in the bulk of the body. Arguments relating to the theory of *material forces* have led Maugin and Epstein (1991) to base their reasoning on (9.12.259). In any case, following along the same reasoning as in Sec. 8.2 or Paragraph 8.4D, we shall obtain the global energy balance as

$$\int_{\Omega_\Gamma} \dot{W}^E dV + \mathcal{G}^E = \int_{\partial\Omega} \mathbf{N} \cdot [(\mathbf{T}^E + \mathbf{T}^F) \cdot \mathbf{v} + \mathfrak{D}\dot{\varphi}_R] dA\,, \tag{9.12.260}$$

if we start with (9.12.258), and

$$\int_{\Omega_\Gamma} \dot{\Sigma} dV + \bar{\mathcal{G}}^E = \int_{\partial\Omega} \mathbf{N} \cdot [(\mathbf{T}^E \mathbf{v}) + \Pi\dot{\varphi}_R] dA + \int_{\Omega} H dV\,, \tag{9.12.261}$$

if we start with (9.12.259). Here we have introduced the following *energy-release rates*:

$$\mathcal{G}^E := \lim_{\Gamma\to 0} \int_{\Gamma} \mathbf{N} \cdot [W^E \bar{\mathbf{V}} + (\mathbf{T}^E + \mathbf{T}^F) \cdot \mathbf{v} + \mathfrak{D}\dot{\varphi}_R] dA\,, \tag{9.12.262}$$

and

$$\bar{\mathcal{G}}^E := \lim_{\Gamma\to 0} \int_{\Gamma} \mathbf{N} \cdot [\Sigma \bar{\mathbf{V}} + \mathbf{T}^E \cdot \mathbf{v} + \Pi\dot{\varphi}_R] dA\,, \tag{9.12.263}$$

where $\bar{\mathbf{V}}$ is the material velocity of propagation of the tip of the crack, and thus of the shrinking region V_Γ that moves rigidly with it. Obviously, the quantities $\mathcal{G}^E$ and $\bar{\mathcal{G}}^E$ are just expressions of the rate of *global dissipation* occurring during the quasi-static progress of the crack at material velocity $\bar{\mathbf{V}}$.

As in the purely mechanical case, it is possible to establish relationships between the above results and *contour-independent integrals* and the notion of *Eshelby* stress properly generalized to the electroelastic case. To do so we must first notice the following behavior of the *electroelastic* solution in the neighborhood of the crack tip (this can be proved only in the *linear theory*, say in *piezoelectricity* or piezoelectricity induced by *electrostriction* in a bias electric field, for a simple mode of cracking — cf. Dascalu and Maugin, 1994b):

$$\dot{\mathbf{u}} = -\bar{\mathbf{V}} \cdot \nabla_R \mathbf{u} + \mathbf{w} ,$$

$$\dot{\varphi}_R = -\bar{\mathbf{V}} \cdot \nabla_R \varphi_R + g ,$$

where $\mathbf{w}$ and g have no singular behavior at the tip of the crack. Then we can rewrite $\mathcal{G}^E$ and $\bar{\mathcal{G}}^E$ as

$$\Phi^E = \mathcal{G}^E = \bar{\mathbf{V}} \cdot \mathcal{F}^E , \qquad \mathcal{F}^E = J^E \mathbf{E}_I , \tag{9.12.264a}$$

or

$$\bar{\Phi}^E = \bar{\mathcal{G}}^E = \bar{\mathbf{V}} \cdot \bar{\mathcal{F}}^E , \qquad \bar{\mathcal{F}}^E = \bar{J}^E \mathbf{E}_I , \tag{9.12.264b}$$

where we have defined J-integrals by

$$\begin{aligned} J^E &:= \lim_{\Gamma \to 0} \int_\Gamma \mathbf{N} \cdot [W^E \mathbf{1}_R - (\mathbf{T}^E + \mathbf{T}^F) \cdot (\nabla_R \mathbf{u})^T - \mathfrak{D} \otimes \nabla_R \varphi_R] \cdot \mathbf{E}_I dA \\ \bar{J}^E &:= \lim_{\Gamma \to 0} \int_\Gamma \mathbf{N} \cdot [\Sigma \mathbf{1}_R - \mathbf{T}^E \cdot (\nabla_R \mathbf{u})^T - \Pi \otimes \nabla_R \varphi_R] \cdot \mathbf{E}_I dA . \end{aligned} \tag{9.12.265}$$

The first of these was formulated by Pak and Herrmann (1986) while the second was obtained by Maugin and Epstein (1991). The path independence of the integrals present in Eq. (9.12.265) follows if appropriate homogeneous boundary conditions hold at the faces of the crack. On account of the limit result (8.4.61), we can also rewrite Eqs. (9.12.265) in the following enlightening form [cf. $(8.4.59)_2$]:

$$\begin{aligned} J^E &= \lim_{\Gamma \to 0} \int_\Gamma \mathbf{N} \cdot \mathbf{b}^{em} \cdot \mathbf{E}_I dA , \\ \bar{J}^E &= \lim_{\Gamma \to 0} \int_\Gamma \mathbf{N} \cdot \bar{\mathbf{b}}^{em} \cdot \mathbf{E}_I dA , \end{aligned} \tag{9.12.266}$$

where $\mathbf{b}^{em}$ and $\bar{\mathbf{b}}^{em}$ are *electroelastic* versions of the quasi-static *Eshelby stress tensor*:

$$\begin{aligned}\mathbf{b}^{em} &= W^E\mathbf{1}_R - (\mathbb{S}^E + \mathbf{T}^F\mathbf{F}^T)\cdot\mathbf{C} + \mathfrak{D}\otimes\mathfrak{E} \\ \bar{\mathbf{b}}^{em} &= \Sigma\mathbf{1}_R - \mathbb{S}^E\cdot\mathbf{C} + \Pi\otimes\mathfrak{E} = \Sigma\mathbf{1}_R - [\mathbb{S}^E - \Pi\otimes(\mathfrak{E}\cdot\mathbf{C}^{-1})]\cdot\mathbf{C}\,.\end{aligned} \tag{9.12.267}$$

The last expression was found by Maugin (1990c; Eq. 25) in the general dynamical case — with additional magnetic terms — by generalizing Eq. (8.4.43) to the dynamical case. The *electroelastic* quasi-static version $(9.12.265)_2$ is due to Maugin and Epstein (1991) who obtained it by using an invariance geometric argument. Indeed, for instance, in quasi-statics, by left mutliplication of Eq. $(9.12.249)_1$ and integration by parts at all *regular points* in the bulk of the material, there hold the *following material balance laws*

$$\operatorname{div}_R \mathbf{b}^{em} = \mathbf{0} \qquad \text{and} \qquad \operatorname{div}_R \bar{\mathbf{b}}^{em} = \mathbf{0}\,. \tag{9.12.268}$$

The second of these can be interpreted by saying that the *material manifold* $\mathcal{M}^3$ is *transparent to the pure field contributions* at all *regular material* points (Maugin and Epstein, 1991; see also Chapter 8 in Maugin, 1993a). In other words, it captures the action of electromagnetic fields $\mathfrak{E}$ and $\mathfrak{B}$ only in so far as *electric polarization* or *magnetization* (two true *material*, *thermodynamically extensive* fields) enter in combinations with them.

To conclude we note that the expressions (9.12.264a) are again in the traditional *bilinear form* of irreversible thermodynamics, so that *thermodynamically based* criteria of progress of "electroelastic" cracks can be devised. We refer the reader to the original papers for the *magnetoelastic* case (Maugin, 1990c; Maugin and Trimarco, 1991; Maugin, Epstein and Trimarco, 1992a,b; Sabir and Maugin, 1996, for soft ferromagnets, Fomethe and Maugin, 1997b, for hard ferromagnets) and the *dynamical electro-magneto-elastic case* which involves an *electromagnetic pseudomomentum* and a Legendre transformation in the style of (8.4.67) (Maugin, 1994a).

9.13. Concluding Remarks

We are afraid that the developments reported above demonstrate that the irreversible thermodynamics of electromagnetic materials is not always a very easy matter. Pierre Duhem was certainly right in thinking that this is indeed difficult, but it is not altogether *nonsensical* as something can be done about it, as we have tried to show. The reader will realize that its takes some time and several trials to capture the beauty and complexity of the subject matter, two arguments which will always attract researchers in the field. In summary, the most expedient ways to build a coherent set of *field equations* are the use of a *Lagrangian–Hamiltonian* principle when the material itself is not dissipative, and the use of a generalized version of the *principle of virtual power* when the material may dissipate and, above all, when there exist additional degrees of freedom of purely mechanical or *electromagnetic* origin. Both *T.I.P.* and *T.I.V.* have been proven to be powerful tools in the study of an extremely wide range of dissipative behaviors in both solids and fluids. Many examples have been presented in a more or less detailed manner. The number of such examples had to be limited, a limitation that is due both to limited space and our own capability.

Chapter 10

WAVES AND REACTION-DIFFUSION SYSTEMS[1]

... physics the subject, makes old hearts fresh;...
W. Shakespeare, (The Winter's Tale, I, i)

10.1. Preliminary Remarks

As thermodynamical internal variables of state introduce additional differential equations which are *first order* in time (they are *evolution equations*) while the usual equations of motions are second order in time (if true generalized coordinates are used), then they are bound to present a special interest in *wave propagation* problems. The reason for this is twofold: on the one hand the introduction of such variables modifies the order of time differentiation of the *overall* system and, on the other hand, they may bring interesting properties in the propagation of *discontinuity waves* where the continuity of a certain order of differentiation, following Hadamard, participates in the very definition of the waves. This was recognized rather early in many cases without introducing a thermodynamical framework but just considering the evolution equation for the additional variables. However, Day (1976) gave a formal structure for these mathematical aspects accounting for thermodynamical restrictions. In this vein, among mathematically inclined papers we find those of Kosinski and co-workers (Kosinski, 1973, 1975a,b; Kosinski and Perzyna, 1972; Kosinski

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[1] This is not a book on *wave propagation*. As a separate book on wave propagation in many structures with special attention to nonlinear effects is in preparation, here we simply comment briefly on the influence of the thermodynamic formulation on essential dynamical properties.

and Wojno, 1973), and Suliciu (1975), while Coleman and Gurtin (1967b), and Bampi and Morro (1980, 1981a,b) and Morro (1980a,b,c,d) paid special attention to the case of dissipative fluids and (heat or electricity) conducting bodies, Brun (1972), Mandel (1974) and Piau (1975) focused on plasticity and viscoplasticity, and McCarthy (1984a,b) and Collet (1983, 1984, 1985, 1987, 1990) concentrated their works on deformable dielectrics, piezoelectrics and ferroelectrics.

In many cases the authors aimed at producing a theoretical framework which endowes the system with *finite speeds* of propagation, i.e. a nice *hyperbolic* feature. This aim is also pursued by other thermodynamic approaches, e.g. extended thermodynamics (cf. Müller and Ruggeri, 1993). In the case of *discontinuity waves* (singular surfaces in the sense of Hadamard), *acceleration waves* (that carry discontinuities in the second-order derivatives of basic fields) may by definition miss phenomena related to *internal variables*. As to *shock waves* (that carry discontinuities in the first-order derivatives, e.g. velocity), they will necessarily be influenced by the evolution equations governing the internal variables. The same holds true for *simple waves* which provide another building block of *nonlinear-wave* solutions. In fact, shock waves may provide a means to measure the relaxation time related to some internal variable as is the case in some dielectric materials (Yakushcov *et al.*, 1968). *Transient nonlinear waves* are also an efficient means to place the effect of *internal-variable relaxation* on the wave process in evidence. This was particularly well exhibited in the case of nonlinear electroelastic materials in Sec. 9.6 where, in fact, the validity of the working hypothesis of the *local accompanying state* can be tested. In such conditions the propagating *simple waves* of electromechanical nature may be *modulated* by the dissipation mechanism (in this case, polarization relaxation; cf. Collet, 1987).

The presence of relaxing internal variables also favors the existence of additional *induced* discontinuities in the presence of shock waves (for the main field variables) — see, for instance, Collet (1990) in the electrodeformable case. This phenomenon has led to a re-examination of some models of solid viscoelasticity on the basis of internal variables of the *stress type* (Maugin and Morro, 1989a,b).

There is another class of models which are likely to present *wavelike solutions* and also *spatiotemporal patterns* although they are *parabolic* in their linearized form; they are the *reaction-diffusion systems* (for short *RDS'*) which, by their very nature and their occurrence in physico-chemistry and biological systems, must be, and indeed are, amenable via *irreversible thermodynamics*. They are, in fact, the realm of *T.I.V.* and as such they deserve more than passing comments. The bulk of this chapter has the purpose of illustrating this remark by presenting a few examples.[2]

10.2. Simple RDS'

Using the notation of applied mathematics, $u_t = \partial u/\partial t$, $u_x = \partial u/\partial x$, we recall the standard *diffusion equation*

$$u_t = \Delta u\,, \tag{10.2.1}$$

where Δu denotes the Laplacian of the scalar-valued real function $u(t, \mathbf{x})$. This celebrated equation is often called the *heat equation* after its introduction by J. B. Fourier (1822) to describe the "propagation" of heat in a rigid materially homogeneous, isotropic body. This equation became famous because the attempts of Fourier at solving space-time problems on its basis led to the development of *Fourier analysis*. Furthermore, this is the *paragon of parabolic equations* which, in constrast to *hyperbolic* equations, yield an *infinite speed of propagation*, or, in other words, an instantaneous propagation of information. This may be considered as physically nonrealistic and altogether unsound but, again, *time scales* of observation must be introduced to have a truly dispassionate debate about this matter.

An even more interesting equation is the one obtained by adding a contribution $f(u)$, called *reaction*, in the right-hand side of (10.2.1). That is,

$$u_t = \Delta u + f(u)\,. \tag{10.2.2}$$

Systems of this type occur in the theory of *combustion* For example, if

$$f(u) = au + bu^2 + du^3\,, \tag{10.2.3}$$

as may happen in some systems, Eq. (10.2.2) will present both a *dissipative feature* (this we know from heat conduction directly or by analogy) and *nonlinearity*, with a possible *competition* betwen these two effects. This is what occurs with *Fisher's* model of *population dynamics* where, in one dimension of space, we have

$$f = u(1-u)\,. \tag{10.2.4}$$

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[2] For the mathematics of *reaction-diffusion systems*, we recommend the book of Grindrod (1991).

Such equations present *wave-front solutions* which are obtained by trying *simple-wave solutions* in the form $u = \bar{u}(x - ct)$, where c is a speed of propagation. With appropriate f's (e.g. f cubic in u with *ad hoc signs of coefficients*) good fortune leads to such explicit solutions (cf. Grindrod, 1991, Sec. 1.5). More generally, we may consider an f-function that involves space-derivatives of u, e.g.

$$u_t = \Delta u + f(u, \nabla u, \mathrm{x}, t) . \tag{10.2.5}$$

Such is the case of the following equation:

$$v_t = v_{xx} - v v_x \, , \tag{10.2.6}$$

which is indeed of the form (10.2.5) in one space dimension. Now when there is no nonlinearity Eq. (10.2.6) is the diffusion equation which is parabolic. But the whole equation (10.2.6), known as *Burgers' equation* as a model of turbulence is both a *reaction-diffusion equation* of type (10.2.5),[3] hence containing both *dissipation* and *reaction* (or *forcing*) and, as shown in many books (e.g. Maugin, Pouget *et al.*, 1992, Chapter 1), *the one-directional wave equation* or *nonlinear evolution equation* associated with a *true* (bi-directional) wave equation containing both *nonlinearity* and **dissipation**. All this to emphasize the ubiquity of nonlinear-wave processes and the relativity of the definition of both a *dissipative* system and a *hyperbolic* or *parabolic* one. Such qualifications are sensical only in the *linear* framework.

Physically, the variable u or v above can be many things, but the most popular cases are temperature and a *concentration* of a constituent in a *mixture.* In the last case u is noted c. In various chapters we have already witness the occurrence of a *transport equation* such as

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J} + Q \, , \tag{10.2.7}$$

where $\mathbf{J}$ is a flux and Q is a source term which may be one of the above-mentioned *reaction* or *source* terms. The *thermodynamic basis* of the constitutive equation for $\mathbf{J}$ is obvious in *T.I.P.*, e.g.

$$\mathbf{J} = -D\nabla c \, , \qquad c \geq 0 \, , \tag{10.2.8}$$

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[3] Indeed Eq. (10.2.6) has traveling-wave solutions of the form

$$v = \bar{v}(\zeta) = c - a \tanh\,(a\zeta/2), \quad \zeta = x - ct \, ,$$

for any constant $a \geq 0$, with wave speed c.

the celebrated isotropic, linear, materially homogeneous, *Fick law* with diffusivity coefficient D.

Thus Eq. (10.2.7) can be of the general type

$$c_t = D\Delta c + Q(c, \nabla c, \mathbf{x}, t)\,. \tag{10.2.9}$$

Fourier's law is of the same type as Fick's law. Typically, in *T.I.P.*, $\mathbf{J}$ *dissipates* according to the **dissipation inequality**

$$\Phi_c = -\mathbf{J}\cdot\nabla\mu \geq 0, \qquad \mu = \partial\Psi/\partial c\,, \tag{10.2.10}$$

where the second of these is none other than a *law of state*. The first part of (10.2.10) is also true of electricity conduction in quasi-statics, and of heat conduction. In which case $\mathbf{J}$ is replaced by electric conduction current and entropy flux, respectively, and the chemical potential μ is replaced by electrostatic potential and thermodynamic temperature, respectively. Some couplings, especially between the last two, can be expected. We have seen in Secs. 6.4, 9.4, 9.8, and 9.9 examples of theories where a flux of the type of $\mathbf{J}$ is involved. In the next section, however, we would like to present a more subtle application of *irreversible thermodynamics* to the construction of good physical *RDS'*. To illustrate this we still quote three systems which appear in *biological* and *ecological* problems (for the last class we refer to Okubo, 1980, for a comprehensive introduction), and combustion.

Chemiotaxis. This is the phenomenon by which individual biological mobile cells are assumed to move up gradients of a particular concentration, the so-called *chemo-attractant*. Let $v(x,t)$ be the attractant concentration. The attractant is subject to random, so-called unbiased *diffusion*, and linear degradation; $s(u)$ represents the nonlinear secretion of attractant by the cell of concentration $u(x,t)$. We call α^2 and D the diffusivities of the cells and the attractant. The resulting governing *RDS'* reads (cf. Grindrod, 1991, p. 11):

$$\begin{aligned} u_t &= \alpha^2 u_{xx} - (uv_x)_x\,,\\ v_t &= Dv_{xx} - rv + s(u)\,. \end{aligned} \tag{10.2.11}$$

The second equation contains a relaxation effect (coefficient r) and a rather strong *reaction* due to the cell concentration. The first one is a diffusion equation which is nonlinearly coupled to the second equation. In particular, this coupling disappears with a spatially uniform v.

FitzHugh-Nagumo system. This is one possible system used by physiologists to model the conduction of action potentials along unmyelinated nerve fibers (FitzHugh, 1961, Nagumo *et al.*, 1962). Without specifying for the moment the precise meaning of the introduced symbols (see Sec. 10.3), we note that this system couples two diffusion equations (in dependent variables u and v),

$$\begin{aligned} u_t &= u_{xx} + f(u) - v\,, \\ v_t &= \delta v_{xx} + \sigma u - \gamma v\,. \end{aligned} \tag{10.2.12}$$

The coupling is linear. The first equation with diffusivity normalized to one, presents a nonlinear reaction $f(u)$ and a linear reaction due to the second variable. The second equation with diffusivity δ presents a linear reaction from the first variable, and what may be considered as a *relaxation* of its own variable. It is thus possible that the first equation in each pair (10.2.11) and (10.2.12) is in fact a true *wave equation* in which inertia has been discarded.

The two more sophisticated systems presented so far, (10.2.11) and (10.2.12), exhibit a second equation akin to a generalized *relaxation* equation with additional diffusion and couplings. This hints at the fact that this second equation may be a generalized *evolution equation* for the second variable considered as *internal* with respect to the first one, considered as observable, in a thermodynamical framework of the type developed in previous chapters. This is the point of view expanded in Sec. 10.3 below.

Combustion problem. Let $u(x,t)$ represent the temperature distribution and $v(x,t)$ the concentration of some immobile chemical species which is combustible at (positive) temperature like a *burning fuse.* With k a positive constant and $g(u)$ a monotone decreasing function such that $g(0) = 0$, we have the system

$$\begin{aligned} u_t &= u_{xx} + kvg(u)\,, \\ v_t &= -vg(u)\,. \end{aligned} \tag{10.2.13}$$

The coupling is nonlinear and typical of combustion processes as it occurs through the product of functions of the two dependent variables. As announced, there is *no diffusion* of the second entity; this is the fuel that is simply consumed. Its natural fate is to contribute to the heating but its rate of consumption also goes to zero with the temperature going to zero (this arbitrary zero is taken as a threshold), below which nothing further happens.

Although it directly relates to a physical thermodynamical process, this system is much less transparent than the previous two from our point of view of *thermodynamic modeling*.

10.3. Model of Nerve-Pulse Dynamics: A Good Physical Example of Internal-Variable Theory[4]

A. Nerve-pulse transmission

Here our object is nerve-pulse transmission which is classically considered as a *reaction-diffusion system*. The physical description behind this is as follows. Nerve pulses are actually *electromagnetic solitary waves* propagating along nerve fibers at a speed of about 20 m/s. A nerve fiber can be modeled as a thin tube filled with axoplasm that has a certain concentration of ions (potassium and sodium ions, mainly — see Fig. 10.1). The tube wall is called a *membrane* which, due to its special nature, permits ion exchange between axoplasm and the fluid surrounding the fiber. The initial excitation triggers the membrane activity, resulting in "ion pumps" responsible for keeping the progressive pulse propagating in the fiber. An important feature is that small excitations are not able to trigger a progressive pulse. There exists a threshold and every excitation above it leads to the stable progressive wave with a characteristic asymmetric shape — Fig. 10.2. For a full physical description of such a fascinating wave process the reader is referred to Cole (1968) and Scott (1975).

In order to explain this wave process several mathematical models have been produced since the celebrated work of Hodgkin and Huxley (1952) in which the mechanism by which the ion current governs the nerve pulse motion was described. The basic idea of these authors was *telegraph* equations where inductance was neglected. Such equations read

$$\begin{aligned} c\frac{\partial v}{\partial t} + \frac{\partial i_a}{\partial x} + j_1 &= 0\,, \\ \frac{\partial v}{\partial x} + r i_a &= 0\,. \end{aligned} \qquad (10.3.14)$$

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[4] This section is based on the recent work of Maugin and Engelbrecht (1994) and previous works by the second author.

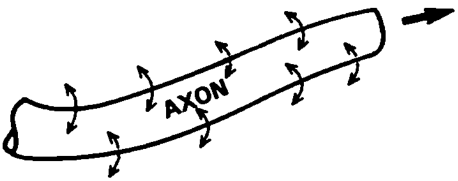

Fig. 10.1. Nerve axon and exchange.

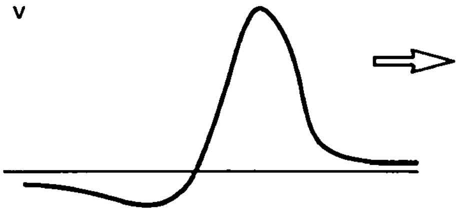

Fig. 10.2. A typical nerve-pulse asymmetric shape.

Here v is the voltage across the membrane, i_a is the total longitudinal current inside the membrane, j_i is the ion current, and c and r are constants. The most ingenious result by Hodgkin and Huxley was to give an *empirical* expression for the ion current depending on (as they call them) *phenomenological* variables, n, m and h. These variables govern : n, the potassium conductance (turning on), and m, h, the sodium conductance (turning on and turning off, respectively). The ion current expression is

$$j_i = g_K n^4 (v - V_K) + g_{Na} m^3 h (v - V_{Na}) + g_L (v - V_L) , \tag{10.3.15}$$

where g_K, g_{Na} and g_L are potassium, sodium and leakage conductances, respectively, and V_K, V_{Na} and V_L are the corresponding equilibrium potentials. The variables n, m and h are governed by the following *kinetic equations*:

$$\begin{aligned} \dot{n} &= -\frac{1}{\tau_n(v)}[n - n_0(v)] , \\ \dot{m} &= -\frac{1}{\tau_m(v)}[m - m_0(v)] , \\ \dot{h} &= -\frac{1}{\tau_h(v)}[h - h_0(v)] . \end{aligned} \tag{10.3.16}$$

Here n_0, m_0 and h_0 are equilibrium values, and τ_n, τ_m and τ_h are characteristic *relaxation times*. As a result of careful experimentation, the empirical relations for these parameters were found (we do not give these expressions here; see Hodgkin and Huxley, 1952). From this, two main directions in the theory of nerve pulse transmission can be distinguished:

(i) to make the mathematical model even more complicated in order to account for all the possible physical and physiological effects;

(ii) to make the mathematical model simpler in order to get simple solutions still preserving the main physical features of a pulse.

Direction (i) is more developed in physiology and cardiac dynamics where the influence of various drugs ("narcotizing") on nerve systems is of interest. The DiFrancesco–Noble (1985) model incorporates as many as twelve different terms in the total ion current, accounting for delayed potassium current, background potassium and sodium currents, background calcium current, potassium-sodium exchange current, etc. The number of *phenomenological variables* may certainly be even higher.

Direction (ii) has its best representation in the FizHugh–Nagumo (for short FHN) model (10.2.12). This model accounts for only one additional variable and the ion current is taken in the form

$$j_i = k_1 v + k_3 v^3 + w\,, \tag{10.3.17}$$

where k_1 and k_3 are constants. The variable w of the phenomenological type is usually referred to as a *recovery variable*. It is governed by a *kinetic equation* of the following type:

$$\dot{w} + c_0 \gamma w = q_0(v + q_1)\,, \tag{10.3.18}$$

where c_0, γ, q_0 and q_1 are constants. Nagumo *et al.* (1962) have used $\gamma = 0$, resulting in a field equation

$$\frac{\partial^3 v}{\partial t \partial x^2} = \frac{\partial^2 v}{\partial t^2} + \mu(1 - v + \varepsilon v^3)\frac{\partial v}{\partial t} + v\,, \tag{10.3.19}$$

where μ and ε are again constants. Later the form with $\gamma \neq 0$ was found to be preferable, but still many works are devoted to the analysis of Eq. (10.3.19) and its variant. There have been also attempts to replace the cubic polynomial in v in (10.3.17) by a piece-wise linear approximation in order to get simpler mathematical expressions.

This approach has been popular in the mathematical analysis of many diffusive systems because the initial equation results from Eq. (10.3.14) as the parabolic equation

$$\frac{\partial v}{\partial t} = D\frac{\partial^2 v}{\partial x^2} + Kj_i , \tag{10.3.20}$$

where D and K are constants.

Within the framework of the second direction, Engelbrecht (1981) has proposed an evolution-equation approach based on *hyperbolic* telegraph equations. As a result of this, the evolution equation

$$\frac{\partial v}{\partial t} + a_1 v + a_2 j_i = 0 , \tag{10.3.21}$$

was derived, where a_1 and a_2 are constants. Together with the ion current, (10.3.14), (10.3.15), the resulting equation in a suitably chosen normalization of variables (with $\gamma = 0$) reads:

$$\begin{aligned} \tfrac{\partial^2 v}{\partial \xi \partial x} + f(v)\tfrac{\partial v}{\partial \xi} + g(v) &= 0 , \\ f(v) &:= b_0 + b_1 v + b_2 v^2 , \\ g(v) &:= b_{00} v , \end{aligned} \tag{10.3.22}$$

where b_0, b_2 and b_{00} are constants and $\xi = c_0 t - x$, so that $(10.3.22)_1$ is written in the frame moving with velocity c_0. The stationary form of $(10.3.22)_1$ is of the Liénard type. The full analysis of this equation is given by Engelbrecht (1991).

Recently (Engelbrecht *et al.*, 1992), a more sophisticated variant of (10.3.18) was proposed. It reads

$$\dot{w} + \phi(w, v)\dot{v} = \psi(w, v) . \tag{10.3.23}$$

This is of a general rate-type relation known in viscoelasticity (see Chapter 8).

To sum up, we notice that in the description given so far, the *observable variable* is, as a rule, the electric potential (voltage). This is the actually measured wave. The other variables introduced are called either *phenomenological*, or *recovery*, or *auxiliary variables.* This last qualification suggests that once eliminated from the formulation via proper operations of differentiation, integration in time, and combinations, they altogether disappear from the final equation. Such variables also present a typical *relaxation*, and they are related in some way to *dissipative processes.* In the formulation given above they seem to come out of the blue, without any thermodynamical support, although they present all the characteristic properties of *internal variables of state* in a good thermodynamics. It is this thermodynamic aspect that we want to examine next. To do so we need to have at hand the *field* equation for the observable variable and then we will draw on a mechanical analogy in a way that W. Thomson would have appreciated. For this purpose we can start from *Lieberstein's* (1967) model also used as a basis for evolution equations. Using the notation of Lieberstein, the *transmission line* equations describing the motion (*telegraph equations*) read:

$$\begin{aligned} \pi a^2 C_a \frac{\partial v}{\partial t} + \frac{\partial i_a}{\partial x} + 2\pi a I &= 0\,, \\ \frac{L}{\pi a^2}\frac{\partial i_a}{\partial t} + \frac{\partial v}{\partial x} + \frac{R}{\pi a^2} i_a &= 0\,, \end{aligned} \tag{10.3.24}$$

where a is the radius of an axon, C_a is the axon self-capacitance per unit area per unit length, L is the axon specific inductance, $I = j_i/(2\pi a)$ is the membrane current density, and $R = (\pi a^2)r$ is the specific resistance of the axon, while r is the resistance per unit length. Combining the two equations (10.3.24), it is easy to obtain the following second-order wave equation with source terms due to $I(t)$:

$$\frac{\partial^2 v}{\partial x^2} - LC_a \frac{\partial^2 v}{\partial t^2} = RC_a \frac{\partial v}{\partial t} + \frac{2}{a} RI + \frac{2}{a} L \frac{\partial I}{\partial t}\,. \tag{10.3.25}$$

The internal variables, if any, must satisfy thermodynamical restrictions and inequalities.

B. Thermodynamics of nerve-pulse dynamics: FHN model

We shall start with the FiztzHugh–Nagumo model. In this model the voltage v is an observable variable somewhat similar to an elastic displacement. We shall exploit this analogy. The *recovery variable* w is considered as an *internal variable of state* (the α of Chapters 4 and 5). Relying, to start with, on the idea of a *hyperbolic* model and accounting for the internal nature of w, with normalized units we expect a *field equation* of the following type ($\mu \geq 0$, but possibly very small):

$$\begin{aligned} \mu v_{tt} - v_{xx} &= \mathcal{F}(v, v_t, w)\,, \\ w_t &= R(v, w)\,. \end{aligned} \tag{10.3.26}$$

The first of these reminds us of some type of generalized *Frenkel–Kontorova model* for a linear elastic chain acted upon by a force $\mathcal{F}$ due to a substratum (interaction with the surroundings), but instead of a simple $\mathcal{F}(v) = \sin v$ (cf. Maugin, Pouget *et al.*, 1992) we have a more complex force expression involving both *friction* (through v_t) and interaction with an additional field w, the latter being governed by the *relaxation equation* $(10.3.26)_2$. We can introduce a Lagrangian density $\mathcal{L}$ such as

$$\mathcal{L} = \frac{1}{2}\mu v_t^2 - W(v, v_x, w) = \frac{1}{2}\mu v_t^2 - \frac{1}{2}v_x^2 - \bar{W}(v, w)\,, \tag{10.3.27}$$

in which we recognize kinetic, elastic, and interaction energies. Contrary to Sec. 4.7 we do not grant any diffusional property to w so that W does not involve w_x. Nor is any inertia associated with w (internal variable!). In the absence of dissipation and discarding thermal effects, Gibbs' equation reads

$$-\frac{dW}{dt} - \mathcal{F}v_t + \sigma v_{xt} = 0\,. \tag{10.3.28}$$

This is valid for any v_t and $\partial(v_x)/\partial t$ so that with the special form of W indicated in the second of (10.3.27) we obtain the *laws of state* (σ is a "stress"):

$$\begin{aligned} \mathcal{F} &= \bar{\mathcal{F}} \equiv -\partial\bar{W}/\partial v\,, \\ \sigma &= \partial W/\partial v_x = v_x\,, \end{aligned} \tag{10.3.29}$$

while the Euler–Lagrange equations of motion takes on the form (10.3.26) but with $\mathcal{F}$ reduced to $\bar{\mathcal{F}}$.

In the presence of dissipation, i.e. when (10.3.28) is replaced by the *Clausius–Duhem inequality*

$$-\frac{dW}{dt} - \mathcal{F}v_t + \sigma v_{xt} \geq 0\,, \tag{10.3.30}$$

we shall assume that there are neither "viscous" stresses nor "anelastic" strains, so that $(10.3.29)_2$ continues to hold. Accounting for the general expression of $\bar{W}$, Eq. $(10.3.29)_2$ and that fact that $\mathcal{F}$ in general depends on v_t, from (10.3.30) we deduce the following *dissipation inequality*:

$$\Phi = -\mathcal{F}^d v_t + \mathcal{R}w_t \geq 0\,, \tag{10.3.31}$$

where we have defined $\mathcal{F}^d$ and $\mathcal{R}$ by

$$\mathcal{F}^d = \mathcal{F} + \partial\bar{W}/\partial v, \qquad \mathcal{R} = -\partial\bar{W}/\partial w\,. \tag{10.3.32}$$

Now we use *T.I.P.* to formulate the laws that govern $\mathcal{F}^d$ and $\mathcal{R}$ in agreement with (10.3.31). Thermodynamic equilibrium corresponds to $\mathcal{F}^d = \mathcal{R} = 0$. Outside (but only slightly outside), equilibrium we assume the existence of a positive *dissipation potential* $\mathcal{D}$, which is homogeneous of degree *two* in v_t and w_t, and such that

$$\mathcal{F}^d = -\partial\mathcal{D}/\partial v_t, \qquad \mathcal{R} = \partial\mathcal{D}/\partial w_t\,. \tag{10.3.33}$$

But we can as well introduce another dissipation potential $\mathcal{D}^*$, by partial Legendre–Fenchel transform of $\mathcal{D}$, such that (see Chapter 5)

$$\begin{aligned} \mathcal{D}^*(v_t,\mathcal{R}) &= \sup\nolimits_{w_t}[\mathcal{R}w_t - \mathcal{D}(v_t,w_t)]\,, \\ \mathcal{F}^d = \partial\mathcal{D}^*/\partial v_t, &\qquad w_t = \partial\mathcal{D}^*/\partial\mathcal{R}\,. \end{aligned} \tag{10.3.34}$$

By way of example, consider the following dissipation potential $\mathcal{D}^*$ and interaction energy $\bar{W}$:

$$\begin{aligned} \mathcal{D}^* &= -\frac{1}{2}\alpha v_t^2 + \frac{1}{2}\beta\mathcal{R}^2, \quad \alpha \geq 0, \quad \beta \geq 0\,, \\ \bar{W}(v,w) &= \mathcal{W}(v) - vw + \frac{1}{2}\gamma w^2\,, \end{aligned} \tag{10.3.35}$$

whence

$$\mathcal{F}^d = -\alpha v_t, \qquad w_t = \beta\mathcal{R}\,. \tag{10.3.36}$$

Setting then

$$f(v) = -\partial\mathcal{W}/\partial v, \quad \tau_w \equiv (\beta\gamma)^{-1}, \quad w_0(v) := \gamma^{-1}v\,, \tag{10.3.37}$$

we obtain Eqs. (10.3.26) in the suggestive form

$$\begin{aligned} \mu v_{tt} - v_{xx} + \alpha v_t &= f(v) + w\,, \\ w_t &= -\frac{1}{\tau_w}[w - w_0(v)]\,, \end{aligned} \tag{10.3.38}$$

which are the two equations of the FHN model up to the polarity of the voltage. According to the general discussion of Sec. 4.7 — *solitons* versus *dissipative structures* (cf. Maugin, 1990a) — the model (10.3.38) is likely to present either solitonic or dissipative structures ($\mu = 0$) in the v variable (the "main" variable of the problem once w has been eliminated as a functional of v), but not directly in w as we are lacking any diffusion term for the latter. Also, if w is indeed an internal variable of state, then the fact that we remain close to equilibrium during true thermo-*dynamical* excursions requires that this internal variable relaxes fast enough compared to a macroscopic time scale, i.e. the Deborah number based on τ_w should be rather small compared to unity. A special case of the above modeling corresponds to $\gamma = 0$ (no self-energy related to w) in which case $(10.3.38)_2$ is replaced by the equation [not a relaxation equation, *per se*, cf. (10.3.18)]:

$$w_t = \beta v \,. \tag{10.3.39}$$

This is an often considered simplified model (Nagumo *et al.*, 1962).

C. Hodgkin–Huxley model

Can we give a true thermodynamical guise to the Hodgkin–Huxley (HH) model of nerve-pulse propagation? A simplified version of the HH model can be obtained by generalizing the model of the foregoing paragraph. This generalization consists in increasing the number of internal variables from one (w) to three (n, m, h) and introducing the appropriate generalization of the interaction potential $\bar{W}(v, w)$ as $\bar{W}(v, n, m, h)$, e.g.

$$\begin{aligned}\bar{W}(v,n,m,h) = W(v) + \frac{1}{2}[a_1(v - V_{\mathrm{K}})^2 n^4 + a_2(v - V_{\mathrm{Na}})^2 m^3 h \\ + a_3(v - V_L)^2] - (b_1 n + b_2 m + b_3 h)\,,\end{aligned} \tag{10.3.40}$$

while (10.3.31) is transformed to

$$\Phi = -\mathcal{F}^d v_t + \mathcal{N} n_t + \mathcal{M} m_t + \mathcal{H} h_t \geq 0\,, \tag{10.3.41}$$

wherein

$$\mathcal{N} = -\partial\bar{W}/\partial n, \quad \mathcal{M} = -\partial\bar{W}/\partial m, \quad \mathcal{H} - -\partial\bar{W}/\partial h\,. \tag{10.3.42}$$

With a simple dissipation potential [more complicated ones can be imagined in so far as they still satisfy (10.3.41)]

$$\begin{gathered}\mathcal{D}^*(v_t, \mathcal{N}, \mathcal{M}, \mathcal{H}) = -\frac{1}{2}\alpha v_t^2 + \frac{1}{2}(\beta_1 \mathcal{N}^2 + \beta_2 \mathcal{M}^2 + \beta_3 \mathcal{H}^2)\,, \\ \alpha_i, \beta_i \geq 0\,, \quad i = 1, 2, 3\,,\end{gathered} \tag{10.3.43}$$

this will naturally reproduce the contribution (10.3.15) to (10.3.26) — in the HH model, $\mu = 0$ — up to the notation, while the relaxation equations (10.3.17) with voltage-dependent relaxation times will come out but with necessarily simplified expressions for the many involved factors. This clearly exhibits a difficulty at representing experimental data in both field and relaxation equations via the thermodynamical model which is rather rigid as everything seems to be decided by the expressions of $\bar{W}$ and $\mathcal{D}$.

D. More complex relaxation equations

Let us examine briefly the possible consistency of more sophisticated equations such as (10.3.23) with thermodynamics. If this is well-known in viscoelasticity, this type of formulation requires here some caution and an altogether nontrivial approach. To that effect we propose to first remind the reader that v has the nature of a voltage while w has that of a current. Assume now that the additional variable w is additively decomposed as $w = w_1 + w_2$ and that the first part w_1 *relaxes* whereas the second part w_2, in the observable (voltage) field v, causes dissipation of the Joule type. Consequently, the transition from thermodynamical equilibrium [Eq. (10.3.28)] to dissipation is effected by considering that (10.3.30) generalizes to

$$-\frac{d\bar{W}}{dt} - \mathcal{F}v_t + w_2 v + \sigma v_{xt} \geq 0\,, \tag{10.3.44}$$

where we immediately recognize a *Joule effect* in the third contribution. Only w_1 is essentially internal so that we can write $\bar{W} = W(v, w_1)$. On computing W_t and accounting for $(10.3.29)_2$ we are led to the following dissipation inequality:

$$\Phi = -\mathcal{F}^d v_t + w_2 v + \mathcal{R}_1 w_{1t} \geq 0\,, \tag{10.3.45}$$

wherein

$$\mathcal{F}^d = \mathcal{F} + \partial\bar{W}/\partial v, \quad \mathcal{R}_1 = -\partial\bar{W}/\partial w_1\,. \tag{10.3.46}$$

For example, on taking ($\alpha \geq 0$, $\beta > 0$, $\gamma \neq 0$)

$$\begin{aligned}\bar{W}(v, w_1) &= \mathcal{W}(v) - vw_1 + \frac{1}{2}\gamma w_1^2\,,\\ \mathcal{D}^*(v_t, \mathcal{R}_1, w_2) &= -\frac{1}{2}\alpha v_t^2 + \frac{1}{2}\beta\mathcal{R}_t^2 + \frac{1}{2}kw_2^2\,,\end{aligned} \tag{10.3.47}$$

we have

$$\mathcal{F}^d = \frac{\partial\mathcal{D}^*}{\partial v_t}, \quad v = \frac{\partial\mathcal{D}^*}{\partial w_2}, \quad w_{1t} = \frac{\partial\mathcal{D}^*}{\partial\mathcal{R}_1}\,. \tag{10.3.48}$$

We recognize in the second of these an equation of the type of Ohm's law. With $k \neq 0$ and using the decomposition of w, from $(10.3.48)_2$ we obtain the following generalized *relaxation equation.*

$$w_t - k^{-1}v_t = -(\beta\gamma)(w - \nu v), \tag{10.3.49}$$

wherein $\nu = \gamma^{-1} + k^{-1}$. Simultaneously, the field equation for v is obtained as

$$\mu v_{tt} - v_{xx} = -\alpha v_t + \bar{f}(v) + w, \tag{10.3.50}$$

where $\bar{f}(v) = f(v) - k^{-1}v$. Equation (10.3.49) is the simplest (linear) version of Eq. (10.3.23). Equation (10.3.50) is just the same as in Paragraph **B.** The full case of that paragraph follows in the limit of large k's for which v remains bounded only if $w_2 = 0$ (a condition of the same type as for *perfect conductors*). There may exist many ways to generalize (10.3.49) to the nonlinear form (10.3.23) but, again, the thermodynamical framework imposes severe restrictions as is must be simultaneously consistent with the v-field equation. For instance, the simple form (10.3.49) already indicates that the principal (constant) contribution to the function $\phi(v, w)$ in (10.3.23) must be negative as $k > 0$.

E. Some conclusive remarks

In this section we have checked that some simple models for nerve-pulse dynamics enter the general framework of *T.I.V.* when the additional recovery variables are identified with the internal variables of *T.I.V.* On the basis of this thermodynamical admissibility, there essentially follow guidelines and prescriptions as to which processes do in fact respect the statement of the second law of thermodynamics. These prescriptions are rather strong statements as they at once cast the expression of thermodynamically coupled contributions which are to appear simultaneously in both field equations for observable variables and evolution equations for internal vraiables. It is easily conceived that agreement with *a priori* set contributions, or contributions to these two types of equations which were more or less guessed, or were developed independently of one another, is rarely met. This is the case even for the relatively simple FitzHugh–Nagumo model, so that agreement between the rather rigid thermodynamical theory like the ones presented and a more complicated model such as the Hodgkin–Huxley one is not to be expected before hand. The difficulty is of the same order as the one already encountered in the thermodynamical description of dilute solutions of macromolecules in Sec. 6.4.

10.4. Coherent Phase-Transition Fronts: Another Example of Thermodynamics of Material Forces

A. The general problem

A propagating *phase-transition* front in a three-dimensional *elastic* body may be looked upon using from different points of view. In metallurgy it is often conceived as a *diffusion process* according to which a certain elastic phase α grows to the expense of another elastic phase β. Introducing then the concentrations of the two phases we have to examine a mixture of a certain type with *reaction-diffusion equations* for the two phases. From the point of view of continuum mechanics, the front with negligible thickness may be viewed as a propagating *discontinuity wave*, the material being elastic but possibly with different symmetries, on both sides of the singular surface that geometrically represents this discontinuity wave. Does this mean that no dissipation occurs in the process? Obviously not. The progress of the front consumes energy which is provided in any suitable form (applied forces, heating, etc). Thus there indeed is dissipation, but the latter takes place *at the interface*, somewhat like the dissipation occurring in brittle fracture which is concentrated at the tip of the crack that progress in an otherwise nondissipative material. This will be examined in Paragraphs **B** and **C**. For the moment we also note that in one dimension of space the phase-transition front can be viewed as a very much *localized, rapid variation* of the mechanical state of the material which present both *elementary dissipation* of the *viscosity* type and some *dispersion* (also called *capillarity effects*) that accounts for some weakly *nonlocal interactions.* This was masterly examined by Truskinowsky (1992, 1994). In this case one considers a time-dependent problem in one dimension x with a stress "tensor" of single component σ, displacement u, velocity v, and strain e. We have

$$\sigma = \frac{\delta W}{\delta e} + \sigma^D, \quad v = u_t, \quad e = u_x\,, \tag{10.4.51}$$

where

$$\frac{\delta W}{\delta e} = \bar{\sigma} - \left(\frac{\partial W}{\partial e_x}\right)_x, \ \bar{\sigma} = \frac{\partial W}{\partial e}, \ W = \bar{W}(e, e_x), \ \sigma^D = \frac{\partial \mathcal{D}}{\partial v_x}\,, \tag{10.4.52}$$

and

$$\bar{W} = \hat{W}(e) + \varepsilon(e_x)^2, \quad \mathcal{D} = \frac{1}{2}\eta_v(v_x)^2 \geq 0\,, \qquad \sigma = \bar{\sigma}(e) + \eta_v v_x - 2\varepsilon e_{xx}\,. \tag{10.4.53}$$

Here η_v is a viscosity coefficient and ε is the square of a characteristic length (the thickness of the above mentioned localized solutions). It is possible to construct a nondimensional number

$$\omega = \eta_v/\sqrt{\varepsilon}\,, \tag{10.4.54}$$

which compares viscous effects to dispersive ones. The energy function $\hat{W}$ is of sufficiently high order so that $\bar{\sigma}(e)$ is *not* linear in e. The equation of motion (balance of physical momentum) in the absence of force reads (mass density is normalized to one):

$$v_t = \sigma_x, \qquad v_x = e_t\,, \tag{10.4.55}$$

where the second equation represents the kinematical compatibility. Imagine that the material body occupies the whole real line $\mathbb{R}$ so that we can think in terms of asymptotic values at + and − infinity. Truskinowsky (1992) has shown that Eqs. (10.4.55) possess strongly localized solutions (over a length scale of the order of $\sqrt{\varepsilon}$) which allows passing from one limit ($e(+\infty) = e_+$, $e_x(+\infty) = 0$) representing say phase α, to the other limit ($e(-\infty) = e_-$, $e_x(-\infty) = 0$) representing then phase β. Such dynamical solutions $u = \bar{u}(\xi = x - ct)$ propagate at speed c given by

$$c^2 = \frac{[\bar{\sigma}]_{-\infty}^{+\infty}}{[e]_{-\infty}^{+\infty}}\,. \tag{10.4.56}$$

This would be the *Rankine–Hugoniot equation* if the jumps were taken between sides of a true discontinuity. Here the jumps are defined in terms of asymptotic values but these are also practically valid up to a distance of the order of $\sqrt{\varepsilon}$ of the wave front. On account of this, the equation of motion $(10.4.55)_1$ provides then the following *nonlinear eigenvalue problem* with respect to e_- if e_+ is known:

$$2\varepsilon\frac{d^2e}{d\xi^2} + \eta_v c\frac{du}{d\zeta} = \bar{\sigma}(e) - \bar{\sigma}(e_+) - c^2(e - e_+)\,. \tag{10.4.57}$$

The specification of the points of *discrete spectrum* for this eigenvalue problem constitutes the desired *kinetic relation* for the wave front transiting from e_+ to e_- as it provides c in terms of the "driving force" acting on the solution (the jump in $\bar{\sigma}$). We refer the reader to Truskinowsky for this discussion and the relationship with commonly admitted *laws of growth* of such *phase boundaries.* But we retain from this the notion of *driving force* which manifests itself almost automatically in the continuum-physics context.

B. Quasi-static progress of a coherent phase-transition front[5]

We first neglect inertia and discard any temperature effect. The phase-transition front is viewed in Fig. 10.3 as a deformable elastic body (one phase, on one side of the surface Σ, say on Σ_-) growing at the expense of another deformable elastic body (the other phase) situated on side Σ_+. Alternately, we may also say that the body V_+ on side Σ_+ sees the other body V_- as an expanding *defect.* The hypothesis of *coherence* between the two phases at Σ (correspondence of lattice sites) imposes some restriction on the jump of characteristic quantities.

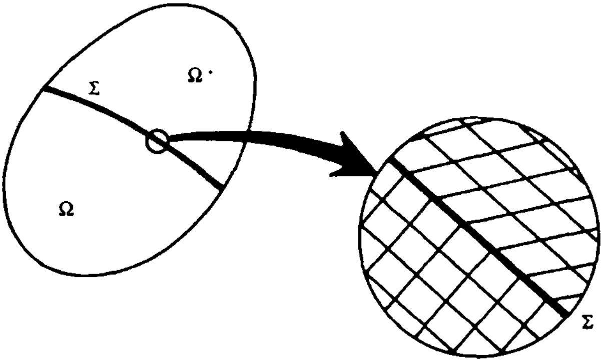

Fig. 10.3. Coherent phase-transition front.

Let $\mathbf{F}$ the direct-motion gradient and $\mathbf{N}_\Sigma$ the local unit normal to Σ pointing toward V_+. Then the Maxwell-Hadamard lemma of singular-surface theory yields

$$[\mathbf{F}] = \mathbf{f} \otimes \mathbf{N}_\Sigma, \qquad \mathbf{f} = [\mathbf{F}] \cdot \mathbf{N}_\Sigma, \tag{10.4.58}$$

---

[5] We follow the derivation of Maugin and Trimarco (1994).

where $[\ldots]$ denotes the jump across Σ, i.e. $[A] = A^+ - A^-$ where $A^\mp$ denote the uniform limits of A in approaching Σ along its normal on it *minus* and *plus* sides. Here $\mathbf{f}$ is a vector field in physical space. The field equations read:

$$\begin{gathered} \operatorname{div}_R \mathbf{T}^\pm = 0 \text{ in} V^\pm, \quad \mathbf{T}^\pm = \partial W^\pm / \partial \mathbf{F}, \\ \mathbf{N} \cdot \mathbf{T} = \mathbf{T}^d \text{ at } \partial V - \Sigma, \\ \mathbf{N}_\Sigma \cdot [\mathbf{T}] = \mathbf{0} \text{ at } \Sigma. \end{gathered} \tag{10.4.59}$$

In order to evaluate the *elementary dissipation* in an *irreversible* progress of Σ, we shall follow the same method as the one sketched out in Paragraph 8.4B for a crack. But now we should write

$$\delta\Phi = \int_{\partial V} (\mathbf{N} \cdot \mathbf{T}) \cdot \delta_{\mathbf{X}} \chi dA - \delta_{\mathbf{X}} \int_V W(\mathbf{F}) dV \tag{10.4.60}$$

where, indeed,

$$\int_V W(\mathbf{F}) dv = \int_{V+} W^+(\mathbf{F}) dV + \int_{V-} W^-(\mathbf{F}) dV, \tag{10.4.61}$$

as the two *elastic phases* are essentially different materials, and Σ is *material* for both bodies. Assuming that it is V^- that progresses into V^+, we use twice the "transport theorem" (8.4.54a) to write

$$\delta_{\mathbf{X}} \int_{V\pm} W^\pm(\mathbf{F}) dV = \int_{V\pm(\text{fixed})} \delta_{\mathbf{X}} W^\pm dV - \int_{\Sigma\pm} W^\pm (\mathbf{N}^\pm \cdot \delta_{\mathbf{X}} \mathbf{X}^\pm) d\Sigma, \tag{10.4.62}$$

where we note that $\mathbf{N}_\Sigma \equiv \mathbf{N}^- = -\mathbf{N}^+$, so that we can write the second contribution to (10.4.60) as

$$\delta_{\mathbf{X}} \int_V W(\mathbf{F}) dV = \int_{V+\cup V-} \delta_{\mathbf{X}} W(\mathbf{F}) dV + \int_\Sigma \mathbf{N}_\Sigma \cdot [W \delta_{\mathbf{x}} \chi^{-1}] d\Sigma. \tag{10.4.63}$$

Now in computing the first contribution to (10.4.62) we have

$$\begin{aligned} \int_{V+\cup V-} \delta_{\mathbf{X}} W^\pm(\mathbf{F}) dV = &- \int_{V-\Sigma} (\operatorname{div}_R \mathbf{T}) \cdot \delta_{\mathbf{X}} \chi + \int_{\partial V - \Sigma} (\mathbf{N} \cdot \mathbf{T}) \cdot \delta_{\mathbf{X}} \chi dA \\ &+ \int_\Sigma \mathbf{N}_\Sigma \cdot [\mathbf{T} \cdot \delta_{\mathbf{X}} \chi] d\Sigma, \end{aligned} \tag{10.4.64}$$

where the jump term comes from the application of the divergence theorem to both V^+ and V^- and the gluing back of the two resulting terms. Now we can account for Eqs. (10.4.59), so that collecting nonvanishing contributions we obtain

$$\delta\Phi = -\int_{\Sigma} \mathbf{N}_{\Sigma} \cdot [W\delta_{x}\chi^{-1} + \mathbf{T} \cdot \delta_{\mathbf{x}}\chi] d\sigma \tag{10.4.65}$$

At this point we follow Hill (1986) by selecting the virtual variations in *direct* and *inverse* motions in such a way that the jump in $\delta_{\mathbf{X}}\chi$ is not zero (we cannot control the *direct motion* which can suffer a jump in its first variation; this has the same properties as a gradient), whereas $\delta_{x}\chi^{-1}$ should be taken as continuous across Σ on the material manifold so as to respect the continuity of *lattice sites* at a coherent front, i.e.,

$$[\delta_{\mathbf{X}}\chi] = -[\mathbf{F}] \cdot \delta_{x}\chi^{-1} . \tag{10.4.66}$$

That is, we have taken the jump of the general compatibility relation (8.4.56), considering a continuous $\delta_{x}\chi^{-1}$. On account of the fact that

$$\begin{aligned} [\mathbf{N}_{\Sigma} \cdot \mathbf{T} \cdot \delta_{\mathbf{X}}\chi] &= -[\mathbf{N}_{\Sigma} \cdot \mathbf{T} \cdot \mathbf{F} \cdot \delta_{x}\chi^{-1}] \\ &= -[\mathbf{N}_{\Sigma} \cdot \mathbf{T} \cdot \mathbf{F}] \cdot \delta_{x}\chi^{-1} \\ &= -\langle \mathbf{N}_{\Sigma} \cdot \mathbf{T} \rangle \cdot [\mathbf{F}] \cdot \delta_{x}\chi^{-1} , \end{aligned} \tag{10.4.67}$$

since $(\langle A \rangle \equiv \frac{1}{2}(A^{+} + A^{-}))$

$$[AB] = \langle A \rangle [B] + [A] \langle B \rangle \equiv \langle A \rangle [B] , \tag{10.4.68}$$

for A continuous across Σ, we can rewrite our final result as

$$\delta\Phi = \int_{\Sigma} \mathbf{f}_{\Sigma} \cdot \delta_{x}\chi^{-1} d\Sigma , \tag{10.4.69}$$

where the *material force* $\mathbf{f}_{\Sigma}$, *with support* Σ, is defined as

$$\mathbf{f}_{\Sigma} := -\mathbf{N}_{\Sigma} \cdot [\mathbf{W}(\mathbf{F})\mathbf{1}_{R} - \langle \mathbf{T} \rangle \cdot \mathbf{F}] \equiv -\mathbf{N}_{\Sigma} \cdot [\mathbf{b}] , \tag{10.4.70}$$

where $\mathbf{b}$ is none other than the quasi-static *material Eshelby stress tensor* defined by (cf. (8.4.45)):

$$\mathbf{b} = W(\mathbf{F})\mathbf{1}_{R} - \mathbf{F}^{T} \cdot \mathbf{T}, \quad \mathbf{bC} = \mathbf{Cb}^{T} , \tag{10.4.71}$$

where the second equation reminds us of the *symmetry property* of $\mathbf{b}$.

For *coherent phase-transition fronts*, we have to account for the condition (10.4.58) and the fact that the elementary material displacement $\delta_{\mathbf{x}}\chi^{-1}$ reduces to a *normal component*. Passing to (material) time derivatives instead of infinitesimal variations, we can rewrite (10.4.69) as

$$\Phi(\Sigma) = \int_{\Sigma} f_{\Sigma}\mathcal{V}_{\Sigma} d\Sigma\,, \tag{10.4.72}$$

where $\mathcal{V}_{\Sigma}$ is a scalar speed of progress, and

$$f_{\Sigma} = -\mathbf{N}_{\Sigma} \cdot [\mathbf{b}] \cdot \mathbf{N}_{\Sigma} = -[W(\mathbf{F})] - \langle \mathbf{N}_{\Sigma} \cdot \mathbf{T} \rangle \cdot \mathbf{f}\,. \tag{10.4.73}$$

It is possible that *no dissipation occurs* at Σ. In this case we must have a vanishing force f_{Σ}, i.e.,

$$f_{\Sigma} = -[W(\mathbf{F}) - \langle \mathbf{N}_{\Sigma} \cdot \mathbf{T} \rangle \cdot \mathbf{F} \cdot \mathbf{N}_{\Sigma}] = 0\,. \tag{10.4.74}$$

Such a relation closely resembles the *Hugoniot* relation that *shock waves* have to satisfy in elastic solids (cf. Maugin, Pouget *et al.*, 1992, p. 171), when thermal effects are discarded. For *phase transitions*, Eq. (10.4.74) accounts for the classical *Maxwell rule* (cf. Grinfeld, 1991; Truskinowsky, 1992). If f_{Σ} does not vanish, then we have dissipation. The elementary dissipation per unit area of Σ reads

$$\varphi_{\Sigma} = f_{\Sigma}\mathcal{V}_{\Sigma} \geq 0\,, \tag{10.4.75}$$

which is in the traditional *bilinear form* of "force" multiplied by a "velocity". In particular, f_{Σ} may be called the *thermodynamical driving force* of the front, a *material force* (with components on the material manifold $\mathcal{M}^3$), as to have nonzero dissipation we have to write a relationship between f_{Σ} and $\mathcal{V}_{\Sigma}$. This is the *kinetic relation* looked for. From the experience gathered in other chapters, we know that this relationship may be of the "viscous", "plastic", or "viscoplastic" type, i.e. involving either a time-scale or a threshold, or both. The most relevant type is the "plastic" one, for which (cf. Chapter 5) there exists a critical f_{Σ}^{c} such that $f_{\Sigma} < f_{\Sigma}^{c}$, no progress, while for $f_{\Sigma} = f_{\Sigma}^{c}$ there is *possible* progress, and we can write in more abstract terms (compare the formalism of Chapters 5 and 7)

$$\mathcal{V}_{\Sigma} \in \mathrm{N}_{C}(f_{\Sigma}), \quad \mathcal{D}^{*} = \mathrm{Ind}\; C(f_{\Sigma}), \; C(f_{\Sigma}) = [0, f_{\Sigma}^{c}] \in \mathbb{R}\,, \tag{10.4.76}$$

where $\mathcal{D}^{*}$ is a *pseudo-potential of dissipation*. In general we would write the second of (10.4.76) as

$$\mathcal{V}_{\Sigma} = \frac{\partial \mathcal{D}^{*}}{\partial f_{\Sigma}}\,, \tag{10.4.77}$$

where the degree of homogeneity of $\mathcal{D}^{\bullet}$ depends on the behavior. The first work to give the velocity of a transition front was by Malomed and Rumanov (1984). The same idea was propounded in Cherepanov (1985). Note that the critical f_{Σ}^{c} is in fact an *energy* per unit volume (Maugin and Trimarco, 1994). Thus f_{Σ} is a quantity akin to the *energy-release rate* of fracture. Expressions such as (10.4.71) were in fact obtained for the *driving force* acting on *damage* and *delamination surfaces* by various authors (cf. Dems and Mroz, 1985; Pradeilles-Duval and Stolz, 1991).

Now the above derivation neglects inertia and temperature effects so that it is unsatisfactory if we think that many phase transitions are also driven by *temperature*. Furthermore, the inclusion of this parameter may help to make the distinction between the above wave fronts and *shock waves*. To elucidate this point we examine next the direct approach through the basic jump relations of thermomechanics.

C. Heat-conducting case.

We consider anew the same problem as in the previous paragraph but we account for material inertia, heat conduction and, therefore, the local expression of the second law of thermodynamics. The surface Σ separating the two phases is viewed as a discontinuity surface propagating at material velocity V_N. It apparently does not present, by itself, any structure and thermodynamic properties (e.g., surface energy, surface tension, dissociation and recombination rates of species,etc). At any regular point $\mathbf{X}$ outside Σ and with the appropriate internal energy $e(\mathbf{F},\eta)$ for each homogeneous phase, we have the following *balance laws* [cf. Eqs. (8.4.39) and (8.4.40)]

$$\left.\frac{\partial \rho_0}{\partial t}\right|_{\mathbf{X}} = 0\,, \tag{10.4.78}$$

$$\left.\frac{\partial}{\partial t}\mathbf{P}\right|_{\mathbf{X}} - \mathrm{div}_R \mathbf{T} = \mathbf{0}\,, \quad \mathbf{p} \equiv \rho_0 \mathbf{v}\,, \tag{10.4.79}$$

$$\left.\frac{\partial}{\partial t}\rho_0\left(e + \frac{\mathbf{v}^2}{2}\right)\right|_{\mathbf{X}} - \nabla_R \cdot (\mathbf{T}\cdot\mathbf{v} - \mathbf{Q}) = 0\,, \tag{10.4.80}$$

and the inequality of Clausius–Duhem in its primitive form:

$$\left.\frac{\partial}{\partial t}S\right|_{\mathbf{X}} + \nabla_R \cdot \mathbf{S} \geq 0, \quad S = \rho_0\eta, \quad \mathbf{S} = \mathbf{Q}/\theta\,, \tag{10.4.81}$$

where $\mathbf{Q}$ is the material *heat flux.* It was assumed that there are neither body force nor body heat supply. Corresponding to Eqs. (10.4.78) through (10.4.81) we have *jump relations across* Σ which, for equations that occur as true conservation laws, are formally obtained from them by replacing the operators $\partial/\partial t$ and ∇_R by $-\bar{V}_N[\ldots]$ and $\mathbf{N}_\Sigma\cdot[\ldots]$ (cf. Maugin, 1988, Chapter 5), where $\bar{V}_n = \bar{\mathbf{V}}\cdot\mathbf{N} = \mathcal{V}_\Sigma$ is the normal (material) speed at Σ. Thus we have the so-called *Rankine–Hugoniot* jump relations:

$$\mathbf{N}_\Sigma\cdot[\rho_0\bar{\mathbf{V}}] = 0 \text{ or } m = \text{const.} \tag{10.4.82}$$

$$\bar{V}_N[\mathbf{p}] + \mathbf{N}_\Sigma\cdot[\mathbf{T}] = 0\,, \tag{10.4.83}$$

$$\bar{V}_N\left[\rho_0\left(e + \frac{\mathbf{v}^2}{2}\right)\right] + \mathbf{N}_\Sigma\cdot[\mathbf{T}\cdot\mathbf{v} - \mathbf{Q}] = 0\,, \tag{10.4.84}$$

and

$$\bar{V}_N[\rho_0\eta] - [\mathbf{Q}\cdot\mathbf{N}_\Sigma/\theta] = \sigma_\Sigma \geq 0\,. \tag{10.4.85}$$

Here $m = \rho_0\bar{\mathbf{V}}_N$ is the mass flux. We consider that the transition across Σ is *homothermal*, so that

$$[\theta] = 0, \quad \text{or} \quad \theta = \theta^+ = \theta^- = \bar{\theta} \text{ at } \Sigma\,. \tag{10.4.86}$$

The relevant constitutive equations are given by Eq. (8.6.86) and (8.6.87) with a free energy $W = \bar{W}(\mathbf{F},\theta)$ in each homogeneous phase. The energy equation in the bulk of each phase can also be written in the form of the *heat equation* (8.6.85):

$$\theta\left.\frac{\partial S}{\partial t}\right|_{\mathbf{X}} + \nabla_R\cdot\mathbf{Q} = 0\,, \tag{10.4.87}$$

because there is neither heat body source nor intrinsic dissipation. Finally, the balance of pseudomomentum (8.6.88) is reduced to

$$\left.\frac{\partial}{\partial t}\mathcal{P}\right|_{\mathbf{X}} - \mathrm{div}_R\,\mathbf{b} = \mathbf{f}^{\mathrm{th}}\,, \tag{10.4.88}$$

where $\mathbf{f}^{\mathrm{th}}$ is given by $(8.6.89)_1$. Both equations (10.4.87) and (10.4.88) are *nonconservative.* Therefore, the corresponding jump relations across Σ should exhibit *source terms,* respectively q_Σ and $\mathbf{f}^{\mathrm{th}}_\Sigma$, to be jointly determined by the thermodynamical study:

$$\bar{\theta}\bar{V}_N[S] - \mathbf{N}_\Sigma\cdot[\mathbf{Q}] - q_\Sigma = 0\,, \tag{10.4.89}$$

$$\mathbf{N}_\Sigma\cdot[\mathbf{b} + \bar{\mathbf{V}}\otimes\mathcal{P}] + \mathbf{f}^{\mathrm{th}}_\Sigma = \mathbf{0}\,. \tag{10.4.90}$$

On account of (10.4.86) and comparing (10.4.85) and (10.4.89) we see that

$$\sigma_\Sigma = q_\Sigma/\bar\theta \quad \text{at} \quad \Sigma. \tag{10.4.91}$$

Now we can estimate $\mathbf{N}_\Sigma \cdot [\mathbf{Q}]$ from (10.4.84) and, in parallel, compute the power expanded by $\mathbf{f}^{\mathrm{th}}_\Sigma$ in the continuous velocity field $\mathbf{V}$ at Σ. In performing the first computation we obtain

$$\mathbf{N}_\Sigma \cdot [\mathbf{Q}] = V_n \left[\rho_0 e + \frac{1}{2}\rho_0 \mathbf{v}^2\right] + \langle \mathbf{N}_\Sigma \cdot \mathbf{T}\rangle \cdot [\mathbf{v}] + \mathbf{N}_\Sigma \cdot [\mathbf{T}] \cdot \langle \mathbf{v}\rangle .$$

But Eq. (10.4.83) yields at once

$$\mathbf{N}_\Sigma \cdot [\mathbf{T}] \cdot \langle \mathbf{v}\rangle = -\bar V_N [\rho_0 \mathbf{v}] \cdot \langle \mathbf{v}\rangle = -\bar V_N \left[\frac{1}{2}\rho_0 \mathbf{v}^2\right] ,$$

from which it follows that

$$\mathbf{N}_\Sigma \cdot [\mathbf{Q}] = \bar V_N [\rho_0 \mathrm{e}] - \langle \mathbf{N}_\Sigma \cdot \mathbf{T}\rangle \cdot [\mathbf{F}] \cdot \mathbf{V} , \tag{10.4.92}$$

according to the fact that while both $\mathbf{v}$ and $\mathbf{F}$ are discontinuous across Σ, the *coherence condition* (continuity of lattice sites at Σ) requires that $\mathbf{V}$ be continuous, so that the relation $\mathbf{v} + \mathbf{F}\cdot\mathbf{V} = 0$ at regular points yields the jump relation

$$[\mathbf{v}] = -[\mathbf{F}] \cdot \mathbf{V} \quad \text{at} \quad \Sigma. \tag{10.4.93}$$

It is readily noticed that

$$\mathbf{V} \cdot \mathbf{N} = \bar{\mathbf{V}} \cdot \mathbf{N} = \bar V_N = \mathcal{V}_\Sigma \tag{10.4.94}$$

On substituting from (10.4.92) into (10.4.85) we arrive at the following result:

$$\bar\theta \sigma_\Sigma = -\mathcal{H} \mathcal{V}_\Sigma \tag{10.4.95}$$

where we have defined the so-called *Hugoniot-Gibbs* driving force $\mathcal{H}$ by

$$\mathcal{H} := [W(\mathbf{F},\theta) - \langle \mathbf{N}_\Sigma \cdot \mathbf{T}\rangle \cdot \mathbf{F} \cdot \mathbf{N}] . \tag{10.4.96}$$

This can also be written in the following alternate forms:

$$\mathcal{H} = [W(\mathbf{F},\theta)] - \langle \mathbf{N}_\Sigma \cdot \mathbf{T}\rangle \cdot \mathbf{f} = [W(\mathbf{F},\theta) - \mathrm{tr}\,(\langle \mathbf{T}\rangle \cdot \mathbf{F})] . \tag{10.4.97}$$

To prove the last of these, we perform some simple manipulations which are more transparent in components, for we have:

$$\langle \mathbf{N}_K \mathbf{T}^{K}_{\cdot i} \rangle [\mathbf{F}^{i}_{\cdot H}] = \langle \mathbf{N}_K \mathbf{T}^{K}_{\cdot i} \rangle \mathbf{f}^{i} \mathbf{N}_H = \mathbf{N}_H \langle \mathbf{T}^{K}_{\cdot i} \rangle \mathbf{f}^{i} \mathbf{N}_K = \mathbf{N}_H \langle \mathbf{T}^{K}_{\cdot i} \rangle [\mathbf{F}^{i}_{\cdot K}] \, .$$

We also note that the quantity $\mathcal{H}\mathcal{V}_\Sigma$ can also be written as

$$\mathcal{H}\mathcal{V}_\Sigma = m[\psi(\mathbf{F}, \theta) - \langle \psi_{,\mathbf{F}} \rangle^T : \mathbf{F}] \, , \tag{10.4.98}$$

where m is the mass flux and ψ is the free energy per unit mass at the reference configuration.

The second calculation consists of evaluating

$$P(\mathbf{f}^{\mathrm{th}}_\Sigma) := \mathbf{f}^{\mathrm{th}}_\Sigma \cdot \bar{\mathbf{V}} \tag{10.4.99}$$

from (10.4.90). We let the reader directly check that this yields (Maugin and Trimarco, 1994b)

$$P(\mathbf{f}^{\mathrm{th}}_\Sigma) = q_\Sigma = -\mathcal{H}\mathcal{V}_\Sigma \, , \tag{10.4.100}$$

where $\mathcal{H}$ is indeed given by (10.4.96) or (10.4.97).

The results obtained deserve the following comments. First, there is *no* inertial term in the expression of $\mathcal{H}$ even in full dynamics. This agrees with Gibbs' and Duhem's views that only the thermodynamic equivalent of the mechanical *potential* energy, here the *free energy*, should describe local changes in properties. As a matter of fact, in the *unidimensional* case where the $\langle \ldots \rangle$ brackets may be ignored, the quantity within squared brackets in Eq. (10.4.98) is indeed the *Gibbs free enthalpy* per unit mass. But the expression of $\mathcal{H}$ reminds us of the *Hugoniot* relation appearing in the thermodynamic study of shocks in nonlinear elasticity (see, Maugin, Pouget *et al.*, 1992, Chapter 4) except that it is the internal energy rather than the free energy which is involved there (unless one studies *detonation waves*). The power (10.4.100) appears to be a non-negative *heat source* localized at the transition front. The result (10.4.100) exhibits the relationship between Eqs. (10.4.89) and (10.4.90) as these two equations which, in fact, represent the time and space components of a single four-dimensional equation, can only be consistent with the condition (10.4.100). An equation such as (10.4.89) with a source term was pointed out by Stolz (1994), but this author did not remark the connection with the heat equation, nor did he use the pseudomomentum argument and the notion of thermal inhomogeneity force at all. Finally, what thermodynamics says here is that $\mathbf{f}_{\Sigma}^{\text{th}}$ and $\mathbf{V}$, or $\mathcal{H}$ and $\mathcal{V}_{\Sigma}$, must be related in such a way as not to contradict the second law of thermodynamics at Σ. Once $\mathcal{H}$ has been expressed in terms of $\mathcal{V}_{\Sigma}$, then the system of field and jump equations is entirely closed. Imagine that we know the solution of the thermoelastic problem at time t on each side of Σ. Then we can compute $\mathcal{H}$, and $\mathcal{V}_{\Sigma}$ shall be such that the second law is respected. This dictates the sign of $\mathcal{V}_{\Sigma}$ along the unit normal to Σ, and thus the direction of progress of the front, i.e. which phase is progressing into the other. The progress can be studied incrementally in time, just as we study the progress of plastic zones in elastoplasticity or the extension of cracks in fracture (cf. Maugin, 1992a).

Consider the case of quasi-statics and the front Σ propagates normally to itself. Thus, when $\mathcal{V}_{\Sigma}$ is not zero, the two expressions (10.4.99) and (10.4.100) provide the following *balance*

$$\mathcal{H} + f_{\Sigma} = 0\,, \qquad f_{\Sigma} = \mathbf{f}_{\Sigma}^{\text{th}} \cdot \mathbf{N}\,, \tag{10.4.101}$$

between the Hugoniot–Gibbs *driving* or *configurational* force $\mathcal{H}$ and the surface thermal force of quasi-inhomogenities f_{Σ}. In fact these two quantities have a different status: $\mathcal{H}$ is a *field quantity*, which can be computed once we know all fields on both sides of Σ, while f_{Σ} is a *constitutive quantity* whose expression is given by a *kinetic law*, e.g. (10.4.77), i.e. a closure hypothesis respecting the second law of thermodynamics. This can be compared to the approach of Truskinowsky (1994) based on kink/shock solutions of the one-dimensional model (10.4.57). For a given functional dependence of the free energy (e.g. quartic in e), this author was able to find a functional relationship between the "force" f_{Σ} and the speed $\mathcal{V}_{\Sigma}$. This relationship depends on the nondimensional number ω defined by (10.4.54). The result is given in Fig. 10.4 in which we have also given the "Griffith" type (or *perfect-plasticity* type) of law (10.4.76). An adjustment of the *pseudopotential of dissipation* $\mathcal{D}^{*}$ in (10.4.77) would permit one to reproduce the whole range of variation with ω.

The results given above for thermoelastic conductors can be generalized to the case of *electromagneto-thermoelastic* conductors of heat and electricity at some cost in computation. The results (10.4.95) and (10.4.87) are left formally unchanged but the expression of $\mathcal{H}$ will obviously be more involved due to the presence of electromagnetic fields. For instance, in perfect agreement with the elements of electroelastic fracture given in Sec. 9.12, it is shown for the case of the electroelasticity of dielectrics in the quasi-electrostatic approximation that

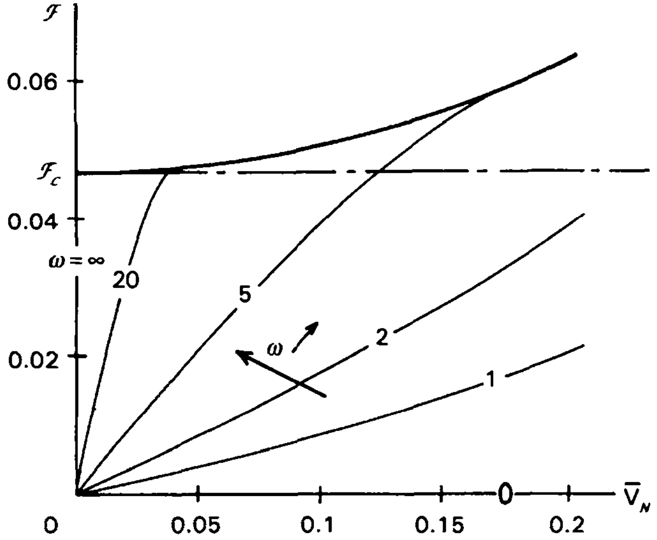

Fig. 10.4. Kinetic curves f_Σ versus nondimensional V_Σ for different values of ω and a cubic $\bar{\sigma}(e)$ — after Truskinowski (1994). The graph —·— represents a Griffith-like criterion corresponding to a plateau similar to plastic flow [lack of uniqueness in speed — Eq. (10.76)].

$\mathcal{H}$ has an expression given by (Maugin and Trimarco, 1995, 1997):

$$\mathcal{H} = [W(\mathbb{E}, \mathfrak{E}, \theta) - \mathbf{N} \cdot (\langle \mathbf{T}^E + \mathbf{T}^F \rangle \cdot \mathbf{F} - \langle \mathfrak{D} \rangle \otimes \mathfrak{E}) \cdot \mathbf{N}] . \tag{10.4.102}$$

Establishing this expression requires the exploitation of the jump relations associated with the energy equation (9.12.258) and the first of the Eshelby stress tensors (9.12.267). Such a result can be used in a criterion for the progress of transition fronts in some *ferroelastic materials* which are also *ferroelectrics* (such materials admit two different order parameters; cf. Maugin, Pouget *et al.*, 1992, Appendix). A similar development is given in elastic ferromagnets by Fomethe and Maugin (1997) with soft ferromagnets as special cases. Recent works consider the case of *noncoherent fronts* (nonvanishing [V]) — so that the fronts themselves present *defects* akin to *dislocations* (jump discontinuities in material displacement) — as also the effect of a *surface tension* akin to *capillarity* at Σ. Both additional effects relate to the not necessarily *normal growth* of one phase with respect to another [only $\bar{V}_N$ was involved in the growth condition (10.4.75) or (10.4.95)], which in turn leads to the problem of the lateral stability of the fronts.

For the sake of completeness the reader may consult works such as those of Daher and Maugin (1986a,b; 1987) for the case of *thermodynamic interfaces* which manifest various properties including surface tension, electric field, electric polarization and magnetization, etc., and for which a surface Clausius–Duhem inequality is used. The resulting complicated modeling is not related to phase-transition fronts, *per se*, but it is particularly useful in the study of *junctions* in deformable semiconductors as a host of exchanges and interactions take place right on the interface.

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