THE DUHEM–HADAMARD HYPOTHESIS IN THERMOFLUIDDYNAMICS*

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Abstract—The Duhem–Hadamard hypothesis (DHH) states that in a fluid flow the same equation relates the pressure, the mass density, and the temperature as in equilibrium. The entire theory of bodies concerning flow processes in engineering science and practice rests upon it. Our recent work on fundamentals of non-equilibrium phenomena suggests that the hypothesis are only approximate in some sense, but its mathematical formulation does not make clear what is being approximated. To get a preliminary clarification, the paper deals with two items: first, a theoretical basis is worked out to yield appropriate presuppositions for an efficient experimental program and, second, provisional experimental data are established by a new and precise set-up. Our theoretical examinations admit to derive definite distinguishing features of both non-equilibrium and equilibrium processes. The latter appear as a limiting case of the former and are identified with the hypothetical fluid state at rest. Only for this special state the thermal equation of state is representative of thermodynamic equilibrium. Yet, there is a second kind of equilibrium: the kinetic equilibrium defined for reversible flows. All theoretical considerations lead us to the conclusion that the DHH can only be justified for kinetic equilibria. The first phase of our research program allowed to learn that our high-precision measurement devices need to be improved in order to decide, whether this special kind of reversible flow exists as a real limiting case. Unlike this, our experiments prove that non-equilibrium states induced by the motions of the fluid cannot be described by the DHH. © 1998 Published by Elsevier Science Ltd. All rights reserved

1. PRELIMINARY REMARKS AND INTRODUCTION

To deal with classical fluid dynamics by means of a set of conservation laws, a relation between the pressure and the density of the flowing matter is needed. For a gas in local equilibrium such a relation additionally depends upon the corresponding local temperature. When Euler faced this problem over more than 200 years ago, he had only been able to suggest the temperature as an assigned function of place. In this way he explained steady-state convection in a tube under the condition that the temperature is an overall property of the flow problem. It may be compared with the role of the mass density as an index of an incompressible flow as a whole.

This is also true for the founders of the vectorial Navier–Stokes equation of motion. A lack of precise thermodynamical relationships prevented them from treating correctly the more realistic flow of a fluid. Its local values of temperature could only be assigned to the flow field by heuristic rules, provided that the latter was solved for the velocity–pressure–density variables as functions of place and time in agreement with the boundary and initial conditions.

Only when the energy balance was explicitly introduced into the classical field theories, this special kind of solutions went out of fashion and is now restricted to approximations concerning some properties of certain liquid flows. To deal with compressible fluids, however, the existence of characteristic equations of state must be considered. These fundamental informations on constitutive relationships between the intensive local variables cannot, as a rule, theoretically be determined with sufficient accuracy except for idealized materials in thermodynamic equilibrium, e.g. ideal solids and gases. Hence, the problem arises whether these equilibrium relationships can be used for dissipative flow processes which are obviously running outside local equilibrium conditions.

Contributed by W. F. Ames.
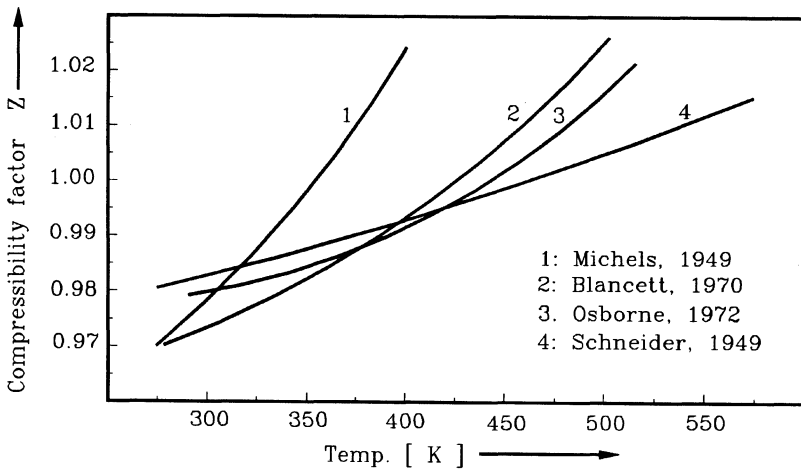*Dedicated to Alfred Walz on the occasion of his 90th birthday.

Fig. 1. Characteristic deviations of precise p, ρ, T-data of argon.

Euler did not know the general principle of energy. Duhem and Hadamar did (e.g. ref. [1], p. 60). Consequently, they were motivated to state the hypothesis—and they stressed that it was nothing more than a hypothesis—that for a gas, subject to any change of state at rest or in a flow, the same equations of state hold, relating the pressure p and, respectively, the specific enthalpy h to both the mass density ρ and temperature T in the same way as in thermodynamic equilibrium. Thus, by means of Duhem and Hadamard's proposition, conventional rational fluid dynamics is allowed to be mathematically represented by a *complete* set of algebraic and differential equations.

This decisive step has sometimes been questioned in the literature, but rarely by specialist in gas dynamics. Nowadays, it is often put forward as the assertion that in each volume element of a flow region each real fluid is subject to local quasi-static processes associated with thermal and caloric changes of state. From this point of view such an infinitesimal volume element may be regarded as a thermodynamic system in local equilibrium.

Can this common hypothesis, widely used in flow mechanics to equate the pressure or the enthalpy with the equilibrium equations of state, be founded theoretically on the general principles alone? May it be justified by theoretical results derived from Maxwell's "Kinetic Theory" or even from new fundamentals or by means of experiments like $p\rho T$-measurements?

As seen from Fig. 1, comparison of allegedly very precise p, ρ, T-data demonstrates deviations up to 1%, though the same substance measured by different authors for the same domain of the density and the temperature variables was observed (cf. ref. [2], p. 4). These significant differences can be explained in no way by the uncertainty of measurements believed to be better than 0.1%. Hence, the discrepancy between the determined state quantities has to be associated with the time behavior of these quantities in the course of their trend to equilibrium.

This paper reports on first results concerning the validity of the Duhem–Hadamard hypothesis. The efforts of our research program were focused on a theoretical study of the problem combined with an analysis of new p, ρ, T-measurements. The latter were made with a new p, ρ, T-apparatus.

2. BASIC ELEMENTS OF THE ALTERNATIVE THEORY

2.1. *Gibbs–Falkian thermodynamics*

A new thermodynamic theory, the so-called Alternative Theory (AT) was developed by Straub [3] based on G. Falk's Extended Gibbsian Thermodynamics [4] and motivated by Prigogine's new way From Classical Chaos to Quantum Chaos [5].

This new theory enables us to describe the dynamics of any non-equilibrium phenomena in physics. Applications cover all macroscopic fields including mechanics, fluid dynamics and thermodynamics, and electromagnetism. As a rule, equilibrium states and processes do

only exist as limiting cases within the frame of a generally valid theory of non-equilibrium motion.

The Gibbs–Euler function constitutes the (total) energy E depending on extensive variables exclusively. Under the condition that the selected quantities represent a complete set of l variables Z_i [$i = 1(1)l$], then $E = \hat{E}(Z_1; \ldots; Z_l)$ contains the complete physical information on the system under consideration. The notion system represents always a mathematical description of an object assumed to be part of nature or human inventions. The special kind synonym is not, however, a copy of the original object, but rather an abstract model, a mathematical construction by means of a finite number of variables usually ignoring one or more less important aspects of the real situation.

The energy E which is connected with an energy transport during a process appears as a sum of a finite number l of energy forms. Each of the latter is abbreviated by the following kind of mathematical construction:

$$(\mathrm{EF})_i := \zeta_i \, dZ_i, \quad i = 1(1)l, \tag{1}$$

where dZ_i is the total differential of the extensive variable Z_i and ζ_i denotes its intensive conjugate. Both these quantities refer to the ith energy form $(\mathrm{EF})_i$ identifying the contribution of energy E to be exchanged exactly by means of this energy form. Note that this transported amount of energy relates only to its assigned energy form and not to the stored energy E of the system.

Since energy is an extensive quantity of a system in motion, the following Gibbs main equation (GME, also known as Pfaff's form)

$$dE = \sum_i \zeta_i \, dZ_i, \quad i = 1(1)l \tag{2}$$

is derived as a consequence of the complete set of l variables Z_i ($i = 1(1)l$).

For the concrete case of single phase-multicomponent-body field system the corresponding Gibbs–Euler function reads

$$E - E_{\#} = E(\mathbf{P}; \mathbf{r}; S; V; N_k \,|\, k = 1(1)K), \tag{3}$$

where $\mathbf{r}$ stands for the displacement vector of the field, and $\mathbf{P}$, S, V, and N_k denote the linear momentum, entropy, volume, and the kth species particle number of the moved body, respectively. With $E_{\#}$, a reference energy amount is marked.

The respective intensive variables ζ_i are obtained by differentiating the Gibbs–Euler function E with respect to its corresponding extensive variables Z_i of the system in motion. The partial derivatives represent the field force $\mathbf{F}$, the flow velocity $\mathbf{v}$, the pressure p_*, the temperature T_* and the chemical potential per particle μ^t_{k*}, respectively. The asterisks $*$ serve to denote such quantities in their non-equilibrium states that fulfill special conditions in equilibria. Table 1 lists these quantities along with the corresponding terms of the energy form assigned (cf. ref. [3] p. 107).

Starting from the Pfaffian (2) of the Gibbs–Euler function (3),

$$dE = \mathbf{v} \, d\mathbf{P} - \mathbf{F} \cdot d\mathbf{r} + T_* \, dS - p_* \, dV + \sum_k \mu^t_{k*} \, dN_k, \tag{4}$$

Table 1. Important intensive and extensive variables of a thermofluid dynamic system

Energy form $\xi_i \, dZ_i$	Intensive variable	Extensive variable
Displacement	$-\mathbf{F}$	$\mathbf{r}$
Motion	$\mathbf{v}$	$\mathbf{P}$
Compression	$-p_*$	V
System configuration	T_*	S
Chemical	u^t_{k*}	N_k

a Legendre transformation of E with respect to volume V,

$$E_*^{[V]} = E - V \left(\frac{\partial E}{\partial V} \right)_{\mathbf{P}, \mathbf{r}, S, N} = E + V p_*, \tag{5}$$

leads to the Massieu–Gibbs function (M–G function; cf. ref. [4], p. 216) $E_*^{[V]}(\mathbf{P}; \mathbf{r}; S; p_*; N_k)$ of the system in question as well as to its corresponding GME,

$$dE_*^{[V]} = \mathbf{v} \cdot d\mathbf{P} - \mathbf{F} \cdot d\mathbf{r} + T_* \, dS + V \, dp_* + \sum_{k=1}^{K} \mu_{*k}^t \, dN_k. \tag{6}$$

Forming the double limit $\mathbf{P} \Rightarrow \mathbf{0}$ and $\mathbf{r} := \mathbf{r}_\# \equiv$ constant, assumed to be true for all changes of the other variables of the system, one obtains from equation (6)

$$dH = T \, dS + V \, dp + \sum_{k=1}^{K} \mu_k^t \, dN_k, \tag{7}$$

where a new symbol H is introduced for $E_*^{[V]}$ if this double limit is actually affected. Of course, H means the well-known enthalpy depending on the variables S, ρ, and N_k each. By dropping the asterisks in equation (6) an essential result is anticipated which will be stated below: *The M–G function $H(S; p; N_k)$ does exist only for the absolute state at rest defined by the double limit $\mathbf{P} \Rightarrow \mathbf{0}$ and $\mathbf{r} := \mathbf{r}_\# \equiv$ constant. This case may be referred to as the common state of thermodynamic equilibrium.* In the Gibbs space any moving multicomponent single-phase BFS, defined by its Gibbs–Euler function (3), has to be described explicitly by equation (6). Its mapping onto the configuration space by means of parametrization, using time as a curve parameter, leads to an expression which allows to be combined with the common balance equations of energy, momentum, and partial masses.

2.2. *Characteristic properties of non-equilibrium states*

First of all, a new way should be opened to discern more precisely non-equilibrium states from any equilibria. The basic idea is simple: provided that only systems are considered which can generally be characterized as non-relativistic ones, it is suitable to introduce the notion of kinetic energy as usual. This procedure follows Einstein's mechanics (cf. ref. [3], p. 94) and is defined to lead to the separation of the total energy E from the rest energy E_0:

$$E_{\mathrm{kin}} := E - E_0. \tag{8}$$

The reader should now be aware that with regard to Gibbs–Falkian theory the

$$E_{\mathrm{kin}} := \tfrac{1}{2} m^{\mathrm{B+L}} \mathbf{v}^2 \tag{9}$$

additional introduction of the term "kinetic energy", according to the common equation is a mere definition, associated with the constant mass $m^{\mathrm{B+L}}$ of all baryons and leptons which constitute the diverse particles of the system. Certainly, there are some well-founded arguments to employ this definition in practice, but there is no theoretical need to do so. For this reason, it is necessary to accept definitions (8) and (9) without any intrinsic inconsistency with the Gibbs–Euler function of the system under consideration and its mathematical derivatives. In order to fulfill this condition for all real and virtual changes of state, an interesting differential equation† can be derived as follows: Starting with the kinetic energy E_{kin} defined by equation (8), then equation (9) can be written as

$$\frac{E_{\mathrm{kin}}}{\tfrac{1}{2} m^{\mathrm{B+L}}} = \mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2$$

$$= \left(\frac{\partial E_{\mathrm{kin}}}{\partial P_x} \right)_{\mathbf{r}, S, V, N_k}^2 + \left(\frac{\partial E_{\mathrm{kin}}}{\partial P_y} \right)_{\mathbf{r}, S, V, N_k}^2 + \left(\frac{\partial E_{\mathrm{kin}}}{\partial P_z} \right)_{\mathbf{r}, S, V, N_k}^2, \tag{10}$$

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†A similar differential equation may be deduced for the motion of an electrically charged particle within a magnetic field [6, p. 182]. This problem concerns a simple, but important, system of the second kind, i.e. its velocity does not only depend on the conjugated variable $\mathbf{P}$, but also on the field coordinate $\mathbf{r}$.

where the generally valid derivative $\mathbf{v} = (\partial E/\partial \mathbf{P}) \ldots$ can be replaced by $\mathbf{v} = (\partial E_{\mathrm{kin}}/\partial \mathbf{P}) \ldots$, because $E_0(\mathbf{r}; S; V; N_k)$ is independent of $\mathbf{P}$. Equation (10) is a non-linear partial differential equation for E_{kin} with respect to the three Euclidean components of the momentum $\mathbf{P}$. By means of the vectorial form

$$\frac{2E_{\mathrm{kin}}}{m^{\mathrm{B+L}}} = \left(\frac{\partial E_{\mathrm{kin}}}{\partial \mathbf{P}}\right)^2_{\mathbf{r}, S, V, N_k}, \tag{11}$$

equation (10) is written in a more compact manner. It is easy to find a general solution of equation (11), as the reader may simply prove differentiating and inserting the formula

$$m^{\mathrm{B+L}}E_{\mathrm{kin}} = \tfrac{1}{2}[\mathbf{P} + \phi]^2, \tag{12a}$$

$$\phi = \phi(\mathbf{r}; s; \rho^{-1}; \omega_k) \tag{12b}$$

into the differential equation (11). The vector ϕ evidently follows from the integration and depends on the system variables assumed to be constant for the purpose of integration. This is a typical example for the so-called principle of equipresence

"as a rule to guide us when . . . we set up constitutive equations." [1, p. 300].

According to this "principle" it is indeed reasonable to assume for any constitutive quantity to depend on the complete set of the independent state variables, always provided that there are no reasons to exclude some of them—as it is done with the momentum in equation (12b).

It is, however, more illustrative to use specific quantities: In this case the reader may verify that with $e_{\mathrm{kin}} = E_{\mathrm{kin}}/m^{\mathrm{B+L}} = \tfrac{1}{2}\mathbf{v}^2$, equation (12) immediately becomes

$$\mathbf{v} = \mathbf{i} + \varphi, \qquad \varphi = (\mathbf{r}; s; \rho^{-1}; \omega_k) \tag{13}$$

The specific momentum, entropy, the mass density and the mass fraction of the kth species are denoted as usual with $\mathbf{i}$, s, ρ, and ω_k, respectively.

Just like the flow velocity $\mathbf{v}$ and the specific momentum $\mathbf{i}$, the vectorial quantity φ also has the unit of a velocity variable. For this and other reasons to be discussed below it may be permitted to term the quantity φ, a dissipation velocity.

Note that equation (13) is immediately derived from two "icons" of classical physics, viz., the decomposition of energy (8) along with the familiar one-half vis-à-vis equation (9), always provided that a proper Gibbs fundamental equation $\Gamma(E, \mathbf{P}, \mathbf{r}, \ldots) \equiv 0$ is accepted. From this point of view, it is puzzling that the scientific community still adheres to the very special solution $\varphi(\ldots) \equiv 0$ for nearly all actual cases without serious theoretical or experimental necessity. Concerning the general solution of any mathematical problem, each kind of discussion is actually a pure truism for every mathematician or theoretical physicist. Therefore, it is hard to grasp why a dispute about a possible more general expression than the constituent $\mathbf{v} = \mathbf{i}$ of the mass-point definition never has taken place.

Perhaps the force of habit, along with the predominance of mechanical paradigms over all branches of physics are responsible for this omission. These rather psychological influences seem to have prevented traditional science to ask for the consequences of a fundamental relation $\Gamma(E, \mathbf{P}, \mathbf{r}, \ldots) \equiv 0$ with respect to the universally accepted terms of kinetic energy and momentum originally founded only for Newton–Eulerian mass-point mechanics.

As a first result it is remarkable that the "velocity" φ simply explains an important fact normally experienced in all real flows along any given walls: On account of the wall adhesion of any viscous flow, maximum dissipation occurs at the wall if the flow velocity $\mathbf{v}$ tends toward zero. In this case, the corresponding specific momentum $\mathbf{i}$ locally equals φ, though furnished with opposite signs. In our opinion, this important example convincingly proves the conclusion that, unlike traditional physics puts it, there is a physically fundamental difference between the two key terms "linear momentum" $\mathbf{P}$ and that property $m_{\neq}\mathbf{v}$, originally labeled as "quantitas motus" by Issac Newton in 1687.

There is no opportunity to offer detailed information about the diverse properties of the dissipation velocity φ. With regard to the mathematical structure of the dependency on its variables, this holds especially true. Therefore, let us take the first step in this direction by some respective preparations.

Starting with the total derivative of the specific kinetic energy e_{kin}, according to definition (9), the idea suggests itself to combine de_{kin} with the total derivative $d\varphi$ of the dissipation velocity φ. In particular, one obtains the following formulas:

$$de_{\mathrm{kin}} = \mathbf{v} \cdot d\mathbf{v} = \mathbf{v} \cdot d\mathbf{i} + \mathbf{v} \cdot d\varphi = \mathbf{v} \cdot d\mathbf{i} + \mathbf{i} \cdot d\varphi + \varphi \cdot d\varphi, \tag{14}$$

$$d\varphi = \left(\frac{\partial \varphi}{\partial \mathbf{r}}\right)_{s, \rho, \omega_k} d\mathbf{r} + \left(\frac{\partial \varphi}{\partial s}\right)_{\mathbf{r}, \rho, \omega_k} ds + \left(\frac{\partial \varphi}{\partial \rho}\right)_{s, \mathbf{r}, \omega_k} d\rho + \sum_{k=1}^{K} \left(\frac{\partial \varphi}{\partial \omega_k}\right)_{s, \rho, \mathbf{r}, \omega \neq k} \cdot d\omega_k. \tag{15}$$

The reader may be reminded of the Gibb's main equation (4) related to constant mass $m^{\mathrm{B+L}}$ of all baryons and leptons. The resulting Pfaffian,

$$\rho \, de = \mathbf{v} \cdot \rho \, d\mathbf{i} + \rho \mathbf{f} \cdot d\mathbf{r} + T_* \rho \, ds + (p_* \rho^{-1}) d\rho + \sum_k \mu_{*k} \rho \, d\omega_k, \quad k = 1(1)K, \tag{16}$$

is presumed to be valid for any multicomponent single-phase BFS and represented by specific variables. Inserting the energy form of motion $\mathbf{v} \cdot d\mathbf{i}$ given by equations (14) and (15) and using some simple algebraic manipulations, this Pfaffian can be transformed into

$$de = de_{\mathrm{kin}} - \varphi \cdot d\varphi - [\mathbf{f} - \mathbf{i} \cdot (\partial \varphi / \partial r)_{s, \rho, \omega_k}] \cdot d\mathbf{r} + [T_* - \mathbf{i} \cdot (\partial \varphi / \partial s)_{\mathbf{r}, \rho, \omega_k}] ds$$

$$+ \rho^{-2} [p_* - \rho^2 \mathbf{i} \cdot (\partial \varphi / \partial \rho)_{\mathbf{r}, s, \omega_k}] d\rho + \sum_k [\mu_{*k} - \mathbf{i}(\partial \varphi / \partial \omega_k)_{\mathbf{r}, \rho, s, \omega \neq k}] d\omega_k. \tag{17}$$

Only for reasons of simplicity a possible dependency of φ on the field vector $\mathbf{r}$ may be dropped in the following part. Furthermore, the specific field force $\mathbf{f}$ is presupposed to be conservative. This means that $\mathbf{f}$ only depends on the conjugated variable $\mathbf{r}$ which is equivalent to the fact that there exists a total derivative

$$de_{\mathrm{pot}} := -\mathbf{f}(\mathbf{r}) \cdot d\mathbf{r}, \tag{18}$$

called the specific potential energy.‡ A further simplification may be obtained by partial integration of the energy form $-\varphi \cdot d\varphi$. The result is termed as the "specific dissipation energy":

$$e_\varphi := -\tfrac{1}{2} \varphi^2. \tag{19}$$

Looking back at equation (17), let us build in the last two definitions. Hence, the following set of relationships will arise:

$$e - e_\# := u + e_{\mathrm{kin}} + e_{\mathrm{pot}} + e_\varphi, \tag{20}$$

$$du = T \, ds + p\rho^{-2} \, d\rho + \sum_k \mu_k \, d\omega_k, \tag{21}$$

$$T := T_* - \mathbf{i} \cdot \left(\frac{\partial \varphi}{\partial s}\right)_{\rho, \omega_k}, \quad p := p_* - \rho^2 \mathbf{i} \cdot \left(\frac{\partial \varphi}{\partial \rho}\right)_{s, \omega_k}, \quad \mu_k := \mu_{*k} - \mathbf{i} \cdot \left(\frac{\partial \varphi}{\partial \omega_k}\right)_{s, \rho, \omega \neq k}. \tag{22}$$

There is, of course, more in this set than mere abbreviations; in fact, the set is essentially identical to the last three bracket terms of equation (17). For this reason we cannot identify

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‡ The existence of conservative body forces is needed, provided a viscous flow within a corresponding force field could be described by Euler's law of motion in the frictionless limiting case. This case is theoretically consistent with the thermodynamic principles only if local equilibrium prevails. Such a condition is allowed to be satisfied by equation (18) (cf. ref. [7], p. 36) and the derivation of the Bernoulli equation.

equation (21) with the usual form used in conventional physics. This is also evident from equation (20), by which the common notion of specific internal energy may be defined, but a significant divergence from the norm is indicated. In other words, the classical result only appears under the condition that the vanishing of the dissipation velocity may be justified physically. However, the general case implies that moving systems which do not consist of Eulerian mass points are characterized by an additional kind of energy, viz., e_φ, provided that the specific kinetic energy e_{kin} of those systems is introduced by definition. Very recently, two authors [8, p. 1773] published a similar result arising from the Lagrange multiplier of the entropy generation balance for consistent treatment of irreversible processes via a variational formalism.

The remarkable triplet (22) elucidates the difference between the thermal quantities assigned obviously to different states with respect to motion. Indeed, there exist two ways to identify each of the state quantities with its associate marked by an asterisk. Theoretically, both options may be realized by a zero vector either of the specific momentum $\mathbf{i}$ or the dissipation velocity φ. For this reason it is convenient for the following considerations to introduce symbolically the two items:

■ state at rest:

$$\boxed{\mathbf{i} \to \mathbf{0} \Longleftrightarrow \begin{cases} \varphi \to \mathbf{0} \\ \mathbf{v} \to \mathbf{0} \end{cases}} \tag{23a}$$

■ reversible process:

$$\boxed{\varphi \to \mathbf{0} \quad \Longleftrightarrow \quad \mathbf{i} \to \mathbf{v}.} \tag{23b}$$

A more profound understanding of the above properties and statements is the subject of the subsequent sections. Nevertheless, both items help us begin *to discern in a basic way equilibrium states or processes from non-equilibrium phenomena*. The main argument rests on the *general axiom* that equilibrium is always connected with reversibility, whether the system is in motion or not. Consequently, equilibrium exists only under the condition that relation (23b) is fulfilled. The converse is also assumed to be true: If equation (23b) is not satisfied, the system is in a non-equilibrium state described by the differential form equation (17) for the case of any multicomponent single-phase body-field system.

In view of our research program, a direct consequence of relationships (22) along with the limiting relations (23a) and (23b) arises: The equilibrium pressure p related to the corresponding state at rest, equation (23a), is equivalent to the familiar equation of state $p(T, \rho, \omega_k)$ of the mixture. In contrast to this basic information to be gained by experiments at rest state or by means of statistical physics, the general case of any non-equilibrium event is characterized by the non-equilibrium pressure

$$p_* = -\left(\frac{\partial E}{\partial V}\right)_{\mathbf{P}, \mathbf{r}, S, N_k} \tag{24}$$

according to the GME (4). The respective version of the Gibbs–Duhem relation (cf. ref. [3], p. 134) leads to a dynamic state function $p_*(T_*, \rho, \mu_*, \mathbf{f}, \mathbf{v})$, which significantly diverges from the common equation of state $p(T, \rho, \omega_k)$ by additional characteristic dependencies on the local field strength $\mathbf{f}$ and the flow velocity $\mathbf{v}$. As a rule, it is impossible to determine this dynamic state function with sufficient accuracy for any non-equilibrium phenomena in physics.

These statements are generally true, but they are also inconsistent with the Duhem–Hadamard hypothesis. Consequently, the problem remains whether there are some kind of flow processes, for which applications of this hypothesis may be justified theoretically or, at least, in practice. Clearly, its solution is of far-reaching importance with regard to flow mechanics and thermofluiddynamics. For this reason, first we intend preparing this paper in view of some theoretical aspects concerning kinetic equilibria in

fields. However, the main subject of our paper concerns some efforts to investigate experimentally the influence of motion on the p, ρ, T-behavior of real fluids.

3. KINETIC EQUILIBRIUM IN STATISTICAL MECHANICS

3.1. *Ambivalence between gas kinetics and continuum mechanics*

Thermostatic equilibria and criteria of stability of fluids as well as their mathematical conditions are well-known (cf. ref. [3], p. 39). Both special states are normally restricted to simple thermostatic systems and formulated by means of the Gibbsian thermostatics. Notably, this kind of equilibria yields the theoretical background underlying the concept of local equilibrium states in moving matter. For this reason, it seems desirable to answer the question whether an equilibrium state exists that is formally consistent with fluid dynamics without any recourse to hypotheses like that of Duhem and Hadamard.

The first correct answer was given by J. Clerk Maxwell in 1867, the year in which he published his second kinetic theory as a very special example of predictive statistical mechanics. Irreversibility is built into the kinetic approach and, in particular, into its definition of the collisions operator.

Although Maxwell's second kinetic theory can scarcely be assessed as explaining irreversibility, it is among the standard parts of statistical mechanics the only one to approximate even some of the physical phenomena typically regarded in researches on simple and complex fluid dynamics. The latter include dissipative transfer processes like local friction, heat conduction, and diffusion. Hence, the physical conditions are of interest, which allow to prove the existence of a special state of local equilibrium occurring in any gas or liquid flow. That is why the limiting case figures in our paper. In this section, we aim only to find out what Maxwell's second kinetic theory predicts in view of such so-called kinetic equilibrium states. This well-known theory is designed to represent a moderately rarefied, monatomic gas flowing under certain boundary conditions. The next section is devoted to the same problem, but now solved by means of a familiar method resulting from the classical field theories of fluid dynamics.

Kinetic theories of gases and, as a part of them, the Maxwell–Boltzmann equation concern a level of physical description which apparently belongs to both the macro- and microscopic state of matter. This means that a mesoscopic level of representation is thought to be tenable, where physical reality may be modelled by the help of a microscopic view of matter described mathematically by the rules of macroscopic mass-point mechanics. This "molecular picture" is quite in accordance with those of Navier, Poisson, and Cauchy,

> in which fluids and solids are represented as static or nearly static arrays of point centers of force. Although correct if somewhat special equations were drawn from such hypotheses by those mathematicians, physicists later rejected the molecular models on which they rest, entirely in the case of fluids, and with such qualifications for solids as to bury the starting point. Scientists should use these theories as examples to show that one man's molecules may be another man's poison [1, p. 407].

At present, kinetic theory means different things to different people. Some regard it as the only mathematical method to calculate reliably such transport properties as the viscosity of a gas. Others use it as a special theory, which, while designed to model only the flows of a simple gas, should make it possible to calculate everything about such flows by mathematics alone. Members of a third group focus all efforts on the equilibrium states of liquids and fluids in general.

Notably, the first point of view was rejected by Maxwell and Boltzmann because all methods used for the calculations of transport coefficients did not lead to conclusions independent of the user. It does no better today. The second objective is associated with detailed examinations of arbitrarily great departures from equilibrium. Of the three aspects the last is still actual in view of the famous problem of the trend to equilibrium which is unsolved today. Problems like the difference between gross equilibrium and kinetic equilibrium are of great interest, just as much as all forms of perturbated equilibria.

As to the problem under consideration, it is sufficient to compile a minimum of the voluminous mathematical apparatus usually applied to kinetic theories of gases. In this context, we recommend the concise presentation of Truesdell [1].

Today's kinetic theories of gases take on a definite formal structure in terms of the molecular density F. Presumed to be known, F is defined by the average or the expectation $\bar{u} = \bar{u}(\mathbf{x}; t)$ of a function $u(\mathbf{x}; \mathbf{v}; t)$

$$n\bar{u} := \int uF \, \mathrm{d}\mathbf{v}, \tag{25}$$

where expectations are marked by an overbar. The abbreviations

$$F := F(x_1, x_2, x_3; v_1, v_2, v_3; t), \tag{26}$$

$$\int \ldots \mathrm{d}\mathbf{v} := \int_{-\infty}^{+\infty} \ldots \mathrm{d}v_1 \, \mathrm{d}v_2 \, \mathrm{d}v_3 \tag{27}$$

are introduced for an integral over all components of particle velocities varying between the given limits. The molecular density F denotes the probable number of particles per unit volume in the six-dimensional space $\mathscr{E} \times \mathscr{V}$ of pairs $(\mathbf{x}; \mathbf{v})$ that at time t occupy the place $\mathbf{x}$ in the Euclidean space $\mathscr{E}$ and possess the velocity $\mathbf{v}$ in the vector space $\mathscr{V}$.

The expectations are stochastic and identical to the macroscopically observable quantities by definition. For $u \equiv 1$, we obtain the direct connection between F and the number density $n(\mathbf{x}; t)$ of the particles assuming $n > 0$, provided that $F \geqslant 0$. Then, the mass density ρ is simply $\rho = nm^t$, where m^t is the particle mass. The local gas flow velocity $\dot{\mathbf{x}}$ is the expectation of the local particle velocity $\mathbf{v}(\mathbf{x}; t)$. As its main if not whole concern is to find the constitutive equations of the classical field theories, gas kinetics should be able to define the pressure tensor Π and the heat flux vector $\dot{\mathbf{q}}$ as expectations, too. Whereas the latter is nothing more than a gross manifestation of transfer of the particles' kinetic energy; relative to $\dot{\mathbf{x}}$, the former is, likewise, nothing more than a gross manifestation of transfer of momentum.

The molecular density function F with given velocity $\mathbf{v}$ and position $\mathbf{x}$ at time t changes in two ways: Due to the motions that the particles undergo from the action of a field of body force $\mathbf{b}$ per unit mass, and due to the motions resulting from forces the particles exert on each other. The rates of increase of these two kinds equal one another, since the particles are assumed to be not created or destroyed. The corresponding formula

$$\partial_t F + \mathbf{v} \cdot \partial_{\mathbf{x}} F + \mathbf{b} \cdot \partial_{\mathbf{v}} F = \mathbb{C}[F], \tag{28}$$

first derived from Boltzmann, manifests precisely these physical mechanisms.

Maxwell has modelled the collision term $\mathbb{C}[F]$ being the rate of increase of F due to molecular interactions. In kinetic theories, these interactions are called collisions and are visualized as motions of pairs of molecules subject alone to their mutual attraction or repulsion. In other words, the elementary two-particle interaction between all particles dominates the collisions and constitutes the constraints concerning the validity of the kinetic theory of gases, i.e. is the application to transport phenomena and the size of departures from equilibrium. Above all, this statement agrees with the intention to describe only moderately rarefied monatomic gases as mentioned above. As to the collision operator $\mathbb{C}[F]$, it is sufficient to refer the reader to the modern textbooks of gas kinetics (cf. ref. [9]). Notwithstanding, two points should be stressed.

Using daring stochastic assumptions in reference to the local two-particle collisions only, Maxwell inferred a very special form for $\mathbb{C}[F]$. Inserting this "law" into Boltzmann's balance the famous Maxwell–Boltzmann equation (MBE) results. This is an integro-differential equation distinguished by enormous complexity, for which no one single exact solution exists under realistic conditions.

As the theory presently stands, the MBE is a definition. This is true, for instance, in accordance with Eulerian hydrodynamics, where the formula $\Pi = p_{\mathrm{E}}\mathbf{1}$ is a definition of the hydrostatic pressure p_{E}, which reduces the pressure tensor Π to the tensor unit $\mathbf{1}$. This means that

the arguments of Maxwell and Boltzmann cannot be assessed rationally as anything but heuristic [1, p. 411].

Indeed, we know today that microscopic physics of particles is ruled by the laws of quantum mechanics. The kinetic theory contradicts these laws. The latter obey the reversibility theorem, whereas the kinetic theory represents the gas as a dissipative material system, not just sometimes or probably, but invariably and certainly. Nevertheless, there is nowadays a great interest in kinetic theories, because they are consistent with classical continuum mechanics and afford a special case of it. A kinetic theory is not a theory of molecules;

rather, it affords us a means of taking a certain, very limited account of molecular constitution in formulation a continuum theory of gases [1, p. 412].

It is a theory whose outcome is just one single constitutive equation as an alleged key for the foundation of modern continuum mechanics. Both theories seek the same end, viz., correct relations among gross fields such as the pressure tensor or the evolution of the local specific momentum and specific kinetic energy. However, the reader should bear in mind that the kinetic theory is purely rational, not physical, because its basic physical pictures no longer agree with those of modern nuclear and particle physics. For this reason, its results are much the same in kind as those in ordinary continuum mechanics, they are thoroughly different in detail. First, different gases are above all classified by molecular masses and intermolecular parameters, not by gross quantities. The latter may then be extracted by means of the the MBE. Second, transport coefficients such as viscosity, which in common continuum mechanics are regarded as disposable and available only by experiments, have specific, unalterable forms and values to be determined by mathematical proof and calculation.

3.2. *Maxwell–Boltzmann equation and kinetic equilibrium*

The MBE is a convenient tool to solve the problem of this section, namely, to find the presuppositions of kinetic equilibrium and, then, its consequences for the field equations. Let us start with the total collision operator $\mathbb{C}$ defined by

$$\mathbb{C}u \equiv \int u\mathbb{C}[F]\,\mathrm{d}\mathbf{v} \tag{29}$$

and applied to an arbitrary function $u(\mathbf{x}; \mathbf{v}; t)$. It yields a special change in that function due to all possible collisions, provided that the molecular density before each encounter is F. Maxwell proved a remarkable theorem: Inserting a very special form of $\mathbb{C}[F]$, definition (29) becomes

$$\mathbb{C}u \equiv 0 \tag{30}$$

for distinguished functions $u(\mathbf{x}; \mathbf{v}; t)$.

Identity (30) follows from the requirement that each of these distinguished functions be conserved in any law of encounter admitted in the kinetic theory. Hence, mass, linear momentum, and kinetic energy may be considered. Reduced to the mass unit, the following distinguished functions result:

$$U_{\mathrm{conserved}} = 1,\ \mathbf{v},\ \tfrac{1}{2}\mathbf{v}^2. \tag{31}$$

Clearly, the vanishing of $\mathbb{C}u$ reflects the balance of these state quantities in the gas as a whole, no matter what solution F of the MBE will be considered.

Another important result may be derived from the MBE, which is quite unaffected by the explicit knowledge of $\mathbb{C}[F]$ as well as F itself. Indeed, after multiplying the MBE (28) by a function $u(\mathbf{v})$ of local particle velocity $\mathbf{v}$ and integrating over $\mathbf{v}$-space, one obtains Maxwell's well-known equation of transfer (cf. Truesdell [1], p. 413)

$$(\rho\bar{u})^{\boldsymbol{\cdot}} + \rho\bar{u}\nabla\cdot\dot{\mathbf{x}} + \nabla\cdot(\rho\overline{(\mathbf{v}-\dot{\mathbf{x}})u}) = -m^t\!\int u\mathbf{b}\cdot\partial_v F\,\mathrm{d}\mathbf{v} + m^t\mathbb{C}u, \tag{32}$$

the superscript dot on the first summand denotes the material derivative.

If we put functions (31) one after the other and use identity (30), the following field equations result:

$$\dot{\rho} + \rho\,\nabla\cdot\dot{\mathbf{x}} = 0, \tag{33a}$$

$$\rho\ddot{\mathbf{x}} = -\nabla\cdot\Pi + \rho\mathbf{b}, \tag{33b}$$

$$\rho\dot{\varepsilon} = -\,\Pi\cdot\nabla\dot{\mathbf{x}} - \nabla\cdot\mathbf{q}. \tag{33c}$$

These partial differential equations are of just the same form as those expressing the balance of mass, linear momentum, and total energy in the continuum mechanics of a single medium devoid of body heating. Thus, the kinetic gas appears to be a special kind of continuum as far as pure mechanics is concerned. However, thermodynamics is another matter. This is indeed a crucial point, because there are many misconceptions about the role of mechanically motivated pictures for kinetic theories. As to the "kinetic" equations (25)–(33), Truesdell advisedly refrained from use of temperature because

in the kinetic theory of monatomic gases it is simply a multiple of the energetic. We wished to leave nobody a chance to miss the strictly mechanical character of the kinetic theory [1, p. 405].

In other words, temperature, like energetic ε, is regarded as but another name for expected kinetic energy of relative motion, i.e.

$$\tfrac{3}{2}k_{\mathrm{B}}T := \tfrac{1}{2}m^{t}\mathbf{c}^{2}, \quad \mathbf{c} := \mathbf{v} - \dot{\mathbf{x}}, \tag{34}$$

where k_{B} is the Boltzmann constant.

Originally, entropy S has not yet been defined in the kinetic theory. Hence, the usual canonical relationship between T and S cannot be established. As a consequence, the common relationship between entropy and thermodynamic equilibrium is unavailable. For this reason, a concept of equilibrium is needed first to arrive at a basis for thermodynamic elements within the concept of the kinetic theory presented.

Following Maxwell, current kinetic approaches regard as being appropriate to equilibrium any molecular-density function F^{equ} such as to be unaltered by collisions. This means that the right-hand side of the MBE identically vanishes. As an inference from this identity,

$$\mathbb{C}\left[F^{\mathrm{equ}}\right] \equiv 0, \tag{35}$$

it can be rigorously proved that any such function F^{equ} is of the general form

$$F^{\mathrm{equ}} = a\exp(-b\mathbf{c}^{2}) \tag{36}$$

in which a and b are positive functionals of some parameters such as the mass density ρ, the particle mass m^{t}, and the temperature T according to equation (34) and implicitly depending on position $\mathbf{x}$ and time coordinates t. Such an F^{equ} is called a Maxwellian molecular density.

As to the topic of this section, the most interesting consequence of definition (35) along with solution (36) concerns concrete statements about the pressure tensor and the heat flux vector $\dot{\mathbf{q}}$. For kinetic equilibrium, defined by identity (35), these two non-equilibrium quantities and $\dot{\mathbf{q}}$ tend towards the hydrostatic pressure p_{E} and vanishing $\dot{\mathbf{q}}$. Inserting these limiting quantities

$$F \to F^{\mathrm{equ}} \Rightarrow \Pi \Rightarrow p_{\mathrm{E}}^{*}\mathbf{1}, \quad \dot{\mathbf{q}} \Rightarrow \mathbf{0}, \tag{37}$$

another characteristic feature of gas kinetic appears: The main pressure p^{*} defined as the trace of Π (i.e. $\mathrm{tr}\,\Pi$) is related to the kinetic temperature in such a way that the ideal gas law holds for every condition of the gas. Hence, it is also true for non-equilibrium states.

The relationships

$$p^{*} := \frac{k_{\mathrm{B}}}{m^{t}}\rho T = \frac{2}{3}\rho\varepsilon \tag{38}$$

serve as a double definition for the main pressure p^{*} and the energetic ε. Hence, there is a difference $\Delta p := p^{*} - p_{\mathrm{E}}^{*}$ between these two pressures, at which Δp only vanishes under dissipationless equilibrium conditions according to equations (35) and (37). This result does formally agree with equations (22) and (23) derived from AT.

Nevertheless, a significant divergence arises, provided that, for instance, the pressure tensor Π, postulating the scalar functions—hydrostatic pressure ϖ, shear viscosity μ as well as the second viscosity μ_v—of the Navier–Stokes–Fourier equation of motion [1, p. 426], is defined as

$$\Pi := \varpi\mathbf{1} - \{\mu_v(\mathrm{tr}\,\mathbf{D})\mathbf{1} + 2\mu\mathbf{D}\}. \tag{39}$$

As usual, the stretching $\mathbf{D} \equiv \frac{1}{2}[\nabla\dot{\mathbf{x}} + (\nabla\dot{\mathbf{x}})^{\mathsf{T}}]$, and ϖ, μ, and μ_v are functions of ρ and T. The scalar functions are assigned by hypothesis or determined by experiments.

Taking the trace of equation (39), the result yields, along with equation (37) the formula

$$p_{\mathrm{E}}^* = \varpi - (\mu_v + \tfrac{2}{3}\mu)\mathrm{tr}\,\mathbf{D}. \tag{40}$$

Truesdell's comment is remarkable [1, p. 409]:

> If $\mu_v + (2/3)\mu \neq 0$, equation (40) implies the ridiculous conclusion $\mathrm{tr}\,\mathbf{D} = \mathbf{f}(\rho, T)$; that is, the expansion is determined by the density and temperature. In order for arbitrary expansions at any given density and temperature to be possible, it is thus necessary that the Stokes relation hold:

$$(\mu_v + \tfrac{2}{3}\mu) \equiv 0. \tag{41}$$

There is no reason to accept Truesdell's conclusion, provided that ϖ is assumed as a non-equilibrium pressure. In this case, equation (40) formally confirms equation (22b) of the AT, but also reveals the inconsistency between the kinetic theory and the Navier–Stokes approach: Equation (40) cannot tend to the identity $p_{\mathrm{E}}^* \equiv \varpi$, because there is no quantity such as the dissipation velocity φ which admits the vanishing of its last term without using the Stokes relation.

That is not all. Clearly, solution (36) of the RHS of equation (28) implies a corresponding solution of the LHS of the MBE. In other words, F^{equ} also has to satisfy the equation

$$\partial_t F^{\mathrm{equ}} + \mathbf{v} \cdot \partial_{\mathbf{x}} F^{\mathrm{equ}} + \mathbf{b} \cdot \partial_{\mathbf{v}} F^{\mathrm{equ}} \equiv 0. \tag{42}$$

In the special case when the body force $\mathbf{b} \equiv \mathbf{0}$, it is easily proved that the most general Maxwellian solution of equation (42) corresponds to the velocity field

$$\dot{\mathbf{x}} = [\tfrac{1}{3}d(t)\mathbf{1} + \mathbf{W}(t)] \cdot \mathbf{x} + \mathbf{e}(t), \tag{43}$$

where the scalar $d(t)$ is the expansion, the skew tensor $\mathbf{W}(t)$ is the spin, and $\mathbf{x}$ is the position vector with respect to some origin. The vector $\mathbf{e}(t)$ denotes an indeterminate integration function. A flow described by equation (43) represents a uniform dilatation superposed upon a rigid motion. Since $\mathbb{C}[F^{\mathrm{equ}}] \equiv 0$, flows of this special kind are isentropic by definition, that is dissipationless in accordance with equation (37). Consequently, the field equations (33a)–(33c) become

$$\dot{\rho} + \rho d(t) = 0, \tag{44a}$$

$$\rho\ddot{\mathbf{x}} = -\nabla p_{\mathrm{E}}^* + \rho\mathbf{b}, \tag{44b}$$

$$\rho\dot{\varepsilon} = -p_{\mathrm{E}}^* d(t), \tag{44c}$$

where the continuity equation (33a) and the energy equation (33c) are modified by means of the relation $d(t) = \nabla \cdot \dot{\mathbf{x}}$ following from solution (43). Note that equation (44b) is reduced to the form of the famous Euler equation of motion. It is true though that in those days Euler used the hydrostatic pressure introduced by himself in 1738.

It is easy to see that for a rigid motion defined by $d(t) \equiv 0$ the strong restrictions

$$\rho = \text{constant}; \quad \varepsilon = \text{constant}; \quad T = \text{constant}; \quad \rho = \text{constant}$$

follow directly from equations (33a), (44c), (34) and (38). A second, more realistic approach results from combining the equations (44a) and (44c) along with equation (38):

$$\dot{\rho} - \frac{\rho^2}{p_{\mathrm{E}}^*}\dot{\varepsilon} = 0 \Rightarrow (\ln\dot{\rho}) - \frac{3}{2}(\ln\dot{\varepsilon}) = 0. \tag{45}$$

This set of differential equation for an interval of time yields the general solution

$$p_E^* \rho^{-5/3} = \text{constant}, \tag{46}$$

and so these motions are isentropic expansions of a perfect gas having $5:3$ as the ratio of its specific heats, assumed constant. In other words, the right-hand side of the MBE is directly responsible for the equilibrium concept of the kinetic theory, whereas its left-hand side leads to an isentropic process of the gas flow. It is evident that the process is running along a path of local equilibrium states.

Of course, this far reaching consequence is due to the equilibrium distribution function resulting from $\mathbb{C}[F]$ and escorted by zero-valued transfer of such properties as heat conduction and viscous shearing. Such an equilibrium solution refers to time- and space-dependent velocity fields, wherein some gradients like those of local pressure and flow velocity exist.

To sum up this section, the following items may be stated

- Despite definitely existing gradients, an equilibrium flow of real fluids may occur. This matter of fact is phenomenologically demonstrated for a prototype of kinetic equilibria and its description: Euler's equation of motion.
- Kinetic equilibrium may be realized as the reversible limiting case of real, and this can only mean, dissipative flow.
- As for the concept of the AT, the results derived from kinetic theory of gases are inconsistent with the approach of the Navier–Stokes theory for compressible fluids.

Although these statements follow from a very special kind of physical imagination along with an unrealistic model of matter, the main results of the analysis well agree with experience. They may be summarized by Wang's definition of local kinetic equilibrium [1, p. 415]:

$$F^{\text{equ}}(\mathbf{x}; \mathbf{v}; t) = F^{\text{equ}}(\mathbf{x}; \mathbf{v}) = F^{\text{equ}}(\mathbf{x}; -\mathbf{v}). \tag{47}$$

That is, F^{equ} shall be steady and invariant under reversal of velocities. But, in contrast to the ordinary version of thermodynamic equilibrium, kinetic equilibrium includes the existence of certain gradients like those of local velocity and pressure. Obviously, it is desirable to know another and independent proof of that notable result that is more trustworthy with respect to its physical fundamentals. The next section offers a corresponding approach.

4. KINETIC EQUILIBRIUM IN FIELDS

Now as before, classical hydrodynamics is lacking in modern designations for the comprehension of basic terms like equilibrium, steady state, dissipation, reversibility, etc. Fortunately, modern methods enable us to design a mathematically consistent field theory that avoids paradoxes similar to those discussed below. Here, we prefer the so-called Gibbs–Falkian dynamics (cf. ref. [3], p. 166). But let us first make some remarks on the common practice to take the limit of vanishing viscosity as an allowed path to reversible processes in the sense of Wang's definition of local kinetic equilibrium.

There are only a few ambitious treatises on rational hydrodynamics that deal with perfect fluids defined as frictionless (i.e. reversible) flows. It is characteristic for those mathematical theories to look upon any dissipationless flow as one of the various paradoxes of fluid dynamics (cf. ref. [10]). In one of his famous Princeton lectures, Weyl, the great mathematician and natural philosopher, outlined this prejudice in a few words: "The following paradox arises in connection with viscous fluids: If a perfect fluid is to be regarded as the limit of a viscous one as the viscosity $\eta \to 0$, then how is it that the viscous fluid sticks to the boundary, even with small η, while the perfect fluid glides smoothly?" [11, p. 61]. Unfortunately, little else can be found on this topic in modern textbooks. Of course, Weyl's question is part of the fundamental problem of what extent Euler's equation of motion may be considered as a limiting case of the Navier–Stokes equation of motion. This is particularly true with regard to the fact that the viscosity of a fluid as well as its heat capacity is unanimously treated either as a constant or as a material function only depending on the

local state variables. Under such a premise, however, the limit $\eta \to 0$ may perhaps be justifiable mathematically, but in principle it is physically inadmissible.

In order to consider equilibria in extended and continuous regions, it is sufficient to regard the limiting case of field quantities, i.e. infinitesimal phases according to the familiar rules. For this purpose, all extensive quantities Z_i have to be replaced by the pertaining densities $\xi_{V,i}$ ($i = 0, 1, \ldots, l$), which may be treated as functions of space and time. As an example, the entropy density S_V may be mentioned.

Given the $\xi_{V,0} = G_V(\xi_{V,1}(x), \ldots, \xi_{V,l}(x), x)$, assumed to be substantial for any infinitesimal volume element dT of the region $\mathscr{B}$, the reader should take into account that the dependent quantity $\xi_{V,0}$ may be explicitly independent of the position vector $\mathbf{x}$. In this special case the density function G_V will describe the same infinitesimal system at all places of $\mathscr{B}$. Consequently, $\xi_{V,0}$ only depends implicitly on the $\mathbf{x}$-functions of the other variables.

By integration of each density $\xi_{V,i}$ over the whole region $\mathscr{B}$,

$$\xi_i = \int_{\mathscr{B}} \xi_{V,i} \, dV, \quad i = 0(1)l, \tag{48}$$

the extensive quantities Z_i assigned to $\mathscr{B}$ will result. Within this region exchange processes occurring between infinitesimal phases tend towards phase equilibria defined by the general variational condition

$$\delta E = \int_{\mathscr{B}} \xi_{V,i} \, dV \equiv 0, \quad i = 0(1)l, \tag{49}$$

which expresses the mutually unrestrained interaction of the ith density $\xi_{V,i}$ between the volume elements dT. Let $\xi_{V,0}$ be the energy density, then the total energy E determined by equation (48) has to be minimized corresponding to the basic problem

$$\delta E = \int_{\mathscr{B}} \delta E_V[\xi_1(\mathbf{x}), \ldots, \xi_l(\mathbf{x}), \mathbf{x}] \, dV \equiv 0. \tag{50}$$

of the variational principle.

By means of Lagrange's method of multipliers λ_i, it is easy to incorporate the finite number of supplementary conditions (49) into the optimization

$$\int_{\mathscr{B}} \left\{ \left(\frac{\partial E_V}{\partial \xi_{V,1}} - \lambda_1 \right) \delta \xi_{V,1} + \cdots + \left(\frac{\partial E_V}{\partial \xi_{V,l}} - \lambda_l \right) \delta \xi_{V,l} \right\} dV \equiv 0 \tag{51}$$

yielding the solutions

$$\frac{\partial E_V}{\partial \xi_{V,l}} = \lambda_i, \quad i = 1(1)l, \tag{52}$$

which are the corresponding intensive variables, i.e. $\lambda_i \equiv \zeta_i$ for all values of the index i.

This means that for equilibrium of region $\mathscr{B}$ the conjugates of the variables $\xi_i(x)$ with respect to the total energy E have an identical value λ_i ($i = 1, \ldots, l$) for all x in $\mathscr{B}$. The resulting statement turns out to be in no way trivial and will be demonstrated below:

> ✱ Inside any spatially extended region $\mathscr{B}$ each *intensive* variable ζ_i which is conjugated to the density $\xi_{V,i}$ has the same value everywhere, provided that local *kinetic equilibrium* prevails in $\mathscr{B}$.

It is remarkable that this theorem completely agrees with the findings following from the Boltzmann equation mentioned above. Thus, in kinetic equilibrium, for example, the existence of an entropy density enforces an isothermal region $\mathscr{B}$ for which local heat fluxes are suppressed. Hence, the derived assertion about kinetic equilibrium is a *limiting value theorem concerning non-equilibrium phenomena.*

By Legendre transformation of equation (16) with respect to the mass density ρ, we get the Pfaffian for the Legendre-transformed specific energy $e[\rho]$,

$$\rho \, de^{[\rho]} = \mathbf{v} \cdot \rho \, di - \rho \mathbf{f} \cdot d\mathbf{r} + T_* \rho \, ds + d\rho_* + \sum_k \mu_{*k} \rho \, d\omega_k, \quad k = 1(1)K. \qquad (53)$$

Note that this Pfaffian contains a single energy form without a conjugate variable. As this differential form also holds true for any constant mass density ρ, equation (53) may thus be expressed by densities $\xi_{V,i}$ as variables. Hence, the boxed statement is inapplicable for the pressure p_*. But it may be applied the other way round: Assuming an explicit dependency of the Legendre-transformed energy density $E_{*V}^{[V]} = \rho e_*^{[\rho]}$ on the position vector $\mathbf{x}$, the pressure p_* is a generally well-defined and non-constant function of $\mathbf{x}$, provided that kinetic equilibrium prevails in $\mathscr{B}$. Simultaneously, a second energy form loses its conjugate variable: According to equation (23) the specific momentum $\mathbf{i}$ equals the flow velocity $\mathbf{v}$ under the condition that kinetic equilibrium may be identified with a reversible process. Then again for constant density ρ, the energy form of motion will change from $(\rho \mathbf{v} \cdot \mathbf{i})$ to $dE_{\mathrm{kin,v}}$ with the consequence that this special kind of energy density also is a well-defined and non-constant function of $\mathbf{x}$. For this reason, in a region $\mathscr{B}$ presumed to be subject to kinetic equilibrium, there may be simultaneously existing gradients of pressure and velocities. Naturally, they cause flow of the kind described by the Euler equation of motion.

This result is inconsistent with the more naive postulates preferred by some adherents of rational mechanics and exemplified as follows: A steady state with time independent variables and no temperature gradient, no symmetric velocity gradient and no dissipative fluxes is called an equilibrium (cf. ref. [12]).

5. A NEW APPARATUS FOR p, ρ, T-MEASUREMENTS

5.1. *The experimental equipment*

During the last decade, a new apparatus for precise pressure–density–temperature measurements of fluids was designed and installed at our institute. It enables us to execute repeatable experiments with a fluid in an equilibrium state.

The core of the whole set-up is sketched in Fig. 2. The measuring cell was constructed as a cylinder with a piston allowing to vary its volume V. For a constant amount of the fluid's mass its density ρ may be changed by variations of V. Working with very small increments of V even reliable values of derivatives may be determined with respect to the pressure or
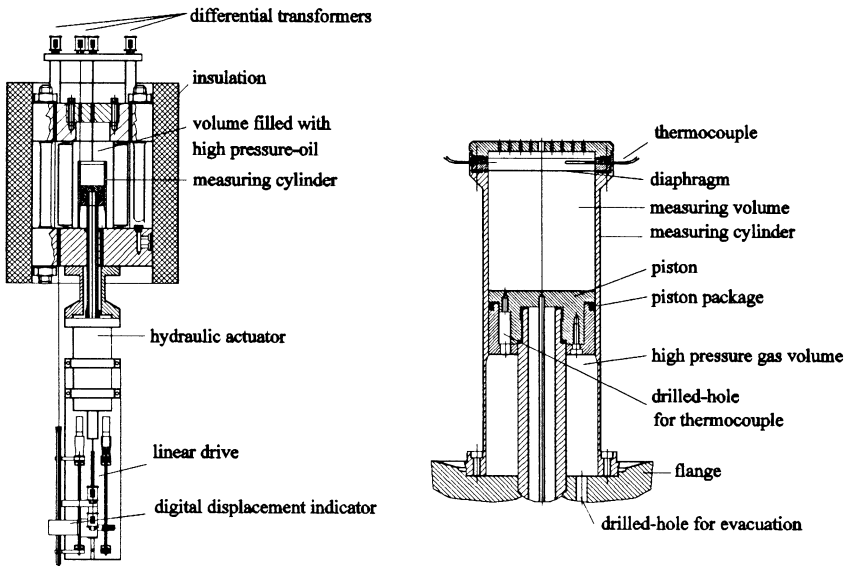

Fig. 2. Cross-sectional view of high-pressure autoclave with piston positioning system and the measuring cell mounted inside the autoclave.

temperature of the fluid. With the option to vary the sample density, a large area of the p, ρ, T-surface can be measured in a short time.

The p, ρ, T-measuring system is equipped with a computer-aided data acquisition and controlling device. It admits the fully automatic operation of the apparatus up to 60 MPa in a temperature range from ambient temperature condition to 600 K.

The measuring cylinder is vertically mounted inside a high-pressure autoclave. The free volume between the cylinder surface and the inner wall of the autoclave is filled with oil. Pressure equality between the sample fluid and the oil is realized by a 50 μm diaphragm on the upper side of the measuring cylinder and maintained by a safety and control device. The adjustable piston on the lower side of the measuring cell can be moved by means of hydraulic actuator with a precision of 1 μm.

The uncertainty of the volume measurement is less than 0.01%. To reduce the leakage of the sample fluid through the piston packing, the free volume below the piston is filled with a blocking gas which is always kept by separate monitoring on the same pressure level as the sample fluid. This is additionally necessary to achieve zero stress condition in the cylinder wall. Thus, the latter cannot be deformed by mechanical stress, and, therefore, the cylinder wall can be produced very thin.

5.2. *Experimental procedure and results*

Using the new set-up, an open basic problem in physics, the trend to the thermodynamic equilibrium can be investigated by means of precise p, ρ, T-measurements. In fact, we only report on our first, provisional experiments. For future work, we plan to equip the set-up for more detailed and refined measuring procedures.

First, the starting point of the temperature–density profile to be prepared in time within the measuring cell is fixed as input parameter for the control program. The latter also controls the positioning of the piston and powersetting of the heaters. After fixing the input parameter, the corresponding values of the fluid temperature and density tend to achieve an equilibrium state. It is defined by zero convection within the measuring cell and experimentally proved by overall constant values of temperature and pressure. Changes of state start and run in reference to the initial profile. The p, ρ, T-triple of values is automatically registered, and the control program then heads for the next preprogrammed set-point. Recording of the p, ρ, T-data is done continuously.

Capability and reliability of the apparatus were demonstrated by means of measurements of nitrogen (N_2), carbon dioxide (CO_2) and propane (C_3H_8). The accuracy of the measurements is within the desired limit of 0.05%. In addition to these measurements, the universal trend to the thermodynamic equilibrium has been investigated for propane. To realize a lot of well-defined non-equilibrium states, the temperature of the fluid is varied by compressing or decompressing the sample gas by moving the piston, while the high-pressure oil temperature is kept constant.

Figure 3 shows a temperature rise in the measuring cell, while the sample gas is compressed by moving the piston upward. The temperature starts rising up to a certain limit and remains constant as long as the compression process is going on. In this period, the heat flux through the cylinder wall is as large as the power consumption of the system due to compression for the case that the temperature of the high-pressure oil is kept constant.

This characteristic intermediate course of the temperature profile runs into the final course of the process defined as the universal trend to thermodynamic equilibrium. Note that for small changes of state, a well-posed experimental status can be observed, i.e. the measuring procedure is distinguished by sufficient accuracy along with high reproducibility. This experience led us first to select processes allowing only small changes of state properties. The latter may be preferred because they meet the main requirement on the quality of the test results, viz., to be reliable with regard to statements concerning the Duhem–Hadamard hypothesis.

In order to establish the final state at rest of the fluid, a resistance thermometer as well as several thermocouples are installed inside the measuring cell. In addition, its wall is equipped by a series of thermocouples applied to control the heat transfer densities between
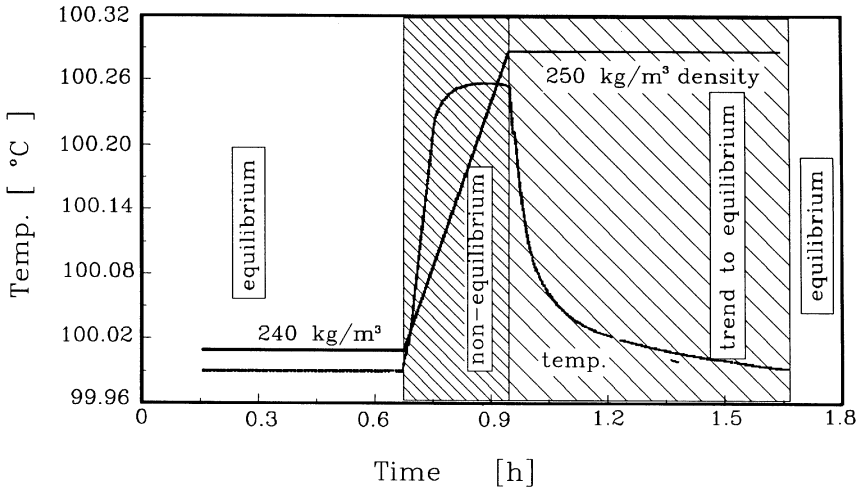
Fig. 3. Temperature–time course during compression and expansion of propane.

the fluid and the high-pressure oil outside the cell. One of the decisive criteria to constitute experimentally the state of thermodynamic equilibrium is fulfilled under the condition that, in principle, all local temperature gradients with respect to the direction of each radius of the test cylinder become approximately zero at the cylinder wall. In practice, this requirement is controlled by only a few temperature sensors built in the wall at various representative positions. Simultaneously, the thermometers installed inside the fluid must agree on their local values of temperature. In other words, the fluid is considered to be in thermodynamic equilibrium when the temperature of the fluid remains unchanged for 1 h at least, while the overall pressure and the density of the fluid is kept constant.

At the beginning of a test sequence the pressure of the real fluid is first determined for an equilibrium state. It may be described by its thermal equation of state

$$p_{\text{equ}} := Z(T, \rho)RT\rho, \tag{54}$$

where $Z(T, \rho)$ means the real gas factor of the fluid in question. Generally, it is experimentally established. For propane as test fluid the function $Z(T, \rho)$ is well known.

The test procedure is initiated by a well-defined change of the density ρ. It is realized by means of the piston to be moved for a prescribed distance during a definite time interval. Meanwhile, the temperature of the heat bath around the measuring cell is kept constant and agrees with the initial equilibrium value of the fluid temperature. This constraint guarantees that the disturbed fluid temperature finally tends again to that initial value. This means that the whole measuring period runs from the starting point until the point in time, where the new state of thermodynamic equilibrium is proved to have been reached.

The mean value of the mass density is linearly changed from its initial value to its final value. Simultaneously, all temperatures and pressures of the fluid change their values. They may be measured as functions of time at some arbitrary, but representative positions inside the measuring volume filled with a definite amount of mass.

For the analysis of the data, it is convenient to introduce the differences Δp and ΔT,

$$\Delta p := p_{\text{equ}} - p_*,$$

$$\Delta T := T_* - T_{\text{equ}}, \tag{55}$$

between the two pressures p_{equ} and p_* and the respective temperatures. The quantity p_* is determined in any reachable non-equilibrium state as a function of time, whereas the equilibrium pressure p_{equ} means the flexible reference value computed by equation (54) for the corresponding time-dependent values of T_* and ρ. On the contrary, the reference temperature T_{equ} may be simply fixed by the constant initial temperature prescribed to be equal to the limiting temperature of the universal trend towards thermodynamic equilibrium.

As a rule, measured values were recorded at 15 min intervals; shorter time intervals were needed during considerable increases of the deviation between the actual non-equilibrium values and their flexible reference values; long time intervals are sufficient near actual equilibrium states. For all cases, each sensor for the temperature measurements inside the test chamber indicates a reliable and accurate result at the respective measuring junction selected. It is a crucial point for the measuring procedure that the corresponding time-dependent temperature values registered simultaneously by all sensors at different positions only disagree in such a way that the averaged differences are relatively small compared to the absolute value of the averaged fluid temperature.

This observation enables us to restrict our measuring procedure to a single measuring junction, where the fluid is allowed to be characterized by the value of the local measured temperature and the mean density value, provided that the pressure is uniform inside the test cell. This assumption is well-founded by the fact that changes in pressure are propagated with speed of sound. As a consequence, the time-dependent value of the fluid pressure may be determined at an arbitrary measuring junction. Our measurement device offers the option to record the actual pressure value by means of the pressure balance technique described above.

Figure 4 shows the deviations Δp as a function of time. There are three time zones differing in that considerable divergences appear with respect to the time dependency of all thermal properties. Clearly, the first period substantiates the common equilibrium behavior. The second and third periods reveal characteristic patterns of non-equilibrium phenomena: With the beginning of the compression the differences Δp between the non-equilibrium values and the equilibrium data start raising. Then, when the compression gets stopped, the temperature difference between the fluid and the surrounding oil continuously reduces towards zero due to unsteady heat fluxes between the two partial systems. In other words, even when the fluid temperature remains constant, Δp is increasing, though the fluid still gets compressed.

The last period relates to the universal trend towards thermodynamic equilibrium. Obviously, the courses of the fluid temperature and pressure seem similar to the idealized results first derived from Maxwell and later extended by Truesdell to the theorem that there is

an analytical function of time which relaxes exponentially to its equilibrium value, and no relaxation time is longer than that for the flux of energy [1, p. 456].

Summing up the experimental results, characteristic differences between equilibrium and non-equilibrium quantities could be clearly revealed. This result is predicted by the "Alternative Theory" and attributed to fluid convection: Suprisingly, those differences even occur if the fluid system is weakly disturbed. This observation agrees with Falk's analysis according to which any system outside an equilibrium state obeys thermodynamic basic
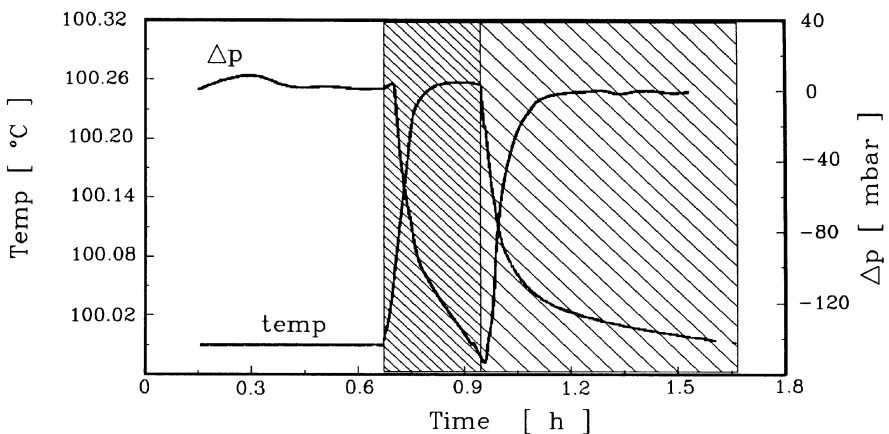

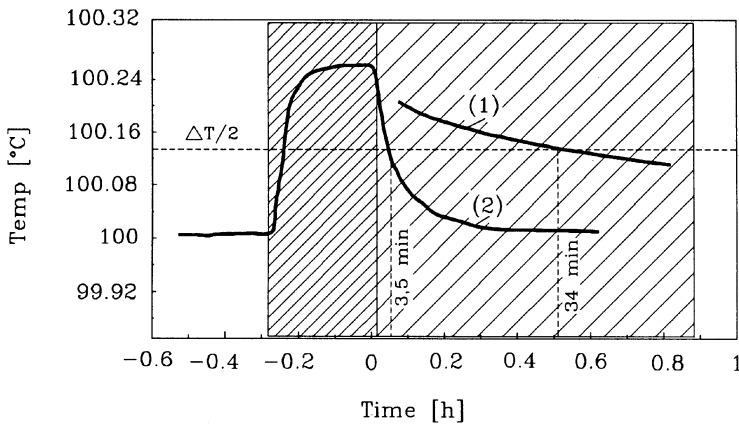Fig. 4. Pressure difference Δp during the non-equilibrium process.

Fig. 5. Temperature equalization by (1) pure conduction and (2) real conduction.

laws proved to be dependent on flow velocity of the fluid also for small values [4, S. 325]. For this reason, local dissipation arises and prevents all real flows from running reversibly or in a quasi-static way from state to state. Consequently, our provisional experiments lead us to suppose that *the Duhem–Hadamard hypothesis cannot experimentally be justified*, not even for small disturbances of convective motions.

However, such an inference does not mean that the use of the equations of state for flow description is erroneous. An essential part of the AT deals with the problem to transform the basic constitutive equations of the field theories in such a way that equations of state established for thermodynamic equilibrium are allowed to be applied to flow mechanics (cf. ref. [3], p. 183f).

Although the experimental facts speak for themselves, it may be useful to estimate the order of magnitude of the occurring flow velocities. Of course, their values are small in accordance with the largest pressure difference of about 150 mbar along the second time zone (cf. ref. [2], p. 60). Even so, nothing indicates that this creeping flow can be approximately described by the Eulerian equation of motion, provided that kinetic equilibrium is supposed to be only an unrealistic limiting case. However, our data are not sufficient with respect to their extent and quality in order to decide, whether there is a flow region, where kinetic equilibrium prevails. To do so, a subtly differentiated investigation is needed concerning the differences between the mean mass density of the fluid and its local density as a time-dependent function of the respective local temperature.

Another crude approximation should be noticed concerning non-stationary heat conduction for comparison. It is assumed that the fluid inside the measuring cell is allowed to be idealized as a kind of cylindrical solid body of an overall mean fluid density and with unlimited length in order to guarantee a spatially one-dimensional arrangement. Furthermore, a spatially unified temperature difference between the body and its surrounding heat bath is presupposed to consider the overall heat transfer between them. Then, the transient motion towards thermodynamic equilibrium may be estimated by means of the algebraic solution for the respective pure heat conduction problem as given in many textbooks (e.g. ref. [13], p. 53f).

The corresponding curve resulting from integration of that solution with respect to the cylinder radius is also sketched in Fig. 5. It is evident that pure conduction in the fluid is not sufficient to generate a heat flux causing the measured temperature profile. As a conclusion, convection may be supposed to become the essential mechanism even for small values of flow velocities.

6. CONCLUSION

A new apparatus for p, ρ, T-measurements was recently developed and successfully tested by precise experiments for some substances and their mixtures. The measurement range

runs from ambient temperature and pressure up to $180°C$ and 150 bar, respectively. The pecularity of the set-up concerns the option to vary freely the mass density of the fluid to be measured. Thus, it is possible to investigate experimentally an open issue of fluid dynamics, the so-called Duhem–Hadamard hypothesis, i.e. the assessment that the pressure of a dissipative flow system is allowed to be replaced by the fluid's equation of state established only for states at rest.

In a first series of provisional measurements, the test results are supposed to contradict Duhem's and Hadamard's expectations. The new set-up admits to induce a sequence of definite non-equilibrium states by means of a piston moved in the cylindrical measuring volume. The piston changes the mass density of the fluid in question in a precise manner and disturbs simultaneously the initial equilibrium state of the fluid. As the temperature of the heat bath wherein the measuring volume is embedded, is kept constant, the fluid tends to a new state of thermodynamic equilibrium fixed by the initial and unchanged temperature. This universal transient motion is characterized by profiles of temperature and pressure as time functions, which cannot be described by the corresponding equation of equilibrium states. With the reservation that improved experiments will confirm our data in more detail, the interpretation of the experimental results obeys the theoretical prediction offered in particular by the Alternative theory. It concerns, above all, the decisive difference between equilibrium and non-equilibrium states of a flow caused by dissipative transfer modes even for small flow velocities inside a vessel where no-slip conditions prevail at the walls.

A last point should be noted: both Maxwell's second kinetic theory of gases and the Gibbs–Falkian thermodynamics predict a flow region, where states of kinetic equilibrium exist. Unfortunately, the extent and quality of our data are not sufficient to confirm at present this important theoretical result. For this reason, improved measurement devices are in preparation.

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