STUDIES IN STATISTICAL MECHANICS

VOLUME VI

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THE KIND OF MOTION WE CALL HEAT

A HISTORY OF THE KINETIC THEORY OF GASES IN THE 19th CENTURY

BOOK 1

Physics and the Atomists

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Preface

These two books bring together the contents of 15 articles (and parts of three others) on aspects of the history of kinetic theory and statistical mechanics, published in various places during the last two decades. The introductory chapter and the bibliographical survey at the end, as well as several other sections, have been added to provide a reasonably comprehensive and coherent picture of the entire subject, though without attempting to go beyond the boundaries of the 19th century or to cover in depth the numerous applications of the theory even within that century. All chapters have been revised in the light of my own current research and the secondary literature up to June 1975. The organization of the books is explained in §1.1.

The project originated as a paper for Thomas Kuhn's seminar at Harvard in 1954, and I have profited from his advice and criticism on numerous occasions since. My colleague C. W. F. Everitt has generously made available his extensive fund of information on James Clerk Maxwell and the Victorian scientific community, and is the co-author of §5.5. Several chapters have been improved and some serious errors avoided thanks to the technical and editorial scrutiny of C. Truesdell, whose encouragement has been especially appreciated. Elliott Montroll first urged me to put together the books in the present form. Other colleagues have contributed valuable suggestions and information: S. R. de Groot, W. Flamm, E. W. Garber, D. ter Haar, F. C. Haber, R. Hahn, Sir Harold Hartley, E. Hiebert, Gerald Holton, H. Kangro, Martin J. Klein, J. L. Lebowitz, P. E. Liley, E. A. Mason, E. Mendoza, A. Michels, R. G. Olson, N. H. Robinson, J. S. Rowlinson, J. V. Sengers, H. I. Sharlin, and J. D. van der Waals Jr.

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CHAPTER 1

The Kinetic Theory in the History of Physics

When Max Planck and Albert Einstein introduced the quantum theory of radiation at the beginning of this century, they used the statistical methods of James Clerk Maxwell and Ludwig Boltzmann to derive observable properties from their hypotheses. And the extensive development of the kinetic-molecular theory of matter in the late 19th century had familiarized many scientists with a probabilistic viewpoint, in contrast to the earlier presumption that all the details of atomic behavior are determined, at least in principle, by mechanical laws and boundary conditions. Thus the kinetic theory played an important part in the transition from classical to quantum physics, on the computational as well as the conceptual level.

At the same time it is fair to say that the kinetic theory of gases was one of the most typical and comprehensive applications of the mechanistic approach in science, very much in the spirit of the 17th-century "mechanical philosophers" – Boyle, Descartes, and Newton (though its physical assumptions differed in important details from the way those thinkers described the atomic structure of matter). For this reason, it has often been associated with the corpus of classical theory that was replaced, as a set of fundamental principles, by 20th-century quantum mechanics and relativity. The "billiard-ball" atom and the luminiferous ether are now supposed to be obsolete.

It is true that the Maxwell–Boltzmann kinetic theory failed to provide a completely consistent mechanical explanation of all properties of gases, the most notorious difficulty being the ratio of specific heats of polyatomic gases. Although in retrospect we can see that this failure resulted from the invalidity of Newton's laws at the atomic level, I do not think it was regarded as an anomaly serious enough to justify either rejecting those laws or discarding the kinetic theory which had been successful in most other applications. Nor was the hypothetical "ultraviolet catastrophe" of black-body radiation (a deduction from Maxwell–Boltzmann statistical mechanics) considered a fatal defect of classical physics, leading to its replacement by quantum theory, as one so often reads in modern textbooks and popular histories of physics. While the development of kinetic theory did stretch Newtonian mechanics beyond its limits of validity, the immediate result of this process was a plastic yielding, not a sharp break.

Most of the basic features of modern kinetic theory can be recognized as direct outgrowths of the work of Maxwell and Boltzmann, building on the more intuitive ideas of Rudolf Clausius and J. D. van der Waals. The quantum theory of matter can be incorporated into the theory without changing its overall character, except insofar as phenomena such as superconductivity and the superfluidity of liquid helium allow this quantum nature to manifest itself in a more spectacular way on the macroscopic level.

The secure place of kinetic theory in modern physics is evident from the most cursory examination of textbooks and departmental curricula. More surprising perhaps is the widespread influence of the mode of thought characteristic of 19th-century kinetic theory on many areas of 20th-century science. This goes beyond explicit analogies such as the "kinetic theory of traffic flow," and affects the way people discuss scientific methods and the kinds of results they expect to get from scientific theories. The kinetic derivation of the ideal gas law is still frequently cited as a paradigm of scientific explanation by teachers and philosophers, despite (or perhaps because of) the fact that it is hard to find such simple connections between microscopic models and macroscopic properties in modern physical science.

1.1 Organization of this book

To the reader who might be expecting some enlightenment on problems of current interest, I must point out that this book is primarily concerned with the history of kinetic theory and related topics in 19th-century physics, not with the role of the theory in 20th-century physics.[1] To the reader who might be expecting a purely historical monograph, giving an account of what happened in the 19th century but scrupulously abstaining from interpretations based on knowledge of what was to happen in the 20th, I must confess that I could not so easily put aside my interest in more recent developments; the presentation differs in many obvious ways from that of an historian who knows nothing of quantum theory.[2]

The history of the kinetic theory was intertwined with changes in ideas about the nature of heat as well as gases, and with the development of mathematical as well as experimental methods. Advances in theory were inspired by concern with problems that now seem to have little or no connection with gas properties, for example the nature of gravitational forces. Sharp criticism from now-forgotten skeptics sometimes stimulated major improvements or clarifications of the theory; vaguely formulated philosophical objections or cultural influences may have discouraged some potential contributors from doing their share. A scientist's work in other fields may have been an important factor in determining what he did in kinetic theory or how much attention would be paid to what he had to say about it. Even though I have abstained from delving into the external history of the subject (social and cultural influences, etc.) any more than seemed absolutely necessary to clarify the internal history,[3] I found that the above-mentioned complexities made it impossible to stick to a simple chronological presentation.

The structure of the book represents an attempt to combine the chronological or biographical approach with the topical approach.[4] First, this introductory chapter gives a brief overview of the main events, with references to individual sections in the later chapters where more detailed accounts are given. Part B is a series of essays on the writings of individual scientists, concentrating on the special problems that stimulated their contributions, their interactions with contemporaries, and the development of their personal careers and reputations. Part C, on the other hand, is a collection of case histories, in each of which a particular problem or group of phenomena is traced throughout the entire century. In a few cases the account is extended a few years into the 20th century in order to reach a natural stopping point, but in general the exposition omits the radical changes in physical theory associated with the names of J. Willard Gibbs and Max Planck.

Part D consists primarily of a bibliography giving details of publications which are cited in abbreviated form in footnotes, but also includes a discussion of some quantitative conclusions that can be drawn from a rather complete search of the literature in one major area of science in a limited time period. Publications mentioned by year only in the text of Parts A, B, or C – *e.g.* "Boltzmann (1872)" – without a footnote reference, may be located in the bibliography of primary sources in Part D. References to biographical articles are usually given only when specific information is cited, or when the publication cannot be easily located in either the *Dictionary of Scientific Biography*[5] or the *Isis Cumulative Bibliography*.[6] Several long quotations from sources have been omitted on the assumption that the reader has available a set of my series, *Kinetic Theory*.[7]

The structure of Parts B and C, suggested in part by the circumstance that most of the chapters were originally published as separate articles, obviously entails considerable redundancy. That may not be a disadvantage in view of the technical nature of some of the material. A clear advantage is that after going through ch. 1, the reader can jump into the other chapters in almost any order, as his or her own interests and available time dictate, without losing too much of the overall picture. The following table, a chronological listing of what I consider the most important contributions to kinetic theory through 1900, may also help as a guide.

Table 1.1-1. 39 important papers

Author and date of publication (see §16.3 for reference)		Subject	Section of book where discussed
1. Bernoulli	1738	Pressure-volume relation	1.3
2. Herapath	1821	Collisions, gas properties	2.2
3. Herapath	1821a	Temperature, phase transitions	2.2
4. Herapath	1836	Speed of molecule and of sound	2.4
5. Waterston	1843	Molecular motions and collisions	3.1
6. Waterston	1846	Equilibrium theory	3.2, 10.1
7. Herapath	1847	Systematic exposition, various applications to gas properties	2.5
8. Joule	1848	Physical arguments for Herapath theory	4.1
9. Krönig	1856	Elementary derivation of gas law	4.2
10. Clausius	1857	General exposition, phase transitions	4.3, 10.2
11. Clausius	1858	Mean-free-path, slowness of diffusion	4.4
12. Maxwell	1860	Velocity distribution, mean-free-path theory of transport coefficients	5.2, 10.3, 12.2, 13.4
13. Loschmidt	1865	Size of molecule from mean-free-path	1.8

Table 1.1-1. (*Contd.*)

Author and date of publication (see §16.3 for reference)		Subject	Section of book where discussed
14. Maxwell	1867	Transport equations, coefficients for inverse 5th power forces	12.3
15. Boltzmann	1868	Effect of forces on distribution	6.1, 10.5
16. Clausius	1870	Virial theorem	11.5
17. Stefan	1871	Diffusion	
18. Maxwell	1871	"Demon" paradox for 2nd Law	14.4
19. Boltzmann	1872	Transport equation, "H-theorem"	6.2, 12.4
20. Van der Waals	1873	Equation of state, critical point	7.4, 11.5
21. Maxwell	1873	Proof of general distribution law	10.6
22. Kelvin	1874	Reversibility paradox	14.5
23. Boltzmann	1877	Reversibility paradox	6.3, 14.5
24. Boltzmann	1877a	Entropy and probability	14.5
25. Meyer	1877	General exposition with many applications including diffusion theory	
26. Maxwell	1879	Rarefied gas dynamics, stresses due to temperature gradients	5.5
27. Reynolds	1879	Rarefied gas dynamics, thermal transpiration	5.5
28. Maxwell	1879a	Equilibrium theory	10.10
29. Boltzmann	1884	Equilibrium theory, "Ergoden"	6.4, 10.10
30. Poincaré	1890	Recurrence theorem	14.7
31. Sutherland	1893a	Transport coefficients for spheres with attractive forces	12.2
32. Burbury	1894a	Randomness and irreversibility	14.6
33. Boltzmann	1896b	Exposition of transport theory	
34. Zermelo	1896	Recurrence paradox	14.7
35. Boltzmann	1896c	Recurrence paradox	6.3, 14.7
36. Smoluchowski	1898	Heat conduction in rarefied gases	13.8
37. Boltzmann	1898	Exposition of equilibrium theory	
38. Rayleigh	1900	Temperature-dependence of transport coefficients	12.2
39. Kelvin	1900	Equipartition problem	10.9

Notes for §1.1

1. The latter topic is discussed to some extent in vol. 3 of the series cited below, note 7.
2. For an excellent example of the history of kinetic theory as seen by an intellectual historian writing at the end of the 19th century, see J. T. Merz, *A History of European Thought in the Nineteenth Century* (Edinburgh: Blackwood, 1904–1914), **1**, ch. V; **2**, chs. VI, VII, XII. An internal history of the kinetic theory written about the same time is A. Klaus, *Über die Entwicklung der kinetischen Gastheorie und ihre Bedeutung für die moderne Physik* (Freiburg i. Br.: Henn, 1904).

3. Some of the connections with cultural movements are discussed in my article "Thermodynamics and History," *Graduate Journal* (University of Texas), 7, 477 (1967).
4. Both approaches are "Lagrangian" – following a person or problem through the appropriate time span – as contrasted with the "Eulerian" approach – looking at several people and activities at a particular time and place. See Walter Rand's paper, "Eulerian and Lagrangian Analogy applied to the History of Science and Technology," presented at the *XIII^e Congrès International d'Histoire des Sciences* (Moscow, 1971), §1. [*Actes* I, 176 (Moscow, 1974)].
5. C. C. Gillispie, ed., *Dictionary of Scientific Biography* (New York: Charles Scribner's Sons, 1970–), cited as *DSB.*
6. M. Whitrow, ed., *ISIS Cumulative Bibliography, A Bibliography of the History of Science formed from ISIS Critical Bibliographies 1–90, 1913–65* (London: Mansell, in conjunction with the History of Science Society, 1971), vols. 1 and 2, Personalities A–Z and Institutions A–Z cited as *Isis Cum. Bib.*
7. S. G. Brush, *Kinetic Theory,* **1**: *The Nature of Gases and of Heat,* **2**: *Irreversible Processes,* **3**: *The Chapman–Enskog solution of the transport equation for moderately dense gases* (Oxford, New York, etc.: Pergamon Press, 1965–72). German edition: *Kinetische Theorie,* **1**: *Die Natur der Gase und der Wärme,* **2**: *Irreversible Prozesse,* hrsg. G. Eisenreich, übersetz. R. Hofmann, Th. Gornitz, and G. Eisenreich (Berlin: Akademie-Verlag/Oxford: Pergamon Press/Braunschweig: Vieweg & Sohn, 1970).

1.2 Air pressure

One might have expected a history of the kinetic theory of gases to begin with the atomic philosophers of ancient Greece, continue with the great poem *De Rerum Natura* of Lucretius, and then describe the revival of atomism in 17th-century Europe. But the history of early atomism has been competently treated by many other writers,[1] and we shall simply take it for granted that the idea that matter consists of tiny particles is one of the oldest in human history. What concerns us here is the transformation of atomism from philosophical speculation to testable physical theory; the older atomism is significant mainly insofar as it was known to modern scientists and was associated with certain other attitudes such as atheism and materialism.

It was not belief in continuous matter which the kinetic theory had to displace, but rather an opposing doctrine about the nature of heat. The proponents of the caloric theory of heat were also in many cases atomists, but they attributed the expansive force of a gas to the repulsion of its atoms rather than to their free motion. The kinetic theory could not flourish until heat as substance had been replaced by heat as atomic motion. Hence a thorough development of the kinetic theory had to wait until the second half of the 19th century; it was only in the middle of that century that the convertibility of heat and work, and the generalized Law of Conservation of Energy, were firmly established. (Note that one should distinguish between the rather vague statements that heat is some kind of molecular motion, which were prevalent in the 17th century and continued into the 18th, and the Law of Conservation of Energy, which is at the same time more general and more precise; similarly one must distinguish the kinetic theory of gases from the general idea that heat is some kind of molecular motion, perhaps vibrational and perhaps entangled with the motion of an ether.)

A convenient starting point is the notion of "air pressure" which arose in the 17th century through the work of Torricelli, Pascal, and Boyle. By a combination of experiments and theoretical reasoning they persuaded other scientists that the earth is surrounded by a "sea" of air that exerts pressure in much the same way that water does, and that air pressure is responsible for the phenomena previously attributed to "nature's abhorrence of a vacuum." We may view this development of the concept of air pressure as part of the change in attitudes that led to the mechanico-corpuscular view of nature, associated with the names of Galileo, Descartes, Boyle, and Newton.[2] Instead of postulating "occult forces" or teleological principles to explain natural phenomena, scientists started to look for explanations based simply on matter and motion.

It was well known in the time of Galileo Galilei (1564–1642) that water will not rise more than 34 feet in a pump, although Galileo himself seems to have been the first to put this fact on record in 1638.[3] A few years later (1643 or 1644) his student Evangelista Torricelli (1608–47) devised an experiment to illustrate the same effect in the laboratory. Since mercury is about 14 times as dense as water, one might expect that it can be lifted only about $\frac{1}{14}$ as far. This is indeed what is observed, and this fact tends to make plausible the mechanical explanation based on air pressure. Taking a glass tube about a yard long with one end closed, Torricelli filled it with mercury to the top; then, placing a finger over the open end, he inverted the tube so that the open end was immersed in an open dish of mercury. When he removed his finger from the open end, the mercury in the tube fell until the top of the mercury column was about 30 inches above the level of the mercury in the open dish. Between the top of the mercury column and the upper end of the tube was an open space, which became known as the "Torricellian vacuum."[4]

According to Torricelli, it is just the mechanical pressure of the air that raises the mercury in the tube. Blaise Pascal (1623–62), the celebrated philosopher and mathematician, then pointed out that – by analogy with the laws of hydrostatics – the pressure of air should be less on top of a mountain than at sea level.[5] An experiment to test this prediction was carried out by Pascal's brother-in-law, Florin Perier, in 1648, according to Pascal's instructions, and the results conformed to expectations.[6] Further experiments with Torricelli's "barometer" were conducted by Otto von Guericke (1602–86), who also constructed a suction pump and performed the famous experiment of the Magdeburg hemispheres in 1654.[7] In this experiment, two hollow bronze hemispheres were fitted carefully edge to edge, and the interior was evacuated. A team of eight horses was harnessed to each hemisphere and the two teams were driven in opposite directions, but they were unable to pull the hemispheres apart.

The science of pneumatics was considerably advanced by the English physicist Robert Boyle (1627–91).[8] His fortune, derived from the family property in Ireland, was put to good use in buying expensive scientific apparatus and in paying the salaries of ingenious assistants or colleagues. One of these was Robert Hooke (1635–1703), an excellent experimentalist who soon became known as a major scientist in his own right. Hooke constructed an improved air pump for Boyle about 1658. It was with this "pneumatic engine" or "sucker" that Boyle performed the experiments recorded in his book, *New Experiments Physico-Mechanical, touching the spring of the air, and its effects.*[9] Among other things, Boyle wanted to prove that air has elasticity ("spring")[10] and can exert a mechanical pressure great enough to support a column of water or mercury.[11]

Boyle considered that the crucial experiment in pneumatics was his No. 17, in which he enclosed the lower part of the Torricellian barometer (a column of mercury in a glass tube sitting in a dish of mercury) in a container from which air could be removed by means of his pump.[12] As the air was exhausted, the mercury in the tube fell nearly to the level of that in the dish. This was interpreted to mean that the mercury had in fact been supported by air pressure, or rather by the difference between atmospheric pressure and the negligible pressure of the Torricellian vacuum at the top of the tube. It was therefore supposed to be a refutation of the notion that the vacuum itself had any positive power to "suck up" the mercury, since such a power could hardly be affected by circumstances outside the tube. (Of course someone who really wanted to retain the old theory could still insist that in Boyle's experiment he was simply balancing one *horror vacui* against another.)

Boyle also tried what might have been a crucial experiment to distinguish between the kinetic and static theories of gas pressure, had these been sufficiently worked out at the time. In his Experiment No. 26, he placed a pendulum in the evacuated chamber and discovered, to his surprise, that the presence or absence of air makes hardly any difference to the period of the swings or the time needed for the pendulum to come to rest.[13] Two centuries later, Maxwell deduced from the kinetic theory of gases the prediction that the viscosity of a gas should be independent of its density, at least over a large range of densities (Maxwell, 1860; see §§5.2 and 12.2 in this book).

Another experiment supposedly proved that air is needed for the propagation of sound: a bell ringing inside the evacuated space could not be heard. In fact sound *can* be transmitted through air at the low pressures attained in Boyle's experiments; according to R. B. Lindsay, Boyle's experiment shows only that there is an "impedance mismatch between transducer and surrounding medium."[14] Nevertheless it is probably just as well for the progress of science that Boyle was able to establish the principle that sound is propagated by air rather than the ether, even though his experimental evidence was misinterpreted.

After publishing his account of these experiments in 1660, Boyle might well have turned to one of the many other subjects in which he was interested, without ever working on the pressure-volume law for which he is now chiefly remembered. But in 1661 Franciscus Linus disputed the conclusions Boyle had drawn from his results and suggested an alternative theory.[15] Inside the evacuated space above the mercury column in Torricelli's barometer, he postulated an invisible entity, the *funiculus* (diminutive of Latin *funis*, rope), which pulls on the mercury, trying to close up the space, and preventing it from falling all the way down. (If you use your finger to close the evacuated space, you can *feel* the funiculus pulling in the flesh!)

Boyle did not ignore Linus' criticism; instead he published another book in 1662, answering them in great detail, attacking the funiculus theory, and reporting some further experiments to bolster his own theory of air pressure. Among these was the set of measurements of volumes occupied by a sample of air at various pressures, confirming the hypothesis that the product pressure × volume = constant.[16]

Although this hypothesis is generally known as Boyle's law, Boyle does not himself claim the credit for it. Instead he says that he had not been able to see any simple relation between the pressures and volumes before he received a paper written by Richard Townley, in which just this hypothesis was proposed.[17] Boyle's own experiments gave results in reasonably good agreement with it.

It has recently been established by C. Webster that the Townley paper mentioned by Boyle was actually written by Henry Power, who had done the original experiments with Townley in 1653.[18] When Boyle's first book on vacuum experiments appeared in 1660, Power took a renewed interest in the subject, and sent an account of this earlier work to William Croune in London. Croune sent it to Boyle in Oxford but apparently neglected to mention the fact that Power was the author! Boyle could only go by the title, which mentioned experiments performed at Townley Hall "by the advice and assistance of that Heroick and Worthy Gentleman, Mr. Richard Townley, Esqr. and those Ingenious Gentlemen Mr. John and Mr. Charles Townley and Mr. George Kemp." Power published the experiments in his own book, *Experimental Philosophy*, in 1663.[19]

It now appears that the equation $PV = \text{constant}$ should be called the "Power–Townley" law, but it has also been argued that Robert Hooke, and perhaps others, probably discovered it independently,[20] and in any case Boyle helped to establish it in the scientific community, so some clumsy combination like "Power–Townley–Hooke–Boyle Law" seems inevitable if we are going to be fair to everyone. But it is usually futile for historians of science to try to change established nomenclature,[21] so I will continue to use the label "Boyle's Law."[22]

Boyle probably did not realize that he was losing his grip on such an important possession when he gave Townley the credit for this hypothesis. It was only much later that the *quantitative* law of gas pressure was considered the most significant discovery to emerge from the work of Torricelli, Pascal, Boyle, Hooke, Power, and Townley. At the time it must have seemed far more crucial to establish the *qualitative* fact that air pressure exists and is strong enough to account for the phenomena of suction, thereby enabling the Aristotelian *horror vacui* to be replaced by a mechanistic explanation more plausible to 17th-century scientists. But afterwards it was largely forgotten that any other explanation had ever been seriously contemplated, and so the *qualitative* achievement was not properly appreciated. We may conclude that Boyle *does* deserve full credit for his work on air pressure but usually gets it for the wrong reason.

I think this situation is not uncommon in the history of science, especially when we are dealing with discoveries made at a time when the world view (or Kuhnian paradigm) is changing. Another example from the same period is Rømer's discovery of the speed of light. According to the textbooks, Rømer obtained a value equivalent to 2×10^8 m/sec in 1676, using the delay in time of observation of eclipses of Jupiter's satellites from different places in the earth's orbit.[23] This is supposed to be the first time anyone had estimated a value of the same order of magnitude as the correct one (3×10^8 m/sec), and thus a quantitative discovery of great importance in physics and astronomy. Unfortunately Rømer's 1676 paper[24] does not mention any speed at all, but merely says that it would take light about 22 minutes to cross the earth's orbit. Rømer should have had the necessary distance measurements available to him so that he could have calculated the actual speed, but the fact remains that he did not do so in his paper, and it was apparently Huygens who first published the number usually attributed to Rømer.[25] This episode becomes a little more comprehensible if we recall that in the mid-17th century the crucial question was *whether the speed of light is infinite or finite.* Descartes had been so certain that light is propagated instantaneously (by displacement of a rigid intervening medium) that he declared that if it were shown to be otherwise he would have to admit that he did not know anything about philosophy![26] So the *qualitative* fact that the speed of light is finite was much more important – at that time – than the actual numerical value; it is only later, when everyone agrees that it is finite, that the numerical value may become of some interest.[27]

* * *

Boyle in 1660 was by no means a mere empiricist whose only concern was to establish relations between observable quantities. He discussed at length the possible atomistic interpretations of air pressure, mentioning Descartes' suggestion that whirling particles might drive away neighbors who get too close, but giving his preference to a more static conception of gas structure. Like earlier writers such as Pecquet,[28] Boyle compared air particles to coiled-up balls of wool or springs which would resist compression and expand into any available space. The air near the earth's surface is already compressed to a great degree by the weight of the atmosphere sitting on top of it; hence, like a squeezed spring, it exerts a strong force outwards.[29]

Boyle's theory was cast into a simple mathematical form by Isaac Newton. In Book II, §V of the *Principia* (1687), Newton stated the theorem: *if* a gas is composed of particles that exert repulsive forces on their neighbors, the magnitude of the force being *inversely as the distance, then* the pressure will be inversely as the volume.[30] He did not claim that the converse of the theorem is true, but stated that it was a physical problem to determine whether gases are in fact made up of particles with such repulsive forces.[31] Newton was also well aware that the action of these forces had to be restricted to a small number of neighbors, otherwise there would be an indefinitely large pressure depending on the shape of the container as well as its volume.

In his other writings, Newton did not adhere to this interatomic force law; in one frequently quoted passage (*Opticks*, Qu. 31) he asserted that atoms must be perfectly hard, and elsewhere he attributed short-range *attractive* forces to them.[32] Nevertheless the repulsive force model was the first one that seemed to give a direct explanation of Boyle's law, and it remained in favor well into the 19th century. It may be regarded as the first stage of the Newtonian program to determine the forces between particles by analyzing the macroscopic properties of matter. (See §11.2.)

Newton's writings were frequently cited in the 19th century in connection with several other physical concepts and laws. In particular he gave the standard definition of viscosity (§12.1); he proposed a law of cooling for hot bodies (§§13.1, 14.2); and he speculated on the transmission of radiant heat by the ether (§§9.1, 13.1). Even more important for our purposes is the fact that Newton's laws of mechanics were ultimately the basis of the kinetic theory of gases, though this theory had to compete with the repulsive theory attributed to Newton.

As has recently been pointed out by historians, the equation $F = ma$, though known as "Newton's Second Law," is nowhere to be found in Newton's own writings; it does not appear explicitly until 1750 in a paper of Euler.[33] Newton formulated his laws first in terms of instantaneous momentum changes caused by impacts (something like $F = \Delta p$, with the time interval, Δt, either equated to one or absorbed into the definition of F). He would then go to a limit of infinitesimal impacts occurring infinitely often in order to deal with continuous force laws, as in the derivation of Kepler's second law from the inverse-square gravitational force.[34]

The standard derivation of the ideal gas law in kinetic theory runs into difficulty if the atoms are regarded as absolutely hard spheres, since the *force* would seem to be infinite at the instant when the atom hits a wall or another atom, but is zero otherwise. One avoids this by using the *momentum change*, Δp, divided by the time between collisions, Δt, to get the *average* force on the wall rather than the instantaneous force $F = ma$. As it happens this approach is completely in harmony with Newton's original impact version of the second law. It was thus rather amusing to see that in his original derivation of the formula for centripetal acceleration, in a manuscript recently published by J. Herivel, Newton used a procedure very similar to that followed in the kinetic theory.[35] In particular the v^2 term comes in, divided by a distance, for precisely the same reason in both derivations: the velocity change at each impact is proportional to v, and the collision rate is proportional to v divided by the distance travelled between collisions.

The theoretical basis for the kinetic theory of gases was available by the end of the 17th century, though quantitative studies of the relation of pressure and volume to temperature were only just beginning. The progress made in this century was quite sufficient to justify Henry Power's exuberant praise of the mechanical philosophers, whom he likened to Boyle's air particles:[36]

> You are the enlarged and elastical Souls of the world, who, removing all former rubbish, and prejudicial resistances, do make way for the Springy Intellect to flye out into its desired Expansion....
>
> ...This is the Age wherein (me-thinks) Philosophy comes in with a Spring-tide.... I see how all the old Rubbish must be thrown away, and carried away with so powerful an Inundation. These are the days that must lay a new Foundation of a more magnificent Philosophy, never to be overthrown: that will Empirically and Sensibly canvass the *Phaenomena* of Nature, deducing the causes of things from such Originals in Nature, as we observe are producible by Art, and the infallible demonstration of Mechanicks; and certainly, this is the way, and no other, to build a true and permanent Philosophy.

Notes for §1.2

1. K. Lasswitz, *Geschichte der Atomistik vom Mittelalter bis Newton* (Hamburg and Leipzig, 1890). C. Bailey, *The Greek Atomists and Epicuros* (Oxford, 1928). S. Sambursky, *The Physical World of the Greeks* (New York: Macmillan, 1956); *The Physical World of Late Antiquity* (London: Routledge & Kegan Paul, 1962). R. H. Kargon, *Atomism in England from Hariot to Newton* (Oxford: Clarendon Press, 1966). R. A. Horne, *Ambix* **8**, 98 (1960). A. G. van Melsen, *From Atomos to Atom* (Pittsburgh: Duquesne University Press, 1952). T. M. Lindsay and W. R. Smith, *B. A. Rep.* **41**, 30 (1871).

   On the history of the concept of the gaseous state of matter see M. Crosland, *Proc. 10th Int. Cong. Hist. Sci.* **2**, 851 (1962); J. B. Gough, *The Foundations of Modern Chemistry* (Ph.D. Dissertation, Cornell, 1971).

2. M. Boas, *Osiris* **10**, 412 (1952). E. J. Dijksterhuis, *The Mechanization of the World Picture* (Oxford: Clarendon Press, 1961). E. A. Burtt, *The Metaphysical Foundations of Modern Physical Science* (Garden City, N.Y.: Doubleday Anchor, 1954, reprint of the 2nd ed., 1932).
3. Galileo Galilei, *Discorsi e dimostrazioni matematiche, intorno a due nuoue scienze, attenenti alla mecanica et i movimenti locali* (Leiden, 1638); English trans. by H. Crew and A. de Salvio, *Dialogues concerning Two New Sciences* (New York: Dover Pubs., 1952, reprint of the 1914 ed.), pp. 12–17. On the background of Galileo's ideas see C. Webster, *Arch. Hist. Exact Sci.* **2**, 441 (1965).
4. E. Torricelli, "Esperienza dell'Argento vivo" (Correspondence with Ricci: June 11, 18, and 24, 1644). See his *Opere* (Faenza: Montanari, 1919), **3**, 186–88, 193–95, 198–201, where letters to other scientists announcing Torricelli's discoveries may also be found. There is an English translation by V. Cioffari in *The Physical Treatises of Pascal, etc.* (New York: Columbia University Press, 1937), p. 163. A formal account was published by the Accademia del Cimento, in *Saggi di naturali Esperienze faite nell'Accademia del Cimento* (Firenze, 1666). This is reprinted, with the above-mentioned letters, in *Neudrucke von Schriften und Karten über Meteorologie und Erdmagnetismus*, ed. G. Hellmann, No. 7 (Berlin, 1897). See also: C. de Waard, *L'experience barometrique* (Thouars, Deux-Sèvres: Imprimerie Nouvelle, 1936); W. E. K. Middleton, *Isis* **54**, 11 (1963); M. B. Hall, *Nature and Nature's Laws* (New York: Harper & Row, 1970), p. 184.
5. B. Pascal, *Traités de l'Equilibre des Liqueurs, et de la Pesanteur de la Masse de l'Air* (Paris, 1663); reprinted in his *Oeuvres*, eds. L. Brunschvicg and P. Boutroux (Paris: Hachette, 1908–21), **2**, 53; and in *Oeuvres Complètes*, ed. J. Chevalier (Paris: Gallimard, 1954), p. 362.
6. B. Pascal and F. Perier, *Récit de la Grande Expérience de l'Equilibre des Liquers, etc.* (Paris, 1648); reprinted, with Pascal's other works on hydrostatics, in his *Oeuvres*, **2**, 147, 349 and in *Oeuvres Complètes*, p. 392. See also *The Physical Treatises of Pascal, etc.*, trans. I. H. B. and A. G. H. Spiers, introduction and notes by F. Barry (New York: Columbia University Press, 1937).
7. O. von Guericke, *Experimenta nova (ut vocantur) Magdeburgica de vacuo spatio primum a R. P. Gaspare Schotto* (Amsterdam, 1672); German trans. by F. Danneman, *Otto von Guericke's neue "Magdeburgische" Versuche über den leeren Raum (1672)* (Leipzig, 1894).
8. On Boyle and his work with air pressure see M. B. Hall, *DSB* **2**, 377 (1970); *Robert Boyle on Natural Philosophy* (Bloomington, Ind.: Indiana University Press, 1965); *Robert Boyle and Seventeenth-Century Chemistry* (Cambridge University Press, 1958); *Sci. Am.* **217** (2), 97 (1967). R. E. W. Maddison, *The Life of the Honourable Robert Boyle, F. R. S.* (London: Taylor & Francis, 1969). M. E. Crowley, *The notion of nature in the corpuscular philosophy of Robert Boyle* (Dissertation, Marquette University, 1970). G. Wilson, *Edinburgh New Phil. J.* **46**, 330 (1849). R. G. Neville, *J. Chem. Educ.* **39**, 356 (1962). J. B. Conant, in *Harvard Case Histories in Experimental Science*, ed. J. B. Conant (Cambridge, Mass.: Harvard University Press, 1950), 1. C. Webster, *Arch. Hist. Exact Sci.* **2**, 441 (1965).

   Older works are listed in J. F. Fulton, *A Bibliography of the Honourable Robert Boyle* (Oxford: Clarendon Press, 2nd ed., 1949).
9. Oxford, 1660; reprinted in *The Works of the Honourable Robert Boyle* (London, 1772), **I**, 1. Extensive extracts in Conant, *op. cit.*

10. Both the concept and the terminology seem to be derived from the writings of Jean Pecquet (1622–74), whose *Experimenta Nova Anatomica* (Paris, 1651) was translated into English in 1653. Webster, *op. cit.* M. B. Hall, *Nature and Nature's Laws*, p. 186 (extract from English translation).
11. In modern units, the height of the column of mercury is about 0.76 meters; if its cross-sectional area is A, its volume is $0.76A$ m^3. Since a liter of mercury has a mass of 13.6 kilograms, the mass of the column is $10336\,A$ kg, and it will exert a force equal to

    $$\begin{aligned} F = mg &= (10336A \text{ kg}) \times (9.8 \text{ m/sec}^2) \\ &= 101300A \text{ (kg} \cdot \text{m/sec}^2) \\ &= (1.013A) \times 10^5 \text{ newtons} \end{aligned}$$

    The pressure exerted by the column is

    $$P = F/A = 1.013 \times 10^5 \text{ newtons/m}^2 \text{ (approximately 15 lb/in}^2)$$

    In meteorology the *bar* is defined as exactly 10^5 newtons/m^2.
12. Boyle's *Works* **I**, 33.
13. *Ibid.*, p. 61.
14. R. B. Lindsay, *Am. J. Phys.* **16**, 371 (1948). Conant (*op. cit.*, see pp. 30–38) gives extensive extracts from Boyle's account of this experiment (No. 27 in the 1660 book) and from a similar one published in 1669, but does not indicate that there is any reason to doubt Boyle's conclusions.
15. F. Linus, *Tractatus de corporum inseparabilitate, in quo experimenta de vacuo tam Torricelliana quam Magdeburgica et Boyliana examinantur* (London, 1661). On the career of Linus, see C. Reilly, *Osiris* **14**, 222 (1962); *Francis Line, S. J., An Exiled English Scientist* 1595–1675 (Rome: Institutum Historicum S. J., 1969).
16. Robert Boyle, *A Defence of the Doctrine touching the spring and weight of the air, proposed by Mr. R. Boyle in his New Physico-Mechanical Experiments*; *Against the objections of Franciscus Linus, wherewith the Objector's Funicular Hypothesis is also examined* (Oxford, 1662); reprinted in Boyle's *Works* (London, 1744, 2nd ed., 1722), **I**, 118.

    Huygens, who received a copy of the book, wrote to Moray that he was "at first astonished to see that he has taken the pain to write so big a book against objections so frivolous as those of his two adversaries [Linus and Thomas Hobbes, who also published a criticism in 1661], but having begun to peruse it, and seeing that among his refutations he had inserted many new discoveries and observations not yet seen, I wished it had been bigger." *Correspondence of Scientific Men of the Seventeenth Century*, ed. S. P. Rigaud (Oxford, 1841; reprinted by G. Olms, Hildesheim, 1965), **1**, 92–93.
17. Boyle's *Works*, p. 160. The reader is warned that the section of Boyle's book in which the evidence for "Boyle's Law" is presented is frequently reprinted in anthologies, but the following paragraph in which Boyle gives Townley the credit for the hypothesis is usually omitted. Presumably the anthologists themselves have seen the reference to Townley but they prefer to ignore it and, by omission, give all the credit to Boyle.
18. C. Webster, *Nature* **197**, 226 (1963); *Arch. Hist. Exact Sci.* **2**, 441 (1965); *Ambix* **14**, 150 (1967). For further discussion of the discovery of "Boyle's Law" see E. Gerland,

in *Beiträge aus der Geschichte der Chemie dem Gedächtnis von Georg W. A. Kahlbaum*, hrsg. P. Diegart (Leipzig and Wien: Deuticke, 1909), p. 350; W. S. James, *Science Progress* **23**, 261 (1928); J. B. Conant, *op. cit.*; R. G. Neville, *J. Chem. Ed.* **39**, 356 (1962); I. B. Cohen, *Nature* **204**, 618 (1964). On Townley see C. Webster, *Trans. Hist. Soc. Lancashire and Cheshire* **118**, 51 (1966).

19. Reprinted with a new introduction by M. B. Hall (New York: Johnson Reprint Corp., 1966).
20. C. Webster, note 169 of his paper in *Arch. Hist. Exact Sci.* **2**, 441 (1965).
21. My attempt to add the name of Wilhelm Lenz to the "Ising Model" in statistical mechanics [*Rev. Mod. Phys.* **39**, 883 (1967)] has been a failure.
22. At least one can take some satisfaction in the fact that it is no longer called "Mariotte's law."
23. Since I first discussed the myth of Rømer's determination of the speed of light [*Physics Teacher* **7**, 271 (1969)] the following texts have repeated the myth: J. G. Reilly and A. W. Vander Pyl, *Physical Science* (Reading, Mass.: Addison-Wesley, 1970), p. 151; R. L. Murray and G. C. Cobb, *Physics, Concepts and Consequences* (Englewood Cliffs, N.J.: Prentice-Hall, 1970), p. 531; K. R. Atkins, *Physics* (New York: Wiley, 2nd ed., 1970), p. 391; G. Shortley and D. Williams, *Elements of Physics* (Englewood Cliffs, N.J.; Prentice Hall, 5th ed., 1971), pp. 713–14.
24. O. Rømer, *J. Scavans*, p. 233 (7 Dec. 1676); *Phil. Trans.* p. 893 (25 June 1677); both reprinted with extensive commentary and other documentation by I. B. Cohen, *Isis* **31**, 327 (1940). Extracts in: W. F. Magie, *A Source Book in Physics* (Cambridge, Mass.: Harvard University Press, 1963, rept. of 1935 ed.), pp. 335–37; H. Shapley and H. E. Howarth, *A Source Book in Astronomy* (New York: McGraw-Hill, 1929), pp. 70–71. (I gather that source books are not consulted frequently by textbook authors.) For other articles on Rømer see *Isis Cum. Bib.*
25. Christiaan Huygens, *Traité de la Lumiere* (Paris, 1690); *Treatise on Light* (New York: Dover Pubs., 1962, rept. of 1912 English trans.), pp. 7–10.
26. Letter from Descartes to Beeckman or Hortensius, 22 Aug. 1634; see J. G. Burke, *Am. J. Phys.* **34**, 390 (1966).
27. There is a discussion of the importance of qualitative discoveries in science by David Hawkins, in *Science and the Creative Spirit*, ed. H. Brown (Toronto: University of Toronto Press, 1958), p. 127.
28. See note 10.
29. See the extract from Boyle's book in Brush, *Kinetic Theory* **1**, 43–51.
30. Brush, *Kinetic Theory* **1**, 52–56 (reprinted from the Motte–Cajori trans.).
31. He was less cautious in writing a manuscript "De aere et aethere" (1674) where one finds the flat assertion that bodies do repel each other at a distance. See A. R. and M. B. Hall, *Unpublished Scientific Papers of Isaac Newton* (New York: Cambridge University Press, 1962), pp. 214–28.
32. Isaac Newton, *Opticks* (London, 4th ed., 1730; New York: Dover Pubs., 1952), pp. 375–402; manuscript published in *Unpublished Scientific Papers of Isaac Newton*, pp. 334–44 and in M. B. Hall, *Nature and Nature's Laws*, pp. 323. I have quoted the statement about hard atoms in §2.2, note 6. A. E. Shapiro [*Stud. Hist. Phil. Sci.* **5**, 275 (1975)] has noted that Newton abandoned his particle theory of fluids when he found it more convenient to use a continuum theory.
33. L. Euler, *Mem. Acad. Sci. Berlin* **6**, 185 (1752, read 1750); C. Truesdell, *Rational Fluid Mechanics 1687–1765*, Editor's introd. to vol. **II.12** of Euler's *Works* (Zürich: Füssli, 1954), p. XLII; T. L. Hankins, *Arch. Int. Hist. Sci.* **20**, 43 (1967).

34. *Principia*, Book I, Section II, Prop. I, Theorem I.
35. J. Herivel, *Isis* 51, 546 (1960); L. Rosenfeld, *Arch. Hist. Exact Sci.* 2, 365 (1965); J. Herivel, *The Background to Newton's Principia* (Oxford: Clarendon Press, 1965), pp. 11–12.
36. *Experimental Philosophy*, p. 192.

1.3 The kinetic theory in the 18th century

The historiography of kinetic theory has suffered considerably from "precursoritis"–the tendency to attribute the discovery of the theory to early scientists who merely made casual remarks about heat and molecular motion. Once the Power–Townley law of gas pressures had been established by Boyle in 1662, there was a definite quantitative result which any theory of gases was obliged to explain. Nevertheless, it is still not sufficient to establish a connection between the motion of particles and the equation $PV = \text{constant}$; it is also necessary to postulate that the particles move freely through space at constant velocity except for occasional collisions with each other or with the sides of the container, and it is necessary to show that the pressure is proportional to the mean-square speed of the particles. By this set of criteria we have to eliminate, for example, Robert Hooke's theory, which P. G. Tait in 1885 mistakenly called an "anticipation of the kinetic theory":[1]

> The air then is a body consisting of particles so small as to be almost equal to the particles of the Heterogeneous fluid medium incompassing the earth. . .. If therefore a quantity of this body be inclosed by a solid body, and that be so contrived as to compress it into less room, the motion thereof (supposing the heat the same) will continue the same, and consequently the Vibrations and Occursions will be increased in reciprocal proportion, that is, if it be condensed into half the space the Vibrations and Occursions will be double in number . . .. Again, if the containing Vessel be so contrived as to leave it more space, the length of the vibrations will be proportionably inlarged, and the number of Vibrations and Occursions will be reciprocally diminished . . .. These explanations will serve *mutatis mutandis* for explaining the spring of any other body whatsoever.[2]

Early in the 18th century, semi-kinetic theories of the nature of gases were published by Jacob Hermann, Leonhard Euler, and others.

Most of these theories were based on the assumption that the atoms in a gas are suspended in the ether, or consist of ether vortices, so that the type of motion considered is vibrational or rotational rather than translational. Since these theories have recently been analyzed rather thoroughly by Talbot and Pacey and by Truesdell,[3] there seems to be no point in discussing them here. Instead we need only mention what is generally considered the first quantitative version of the modern kinetic theory, proposed by Daniel Bernoulli (1700–82) in 1738.[4]

Bernoulli's kinetic theory was developed in the 10th section of his book on *Hydrodynamics*, a work that was widely known among mathematical physicists of the 18th century and afterwards,[5] though a complete English translation has only recently been published.[4] One has therefore to answer the historical question: Why was the theory forgotten until it was revived in the middle of the 19th century?

A fairly obvious reason is that Newton's theory, based on repulsive forces between gas atoms, had already been firmly established as the explanation of Boyle's law, both by the reputation of Newton and by its simplicity. Bernoulli's theory did not really go much further in explaining or predicting additional properties of gases. Even though Bernoulli did show that the pressure of a gas should be proportional to the square of the molecular velocity, he was not able to connect this fact in any convincing way with an accepted temperature scale. Although a modern reader of Bernoulli is likely to jump to the conclusion that he identified the heat content or temperature of a gas with molecular kinetic energy, this conclusion was not stated explicitly. One of the handful of 18th-century scientists known to have mentioned Bernoulli's gas theory, Jean Trembley, was willing to accept the kinetic explanation of gas pressure, yet still complained that Bernoulli had not explained *how* heat increases the motion of particles.[6]

A second reason why Bernoulli's theory may have appeared unattractive to his contemporaries is that the assumption that gas atoms move freely through space contradicted the prevailing belief that space was filled with ether or vortices. A third reason could be the fact that heat is clearly not "just" the kinetic energy of molecular motion, since it can be transmitted across empty space (as from the sun to the earth) without any accompanying motion of molecules. A fourth reason[7] might be that Bernoulli's was only one of several kinetic theories (*i.e.* theories based on the general idea of some kind of molecular motion) and at the time there was no particular reason to prefer it. A fifth reason[8] may be that it was published at a time when scientists were beginning to abandon the Cartesian notions of billiard-ball impacts on which it was based in favor of Newtonian forces. Finally, it has been suggested that many Continental scientists were becoming skeptical of all explanations based on hypothetical corpuscles at this time.[9]

The kinetic theory was kept alive by the writings of such scientists as Lomonosov in Russia, and J. A. DeLuc and G. L. LeSage in Geneva.[10] But, as mention of LeSage may suggest to some historians of science, the kinetic theory was more popular as an explanation of gravity than as an explanation of gas pressure at the end of the 18th century. LeSage's "ultramondane corpuscles" bombarding the planets from all sides, but shielded by nearby planets or the sun, were supposed to account for gravitational attraction between bodies that shield each other. This idea has been frequently revived during the past two centuries but has never been developed into a successful quantitative theory of gravity;[11] nevertheless it played an important role in the history of kinetic theory, by stimulating Herapath and Waterston to think about forces resulting from the bombardment of particles. The popularity of kinetic theories of gravity is also an indication of the general desire of scientists to get rid of action at a distance in physics; perhaps for this reason, even respectable physicists such as Maxwell have been reluctant to reject such theories in spite of their obvious defects.[12]

Needless to say there was no possibility of direct verification of the postulates of kinetic theory until early in the 20th century, when the refinement of experimental techniques permitted measurements (if not "observations") of the behavior and properties of individual atoms.[13] Most scientists (with a few exceptions to be discussed in §§1.7 and 1.9) were quite willing to accept the theory long before such verification was available, just as most scientists in the 17th and 18th centuries accepted the heliocentric system before direct astronomical observations of the earth's motion (parallax effects, etc.) had been made.

Notes for §1.3

1. P. G. Tait, *Proc. R. S. Edinburgh* 13, 118 (1885); *Scientific Papers* (Cambridge University Press, 1900), 2, 122.
2. Robert Hooke, *Lectures de Potentia Restitua* (London, 1678), pp. 15–16.

   A similar derivation was published in 1750 by M. V. Lomonosov; see H. M. Leicester, *Mikhail Vasil'evich Lomonosov and the Corpuscular Theory* (Cambridge, Mass.: Harvard University Press, 1970), p. 217.

3. G. R. Talbot and A. J. Pacey, *Brit. J. Hist. Sci.* **3**, 133 (1966); C. Truesdell, *Essays in the History of Mechanics* (New York: Springer-Verlag, 1968), p. 272. Cherbuliez, *Mittheilungen, Naturforschende Gesellschaft, Bern*, 291 (1871). The relevant portions of Hermann's work were translated by W. E. K. Middleton, *Brit. J. Hist. Sci.* **2**, 247 (1965).
4. Daniel Bernoulli, "De affectionibus atque motibus fluidorum elasticorum, praecipue autem aeris," Sectio Decima in his *Hydrodynamica, sive de viribus et motibus fluidorum commentarii* (Argentorati, 1738); English trans. of entire book together with Johann Bernoulli's *Hydraulics* by T. Carmody and H. Kobus with preface by H. Rouse (New York: Dover Pubs., 1968); English trans. of the section on kinetic theory in Brush, *Kinetic Theory* **1**, 57. Bernoulli's theory is discussed in the papers cited in note 3 above, and by A. J. Pacey and S. J. Fisher, *Brit. J. Hist. Sci.* **3**, 388 (1967).
5. See Hunter Rouse and Simon Ince, *History of Hydraulics* (Iowa City: Iowa Institute of Hydraulic Research, 1957; New York: Dover Pubs., 1963), ch. VIII; Truesdell, *Rational Fluid Mechanics 1687–1785*, Part IV.
6. Jean Trembley, *Memoires de l'Academie Royales des Sciences et Belles-Lettres, Berlin*, p. 67 (1796).
7. Truesdell, *op. cit.*, p. XXV; Talbot and Pacey, *op. cit.* (note 3), p. 141.
8. Henry Guerlac, in *John Dalton and the Progress of Science*, ed. D. S. L. Cardwell (New York: Barnes & Noble, 1968), p. 57, esp. note 27 on p. 87.
9. Talbot and Pacey, *op. cit.*, p. 141.
10. See for example De Luc's review of Bernoulli's theory in his *Recherches sur les Modifications de l'Atmosphere* (Geneva, 1772), pp. 165–71.
11. George Louis LeSage, *Nouveaux Memoires de l'Academie Royale des Sciences et des Belles-Lettres, Berlin*, p. 404 (1782), English trans. in *Smiths. Rep.*, p. 141 (1898); "Physique Mecanique" in *Deux Traites de Physique Mecanique* by P. Prevost (Geneva, 1818); S. Aronson, *Natural Philosopher* **3**, 51 (1964); Blair, *Scientific Aphorisms* (1827), cited by Preston, *Phil. Mag.* [5] **4**, 367 (1877); A. M. Bock, *Inauguraldissertation* (München, 1891); C. Isenkrahe, *Abhandlungen zur Geschichte der Mathematik* [suppl. to *Z. Math. Phys.* **37**] (6) (Leipzig, 1892); C. Isenkrahe, *Das Räthsel von der Schwerkraft* (Braunschweig, 1879). A large number of periodical articles published during the 19th century are listed in the Royal Society *Catalogue*, index vol. **III**, *Physics*, category 0700. For articles published in the period 1900–13 see the *International Catalogue of Scientific Literature*, registeration number 0700. There have been more recent attempts to revive the theory: C. F. Brush, *J. Franklin Inst.* **206**, 143 (1928), *Proc. Am. Phil. Soc.* **67**, 105 (1928), **68**, 55 (1929); James MacKaye, *The Dynamic Universe* (New York: Scribner, 1931); V. V. Radziyevskii and I. I. Kagal'nikova, *Bull. Vsesoyuz. Astronomo-Geod. Obshchestva* (Moscow) **26**, 3 (1960), English trans. in U.S. Government document FTD-TT-64-323/1 + 2 + 4 [AD-601762].
12. J. C. Maxwell, art. "Atom" in *Encyclopedia Britannica* (9th ed., 1878); Maxwell's *Scientific Papers* (Cambridge, 1890), **2**, 445. See also Maxwell's letter to Tait, concerning a molecular ether, published by D. J. Price in *Notes and Records of the Royal Society of London* **10**, 139 (1953) and Maxwell's review of a book by Challis in *Nature* **8**, 279 (1873). According to S. P. Langley, modern thought goes in the direction of LeSage's theory; see *Smiths. Rep.*, p. 139 (1898).
13. The experiments of Dunoyer (1911) and Stern (1920) may be mentioned in this connection; see F. L. Friedman and L. Sartori, *The Classical Atom* (Reading, Mass.: Addison-Wesley, 1965), **12**, 29–30.

1.4 Absolute temperature and the thermal expansion of gases

It was recognized in the 17th century (and probably much earlier) that heat causes gases to expand, but serious attempts to find a quantitative relation between volume and temperature did not begin until the 18th century. The development of this subject is closely intertwined with the development of temperature scales, in particular that based on the air thermometer, and with meteorology.[1]

A general law of expansion of gases was proposed at the beginning of the 18th century by the French physicist Guillaume Amontons (1663–1705), who also provided some experimental justification for it. Amontons suggested that since the pressure of a given amount of air (or volume at a fixed pressure) is proportional to the amount of heat contained in the air, one could conceive of an "absolute zero" of temperature at which air has no pressure or volume at all.[2] From Amontons' data, historians have deduced that absolute zero should be at −248°C or at −239.5°C.[3,4] According to another historian of the subject: "However, scientists of the time were skeptical of his [Amontons'] conclusions, and this suggestion of an absolute thermometric scale remained largely unnoticed."[5] One can see why scientists might well be skeptical if one examines some of the subsequent attempts to calculate zero late in the 18th century. These range from rather cautious analyses of the data to rash extrapolations from dubious experiments.[6]

The modern form of the law of thermal expansion of gases was established at the end of the 18th century by the work of J. A. C. Charles (1746–1823) and J. L. Gay-Lussac (1778–1850). Both were interested in the properties of the atmosphere, among other possible applications of the gas laws, and there is some evidence that Gay-Lussac's systematic work was conducted to satisfy the needs of astronomers such as Laplace for atmospheric-refraction corrections to their observations.[7] The law of Charles and Gay-Lussac[8] states that the pressure (at constant volume) or the volume (at constant pressure) is proportional to $(t + c)$, where t is the temperature measured on some arbitrary scale such as Fahrenheit's or Celsius', and c is a constant which depends on the scale chosen. Once such a law is admitted to apply universally for all gases at all temperatures, then (as Amontons had already pointed out a century earlier) it is natural to redefine $t + c$ as an "absolute temperature" whose zero will be the lowest attainable temperature, corresponding to condensation of the gas to practically nothing.

Nevertheless it is not true *historically* that the establishment of this law immediately led to the acceptance of the modern scale of absolute temperatures; confusion on this point has, I think, led to some misunderstanding of the basis of the unfavorable reception of Herapath's kinetic theory of gases.

To illustrate the problem as it stood at the beginning of the 19th century, we may recall that the law of thermal expansion was also discovered independently, though not in quite the same form, by John Dalton in 1801.[9] Dalton immediately offered a theoretical explanation of the law:

> ... let us assume an hypothesis that the repulsive force of each particle is exactly proportional to the whole quantity of heat combined with it, or in other words to its temperature reckoned from the point of total privation.

Dalton then noted that the expansion data could be used to determine this "point of total privation" or absolute zero of temperature. Having found that air expands by 32.5% between 55°F and 212°F, he argued:

> since the diameter of each particle's sphere of influence is as the cube root of the space occupied by the mass we shall have $\sqrt[3]{1000}$: $\sqrt[3]{1325}$ (10:11, nearly): the absolute quantity of heat in air at 55°: the absolute quantity in air of 212°. This gives the point of total privation of heat, or absolute cold, at 1547° below the point at which water freezes.[10]

Note the assumption that the amount of heat contained in a particle is proportional not to its volume but to its diameter. Why did Dalton make this assumption, especially since it led to consequences that contradicted his own data?

> ... it necessarily requires the augmentation of elastic fluids for a given quantity of heat to be greater in the higher temperatures than in the lower, because the cubes of a series of numbers in arithmetical progression differ more the larger the numbers or roots; but it has just been shown that in fact an augmentation of the contrary kind is observed.

Presumably his commitment to the Newtonian repulsive-force model of gases persuaded him that there must be a linear relation between repulsive force and distance, even though in Newton's model it was actually a reciprocal relation. To explain away the discrepancy between theory and experiment, Dalton had to make the additional hypothesis that "equal increments of heat cause a greater expansion in mercury in the higher than in the lower temperatures."[11] With this modified temperature scale everything was consistent.

Contrary to the impression one gets from most expositions of kinetic theory, I suspect that, at least at the beginning of the 19th century, the notion of an absolute temperature scale was tied up more closely with the idea that heat is a substance than the idea that heat is motion.[12] There is some support for this view in Count Rumford's paper, advocating the theory that heat is molecular motion, presented to the Royal Society in 1804:

> *Hot* and *cold*, like *fast* and *slow*, are mere relative terms; and, as there is no relation or proportion between motion and a state of rest, so there can be no relation between any degree of heat and absolute cold, or a total privation of heat; hence it is evident that all attempts to determine the place of *absolute cold*, on the scale of a thermometer, must be nugatory.[13]

Most of the older methods for determining absolute temperatures ran into difficulty as soon as it was realized that the specific heats of all substances vary somewhat with temperature. By 1818, Dulong and Petit published a detailed study of this problem in connection with the choice of a suitable temperature scale for studying the law of cooling (§13.2).[14] Among other conclusions, they suggested that it might even be possible to locate the absolute zero an infinite number of degrees below any measurable temperature. This would not mean that a body contains an infinite amount of heat, since it had been found that the specific heat decreases at low temperature, hence one could suppose that its integral over a semi-infinite temperature range is still finite.

Shortly after this, Gay-Lussac published a note on the possibility of reaching indefinitely low temperatures by expanding compressed gases; he remarked that:

> If it is incontestable that, by the dilation of gases, one can produce an unlimited amount of cold, the determination of the absolute zero of heat would appear to be a question altogether chimerical.[15]

From the above discussion it should be evident that in 1820, when John Herapath sent his paper on kinetic theory to the Royal Society, proposing yet another absolute temperature scale (§2.2), it was not safe to assume that the concept of absolute temperature (or absolute zero) had been securely established. There was no general agreement on a satisfactory method for determining absolute temperatures, and the vast discrepancies among the various methods proposed was sufficient to make any scientist tread cautiously on this ground. The example of Rumford shows that someone who thought of heat as a mode of motion would not necessarily accept the idea of "total privation of heat." With all this in mind we can perhaps be more sympathetic to Humphry Davy's protest, quoted in §2.3, that there is no basis for the concept of absolute zero, and that "temperature does not measure a quantity, but merely a property of heat."

Notes for §1.4

1. For general surveys see: W. E. K. Middleton, *A History of the Thermometer and its use in Meteorology* (Baltimore: Johns Hopkins Press, 1966); E. Mach, *Open Court* **16**, 641, 733 (1902) (trans. from his *Principien der Wärmelehre*); P. Duhem, *Revue des deux mondes* **129**, 869 (1895); A. Wolf, *A History of Science, Technology, and Philosophy in the 18th Century* (New York: Macmillan, 1938, 2nd ed., 1952), ch. VIII; F. S. Taylor, *Ann. Sci.* **5**, 129 (1942); C. B. Boyer, *Sci. Mon.* **57**, 442 (1943); M. K. Barnett, *Osiris* **12**, 269 (1956).
2. G. Amontons, *Mem. Acad. Roy. Sci. Paris* **112** (1699). G. R. Talbot and A. J. Pacey, *Centaurus* **16**, 20 (1971).
3. Middleton, *op. cit.*, p. **111**.
4. F. Cajori, *A History of Physics* (New York: Macmillan, 1929; Dover rept. 1962), p. 114.
5. C. B. Boyer, *op. cit.* (note 1).
6. George Martine, *Essays and Observations on the construction and graduation of thermometers, and on the heating and cooling of bodies* (Edinburgh, 4th ed., 1787). Essay IV (1738–39), pp. 95–103. Jean Andre Deluc, *Recherches sur les modifications de l'Atmosphere* (Geneva, 1772), **I**, 223, **II**, 180. The publications of J. A. Braun (1759), J. H. Lambert, W. Irvine, A. Crawford, and J. Gadolin are discussed by Middleton, *op. cit.*, pp. 110–111; Barnett, *op.*, p. 322; and Wolf, *op. cit.*, p. 189.
7. J. L. Gay-Lussac, *Ann. Chim.* **34**, 137 (1802); Laplace, *Celestial Mechanics*, trans. N. Bowditch (Boston, 1839), **4**, 527.
8. W. S. James, *Science Progress* **24**, 57 (1929). J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, 1949), **I**, 592–93. W. W. Randall, ed. and trans., *The expansion of gases by heat. Memoirs by Dalton, Gay-Lussac, Regnault and Chappuis* (New York: American Book Co., 1902).
9. J. Dalton, *Manchester Mem.* **5**, 535 (1802, read 1801). For further details of this and other works of Dalton see A. L. Smyth, *John Dalton 1766–1844. A Bibliography of Works by and about him* (Manchester University Press, 1966).
10. Dalton, *op. cit.*, p. 601. A detailed discussion of the basis of Dalton's calculation has been given by R. Fox, in *John Dalton and the Progress of Science*, ed. D. S. L. Cardwell (Manchester: Manchester University Press, 1968), p. 187.
11. Dalton, *op. cit.*, p. 602. For further discussion of this point see an anonymous letter comparing Dalton's hypothesis with various other current calculations of absolute zero, in *Nicholson's J. Nat. Phil.* **4**, 221 (1803), and Dalton's reply, *ibid.* **5**, 34 (1803). The problem is taken up again in Dalton's *A New System of Chemical Philosophy* (1808), **1**, ch. I.

12. For general background see R. Fox, *The Caloric Theory of Gases from Lavoisier to Regnault* (Oxford: Clarendon Press, 1971).
13. Rumford, *Phil. Trans.* 94, 77 (1804); *Collected Works*, ed. S. C. Brown (Cambridge, Mass.: Harvard University Press, 1968–), I, 323 (quotation from pp. 405–6 of this edition).
14. P. L. Dulong and A. T. Petit, *Ann. Chim.* [2] **7**, 113, 225, 337 (1818): *Ann. Phil.* **13**, 112, 160, 241, 321 (1819); see p. 259 of the original French version. This work is discussed by Barnett, *op. cit.* (note 1); see also R. Fox, *Brit. J. Hist. Sci.* **4**, 1 (1968).
15. Gay-Lussac, *Ann. Chim.* [2] **9**, 305 (1818). Gay-Lussac's arguments were contradicted by Clément and Desormes, who obtained the value −267.5°C for absolute zero from their work on the "caloric of the vacuum," in good agreement with the value of −266.66°C inferred from Gay-Lussac's expansion coefficient for gases. *J. phys. chim. hist. nat.* **89**, 321, 428 (1819). P. Costabel, *Arch. Int. Hist. Sci.* **21**, 3 (1968). J. Payen, *DSB* **3**, 315 (1971). Person, *C. R. Paris* **23**, 336 (1846). A. de la Rive, *Arch. Sci. Phys.* **9**, 5 (1848).

1.5 Opinions on the nature of heat before 1840

As I have pointed out in Part B of this book, the kinetic theories proposed by Herapath (1820) and Waterston (1845) were rejected before publication by the scientists in the Royal Society to whom they were submitted, whereas the theories of Krönig, Clausius, and Maxwell were almost immediately accepted in the late 1850's. It seems that this difference in reception must be attributed at least in part to the change in ideas about heat and energy that occurred in the period 1840–55. To understand the history of kinetic theory we must therefore know something about prevalent theories of heat in the early 19th century, as well as the events that led to the replacement of those theories. Fortunately this subject has already been studied rather intensively by historians of science, so it is not necessary to present more than a brief summary here. My own reading of a few of the primary sources suggests a few points on which the standard interpretations do need some correction or change of emphasis, and it is perhaps well to mention these at the outset.

First, I have been impressed by the great caution and open-mindedness with which many scientists presented their views on heat, particularly some of the ones who are usually labeled as supporters of the caloric theory. It was very common to say that most of the phenomena can be explained equally well by considering heat as a substance or as a mode of motion; even if the former view was to be adopted for the sake of convenience, it was not to be regarded as firmly established beyond any doubt. Furthermore, even if heat is really a fluid substance, there were hints that it might have some association with molecular motion.[1]

Second, there was a rather close connection between heat theory and ideas about heat *radiation*, and thus indirectly a connection with ideas about the nature of light.[2]

Third, even though historians have now recognized that Rumford and Davy did not kill the caloric theory at the beginning of the 19th century (as used to be supposed), they have not, in my opinion, given an adequate explanation of what happened to the caloric theory after 1830, aside from the obvious fact that it was eventually replaced by thermodynamics.

* * *

The notion that heat is a substance has been traced back to Lucretius and Heraclitus,[3] but what concerns us here is its reemergence in the 18th century in competition with the 17th-century theories of heat as molecular motion.[4] One major reason for this revival was the discovery of latent and specific heats by Joseph Black around 1760;[5] although Black's work was not officially published until after his death, in 1803,[6] he lectured on heat and other topics in chemistry to medical students in Edinburgh during the last third of the century. Since a number of the major British scientists of the late 18th and early 19th centuries received some part of their education at Edinburgh,[7] Black was in a good position to propagate his ideas. Indeed, the doctrine that every substance has a "capacity" for holding heat, and the idea that a gas "contains" the latent heat that was added to a liquid to vaporize it (as well as the latent heat that was added to a solid to melt it), became so well established that it is hard to avoid them even in teaching physics today.[8] Although Black did not strongly advocate a definite theory of heat, he mentioned Cleghorn's caloric theory with approval,[9] and remarked that if heat were simply related to molecular motion one would expect denser substances to have larger heat capacities, contrary to experience (*e.g.* mercury and water).[10]

Bryan Higgins was probably one of the first writers to suggest (1775) that atoms are surrounded by atmospheres of heat which repel the atmospheres of other atoms; similar ideas were expressed by Torbern Bergman about the same time.[11]

William Cleghorn, in his Dissertation at Edinburgh (1779), published what has been called "the first detailed exposition of the material theory of heat later known as the caloric theory."[12] According to Cleghorn, "fire is a fluid *sui generis* and perhaps the only substance in which fluidity is essential"; "there is a repulsive force between the particles of fire by which they repel one another"; and "there are forces attracting fire in almost all bodies," though the forces differ in different bodies. Finally, "all the phenomena of heat arise from change in the repulsive forces of the fire-particles, or from change in the attractions between fire and bodies due to the change of state of the latter"; "fire is never generated *de novo*; but . . . a certain force of fire was created with the world by the word of God."[13]

Against the theory that heat is motion, Cleghorn argued that "if it depended on motion, then fire impressed on a body would pass quickly through its whole mass, and if the body were elastic, in a moment of time; but heat, after the manner of fluids, moves slowly." Similar objections were later made to the kinetic theory of gases: that heat conduction ought to be so rapid that any temperature differences would be immediately smoothed out, contrary to experience. Cleghorn had another objection on this point: "If heat depended on vibration, then, when an impulse has been given, it ought to be communicated to a body in proportion to the quantity of matter in the body; this is completely refuted by experiments made on the quantity of fire in a great number of bodies." On the other hand it was known that fire can pass through a vacuum and thus exists apart from other matter.[14]

The name "*calorique*" was proposed in 1787 by De Morveau, Lavoisier, Berthollet and Fourcroy in their influential *Méthode de Nomenclature Chimique*, and Lavoisier included *calorique* as one of the elements in his *Traité élémentaire de Chimie* (1789). The first chapter of the *Traité* was devoted to an exposition of the caloric theory; as in Cleghorn's theory, the particles of caloric were considered to repel each other but to attract matter in various degrees.

At the beginning of the 19th century, caloric was the keystone of anti-phlogistic chemistry, and was used in explaining phenomena such as thermal expansion, specific heat, change of state, latent heat, and the heat evolved in chemical reactions, even though one could not say that the majority of scientists considered the theory firmly established.[15] It seemed to be a basic part of Dalton's thinking about atoms.[16] The chief opponents of the caloric theory at this time were Rumford and Humphry Davy; they produced a number of famous experiments (boring of cannon, melting of ice by friction, etc.) in support of the doctrine that heat is motion.[17,18] Rumford and others also attempted to undermine the materiality of heat by showing that it has no weight.[19]

The caloric theorists attacked Rumford and Davy with considerable force, and claimed that the same experiments could be explained by assuming heat to be a fluid, whereas other experiments such as the passage of heat through a vacuum could not be explained by the motion theory.[20] Cajori has cited a number of American and German authors who favored the caloric theory during the period 1800–30, and Brown has shown how this theory can be presented in a logically coherent, semiquantitative manner to modern physics students, thereby forcing them to think through more carefully than is usually done the reasons for replacing it by thermodynamics.[21]

The explanation of the gas laws of Boyle and Gay-Lussac was not a major concern of the caloric theorists, perhaps because these laws seemed to be so simple that any reasonable hypothesis about caloric could be made to explain them. For example, if one assumes that the caloric atmospheres of atoms produce a repulsive force that varies inversely as the distance between the centers of the atoms, one can then rely on Newton's derivation of Boyle's law mentioned in §1.2.[22] This type of explanation would interfere with the desire of Laplace and others to postulate short-range *attractive* forces between molecules in order to explain phenomena such as capillarity; thus there was a tendency to assume that the repulsive force of caloric operated at *greater* distances than these attractive forces. Yet there still had to be a limitation on the range of these forces so that in integrating the effects of all molecules on a piston one could get a finite result. This problem was discussed in 1815 by Ampère who argued that one could derive Mariotte's [Boyle's] law without specifying a particular force law, as long as one assumes that the integral over infinite distance is a finite constant. Then the total pressure on a piston would be proportional simply to the *number* of molecules in the gas.[23] By inserting the words "in a given volume" after "number of molecules" Ampère fooled himself into thinking he had proved that the total pressure would increase as the volume containing a fixed number of molecules is decreased (the argument to this effect in the last paragraph of his paper is based on an assumption that contradicts his earlier ones).

It was also possible to explain the gas laws in terms of an equilibrium of absorption and emission of radiant caloric by individual molecules, as Laplace proposed to do in 1821; but Herapath pointed out some serious defects in that explanation.[24] One could avoid all these difficulties by simply postulating that pure caloric is an ideal gas, so that molecular interactions would yield only negligible corrections to the equation of state; by using a mathematical model due to Poisson, the Swiss physicist Ritter was able to calculate such corrections in 1845 (§11.3).

A major accomplishment of the caloric theory was its use by Laplace and Poisson to elucidate the relation between the ratio of specific heats of a gas (at constant volume and at constant pressure) and the speed of sound, in the context of a general theory of adiabatic compression.[25] This relation survived the death of caloric theory and was ultimately considered to be valid, independent of any molecular model, though 20th-century kinetic theory helped to clarify the reasons why it breaks down under certain physical conditions.

We should also recognize that two other permanent contributions to physics grew out of the caloric theory and did not suffer any serious changes when that theory was abandoned: Fourier's theory of heat conduction (§14.2) and Carnot's theory of the motive power of heat in steam engines (§14.3). Fourier's theory applies to a large number of situations in which heat can be treated as a conserved substance; while Carnot's theory led to correct results (now embodied in the Second Law of Thermodynamics) in spite of the fact that Carnot originally assumed that mechanical work can be done by means of heat without destroying any of the heat.[26]

We must now face the question: What factors led to the overthrow of the caloric theory? It seems clear that the experiments of Rumford and Davy, whatever later scientists may think they proved, were not regarded at the time as refuting the caloric theory by most scientists. Gay-Lussac's experiment on the free expansion of gases (1807) was later interpreted as a refutation of the idea that gas pressure is due to repulsive forces between particles, but it does not seem to have been used as an argument against the caloric theory before 1840.[27] L. Pearce Williams has suggested that Kant and the ideas of German *Naturphilosophie* may have had some influence in breaking down the beliefs of scientists in material fluids such as caloric.[28] But the only definite evidence in favor of this suggestion, as far as I know, is the case of the Russian chemist A. N. Scherer, who abandoned the caloric theory and explained heat simply in terms of forces in 1795,[29] and the Danish physicist H. C. Oersted, who advanced similar opinions in 1812.[30] I think we must look elsewhere.

My conclusion, based on material presented in detail in ch. 9, is that the caloric theory of heat was rejected by most scientists by 1840, not because of any difficulties in explaining thermal phenomena, but because the particle theory of light had been replaced by the wave theory of light. Because of the great interest in *radiant* heat during the period 1800–40, and several key experiments which indicated that radiant heat had the same qualitative properties as light, it was generally accepted that both light and heat must be explained by the same kind of theory. So, when the Young–Fresnel theory was accepted after 1820, it seemed to follow logically that heat too is a form of ether vibration; hence the rise of the "wave theory of heat."

The transition from the caloric to the wave theory of heat was not too difficult, since many of the properties formerly assigned to caloric could now be attributed to ether; other properties were simply reexpressed in terms of the "motion" of the ether rather than the "amount" of caloric. This had the great advantage that only one imponderable fluid was needed instead of two; and indeed the desire for unity in 19th-century natural philosophy expressed itself in many cases by making a single fluid do the jobs previously assigned to several separate ones.

Early supporters of the wave theory of heat were careful to note that they were *not* simply returning to the Rumford–Davy theory of heat as *molecular* motion; that theory was not satisfactory in explaining the phenomena of *radiant* heat. But once it became customary again to think of heat as the motion of some kind of material substance, it was hard to resist the further conclusion that heat does involve molecular motion in some way. Although the primacy of ether vibrations was subsequently abandoned in thermodynamics, there remained throughout the rest of the century the vague idea that the ether might be useful in explaining how energy gets exchanged and equilibrated between particles of matter.

Notes for §1.5

1. See §9.2, note 2.
2. Since we are now very careful to point out the distinction between the thermal energy contained in a body and the infrared electromagnetic radiation which produces thermal effects when it strikes a body, we may be in danger of forgetting that such a distinction hardly existed before 1850, and thus we miss a connection between light and heat that was historically of great importance. The older histories of heat, written by Whewell and Langley, however inadequate they may be in other respects, at least do have the advantage of recognizing this connection. W. Whewell, *History of the Inductive Sciences* (London, 1837), II, Book X (the 3rd ed., 1856, recognizes the distinction in an additional note to Book X on "The Dynamical Theory of Heat"). S. P. Langley, *Pop. Sci. Monthly* **34**, 212, 385 (1889).
3. F. Cajori, *Isis* **4**, 483 (1922). M. K. Barnett, *Sci. Monthly* **62**, 165 (Feb. 1946).
4. R. Fox, *The Caloric Theory of Gases* (Oxford: Clarendon Press, 1971). R. J. Morris, Jr., *Eighteenth-Century Theories of the Nature of Heat* (Ph.D. Dissertation, University of Oklahoma, 1965); *Proc. Oklahoma Acad. Sci.* **42**, 195 (1962); *Brit. J. Hist. Sci.*

6, 1 (1972). A. Wolf, *A History of Science, Technology, and Philosophy in the 18th Century* (New York: Macmillan, 2nd ed., 1952), I, ch. VIII. P. Duhem, *Rev. deux Mondes* **129**, 869 (1895). G. Ronge, *Math.-Physik. Semesterberichte zur Pflege des Zusammenhangs von Schule und Universität* **5**, 92 (1956).

5. D. McKie and N. H. deV. Heathcote, *The Discovery of Specific and Latent Heats* (London: Arnold, 1935). D. Roller, in *Harvard Case Histories in Experimental Science*, ed. J. B. Conant (Cambridge, Mass.: Harvard University Press, 1948), I, 119. On the question of Watt's independent discovery of latent heat in connection with the properties of steam, see James Watt, *Edinburgh Phil. J.* **2**, 1 (1820); M. Kerker, *Tech. and Culture* **2**, 381 (1961). For the work of Cavendish see W. V. Harcourt, *B. A. Rep.* **9**, 45 (1839).
6. Joseph Black, *Lectures on the Elements of Chemistry* (Edinburgh, 1803).
7. Thomas Young, Thomas Thomson, William Henry, Peter Mark Roget, etc.
8. The retention of terms such as "specific heat," "latent heat," and "heat content" obscures the main point of thermodynamics, *viz.* that heat is not a function of state, hence a body cannot be said to *contain* a certain amount of heat; it is possible to go from one state to another (including liquid to gas or solid) by purely mechanical processes–expansion or compression–without any transfer of heat.
9. Black, *op. cit.* (6), pp. 33–34, quoted by McKie and Heathcote in their introduction to Cleghorn's *De Igne. Ann. Sci.* **14**, 1 (1958).
10. Roller, *op. cit.* (note 5), p. 153. For a detailed study of Black's ideas on heat consult David R. Dyck, *The Nature of Heat and its Relationship to Chemistry in the Eighteenth Century* (Ph.D. Dissertation, University of Wisconsin, 1967).
11. B. B. Kelham, in *John Dalton and the Progress of Science*, ed. D. S. L. Cardwell (Manchester: Manchester University Press, 1968), p. 109. Bryan Higgins did not approve of the phrase "latent heat"–see *A Philosophical Essay concerning Light* (London, 1776), I, xliv (I am indebted to Mrs. Emily van Zee for this reference).
12. D. McKie and N. H. deV. Heathcote, *Ann. Sci.* **14**, 1 (1958). This article contains the text of the original Latin dissertation with English translation, commentary, and notes.
13. *Ibid.* p. 43.
14. *Ibid.* p. 15.
15. S. Lilley, *Actes* 5^e *Cong. Int. d'Hist. Sci.* (Lausanne, 1947), p. 130; *Arch. Int. Hist. Sci.*, p. 630 (1948).
16. John Dalton, *A New System of Chemical Philosophy* (London, 1808), I, ch. I. R. Fox, in *John Dalton and the Progress of Sciences*, ed. D. S. L. Cardwell (Manchester: Manchester University Press, 1968), p. 187. L. K. Nash, in *Harvard Case Histories in Experimental Science*, ed. J. B. Conant (Cambridge, Mass.: Harvard University Press, 1948), I, 215.
17. *Collected Works of Count Rumford*, ed. S. C. Brown (Cambridge, Mass.: Harvard University Press, 1968), I. S. C. Brown, *Benjamin Thompson–Count Rumford, Count Rumford on the Nature of Heat* (Oxford and New York: Pergamon Press, 1967). S. C. Brown, *Count Rumford: Physicist Extraordinary* (Garden City, N.Y.: Doubleday Anchor, 1962). W. J. Sparrow, *Count Rumford of Woburn, Mass.* (New York: Crowell, 1965). S. C. Brown, *Am. J. Phys.* **20**, 331 (1952). M. Watanabe, *Isis* **50**, 141 (1959).
18. Humphry Davy, "An Essay on Heat, Light, and the Combinations of Light" in *Contributions to Physical and Medical Knowledge, primarily from the West of England*, ed. T. Beddoes (Bristol, 1799), reprinted in Davy's *Collected Works* (London, 1839), **2**, 9. H. Davy, *Elements of Chemical Philosophy* (London, 1812), I.

Extracts reprinted in John Tyndall's *Heat a Mode of Motion* (London, 1863, 4th ed., 1873), App. to ch. III. E. N. da C. Andrade, *Nature* **135**, 358 (1935). D. McKie, *Nature* **135**, 878 (1935).

19. Experiments to determine the weight of heat were reviewed by W. Heintz, *Z. ges. Naturw.* **1**, 417 (1853); Heintz concluded that there is definitely no change of weight in chemical reactions involving heat. Hans Landolt reinvestigated the question at the end of the 19th century with more accurate methods, and in 1909 concluded that the law of conservation of mass is correct to within an error of less than a thousandth of a milligram (the relativistic mass changes predicted by Einstein in 1905 would be much less than this amount in the chemical reactions studied by Landolt). See A. Hermann, *1966 Kalendar der Bad. Anilin und Sodafabrik.*

    Another argument was that if heat from the sun had weight it would have momentum and thus produce an observable effect on the motions of the planets; since no such effect is observed, heat does not have weight. P. W. Holland, *Phil. Mag.* [3] **9**, 396 (1836). (This argument seems to be endangered by the tendency to explain the fact that comets' tails point away from the sun as an effect of heat radiation.)
20. William Henry, *Manchester Mem.* **5** (2) 603, 679 (1802). Tilloch, *Phil. Mag.* **9**, 158 (1801) [quoted by S. C. Brown, *op. cit.* (note 21)]. J. B. Emmett, *Ann. Phil.* **9**, 421 (1817) and later papers in this journal. G. Gregory, *The Economy of Nature* (London, 1796), passage reprinted in Brush, *Kinetic Theory* **1**, 66. Robert Hare, *Am. J. Sci.* **4**, 142 (1819) and subsequent discussion by Olmsted and Hare in *Am. J. Sci.* **11–13** (1826–28). Thomas Graham, *Ann. Phil.* **12**, 260 (1826). On Hare's criticism of Davy see §2.2
21. S. C. Brown, *Am. J. Phys.* **18**, 367 (1950).
22. Emmett, *Ann. Phil.* **21**, 243 (1823).
23. Ampère, *Ann. Chim. Phys.* **94**, 145 (1815).
24. Brush, *Kinetic Theory* **1**, 11–16.
25. See §3.3, note 8. According to C. Truesdell [*Rational Fluid Mechanics 1765–1788*, p. CIV] the Laplace–Poisson treatment is unsatisfactory: "The usual modern explanation in terms of an adiabatic process was not attained until after the formulation of thermodynamics."

    For further quantitative developments of the theory see W. S. Sankey, *Edinburgh J. Sci.* [2] **1**, 17 (1829); O. F. Mossotti, *Sur les Forces qui régissent la Constitution intérieure des Corps, aperçu pour servir à la Determination de la Cause et des Lois de l'Action Moléculaire* (Turin, 1836); P. Kelland, *Trans. Cambridge Phil. Soc.* **7**, 25 (1839). These and other papers are summarized by Isaac Todhunter, *A History of Elasticity* (Cambridge, 1886), I. Although Kelland and others refer to caloric particles, they are now concerned not so much with the theory of heat as with the elastic properties of solids as they can be related to molecular forces.
26. Since Carnot did later abandon the caloric theory, it has sometimes been suggested that Carnot's discussion in the *Reflexions* should be considered as a "correct" modern thermodynamic analysis, by reinterpreting his term "calorique" as "entropy." I think T. S. Kuhn has effectively disposed of this suggestion by showing that whatever pedagogical value it may now have, this reinterpretation has no basis whatsoever in Carnot's own exposition of his theory, and can only confuse our historical understanding of the subject. *Am. J. Phys.* **23**, 91, 387 (1955).
27. The connection between Gay-Lussac's experiment and Mayer's work on the mechanical equivalent of heat is discussed by J. T. Merz, *A History of European Thought in the Nineteenth Century* (Edinburgh: Blackwood, 1904–12), II, 109, note 1.

The free-expansion experiment was done somewhat more accurately by J. P. Joule and William Thomson in 1853; they found that in some cases there is a slight cooling effect, indicating that in the process of expanding the gas, work has been done against long-range intermolecular *attractive* forces. According to Merz, the Joule–Thomson experiment was the "real proof" that the kinetic rather than the static Newton–Boyle conception of gas structure is correct (*op. cit.*, I, 434, note 2).

28. L. Pearce Williams, *Hist. Sci.* **1**, 1 (1962).
29. R. Kargon, *Centaurus* **10**, 253 (1964).
30. H. C. Oersted, *Ansicht der chemischen Naturgesetze* (1812), cited by Kargon, *op. cit.*; *Recherches sur l'Identité des Forces Chimiques et Électriques* (Paris, 1813), pp. 159–200. See also Zerah Colburn, *An Inquiry into the Nature of Heat*... (London, 1863); Francois Zantedesche, *Trattato del Calorico e della Luce* (Venice, 1846) [rev. by E. Wartmann in *Arch. Sci. Phys.* **2**, 25 (1846)].

1.6 The Second Scientific Revolution 1800–1950

The acceptability of a kinetic theory of gases depended primarily on its compatibility with prevailing theories in other areas of physical science, rather than on the details of the theory itself. Thus John Herapath, despite persistent efforts from 1820 to 1848, was unable to obtain serious consideration of the theory by other scientists (see ch. 2), and J. J. Waterston could not even get his major paper published as late as 1846 (see ch. 3); but when the theory was revived in the 1850's by Krönig, Clausius, and Maxwell, it was favorably received and quickly absorbed into the mainstream of physics (chs. 4 and 5). What had happened in the meantime was the establishment of the generalized law of conservation of energy by Mayer, Joule, and Helmholtz in the 1840's, and the formulation of the laws of thermodynamics by Clausius, Thomson, and Rankine in the early 1850's; it was now an obvious step to describe heat as a form of mechanical energy rather than as a separate substance.

In this section I try to put these events into a still larger context: the transition from classical (Newtonian) to modern science which may be designated the "second scientific revolution." In order to do this it will be necessary to challenge the traditional view, that 19th-century physical science was a relatively peaceful continuation of the Newtonian era, and that the revolutionary changes began only at the beginning of the 20th century. On the contrary, I will claim that the Second Scientific Revolution really began at the beginning of the 19th century, and was essentially complete around the middle of the 20th century; and that the dramatic events of 1900 and 1905 were only the more visible manifestations of a larger historical process that was already well under way.

The present topic is one that is best approached by defining terms. To begin, I refer to the *second* scientific revolution, on the assumption that the reader accepts the usual view of historians of science that the *first* one took place during the period 1500–1800, and that nothing before that could properly be called a scientific revolution. This view is explicit in the title of A. Rupert Hall's authoritative survey, *The Scientific Revolution 1500–1800.* In particular, one assumes that:

(1) the Aristotelian/Ptolemaic theory of the universe, which was generally accepted up to about 1500, developed slowly out of a common-sense interpretation of natural phenomena, and never had to replace a previously well-entrenched theory;

(2) the various changes in the physical sciences that occurred during the period 1500–1800 are best described as successive or overlapping stages of a single process: thus the revolution began in astronomy, continued in physics, and ended in chemistry, with repercussions in the biological sciences and in philosophy. The end result was a more-or-less unified viewpoint about science, which was eventually to be challenged in all areas by the second scientific revolution.

But why are we justified in using the word *revolution* in talking about developments in *science*? Does a scientific revolution have any similarity to political revolutions, for example? If you think of a revolution as something that occurs suddenly, and is accompanied by considerable violence as the old regime is overthrown by its opponents, then you might well wonder why it is legitimate to apply the term to changes in abstract ideas that take place over a period of two or three centuries. Are we not being overdramatic in talking about scientific revolutions? That would seem to be the viewpoint of Stephen Toulmin, who has recently proposed the phrase "evolutionary development of natural science"[1] in contrast to the well-publicized emphasis on "scientific revolutions" in the book of Thomas S. Kuhn.[2]

On the other hand, if we look at what historians have been saying about revolutions, we find that some of them paint an entirely different picture. According to writers such as Lyford P. Edwards[3] and Crane Brinton,[4] who have studied and compared the major English, American, French, and Russian revolutions, a revolution is best regarded as a *slow* process of change. There is very little actual violence, compared to a war. Instead, there is a long preliminary period, extending over several generations, during which intellectual propagandists spread the idea that the established regime is corrupt and tyrannical. In fact, the regime may well be extremely corrupt and unsuited to the needs of the people, but it also becomes so weak and inefficient that it can no longer succeed in being tyrannical. When it finally collapses, the transfer of power is almost bloodless. The government is now taken over by a group of moderate reformers, who often do not even think of themselves as revolutionaries; they are simply trying to restore the old system by patching up some of its more obvious deficiencies. But this moderate provisional government cannot stay in power very long, since both the conservatives and the radicals see it as an unsatisfactory compromise. Either the radicals take over (in which case we say that the revolution was successful) or else the conservatives come back (in which case we say the revolution failed and we tend to forget about it). It is only at this point that any violence is likely to occur, as some of the conservatives or moderates now realize that things have gone much farther than they expected, and they try to stage a counter-revolution which the radical government must suppress by force. Partly as a result of this phenomenon, the new radical regime tends to be much more dictatorial and intolerant of dissent, at least in the first few years, than was the old conservative regime in the years just before it was overthrown.

The first scientific revolution did have many of the characteristics of political revolutions (as schematized by Edwards and Brinton) though of course there are many features of the Edwards–Brinton analysis that have no obvious counterparts in science. There was a prolonged period of critical discussion of the physical and astronomical theories of Aristotle and Ptolemy, extending through the 14th, 15th, and 16th centuries, so that by the early 17th century few reputable scientists still accepted them in their original form. This is not to say that perceived "anomalies" had created a crisis situation that would induce a large number of scientists to abandon the basic world view of Aristotle and Ptolemy.

Copernicus and Tycho Brahe, who actually started the revolution in the sense that they persuaded a majority of astronomers to abandon the fundamental postulate that everything revolves around the earth, nevertheless accepted most of the features of the old system that were later to be abandoned as a result of their own work. Copernicus still insisted on using circles and combinations of circles (epicycles) to explain planetary motion; his methods of calculation and his physical arguments were almost identical to those of Ptolemy. He stated quite explicitly that the Ptolemaic system was consistent with the observational data; its fatal defect was that it was "neither sufficiently absolute nor sufficiently pleasing to the mind" because the fundamental principle of uniform circular motion had been sacrificed when the "equant" device was introduced, making the motion of a planet uniform only with respect to an imaginary point which is not the center of its circular orbit.[5] Nothing could have been farther from the thoughts of Copernicus than a revolution that would throw out circular orbits entirely and discard the whole system of Aristotelian physics and philosophy.

Even the single innovation of making the earth go round the sun was too radical for Tycho Brahe. Instead, he proposed a compromise system that retained the mathematical advantages of the Copernican system while avoiding the physically unreasonable hypothesis that the earth moves: Tycho assumed that the planets Mercury, Venus, Mars, Jupiter, and Saturn go around the sun, but the sun itself goes around a stationary earth. The Tychonic system was quite popular for a short period at the beginning of the 17th century, and may be regarded as the "provisional government" in the early stages of the revolution. (The theories of René Descartes played a somewhat similar role in physics and philosophy, though Descartes went further in abandoning the Aristotelian world view.)

The only real violence during the first scientific revolution was committed by the Roman Catholic Church, in burning Giordano Bruno in 1600 and in silencing Galileo under threat of torture in 1633. These actions, which were directed not so much against the substantive content of the new theories as toward a perceived threat to the Church's authority, came much too late to stop the revolution, and indeed they are quite analogous to what Edwards describes as "the violent outbreaks . . . due to that conservatism which makes the economically favored classes unwilling to recognize the fact that a real and peacable revolution has already occurred."[6]

Just as political revolutions are usually undertaken under the banner of freedom and democracy, scientific revolutions may begin with an attack on the tyranny of traditional authority in the realm of thought, and promise to create a healthier atmosphere in which reason and experiment will be the only tests of the validity of new theories (cf. Power's view quoted above, end of §1.2). Yet the authority of Newton was much stronger in the 18th century (once Descartes had been defeated) than was the authority of Aristotle and Ptolemy in the 16th. It was in part the revival of Platonism, coming *before* there was any general dissatisfaction with geocentric astronomy, that prepared the way for the first scientific revolution; the very fact of that revival seems to demonstrate that the Aristotelians did *not* have such a stranglehold on the intellectual community as was alleged by their opponents. It would be entirely misleading to infer from the trial of Galileo in 1633 that the Catholic Church had tried to suppress the new scientific theories when they appeared earlier in the 16th century. There was considerable opportunity for expressing heretical scientific opinions during the last days of Aristotelian domination; but once the Newtonians were in power, no prudent scientist (at least in England) would dare to contradict the real or supposed opinions of the "autocrat of science"[7] until late in the 19th century. (The extraordinary resistance encountered by early writers on the kinetic theory of gases who were attempting to displace Newton's casual ideas about gas pressure provides a good example of this.)

Having reassured ourselves that the term "revolution" may have some relevance to the history of science, let us now proceed to describe the beginnings of the Second Scientific Revolution.

The old regime in 1800 was of course what we now call "classical mechanics," or rather the Newtonian synthesis of physics and astronomy, recently extended to chemistry by Lavoisier and more or less influential in the other sciences; but still lacking the fully developed wave theory of light, generalized energy concept (including thermodynamics), and Maxwellian electrodynamics. Although in the 17th century the most spectacular successes of Kepler, Galileo, and Newton had been achieved by sophisticated analysis of *motion*, so that today we refer to "Newton's laws of motion" as the epitome of classical physics, there had been hardly any advances in the treatment of motion during the 18th century. (The works of Euler and the Bernoullis on fluid dynamics should perhaps be considered an exception to this statement.) Whenever scientists were confronted with new phenomena, whether in electricity or in chemistry, they tended to seek an explanation in terms of new kinds of *matter* or new kinds of *forces* rather than new kinds of *motion*. Thus there was a proliferation of ethers and effluvia and chemical elements around the end of the 18th century; although the general approach was mechanistic, it was in fact the opposite of reductionist, since all the elements and all the fluids (electric, magnetic, thermal, etc.) were seen as distinct kinds of substance.[8] It seemed for a while that the physical scientists had lapsed into the mania for classification of species and minerals that afflicted the natural scientists of the 18th century.

This tendency to look for explanations based on different kinds of matter may be characterized as *materialism* (with apologies to philosophers who are accustomed to a slightly different usage of that word); it is distinct from, though often overlaps, what is known as *mechanism.*[9] It is also distinct from the tendency to look for explanations based on different kinds of *forces,* which is sometimes called *dynamism.*[10] Finally, I would like to use the rather inelegant term *kineticism* (or "kinetic world view") to denote the tendency to look for explanations based on motion; the kinetic theory of gases is an example, but in its later forms combines elements of both materialism and dynamism in specifying molecular models.

The Newtonian mechanistic world view seemed to be compatible with moderate amounts of materialism, dynamism, and kineticism; yet an excessive concentration on any one of these aspects to the exclusion of the others could undermine its stability.

Newtonian mechanics, as of 1800, also included the notions of *determinism* and *reversibility,* but these were usually not made explicit until confronted with possible opposites. Despite the fact that randomness and irreversibility were introduced in the world view that displaced the Newtonian, these concepts could also be incorporated into a Newtonian kinetic theory (see ch. 14); whether their introduction made a revolution inevitable is an open question.

At this point it is appropriate to say something about how the biological sciences fit into the Second Scientific Revolution. I will not say very much, for a very good reason: I know practically nothing about 20th-century biology, and very little about 19th-century biology. Nevertheless, I have to say that biology played a much more important role in the second revolution than it did in the first. After all, one of the basic metaphors of modern science is the "evolutionary process" which replaces the "clockwork mechanism" of Newtonian science.[11] Of course "evolutionary" is a very vague term, and in the physical sciences it may mean nothing more than "irreversible." In any case, the principle of irreversibility came into 19th-century physics to a large extent through geological considerations (§14.2), so we must at least include some aspects of geology in discussing the basic ideas of the second scientific revolution. Curiously enough, it was just those aspects–*e.g.* calculations of the age of the earth from heat-conduction theory–that appeared at the time to be opposed to Darwin's version of evolutionary biology.[12] Let us take this as a warning that an accurate treatment of the relations between the natural and physical sciences during the past two centuries will have to go far beyond a superficial identification of concepts and tendencies.

Although broad themes like "clockwork mechanism" and "evolutionary process" are helpful in characterizing scientific revolutions as a whole, they may not be very useful in describing the detailed sequence of events that constitutes a revolution. It is probably better to identify and focus on certain crucial problems that scientists considered especially important at a particular time, and to see how the solution of one led on to a certain preferred method for attacking the next one.

For the first revolution, these problems appeared to be, first, the apparent motions of the sun, stars, and planets; and second, the collisions of small hard spheres. Copernicus, Brahe, Kepler, and Galileo approached the first problem, not with the intention of using it to demolish the philosophical-scientific systems they inherited from Aristotle and Plato, but with the hope of finding a more satisfactory solution of the problem at the cost of only minimal changes in those systems. For example, it required a deep commitment to discovering the mathematical harmony of the universe, in the Pythagorean sense, to induce Kepler to abandon the circles so dear to the earlier astronomers' hearts; if he had not devoted himself to a massive attack on a highly technical problem, the orbit of Mars, he would not have been forced to introduce the ellipse into astronomy.

About 70 years later, in 1668, it became so obvious to the leaders of the Royal Society of London that the further development of the mechanical philosophy (in the then popular Cartesian formulation) required exact knowledge of the laws of impact that they initiated a cooperative effort to solve the problem.[13] The outcome of this subject–the publication of the principle of conservation of momentum by Wallis, Wren, and Huygens–provided a firm base for Newton's dynamics that was eventually to overthrow the Cartesian system of physics.

Often in the history of science we find that a scientist dives into a problem, carrying one set of philosophical baggage; when he finally surfaces with the solution, the baggage has become so waterlogged that it is no longer attractive to other scientists who come to value the solution of the problem for its own sake, regardless of philosphical aspects. In this way, major changes in scientific concepts may take place in the absence of a debate about the concepts themselves.

I suggest that the key problems of the second revolution for physicists were: first, the propagation of light and heat radiation and their interactions with matter; second, the connection between electricity and magnetism. (As it turned out the problems converged.) To emphasize my disagreement with other interpretations, let me add that I think both of these were much more important than the microstructure of matter or the nature of space and time, or the question of whether heat is molecular motion or a substance. The latter were problems that physicists liked to *discuss* at various times during the first revolution as well as the second, and in each case the revolution appeared to yield finally a fairly definite solution. Yet I would argue that a direct attack on these problems was almost always fruitless, and solutions were usually obtained only as byproducts of the solutions of the key problems mentioned above.

A third key problem that 19th-century physicists shared with geologists, astronomers, and engineers was that of the balance and flow of energy–on a large scale in the earth–sun system, in space, and in situations affecting man. The energy problem interacted with the other problems in various ways, sometimes stimulating the development of mathematical methods that were later useful in theoretical physics (such as Fourier's theory of heat conduction), sometimes providing a technological incentive (energy conservation and thermodynamics), and sometimes posing challenges to fundamental ideas (irreversibility).

Often the turning point in a revolution is not a new physical idea but the unexpected result of a mathematical calculation. Just as a political revolution, once it is underway, seems to acquire an irresistible momentum which pushes along its nominal leaders perhaps faster than they wanted to go, so his mathematical derivations may force a physicist to accept conclusions for which his physical intuition has not yet prepared him. Despite the frequently repeated assurance that mathematics, if done correctly, is pure tautology–it cannot give you back any more information about the physical world than you put into it–it is precisely what Eugene Wigner has called "the unreasonable effectiveness of mathematics in the natural sciences"[14] that has provided a significant driving force in scientific revolutions.

In 1818, Augustin Fresnel (1788–1827) presented to the Academie des Sciences of Paris his memoir on the wave theory of light, as an entry in a prize competition on the subject of the diffraction and interference of light.[15] The jury was stacked against him: Laplace, Poisson, and Biot were strong supporters of the particle theory, while Gay-Lussac was neutral and only Arago was sympathetic to the wave theory. But revolutions in science, as in politics, are precipitated by the actions of individual men rather than by a popular vote. Often it is a leader of the old regime who unwittingly sets in motion the train of events leading to the downfall of his government. Simon Denis Poisson (1781–1840) was one of the outstanding French geniuses in mathematical physics at the beginning of the 19th century, second only to

Laplace. He had developed the major part of the modern theory of electrostatics and magnetostatics, using the device of a function defined everywhere in space, satisfying a differential equation containing the charge distribution specified in a particular problem.[16] (This function, a generalization of a similar function used by Laplace in gravitational theory, was given its present name "potential" by the British mathematician George Green in 1828. It was later to appear as the precursor of the "field" concept of Faraday, Kelvin, and Maxwell.) Poisson's contribution to the theory of sound has already been mentioned (§1.5).

Poisson was not only a staunch defender of the reigning Newtonian theories of electricity, magnetism, and heat; he was also a supporter of the particle theory of light. When he examined Fresnel's memoir on the wave theory, his sharp eye caught a mathematical consequence that had escaped Fresnel himself: if a beam of light encounters a circular disk there should be a singular diffraction pattern characterized by a tiny bright spot at a certain distance directly behind the disk.[17] But Poisson had never heard of anyone observing such a bright spot.[18] So he proposed this to Fresnel as an experimental test of his theory, presumably in the belief that there would *not* be any such bright spot and thus the wave theory would be refuted. The experiment was performed, and the bright spot appeared just where the mathematics predicted! This surprising result, taken with the success of Fresnel's theory in treating many other optical phenomena, forced Poisson and Laplace to award the prize to Fresnel; even though they did not abandon the particle theory themselves, the rest of the scientific world soon adopted the wave theory of light.

That was the first major step in the Second Scientific Revolution. But we must look elsewhere for the second step; further development of the wave theory of light quickly became entangled in the snares of Newtonian physics. When Thomas Young and Fresnel proposed to explain polarization phenomena by the hypothesis of transverse vibrations–in itself a perfectly plausible hypothesis–it appeared that the ether would now have to be conceived as an elastic solid rather than as a fluid. The search for a consistent mechanical model of the ether turned out to be a wild goose chase which dissipated the energies of many talented 19th-century mathematical physicists (though it produced, as a valuable byproduct, some theorems in continuum mechanics); aside from the discoveries of Maxwell, the theory of light did not play a significant role in the revolution again until the end of the century.

The second step has already been mentioned in the preceding section: because it was generally believed in the 1820's and 1830's that light and heat are merely qualitatively different aspects of the same phenomenon (because of the experiments on radiant heat conducted during that period), the adoption of a wave theory of light entailed the adoption of a wave theory of heat. More generally, it meant a shift from the materialist style of explanation to the kineticist style, though a kinetic theory in the modern sense was not yet acceptable as long as the ether was assigned a dominant role.

Equally important from this viewpoint were the discoveries in electromagnetism made by Hans Christian Oersted, André-Marie Ampère, and Michael Faraday in the 1820's and 1830's. Oersted's discovery indicated that while electric and magnetic matter *at rest* exerted no forces on each other, electric charges *in motion* could act on a magnet. Faraday found that an electric current could be induced by another current only if the other current was *changing*, or by a magnet only if it was *moving* relative to the conducting wire. Ampère, in addition to demonstrating the force between two currents that one might expect to find as a consequence of Oersted's discovery, proposed that magnetism itself might be regarded not as a separate entity but as an effect of the motion of electricity.[19] That suggestion was not taken seriously until after the establishment of the energy-conservation law, when it could be seen as an integral part of the kineticist world view. To illustrate this point we have William Thomson's testimony, dated 1872:

> From twenty to five-and-twenty years ago, when the materials of the present compilation were worked out, I had no belief in the reality of this theory [Ampere's molecular-current model of magnetism]; but I did not then know that motion is the very essence of what has been hitherto called matter. At the 1847 meeting of the British Association in Oxford, I learned from Joule the dynamical theory of heat, and was forced to abandon at once many, and gradually from year to year all other, statical preconceptions regarding the ultimate causes of apparently static phenomena.[20]

According to Einstein and Infeld, it was the discovery of Oersted and Faraday that electromagnetism involves *non-central forces*, together with the difficulty in constructing a plausible model of an ether that could propagate transverse light waves, that led to the downfall of the mechanical view of nature.[21] While Einstein of course did not claim to be an historian of science, his opinion about the origins of the revolution in which he played such an important role cannot be ignored. Einstein and Infeld further asserted that the formulation of Maxwell's electromagnetic field equations, which led to a theory of transverse light waves explicitly based on non-central electromagnetic interactions, was "the most important event in physics since Newton's time."[22] Maxwell's theory led physicists away from the assumption that the world consists of pieces of matter from which forces emanate, toward the notion that force-determining fields have a real existence in space, independent of the presence of matter. That meant pushing the viewpoint of *dynamism* to its extreme limits. Yet it took quite a long time before this consequence of the Oersted–Faraday discoveries was taken seriously; it was not until 1888 that Heaviside pointed out that, contrary to the impression created by a statement of Maxwell, modern electrodynamics does *not* follow Ampère in postulating a central force between current elements.[23] For Ampère, Faraday's circular "lines of force," floating in space rather than anchored to atoms, were incompatible with Newtonian physics; they could be avoided by making a different postulate about the (unobservable) forces between hypothetical pieces of current-carrying wire, designed to lead on integration to the correct net force between complete circuits.[24] Yet the theorists who rejected Ampère's postulate in the 19th century did not seem to think that their own postulates were incompatible with Newtonian physics.[25]

* * *

To illustrate my assertion that the microstructure of matter was *not* one of the crucial problems at the beginning of the 19th century, I mention the rather odd outcome of Dalton's work on the chemical atomic theory. Recall that Dalton had originally been interested in the problem of the uniform composition of the atmosphere: what keeps gases of different specific gravity (oxygen and nitrogen) from separating out?[26] After pursuing various related investigations which led him eventually to develop a table of atomic weights for the elements, he returned to this problem in 1804 or 1805 and developed a new theory of mixed gases. This theory was based on the idea that the sizes of particles of fluids are different, because they have different affinities for heat. The size of a particle depends on the space occupied by its atmosphere of heat, and each atmosphere was assumed to be in contact with the atmospheres of neighboring particles. This conception led Dalton to an explicit denial of the "confused idea" which he reports he had previously shared with many of his contemporaries, that every elastic fluid at the same pressure and temperature contains the same number of particles:

> It is evident the number of ultimate particles or molecules in a given weight or volume of one gas is not the same as in another: for, if equal measures of azotic and oxygenous gases were mixed, they would form nearly two measures of nitrous gas, having the same weight as the two original measures; but the number of ultimate particles could at most be one half of that before the union. No two elastic fluids, probably, therefore, have the same number of particles, either in the same volume or the same weight.[27]

In his new theory of mixed gases, it was the differences in diameters of different kinds of particles that were responsible for keeping them mixed up; in Dalton's mind these differences were also responsible for excluding what later came to be known as "Avogadro's hypothesis."

His theory of particle diameters was only one aspect of the complex of theoretical preconceptions that prevented Dalton from recognizing the significance of the work of Gay-Lussac and Avogadro. In addition to rejecting Gay-Lussac's law of combining volumes,[28] Dalton refused to accept the suggestion that gaseous molecules of hydrogen or oxygen may consist of more than one atom. That suggestion had been made by Amedeo Avogadro in order to explain reactions such as the formation of two volumes of water vapor from one volume of oxygen and two volumes of hydrogen.[29] According to Avogadro's hypothesis, the reaction product must contain twice as many particles of water vapor as there had been particles of oxygen in the original reagent, if equal volumes of different gases contain the same numbers of particles.[30] Since each particle of water vapor contains oxygen, one must assume that a particle of oxygen in the original reagent splits into two smaller particles of oxygen in order to combine with hydrogen particles. If the original particles are "molecules" containing two atoms, one can then write the reaction equation (in modern notation) as

$$O_2 + 2H_2 = 2H_2O$$

But Dalton believed that the forces between like atoms were repulsive, thinking that Newton had proved this from the theory of gas pressure.[31] The absence of such a repulsion between *unlike* atoms had been the theoretical basis of his "law of partial pressures,"[32] and an *attraction* between certain combinations of unlike atoms might be invoked to explain chemical combination, but the idea that two oxygen atoms could join together in a stable molecule seemed completely contrary to Dalton's understanding of the nature of gases.

Avogadro's theory of gases might have provided a favorable environment for the reception of a kinetic theory, since he recognized that in order to justify giving equal volumes to molecules of different kinds, one must abandon the assumption that the molecules are in contact with each other. One must assume that the space occupied by a molecule depends on general properties such as pressure and temperature rather than on the size of the molecule itself. To express this assumption Avogadro did not reject the common notion that atoms have atmospheres of caloric, but proposed a convenient modification of it:

> . . . it is very well conceivable that the molecules of gases being at such a distance that their mutual attraction cannot be exercised, their varying attraction for caloric may be limited to condensing a greater or smaller quantity around them, without the atmosphere formed by this fluid having any greater extent in the one case than in the other, and, consequently, without the distance between the molecules varying; or, in other words, without the number of molecules contained in a given volume being different.[33]

Up to this point it might seem that the revolution in chemical theory was going to follow the pattern described earlier, with Dalton playing the role of the conservative reformer who refuses to accept the logical consequences of his own innovation, while Gay-Lussac and Avogadro are willing to forge ahead even at the cost of abandoning older ideas about interatomic forces. Indeed there were a number of chemists who saw the advantages of adopting Avogadro's hypothesis together with the assumption that many elements form polyatomic molecules in the gaseous state; by 1834, William Prout could assert that "such a mass of evidence exists in favour of the hypothesis . . . that nothing but a mathematical demonstration that it *cannot* be true, will at present convince me of its error."[34] But the old guard of Daltonians like W. C. Henry, who maintained that "the self-repulsive gaseous molecule as . . . the ultimate chemical atom" provided a fatal objection to Avogadro's hypothesis,[35] did not have to fight the battle alone. They were joined by a younger generation of chemists who followed the dualistic electrochemical theory of J. J. Berzelius. If chemical combination was to be explained by invoking electrostatic forces between positively and negatively charged atoms, there was a new reason for rejecting the idea that molecules such as O_2 or N_2 can have a stable existence in gases.[36] Here the contemporary enthusiasm for electrical explanations of phenomena worked against the adoption of an atomic theory that was in harmony with most chemical and physicochemical evidence, and thus the revolution was delayed until around 1860 when Cannizzaro revived the theory that could have been adopted as early as 1814 when Ampère lent his prestige to it.[37] The fact that Herapath's kinetic theory, the only one generally known in the 1820's (and 1840's), happened to contradict Avogadro's hypothesis (see §2.2) was probably only a minor factor in the situation since few chemists paid any attention to Herapath. On the other hand the hypothesis did profit after 1857 from the fact that it could be derived from the kinetic theory of Clausius and Maxwell (§4.3), since that theory was part of the prestigious mainstream of physics from its birth.

* * *

One last example shows that no matter how appealing a new world view may be, it cannot by itself bring about a revolution if it is not relevant to the problems that a generation considers crucial, even though it may be quite appropriate to a problem *previously* considered crucial. Surely the epitome of kineticism is the "kinetic theory of gravity," proposed by G. L. LeSage (1724–1803), which purports to "explain" the force of gravitational attraction by postulating that space is filled with invisible particles moving rapidly in all directions; when two macroscopic objects are close to each other, each shields the other from the bombardment on the near side, so there is a net push forcing them together.[38] This theory has been proposed so frequently that it must occur naturally to almost anyone who thinks seriously about the cause of gravity in a mechanistic way.[39] It is clearly associated with the Cartesian program to abolish action at a distance in favor of contact action, yet it has survived the defeat of most other Cartesian schemes. Even Maxwell was unwilling to reject it,[40] and it has recently been revived in the U.S.S.R.[41] But its primary historical interest is that some of the thinkers who proposed the kinetic theory of gravity were then led to contemplate a kinetic theory of gases (LeSage, DeLuc, Herapath, and Waterston). Nevertheless the early kinetic theorists were not able to convert the intuitive appeal of this explanation of gravity into support for their explanation of gas pressure, and the kinetic theory of gravity was of little importance in the revival of the kinetic theory of gases after 1845.

Notes for §1.6

1. S. Toulmin, *Am. Scient.* **55**, 456 (1967).
2. T. S. Kuhn, *The Structure of Scientific Revolutions*, International Encyclopedia of Unified Science, ed. O. Neurath (Chicago: University of Chicago Press, 1962, 2nd ed., 1970), Vol. 2, No. 2.
3. L. P. Edwards, *The Natural History of Revolution* (Chicago: University of Chicago Press, 1927).
4. Crane Brinton, *The Anatomy of Revolution* (New York: Norton, 1938).
5. The *Commentariolus* of Copernicus, trans. E. Rosen, in *Three Copernican Treatises* (New York: Dover Pubs., 2nd ed., 1959), p. 55 (quotation from pp. 57–58).
6. Edwards, *op. cit.*, p. 9.
7. This is the title of ch. 13 of F. E. Manuel, *A Portrait of Isaac Newton* (Cambridge, Mass.: Belknap Press of Harvard University Press, 1968).
8. L. P. Williams, *Hist. Sci.* **1**, 1 (1962). For a different interpretation, emphasizing the role of Laplace, see R. Fox, *Hist. Stud. Phys. Sci.* **4**, 89 (1974).
9. R. E. Schofield, *Mechanism and Materialism, British Natural Philosophy in an Age of Reason* (Princeton, N.J.: Princeton University Press, 1970).
10. See §8.1.
11. This theme is extensively developed in the writings of Alfred North Whitehead. See also R. G. Collingwood, *The Idea of Nature* (Oxford: Clarendon Press, 1945); F. C. Haber, in *The Study of Time*, eds. J. T. Fraser, F. C. Haber, and G. H. Müller (New York: Springer, 1972), p. 383; M. Mandelbaum, *History, Man, and Reason* (Baltimore: Johns Hopkins Press, 1971); R. L. Schanck, *The Permanent Revolution in Science* (New York: Philosophical Library, 1954); R. A. Nisbet, *Social Change and History, Aspects of the Western Theory of Development* (New York: Oxford University Press, 1969). R. Baker, *New York Times*, Jan. 19, 1969.
12. Brush, *Grad. J.* **7**, 477 (1967). In his recent article on this subject, H. I. Sharlin somewhat exaggerates the extent to which Lord Kelvin opposed the theory of evolution: *Ann. Sci.* **29**, 271 (1972). In his 1871 address to the British Association he implied that he would be willing to accept a theory of evolution if the random aspect of natural selection were replaced by "design"–see the extract in *Victorian Science*, eds. G. Basalla *et al.* (Garden City, N.Y.: Doubleday Anchor, 1970), pp. 127–28.
13. A. R. Hall, *Brit. J. Hist. Sci.* **3**, 24 (1966).
14. E. P. Wigner, *Comm. Pure and App. Math.* **13**, 1 (1960).
15. R. H. Silliman, *Augustin Fresnel (1788–1827) and the Establishment of the Wave Theory of Light* (Ph.D. Dissertation, Princeton University, 1968). P. S. Epstein, *Science* **63**, 387 (1926). E. Whittaker, *A History of the Theories of Aether and Electricity* (London: Nelson, 2nd ed., 1951), **1**, 107–8.
16. Whittaker, *op. cit.*, pp. 60–65.
17. *Oeuvres d'Augustin Fresnel* (Paris, 1866–69), **I**, xlii (E. Verdet), 236, 245, 365. S. D. Poisson, *Ann. Chim.* **22**, 270 (1823). M. Born and E. Wolf, *Principles of Optics* (Oxford: Pergamon Press, 3rd ed., 1965), p. 375.
18. According to Whittaker (*op. cit.*, p. 108) the bright spot had been observed in the early part of the 18th century by J. N. Delisle; according to Born and Wolf (*op. cit.*, p. 375) it had been observed by Maraldi. It was fortunate that no one remembered these observations in 1818.
19. Reprints or translations of the original papers, with extensive commentary, may be

found in the two books compiled by R. A. R. Tricker: *Early Electrodynamics* (Oxford and New York: Pergamon Press, 1965) and *The Contributions of Faraday and Maxwell to Electrical Science* (Oxford and New York: Pergamon Press, 1966). See also Whittaker, *op. cit.*, pp. 81–88, 170–73; L. Pearce Williams, *Michael Faraday* (New York: Basic Books, 1965) and *The Origins of Field Theory* (New York: Random House, 1966).

20. *Reprint of Papers on Electrostatics and Magnetism* (London, 1872), p. 419. Maxwell said that "we know of few statements so full of meaning" as this statement (*Scientific Papers* **2**, 305).

    For other examples of the kinetic world view see P. de Saint-Robert, *Rev. Cours. Sci.* **2**, 985 (1872); C. H. D. Buys-Ballot, *Verh. Ges. D. Naturf. Aerzte* **33**, 164 (1857); W. Thomson, *Proc. Roy. Inst.* **9**, 520 (1881) [on elasticity as a mode of motion]; D. R. Topper, *Arch. Hist. Exact Sci.* **7**, 393 (1971) [on J. J. Thomson.] [H. Holland] *Edinb. Rev.* [Am. ed.] **108**, 41 (1858); H. Sharlin, *Ann. Sci.* **32**, 133 (1975) [on Kelvin]; J. H. Jellett, *Nature* **10**, 320 (1874).
21. Albert Einstein and Leopold Infeld, *The Evolution of Physics* (New York: Simon & Schuster, 1938).
22. Einstein and Infeld, *op. cit.*, p. 143.
23. Quoted by Whittaker, *op. cit.*, p. 88.
24. Tricker, *Early Electrodynamics*, pp. 48–57. Whittaker, *op. cit.*, pp. 85–87. Williams, *Michael Faraday*, p. 161.
25. See Tricker's discussion in *Early Electrodynamics*, ch. IV, and the 1845 paper by Grassmann translated at the end of Tricker's book.
26. John Dalton, *Meteorological Observations and Essays* (Manchester and London, 1793, 2nd ed., 1834); *Manchester Mem.* **5**, 535 (1801). F. Greenaway, *John Dalton and the Atom* (Ithaca: Cornell University Press, 1966), pp. 113–18.
27. Dalton, *New System of Chemical Philosophy* (London, 1808; New York: Citadel Press, 1964), **57**, 144; see also *Foundations of the Molecular Theory* (Alembic Club Reprints No. 4), pp. 5–7.
28. J. L. Gay-Lussac, *Mem. Soc. Arcueil* **2**, 359 (1809); *Foundations of the Molecular Theory*, p. 15. L. K. Nash, in *Harvard Case Histories in Experimental Science*, ed. J. B. Conant (Cambridge, Mass.: Harvard University Press, 1950), pp. 260, 264–75. It may be noted that Dalton had earlier relied on Gay-Lussac's balloon flight for evidence that the composition of the atmosphere is the same at a height of 4 miles as it is at ground level: *Manchester Mem.* [2] **1**, 258 (1805).
29. This reaction had been investigated by Gay-Lussac and Humboldt in 1805 and is considered one of the first examples of the law of combining volumes to be firmly established. J. R. Partington, *History of Chemistry* (London: Macmillan, 1964), **4**, 78–79.
30. A. Avogadro, *J. phys. chim. hist. nat.* **73**, 58 (1811); Nash, *op. cit.* (note 28), pp. 275–290. *Foundations of the Molecular Theory*, p. 28.
31. Dalton, *Manchester Mem.* **5**, 540–41.
32. Dalton, *Manchester Mem.* **5**, 536, 545.
33. *Foundations of the Molecular Theory*, p. 29.
34. W. Prout, *Phil. Mag.* [3] **5**, 132 (1834). For discussion of the use of Avogadro's hypothesis by other chemists see A. J. Ihde, *The Development of Modern Chemistry* (New York: Harper & Row, 1964), pp. 150–53, 207; D. M. Knight, *Atoms and Elements* (London: Hutchinson, 1967), pp. 69, 89–94.
35. W. C. Henry, *Phil. Mag.* [3] **5**, 33 (1834).

36. Ihde, *op. cit.*, p. 121; Partington, *op. cit.*, ch. V.; Nash, *op. cit.*, p. 310. On the failure of various writers to mention the hypothesis at all see J. T. Merz, *History of European Thought*, 1, 428–29 (footnote). Reasons for rejecting it are analyzed by R. L. Causey, *J. Chem. Ed.* **48**, 365 (1971).
37. Ihde, *op. cit.*, pp. 226–230. The famous Karlsruhe congress of 1860 is described in some detail by C. deMilt, *J. Chem. Ed.* **28**, 421 (1951).
38. G. L. LeSage, *Nouveaux Memoires de l'Academie Royale des Sciences et Belles-Lettres, Berlin*, p. 404 (1782); *Deux Traites de Physique Mécanique*, ed. P. Prevost (Geneve, 1818). S. Aronson, *Natural Philosopher* 3, 51 (1964).
39. See §1.2, note 11.
40. J. C. Maxwell, art. "Atom" in *Encyclopedia Britannica* (9th ed.), 3, 36 (1875), rept. in *The Scientific Papers of James Clerk Maxwell* (Cambridge, 1890), 2, 445. See also Maxwell's letter to Tait, concerning a molecular aether [D. J. Price, *Notes and Rec. R. S. London* **10**, 139 (1953)] and his review of a book by Challis in *Nature* **8**, 279 (1873).
41. V. V. Radziyevskiy and I. I. Kagal'nikova, cited in note 11 to §1.3.

1.7 Nature philosophy and the reaction against materialism

In recent years there has been considerable interest in the relations between the popularity of various scientific theories and general cultural or philosophical movements, especially Romanticism and *Naturphilosophie* at the beginning of the 19th century.[1] It has been argued, on fairly good evidence, that Oersted's discovery of electromagnetism in 1820 was motivated by his convictions about the unity of natural forces, deriving from the *Naturphilosophie* of Schelling.[2] The same idea of the unity of forces has also been credited with creating a favorable intellectual climate for the acceptance of a generalized principle of energy conservation in the 1840's.[3] Since *Naturphilosophie* was strongly opposed to the Newtonian mechanistic world view, one might expect it to have played some part in the second scientific revolution. However, my own interpretation is that such direct opposition was premature in the early 19th century, and that *Naturphilosophie* contributed to the revolution only to the extent that it inspired discoveries or principles that could be incorporated into the existing framework of Newtonian physics. That was indeed the case with electromagnetism and energy conservation: it was not apparent until much later that such developments could seriously undermine the Newtonian world view, and then only as a result of other events that had little to do with *Naturphilosophie.* Subsequent revivals of the Romantic philosophy in the late 19th century ("Neo-Romanticism") and in Weimar Germany after World War I may have helped to create an atmosphere of distrust in mechanistic or causal explanations in science, thereby contributing in a negative way to the final stages of the Second Scientific Revolution.[4]

The origin of the term "Romantic," according to A. O. Lovejoy, is to be found in Friedrich Schlegel's essays on ancient and modern literature, written in the 1790's.[5] Schlegel at first shared the prevailing spirit of Classicism with its admiration for ancient as opposed to modern art, and he set up the antithesis: *die schöne Poesie* vs. *die interessante Poesie*, in order to sharpen the distinction. The first type of poetry displays beauty as an objective attribute; and, in general, aesthetic values are conceived to be of universal validity independent of the individuals who create or perceive them. The principle of classical art is one of self-limitation–exclusion of the intrinsically ugly and of anything that may be inconsistent with the unity of the work of art itself. In order to sharpen the definition of classical art, Schlegel also described the opposite type, which rejects limitations and forsakes universal validity in order to express the richness and individuality of life and nature, including the grotesque as well as the beautiful. The foremost example of *interessant* art is found in Shakespeare's works, but the same general characteristics were attributed to medieval and early modern, *i.e.* late 18th-century, literature.

After 1796, Schlegel himself was converted to the new doctrine which he had previously described with disapproval, and he now needed a term that would characterize it better than *interessant*. He therefore selected the term *Romantische*, which he had previously used in describing medieval and contemporary literature, and attached it to the modern tendency which he now wanted to establish as the highest form of art.

The nature of the Romantic movement in the arts can be seen in the emphasis on the individual and the unique as opposed to the general; freedom from the restrictions of classical rules of form and structure; direct expression of the emotions; antipathy to academic analysis; and an insistence that the whole is greater than the sum of its parts because it is pervaded by a spirit that cannot be rationally explained but can only be intuitively felt. It is these features that also characterize the Romantic view of science, usually known as *Naturphilosophie*. The philosophy of nature, as formulated by Fichte, Scheling, and others, is directly opposed to the mathematical-empirical tradition of the 17th and 18th centuries. It was most influential in biology where it was associated with vitalism. Its role in the history of the physical sciences has been quite obscure, and has only recently been seriously investigated by historians of science.

The Romantic viewpoint in science favors the interpretation of all phenomena in terms of a single basic principle, or perhaps two basic contrasting principles. As it happened, such a viewpoint could be quite fruitful at certain stages in the development of science, although at other stages it might be sterile. Biology was not quite ready for it at the beginning of the 19th century: there was still too much yet to be discovered and classified before it would be possible for a grand generalization to produce anything but confusion. Chemistry could profit by it to some extent, although even there it was dangerously easy to carry speculation too far, and the net result was a relapse into empiricism which discouraged theorizing in chemistry later in the century. It was primarily in physics that conditions were favorable for a leap of the imagination. By the end of the 18th century a great deal was known about light, electricity, magnetism, heat, and gravity, and this knowledge could be described by an atomic theory in which each atom was surrounded by several imponderable fluids–the "materialistic" approach mentioned in the preceding section. But the model was becoming clumsy, and it must have occurred to many scientists that there should be a simpler theory which would exhibit all these different phenomena as manifestations of one or two basic principles. The Romantics found the answer in the dynamism of Immanuel Kant or Roger Boscovich–a philosophy which proposed to replace the mechanical picture of atoms moving through empty space by a system of attractive and repulsive forces.[6] These forces fill all space and make the separate existence of matter almost unnecessary. Atoms, if they exist at all, are merely centers of force, having no independent existence apart from the forces.

According to L. Pearce Williams (whose views have been disputed by other historians of science), German Romantic philosophy, including Schelling's development of the dynamic physics of Kant as opposed to the mechanistic or materialist physics of Laplace and other French scientists, was transmitted to England by various means, one of which was the direct personal influence of Samuel Taylor Coleridge.[7] Coleridge visited Germany in 1798 and became an enthusiastic adherent of Schelling's philosophy; when he returned to England he met Humphry Davy, who was beginning to doubt the theory of imponderable fluids and was apparently receptive to the dynamic viewpoint. Davy, in turn, influenced his pupil Michael Faraday, and in this way the notion of a physical universe dominated by various manifestations of underlying attractive and repulsive forces provided the motivation for some of the most important work in experimental physics in the first part of the 19th century. It must of course be conceded that, despite Faraday's occasional remarks favoring the Boscovichean atomic model, there were significant differences between his conception of matter and that of Kant–Boscovich dynamism.[8]

Another example of the Romantic influence is the work of Oersted, who sought for many years, and finally found, a connection between electricity and magnetism because Schelling's *Naturphilosophie* gave him the conviction that such a connection must exist.[2]

The idea that the discovery of the energy-conservation principle owes something to *Naturphilosophie* is by no means accepted by all historians of science, and it is certainly true that other factors were involved.[9] The reader who wishes to investigate this question for himself is advised to start by reading Robert Mayer's paper of 1842, "Remarks on the Forces of Inorganic Nature," which is generally regarded as being one of the first explicit general statements of the principle of energy conservation.[10] The metaphysical arguments with which Mayer supported this principle were not much appreciated by physicists of the mid- and late-19th century, and did little to help the adoption of the principle.[11] Mayer also rejected any mechanist or kineticist interpretation of the energy principle, refusing to regard any of the observed forms of energy as being more fundamental than the others; other scientists soon jumped to the conclusion that all forms of energy could be represented as *mechanical* energy, and thus heat could be considered as nothing but the kinetic energy of atomic motion. This new version of the mechanical philosophy did not insist on excluding forces between the atoms (with a few exceptions[12]) though it preferred to describe long-range forces as being mechanically transmitted through some kind of intervening fluid (the aether). The historic "problem of action at a distance" remained unresolved.[13]

The identification of Humphry Davy as a Romantic scientist may help to explain his hostility to John Herapath's kinetic theory of gases (§2.3). Despite his earlier criticism of the caloric theory and support for the qualitative idea that heat is related to atomic motion, Davy rejected Herapath's theory as being "too speculative," which we may interpret as meaning "too mechanistic" or "too materialistic." While Herapath, like the Romantics, wanted to reduce all phenomena to a single principle, his choice of bouncing billiard-ball atoms could not be considered a very sublime principle.

* * *

Romanticism was followed by another movement, which I call, somewhat arbitrarily, "Realism" (there seems to be no generally accepted label for the movement as a whole). It included realism and naturalism in the arts, atomism, materialism, mechanism, kineticism, and certain aspects of positivism. Realism was the opposite of Romanticism in many respects, but because it was influenced by Romanticism it was not simply a return to the 18th-century Enlightenment or Classicism.[14] This movement reached its height around 1870 and declined thereafter; it was followed by reactions in various directions.

The term "Neo-Romanticism" will be used to refer to a collection of theories and tendencies that arose in the last part of the 19th century: aestheticism, decadence, empiriocriticism, energetics, idealism, impressionism, mysticism, sensationalism, and symbolism. Neo-Romanticism differs from Romanticism primarily because it has such a negative character–almost the only common feature of the components mentioned is that they represent some kind of reaction against Realism. The later movement was never able to attain that unity of thought and feeling which had characterized the earlier one.

The Realist period of the mid-19th century saw a great burst of activity and enthusiasm in the sciences, and considerable confidence that the methods of the physical sciences could be successfully applied in the biological and social sciences. In physics, the energy-conservation principle spawned the "mechanical theory of heat," including macroscopic thermodynamics and the microscopic kinetic theory of gases. Maxwell, following William Thomson, translated Faraday's dynamic field theory into Newtonian mechanism, and succeeded in achieving a magnificent synthesis with his electromagnetic theory of light. The valence theory of chemical bonds (Frankland, Kolbe, Couper, Kekulé) was developed during this period, and it may perhaps be characterized as a mechanistic theory in contrast to the earlier "dualistic" electrochemical theory of Davy and Berzelius, which had attempted to explain all chemical combination by means of simple attractive and repulsive forces. There were explicit attempts to introduce physical and chemical methods into physiology (Helmholtz, Ludwig, DuBois-Reymond) and sensory psychology (Helmholtz, Weber, Fechner). The atomistic spirit can be seen in the cell theory (Schwann and Schleiden) and in the germ theory of disease (Koch, Pasteur). Darwin's theory of evolution by natural selection, though not yet satisfactory to physicists, was seen by many others as a materialistic campaign to explain the development of all life, including man himself, in terms of impersonal physical law. And with Quetelet and

Galton we have the first serious attempts to apply statistical theories to the study of society and of human heredity.

Since I have suggested in the preceding section that atomism was *not* a problem of primary importance in stimulating the revolution that led to modern physics (though a new atomic theory was one of the most striking *results* of that revolution), it is well to emphasize here the significance of atomism in influencing the attitude of nonscientists toward science. For this purpose we must recall some of the historic associations of atomism with various philosophical doctrines.

Before about 1870, there was little or no connection between the research that scientists were doing on atomic theories such as the kinetic theory of gases, and the controversies among philosophers about the nature of matter, even though both were apparently discussing the properties and motion of atoms. The atom of the chemists and physicists, which was employed to express quantitative relationships between observable properties of matter, was entirely distinct from the atom of the philosophers, which symbolized a doctrine about the real nature of matter. As long as both atoms remained entirely hypothetical and unobservable, there did not need to be any conflict between them. But when William Thomson and others started to estimate numerical values for the size, mass, and charge of atoms, as though atoms really existed and might some day be observed through a microscope, the situation changed. Many sensitive intellectuals were becoming alarmed at the whole tendency of physical and biological science since the middle of the century. The idea had become prevalent that science would soon be able to provide a mechanistic explanation of all the phenomena in the universe in terms of the motions of atoms and the ether. At the same time it was being asserted that everything that was *not* susceptible to mechanical explanation could never be understood at all. This combination of attitudes can hardly be called a philosophical system, yet philosophers have expended prodigious efforts trying to refute it. It is most often labeled "materialism" although the multitude of meanings which have been attached to this word make it practically useless except as an epithet. Hardly anyone will admit to being a materialist himself, and therefore most definitions have been proposed by writers who were trying to describe a view which they detested.

In the usual classification scheme, *Idealism* is the opposite of Materialism. The former holds that only mental concepts and things of the spirit are real, whereas the latter holds that only matter is real. Idealism and Materialism are the philosophical components of the movements that we call Romanticism (or Neo-Romanticism) and

Realism, respectively. The corresponding scientific viewpoints, which might be called Positivism (or Empirio-criticism) and Scientific Materialism, are not so much concerned with what is "real" as with what can be employed to construct a useful scientific theory.[15]

To clarify our definitions of terms, we must note also the popular usages of the terms Materialism and Idealism as exemplified in the following statement of Theodore Roosevelt, made in 1918 and recently reprinted (*This Week* magazine, December 18, 1960):

> Surely all of us ought to realize the need in this country of a loftier idealism than we have had in the past; and the further and even greater need that we should in actual practice live up to the ideals we profess. The things of the body have a rightful place and a great place. But the things of the soul should have an even greater place. Materialism, in the end, eats like an acid into all the finer qualities of our souls.

It should be evident that Materialism and Idealism as used here have almost nothing to do with the philosophical terms defined above; nevertheless, the popular connotations tend to confuse discussions of the philosophical ideas. Perhaps we should use the label "*crass* materialism" for the attitude that only the possession of material wealth and the enjoyment of sensual pleasure are of value in life, and "*fine* idealism" for the opposite belief that only adherence to ideals and concern for things of the soul are important. The disgust for *crass* materialism was, however, due partly to the mechanization of work and life in general that accompanied the rise of industrialism in the 19th century, together with the loss of faith in traditional religion. Some of this disgust was transferred to *scientific* materialism, especially in the biological sciences.[16]

The kinetic theory of gases may be considered the outstanding representative of Materialism in physics (though in our own scheme it must be distinguished from the materialism of proliferating fluids–see above, §1.6) and its ups and downs are strongly correlated with trends of opinion in biology, geology, politics, and the arts. It is probably futile to try to determine any rigorous cause-and-effect relationship when interactions among human activities are involved; nevertheless it is tempting to suggest that the success of the mechanistic world view introduced by 17th-century physics encouraged Materialistic explanations in the natural sciences, and that when biological theorizing was carried to such an extreme that if offended public opinion, the "backlash" against Materialism was so strong that it also affected physics. Regardless of how much truth there may be in this, it is undeniable that the theory of Natural Selection–which purported to provide a mechanism by which the evolution of man from the simplest forms of life, and perhaps ultimately from inanimate matter, might be explained–was the most important scientific theory in the 19th century from the viewpoint of the nonscientific public. It certainly aroused much stronger feelings that the viscosity of gases, or the frequency spectrum of black-body radiation, or the law of combining proportions, and therefore it seems that one cannot properly study the history of any part of 19th century science without paying some attention to the possibility of interactions with biology. (It should also be remembered, of course, that the biologists themselves were somewhat aware of what was happening in physics and influenced by it; thus Alfred Russel Wallace, co-founder of the theory of evolution, noted in his book *The Wonderful Century* [1898] that the two most important theoretical discoveries in physics of the century were the conversion of forms of energy, and the molecular theory of gases.)

* * *

While popular Scientific Materialism claimed to encompass all nature and reduce spirit to matter in motion, the pronouncements of scientists who were regarded as Materialists display considerable reluctance to bite off such an indecently large mouthful. On the contrary, they emphasize our ignorance of everything except a few properties of dead matter, and assert that the methods of science are unable to deal with much else except these properties. The essence of their Materialism is in their contention that where mechanistic science fails, nothing else can succeed. Thus not atheism but Agnosticism was the characteristic stance of these scientists (the word itself was coined by T. H. Huxley in 1869[17]). A famous statement of this position is contained in the lecture of the physiologist Emil du Bois-Reymond, *Ueber die Grenzen des Naturerkennens* (1872). Du Bois-Reymond maintains that the only true and exact science is mechanics; all other modes of investigation based on qualitative principles (moral, aesthetic, etc.) can never lead to reliable results. Hence the limits of our possible knowledge of the world are determined by the extent to which purely mechanical principles can be applied. As for everything else, not only do we know nothing, but we can never hope to know anything; the lecture ends with the slogan: "Ignorabimus."[18]

In England, two of the most influential popularizers of science, John Tyndall and Thomas Huxley, were bold enough to risk the onus of Materialism in lectures delivered in 1868.[19] Huxley predicted that physiology will eventually "extend the realm of matter and law until it is coextensive with knowledge, with feeling, and with action.... The consciousness of this great truth weighs like a nightmare, I believe, upon many of the best minds of these days. They watch what they conceive to be the progress of materialism, in such fear and powerless anger as a savage feels when, during an eclipse, the great shadow creeps over the face of the sun. The advancing tide of matter threatens to drown their souls; the tightening grasp of law impedes their freedom; they are alarmed lest man's moral nature be debased by the increase of his wisdom." Tyndall insisted that mechanical laws apply even to the growth of a grain of corn: "Given the grain and its environment, with their respective forces, the purely human intellect might, if sufficiently expanded, trace out *a priori* every step of the process of growth, and by the application of purely mechanical principles, demonstrate that the cycle must end, as it is seen to end, in the reproduction of forms like that with which it began. A necessity rules here, similar to that which rules the planets in their circuits round the sun."

The Realist movement believed that such Materialistic explanations were the ultimate goal of science, though few would state their opinions as explicitly as Tyndall and Huxley. The "reaction against Materialism" was therefore one of the major themes of the Neo-Romantic movement.

Just as the transition from Romanticism to Realism can be followed under various names and aspects just before the middle of the 19th century, so we can identify a transition from Realism to Neo-Romanticism in the arts and sciences in the late 19th century.[20] Of particular interest here is a small group of theories and philosophical positions that grew out of the dissatisfaction with classical physics, and were to have an important influence on the philosophical interpretation of science in the 20th century. We now sketch some of these theories and then illustrate how they were applied to the criticism of kinetic theory.

Positivism. This word has been used in various senses; it can denote simply the attitude that the methods of experimental science should be applied in sociology, history, and literature, instead of the methods of moral theology and metaphysics. In this sense it merges with "naturalism," "realism," and "materialism," and represents simply the influence of science on culture in the mid-19th century. But in philosophy, and to some extent in science itself, positivism is opposed to materialism, and comes to be synonymous with "idealism" or "empiricism." Positivists claim that materialism is "a metaphysical doctrine which goes beyond the limits of observation by asserting that all phenomena derive from a material 'substance,'" whereas positivism rejects all hypotheses about the unknowable (E. Littré, "Preface d'un disciple" in the 1864 edition of Comte's *Cours de Philosophie Positive*). Thus while positivists may advocate scientific methods in the study of society and the arts, they would place severe restrictions on the methods which can properly be used in science.[21]

Positivism as a 19th-century movement derives from the writings of August Comte (1798–1857), who was at first more influential in England (with the support of J. S. Mill) than in his own country, France.[22] While Comte did not make any significant contributions to physics, his opinions on physics are of some interest in view of later interpretations based on positivism. In his *Cours de Philosophie Positive*, vol. **II**, p. 206 (1830 edition) he says: "The physical phenomena observed in bodies are only the sensible results of those which occur among their smallest particles"–an opinion which is hardly consistent with the positivism of Mach and Ostwald (see below). While Comte believed in atoms, he objected to the widespread use of supposed "agents" like the aether as a basis for classification of phenomena.

Of the two senses of the word "positivism" mentioned above, the second one–a critical attitude toward scientific theories which attempt to go beyond the immediate facts of experience–became more common after 1870, and indeed positivism provided one component of the reaction against materialism with the object of reforming and reformulating the foundations of science. The older form of positivism came to be known as "scientism," an epithet connoting a misguided attempt to extend scientific terminology to subjects in which the scientific method cannot be applied. This pseudoscience merges with popular materialism, and many of the attacks on materialism are really attacks on scientism.[23]

While scientific materialism would have set up boundaries within which the scientific method was applicable, but beyond which no sure knowledge was possible, the new positivism attempted to prove that the metaphysical mysteries of life and the universe supposedly lying beyond those boundaries are nonexistent. A distrust for metaphysical speculation was accompanied by suspicion of "intellectualism": the scientific and mechanical models constructed by the human mind were denounced as unreal, frivolous, misleading, and worthless. While the

Materialists might advance a physical explanation of biology, the positivists emphasized instead a biological explanation of physics. The latest researches in physiological psychology were adduced to prove that all perceptions, whether of color, smell, weight, or distance, are on an equal footing as combinations of sensations, and that there is no justification for choosing mass, distance, force, and time as physical quantities more fundamental than the others.[24] If the human mind is, as the Materialists asserted, merely another product of biological evolution, then obviously everything which has been developed by the human mind–including mechanical models and Scientific Materialism–is likewise simply a product of Evolution.

Empirio-criticism is the doctrine of Avenarius, Mach, and their followers; it asserts that reality is a combination of sensations standing in a definite relation to each other. The true elements of the world are thus colors, sounds, durations, pressures, smells, and spaces–not *things*. The idea of a thing-in-itself from which these qualities emanate is rejected as an illusory human through-construct. A concept (or a name which appears to refer to a thing) is useful in summing up a set of experiences or sensations; and a scientific theory is likewise useful as long as it systematizes our concepts in a certain area. The goal of science is not to understand some mythical "reality" but to economize efforts of thought. Empirio-criticism held that the method of mechanical analogies had outlived its usefulness in science, because the attempts to explain phenomena by reducing them to hypothetical atomistic models had not led to simplicity but rather to greater complexity. In the case of heat, for example, the fact that heat can be transformed into mechanical work, and conversely, does not imply that heat has anything to do with mechanical processes or motion. (This was also the view of Robert Mayer.) It is quite irrelevant for scientific purposes whether we consider heat a substance or a mode of motion. That which we imagine to lie behind the appearances exists only in our minds and will vary from person to person, from culture to culture, and from time to time.[24,25]

The establishment of the Conservation of Energy was considered by many scientists to have put the kinetic theory on a legitimate foundation, and to suggest that ultimately all forms of energy might be reduced to the kinetic energy of matter in motion and the potential energy of forces between atoms. The school of *Energetics* (Helm, Ostwald, Duhem, and others) maintained on the contrary that the equivalence of all forms of energy, far from authorizing us to reduce one of these forms to another, places them instead all on the same level. Whereas the Empirio-critics would have accepted the reduction of all forms of energy to one form, provided that this reduction leads to a genuine economy of thought, the Energetists were unwilling to accept any reduction at all. Instead, they assigned to energy itself the most fundamental reality. The appellation Neo-Romantic is rather appropriate for Energetics, since this doctrine is quite similar to the notion of unity of natural forces in *Naturphilosophie* which had preceded the establishment of the Conservation of Energy. Ostwald even founded a journal which he called *Annalen der Naturphilosophie.* We should mention here the argument of Energetics against the mechanical theory, based on the Second Law of Thermodynamics: energy is subject to irreversible dissipation in all natural transformations, a property which is not shared by a mechanical system of particles obeying Newton's laws of motion. Finding a contradiction between the absolute validity of thermodynamics and the kinetic theory, the Energetists proposed to reject the latter.[26]

Laymen were often alarmed by the deterministic attitude that scientists took toward the physical world, and supposed that science had adopted fatalism and rejected free will. Such statements as that of Laplace, that the entire past and future history of the world could be predicted from its present state by a being with sufficient intelligence (*Essai Philosophique sur les Probabilités*, 1814), were unacceptable to many, and some writers tried to reconcile free will with the Conservation of Energy.[27] The philosophical doctrine of *Voluntarism* need not be discussed here, since it had little influence on science.[28] However, we should mention briefly the writings of the American philosopher C. S. Peirce, who opposed to determinism not voluntarism but *chance*; his views have a special significance for the kinetic theory in both its classical and modern (*i.e.* quantum-mechanical) versions. In 1891 he wrote (after noting the idea of Epicurus that atoms swerve randomly from their courses): "the peculiar function of the molecular hypothesis in physics is to open an entry for the calculus of probabilities." Whereas determinists postulate that "certain continuous quantities have certain exact values," anyone who has ever worked in a physical laboratory knows that it is impossible to determine any quantity by observation with zero error. One might think that if there were an element of randomness in the universe, it would occasionally produce effects that would be observed; yet the kinetic theory of gases is based on the assumption that atoms move about as if by chance, and "by the principles of probabilities there must occasionally happen to be concentrations of heat in the gases contrary to the Second Law of

Thermodynamics, and these concentrations, occurring in explosive mixtures, must sometimes have tremendous effects. Here, then, is in substance the very situation supposed; yet no phenomena ever have resulted which we are forced to attribute to such chance concentrations of heat, or which anybody, wise or foolish, has ever dreamed of accounting for in that manner." Peirce thus supports Boltzmann's statistical interpretation of the Second Law of Thermodynamics, though for not quite the same reasons. In another article, he doubted "whether the fundamental laws of mechanics hold good for single atoms," and suggested that instead of precise universal laws one should look for approximate laws of nature which may be the "results of evolution," thus introducing "an element of indeterminacy, spontaneity, or absolute chance in nature."[29]

* * *

During the second half of the 19th century many criticisms of the kinetic theory appeared in the scientific and philosophical literature. Much of this criticism deserves no more than passing notice, since it came from writers who lacked the technical qualifications to make a sound judgment of the scientific value of the theory, and were simply reflecting the general reaction against Materialism.

We must now note the objections of J. B. Stallo, which may be viewed as a concrete application of the ideas of Positivism and Empirio-criticism mentioned above. His book, *The Concepts and Theories of Modern Physics* (1882) is a remarkably penetrating analysis of the foundations of classical physics, which gained the admiration of Ernst Mach and went through 15 printings in six different languages within 30 years of its original appearance; it was reprinted again in 1960 by Harvard University Press with an introduction by P. W. Bridgman.[30] Stallo's systematic attack on the mechanical theory of the universe includes several substantial arguments against the validity of the atomic hypothesis and the kinetic theory of gases in particular, which may be summarized as follows:

(1) If atoms are absolutely hard, they cannot be "elastic" since elasticity involves the motion of parts; in the collision of ordinary bodies there is a temporary loss of motion which is accounted for by conversion of energy of large-scale motion into energy of motion of the constituent parts, but this is impossible in the case of atomic collisions. The kinetic theorists, in order to maintain the principle of Conservation of Energy, had to assume that atoms are perfectly elastic, which is contradictory to the concept of an atom.[31]

(2) The postulate that atoms are indestructible and impenetrable cannot legitimately be inferred from experiences with ordinary solids, liquids, and gases.

(3) A satisfactory scientific theory must explain obscure facts by means of familiar facts; "a valid hypothesis reduces the number of the uncomprehended elements of a phenomenon by at least one." (Quoted by Stallo from Zoellner's *Ueber die Natur der Kometen*, 1872.) In the case of gas theory we have to explain first of all the existence of elasticity, *i.e.* resistance to compression, and the tendency toward expansion when external constraint is removed. Yet the kinetic theory proposes to explain this by invoking the supposed elasticity of invisible solid particles, which is more complicated and less comprehensible than the elasticity of gases, since a solid shows resistance to both compression and dilation, and also to change of shape. In order to compensate for this defect and try to explain the tendency of a gas to expand, the kinetic theory must resort to still more hypotheses, which are likewise remote from experience. It is assumed that the atoms are endowed with incessant rectilinear motion, and that they exert no forces on each other except when in contact; but we have no knowledge of such behavior in the real world. Thus the kinetic theory only complicates the phenomena which it professes to explicate; it represents "an unraveling of the Simple into the Complex, an interpretation of the Known in terms of the Unknown, an elucidation of the Evident by the Mysterious, a reduction of an ostensible and real fact to a baseless and shadowy phantom."

(4) The various artificial force laws introduced in order to account for certain properties of gases are "fatal to all claims of simplicity preferred on behalf of the kinetic hypothesis, and are in no sense an outgrowth of its original postulates.... They are both mere stop-gaps of the hypothesis, peace-offerings for its noncongruence with the facts, pure inventions to satisfy the emergencies created by the hypothesis itself."[32]

(5) There are no logical, mathematical, or other grounds for applying the statistical method to the *velocities* of the molecules instead of to their *weights* or *volumes*.[33]

(6) The theory fails to explain the relation between the thermal properties of gases and the internal motions of atoms in molecules.

In conclusion, Stallo says: "It may seem strange that so many of the leaders of scientific research, who have been trained in the severe schools of exact thought and rigorous analysis, should have wasted their efforts upon a theory so manifestly repugnant to all scientific sobriety–

an hypothesis in which the very thing to be explained is but a small part of its explanatory assumptions. But even the intellects of men of science are haunted by pre-scientific survivals, not the least of which is the inveterate fancy that the mystery by which a fact is surrounded may be got rid of by minimizing the fact and banishing it to the regions of the Extra-sensible. The delusion that the elasticity of a solid atom is in less need of explanation than that of a bulky gaseous body is closely related to the conceit that the chasm between the world of matter and that of mind may be narrowed, if not bridged, by a rarefaction of matter, or by its resolution into 'forces.' The scientific literature of the day teems with theories in the nature of attempts to convert facts into ideas by a process of dwindling or subtilization. All such attempts are nugatory; the intangible specter proves more troublesome in the end than the tangible presence. Faith in spooks (with due reverence be it said for Maxwell's thermodynamical 'demons' . . .) is unwisdom in physics no less than in pneumatology."

Notes for §1.7

1. This section is based in part on my article in the *Graduate Journal* (University of Texas), 7, 477 (1967), which includes an extensive bibliography. I cite here only a few works that have appeared since then: D. M. Knight, *Studies in Romanticism* **6**, 65 (1967); *Ambix* **14**, 179 (1967); *Actes XIIe Cong. Int. Hist. Sci.* (Paris, 1968), p. 49; *Hist. Sci.* **9**, 54 (1970). B. Hoppe, *Naturwiss. Rundschau* **20**, 380 (1967). G. Eriksson, *Romantikens världsbild speglad i 1800-talets Svenska vetenskap* (Stockholm: Wahlström & Widstrand, 1969). A. Hermann, *Phys. Bl.* **23**, 343 (1967). H. Pietschmann, *Philosophia Nat.* **12**, 80 (1970). W. D. Wetzels, *Johann Wilhelm Ritter: Physik im Wirkungsfeld der deutschen Romantik* (Ph.D. Dissertation, Princeton University, 1968); *Studies in Romanticism* **10**, 44 (1971). H. A. M. Snelders, *Studies in Romanticism* **9**, 193 (1970); *Isis* **62**, 328 (1971). B. Gower, *Stud. Hist. Phil. Sci.* **3**, 301 (1973).
2. R. C. Stauffer, *Isis* **44**, 307 (1953), **48**, 33 (1957). L. Rosenfeld, *N. Cim.* [10] **4**, Suppl. 5, 2 (1956).
3. T. S. Kuhn, in *Critical Problems in the History of Science*, ed. M. Clagett (Madison, Wisconsin: University of Wisconsin Press, 1959), p. 321.
4. P. Forman, *Hist. Stud. Phys. Sci.* 3, 1 (1971).
5. A. O. Lovejoy, *Essays in the History of Ideas* (Baltimore: The Johns Hopkins Press, 1936), p. 15f and note 4 to ch. 7.
6. Immanuel Kant, *Metaphysischen Anfangsgründe der Naturwissenschaft* (Riga, 1786); English trans. by J. Ellington, *Metaphysical Foundations of Natural Science* (Indianapolis: Bobbs-Merrill, 1970). Roger Joseph Boscovich, *Theorie Philosophiae Naturalis redacta ad unicam legem virium in natura existentium* (Vienna, 1758; 2nd ed., Venice, 1763); English trans. by J. M. Child, *A Theory of Natural Philosophy* (Chicago: Open Court Pub. Co., 1922, reprinted by MIT Press, Cambridge, Mass.,

1966). L. P. Williams, *Michael Faraday* (New York: Basic Books, 1965), p. 60f. Essays by L. L. Whyte, Z. Marković, L. P. Williams, and R. E. Schofield in *Roger Joseph Boscovich*, ed. L. L. Whyte (London: George Allen & Unwin, 1961), pp. 102, 127, 153, 168.

7. L. P. Williams, *Michael Faraday*, p. 60f.
8. J. B. Spencer, *Arch. Hist. Exact Sci.* **4**, 184 (1967).
9. T. S. Kuhn, *op. cit.* (note 3) and comments on Kuhn's paper by C. B. Boyer and Hiebert, pp. 384 and 391 in the same volume. Y. Elkana, *Arch. Int. Hist. Sci.* **23**, 31 (1970).
10. J. R. Mayer, *Ann. Chem. Pharm.* **42**, 233 (1842); English trans. in Brush, *Kinetic Theory* **1**, 71.
11. "To me it seems as if many of those who are discussing this question of the conservation of force are plunging into the fog of mysticism"–W. B. Rogers to H. Rogers, Nov. 2, 1858, in *Life and Letters of William Barton Rogers*, edited by his wife with the assistance of William T. Sedgwick (Boston, 1896), p. 393. P. G. Tait complained about Mayer's "false analogy and his *a priori* reasoning" and claimed that "his premises (though now known to be true) had no basis better than a piece of bad Latin"–see C. G. Knott, *Life and Scientific Work of Peter Guthrie Tait* (Cambridge: At the University Press, 1911), pp. 212, 216.
12. Hertz's attempt to eliminate force from mechanics is well known. On J. J. Thomson's attempt to reduce potential energy to kinetic energy see D. R. Topper, *Arch. Hist. Exact. Sci.* **7**, 393 (1971).
13. *The Scientific Papers of James Clerk Maxwell*, ed. W. D. Niven (Cambridge, 1890; reprinted by Dover Pubs., 1965), **2**, 311, 485. M. B. Hesse, *Forces and Fields, The Concept of Action at a Distance in the History of Physics* (London: Nelson, 1961). M. Jammer, *Concepts of Force* (Cambridge, Mass.: Harvard University Press, 1957).
14. For a somewhat similar attempt to divide 18th-century natural philosophy into three periods, see R. E. Schofield, *Mechanism and Materialism* (Princeton, N.J.: Princeton University Press, 1970).
15. While Susan Stebbing complains that "most physicists who have attempted to construct a philosophy upon the basis of physical researches have ended by elaborating some form of idealism," Philipp Frank points out that professional philosophers have always tended to interpret a transition from a mechanical to a more formal mathematical theory as a movement towards idealism. It has been claimed, for example, that the use of abstract mathematical representations in quantum mechanics and relativity indicates that it is mental concepts rather than atoms which are being invested with reality. Frank asserts that Mach's views, and modern positivist physics, have nothing to do with idealism, despite the impression which one might gain from some of the careless statements occasionally made by Mach and other physicists. S. Stebbing, *Philosophy and the Physicists* (London: Methuen, 1937; New York: Dover Pubs., 1958), pp. 265–66. P. Frank, *Phil. Sci.* **4**, 41 (1937).
16. "I grew up as a disciple of science. I know its fascination. I have felt that godlike power man derives from his machines . . .. Now I have lived to experience the early results of scientific materialism. I have watched men turn into human cogs in the factories they believed would enrich their lives. I have watched pride in workmanship leave and human character decline as efficiency of production lines increased . . ."–C. A. Lindbergh (1948), quoted by V. Packard, *The Waste Makers* (New York: McKay, 1960), p. 318.

It is rare to find anyone explicitly defending the materialist viewpoint, but here is one example: "What is a materialist? In the popular view I suppose a materialist is a pretty unpleasant person who gobbles babies for breakfast. This is a view I do not agree with. I am a materialist and I haven't gobbled any babies, yet. . . . The essence of materialism lies in a refusal to separate Man and his environment into the mutually exclusive categories of 'spiritual' and 'material.' Man is regarded as belonging to the Universe, not necessarily insignificantly, as a star or a galaxy belongs to the Universe. Star, galaxy, man, are all expressions of the structure of the Universe. No attempt is made to introduce the notions of value or importance. . . . The materialist . . . will only secure a complete victory over his opponents if he is able to show that the behavior of Man can indeed be understood with precision." – F. Hoyle, *Men and Materialism* (New York: Harper and Brothers, 1956), p. xix.

17. See J. A. H. Murray, *A New English Dictionary on Historical Principles* (Oxford: Clarendon Press, 1888), vol. I, Part I, p. 186.
18. E. Du Bois-Reymond, *Tageblatt der 1872 Versammlung Deutscher Naturforscher und Aerzte*, p. 85 (1872); English trans. in *Popular Science Monthly* **5**, 17 (1874). See E. Cassirer, *Determinism and Indeterminism in Modern Physics: Historical and Systematic Studies of the Problem of Causality* (translated from German) (New Haven: Yale University Press, 1956), Part 1.
19. These and other lectures are reprinted in: T. H. Huxley, *Collected Essays* (New York: Appleton, 1896–1916); J. Tyndall, *Fragments of Science* (New York: Appleton, 1897). See Huxley, vol. I, p. 130, and Tyndall, vol. II, ch. VI.
20. Further discussion and references are given in my article in the *Graduate Journal* already cited.
21. Maurice Mandelbaum gives a useful discussion of the distinction between these two usages of "positivism" and the transition from one to the other that took place near the end of the 19th century. M. Mandelbaum, *History, Man, and Reason* (Baltimore: The Johns Hopkins Press, 1971), p. 20.
22. In the lecture cited in note 19, Huxley said that he had found little of scientific value in Comte's Positive Philosophy, "and a great deal which is as thoroughly antagonistic to the very essence of science as anything in ultramondaine Catholicism. In fact, M. Comte's philosophy in practice might be compendiously described as Catholicism *minus* Christianity." Comte was defended in an article by Richard Congreve in the *Fortnightly Review* (April 1869); Huxley's reply, in the same magazine, was an article on *The Scientific Aspects of Positivism* in which he quoted a passage from Comte advocating Catholic organization but not Catholic doctrine, which had been the basis for Huxley's phrase quoted above. He then continued with a full-scale attack on Comte's philosophy; but according to Huxley's biographer [H. Peterson, *Huxley, Prophet of Science* (London: Longmans, Green, 1932)] the mere phrase "Catholicism *minus* Christianity" had such a poisonous influence, regardless of any rational argument on either side, that it was "one of the most damaging blows that the Positivists received in England" and helped to reduce Positivism from a respectable intellectual position to the status of mere cultism." See also C. Ayres, *Huxley* (New York: Norton, 1932), p. 118ff.

    For further discussion of the propagation of Comte's Positivism in England see F. S. Marvin, *Isis* **6**, 387 (1924).
23. H. E. Guerlac, *Science and French National Strength*, p. 81 in *Modern France* (E. M. Earle, editor) (Princeton University Press, 1951); F. W. Matson, *The Broken Image: Man, Science, and Society* (New York: Braziller, 1964); F. A. Hayek, *The Counter-*

Revolution of Science: Studies on the Abuse of Reason (Glencoe: The Free Press, 1952).

Here is one way the criticism was expressed: "Physical science, cultivated exclusively for its own sake and as an end, inevitably tends, in our poor nature, to contract, to carnalise, and, in some cases, even to embrutify, if we may so speak, the judgment of its devotees: the mind becomes insensibly impregnated with the muddy qualities of the evil through which it rises, so that when applied to questions of human life, it becomes confused, giving birth to a monstrous flood of misshapen revelations." (From the *British and Foreign Evangelical Review*, quoted by J. Young in the *Transactions of the Geological Society of Glasgow* **3**, 344 (1871).)

24. See the works of Ernst Mach, cited in ch. 8, and John Blackmore's recent book, *Ernst Mach* (Berkeley: University of California Press, 1972).
25. R. H. L. Avenarius, *Kritik der reinen Erfahrung* (Leipzig: Fues, 1888–90); *Philosophie als Denken der Welt gemäss dem Prinzip des kleinstein Kraft-masses* (Leipzig: Fues, 1876). K. Pearson, *The Grammar of Science* (London: Block, 1892). H. Poincaré, *La Science et l'hypothese* (Paris: Flammarion, 1902); *La Valeur de la Science* (Paris: Flammarion, 1904); *Science et Methode* (Paris: Flammarion, 1909). J. Ward, *Naturalism and Agnosticism* (New York: Macmillan, 1899). H. Bergson, *Essai dur les donnees immediates de la conscience* (Paris: Alcan, 1889). (English translation: *Time and Free Will*) P. Duhem, *La Théorie Physique, son objet et sa structure* (Paris, Chevalier et Riviera, 1906). E. Carpenter, *Civilisation: Its Cause and Cure* (London: Sonnenschein, 1889).
26. F. Wald, *Die Energie und ihre Entwerthung* (Leipzig: Engelmann, 1889), p. 104, E. Mach, *Die Prinzipien der Wärmelehre* (Leipzig: Barth, 1896), p. 362. G. Helm, *Die Lehre von der Energie historisch-kritisch entwickelt* (Leipzig: Felix, 1887); *Grundzüge der mathematischen Chemie: Energetik der chemischen Erscheinungen* (Leipzig: Engelmann, 1894); *Die Energetik nach ihrer geschichtlichen Entwickelung* (Leipzig: Veit, 1898). W. Ostwald, *Abhandlungen und Vorträge allgemein Inhaltes* (1887–1903) (Leipzig: Veit, 1904) (see esp. p. 220, reprint of his 1895 lecture "Die Ueberwindung des wissenschaftlichen Materialismus," or the English trans. in *Science Progress* **4**, 419 (1896); *Die Energie* (Leipzig: Barth, 1912), and many other articles and books. Pierre Duhem, *Traité d'Energetique* (Paris: Gauthier-Villars, 1911). H. Poincaré, *Thermodynamique* (Paris, 1892); Nature **45**, 414, 485 (1892).

    There is a recent review of the energetics controversy by E. N. Hiebert, in *Perspectives in the History of Science and Technology*, ed. D. H. D. Roller (Norman: University of Oklahoma Press, 1971), p. 67.
27. J. Croll, *Phil. Mag.* [4] **44**, 1 (1872); *The Philosophical Basis of Evolution* (London, 1891), 5, 29, 33ff. X. Clark, *Open Court* **2**, 975 (1888). See also the discussion in *Nature* (1891) by Lodge, Morgan, Dixon, Wetterham, and Sherlock.
28. A. Aliotta, *The Idealistic Reaction against Science*, trans. A. McCaskill (London: Macmillan, 1914), Part I, ch. II. A. J. E. Fouillee, *La Liberté et le Déterminisme* (Paris, 4th ed., 1895).
29. C. S. Peirce, *Monist* **1**, 162 (1891), **2**, 321 (1892). See the comments in the same journal by Carus (1, 243) and Mach (1, 399). On the contrasting views of another American philosopher of this period see E. H. Madden, *Chaucey Wright and the Foundations of Pragmatism* (Seattle: University of Washington Press, 1963), ch. 4. Wright was one of the first to cite Kelvin's determination of atomic size, in an article on "The Genesis of Species," *North Am. Rev.* **113**, 63 (1871).
30. See also S. Drake, in *Men and Moments in the History of Science*, ed. H. M. Evans (Seattle: University of Washington Press, 1959), p. 22.

31. See the extensive discussion of this problem by Wilson L. Scott: *The Conflic between Atomism and Conservation Theory* 1644 to 1860 (New York: Elsevier 1970).
32. Cf. S. G. Brush, *Arch. Rat. Mech. Anal.* **39**, 1 (1970).
33. This point was discussed by Maxwell: *Scientific Papers* **2**, 478–84.

1.8 Triumphs and failures of the kinetic theory

Up to now we have been referring to the "kinetic theory of gases" as if it were the same collection of assumptions, derivations, and formulas that one finds grouped together under that title in beginning physics or chemistry textbooks. Stallo's criticism pertains to this elementary version of the theory, which was almost as familiar to persons with a general physical-science background at the end of the 19th century as it is today. But an intelligent response to his criticism, that is to say an assessment of the theory as of 1890 or 1900, requires a more detailed knowledge of the achievements of Herapath, Waterston, Clausius, Maxwell, Boltzmann, and van der Waals. The present section will provide a rather condensed summary of these achievements, most of which are discussed in greater depth in the rest of the book.

Herapath, in his paper submitted to the Royal Society in 1820, obtained the pressure formula first found by Daniel Bernoulli in 1738:

$$PV = \tfrac{1}{3} Nmv^2$$

He went further than Bernoulli in stating unequivocally the idea of an absolute temperature depending on molecular velocities. Unfortunately, he convinced himself that temperature should be proportional to velocity, rather than to velocity squared. His theory of the collision of hard bodies, though not quite correct, was good enough for his purposes; it at least avoided the paradox that a body cannot be at once absolutely hard and perfectly elastic. Herapath was the first to show that the kinetic theory could provide a simple qualitative explanation for many diverse phenomena, such as changes of state, diffusion, and the propagation of sound.

In 1832 Herapath made what is in effect the first direct calculation of molecular speeds from the above formula, assuming that the average speed of a molecule is of the same order of magnitude of the speed of sound. J. P. Joule, who is usually credited with this calculation, seems to have based his 1848 paper directly on Herapath's theory, as expounded at length in the latter's book *Mathematical Physics* (1847).

In his *Mathematical Physics*, Herapath also gave a detailed discussion of diffusion phenomena and was able to give a satisfactory explanation of the laws discovered experimentally by Thomas Graham.[1] On the assumption that the particles of air are spheres of finite size rather than points, he showed that there should be departures from Boyle's law, the pressure increasing more rapidly than the density; but his formula was not essentially different from Daniel Bernoulli's result.

According to Herapath, the force of gravity by itself produces a temperature variation in a vertical column of air, namely a decrease of about 1°F for every 100 yards increase in height above the earth's surface (assuming perfectly dry air); the "total altitude of the air" would thus be approximately 31 miles, if it terminates when the temperature has dropped to absolute zero.

Herapath's work was refused publication by the Royal Society of London but seems to have had ample publicity through its appearance in several issues of the *Annals of Philosophy*, further discussion and application in Herapath's *Railway Journal*, and the comprehensive exposition in *Mathematical Physics*. The latter was published at about the right time to be read by physicists such as Joule who were thinking along similar lines in consequence of the establishment of the equivalence of heat and mechanical work as forms of energy, so Herapath did get some mention as a precursor in the writings of Maxwell and others, before he died.

In 1843, J. J. Waterston published anonymously a book titled *Thoughts on the Mental Functions*, in which he gave a brief outline of the kinetic theory of gases without mentioning the previous writings of Bernoulli and Herapath. He suggested a connection between temperature and molecular *vis viva* (mv^2), and stated that a medium of elastic spheres would exert an elastic force proportional to the square of the velocity of the spheres and to the density. He showed that the distance traveled by a molecule, after hitting one molecule and before encountering another, should be inversely as the density of the medium and also inversely as the square of the diameter of the molecules. He discussed the constitution of the earth's atmosphere and mentioned that, if the atomic weight of air were as small as that of hydrogen, the earth's attraction could not retain it, and it would evaporate into space, just as the moon's atmosphere has already done. The mean velocity of the molecules of air at 60° was estimated to be 2282 feet per second, and the velocity of sound just half this.

In 1845 Waterston sent a long paper on the kinetic theory to the

Royal Society of London. Here he stated somewhat more explicitly that the absolute temperature of his medium of elastic spheres, if regarded as a model for real gases, should be proportional to v^2. He also gave the first statement of the "equipartition theorem" of statistical mechanics: in a mixture of gases containing molecules of different specific weights, the mean-square molecular velocity of each kind of gas is inversely proportional to its specific weight. In other words, the average value of mv^2 is the same for all molecules in thermal equilibrium.

Waterston attempted to calculate the ratio of specific heats at constant pressure and at constant volume, but because of a numerical error he obtained the result $\frac{4}{3}$ instead of $\frac{5}{3}$ (for a monatomic gas). The former value was in fairly good agreement with the experimental data then available; he thus failed to encounter the discrepancy which plagued later kinetic theorists.

Like Herapath, Waterston thought that one should be able to explain the thermal structure of the earth's atmosphere by simply incorporating the force of gravity into the kinetic theory. He came to a similar conclusion, that there should be a uniform diminution of temperature with increasing height.

Not only did the Royal Society refuse to publish Waterston's paper: they refused to return it to him. Although he made several attempts to call attention to his work in later years, it remained unknown during his lifetime, and thus had no direct influence on the later development of the theory with the possible exception of Krönig's paper, which may have been partly inspired by it.[2]

Joule's use of the kinetic theory to estimate the velocity of a hydrogen molecule, though it was not a substantial advance beyond what Herapath and Waterston had already done, did serve to dramatize the fact that the theory could give a glimpse into the hitherto obscure world of the atom. Moreover, Joule's own prestige as co-discoverer of the energy-conservation principle helped to make the kinetic theory respectable at a time when Herapath and Waterston were regarded either as crackpots or as naive amateurs.

A. K. Krönig's short paper on kinetic theory, published in 1856, likewise did not represent a theoretical advance but helped to popularize the kinetic viewpoint at a critical period. It had the immediate effect of stimulating Clausius to publish his own ideas on the subject.

Rudolph Clausius, in his 1857 memoir, gave a sophisticated presentation of the elementary kinetic theory in the context of a careful analysis of the physical assumptions involved in the theory and its possible applications to the various properties of gases and liquids. In contrast to the "take-it-or-leave-it" attitude toward the kinetic model often adopted by Waterston and Maxwell, Clausius was willing to make semi-empirical modifications to avoid direct conflicts with experimental data. Thus rather than assume complete equipartition of energy among all mechanical degrees of freedom of his molecules–which would have given clearly the "wrong" value for the ratio of specific heats–he preferred to assume that the ratio of translational to total energy is simply a constant chosen to conform with the experimental values of specific heats.

To meet the criticism of C. H. D. Buys-Ballot, that the kinetic theory predicts much faster mixing of gases than is actually observed, Clausius introduced the "mean-free-path" concept into kinetic theory in 1858. If the molecules are assumed to have a finite diameter d, then (as noted earlier by Waterston) the average distance traveled between collisions with other molecules will be inversely as d^2. It was possible to find values of d large enough to reduce the mean free path to a fairly small value (thus preventing over-rapid diffusion of molecules from one region to another) yet still small enough to avoid any significant departure from the ideal gas laws (derived from kinetic theory on the assumption that each molecule moves through almost-empty space most of the time). But as yet there was no direct way to determine d. Nor did Clausius derive a quantitative relation between d and the rate of diffusion.

Maxwell read an English translation of Clausius' paper in the *Philosophical Magazine* and immediately started to develop his own theory of systems of elastic spheres. He introduced a statistical distribution function for molecular velocities, analogous to the law of errors (normal or bell-shaped curve) developed previously in statistical theory. Although his justification for using this particular distribution function did not have an adequate physical basis at the time, no one could defend the assumption (always used in previous calculations in kinetic theory) that all molecules in a gas at a given temperature have the *same* speed, and it was later found that some observational consequences follow from abandoning that assumption.

Unlike Clausius, Maxwell insisted that the elastic-sphere model (or, more generally, any theory based on collisions of elastic bodies of any form) required complete equipartition of energy among all mechanical degrees of freedom. The theoretical ratio of specific heats is therefore

$$\gamma = c_p/c_v = \frac{2+n}{n}$$

for bodies with n degrees of freedom. For point masses $n = 3$ and $\gamma = \frac{5}{3}$; for bodies that can rotate around three perpendicular axes (but cannot vibrate), $n = 6$ and $\gamma = \frac{4}{3}$. For oxygen, nitrogen, and hydrogen (known to be composed of diatomic molecules in the gaseous state at room temperature) experiments gave $\gamma \approx 1.4$. Hence Maxwell rejected the assumption that such gases are composed of "hard elastic particles." This conclusion is often regarded as a "failure" or "paradox" of the kinetic theory although strictly speaking it is only a refutation of this particular *hypothesis* about molecules; even in the middle of the 19th century scientists did not believe that molecules are accurately represented by such a hypothesis. It is not the *failure* of this naive hypothesis that is surprising, but rather the *success* of the same hypothesis when used to compute many other properties of gases: there lies the paradox.

In the same paper, published in 1860, Maxwell worked out the elementary kinetic theory of "transport processes"–diffusion, viscosity, and heat conduction–using the mean-free-path approximation. His treatment of heat conduction was sloppy and his calculation of diffusion seriously defective, but his theory of viscosity led to a remarkable result: the coefficient of viscosity of a gas composed of elastic spheres should be independent of density (or pressure), and should increase as the square root of the absolute temperature. This was an unexpected conclusion which disagreed with the apparent results of earlier experiments (see §§12.1, 12.2). In particular, the idea that a little bit of gas should offer as much resistance to a solid moving through it as a lot of gas seemed contrary to common sense. Again it seemed that the hypothesis underlying the elementary kinetic theory had been decisively refuted.

In 1862 Clausius published a long memoir, criticizing Maxwell's theory of heat conduction in gases and attempting to develop an improved theory based on the mean-free-path approximation. Clausius noted that the kinetic theory predicts that lighter gases such as hydrogen should conduct heat better than heavier gases (assuming the same specific heats and mean free paths), in agreement with the scanty experimental data available at the time (see §13.3). He also stated explicitly that the heat conduction coefficient for a system of elastic spheres should be proportional to the square root of the absolute temperature and independent of density (like the viscosity coefficient).

Following Clausius' criticism, Maxwell abandoned the mean-free-path method and developed instead a more accurate theory based on the transfer of molecular quantities by motion and collisions; this theory, or the equivalent one developed later by Boltzmann (1872), is still used as the basis of modern transport theory. For reasons of mathematical convenience it turns out to be desirable to abandon the elastic-sphere model and to assume instead that the molecules are point centers of repulsive force varying as the inverse fifth power of the distance. When he made this change around 1865, Maxwell seems to have been completely unaware of its philosophical implications; for him, neither the elastic sphere nor the point-center-of-force represented the real nature of the molecule. Nor did his early use of the phrase "dynamical theory of gases" in his early papers mean that he associated it with what was called "dynamism" on the Continent.

For the inverse fifth power force model–hereafter called "Maxwellian molecules"–Maxwell found that the transport coefficients were still independent of density, but varied directly as the absolute temperature instead of its square root. This result promised to give a means for deciding whether real molecules are more like elastic spheres or Maxwellian molecules. In the meantime Maxwell had conducted his own experiments on the viscosity of air, and had discovered that the coefficient really is independent of density over a fairly wide range. This conclusion was subsequently confirmed by other experimenters, and could be considered strong evidence for the validity of the theory; at least no other theory seemed to be able to explain this property of gases. (The earlier experiments that had been thought to show that the viscosity does vary with density were not actually wrong, but their *interpretation* had been based on the assumption that the viscosity *does* vary directly with density!)

In a last-minute note added to this paper in December 1866, Maxwell stated that he had finally succeeded in proving that a column of air would have the same temperature throughout, despite the influence of gravity. Maxwell did not mention the earlier discussion of this problem by Herapath, and made no attempt to develop a theory that would account for the observed variation of temperature with height in the earth's atmosphere. In 1868, Ludwig Boltzmann generalized Maxwell's derivation of the velocity-distribution law to the case where external forces such as gravity are present; he confirmed Maxwell's conclusion that the temperature should be the same at all heights. At the same time he derived what is now called the "Boltzmann factor" [$\exp(-V/kT)$ in modern notation, where $V =$ potential energy, $k =$ Boltzmann's constant, $T =$ absolute temperature] for the relative probability of molecular arrangements influenced by external or intermolecular forces. This is equivalent to the well-known logarithmic formula relating height and atmospheric pressure, but provides a new basis for calculating thermodynamic properties of molecular systems.

The virial theorem of Clausius (1870) furnished one starting point for J. D. van der Waals (1873) and later theorists who attempted to determine the pressure-volume-temperature relation of a fluid from some assumed intermolecular force law. Together with the Boltzmann factor, the Clausius virial theorem became the basic tool for determining many equilibrium properties of interest to physicists and chemists.

* * *

During the late 1860's, while these basic equations of modern kinetic theory were being established, there was also made a major discovery that greatly enhanced the credibility of the entire atomic viewpoint in science. This was the determination, by several independent methods, of the actual size and other properties of individual atoms. While the kinetic theory at first seemed to be only one of several such methods, it proved to be the most accurate and reliable.

Up to the beginning of the 19th century, there had been numerous attempts to show that matter could be dispersed or spread out to an enormous extent without losing its properties, but these attempts served only to place an *upper* limit on the size of the atom.[3] In 1816 Thomas Young showed that the *range* of molecular forces can be estimated from the surface tension of liquids, and obtained a value equivalent to about 10^{-8} cm, but thought that the actual distance between particles in water would be considerably less than this.[4] Waterston, in 1859, estimated the thickness of a molecule at one two-hundred millionth of an inch [1.25×10^{-8} cm] using a relation between capillarity and latent heat,[5] but other estimates of this type in the 1860's failed to yield consistent or reasonable values.[6]

The first convincing calculation of the size of a molecule was made in 1865 by Josef Loschmidt.[7] He used the mean free path as deduced from viscosity measurements, together with an estimate of the fraction of the total gas volume occupied by the molecules themselves. The latter fraction, known as the "condensation coefficient," was obtained by comparing the density of liquid and gas when both were known for the same substance, or estimating it by empirical rules in other cases. The mean free path depends on Nd^2, while the molecular volume is of the order of magnitude of Nd^3; if both quantities are known, one can solve to find N and d separately. Loschmidt concluded that the diameter of an air molecule is about 0.000001 mm ($= 10 \times 10^{-8}$ cm) which is about four times too large but still fairly close in the light of knowledge available at the time.

The corresponding value of the number of molecules in a cubic centimeter of an ideal gas at standard conditions (0°C, 1 atm pressure) would be $N \approx 2 \times 10^{18}$ using the same data. Although Loschmidt himself did not give this result explicitly, it can easily be deduced from his formula, and so this number is now sometimes called "Loschmidt's number." Its presently accepted value is 2.687×10^{19}. Those who have been educated outside of Germany will be more familiar with "Avogadro's number,"[8] which is defined as the number of molecules per gram-mole, and is equal to $N_{\text{Loschmidt}}/V_0 = 6.02 \times 10^{23}$; V_0 is the standard volume of a perfect gas, 22420.7 cm^3 atm mole^{-1}.

Loschmidt's estimate of N was low; other estimates published in the late 1860's tended to be too high. Dupré[6] thought the number of molecules in a milligram of water is greater than 1.25×10^{20} (modern value would be about one-fourth of that) and L. V. Lorenz published an upper limit of 13.6×10^{20} for this quantity.[9] (Both were based on non-kinetic methods.) G. J. Stoney, taking Clausius' estimate of d which was not much better than pure guesswork, arrived at "not fewer than" 10^{21} molecules in a cubic centimeter of gas at ordinary temperatures and pressures.[10]

The investigation of atomic magnitudes received considerable impetus from William Thomson's publication in 1870 of four independent methods leading to similar estimates of the diameter of a molecule.[11] Thomson had been interested in this problem for at least ten years, but was not able to "come to definite terms" with it when he started to work with the kinetic theory of gases.[12] The four methods were based on the dispersion of light, contact electricity in metals, capillary action in thin films such as soap bubbles, and the Clausius mean free path:

> Jointly they establish with what we cannot but regard as a very high degree of probability the conclusion that, in any ordinary liquid, transparent solid, or seemingly opaque solid, the mean distance between the centres of contiguous molecules is less than the hundred-millionth, and greater than the two thousand-millionth of a centimetre.[11]

From the kinetic theory and the known facts about condensation of gases, Thomson found that

> the diameter of the gaseous molecule cannot be less than

$\frac{1}{500\,000\,000}$ of a centimetre; nor the number of molecules in a cubic centimetre of the gas (at ordinary density) greater than 6×10^{21}.

Maxwell took considerable interest in the problem of estimating atomic magnitudes and reworked his diffusion theory in order to be able to use Loschmidt's experimental data for this purpose. In his influential lecture on "Molecules" to the British Association meeting in 1873, he presented his own results, though warning that they must still be regarded as "conjectural."[12] He found the diameters of molecules to range from 5.8 to 9.3×10^{-8} cm (for hydrogen and CO_2, respectively), and their masses to range from 46 to 1012×10^{-25} g (for the same). He estimated the number of molecules in a cubic centimetre of gas to be 19×10^{18}.

At about the same time in Holland, J. D. van der Waals was completing his dissertation on the theory of the continuity of gaseous and liquid states, which was to provide yet another method for estimating atomic sizes. Van der Waals showed that the volume available to molecules in a gas should be corrected by subtracting a term b, equal (at least at low densities) to four times the volume occupied by the molecules themselves. The effect of intermolecular attractive forces, analyzed along the lines of Laplace's theory of capillarity, was represented by a term proportional to the square of the density (inversely as the square of the volume) which was to be added to the pressure, thus giving the "van der Waals equation of state"

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation was to replace the "ideal gas law" (combined laws of Boyle and Gay-Lussac), $PV = RT$.

Since the van der Waals' equation is a cubic in the variable V, it gives three real solutions for a certain range that could be identified with the region of coexistence of liquid and gaseous states, and predicts very neatly the merging of liquid and gaseous states at the "critical point" previously investigated by Cagniard de la Tour, Andrews, and others (§7.3). Though the van der Waals' equation could not be regarded as a rigorous mathematical deduction from the kinetic theory, it was still a very impressive achievement; previously it had been scarcely conceivable that the same molecular theory could account for the properties of matter in both liquid and gaseous states.

Van der Waals showed that one could infer values of b for air and hydrogen from Regnault's experimental data,[13] and such values were subsequently used in conjunction with estimates of the mean free path to obtain molecular diameters.[14] (The most frequent method in the 1880's was to apply O. E. Meyer's formula, $d = 6\sqrt{2}v\lambda$.) These diameters began to cluster in the range from 1.5 to 5×10^{-8} cm which we would now consider fairly reasonable, while estimates based on non-kinetic methods still varied over a much wider range.

Another method for estimating the condensation coefficient or molecular volume did emerge in the 1880's, thanks in part to the efforts of Clausius, Maxwell, and Boltzmann in areas of physics other than gas theory. Clausius published in 1879 a derivation of Mossotti's formula relating the dielectric constant of a substance to its density, and this became known as the "Clausius–Mossotti formula." At about the same time L. Lorenz and H. A. Lorentz deduced a similar equation relating the density to the refractive index. The two equations become equivalent if one invokes the relation between dielectric constant and refractive index implied by Maxwell's electromagnetic theory of light and confirmed experimentally by Boltzmann. These equations were used by Dorn, Exner, and others, in conjunction with kinetic-theory estimates of the mean free path, to obtain molecular diameters for air, H_2, CO_2, CO, N_2O, and other compounds, in the range from 1 to 2×10^{-8} cm. A critical review of the subject published in 1888 by A. W. Rücker concluded with a calculation of diameters obtained by three independent methods, each based on multiplying a molecular volume v by a mean free path L. Estimates of L from the three transport processes – diffusion, viscosity, and thermal conductivity – were paired with values of v obtained from refractive indices, specific inductive capacities, and the van der Waals' b. With one exception the diameters for air, hydrogen, and carbon dioxide now lay between 1.1 and 1.9×10^{-8} cm. Thus the kinetic theory furnished four of the six pieces of evidence which Rücker considered most reliable for determining molecular sizes.[15]

* * *

Let us now return to the main lines of development of the kinetic theory itself.

The initial success of van der Waals' theory gave an impetus to further experimental investigations of the equation of state of dense gases, and also to more refined calculations of the equation of state for various molecular models (§§11.6, 11.7). The development of a complete equation of state and prediction of phase transitions became one of the major goals of the branch of kinetic theory known as "statistical mechanics" in the 20th century (§11.8).

The ability of kinetic theory to explain equilibrium thermal properties of gases was seen in a new light in 1875, when Kundt and Warburg measured the ratio of specific heats of mercury vapor–a monatomic gas–and found it to be very nearly $1\frac{2}{3}$, the theoretical value appropriate for point masses. Boltzmann (1876) inferred that the mercury atom must behave as if it were a single point, as far as collisions and thermal equilibrium were concerned; if it did in fact have a more complex structure, as was indicated by spectroscopic evidence, this structure clearly did not play any role in thermal phenomena. So he proposed a model for diatomic molecules consisting of two rigidly connected mass points–or, alternatively, two rigidly connected elastic spheres. Such a model would have five degrees of freedom: three of translation and two of rotation. The sixth degree of freedom, rotation about the connecting axis, may be ignored (he thought) because such rotation is unaffected by collisions. The ratio of specific heats for such a model would be $\gamma = (2+5)/5 = 1.4$, in good agreement with experimental data.

While Maxwell did not accept this theory (see §10.8) there seemed to be nothing better available before 1900. (Conversely, in 1898 William Ramsay used the fact that the ratio of specific heats of helium is $\frac{5}{3}$ as evidence that it must be monatomic and hence have atomic weight 4, thus showing his confidence in the kinetic theory of gases.) This and other problems with the equipartition theorem led to the discussion of a number of "test cases" by Kelvin and others–simple examples of mechanical systems in which it should be possible to determine by direct calculation whether the energy is equilibrated among all degrees of freedom (§10.9). At the same time there were speculations on whether general mechanical systems would eventually pass through all possible states consistent with a specified total energy: the so-called "ergodic hypothesis." In various forms this hypothesis was proposed by Boltzmann (1871, 1884, 1887) and Maxwell (1879); the term "ergodic" was originally introduced by Boltzmann to denote a certain kind of "ensemble" (hypothetical collection of systems), but later given its modern definition by the Ehrenfests (see §10.10). To say that a mechanical system is ergodic implies that the $(6n-1)$-dimensional energy surface can be mapped continuously one-to-one onto the one-dimensional time axis; is this a possible mathematical operation? The answer to that question depended on the outcome of researches in set theory, beginning with Georg Cantor in 1878 and concluding with the work of Lebesgue in 1902 and Brouwer in 1910 (§10.11). Using these mathematical results, Rosenthal and Plancherel proved in 1913 that it is impossible for a mechanical system to be strictly ergodic in the sense that the point describing its configuration ($3n$ position and $3n$ momentum coordinates) passes through every point on the energy surface in phase space (§10.12). That conclusion still left open the possibility that the system could be "quasi-ergodic" (passing arbitrarily close to every point on the energy surface) and that this property would be sufficient to imply the equipartition theorem. So there was plenty of work left to do in the 20th century on this problem, though it now seems to be of interest to mathematicians rather than physicists.[16]

Our survey should have demonstrated already that the kinetic theory in the 19th century was an exceptionally fruitful and stimulating scientific enterprise; yet we have scarcely mentioned one of the most important contributions to the theory. This was Ludwig Boltzmann's 1872 memoir, "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen." Despite its title, the memoir is concerned not so much with thermal equilibrium itself as with the irreversible processes by which equilibrium is reached, including the Maxwellian trio, diffusion, viscosity, and heat conduction. Here Boltzmann derived his integro-differential equation for the non-equilibrium velocity distribution function, the famous "Boltzmann equation" that forms the basis of most modern research in the theory of gases, plasmas, and neutron transport. In the same paper Boltzmann proposed what is now called the "H-theorem," which asserts that a certain functional of the velocity-distribution-function, related to the entropy when the system is in equilibrium, changes irreversibly in one direction as a result of molecular collisions. Thus the H-theorem is a microscopic version of the general principle of dissipation of energy, proposed by Kelvin in 1852, and reformulated by Clausius in 1865 in the phrase, "the entropy of the universe tends to a maximum."

To clarify the relation between Boltzmann's theory and Maxwell's, suppose that $f(u, v, w)$ is the velocity distribution function (for velocity components of a single molecule, labeled u, v, w). In general it may vary from one place to another in the gas, so f in the following may be interpreted as $f(x, y, z, u, v, w)$. If Q is any function of the velocity of a molecule, its average value at (x, y, z) is

$$\bar{Q} = \int Qf\,du\,dv\,dw$$

For example, if $Q = \frac{1}{2}m(u^2 + v^2 + w^2)$, then $\bar{Q}$ would be the mean kinetic energy per molecule at this point in space. (Note that we must already assume that the density of the gas is large enough so that we can reasonably define a continuous function f, at least by averaging over a small volume element which contains a large number of molecules; at the same time we must assume that conditions do not change very much in going from one such volume element to the next.) Maxwell then enumerates and estimates the changes in $\bar{Q}$ due to various factors: (1) the motion of molecules into and out of a small region of space, carrying Q with them; (2) actions of external forces on the molecules; (3) collisions between molecules. In this way he derives a set of general transport equations of the form

$$\frac{d}{dt}\bar{Q} = \delta_1\bar{Q} + \delta_2\bar{Q} + \delta_3 Q$$

These equations, written out in detail for particular choices of Q, are then compared with the macroscopic equations, such as the Navier–Stokes equations of hydrodynamics, which contain as variables the fluid velocity, density, pressure, etc. Insofar as one can make a reasonable identification of the microscopic and macroscopic definitions of these variables, and thereby obtain similar equations for them from the kinetic theory and from hydrodynamics, it is possible to deduce values for the coefficients of viscosity, heat conduction, and diffusion.

Boltzmann's derivation of his transport equation is similar to Maxwell's derivation of his equations for changes of $\bar{Q}$, except that the integration over velocities is omitted and one gets just an equation for the change of f itself

$$\frac{df}{dt} = \delta_1 f + \delta_2 f + \delta_3 f$$

If the equation can be solved for f, all macroscopic properties of the system including transport coefficients can be calculated.

The chief difficulty in the theory arises from the fact that δ_3 is not a linear operator on f, but depends on the joint distribution function for pairs of colliding molecules. Thus $\delta_3 f$ really looks something like

$$\iint [f(1',2') - f(1,2)]\psi(1,2,1',2')\,d(1)\,d(2)$$

where we have used (1) and (2) to denote the velocities of molecules 1 and 2 before the collision, (1′) and (2′) to denote their velocities after the collision, and $\psi(1,2,1',2')$ to denote a "scattering cross section," *i.e.* the probability that the collision will change $(1,2)$ to $(1',2')$.

In order to reduce the original equation containing $f(1,2)$ to one for the one-molecule function $f(1)$, Boltzmann (following Maxwell and Clausius) *assumed that there is no statistical correlation between the two colliding molecules*

$$f(1,2)=f(1)f(2)$$

This is sometimes called the hypothesis of "molecular disorder" or "molecular chaos."

Boltzmann defined the H-function (originally denoted by E) as

$$H=\iiint (f\log f)\,du\,dv\,dw$$

and with the help of the above-mentioned assumption of molecular disorder proved that

$$\frac{dH}{dt}\leq 0$$

The equality sign holds only when f is Maxwell's velocity distribution function. In this case H is proportional to $-kS$, where S is the entropy and k is a constant. So one may say that the H-theorem shows that H tends to decrease to a mimumum value as the entropy increases to its maximum value; once these extremum values are attained, corresponding to the state of thermal equilibrium, nothing more can happen if the system is undisturbed.

If one accepts Boltzmann's theory as it was presented in 1872, one would suppose that he had solved the "problem of irreversibility" by providing an atomistic explanation of the principle of dissipation that had emerged from earlier research in geophysics and thermodynamics (§§14.2, 14.3). As is well known things were not so simple; Boltzmann's theory of irreversibility was soon confronted by serious criticisms.

Even before 1872, Maxwell had pointed out that if one accepts the atomic-kinetic viewpoint, the principle of irreversibility cannot be regarded as an absolute law of nature but only as a consequence of human inability to deal with individual molecules. An intelligent being that *could* deal with molecules, the so-called "Maxwell demon," would be able to cause heat to flow from cold to hot, taking advantage of the fact that even a cold gas contains a few fast molecules and even a hot gas contains a few slow molecules (according to Maxwell's velocity distribution law). A demon stationed at a door between two containers, one containing hot gas and the other cold, could open the door to allow fast molecules from the cold side to pass into the hot side, and to allow slow molecules from the hot side to pass into the cold side, closing the door at all other times. Thus the temperature difference would be increased without the performance of any mechanical work, in violation of the Second Law of Thermodynamics.

As a result of the discussion among Maxwell, Tait, and Kelvin on the statistical nature of the Second Law around 1870, Kelvin published a discussion (1874) of what was later called the "Reversibility Paradox." Without specific mention of Boltzmann's H-theorem, Kelvin simply asked the question: How can irreversibility result from molecular motions and collisions which are themselves (according to Newton's laws of motion) strictly reversible in time? For if you imagine a particular sequence of motions and collisions that involves dissipation of energy or mixing of two kinds of gases, there must exist another sequence obtained from the first by reversing all the velocities, which will lead from the final state back to the initial state. But Kelvin pointed out that if the number of molecules involved is very large, the ordered state thereby obtained will become disordered again almost immediately. In any finite system of molecules one expects to find such momentary ordered states as a result of fluctuations, even in the absence of any deliberate reversal of velocities by an external agent; but as the number of molecules involved becomes infinite, the probability of such fluctuations goes to zero. (Note that it was only after reliable estimates of atomic sizes and of "Avogadro's number" became available, as described above, that such statements about the number of molecules were plausible.)

When Josef Loschmidt brought the reversibility paradox to Boltzmann's attention around 1876, in a discussion of the temperature-equilibrium of a column under the influence of gravitational force, Boltzmann quickly converted the apparent difficulty into a new conceptual advance. He asserted that the fundamental reason why systems tend to pass from ordered to disordered states, rather than the reverse, is that the *number* of disordered states is so much greater than the number of ordered states. If you start with an ordered state it is almost certain that it will evolve to a disordered state, after a finite interval of time has elapsed. But if you start with a disordered state, it is also almost certain that it will evolve to another disordered state, since it is quite unlikely that you would have picked one of the extremely small number of disordered states that is the result of evolution from an ordered state in a particular interval of time. This explanation suggested to Boltzmann that *entropy*–previously a rather mysterious quantity–should be interpreted as a measure of *disorder*; the tendency toward increasing entropy is simply a tendency toward increasing disorder. In particular (following the definition of H which he had introduced in 1872) he could define S as being proportional to the logarithm of the relative probability of a macroscopic state,

$$S = k \log W$$

where the probability W could be computed as the number of microscopic configurations corresponding to the given macroscopic state. This equation, which is now engraved on Boltzmann's tombstone, was made the basis of a new formulation of kinetic theory (Boltzmann 1877a), leading toward modern statistical mechanics.

The decade of the 1870's also saw increased interactions between the kinetic theory and experiments on transport processes. Among those most active in this area were Josef Loschmidt, Oskar Emil Meyer, Josef Stefan, Emil Warburg, Albert von Obermayer, and Adolf Winkelman (the absence of British and French names from this list is striking).[17] Among the major results were confirmation of the prediction that viscosity and heat conduction coefficients are independent of pressure over a wide range; initial explorations of the very low pressure regions where this is no longer true and gas-surface interactions become important; determination of the temperature-dependence of the coefficients, the exponent usually falling in between the values of $\frac{1}{2}$ and 1 corresponding to the elastic-sphere and Maxwellian models, respectively; and discoveries of "cross-effects" such as thermodiffusion. In the case of heat transfer, Maxwell's theory helped to disentangle the processes of conduction, convection, and radiation, and thus played a role in the replacement of the old Dulong–Petit radiation cooling law by Stefan's T^4 law (§13.7). But considerable difficulty was encountered in verifying the theoretical relation between heat conduction, viscosity, and specific heats, especially for polyatomic molecules (§§13.4, 13.5). As in the case of the ratio of specific heats, the interchange of energy between internal and translational motions of molecules did not seem to conform to expectations based on any of the molecular models used in the classical kinetic theory.

The inability of Maxwell and Boltzmann to go beyond the mean-free-path approximation except for the special case of Maxwellian molecules did limit the success of the kinetic theory in dealing with properties of gas mixtures. For example, O. E. Meyer developed a theory of diffusion (1877) in which the diffusion coefficient was predicted to change by a factor m_2/m_1 (mass ratio of the two kinds of molecules) as the concentration varied between its possible extreme values. This change was much greater than that observed experimentally. Another theory was proposed by Stefan (1871, 1872) and Maxwell (1873); they argued that in calculating the mean free path which enters into the formula for the diffusion coefficient, one should ignore collisions between molecules of the same kind, since these do not have any effect on the process of diffusion. This reasoning led to an expression for the diffusion coefficient which was independent of concentration. But both the Meyer and Stefan–Maxwell theories were inaccurate since they ignored the effect of nonuniform conditions in the gas on the velocity distribution. This effect was finally taken into account by Sydney Chapman and David Enskog (1916–17) when they developed general solutions for the Maxwell–Boltzmann transport equations valid for various molecular models. They found that while the diffusion coefficient is independent of concentration for Maxwellian molecules, it does vary slightly with concentration for other force laws, in agreement with experiment.[18] One might say that the kinetic theory as of the end of the 19th century had failed to give a satisfactory explanation of the details of diffusion processes, provided one recognizes that the experimental work on this problem was itself largely stimulated by the disagreement between the two earlier theories (Meyer and Maxwell–Stefan).

A more serious criticism of 19th-century kinetic theory is that it failed to predict the important phenomenon of "thermal diffusion," first discovered by Chapman and Enskog when they solved the Maxwell–Boltzmann transport equations, and confirmed experimentally by Chapman and Dootson in 1917.[19] This effect just happens to be absent for Maxwellian molecules, the only case that Maxwell and Boltzmann could work out accurately by their methods.

Another phenomenon which challenged the kinetic theory, and forced some of its further development, was the "radiometer effect" studied by William Crookes in the mid 1870's. The experiments suggested that temperature differences could give rise to pressure differences in a rarefied gas. Maxwell and Osborne Reynolds carried out detailed investigations of this problem; the outcome was Reynolds' discovery of thermal transpiration, and Maxwell's theory of gas-surface interactions and thermal stresses in rarefied gases (§5.5).

In studies of another transport process in gases, the propagation of sound, the kinetic theory contributed much less than might have been expected (§3.3). At first there was some resistance to retaining Laplace's formula relating the speed of sound to the ratio of specific heats, since it appeared to be based on a static theory of gas structure.

Waterston, writing on the theory of sound in 1858, rejected Laplace's theory on the grounds that its assumptions about heat were incompatible with the mechanical theory of heat; he proposed to use Herapath's theory instead. Other kinetic theorists showed little interest in sound propagation until 1876, when S. Tolver Preston sent to Maxwell his extension of Waterston's theory.[20] Maxwell then informed Preston that he had calculated the numerical factor $\sqrt{\frac{5}{3}}$ (corresponding to the factor $\sqrt{\gamma}$ in Laplace's formula, using the theoretical value of γ for a monatomic gas) relating sound speed to average molecular speed.[21] Shortly after this, R. H. M. Bosanquet suggested that the speed of sound in diatomic gases could be explained using a ratio of specific heats consistent with the kinetic theory, provided that one attributed five rather than six degrees of freedom to the molecule by treating it as "a smooth hard solid of revolution." As mentioned above, Boltzmann had already published this proposal for explaining γ though without specifically mentioning its connection with the speed of sound. After the work of H. A. Lorentz (1880)–the only substantial work on the theory of sound from the kinetic-theory viewpoint in the 19th century–kinetic theorists accepted the validity of the Laplace formula. The only remaining problem was thought to be the explanation of the ratio of specific heats of polyatomic gases. Thus the problem of calculating the speed of sound was seen as part of the more general problem of the validity of the equipartition theorem: Why is it that some degrees of freedom of a mechanical system do not acquire their full share of energy in thermal equilibrium? One might ask why no attempt was made to investigate this question by means of measurements of sound velocity at high frequency, but as far as I know this possibility was never seriously considered in the 19th century.[22]

In the meantime, considerable progress in the theory of sound propagation was being made by the use of hydrodynamical theory without reference to atomic hypotheses. In 1845 G. G. Stokes showed that the effect of viscosity on free waves in a fluid would be to *decrease* their speed by an amount proportional to the square of the viscosity, and also proportional to the square of the frequency of the waves.[23] [In modern terminology, any change of speed with frequency is known as "dispersion" by analogy with the corresponding effect in optics–a prism "disperses" light of different frequencies because the speed of light (and hence the index of refraction) depends on frequency. One speaks of "normal dispersion": when (as in the case of light) the speed decreases with frequency.] Stokes also found that the absorption (sometimes called attenuation) of waves is proportional to the viscosity and to the frequency. Stokes, and later investigators up to around 1900, seem to have generally believed that viscous dispersion of sound waves is a negligible effect.

A few years later, Stokes discussed the effect of heat radiation on the absorption and dispersion of forced waves in fluids.[24] (As discussed in ch. 8, it was thought before 1860 that heat *conduction* in gases is insignificant compared to radiation, so Stokes did not bother to discuss the effects of conduction.) He found that the speed of sound increases from the Newtonian value ($\sqrt{p/\rho}$) up to the Laplace–Poisson value ($\sqrt{\gamma p/\rho}$) as a parameter ω/q increases from 0 to infinity ($\omega =$ frequency, and q is proportional to rate of heat radiation). He concluded that this parameter is effectively infinite for audible frequencies.

In 1863, Stefan treated the absorption and dispersion of forced waves in a viscous fluid; his results were similar to those of Stokes except that the dispersion is now anomalous, *i.e.* the sound speed *increases* with frequency.[25] A more complete theory of absorption and dispersion of sound, taking into account both heat conduction and viscosity (but not radiation) was published by Kirchhoff in 1868.[26] According to his equations there should be two distinct kinds of waves, but he assumed that one of them could be ignored because it would be rapidly absorbed within a short distance unless the viscosity and heat conduction coefficients are large. To first approximation, there is no dispersion, and the absorption due to viscosity and heat conduction are additive. The predictions of Kirchhoff's theory were subsequently worked out by Rayleigh, Lamb, Truesdell, and others for arbitrary values of the physical parameters; it appears that the effect of heat conduction alone is to decrease the speed of sound, whereas the effect of viscosity alone is to increase it.

The hydrodynamic theory of sound propagation did not lead to definite predictions about the amount or even the qualitative character of the dispersion to be expected at high frequencies in real gases until the 20th century, and suitable experimental equipment for testing such predictions did not become generally available until after World War II. Thus the problem of determining limits of validity of macroscopic theories, and of working out predictions of kinetic theory in this case, belongs to the fairly recent history of science.[27] On the other hand, some aspects of the problem could have been discussed in the context of 19th-century kinetic theory, and might have led to some interesting consequences. For example, in 1933 E. U. Condon noted that physics textbooks generally state, incorrectly, that the reason for using the adiabatic rather than the isothermal relation between pressure and density is that "sound vibrations are so rapid that the temperature inequalities do not have time enough for equalization." According to Condon, if one analyzes the effect of heat conduction with the mean-free-path theory, one finds the opposite situation: the vibrations of sound are ordinarily *too slow* for equilibration of energy. At very high frequencies when heat conduction does become important, the isothermal assumption seems to be valid.[28] Truesdell has noted that the statement that acoustic changes would be adiabatic at high frequencies and isothermal at low frequencies remained unchanged in the 1896 edition of Rayleigh's *Theory of Sound* in spite of the fact that this edition included an account of Kirchhoff's theory leading to the opposite conclusion.[29] Did Rayleigh's persistent belief that low-frequency vibrations of a medium involve isothermal equilibrium perhaps have something to do with the way in which he introduced his theory of black-body radiation in 1900? Would a better understanding of the predictions of the *classical* theory of high-frequency vibrations of a medium have changed the attitude of physicists toward Planck's quantum theory of radiation in the early 1900's?

My impression is that the failure of kinetic theorists to tackle a number of problems in rarefied gas dynamics and sound propagation was partly a consequence of Maxwell's premature death in 1879. There was a marked decline in the number of major discoveries during the 1880's, although research of high quality continued in the Netherlands under the leadership of van der Waals and Lorentz. In Britain, Germany, and Austria, interest turned to problems in radiation emission, transfer, and absorption, arising from high-temperature technology, meteorology (transmission of the sun's rays through the atmosphere), and laboratory spectroscopy. (This was also a period when American scientists began to take the lead in exploring new directions–Michelson, Gibbs, Ferrel, Langley and others.) The strange phenomena associated with electrical discharges in vacuum tubes–in part an outgrowth of Crookes' experiments with the radiometer–were attracting increasing attention. Those physicists who were still interested in kinetic theory confined their attention to a rather narrow range of problems for which the basic principles had already been established, though elaborate mathematical calculations still seemed to be needed to tie up the loose ends. Boltzmann published hundreds of pages on the theory of viscosity, diffusion, and thermal equilibrium in various kinds of mechanical systems, yet only one short article which he wrote during this decade is still remembered: his theoretical derivation of Stefan's T^4 radiation law in 1884 (§13.7).

It was this loss of momentum and enthusiasm in the 1880's that allowed the critics of kinetic theory to discount its earlier achievements and ask: What have you done for us recently?

Notes for §1.8

1. On Graham's work see E. A. Mason, *Am. J. Phys.* **35**, 434 (1967); *Philos. J.* **7**, 99 (1970); E. A. Mason and B. Kronstadt, *J. Chem. Ed.* **44**, 740 (1967); E. A. Mason and P. G. Wright, *Contemp. Phys.* **12**, 179 (1971).
2. E. E. Daub, *Isis* **62**, 512 (1971).
3. J. R. Partington, *Ann. Sci.* **4**, 245 (1939). M. P. Crosland, ed., *The Science of Matter* (Harmondsworth, Eng.: Penguin Books, 1971), pp. 88–98; *Gold Bull.* **6**, 82 (1973). C. G. Ehrenberg, *Edinburgh New Phil. J.* **13**, 319 (1832). T. Young, *Course of Lectures on Natural Philosophy* (London, 1807), **1**, 608.
4. Young, *Supplement to the Fourth, Fifth and Sixth Editions of the Encyclopedia Britannica*, art. "Cohesion" (Edinburgh, 1824), reprinted in *Miscellaneous Works of the Late Thomas Young*, ed. G. Peacock (London, 1855), **1**, 454. Rayleigh, *Proc. Roy. Inst.* **16**, 204 (1899). G. D. Scott and I. G. Macdonald, *Am. J. Phys.* **33**, 163 (1965). E. A. Mason, *Am. J. Phys.* **34**, 1193 (1966). A. P. French, *Am. J. Phys.* **35**, 162 (1967).
5. See below, §3.1.
6. A. and P. Dupré, *C. R. Paris* **61**, 582 (1865). A. Dupré, *C. R. Paris* **62**, 39 (1866). L. Lorenz, *Ann. Phys.*[2] **140**, 644 (1870); *Phil. Mag.*[4] **40**, 390 (1870). In view of Dupré's work it is ironic that a French historian of science designated the theory of molecular sizes and numbers as purely German with a few English contributions. A. Bordeaux, *Histoire des Sciences Physiques, Chimiques et Géologiques au XIX^e Siecle* (Paris and Liége: Béranger, 1920), pp. 233–34.
7. J. Loschmidt, *Wien. Ber.* **52**, 395 (1865).
8. On the history of this term see R. M. Hawthorne, *J. Chem. Ed.* **50**, 282 (1973). Hawthorne has discussed early estimates (including one possibly by Loschmidt himself) in *J. Chem. Ed.* **47**, 751 (1970).
9. Lorenz, *op. cit.* (note 6). According to M. Pihl [*Dict. Sci. Biog.* **8**, 501 (1973)] he was the first to determine Loschmidt's number from the scattering of sunlight in the atmosphere in 1890.
10. G. J. Stoney, *Phil. Mag* [4] **36**, 132 (1868).
11. Thomson, *Nature* **1**, 551 (1870), reprinted in William Thomson (Lord Kelvin) and Peter Guthrie Tait, *Principles of Mechanics and Dynamics* [formerly titled *Treatise on Natural Philosophy*] (New York: Dover Pubs., 1962, reprint of the 1912 ed.), Part II, App. F.
12. Thomson, *Nature* **2**, 56 (1870).
13. *Over de Continuiteit van den Gas- en Vloeistoftoestand* (1873), pp. 67–68.
14. J. D. van der Waals, *Physical Memoirs* (London, 1890), **1** (Part 3), 436–37 [this is the Threlfall–Adair translation based on Roth's 1881 German edition]. R. Rühlmann, *Handbuch der Mechanischen Wärmetheorie* (Braunschweig: Vieweg, 1885), **2**, 244.
15. J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949–53), **1**, 243–45 [references on sizes of molecules], **4**, 8 [Lorentz–Lorenz equation], 538–39 [Mossotti–Clausius equation]. E. Dorn, *Ann. Phys.* [3] **13**, 378 (1881). F. Exner, *Wien. Ber.* **91**, 850 (1885). A. W. Rücker, *J. Chem.*

Soc. London **53**, 222 (1888). K. F. Herzfeld, *Jahrb. Radioakt. Elektr.* **19**, 259 (1922). R. G. Lunnon, *Proc. Phys. Soc. London* **38**, 93 (1926). S. E. Virgo, *Science Prog.* **27**, 634 (1933). A. J. Berry, *From Classical to Modern Chemistry* (New York: Cambridge University Press, 1954), ch. V.

16. Brush, *Transport Theory and Statistical Physics* **1**, 287 (1971).
17. Partington, *Advanced Treatise on Physical Chemistry*, **1**, §§VIIF-H [detailed survey of early experimental and theoretical research on gas transport properties, with extensive bibliography].
18. Brush, *Kinetic Theory* **3**, 17–18, 109–18, 168–73, 184–88.
19. *Ibid.*, pp. 18–20, 109–10, 117–18, 120–24, 266–70.
20. Letter from Preston to Maxwell, 5/12/76, at Cambridge University. Unfortunately Maxwell did not follow up Preston's remark that Waterston had written on the kinetic theory of gases in 1845 (as Waterston himself states in his paper).
21. S. T. Preston, *Phil. Mag.* [5] **3**, 441 (1877).
22. There are a few remarks about the possible effect of slow equilibration of rotational and vibrational energy on sound speed in the papers by Lorentz (1880) and Rayleigh, *Phil. Mag.* **47**, 308 (1899).
23. G. G. Stokes, *Trans. Camb. Phil. Soc.* **8**, 287 (1845). For a critical review of the early work on this subject see C. Truesdell, *J. Rat. Mech. Anal.* **2**, 643 (1953).
24. G. G. Stokes, *Phil. Mag.* [4] **1**, 305 (1851).
25. J. Stefan, *Wien. Ber.* **53** (2), 529 (1866).
26. G. Kirchhoff, *Ann. Phys.* [2] **134**, 177 (1868).
27. Brush, *Kinetic Theory* **3**, ch. IV.
28. E. U. Condon, *Am. Phys. Teacher* **1**, 18 (1933).
29. Truesdell, op. cit. (note 13); Rayleigh, *Theory of Sound* (Cambridge, 1877; 2nd ed., 1894–96, reprinted by Dover Pubs., New York, 1945), §§247, 348–9.

1.9 *Fin de Siècle* and the resurrection of atomism

If you ask an historian of science "when did modern physics begin?" he would probably say that it started in the 17th century with the work of Galileo, Boyle, Huygens, and Newton. But if you address the same question to a physicist, he would think first of radioactivity and experimental atomic physics, relativity, and quantum mechanics, and so he would assign the origin of modern physics to some date around 1900.

I want to conclude this chapter by discussing one feature of the "origin of modern physics" in the physicist's sense: the establishment of the concept of "atom" in physical science in the years just before the development of the Rutherford–Bohr model. Here one must first distinguish:

(1) experimental atomic physics–discovery of the electron and verification of its discrete particle-like nature; investigations of radioactivity; and construction of various atomic models by

J. J. Thomson, Nagaoka, and others to account for these discoveries

This is what one usually considers as the important work leading to the Rutherford–Bohr model, along with spectroscopic studies going back earlier in the 19th century:

(2) the Einstein–Smoluchowski theory of Brownian movement, and the experiments of Jean Perrin and his colleagues, based on this theory, which were interpreted as providing the first definite proof of the "real existence of atoms"

Concurrent with these two developments is a third, whose relevance to atomic theory became apparent after 1910:

(3) the Planck–Einstein quantum theory of black-body radiation and light, followed by applications by Einstein, Nernst, and Debye to specific heats of solids and gases.

At first glance it appears that (1) and (3) are "new" and essentially non-Newtonian, and it was their combination by Bohr, Heisenberg, and Schrödinger that led to the modern quantum theory of the microstructure of matter. Item (2), on the other hand, is frequently glossed over because it is, from a modern viewpoint, no more than a recovery of lost ground, bringing some scientists back into the fold of orthodoxy; it is hard to understand why anyone would still need to be convinced that atoms exist as late as 1900, when this had apparently been established long before. It was a backward-looking rather than a forward-looking event in the history of science, and therefore of little importance to those who see this history as a cumulative, progressive advance from ignorance to knowledge. On the other hand, I would argue that a study of the reasons why atomism had to be resurrected, rather than simply being taken for granted after 1900, is an essential part of the history of science.[1] Moreover it should be of interest to philosophers of science, for many of the opinions about the nature and methods of science which have been current since 1925 have their roots in the writings of the anti-atomists at the end of the 19th century; this situation certainly has to be taken into account, for example, in any assessment of the doctrines of Ernst Mach (ch. 8).

The argument was not about whether there exist *indivisible* ultimate particles of matter–*atoms* in the classical sense of Democritus, Epicurus, and Lucretius. That had not really been a serious question since the 17th century. Certainly in the 19th century the atomists themselves almost always attributed a more or less complicated structure to the atom, including for example "atmospheres" of various fluids that could be emitted or absorbed in various physical processes; and starting around 1900 they began to propose decomposable models for radioactive atoms.

The question was only partly, "is matter continuous or heterogeneous?"–or, "is there a sharp distinction between matter and empty space?" In fact there were two popular atomic theories based on continuous space-filling entities:

(1) the vortex atom of Helmholtz, Rankine, and Kelvin, in which atoms were treated as permanent vortex motions in the ether (§5.4). This theory had the great advantage, from the viewpoint of scientists such as Maxwell, that it was based on nothing more than "matter and motion"–no occult forces or action at a distance were needed. Since only one kind of ultimate ether-matter was permitted, and all the properties distinguishing different kinds of observable matter were to be explained in terms of different kinds and combinations of vortex motions, this theory should be regarded as an example of *kineticism* rather than *materialism* (cf. §1.6).

(2) The atom as point-center of force, as conceived by Boscovich in the 18th century, and further elaborated by Maxwell, Kelvin, and others in the 19th century (§11.1). As can be seen from these names, it was quite possible for these two contradictory models to be used by the same people; the space-filling force of Boscovich's theory is not so very much different from the space-filling ether-matter of the vortex theory.

Of course the vortex atom was rather far from the traditional concept of an atom; only a theorem of hydrodynamics prevented it from disintegrating into smaller and smaller vortices. Similarly, the Boscovich theory led quite easily to a form of *dynamism* in which atoms could be completely eliminated.

Yet the notion that matter is continuous rather than atomic at the microscopic level had few defenders among 19th-century scientists. The critics of atomism were more often opposed to *any* hypothesis about the microstructure of matter, on the grounds that (a) such a structure is inherently unobservable; (b) phenomenological theories are quite adequate for the legitimate purposes of science. Atomic theories were criticized because (a) there were too many of them, a different model being proposed for each phenomenon to be explained; (b) any results of atomic theory could (it was asserted) be obtained just as well from phenomenological theory; (c) in a few cases the deductions from atomic theories seemed to contradict generally accepted phenomenological principles or experimental facts.

In the preceding section we discussed the triumphs of atomism in kinetic theory, and mentioned the quantitative estimates of atomic magnitudes published late in the 1860's. During the same period the chemists were debating the value of atomic theories. At the Karlsruhe conference in 1860, Cannizarro presented his version of Dalton's theory and apparently found wide acceptance for it. Mendeleev and others published periodic tables of atomic weights[2] and showed that from such tables one could make successful predictions of the properties of new elements. But in England, Benjamin Brodie attacked the "materialistic" tendency of atomic theory (as exemplified by the ball and wire models of molecules that were already being advertised) and proposed an alternative "calculus of chemical operations" which would eliminate atomistic hypotheses. The debate on chemical atomism stimulated by Brodie's attack has been reviewed by W. H. Brock and D. M. Knight[3] and need not be discussed here, especially since it seems to have died down (at least in England) by 1890.[4] The debate did serve to make chemists aware that what are called "atomic" weights are really nothing more than "relative combining weights" which do not depend on the weight of an individual atom, and this fact was the basis of later attempts by Ostwald to eliminate the term "atomic weight" from chemistry.[5]

While scientific opinion was generally favorable to the kinetic theory in the 1860's (§5.4), a few diehards like the American, William A. Norton, continued to advocate the static repulsive theory of gases as late as 1879.[6] Others accepted the idea that gaseous atoms are in motion but felt that certain phenomena could still be more easily explained by a static theory.[7] One of the rare attempts to make a critical comparison of the two theories was published by Wladislaw Gosiewski in 1874.[8] But confrontations between the kinetic and static theories of gas structure played a very minor role in the history of physics.

During the 1880's and 1890's a number of physicists and physical chemists published attacks on the kinetic theory of gases; in most cases, if they had any concrete alternative to offer, it was not the old static theory but one in which postulates about energy or forces replaced postulates about atomic motion. Often the critique of kinetic theory was part of a broader attack on atomism or on mechanistic hypotheses in general. Among the better-known names were those of Ernst Mach,[9] Pierre Duhem, Wilhelm Ostwald, Henri Poincaré, Gustav-Adolph Hirn, Ernst Zermelo, and (listed here with some reservations to be explained below) J. Willard Gibbs.[10,11] The list could be made much longer by including more obscure scientists who also attacked the kinetic theory or proposed non-kinetic theories of gas properties.[12]

Who was on the other side of this battle? Of course many scientists, especially in Britain and Holland, continued to *use* atomic and kinetic theories without bothering to *defend* them in explicit public statements. The only scientist of stature comparable to those listed above who did take it on himself to defend the atomic-kinetic theories was Ludwig Boltzmann. Insofar as there was a real debate, not just a barrage of attacks that were unanswered and eventually forgotten, it centered around the particular problems that Boltzmann himself was interested in, *viz.* the statistical interpretation of thermodynamics. It is in this area that we can find a continuous thread running through the period 1890–1910: a problem is first brought up as a *difficulty* in atomism and finally is resolved in such a way as to provide evidence *for* atomism.

I want to emphasize that many of the problems involved in the origin of modern physics do not have this continuity, since they arose from fairly new experimental results which the old theories did not have to grapple with. It is also rather rare to find a case in which a scientist who takes a fairly strong position on one side of an issue actually changes his mind and goes over to the other side. According to the well-known "Planck rule" in the history of science,[13]

> A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it.

The context of this remark is Planck's own failure to persuade Ostwald of the error of the latter's formulation of thermodynamics. One of the curiosities of the story of the resurrection of atomism is that both Ostwald and Planck provide counter-examples to the Planck rule, since both of them did eventually "see the light" and accept the statistical-molecular interpretation of thermodynamics, reversing their earlier positions.

* * *

In the English-speaking countries, whenever there is widespread public concern about a problem but no one is quite sure who should be responsible for solving it, the custom is to appoint an official commission to investigate the matter. Thus when E. P. Culverwell in 1890 revived the reversibility paradox and other scientists began to question the validity of the equipartition theorem, the British Association for the Advancement of Science charged J. Larmor and G. H. Bryan with the task of looking into "the present state of our knowledge of Thermodynamics, specially with regard to the Second Law." Eventually an outside expert was invited to testify on the subject at the meeting of 1894: none other than Ludwig Boltzmann himself. The outcome of these discussions was the proposal, first published by S. H. Burbury and tentatively adopted by Boltzmann, that in order to derive the principle of irreversibility from kinetic theory one should assume that molecular motions are randomized after each collision. The proposal should not be confused with the earlier attempts to interpret irreversibility as a consequence of human inability to deal with individual molecular states, or of the fact that the great majority of such states correspond to "disorder" rather than "order." Such "statistical" explanations of irreversibility might still be compatible with determinism at the molecular level. What was involved here was a much more specific postulate of molecular disorder–possibly to be attributed to the action of the ether–needed in the proof of Boltzmann's H-theorem (§14.6). Of course there was considerable reluctance to assume that there is an inherent element of randomness at the atomic level, and the British Association would not be expected to give its official approval to such a radical solution. Nevertheless the ice had been broken, and the next time indeterminism was proposed in physical theory it was not quite as shocking an idea.

In the meantime another objection to Boltzmann's H-theorem was being developed. In 1889, Henri Poincaré proved his "recurrence theorem" in dynamics: any mechanical system, confined to a finite space with fixed total energy, must eventually return arbitrarily close to its initial state. The theorem was originally proposed in connection with the problem of the stability of the solar system, but Poincaré and later Zermelo (1896) pointed out its applicability to the kinetic theory. If a gas is really a mechanical system composed of atoms obeying Newton's laws, then it cannot simply go irreversibly toward an equilibrium state and stay there forever; it must return to its initial non-equilibrium state, with the initial values of physical properties such as entropy; hence entropy must eventually *decrease*, contrary to the Second Law of Thermodynamics. For Zermelo and the adherents of Energetics, the only way out of the contradiction was to abandon the assumption that a gas is a deterministic mechanical system of atoms obeying Newton's laws; or, more generally, to abandon the mechanistic view of nature while preserving phenomenological principles such as the Second Law of Thermodynamics.

Boltzmann, in the debate described in §14.7, argued that the recurrence property is not a paradox but a perfectly reasonable consequence of the statistical concept of matter. One can indeed compute the probability of a statistical fluctuation that would return the system to its initial state; but this probability, while finite, is so small that it would happen only once in untold eons of time, and therefore the fact that it is never observed in human experience is perfectly consistent with the kinetic theory. Moreover, if the observer's subjective time-direction is linked to irreversible processes in nature, the change in the direction of entropy-change that occurs during such a fluctuation might in some sense change the direction of time itself, so that the statement "entropy increases with time" is a mere tautology.

After his trip to the British Association meeting in 1894, at which various difficulties of the kinetic theory such as specific heats of diatomic molecules and the problem of ether-interactions were discussed, Boltzmann published a letter in *Nature* to clarify his position on the existence of atoms and the role of hypotheses in physical theory. He explicitly rejected dynamism–the Boscovich-type theories that would claim to explain the universe in terms of centers of force–and said that we really have no way of telling what the atom is like. Nevertheless, the kinetic theory of gases

> agrees in so many respects with the facts, that we can hardly doubt that in gases certain entities, the number and size of which can roughly be determined, fly about pell-mell. Can it be seriously expected that they will behave exactly as aggregates of Newtonian centres of force, or as the rigid bodies of our Mechanics?[14]

Later in 1895 there occurred a memorable debate between Boltzmann, Helm, and Ostwald at the Lübeck meeting of the Naturforschergesellschaft. Arnold Sommerfeld, recalling this debate 50 years later, compared Boltzmann to a bull and Ostwald to a supple bullfighter: he felt that in this case the bull won. "We young mathematicians were all on Boltzmann's side" as Sommerfeld remembered it; "it was at once obvious to us that it was impossible that from a single energy equation could follow the equations of motion of even one mass point, to say nothing of those for a system of an arbitrary number of degrees of freedom."[15] From this one might gather that Ostwald's phenomenological theory, Energetics, was doomed to failure as soon as a satisfactory atomistic substitute could be found.

Boltzmann himself focused on this mathematical objection to Energetics in his paper "On the necessity of atomic theories in physics" (1896).[16] Those who favored phenomenological theories, he wrote, claimed that all one needed was a system of differential equations, which could be formulated and solved without any reference to atomism. But in fact if one goes back to the derivation of such an equation, for example Fourier's equation for heat conduction, he sees that it *is* based on certain hypotheses about the behavior of very small pieces of matter; after stating the hypothesis about pieces of matter or particles of a certain size during a certain time interval, one then takes the limit when size and time interval go to zero. Similarly in *solving* the equation the only rigorous way to proceed (according to Boltzmann) is to work first with systems of a finite number of points or particles, and then let their number go to infinity. For Boltzmann the concept of a continuum was meaningless apart from such atomistic approaches for *mathematical* as well as physical reasons; this attitude was involved in his discussion of ergodicity (§10.10). While it could have been criticized by contemporary mathematicians–in a sense Zermelo's critique of the statistical theory of irreversibility depends on this issue–few physicists around 1900 were mathematically more sophisticated than Boltzmann, so his arguments may well have been persuasive.

When Boltzmann published the second part of his *Lectures on Gas Theory* in 1898, he noted the attacks which had recently been made on this theory, and wrote:

> In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority. I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered.[17]

Thus Boltzmann thought he would deposit a "time capsule" containing the major results of kinetic theory, for the benefit of future generations of scientists who, he expected, would eventually come back to atomism.

At the meeting of the Naturforschergesellschaft in Munich (1899), Boltzmann gave what seemed to be his valedictory address. He reviewed the development of atomistic and mechanistic theories and their recent apparent replacement by phenomenological theories. He admitted that

> the form of research designated classical theoretical physics frequently led to extravagances against which some sort of reaction was imperative. Every Tom, Dick, and Harry felt himself called upon to devise his own special combination of atoms and vortices, and fancied in having done so that he had pried out the ultimate secrets of the Creator.[18]

After reviewing the various physical and philosophical questions being hotly debated at the time, he said: "One regrets almost that one must pass away before their decision." One wonders how far Boltzmann did realize that these questions were well on the way to being settled before he committed suicide in 1906.

* * *

A physicist might have been surprised to see the name of Willard Gibbs on the list of those who opposed atomism (see above), since his work on statistical mechanics was to provide the foundation for a large amount of 20th-century research in this area. The only reason for including Gibbs in the list is the frequently quoted statement in the preface to his *Elementary Principles in Statistical Mechanics* (1902):

> Moreover, we avoid the gravest difficulties when, giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquiries as a branch of rational mechanics. . . . Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.[19]

If you take the trouble to read the context of this quotation, you will see that Gibbs is really in perfect agreement with Maxwell and Boltzmann: the purpose of developing statistical mechanics is to assist "the interpretation of observed phenomena with reference to their evidence respecting the molecular constitution of bodies" although we do not yet have any *single* acceptable hypothesis about the nature of atoms on which we can construct a detailed theory. Just as Maxwell had done earlier in his formulation of statistical mechanics in 1879, and in his later formulation of electromagnetic field theory–and as Boltzmann had attempted in several later papers–Gibbs was using the apparatus of Lagrange–Hamilton dynamics to obtain general theorems about mechanical systems of many degrees of freedom, without committing himself to a particular molecular model.[20] In other words, Gibbs' abstention from "framing hypotheses" is in the same spirit as Newton's, and has given rise to almost as much confusion for those who do not read him carefully.

The marvelous thing about Gibbs is that he was able to make statistical thermodynamics respectable in the 20th century by putting it into an elegant mathematical form, discarding much of the verbiage and computational clutter of Boltzmann's work but retaining precisely those features that were most useful. The mathematical abstractness of his system tended to discourage physicists for a few years until they realized how effective it could be, but it appealed to mathematicians who were skeptical of physical hypotheses. In fact, the German translation of Gibbs' book, published in 1905, was edited by none other than Ernst Zermelo.

The second scientist responsible for the resurrection of statistical thermodynamics around 1900 was Max Planck, who used it in developing his quantum theory. Planck had previously been an advocate of thermodynamics as a research method which could *replace* atomism. As early as 1882 he had emphasized that his results on evaporation, melting, and sublimation were independent of any molecular hypothesis, and argued that one should go as far as possible with thermodynamics before introducing assumptions about the interior constitution of bodies. At the end of the paper he hinted that atomism might eventually have to be abandoned altogether because of its inconsistency with the Second Law of Thermodynamics (§14.8). How then can we explain the fact that Planck was such a master of the *techniques* of statistical thermodynamics that he could make a sophisticated new application of them in relating his radiation law to the quantum hypothesis in 1900?

I suspect the explanation for this goes back to personal circumstances; in fact, the same personal circumstances that caused Planck to become interested in the radiation law in the first place. In 1889, after the death of Gustav Kirchhoff, Planck was called to Berlin to occupy Kirchhoff's chair. It happened that Lummer and Pringsheim were doing experimental work on black-body radiation at Berlin, and so Planck, who had previously been concerned mainly with physical chemistry, became interested in the theory of radiation. Somehow he acquired the assignment of editing Kirchhoff's lectures on theoretical physics for publication. Now Kirchhoff, while by no means an advocate of the kinetic theory, had felt obliged to discuss it in his lectures, and perhaps it was for this reason alone that Planck was first forced to familiarize himself with the detailed mathematics of the subject. This is evidenced by a little dispute with Boltzmann on the proof of the H-theorem in 1894–95. The latent connection between statistical entropy theory and radiation is also indicated by some parts of the development of Planck's radiation theory *before* 1900, where he makes use of a logarithmic entropy formula to prove, in effect, an H-theorem for radiation, in a manner that is mathematically very similar to Boltzmann's proof for gases.[22] Thus, despite his distaste for the statistical interpretation of entropy from a *physical* viewpoint, Planck just happened to be familiar with the *mathematical* side of this interpretation, so he could recognize at once how it could be used in radiation theory when the occasion arose. Subsequently, the success of the mathematical work tended to justify acceptance of the physical conclusions implied by the new theory; I regard this as a good illustration of the subversive role of mathematics in scientific revolutions, mentioned earlier in connection with the Poisson bright spot (§1.6).

Planck was also forced to change (at least temporarily) his ideas about the origin of irreversibility in nature as a result of the discussions on radiation just before 1900. At first he thought it would be possible to derive irreversibility directly from electromagnetic radiation theory, without introducing any statistical assumptions, but Boltzmann pointed out errors in his reasoning. Planck eventually had to admit that he needed an additional postulate, corresponding to molecular disorder or randomness in the kinetic theory.

The third scientist responsible for reviving statistical thermodynamics was Albert Einstein, who wrote three papers in 1902–4 developing many of the results of Boltzmann and Gibbs.[23] Einstein succeeded in doing what Boltzmann and Gibbs had not: he found a physical situation in which the Second Law of Thermodynamics was violated in such a way as to indicate the presence of fluctuations resulting from the atomic structure of matter. (It will be recalled that Boltzmann's defense of his statistical interpretation of the Second Law included the assumption that such violations would *not* be observed in the lifetime of any experimenter.)

As early as 1888 the French physicist Leon Gouy had argued that

Brownian movement provides a possible mechanism for violating the Second Law. It was not until 1904 that Poincaré in his speech to the St. Louis Congress of Arts and Sciences called this argument to the attention of other scientists. He apparently tried to get one of his graduate students, Bachelier, to investigate the mathematical theory, and indeed Bachelier did develop the theory of stochastic processes in connection with stock market speculation, but mentioned the application to Brownian movement only in a footnote (§15.3).

Einstein's theory of Brownian movement was published in 1905, the same year that he announced his special theory of relativity and his quantum theory of light (with applications to the photoelectric effect). Previous attempts to use kinetic theory had been fruitless because of the mistaken notion that one could simply apply the equipartition theorem to estimate the average speed of the microscopic particle in thermal equilibrium with a fluid. Einstein showed that the nature of random particle movement in this case is such that "average speed" has no well-defined value; on the other hand, the net displacement of the particle should vary with the square root of the time interval, with a coefficient of proportionality depending on temperature, the size of the particle, and the viscosity of the fluid (§15.4). The height distribution of particles should be governed by the Boltzmann law for equilibrium under a gravitational force. Smoluchowski published a theory leading to somewhat similar results in 1906 (§15.5).

It was Jean Perrin who undertook to test the Einstein–Smoluchowski theory by an extensive series of experiments. More important, he showed that one could get reasonable values of Avogadro's number by applying the Boltzmann formula to observed height distributions, and argued that the confirmation of the kinetic theory of Brownian movement should be regarded as direct evidence for the real existence of atoms. He was strikingly successful in persuading other scientists of this; even Ostwald gave up his opposition to atomism (§15.6). This must be regarded–historically if not logically speaking–as the final establishment of the atomic nature of matter, thereby settling one of the oldest problems in science.

One might think that this achievement would have made Jean Perrin an immortal hero of science, celebrated in all texts, encyclopedias and histories of science as the man who finally proved that atoms really exist.[24] No such luck! Take a random sample of the science books on your shelf and see how many of them even list Perrin in the index, or mention anything more than his determination of Avogadro's number. As I suggested in §1.2, there is a curious blind spot in our attitude toward the significance of various discoveries in science. Those who are fortunate enough to attach their names to quantitative "laws" or "fundamental constants" are assured of a place in the language of posterity (at least until we decide to abolish eponymy, as a few short-sighted scientists have proposed). But a scientist who establishes a *qualitative* fact or concept–without which those laws and constants would be meaningless–is likely to have his contribution forgotten, though he may still be honored (sometimes inaccurately) for his work on a law or constant associated with his discovery. In order to appreciate the true value of his achievement one has to know enough about the history of science to realize that the qualitative part–the existence of atoms, the existence of air pressure, or the finiteness of the speed of light–was not always taken for granted.

Notes for §1.9

1. There is a useful survey of several aspects of this subject in the article by G. M. Fleck, *J. Hist. Ideas* **24**, 106 (1963). See also H. R. Post, *Phys. Ed.* **3**, 225, 307 (1968); A. Hermann and W. Kaiser, *Rete* **1**, 135 (1972).
2. See the comprehensive account by J. W. van Spronsen, *The Periodic System of Chemical Elements: A History of the First Hundred Years* (New York: Elsevier, 1969).
3. W. H. Brock and D. M. Knight, *Isis* **56**, 5 (1965); W. H. Brock, ed., *The Atomic Debates: Brodie and the Rejection of the Atomic Theory* (New York: Humanities Press, 1967).
4. D. M. Knight, *Atoms and Elements* (London: Hutchinson, 1967), p. 147.
5. W. Ostwald, *Nature* **70**, 15 (1904).
6. W. A. Norton, *Am. J. Sci.* [2] **46**, 167 (1868), **49**, 24 (1870); [3] **3**, 327, 440, **4**, 8 (1872); **17**, 183, 345, 433 (1879).
7. W. F. Stanley, *Experimental Researches into the Properties and Motions of Fluids* (London, 1881), p. 2. A. M. Worthington, *Phil. Mag.* [5] **18**, 334 (1884).
8. W. Gosiewski, *Pamietnik Towarzystwa Nauk Sciclych w Paryzu* **5** (2) (1874); English trans., "Various theories of pressure in gases," UCRL-trans-885(L) (Livermore, Calif.: Lawrence Radiation Laboratory, 1962).
9. See ch. 8.
10. Pierre Duhem, *The Aim and Structure of Physical Theory*, trans. by P. P. Wiener from the second French edition of 1914 (Princeton, N.J.: Princeton University Press, 1954), D. G. Miller, *Physics Today* **19** (12), 47 (1966). W. Ostwald, *Nature* **45**, 293, 415 (1892); *Verh. Ges. D. Naturf. Aerzte* (1), 155 (1895), English trans. in *Science Progress* **4**, 419 (1896). W. D. Bancroft, *J. Chem. Ed.* **10**, 539 (1933). N. R. Holt, *Isis* **61**, 386 (1970). H. Poincaré, *Nature* **45**, 414, 485 (1892). H. Poincaré, *C. R. Paris* **116**, 1017, 1165 (1893); *Science and Hypothesis*, trans. from French ed. of 1902 (New York: Dover Pubs., 1952), p. 129. G. A. Hirn, *Théorie Mécanique de la Chaleur*

(Paris, 1868); *Mem. Acad. Sci. Bruxelles* **43**, 52 (1881), **46**, 97 (1886); *C. R. Paris* **103**, 514, 1232 (1886), **107**, 166 (1888); *La Cinetique Moderne et le Dynamisme de l'Avenir* (Paris, 1887). E. Zermelo, articles on the recurrence paradox, cited in §14.7.

11. See below, note 19.
12. J. Boussinesq, *J. Math.* **18**, 305 (1873). M. Levy, *C. R. Paris* **87**, 449, 488, 554, 649, 676, 826 (1878). A. C. H. Ledieu, *C. R. Paris* **94**, 691 (1882); *Rev. Quest. Sci.* **12**, 156 (1882). Charles Reeder, *Caloric: A Review of the Dynamical Theory of Heat* (Baltimore, 1887). F. Wald, *Die Energie* (Leipzig, 1889), p. 104. L. Poincaré, *Rev. Gen. Sci.* **5**, 700 (1894). Seligmann-Lui, *Annales des Mines* [10] **2**, 144 (1902). E. Dreher, *Die Grundlagen der exakten Naturwissenschaft im Lichte der Kritik* (Dresden: Verlag des "Apollo," 2. Aufl. 1901), p. 69. W. McF. Orr, *Phil. Mag.* **15**, 297 (1908). Letter from E. Federov to N. A. Morozov, 1912, quoted in *Fifty Years of X-Ray Diffraction*, ed. P. P. Ewald (Utrecht: Vosthoek, 1962), p. 346.
13. Cf. the beginning of §14.8 where a slightly different version is quoted, and note 1 of that section where sources of both versions are cited.
14. L. Boltzmann, *Nature* **51**, 413, 581 (1895); for a longer extract see the end of my introduction to *Lectures on Gas Theory* (Berkeley: University of California Press, 1964), pp. 15–17.
15. A. Sommerfeld, *Wiener Chem. Zeitung* **47**, 25 (1944); quoted in introduction to *Lectures on Gas Theory*, p. 14.
16. L. Boltzmann, *Wien. Ber.* **105**, 907 (1896); *Ann. Phys.* [3] **60**, 231 (1897); English trans. in *Monist* **12**, 65 (1901).
17. *Lectures on Gas Theory*, p. 216.
18. *Verh. Ges. D. Naturf. Aerzte* (1) 99 (1899); quoted from T. J. McCormack's English trans. in the *Monist.* **11**, 226 (1901) (see p. 247).
19. *The Collected Works of J. Willard Gibbs* (New Haven: Yale University Press, 1948), **II**, ix–x.
20. J. C. Maxwell, *Trans. Camb. Phil. Soc.* **12**, 547 (1879). L. Boltzmann, *Ann. Phys. Beibl.* **5**, 403 (1881), English trans. in *Phil. Mag.* [5] **14**, 299 (1882). T. K. Simpson, *Stud. Hist. Phil. Sci.* **1**, 249 (1970). M. J. Klein, *Centaurus* **17**, 58 (1972).
21. J. W. Gibbs, *Elementare Grundlagen der statistische Mechanik*, Deutsch bearb. von E. Zermelo (Leipzig: J. A. Barth, 1905). E. Zermelo, *Jahresber. D. Math. Ver.* **15**, 232 (1906).
22. Max Planck, *Physikalische Abhandlungen und Vorträge* (Braunschweig: Vieweg, 1958), **1**, 585–89.
23. Albert Einstein, *Ann. Phys.* [4] **9**, 417 (1902), **11**, 170 (1903), **14**, 354 (1904). M. J. Klein, *Science* **157**, 509 (1967).
24. The first monograph on Perrin's work meeting the standards of modern historical scholarship was published only quite recently: M. J. Nye, *Molecular Reality, A Perspective on the Scientific Work of Jean Perrin* (New York: American Elsevier, 1972). This paragraph is adapted from my review of the book published in *Centaurus* **17**, 174 (1972). One of those who remembered Perrin's contribution to atomism was R. A. Millikan, *Rev. Mod. Phys.* **21**, 343 (1949).

CHAPTER 2

Herapath

2.1 Introduction

John Herapath (1790–1868) was the first important kinetic theorist in the 19th century.[1] He was born in Bristol, the son of a maltster; his cousin was William Herapath, a chemist whose name is preserved in the chemical compound Herapathite. The family name is taken from Harepath or Herapath, a locality in North Devon; the word means military road. He had a scanty formal education but endeavoured to educate himself while working in his father's business. He learned French quite early, and was thus enabled to study the works of the French mathematicians. At the age of 19 he was already known as a mathematical prodigy in the neighborhood, and at that time was introduced by William Perry, at his house at Winterbourne, to Davies Gilbert. Gilbert (who had changed his name from Giddy) was a man of fortune who dabbled in mathematics and physics; he later became President of the Royal Society after Davy resigned in 1827; he had been elected M.P. for Bodmin in 1806, and took a prominent part in parliamentary investigations connected with the arts and sciences.[2] Gilbert apparently gave some encouragement to Herapath in 1809, though they were later to come in conflict.

Herapath, like many other young scientists in the 18th and 19th centuries, started his researches by trying to apply and extend Newton's methods in celestial mechanics. In 1811 he was at work on the

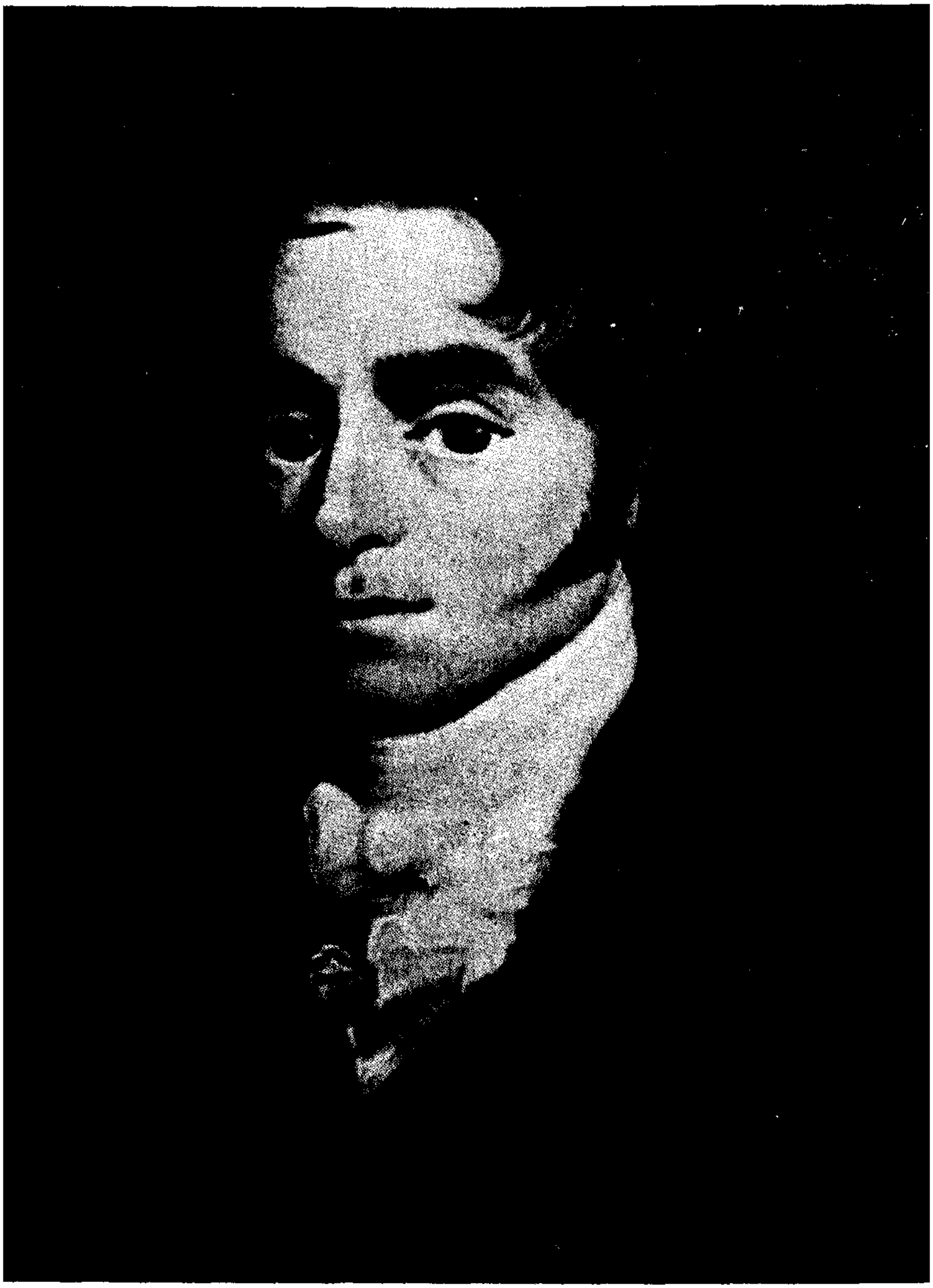

Fig. 2.1-1. Portrait of John Herapath. [Photograph courtesy of E. Mendoza.]

theory of the moon's motion, and he concluded that "the earth's action on the moon is greater about the winter than the summer solstice, or greater when the earth is nearer the sun than when further from it. This difference, if it be so, can only be attributed to a variation of temperature, arising from a change of distance in the earth with respect to the sun."[3]

He was married in 1815, and soon afterwards gave up business and became a teacher of mathematics. Early in 1816 he wrote to Thomas Thomson, editor of the *Annals of Philosophy*, saying that he had developed a mathematical theory of the cause of heat, light, gravity, cohesion, etc.; and that in order to avoid controversy in case his theory should turn out to be not original, he wanted to publish first a problem for mathematicians, which would attract the notice of anyone who was familiar with similar ideas. Thomson's reaction to this proposal is not known, but eventually a short note by Herapath was published in the *Annals*, containing one of the main results of his theory stated as a theorem without proof.[4] While this preliminary announcement seems to have attracted no attention from other scientists, Herapath continued to develop his theory and on May 24, 1820, he submitted a manuscript entitled "A Mathematical Inquiry into the Causes, Laws and Principal Phenomena of Heat, Gases, Gravitation, etc." to Davies Gilbert for publication in the *Philosophical Transactions of the Royal Society*. The subsequent history of this article will be discussed in §2.3.

Notes for §2.1

1. This chapter is based on my articles in *Ann. Sci.* **13**, 188 (1957); *Notes and Rec. Roy. Soc. London* **18**, 161 (1963); and introduction to the reprint of Herapath's *Mathematical Physics* (New York: Johnson Reprint Corp., 1972). The latter contains a bibliography of works by and about Herapath. There is an anonymous obituary of Herapath in *Herapath's Railway Journal* (*Railway Magazine*, Quarto series), **30**, 275, 309 (1868) which contains a large amount of interesting but unverifiable biographical information.
2. According to D. S. L. Cardwell, he opposed attempts to educate the working classes, *e.g.* the Parochial Schools Bill of 1807: *The Organization of Science in England; A Retrospect* (London: Heinemann, 1957), p. 28. For further information on Gilbert see Cardwell, *From Watt to Clausius* (Ithaca: Cornell University Press, 1971); A. C. Todd, *Trans. Newcomen Soc.* **32**, 1 (1959–60); Crabb Robinson, *Diary, Reminiscences, and Correspondence* (London, 1869), **2**, 401.
3. *Ann. Phil.* **8**, 56 (1816), quoted from p. 59. See the Bibliography (Part D of this book) for details of Herapath's papers on kinetic theory, sometimes cited in the text and notes by date only (*e.g.* "Herapath (1816)").
4. Herapath (1816).

2.2 Herapath's 1820 paper

Herapath succeeded in deriving the ideal gas law, apparently without knowledge of Bernoulli's work. He went further than Bernoulli in stating unequivocally the idea of an absolute temperature depending on molecular velocities, although, as will be seen, his temperature scale was based on an erroneous theory of heat. He realized that contemporary ideas about the collisions of hard bodies were inconsistent, and could not be used as the basis of a kinetic theory without considerable revision. He attempted to construct an alternative theory of collisions (somewhat similar to the older theory of Descartes[1]) but this was not completely successful since he did not realize the importance of conservation of energy. He was the first to show that the kinetic theory could provide a simple explanation for many diverse phenomena, such as changes of state, diffusion, and the propagation of sound. His explanations of these phenomena were not always correct, but his ideas were always ingenious–though sometimes hard to follow in detail because of the many neologisms he employed.[2]

According to his own account, Herapath first started to develop his kinetic theory after making some calculations on the motion of the moon, attempting to reconcile Newton's calculations with observations. Having failed to understand the cause of the discrepancies, he turned to Newton's opinion regarding the cause of gravitation: "If, argued I with myself, gravitation depends upon the action of an elastic medium, such as Newton supposes, which grows rarer and rarer as you approach the dense bodies of the sun and planets, there ought to be some reason for this variation of density."[3] He reasoned that if this medium were of the same nature as our atmosphere and other gaseous bodies, then the variation in density might be due to the high temperature of the sun, and to a lesser degree of the planets. Since the earth's distance from the sun varies, therefore the temperature of the earth, and hence its attraction for the moon, will also vary. To develop this theory further it was first necessary "to establish the cause of heat, and reduce its phenomena to mathematical laws."[4]

Herapath had started out with the (then current) idea that heat is an elastic fluid composed of particles which repel each other, but he finally decided to adopt a kinetic theory of gases, in which *impacts* play an essential role. But he soon encountered a well-known paradox of "hard" bodies: if a body is absolutely hard, then it cannot be "elastic" since it cannot (in modern terms) store potential energy by deformation when it collides with another hard body. Thus in a head-on collision of two hard bodies, both must come to a stop at the instant of collision, and apparently they cannot bounce since they are not elastic. How can one conserve energy in such a situation, if there is no possibility of dissipation by excitation of internal motions in the bodies?[5]

Herapath's solution of the paradox, while not entirely correct, is not unreasonable from a modern viewpoint. He is unwilling to reject Newton's opinion[6] that the ultimate atoms of matter must be absolutely hard, and it seems impossible to imagine a microscopic process of deformation and elastic restoration when two such atoms collide. Hence collisions must be instantaneous, and, as Herapath points out, we can determine the result of the collision by using the principle of conservation of momentum, even if we cannot describe what actually happens during the collision. However, although in some of his calculations he also makes use of the conservation of *vis viva* (kinetic energy), he does not seem to regard conservation of energy as being an important principle, and his theory of the temperature of mixtures actually violates this principle. He postulates that the heat of a gas is proportional to the momentum of internal motions of its atoms; this notion seems to come from his theory of collisions which emphasizes conservation of momentum in atomic collisions. Thus a system is in thermal equilibrium when all its atoms have the same momentum.[7]

Herapath defines absolute temperature as the total momentum divided by the number of particles. Thus the elasticity of a gas at constant volume is proportional to the number of particles (which Herapath calls the *numeratom*) and to the *square* of the temperature. The elasticity is just equal to the pressure exerted by the gas on the walls of the container, which is proportional to the intensity of the collisions and to their frequency. The intensity is proportional to the momentum, and the frequency to the velocity so that if the mass of the particles remains the same, the elasticity is proportional to the square of the momentum.[8]

We see that Herapath thus derived an ideal gas law of the form $PV \propto T^2$ instead of the usual $PV \propto T$. The difference is more than just a matter of definition, since Herapath believed that his "true temperature" had the properties usually attributed to the ordinary temperature. Thus, if one mixes two equal portions of the same fluid at different temperatures T_1 and T_2, the temperature of the mixture should be $\frac{1}{2}(T_1 + T_2)$. If one mixes, for example, equal portions of water at 32° and 212° on the Fahrenheit scale (this is Herapath's own example) the temperature of the mixture by conventional theory would be $\frac{1}{2}(32 +$

212) = 122°F. But according to Herapath's theory one should find the absolute temperatures, taking −448°F as the point of "absolute cold," and then compute the true temperatures as the *square roots* of these, $T_1 = \sqrt{448+32}$ and $T_2 = \sqrt{448+212}$. The average true temperature is $\frac{1}{2}(\sqrt{480}+\sqrt{660})$ which can then be converted back to the Fahrenheit scale as $(\sqrt{120}+\sqrt{165})^2 - 448 = 118.4$°F.

Herapath mentioned an experiment of this kind by de Luc, who, according to Ure, obtained the result 119°F. On the other hand, Crawford found that the temperature of the mixture is just the arithmetical mean, 122°F, as one expects from the conventional theory. Herapath concluded that de Luc's experiment was more likely to be correct just because its result was unexpected and therefore must have been carefully checked.[9] Herapath considered such experiments to be crucial to his theory, and later tried to get the Royal Society to sponsor them.

In general, of course, the temperature of a mixture will depend on the specific heats of the components, and these, according to Herapath, depend on the number of separate particles in unit volume. His explanation of latent heat (one of the phenomena that the caloric theory seemed to be able to explain more satisfactorily than the kinetic theory) was also based on this idea. Thus when one heats a solid, the vibrations of the atoms increase, until finally the cohesion holding together the solid begins to be overcome. However, as soon as some particles have broken free, there will be a lowering of the temperature since the same motion (*i.e.* momentum) must be distributed among a larger number of particles. Thus more heat must be added to maintain the same temperature while the melting takes place. In general, melting and evaporation are accompanied by an increase in the number of particles in a given mass of substance, and they will therefore result in a diminution of temperature unless heat is supplied externally.[10] On the other hand, Herapath made the implicit assumption that the specific heat of a liquid remains constant between its melting and boiling points; this is consistent with the simple form of his theory, and is plausible for gases, but not for liquids.[11] So it appears that he was being rash in placing so much confidence in the predictions of his theory for temperatures of mixed liquids, for two reasons. First, averaging mv instead of mv^2 is erroneous; second, in real liquids the temperature of the mixture cannot be calculated by a simple averaging of *either* mv or mv^2. But the experimental errors (loss of heat by radiation from the initially hotter component, etc.) tend to give a result more nearly in agreement with Herapath's theory than with the conventional theory based on averaging mv^2.

The above discussion is misleadingly unhistorical in one important respect: Herapath's contemporaries would have accepted the rule of taking the arithmetical average of the temperature on the Fahrenheit scale, but they did not identify temperature with mv^2 for individual molecules. This was not done until 1845 when J. J. Waterston, in a manuscript presented to the Royal Society but not published until 1893, argued that thermal equilibrium in a system of colliding particles of different masses would correspond to equal average values of mv^2 for all species (§3.2). It was another decade before Clausius, and especially James Clerk Maxwell, established the idea that kinetic energy is equally distributed, on the average, among molecular motions of all kinds; and this "equipartition theorem," combined with the principle of conservation of kinetic energy in elastic collisions, provided the theoretical basis (at least for gases) of the original rule for temperature of mixtures that Herapath had disputed (see ch. 10).

The assumption that thermal equilibrium corresponds to equality of mv rather than mv^2 led to a direct contradiction of Avogadro's hypothesis, though there is no indication that Herapath was aware of that hypothesis. It follows from Herapath's theory that if two gases have the same temperature [*i.e.* same mv], pressure, and volume, then the numbers of particles will be proportional to the square roots of the densities. So "if oxygen is 16 times heavier than hydrogen, there is quadruple the number of particles of oxygen in a given volume than there is of hydrogen."[12]

Notes for §2.2

1. R. Descartes, *Principia Philosophiae* (Amsterdam, 1644), reprinted in his *Oeuvres* (Paris: Cerf, 1905), vol. **8**; French translation (Paris, 1647) reprinted in *Oeuvres*, vol. **9**. There is unfortunately no complete English translation of this work as yet; the Haldane–Ross translation omits most of the sections on physics. The sections on collisions are translated in M. B. Hall, *Nature and Nature's Laws* (New York: Harper, 1970), pp. 264–70.
2. Cardwell has the following comments on style: compared to the publications of Fourier, Gay-Lussac, and Ampère, Herapath's "are not merely old-fashioned: they are archaic . . .. Herapath belongs to the tradition of the English eccentrics . . . a very able but basically undisciplined thinker. His highly idiosyncratic style of presentation suggests that he was also headstrong . . ." *From Watt to Clausius* (Ithaca: Cornell University Press, 1971), **146**, 316. For a detailed analysis of Herapath's theory see E. Mendoza, *Brit. J. Hist. Sci* **8**, 155 (1975).
3. Herapath (1821), p. 276.
4. Herapath (1821), p. 277.
5. Cf. W. L. Scott, *Isis* **50**, 199 (1959); *The Conflict between Atomism and Conservation Theory* 1644–1860 (New York: American Elsevier, 1970). In an earlier paper "On the

Law of Continuity," *Ann. Phil.* **11**, 208 (1818), Herapath objected to Leibniz's law, mentioning the collision of hard bodies which must introduce discontinuities.

6. "... it seems probable to me, that God in the beginning form'd Matter in solid, massy, hard, impenetrable, movable Particles, of such Sizes and Figures, and with such other Properties, and in such Proportion to Space, as most conduced to the End for which he form'd them; and that these primitive Particles being Solids, are incomparably harder than any porous Bodies compounded of them; even so very hard, as never to wear or break in pieces; no ordinary Power being able to divide what God himself made one in the first Creation. While the Particles continue entire, they may compose Bodies of one and the same Nature and Textures in all Ages: But should they wear away, or break in pieces, the Nature of Things depending on them, would be changed. Water and Earth, composed of old worn Particles and Fragments of Particles, would not be of the same Nature and Texture now, with Water and Earth composed of entire Particles in the Beginning. And therefore, that Nature may be lasting, the Changes of corporeal Things are to be placed only in the various separations and new Associations and Motions of these permanent Particles; compound Bodies being apt to break, not in the midst of solid Particles, but where those Particles are laid together, and only touch in a few Points." I. Newton, *Opticks* (London, 4th ed., 1730; reprinted by Dover Pubs., New York, 1952), p. 400.
7. That this error was not unique to Herapath is indicated by a paper by R. Hare (Professor of Chemistry at the University of Pennsylvania), *Am. J. Sci.* **4**, 142 (1819). Hare criticized Davy's theory that heat is motion on the grounds that such a theory would imply equalization of momentum after thermal contact; for example, if equal *weights* of mercury and water were mixed, the temperature of the mixture ought to be the arithmetic mean of the two initial temperatures, whereas in fact it is much closer to the initial temperature of the water. Hence (Hare argued) heat is not proportional to mv, hence Davy's theory is wrong, hence heat is a substance. J. Robert Mayer at first identified mv as "quantity of motion" in his paper "Ueber die quantitative und qualitative Bestimmung der Kräfte" submitted to Poggendorff's *Annalen* in 1841; see Mayer's *Kleiner Schriften und Briefe*, ed. J. J. Wyrauch (Stuttgart, 1893), p. 100.
8. Herapath (1821), p. 404.
9. Researches on the temperatures of mixtures in the 18th century have been reviewed by A. Wolf, *A History of Science, Technology, and Philosophy in the 18th Century* (London: Macmillan, 2nd ed., 1952), pp. 198–206; see also V. P. Zoubov, in *L'Aventure de la Science-Melanges Alexandre Koyré* (Paris: Hermann, 1964), p. 654. The later work of F. Neumann is discussed by J. G. Burke, *Dict. Sci. Biog.* **10**, 27 (1974).
10. Herapath (1821), pp. 256–58; (1847), vol. **1**, p. 233.
11. See J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1951), **2**, 215.
12. *Mathematical Physics* **1**, 260; *Ann. Phil.* **1**, 403. In Herapath's notation, elasticity $E \propto NMS^2 \propto NT^2/M$, where N = number of particles in unit volume, M = mass of one particle, S = speed, T = true temperature = SM. The specific gravity is proportional to $D = NM$. Thus, substituting $M = D/N$ in the expression for E, he finds $E \propto N^2T^2/D$. If two gases have the same E and T, they must have the same ratio of N^2/D, hence N is proportional to the square root of the specific gravity.

2.3 The Royal Society controversy

The fate of Herapath's theory was largely determined by the fact that the Royal Society refused to publish his work, though he was able to appeal to a wider audience through publication in the *Annals of Philosophy*. The Royal Society's decision was in turn primarily determined by the opposition of Humphry Davy. One might have expected Davy to be more favorable to Herapath's theory, since Davy himself was one of the exponents of the idea that heat is a form of atomic motion.[1] However, Davy objected to Herapath's theories on the grounds that they were too speculative, and did not have sufficient experimental justification. It is also possible that Davy had been influenced by the attitudes of Romantic *Naturphilosophie* by this time, and was consequently out of sympathy with the extremely mechanistic viewpoint of Herapath's theory.[2] Another reason may have been that Davy's mathematical skills were not good enough to permit him to understand Herapath's derivations, which–though they involved nothing more than elementary algebra–were presented in a rather clumsy manner.

Herapath himself published parts of his correspondence with Davy and Gilbert (see below), because he wanted to show his critics that the rejection of his work by the Royal Society was not due to any demonstrated faults in his theory.[3] Whatever his contemporaries may have thought of the merits of his case, modern students of the history of 19th-century science should be thankful that Herapath was such an inveterate propagandist and took such pains to put these documents (at least the ones he considered favorable to himself) in the public record. To start with, we learn the following from Gilbert's first letter to Herapath (27 January 1820):

> The usual practice of the Society is as follows:–When a communication is offered, the individual receiving it consults those most conversant with the subject, and is guided by their judgment in presenting it to the Society. If he presents the paper, it is almost always read, after which it is, in its turn, considered by the council, who finally determine on the question of printing. A paper after being read is never returned, but in the event of its not being printed, the author is allowed to have a copy taken if he wishes it.

The rule that papers not printed could not be returned has frequently been criticized;[4] in some cases, for example that of Waterston (ch. 3) it resulted in important work being "buried" in the Royal Society Archives, to the annoyance of their authors and at great loss to the scientific world. This is one instance where the modern reader, who is accustomed to carbon copies and mimeographed preprints, must try to imagine the working conditions of scientists in previous centuries in order to appreciate the significance of such a rule.

Herapath submitted his manuscript to Gilbert on May 24, and on June 6 Gilbert wrote that while he was "not satisfied with the ultimate deduction, yet I was much pleased with the great ingenuity displayed throughout the whole; but I entertained strong doubts on the propriety of laying before the Royal Society anything so abstruse and metaphysical. I, therefore, desired two of the best mathematicians in London to look at the premises; and their opinion confirmed my doubts. They say that such a work should be laid before the public in a separate form. I cannot present it to the Royal Society in opposition to their opinions, and consequently I must wait your direction to dispose of the treatise in any other manner that you may have the goodness to direct."

Herapath went to London at the end of June and had two interviews with Gilbert, in which Gilbert tried to convince him that his theory was wrong. Herapath surmises that "Want of leisure very probably was one cause of Mr. G's not being able to master the paper; but it is also highly probable that the known difficulty of the subject, and the failures of others in the same inquiry, operated to prevent his finding that leisure, and to prejudice him in the belief that, 'where many had failed it is not likely another could succeed.'" At the same time it was also agreed that Herapath should do some experiments on the temperatures of liquids mixed at different temperatures. The results of these experiments were described in another letter to Gilbert in September, but Gilbert was still dubious, and mentioned the opinion of "some members of the Council, who are usually looked up to in such occasions" who considered Herapath's memoir "too theoretical for the Transactions" (Gilbert to Herapath, 25 October 1820). Davy was elected President of the Royal Society at the end of November,[5] and Gilbert (undoubtedly with a sigh of relief) dumped the whole problem in Davy's lap. This turn of events raised Herapath's hopes for the moment, for he knew that Davy had previously published views on heat in agreement with his own.

The following January, Herapath wrote again to Gilbert, mentioning that he had "something more at stake than mere literary fame" because he was running a school of mathematics (partly to prepare young men for the Navy) and hence felt it necessary "to strain every nerve to establish my scientific reputation" for business reasons.

At about the same time Davy wrote to Herapath giving his evaluation of the paper: "highly ingenious as I find your views, I must say I am not impressed with a conviction of their truth." He objects to Herapath's theory of gravity, and wishes that Herapath had restricted himself to developing the doctrine of heat as motion. He also expresses his willingness to communicate the results of Herapath's experiments, which he had heard about (Davy to Herapath, 13 January 1821).

On January 17 Herapath attended one of Davy's Evening Meetings at the Royal Society. "We had a long chat together in the rooms, in which he [Davy] spoke very kindly and encouragingly, and hoped, alluding to my paper, that I would not be discouraged by the *opinions of one or two*, laying an emphasis of contempt on the word 'opinions,' adding, that there are two or three in the Council who are determined it shall not pass. He introduced me to Dr. Young who, on my asking him, said, he had not seen or heard of the paper, yet, in a few minutes after, discussing the mode of making some experiments, he observed, 'but you, in your paper,' (referring to this very one) 'say....'"

After being convinced that the Royal Society would not publish his work, Herapath decided to withdraw it. There were now two separate papers, the original theoretical one, and a second one on his experiments; Herapath wanted to withdraw both of them and publish them elsewhere. Later he suspected that Davy was offended by this move because he had already agreed to communicate the paper on the experiments. In fact, the experimental paper was retained in the archives and was communicated by Gilbert on May 31, 1821,[6] though Herapath does not mention this fact; it was not published in the *Transactions*, but Herapath published a copy of it in his *Railway Magazine* in 1838.[7]

Herapath saw Davy again in February 1821, "and found him very unlike the kind affable man I had seen him at my first visit, January 17th. He affected the great man–talked dictatorially–was going to upset me at once by some experiments of De Luc, but, though I saw the book under his fingers, he would not take it down, probably well knowing he would have confirmed me, as I then told him the experiments he alluded to would." Davy wrote to Herapath on February 28, mentioning a note on Herapath's paper by "a very able philosopher" to whom he had shown it. Herapath says the note was by Roget, and it contains nothing more than a confused criticism of

Herapath's calculation of true temperatures. Another letter from Davy gives a significant statement of his own view on absolute temperatures:

> Having considered a good deal the subject of the supposed real zero, I have never been satisfied with any conclusions respecting it. I cannot see any necessary connexion between the capacity of bodies for heat, and the absolute quantity they contain; and temperature does not measure a quantity, but merely a property of heat. (Davy to Herapath, 6 March 1821.)

As Herapath later remarked when he published this letter, this was the only real objection that Davy ever made to his theory, and on this very point Herapath's view was confirmed soon afterwards by Laplace and by Clément and Desormes. But other scientists were not so certain, and an absolute temperature scale was not generally accepted until the middle of the century (see above, §1.4).

A few months after Herapath's kinetic-theory paper was published in the *Annals of Philosophy*, Laplace announced his derivation of the ideal gas laws based on the caloric theory.[8] Herapath wrote a critique of this theory for the *Philosophical Magazine* in which he remarked that he had sent "an announcement of the publication and objects" of his own paper to Laplace in June 1821. According to Herapath,

> it was obvious from the perfect coincidence of M. Laplace's paper with that of a part of mine, and its being presented to the Royal Academy so long after the printing and notice of my paper, that his communication was in consequence of mine and intended to supersede it.[9]

But Laplace's theory could not supersede Herapath's in the thinking of British physicists of this period: neither made any impact at all until a quarter of a century later when Joule read Herapath's *Mathematical Physics.*[10]

In 1823 Herapath translated Poisson's paper on caloric theory for the *Philosophical Magazine* and remarked in his introduction:

> From this paper and those of M. Laplace it is plain with what ardour the subject of gases and heat is pursued on the continent. Would our English philosophers but lend their aid in the securer course of deciding some of the more important and disputed points by experiments, it is manifest we should speedily come to decisive conclusions respecting the nature and laws of heat.[11]

While he apparently found no difficulty in publishing a series of papers on various subjects in the *Annals of Philosophy* and the *Philosophical Magazine.* Herapath still cherished his grievances against the Royal Society, and in 1826 he resumed the battle. On January 6, 1826, a letter from Herapath, nearly two columns long, appeared in *The Times* under the caption "Sir Humphry Davy's treatment of Mr. Herapath." Among a number of minor complaints against Davy and the Royal Society, he accused Davy of suggesting that he had fabricated his experiments to support his theory, and claimed that because of the "insidious propagation of reports" against his experiments he was unable to get them published in any other journal. "Thus, I was first charged with a most foul action, and not allowed to clear myself, and at length I was prevented from doing that which every one must see it would be to the interest of any enemy to encourage, if he knew me to be wrong.... It was now but too clear that a deep-laid scheme against my private character was in active operation...." Herapath then proposed a series of "Problems of Defiance" to Davy and the Royal Society, the object being to demonstrate their scientific incompetence and vindicate Herapath's reputation. The problems were mainly based on theorems which Herapath had deduced from his own kinetic theory of gases; no one else would be likely to be able to solve them unless he were familiar with the same or some other theory of gases. At the same time the statement of each problem was deceptively simple, and made it appear to be of general scientific interest–for example, to determine the law governing temperature and pressure in the atmosphere surrounding a globe of uniform temperature–so that one can well believe Herapath's assertion that Dalton had shown an interest.

Davy offered no response to Herapath's attacks, even though the Editor of *The Times* tacitly supported them and printed a report that Herapath's cause was "very warmly espoused" in Cambridge.[12] Davy resigned the Presidency of the Royal Society early in 1827, supposedly because of ill health, though his term did not officially end until November 6 of that year. After a brief campaign in which the character of each of the leading candidates (as well as of Davy) was blackened by anonymous letters in *The Times*, Davies Gilbert was elected to the Presidency.[13] Herapath then announced that he wished to conclude his dispute with the Royal Society; apparently he considered that Davy's resignation was a victory for himself. He managed to convince himself and his friends that his controversy with Davy had led to the latter's "expulsion or forced retirement" from the Presidency,[14] although there seems to be no reason to doubt the more conventional version that Davy's retirement was due mainly to his illness.[15]

Notes for §2.3

1. In his *Elements of Chemical Philosophy* (London, 1812), p. 53, Davy wrote: "It seems possible to account for all the phenomena of heat, if it be supposed that in solids the particles are in a constant state of vibratory motion, the particles of the hottest bodies moving with the greatest velocity, and through the greatest space; that in fluids, and elastic fluids, besides the vibratory motion, which must be conceived greatest in the last, the particles have a motion around their own axes, with different velocities, the particles of elastic fluids moving with the greatest quickness; and that in etherial substances the particles move round their own axes, and separate from each other, penetrating in right lines through space. Temperature may be conceived to depend upon the velocities of the vibrations; increase of capacity on the motion being performed in greater space...."

   Davy's "etherial substances" were composed of particles which can move freely through space, yet it was their supposed existence which probably prevented him from ascribing equally free motion to the molecules of gases or "elastic fluids." The belief in a luminiferous ether was indeed one of the major obstacles to complete acceptance of the kinetic theory of gases; for how could molecules move without resistance through a medium which transmits waves generated by their internal motions? It was only by ignoring this problem that the kinetic theorists of the late 19th century were able to develop their doctrine.
2. See L. Pearce Williams, *Michael Faraday* (New York: Basic Books, 1965), pp. 66–80; J. Z. Fullmer, *Chymia* **6**, 102 (1960); D. M. Knight, *Studies in Romanticism* **5**, 185 (1966), **6**, 65 (1967), *Ambix* **14**, 179 (1967).
3. J. Herapath, *Ann. Phil.* [2] **2**, 303 (1821); *Railway Magazine* **2**, 308, 389, **3**, 29, 97, 176 (1837); quoted by Brush, *Notes and Rec. Roy. Soc. London*, **18**, 161 (1963).
4. J. Davy, *Memoirs of the Life of Sir Humphrey Davy* (London, 1836), **2**, 136–37.
5. On Davy's election see A. Treneer, *The Mercurial Chemist: A Life of Sir Humphry Davy* (London: Methuen, 1963), p. 186.
6. I am indebted to Sir Harold Hartley for this information.
7. J. Herapath, *Railway Magazine* **4**, 3, 88, 145 (1838). Cf. Trimmer, *Ann. Phil.* **1**, 417 (1821).
8. Laplace, *Ann. Chim.* **18**, 181 (1821); see S. G. Brush, *Kinetic Theory* (New York: Pergamon, 1965), **1**, 39.
9. J. Herapath (1823); see Brush, *op. cit.*, p. 15, for a summary of Herapath's arguments.
10. I have found only a handful of British references to Laplace's theory: W. C. Henry, *Phil. Mag.* [3] **3**, 33 (1834) (favorable); J. Challis, *Brit. Assn. Rept.* **6**, 225 (1836), and W. Whewell, *History of the Inductive Sciences* (London, 1837), vol. **II**, Book X, ch. LV (both unfavorable).
11. J. Herapath, *Phil. Mag.* **62**, 328 (1823).
12. *Times*, Nov. 18, 1826, p. 2.
13. For a time it appeared that Sir Robert Peel would be elected, on political rather than scientific grounds, much to the disgust of the *Times* and some of its correspondents (see the issues of Nov. 12, p. 3; Nov. 14, p. 3; Nov. 23, p. 2; Nov. 26, p. 2; Nov. 29, p.

2; Nov. 30, p. 2). However, Peel eventually withdrew his candidacy when it appeared that he would not be elected without some opposition. Gilbert served only with some reluctance; he has willing to spend several thousand pounds per annum to promote the objects of the Society, but "declared his inaptitude to undergo the personal fatigue of keeping open house as it were, for that purpose." (*Literary Gazette*, quoted in the *Times*, Nov. 12, p. 3). In 1830 Gilbert managed to turn over the burden to the Duke of Sussex (Augustus Frederick, sixth son of George III) who presided until 1838. *The Record of the Royal Society* (London: Oxford University Press, 3rd ed., 1912), which lists the scientific accomplishments of all the Society's past officers, says of the Duke of Sussex only that "During his tenure he constantly presided at all meetings of the Council and Society," p. 203).

During this period the Royal Society was split between those who wanted the President to be a distinguished scientist, and those who thought that a political leader or member of the Royal Family would be better able to advance the Society's interests. Davy himself apparently held the latter opinion since he would have approved the election of Peel (letter to his wife, June 30, 1827, quoted in *Fragmentary Remains*, ed. J. Davy, London, 1857, p. 288).

14. J. Herapath, *Railway Magazine* **2**, 308 (1837).
15. On Davy's reasons for resigning, see J. Davy, *Fragmentary Remains*, and *Memoirs of the Life of Sir Humphry Davy* (London, 1836), **2**, 218–222. According to another biographer, "to assert that Davy retained his popularity, or to deny that he retired from office under the frown of a considerable party, would be dishonest"–J. A. Paris, *The Life of Sir Humphry Davy* (London, 1831), p. 181. An anonymous correspondent wrote: "... it was said as long ago as October twelvemonth, by one or two of the leading members of the Society, 'that they suppose the end of it would be, that they must get rid of Sir Humphry Davy,' and in January last, it was widely known that Sir Humphrey was to go on the Continent, and then resign. Besides, reports of universal offence by a little too much hauteur have been pretty generally circulated..."–Anti-Humbug, *Times*, Nov. 26, 1827, p. 4. That Davy had many opponents besides Herapath is shown in the article by J. Z. Fullmer, *Chymia* **8**, 147 (1962).

2.4 Railways

Early in 1821 Herapath had confessed to Davies Gilbert that he had "something more at stake than mere literary fame" in his campaign to get his paper published by the Royal Society: he had recently started "a school for mathematics, and for preparing young men for the [universities]" at Cranford, near London[1] and therefore he must "strain every nerve to establish my scientific reputation, as well for the sake of maintaining myself in the good opinion of my friends, as for the benefit which it may be of to my family, in my business."[2] By his own standards this attempt was a failure, though mathematics teaching was his only recorded source of income until 1832. A projected textbook on calculus involved him in some kind of disagreement with Henry

Brougham and was never completed; similarly, his hope of getting a chair at the newly established University College in London came to nothing. Nor did he have any standing in the international scientific community.[4]

In 1829, Herapath became interested in Goldsworth Gurney's steam carriages, and supported the project by publishing a letter to the Duke of Wellington[5] and by letters to *The Times.*[6] Gurney's attempt to develop a steam-driven vehicle using ordinary roads was a failure, mainly because of sabotage and excessive tolls,[7] and Herapath soon turned his attention to railways.[8] In 1835, he published an extensive survey of the engineering aspects of current and projected railway lines in the *Mechanics Magazine.* One of his theoretical results, a formula for the speed acquired by a locomotive going up- or downhill, stimulated a long and rather ridiculous controversy in the pages of this magazine.[9] Some of the anonymous correspondents resurrected the Davy affair as part of their attack on Herapath.[10] Around this time Herapath began to write reports on railways for the *Railway Magazine* (established in 1835) and became its editor in 1836. This occupation provided financial security–the magazine, later titled *Herapath's Railway Journal,* was apparently quite successful–and it also gave him an opportunity to publish his own papers on scientific subjects.[11] But beyond these advantages, one must infer from the numerous pages of the *Railway Magazine* filled by Herapath's writings on railways that this new occupation turned out to provide a perfectly legitimate satisfaction for the needs of his personality. Herapath, as the scientist-turned-journalist, engineer, and operations-researcher, threw himself wholeheartedly into all the excitement and problems of England's railway boom of the 1840's.

What does the kinetic theory of gases have to do with railways? Herapath points out one possible connection in the first issue of the new series of the *Railway Magazine.* According to his theory, the temperature of the atmosphere decreases nearly 1°F for every hundred yards increase in altitude. Since "a single degree will be sufficient to change a damp-rail at the temperature of about 32°F, into one glazed with ice, on which a train could not move, it will evidently be a matter of some consequence in the laying down of these expensive lines to avoid every chance of obstacle or injury to the free working of them, by keeping their summits as low as possible, so as to be the least affected by temperature."[12]

Although Herapath does not give the details of his calculation here, they can be found in §VI, Book III of the *Mathematical Physics.* The argument is plausible but wrong; as Maxwell later showed (1866), a column of air should be in thermal equilibrium at constant temperature throughout under the action of gravity. Of more practical significance is the fact that the earth's atmosphere is not in thermal equilibrium anyway, so that any simple calculation based on kinetic theory is likely to be misleading. But Herapath did not realize this, and no one else at the time could have made this criticism.

On the next page following the end of this paper, Herapath prints an account of his "Exact calculation of the Velocity of Sound," first presented to the British Association meeting at Oxford in 1832 [Herapath 1832, 1836]. In retrospect this work appears to be one of Herapath's major contributions to science, and one for which he has not (as far as I know) been given proper credit. Not only did he obtain essentially the correct first approximation for the speed of sound in an ideal gas (aside from numerical factors, involving, for example, the ratio of rotational to translational energy of diatomic molecules), but at the same time he gave the first explicit value for the speed of a molecule. J. P. Joule, who is usually considered to have been the first to publish the latter estimate, undoubtedly based his own calculation on Herapath's, as published in *Mathematical Physics* (Book III, §II). The values found for the "mean rectilinear velocity of the particles in any given direction; that is . . . the velocity with which sound or any disturbance in air is propagated" are: 1089.6 feet per second for air at 32°F, in excellent agreement with Moll's experimental value of 1089.7; fairly good agreement with results of Parry, Gregory, Arago, and others at various different temperatures; and fairly good agreement with Dulong's values for the speed of sound in other gases, for example, 1266.21 meters per second for hydrogen, compared with the experimental value of 1269.5 meters per second. Herapath's formula gives the correct dependence of speed on temperature and specific gravity.

The force or pressure that air exerts on a solid surface is proportional to the square of the velocity of its molecules, according to the kinetic theory. To Herapath this fact now suggested a new application of kinetic theory to railways, which he published in May, 1836 under the title: "Effect of the atmosphere in resisting a train." He introduces the subject as follows:

> In this age of experiment and research, when men seek to rival birds in the celerity of their motions, and to make tea-kettles their wings, it is rather extraordinary that the effects of one of the

> greatest opponents to their success should have been almost entirely overlooked. But engineers, whose business it is to deal in clods, bricks, and stone, who plume themselves on the power of an engine capable of whirling along at twenty miles an hour, thirty, fifty, or a hundred tons, seem to think themselves omnipotent, and that a body so light as air is utterly unworthy of their notice, overlooking that the very agent they use is little better than half the weight of the body they despise.[13]

On looking over the existing data on wind resistance at various speeds, Herapath noted that the pressure is rather great at high speeds, but little reliable information was available. He realized, however, that he could compute the pressure theoretically since the kinetic theory gives a relation between speed and pressure. A train moving at the speed of sound–*i.e.* at the average speed of an air molecule, according to Herapath's theory–would encounter a resistance equal to atmospheric pressure, in other words about 2120 pounds per square foot at a speed of 1090 feet per second (743 mph). At any lower speed the resisting pressure would be proportionately smaller, the important point being that the pressure varies as the square of the speed.[14] By this simple method Herapath was able to compute theoretical values that were in good agreement with the handful of experimental results available: about 0.75 pounds at 14 mph, and 24.5 pounds at 80 mph. According to Pambour's experiments, the traction on the level is about 8 pounds per ton of load.[15] Since the normal weight of a passenger train was about 30 tons, this meant that the load would be increased by 43% at 30 mph; at 40 mph it would be increased by 23 tons, or 77%.

From these calculations Herapath drew two important conclusions: first, the idea that trains could operate at 60 mph or more (as suggested by Stephenson and others) is absurd; second, every effort should be made to design the shape of the locomotive so as to minimize air resistance. Another way to reduce air resistance, he suggested, would be to lay the railroad line in a moderately deep cutting, so that the air will strike the train at the front where the exposed surface is least.

In subsequent issues of the *Railway Magazine*, Herapath published further applications of kinetic theory to railway problems, miscellaneous articles on the economic and scientific aspects of locomotives and railway lines, and the Royal Society correspondence already mentioned. He did not exclude from his journal a communication that appears to be a satire on his own theories, contributed by

"Philo-Humbug."[16] Nor did he hesitate to take sides on important practical questions such as whether locomotives should have four or six wheels, whether a wider gage should be adopted for the tracks, whether tunnels should be avoided in constructing lines,[17] and so forth. Several times he got embroiled in controversies and even lawsuits as a result of his criticism of various projected railway lines. After 1844 Herapath published little of scientific interest in the *Railway Magazine*, but instead devoted himself to reworking his theories and writing the *Mathematical Physics.*

Herapath's involvement in railway history seems to have left few permanent traces, but it has aroused the interest of Ellis Hadfield, who recently reviewed one of the transportation schemes torpedoed by Herapath. Hadfield gives us this assessment:

> Herapath was bellicose, opinionated, outspoken, and unfair; he was also well-informed, with a nose for news and sympathy for the underdog, a detective of extravagant claims and unsupported statements, and a very competent mathematician and physicist.[18]

Notes for §2.4

1. See the obituary in *Herapath's Railway Journal* **32**, 275, 309 (1868).
2. Herapath to Gilbert, 11 January 1821; published by Herapath in his *Railway Magazine* in 1837.
3. Cf. G. Goodwin, article "Herapath, John" in *Dictionary of National Biography.* Some indication of his family responsibilities during this period may be inferred from a letter he wrote to the *Times,* Nov. 8, 1837, p. 3, discussing vaccination; he says he has 11 children, ages from 1 to 22.
4. G. W. Muncke, reviewing the progress of research on gases in *Gehler's Physikalisches Wörterbuch,* dismissed him in a footnote: "Die Theorie, welche HERAPATH über Wärme und Gasarten in Ann. of Phil. New Ser. Nr. I, II, III und IV, p. 197 aufgestellt hat, übergehe ich, weil sie zu sehr gekünstelt und zu wenig befriedigend ist" (Leipzig, 1828, **4**, 1073).
5. J. Herapath, *A Letter to His Grace the Duke of Wellington on the Utility, Advantages, and National Importance of Mr. Gurney's Steam Carriage* (London: Baldwin & Craddock, 1929).
6. J. Herapath, *Times,* Sept. 8, 1829, pp. 3–4; Feb. 1, 1830, p. 3; March 16, 1830, p. 4; April 18, 1831, p. 3.
7. C. H. Ellis, *British Railway History* (London: Allen & Unwin, 1954), pp. 46, 62.
8. J. Herapath, *Mechanics Magazine* **12**, 167, 169 (1830). An early notebook of "Railroad Scraps" is preserved in the Hopkins Library at Stanford University.
9. J. Herapath, *Mechanics Magazine* **23**, 148, 166, 181, 197, 232, 275, 308, 355, 425, 450, 517; **24**, 20, 51 (1835); I. Maciver, *ibid.* **24**, 15, 43, 64, 123, 195, 219, 250, 275, 323 (1835); **24**, 394, 433, 500; **25**, 14, 106 (1836); J. Combe, *ibid.* **23**, 291 (1835); anonymous

notes published by various correspondents in *Mechanics Magazine* **23**, 500; **24**, 6, 64, 67, 134, 160, 166, 194, 206, 220, 236, 271 (1835); **24**, 297, 382, 416, 433, 448 (1836); **25**, 92 (1836); **27**, 4, 58, 69, 308 (1837); F. M. Meredith, *ibid.* **24**, 319 (1836); **27**, 19, 40 (1837).

10. See especially the letters from "Philo-Davy," *Mechanics Magazine* **27**, 4, 69, 308 (1837): referring to the claim that Davy was the "tool" of Herapath's opponents within the Royal Society, he says–"What opponents? I never knew he had any within the walls of the Royal Society. I remember to have heard the letters he speaks of laughed at for their measureless impudence and conceit–but that, I am sure, was the utmost notice they ever elicited." In his next communication Philo-Davy stated that "Mr. Herapath and his challenges had, in no shape whatever–whether 'expulsion,' 'retirement,' or 'resignation,' anything to do with the termination of Sir Humphry Davy's presidential career. I say this with a perfect knowledge of the real facts of the case."
11. Another interpretation of this move was offered by Iver Maciver, Herapath's opponent in a dispute in the *Mechanics Magazine*: "I observe that this poorest of mathematicians, but most dogmatic and arrogant of all living prigs, has, after being beaten to his utter confusion and disgrace, in the controversy of his own provoking in the *Mechanics Magazine*, started a Journal of his *own*, in order that he may have all his *own* way, and be no more troubled with such inconvenient antagonists as truth, honesty, and common sense. I cordially wish him in his new character and career all the success he *deserves*, and beg, at the same time, with equal cordiality, to congratulate the readers of the *Mech. Mag.* on a capital riddance." [*Mechanics Magazine* **25**, 15 (1836).] The same thought was expressed a little more subtly by "Ursa Major" in calling for an evaluation of a new theory of the universe by the readers of the *Mechanics Magazine*: "I suppose the redoubtable Mr. John Herapath has withdrawn the light of his countenance from us forever; we cannot, therefore, expect to be illuminated as heretofore with the refulgence of his transcendent genius." [*Mechanics Magazine* **25**, 93 (1836).]
12. J. Herapath, *Railway Magazine* **1**, 19 (1836).
13. J. Herapath, *Railway Magazine* **1**, 89 (1836).
14. This is a standard result going back to I. Newton, *Philosophiae Naturalis Principia Mathematica* (London, 1687, 3rd ed., 1726), Book II.
15. Let pressure $P = kv^2$, then if the train moves at the speed of sound, $P = 2120$ lb/ft^2 when $v = 743$ mph, hence $k = 2120/743^2 = 0.00385$. At a speed of 14 mph, $P = 0.00385 \times 14^2 = 0.75$ lb/ft^2. At 30 mph, $P = 0.00385 \times 30^2 = 3.46$ lb/ft^2, so the force on an area of 30 ft^2 would be $3.46 \times 30 = 104$ lbs. This is equivalent to $104/8 = 13$ tons.
16. *Railway Magazine* **1**, 309 (1836).
17. He managed to relate this problem to the contemporary discussions of the internal heat and cooling of the earth (§14.2), using the fact that underground temperature does not change with the seasons as another argument against tunnels. *Railway Magazine* [N.S.] **1**, 57 (1836).
18. E. C. R. Hadfield, *Atmospheric Railways* (Newton Abbot: David & Charles, 1967), p. 30.

2.5 The Mathematical Physics

In 1847 Herapath published a two-volume treatise on *Mathematical Physics*, containing an elaborate development of his earlier theory with new applications and comparison with recent experiments. The publication of experimental work by Joule, Regnault, and Graham in 1845 and 1846 seems to have furnished the immediate stimulus for this attempt to revive his theory,[1] though much of the manuscript had probably been prepared during the previous decade. Herapath's practical interest in railways is reflected in the book–he says that one of its major purposes is "to apply its principles to a correct theory of the operation and economy of steam" (Herapath 1847, **1**, xxxix). But for the most part the subjects treated are the same as in his earlier papers: the collisions of hard bodies, investigated initially with a view toward explaining gravity, but primarily in order to develop a theory of gases; the phenomena of heat and their kinetic interpretation; the temperatures of mixtures; the propagation of sound; and the structure of the atmosphere.

The book includes an extensive discussion of diffusion of gases. Herapath claims that he had proved from his theory, before the publication of Graham's experiments,[2] that the time required for a given volume V of gas to pass through a small hole into a vacuum should be proportional to $VG^{\frac{1}{2}}/T$, where G = specific gravity and T = Herapath's "true" temperature. He says he obtained this result in March 1844, at which time he was not aware of any experiments on the subject.

What Herapath calls "The most remarkable fact of prediscovery" reported in his *Mathematical Physics* is the theoretical prediction of the direction of deviations from Mariotte's [Boyle's] law at high pressures. This prediction may be regarded as a direct consequence of the Cartesian viewpoint of Herapath's theory: "Our theory deprives the particles of repulsion or of any active properties, and merely assumes that airs are composed of small particles moving about in all possible directions, and keeping up their state as airs by their mutual collisions and reflexions from one another, and the sides of the containing vessels." (p. xviii) If the particles have finite diameters–*i.e.* if one does *not* assume, as in the usual first approximation, that the space occupied by the particles is negligible compared to the entire volume of the gas–then it follows that the pressure must increase more rapidly than the density (Herapath 1847, **1**, 266–69). When Herapath first obtained this result from his theory in 1844, existing experimental data indicated that gases depart from Boyle's law in the opposite direction. He was at first inclined to attribute the discrepancy to the effects of cohesion of particles in the gas, but then Regnault's experiments on hydrogen[3] have results agreeing with his original prediction. Since hydrogen is the gas "which all philosophers have looked upon to be the most perfect," Herapath considered this one result a striking confirmation of his theory (pp. 276–77).

Regnault's experiments also led to a new value for the "point of absolute cold," *viz.* 491°F below freezing. [Modern value, 491.6°F below freezing.] Of course this result was independent of the kinetic theory, but provided the basis for many of Herapath's calculations. At the point of absolute cold, he asserted, "all corpuscular motion would cease" (p. 249). In view of Regnault's other experiments, Herapath conjectured that many gases could be solidified: "It would be a curious phenomenon certainly, for us to have solid Atmosphere, solid Oxygen, Nitrogen, and c.; but there is nothing improbable in it." (pp. 277–78)

There is a qualitative discussion of heat transfer in fluids, in which Herapath clearly distinguishes the three modes: conduction, convection, and radiation (see our detailed discussion of this distinction in ch. 13). He states that "the natural tendency of heat is to equal diffusion" (p. 186) but draws no profound conclusions about irreversibility from this phenomenon. He says:

> It was long supposed that fluids could conduct heat only by *convection.* Careful experiments have, however, exploded this notion, and it is now generally admitted that all bodies conduct heat in every direction, but that fluids do it very feebly and slowly. . . . Elastic fluids, as air, vapours, and gases of all sorts, are looked upon to be almost non-conductors of heat. We shall, however, be able to show, that they are the quickest and most perfect conductors we have, but their effects are rendered insensible from their extremely small quantity of matter.

Herapath also suggests that the rate of conduction of heat may increase as the temperature increases. But then there is the curious remark: "the time is not yet arrived to explain our theory of heat. . . . Hereafter, probably, the subject may be resumed." Apparently this subject was to be treated in more detail in the projected third volume of *Mathematical Physics*, which never appeared.[4]

Since a reprint of *Mathematical Physics* is now available, it does not seem necessary to give any further account here of its contents. But the reviews (mostly anonymous) which followed its first publication may be of some interest. Herapath reprinted several extracts from reviews and correspondence in his *Railway Journal.*[5] For example, the *Times*, which had previously helped him to air his grievances against the Royal Society, thought highly of the book (August 26, 1847). A reviewer in the Athenaeum, however, objected that "the author assumes for an established truth what amounts scarcely to a plausible hypothesis" namely the assumption that *force* is the cause of everything; "even admitting . . . that motion and heat are convertible into each other – we must ascend to some cause or causes beyond, to which this manifestation of force is due."[6] Herapath replied that "there is no such hypothesis either assumed or implied in any part of the work."[7] The reviewer then quoted Herapath's "intention . . . to connect . . . heat, light, . . . etc. with gravity . . . and to show how they all follow from only two properties of matter, namely, inertia and absolute hardness." He continues: "Not regarding the revival of the Newtonian doctrine of the origin of matter to be as likely a source of error as the hypothesis of the great agencies of material creation being merely manifestations of force – the one being according to our ordinary perceptions, whilst the other is only arrived at by the metaphysical refinements which have run ahead of inductive science, – on that alone did we raise our objections . . . ."[33] It is unfortunate that we do not know the name of this reviewer, for his comments indicate an opinion prevalent in Britain before 1850. He was criticizing not so much Herapath's particular theory (which he did not really understand) as the philosophy of nature associated with the principle of conservation of energy.

Though Herapath had a small group of supporters who occasionally tried to gain public recognition for him in later years, none of them were influential scientists and most of them did not realize what he had actually done.

Notes for §2.5

1. Cf. G. R. Talbot and A. J. Pacey, *Brit. J. Hist. Sci.* **3**, 133 (1966).
2. T. Graham, *Elements of Chemistry* (London, 2nd ed., 1846). For extensive discussion of Graham's work on diffusion and effusion see the series of papers by Mason and his collaborators: E. A. Mason, *Am. J. Phys.* **35**, 434 (1967); E. A. Mason and B. Kronstadt, *J. Chem. Ed.* 44, 740 (1967); *Philos. J.* **7**, 99 (1970); E. A. Mason and P. G. Wright, *Contemp. Phys.* **12**, 179 (1971).
3. H. V. Regnault, *Compt. Rend. Acad. Sci. Paris* **23**, 787 (1846).
4. See the *Railway Magazine* (Quarto series), Oct. 26, 1861, p. 1105 for a note about this.

5. *Railway Journal* **10**, 66, 197, 896 (1848), **11**, 511 (1849).
6. *Athenaeum*, p. 950 (Sept. 11, 1847).
7. *Athenaeum*, p. 983 (Sept. 18, 1847).
8. *Athenaeum*, p. 1006 (Sept. 25, 1847).

2.6 Herapath's reputation after the revival of the kinetic theory

On the flyleaf of his copy of volume 2 of the *Railway Magazine*, Joseph Henry inscribed the following:

> Mr. Herapath the editor of this magazine was very polite and attentive to me while I was in England in 1837. He gave me the number of this work which I have in my library. He was a man of genius, the author of one of the first investigations of the dynamic theory of heat.[1]

Few of Herapath's contemporaries shared this opinion; his only real influence on the course of science was through J. P. Joule, who read his book and used the kinetic theory formula to compute the velocity of a gas molecule.[2]

J. J. Waterston did not mention Herapath in his early writings on kinetic theory, but in his 1858 paper on the theory of sound he gave extensive extracts from Herapath's 1821 paper. While objecting to Herapath's assumption that temperature is proportional to velocity rather than square of velocity, he asserted that, in the light of his own work on the subject, there is "no doubt that Mr. Herapath's idea of the physical constitution of gases approximates closely to the truth." He closed by appealing to other mathematicians to "acknowledge the value of the idea first struck out by Mr. Herapath, and perhaps saved from oblivion by the *Philosophical Magazine* of that period" (Waterston 1858).

Clausius mentioned Herapath in the historical footnote in his 1862 paper on heat conduction, and again at the beginning of his posthumous treatise *Die Kinetische Theorie der Gase* (1891), but seems only to be reporting Joule's reference and gives no indication of having examined Herapath's writings himself.

There is a brief reference to "Herapath's Principia" by William Thomson in a notebook entry dated 6 January 1859, in connection with a discussion of the repulsion and hardness of atoms, but I have not found any public reference to Herapath by Thomson before 1871.[3] Later in 1859, when a notice of the meeting of the British Association appeared in the *Athenaeum*, announcing that Maxwell was to give a paper on the kinetic theory of gases and a calculation of the velocity of sound from the theory, Herapath wrote a letter to the *Athenaeum* calling attention to his own previous work on the subject.[4]

Though he made no public reply to this reminder, Maxwell did show some interest in Herapath's work a few years later. There is a letter from Herapath, presumably to Maxwell, dated 23 February 1864, explaining his theory of collisions of hard bodies in connection with the thermal properties of gases; it is a reply to an inquiry which does not seem to have survived. Maxwell's memoir "On the Dynamical Theory of Gases" (1866) mentions Herapath, saying that

> His theory of the collisions of perfectly hard bodies, such as he supposes the molecules to be, is faulty, inasmuch as it makes the result of impact depend on the absolute motion of the bodies, so that by experiments on such hard bodies (if we could get them) we might determine the absolute direction and velocity of the motion of the earth. This author, however, has applied his theory to the numerical results of experiment in many cases, and his speculations are always ingenious, and throw much real light on the questions treated. In particular, the theory of temperature and pressure in gases and the theory of diffusion are clearly pointed out.

In 1871, when William Thomson asked Maxwell for a summary of the history of kinetic theory, to be included in his Presidential Address to the British Association, Maxwell listed Herapath as one of a line of precursors (Democritus, Lucretius, Daniel Bernoulli, LeSage, Prevost, Herapath, Joule, Krönig) leading up to the real foundation of the modern theory by Clausius.[6] As a result Thomson awarded a bare minimum of credit to Herapath, while attributing to Joule (as does everyone else) the calculation of molecular speed:

> The greatest achievement yet made in molecular theory of the properties of matter is the Kinetic Theory of Gases, shadowed forth by Lucretius, definitely stated by Daniel Bernoulli, largely developed by Herapath, made a reality by Joule, and worked out to its present advanced state by Clausius and Maxwell. Joule, from his dynamical equivalent of heat, and his experiments upon the heat produced by the condensation of gas, was able to estimate the average velocity of the ultimate molecules or atoms composing it. . . .[7]

It appears that Maxwell was the last major physicist who actually bothered to read Herapath's writings and take any interest in what he had to say. The remaining question to be answered is: Did Herapath succeed in becoming immortal? In other words, did he attain the one permanent reward that every scientist must have in view, or at least in the back of his mind: to "go down in history" as the person who made a particular discovery or proposed an accepted theory?

My impression, based on an unsystematic sampling of 20th-century books on physics and on the history of science, mostly in English, is that Herapath's name is part of the "long list" of founders of the kinetic theory but not part of the "short list."[8] An author who makes any reasonable attempt to look up the historical background of the kinetic theory of gases in order to insert a few sentences in his own book will usually come up with the name "Herapath" following Bernoulli and preceding Waterston, Joule, and Krönig, although if he gropes for a first name he may commit the error of confusing John with the slightly less obscure William Herapath (cf. beginning of §2.1 above). On the other hand if less space is available or there is less inclination to look into origins, the author will usually jump immediately from Bernoulli to Clausius and Maxwell; in a few cases the kinetic theory is even said to begin with Maxwell and Boltzmann. In view of the general level of historical knowledge and standards of accuracy in citing predecessors among modern *scientists*, that is not such a bad showing; but *historians* of science might be accused of unfairly neglecting Herapath until the last two decades.

Notes for §2.6

1. I am indebted to Dr. Nathan Reingold, curator of the Joseph Henry Papers at the Smithsonian Institution, for this information.
2. Joule (1848); there is a comprehensive account of Joule's relation to Herapath in the paper by E. Mendoza, *Mem. Proc. Manchester Lit. Phil. Soc.* **105**, no. 2, 1–13 (1962–63).
3. O. Knudsen, *Centaurus* **16**, 41 (1971).
4. J. Herapath, *Athenaeum*, 722 (1860); reprinted in *Railway Magazine* (Quarto series) **22**, 552 (1960).
5. The letter is in the possession of Professor C. Truesdell, who published a facsimile of part of it in his *Essays in the History of Mechanics* (New York: Springer-Verlag, 1968), p. 287.
6. H. T. Bernstein, *Isis* **54**, 206 (1963).
7. W. Thomson, *Rept. Brit. Ass.* **41**, xxxiv (1871); reprinted in his *Popular Lectures and*

Addresses (London: Macmillan, 1894), **II**, 132, and in part in *Victorian Science*, eds. G. Basalla *et al.* (Garden City, N.Y.: Doubleday Anchor, 1970), p. 98.

8. In order to avoid contaminating the survey with possible effects of the observer on the phenomenon under observation, I considered only those books published before my own first article on Herapath appeared [*Ann. Sci.* **13**, 188 (1957)].

CHAPTER 3

Waterston

3.1 Biography

John James Waterston (1811–83) was another British scientist who worked out for himself the elementary kinetic theory and some of its consequences, but did not succeed in obtaining any recognition for his work in his own lifetime. He was born in Edinburgh in 1811.[1] His father was George Waterston, a well-known manufacturer of sealing-wax and other stationery requisites; George's father, William, had originally been a schoolmaster before going into the sealing-wax business. William Waterston married Catherine Sandeman, who was a niece of Robert Sandeman, a prominent religious leader. Robert Sandeman and his father-in-law John Glas were the originators of the religious body known as Glasites or Sandemanians. One of the English Sandemanians was Michael Faraday's father, and Faraday himself remained throughout his life an active member of the Sandemanian Church in London. Catherine Sandeman was also a sister of George Sandeman, founder of the London firm of port wine merchants.

George Waterston was greatly interested in literature, science, and music; his family thus grew up in an atmosphere of culture, and came into contact with young literary men. John James was the sixth of a family of nine; they were educated at the Edinburgh High School, at that time the leading school in Scotland. On leaving the High School, Waterston became a pupil of Messrs Grainger and Miller, civil engineers, but also attended lectures at the university, and there took an active part in the students' Literary Society. He studied mathematics and physics under Sir John Leslie and was medallist of his year in Leslie's class. He also attended lectures on anatomy, chemistry, and surgery.

Like Herapath, Waterston was interested in the problem of explaining gravity without invoking action at a distance. At the age of 19, he published a paper in which he discussed the properties of a system of colliding cylindrical particles, arguing that these could generate a gravitational force. Some of the ideas developed in this paper were later utilized in his kinetic theory, in particular the idea that collisions could result in a transfer of energy from the rectilinear to the rotatory modes of motion.[2] He notes that the work of Young, Oersted, Seebeck, and others have shown that heat, electricity, magnetism, and light are all intimately connected, and that "the actual principles of nature, if we except perhaps gravitation, interfere with each other in such a manner as to lead us to conjecture they may all be particular modifications of one agent." He cites two opinions entertained by philosophers on motion: the first, that "the absolute quantity of motion in the universe is always the same, suffering neither the smallest increase nor diminution" ((Descartes); the second, that "motion is much more apt to be lost than got" (Newton's *Optics*, 30th query) and that therefore "some other principle is necessary for conserving it," to supply the continued loss incurred "by reason of the tenacity of fluids and attrition of their parts, and the weakness of elasticity in solids." The "other principle" could simply be that visible motion is transferred to invisible; thus one may hope "that matter and motion alone will be found sufficient to explain all the phenomena attending the grand cycle of nature's operations, and that the system of unity and simplicity which the advancement of discovery is always bringing further into view, will at length be completely unfolded, and all the physical sciences eventually traced to the varied development of these two principles." The system can be completed by providing a kinetic explanation for gravity. At the end of the paper Waterston cites Oersted's general principle, deduced from his experiments, "that all effects are produced by a fundamental power operating in different forms of action"[3]–a view with which Waterston is in complete agreement.

At the age of 21 Waterston went to London, where he found employment in drawing and surveying work in connection with the rapidly developing railway system in England. He became an associate

Fig. 3.1-1. J. J. Waterston.

of the Institution of Civil Engineers, and contributed a paper to the transactions of that body on a graphical method of estimating the earthwork in embankments and cuttings. Because[4] he wanted to have more time free to pursue his scientific interests, he obtained a post in the Hydrographers Department of the Admiralty. The head of the Department was Captain, afterwards Admiral, Beaufort, F. R. S., who later communicated Waterston's paper on the kinetic theory to the Royal Society. On Beaufort's suggestion, and with his backing, he applied, in 1839, for the post of Naval Instructor to the East India Company's cadets at Bombay. He was successful, and found the position satisfactory in that he had sufficient leisure and access to scientific books and journals at the Grant College, Bombay. He taught the theoretical aspects of such subjects as navigation and gunnery.

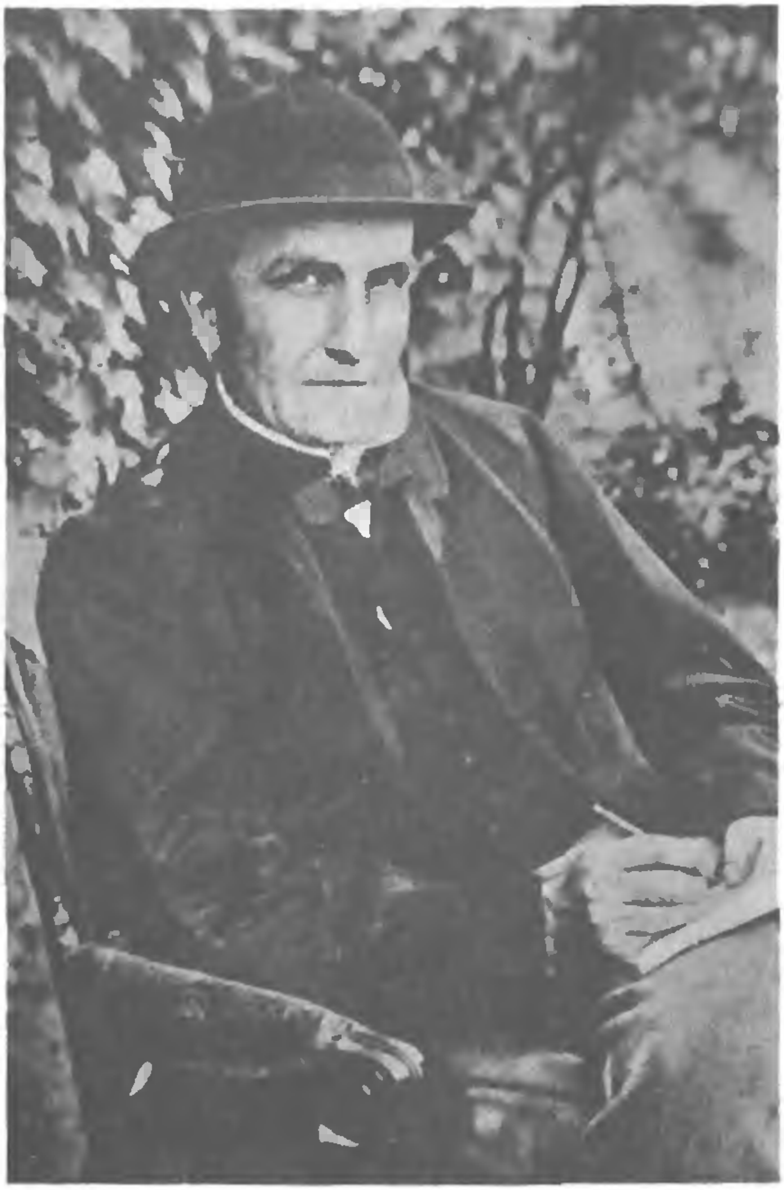

Fig. 3.1-2. J. J. Waterston.

During his stay in India he forwarded home the manuscript of a short book and several scientific papers. The book, an essay on the physiology of the central nervous system, was published anonymously in Edinburgh in 1843. It contains the first expression of Waterston's views on molecules, and on the possible application of molecular theory to biology. He states here some basic principles of the kinetic theory, such as that the pressure of a system of moving particles is proportional to their density and to the square of their velocity. He states that "the proportion of the whole rectilineal to the whole rotatory momentum of the medium is probably constant, and might be found perhaps by calculation." He suggests that increase of temperature in gases might correspond to increase of molecular kinetic energy, and shows that the distance traveled by a molecule, after hitting one and before encountering another, is inversely as the density of the medium and also inversely as the square of the diameter of the molecules. He discusses the constitution of the earth's atmosphere, and mentions that, if the atomic weight of air were as small as that of hydrogen, the earth's attraction could not retain it, and it would evaporate into space, just as the moon's atmosphere has already done.

From his theory Waterston estimated the mean velocity of air molecules at 60° to be 2282 feet per second; the velocity of sound is just half this.

Waterston's remark on the possibility of accounting for all the phenomena of heat, light, electricity, and chemical combination with a single molecular model is not especially original but is worth quoting as an indication of views current at the time:

> Perhaps the most interesting attempt of this kind is that of Mossotti, who derives from the electric theory of Epinus alternations of attractive and repulsive forces which have all the character of molecularity, and leaves a residual attraction that exactly represents gravitation. A medium is supposed to pervade space, consisting of atoms that have an intense mutual repulsion and an intense attraction for the molecules of matter; while these have also a mutual repulsion and a reciprocal attraction to the atoms. It follows, that each molecule will be surrounded with an atmosphere of the medium, condensed toward its centre; and between adjacent molecules there will be a single attraction by means of the reciprocal atmospheres on the molecules, and a double repulsion from the direct mutual action of the molecules themselves, and indirectly from the mutual action of the atmospheres. At small distances the latter forces greatly exceed the former; but there is a point where they mutually balance, and beyond which the attraction preponderates and increases for a short space, and then subsides rapidly.[5]

Though he draws a diagram showing this force law, Waterston is not able to use it in developing his theory, but instead reverts to the model of elastic spherical particles. He does have a fairly concrete idea of the size of his particles: he suggests that "there are one million of molecules in the length of one inch" on the basis of Ehrenberg's microscopic researches.

There is a curious reference to Newton's repulsion theory of gas pressure, possibly designed to convey the impression that the

Newtonian theory is not being rejected:

> Newton's theory makes the law of repulsion to follow the inverse of the distance of the molecules, supposing it not to extend beyond the one adjacent. This is exactly the description of a medium constituted as the preceding; for the expansive force is maintained by the number of collisions in a given time, which varies inversely as the cube of the mutual distance of the molecules, or as the density of the gas.[6]

This is followed by the assertion that, according to experiments, "*the same volume of all simple gases, under the same pressure, require the same absolute quantity of heat to raise them 1° in temperature.*" He can explain this from his kinetic theory by making the hypothesis "that equilibrium of temperature depends on molecules, however different in size, having the same *vis viva*" together with "the chemical theory of volumes." This is the first statement of the "equipartition theorem" of statistical mechanics, though restricted to a special case and apparently contradicted by the statement elsewhere in the same book that different gases will be in thermal equilibrium when the molecular velocities are inversely as the masses.[7] In any case, Waterston also infers from his theory the probable truth of Avogadro's hypothesis (he does not call it that) when he says in the same sentence that the analysis "favours the idea that there are the same number of gaseous atoms in the same volume of all simple gases, and probably of all gases whatever." If one is willing to assume that "the molecules of some of what are esteemed simple bodies are divisible into two or three parts" this hypothesis can be generalized to the statement that there are the same number of *molecules* in the same volumes of all gases, including compounds as well as simple substances. Such a general principle, Waterston suggested, "would certainly introduce great simplicity into the theory of the mechanical and chemical properties of gases."[8]

It should be emphasized that all these results and suggestions were actually published, in a book called *Thoughts on the Mental Functions*, in 1843. There is no evidence that anyone read the book or knew that it proposed a kinetic theory of gases, before Haldane discovered it and had it reprinted in 1928. Even now it is hardly ever referred to.

* * *

While the scientific world can hardly be blamed for failing to notice Waterston's rather rambling and confusing speculations on the theory of gases, buried in an anonymous book with a misleading title, it is quite otherwise with his paper, "On the physics of media that are composed of free and elastic molecules in a state of motion," communicated to the Royal Society in December 1845. The manuscript was first sent to the Reverend Baden Powell, Savilian Professor of Geometry at Oxford; he objected to Waterston's hypothesis though admitting that the paper "exhibits much skill and many remarkable accordances with the general facts as well as numerical values furnished by observation." He did not think it should be published in the *Philosophical Transactions*, but suggested that the final decision should be made by an expert in the field–such as Sir J. Lubbock or Prof. Kelland. The paper was then sent to Lubbock, who said that "the paper is nothing but nonsense, unfit even for reading before the Society."[9] The paper was read in March 1846 (before Lubbock had given his opinion) and an abstract was printed in the *Proceedings* of the Royal Society, but the Society refused to print the paper itself. Waterston was not able to have his paper returned to him.[10] It remained unpublished in the archives of the Royal Society until Rayleigh discovered it in 1891 and had it reprinted with his own comments and corrections. (We postpone a detailed discussion of the paper to the next section.)

During the 1850's, Waterston made several efforts to publicize the kinetic theory and other consequences of the mechanical theory of heat. He circulated a 12-page abstract of his 1845 paper, and presented brief accounts to meetings of the British Association. At the Ipswich meeting in 1851 he spoke at the same section as W. J. M. Rankine, who was at that time advancing his molecular-vortex theory of gases.[11] The result of this coincidence was that Rankine in 1853 published a summary of the hypothesis "proposed by Mr. Herapath and Mr. Waterston," but compared it unfavorably with his own theory. The kinetic theory predicts that the product of pressure × volume of a gas is two-thirds its heat energy, whereas, according to Rankine, this product is actually "only about four-tenths of the equivalent of its total heat." The hypothesis should therefore be modified so as to attribute a larger share of the energy of the gas to rotational motion.[12]

Waterston mentioned the kinetic interpretation of the dynamical theory of heat in a paper "On Dynamical Sequences in Kosmos" presented to the British Association meeting in 1853.[13] It was from this paper that William Thomson first learned the meteoric theory of the sun's heat, according to Thomson's later account.[14] In 1857, Waterston published in the *Philosophical Magazine* a detailed analysis of the Joule–Thomson experiments on the thermal effects of fluids in motion, and challenged Thomson's own interpretation of the results.[15] In a paper in the same journal a year later on the theory of sound, Waterston gave a more extensive discussion of the kinetic theory and mentioned his own unpublished manuscript lying in the Archives of the Royal Society.[16] Yet, despite the fact that Clausius' first paper on kinetic theory had already appeared in the *Philosophical Magazine* and his second was published there in 1859 [Clausius 1857, 1858], Thomson and the other readers of the *Philosophical Magazine* did not bother to look into Waterston's work. In particular it is curious that Maxwell paid no attention to it. Even in 1876, when S. Tolver Preston wrote to Maxwell about Waterston's kinetic theory in connection with its application to the theory of sound propagation, Maxwell seems to have made no response despite his interest in historical antecedents of the kinetic theory.[17] Two brief references to Waterston by Rankine in 1864 and 1869 had no effect either.[18]

The reception of Waterston's work in Germany is of interest in connection with its possible influence on the work of Krönig and Clausius. In a review of various papers on the mechanical theory of heat, published in *Fortschritte der Physik* in 1855, Helmholtz mentioned Waterston's paper "On a general law of density in saturated vapours," published in the *Philosophical Transactions* in 1852, and noted Waterston's reference to his theory of gases, but there is no indication as to where an account of that theory may be found.[19] In the same article, Helmholtz mentioned Joule's paper in which the velocity of hydrogen molecules was calculated by Herapath's method. Krönig was editor of this volume of *Fortschritte* and added a short note at the end of the review about a paper by Goodman, so one would presume that he had at least read the review, though he made no reference to Waterston or Joule in his own paper of 1856. Edward Daub has pointed out the close similarity between Krönig's 1856 theory and the abstract of Waterston's paper published in the *Report* of the British Association meeting of 1851, suggesting that Krönig probably did read about Waterston's work.[20]

The only other reference I have found to Waterston's work on kinetic theory before Rayleigh's famous rediscovery of it is in Max Planck's 1887 monograph on the principle of energy conservation.[21]

In 1857 Waterston resigned his appointment at Bombay, and returned to Scotland; he had apparently saved enough money to be able to devote his time to scientific work. He began to publish papers on the experimental measurement of solar radiation, yielding an estimate of about 13000000 degrees for the sun's temperature[22]; this estimate was frequently quoted in the debate on the sun's temperature in the 1870's (see below, §13.6). He also began some experimental work on liquids, and published a series of papers on physical chemistry, mainly in the *Philosophical Magazine.*

In a paper "On capillarity and its relation to latent heat" (1858) Waterston presented a new estimate of molecular size, based on the assumption that the cohesive force that has to be overcome in evaporating a liquid is the same as that responsible for capillary action; the result was that an inch contains 214778500 molecules.[23]. This estimate was not mentioned by those who attempted to calculate the size of an atom from kinetic theory a few years later, though William Thomson discussed somewhat similar arguments in his 1870 paper.[24]

Apparently Waterston never met any of the scientists who might have recognized the value of his work on the kinetic theory, such as Thomson, Tait, and Maxwell.[25] (Tait especially should have been delighted to find another British kinetic theorist to take the priority away from the Germans, Krönig and Clausius!) His last published paper was dated 1868; this is the same year in which Sir David Brewster, one of the editors of the *Philosophical Magazine*, died, and Haldane suggests that it was only as a result of Brewster's tolerance that he had been permitted to publish there.[26] In 1878 Waterston sent two papers to the Royal Astronomical Society, one entitled "On a solar thermometer to measure the radiant force of sunlight" and the other "On the heat of the stars." Despite the fact that Waterston had gained some reputation for his earlier work in this area, both papers were rejected, and a few months later he resigned from the Society, of which he had been a member since 1852. This event reinforced his isolation from the scientific world.

I conclude with some extracts from a letter about Waterston by his nephew, George Waterston, sent to Lord Rayleigh and reprinted in Rayleigh's biography:[27]

> I have often heard him talk on scientific subjects, but he never mentioned this paper. He talked however in a manner that seemed to me strangely contemptuous of scientific men with but few exceptions. He had not a word of complaint nor did he speak of being neglected or ill-used, but I distinctly remember the Royal Society was characterized in very strong terms useless now to repeat. We have it on record what they thought of his paper. He returned the compliment in no measured terms. He would not attend the meetings of the Royal Society of Edinburgh though

some friends sent him billets, and rather avoided the society of scientific men. He was of a most social, kind disposition, enjoying the society of young people. He never married, and besides his mathematical work he was fond of music, chess, and billiards . . . .

He was man of strong feelings and strong prejudices—especially so in regard to anything that looked like self-seeking in scientific matters.

We could never understand the way in which he talked of the learned societies, but any mention of them generally brought out considerable abuse without any definite reason assigned.

My uncle's disappearance was very remarkable . . . . He was fond of walking out by a new breakwater recently built at Leith, very well exposed to a fine sea breeze, but from its construction very dangerous to foot passengers. At this place the tide runs out very fast, and if he had fallen in he would have been carried out to sea. We know of no place near Edinburgh where he could so easily have disappeared, and no one who knew him thought of suicide as likely in his case.

His friends share your surprise that he should not have put forward more definite claims, but he was of a very retiring disposition. To me he appeared to put forth his papers like some mathematical question for others to tackle, and not being a scientific man I was never sure whether all his contemptuous words of other scientific men were not the fruit of some exaggerated view of the importance of his own work, though he was always so simple and straightforward that I put it down to his not stating his views in a sufficiently practical manner . . . .

The last time I remember him very angry on a scientific subject was in regard to Mr. Crookes and his radiometer, as to which he used some unparliamentary language.

Notes for §3.1

1. We are indebted for biographical information about Waterston mainly to J. S. Haldane, who considered that Waterston's work on the physical chemistry of liquids and on physiological psychology was of such great value as to call for a modern edition of all his publications. See his biographical introduction to *The Collected Scientific Papers of John James Waterston* (Edinburgh: Oliver and Boyd, 1928) and also Haldane, *Gases and Liquids* (Edinburgh: Oliver and Boyd, 1928), ch. I. Despite the considerable effort which Haldane devoted to preparing the *Papers*, he did miss a few of Waterston's shorter publications, including items 14, 22, and 34 in the Royal

Society Catalogue. In addition there are brief reports of Waterston's papers presented at British Association meetings, in *Athenaeum*, p. 776 (1851), p. 980 (1852), p. 1099 (1853). Haldane apparently did not examine the unpublished materials at the Royal Society Archives.

2. J. J. Waterston, *Phil. Mag.* [2] **10**, 170 (1831); *Papers*, p. 531.
3. Waterston's citation of Oersted's "*Identity of Electricity and Chemical Affinity*" is probably based on Oersted's article, "Thermo-electricity" in Brewster's *Edinburgh Encyclopedia* which had just appeared; Waterston began his own paper with a quotation from that article.
4. According to Haldane, in Waterston's *Papers*, p. xxiv.
5. *Papers*, pp. 168–69. On the theory of "Epinus" (*i.e.* Franz Ulrich Theodosius Aepinus, 1724–1802) see J. L. Heilbron, *DSB* **1**, 66 (1970).

   The theory of Ottaviano Fabrizio Mossotti (1791–1863) was published in his book, *Sur les Forces qui regissent la constitution intérieure des corps* (Turin, 1836) and translated into English in Taylor's *Sci. Mem.* **1**, 448 (1837). It was acclaimed as "one of the most remarkable discoveries of the present aera in science" in an unsigned note in *Phil. Mag.* [3] **10**, 320 (1837). (The editors at that time were Brewster, Taylor, and Phillips.) A subsequent paper appeared in *Taylor's Sci. Mem.* **3**, 564 (1843).
6. *Papers*, p. 179.
7. *Papers*, pp. 186, 188. Haldane in his biography of Waterston calls this a "serious error" which he would not have made had he been aware of Graham's experiments on diffusion (*Papers*, pp. xxxiii–xxxiv).
8. *Papers*, pp. 181.
9. I am indebted to Sir Harold Hartley and N. H. Robinson for identifying the referees and sending me copies of their letters preserved in the Royal Society Archives. The complete texts of the letters follow:

Dear Sir,

With reference to the paper on "the Physics of Media and c" submitted to me by the Committee of Physics of the R. Society I beg to report as follows:—

The whole investigation is confessedly founded on a principle entirely hypothetical from which it is the object to deduce a mathematical representation of the phenomena of elastic media.

It exhibits much skill and many remarkable accordances with the general facts as well as numerical values furnished by observation.

In certain cases it is confessed to fail (§26): though in these, by a subsidiary modification (§§27–29) the discrepancies are reconciled.

The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory, *viz.* that the elasticity of a medium is to be measured by supposing its molecules in rapid motion and making a succession of impacts against an elastic gravitating plane.

Upon the whole my opinion is unfavorable to its publication in Philos. Transactions. But I should not feel satisfied without obtaining the opinion of mathematicians whose researches have been specially directed to these subjects–as Sir J. Lubbock or Prof. Kelland.

I remain
Very faithfully yours
B. Powell

To the Secretary of the Committee of Physics, R.S.

9 May 1846

Dear Sir,

I have received a paper, from the clouds for ought I know, but I conjecture that it may have been sent to me by Mr. Weld for a Report.

In my opinion the paper is nothing but nonsense, unfit even for reading before the Society.

I am, dear sir
Yours very sincerely
Lubbock

S. Roget

10. Waterston wrote to the Royal Society on 4 June 1846 requesting the return of his paper as he had kept no complete copy (Royal Society Archives, MC.4.142). Apparently the request was refused.
11. J. J. Waterston, *Brit. Ass. Rept.* **21**, 6 (1851).
12. W. J. M. Rankine, *Trans. R. S. Edinburgh* **20**, 565 (1853); see E. E. Daub, *Isis* **61**, 105 (1970).
13. J. J. Waterston, *Athenaeum*, p. 1099 (1853).
14. W. Thomson, *Popular Lectures and Addresses* **2**, 128; reprinted from *Report of the Glasgow Philosophical Society's Meeting of March 24, 1869.* See also *Popular Lectures* **1**, 364, reprinted from *Macmillan's Magazine*, 1862.
15. Waterston's *Papers*, p. 332.
16. Waterston (1859); see §3.3 for further discussion of this paper. He also cited his Royal Society manuscript in *Phil. Mag.* (1861); see *Papers*, footnote on p. 461.
17. Preston enclosed a copy of Waterston's 1859 paper on sound, and said: "It appears to me a somewhat remarkable fact that Mr. Waterston should already in 1845 (as appears from his paper) have investigated to some extent mathematically the kinetic theory of gases." I am indebted to Dr. C. W. F. Everitt for informing me of this letter which he discovered at Cambridge University. See also Preston's paper on sound (Preston 1877) which discusses Waterston's theory, and indicates that Maxwell has replied to his letter.
18. W. J. M. Rankine, *Proc. Glasgow Phil. Soc.* **5**, 128 (1864); *Trans. R. S. Edinburgh* **25**, 559 (1869).
19. H. von Helmholtz, *Fortschritte der Physik in den Jahren 1850 und 1851* (Berlin, 1855), p. 561.
20. E. E. Daub, *Isis* **62**, 512 (1971).
21. M. Planck, *Das Princip der Erhaltung der Energie* (Leipzig: Teubner, 1887), p. 63, where the abstract in the 1851 British Association *Report* is cited; on p. 65 Planck refers to Waterston's theory of the sun's heat, described in the *Athenaeum* (*op. cit.*, note 11). Planck also mentions Herapath's letter published in the *Athenaeum* in 1860 (*Princip*, 62). It is evident that, despite his own skepticism concerning the molecular interpretation of thermodynamics at this time, Planck was somewhat familiar with the development of this interpretation (cf. §§1.9, 14.8).
22. *Waterston's Papers*, p. 692.
23. *Phil. Mag.* [4] **15**, 1 (1858); *Papers*, p. 407. The estimate is mentioned again in *Papers*, p. 674. For further discussion see J. Satterly, *Phil. Trans. R. S. Canada* **16**, 83 (1922).
24. See §1.8, note 5.
25. In 1860 he wrote to Michael Faraday asking for some information about the temperature scale used in one of Faraday's earlier papers, but did not say much about his own work. *The Selected Correspondence of Michael Faraday*, ed. L. Pearce Williams (London: Cambridge University Press, 1971), **2**, 945–46.

26. Haldane, in Waterston's Papers, p. lxii.
27. R. J. Strutt, *Life of John William Strutt, Third Baron Rayleigh* ((London: Arnold, 1924; reprinted with additions by J. N. Howard, Madison, Wisc.: University of Wisconsin Press, 1968).

3.2 His 1845 paper

The first paragraph of Waterston's 1845 memoir shows that he regards the wave theory of heat (ch. 9) as a direct route to kinetic theory:

> Of the physical theories of heat that have claimed attention since the time of Bacon, that which ascribes its cause to the intense vibrations of the elementary parts of bodies has received a considerable accession of probability from the recent experiments of Forbes and Melloni. It is admitted that these have been the means of demonstrating that the mode of its radiation is identical with that of light in the quantities of refraction and polarization. The evidence that has been accumulated in favour of the undulatory theory of light has thus been made to support with a great portion of its weight a like theory of the phenomena of heat.... The undulatory theory at once leads us to the conclusion that, inasmuch as the temperature of a body is a persistent quality due to the motion of its molecules, its internal constitution must admit of it retaining a vast amount of living force. Indeed, it seems to be almost impossible now to escape from the inference that heat is essentially molecular *vis viva*....

If our assessment of the popularity of the wave theory of heat in the period 1830–45 is accepted (§9.4), it is no longer so easy to explain the suppression of Waterston's kinetic theory by arguing that it was incompatible with current ideas about the nature of heat. On the contrary, Waterston took some pains to show that his theory *was* compatible with current ideas. At the same time he cautiously refrained from asserting that his particular molecular model corresponded to the structure of real gases; he simply proposed to develop the theory of a hypothetical medium "composed of free and perfectly elastic molecules in a state of motion," in order to see if the properties of such a medium bear any resemblance to those of gases.

The 1845 memoir contains a systematic derivation of the results mentioned earlier (§3.1). It is stated quite clearly that "in mixed media the mean-square velocity is inversely proportional to the specific weight of the molecules." Since this conclusion was printed in an abstract of his paper given at a British Association meeting in 1851,[1] he did manage to establish priority for discovery of the equipartition theorem, even though this priority was not generally recognized. His justification for the theorem is of interest in connection with the history of the ergodic hypothesis, and is quoted below in §10.1. He notes that the result is in agreement with Graham's law of diffusion.

The same sentence in the 1851 abstract indicates that Avogadro's hypothesis also follows from the kinetic theory: "Equilibrium of pressure and heat between two gases takes place when the number of atoms in unity of volume is equal, and the *vis viva* of each atom equal." The discussion in the text of the memoir shows that Waterston realized that "molecule" is more appropriate than "atom" in this context, and that he is well aware of the problem of conceiving certain gaseous molecules as being divisible into smaller parts (cf. end of §1.6):

> It seems impossible that the fact of a volume of every gas containing the same number of molecules can ever be inductively established, but all analogy leads us to this conclusion. One volume of oxygen combines with two volumes of hydrogen to form two volumes of aqueous vapour. If we inferred from this that one molecule of oxygen combined with two molecules of hydrogen to form one of steam, we must admit that the molecule of steam occupies double the volume of a molecule of hydrogen or oxygen. If it is admitted, on the other hand, that the oxygen molecule is capable of disintegration, and that half a molecule combines with one of hydrogen to form one of steam, the bulk of the three molecules are equal. This last is the view that is responded to by the hypothetical media. The objection to it is plausible from the natural repugnance to the idea of dividing what has been considered as an ultimate element into parts, and of supposing it possible that an element should have a strong affinity to itself – for this point is also involved. Half molecules of oxygen must have a powerful attraction to each other as they never appear separate. It is the same with all the other simple gases and vapours that combine in half or other fractional volumes.[2]

A consequence of this line of thought is that the same element might be found to occur in the gaseous state with two or more different specific gravities.

Waterston then turned to a rather complicated calculation of the effects of expansion on molecular *vis viva*, leading to the conclusion that

> to effect one increment of expansion in the volume of a medium subsisting under a constant pressure, four-thirds of an increment of *vis viva* are required; one of which thirds is expended in the act and does not appear in the medium: the remaining three-thirds, or one increment, appears in the medium and assists in sustaining its augmented volume.

Thus the ratio of specific heat at constant pressure to that at constant volume should be $\frac{4}{3}$. Unfortunately the result is erroneous because of a numerical slip; or perhaps fortunately, since Waterston's value $\frac{4}{3}$ happened to be in fairly good agreement with experimental data then available for air and other gases,[3] whereas if he had obtained the correct theoretical value $\frac{5}{3}$ he might have been discouraged from developing his theory. In any case it remained for Clausius and Maxwell to discover this discrepancy.

At the end of this section Waterston used the kinetic theory to estimate the mechanical equivalent of heat, and obtained a value of 673 foot-pounds corresponding to 1°F of heat applied to 1 pound of water [modern "Btu"]; he considered this to be in satisfactory agreement with Joule's recent value of 800 foot-pounds.[4]

Later sections of the paper are devoted to applications of the kinetic theory to three special problems: (1) the resistance encountered by a surface moving through a gas; (2) the equilibrium of temperature and density in a vertical column of gas; (3) the propagation of sound. We shall not discuss the first two topics here, except to remark that Waterston's results appear to be erroneous. (We return to the problem of temperature-equilibrium in the atmosphere in §10.6) The third topic is best treated in conjunction with Waterston's later paper on sound.

Some other points of interest in the 1845 paper may be briefly noted. In a note on "Motion Indestructible as Matter," Waterston asks: "Is it not possible to view all forces as inseparable from some form of matter, and all the phenomena of nature, as not consisting of the creation and annihilation of force, but in its transference from one form of matter to the other?" Apparently he still believes that gravity (and other forces) is not "action at a distance" but action transferred by means of a substance. Yet, unlike Herapath, Waterston relegates this suggestion to the end of the paper, perhaps in order not to arouse the opposition of skeptical readers to the kinetic theory of gases which is the main topic. His caution is further justified by the recognition in another note that the supposed existence of an ethereal medium (needed to account for the propagation of light) would seem to be incompatible with the free motion of the molecules of gases through space. Why does the medium not offer any resistance to molecular motion?

Notes for §3.2

1. J. J. Waterston, *B. A. Rep.* **21**, 6 (1851); Waterston's *Papers*, p. 318.
2. *Papers*, pp. 229–30; see also bottom of p. 223.

Waterston mentions two experiments: Clément and Desormes found the result 1.35 for the ratio, and Gay-Lussac and Welter found 1.37. For discussion and references see R. Fox, *The Caloric Theory of Gases* (Oxford: At the Clarendon Press, 1971), p. 170. There is a systematic review of experimental data and theoretical interpretations in the book by J. R. Partington and W. G. Shilling, *The Specific Heats of Gases* (London: Benn, 1924).

On Joule's various values for the mechanical equivalent of heat see Cardwell, *From Watt to Clausius*, pp. 232–36. The modern value is 778 foot-pounds per Btu.

3.3 Theory of sound

Waterston in his 1858 paper on the theory of sound gave an historical survey of earlier theories, as a basis for discussing the question: Can the Newton–Laplace theory of sound propagation be consistent with "modern" ideas of heat? So this is an appropriate place for us to review the history of that subject as a prelude to discussion of Waterston's paper, though in fact it turns out that his own contribution is disappointingly small.[1]

It is well known that Newton attempted a quantitative calculation of the speed of sound in Book II of his *Principia* (1687),[2] arriving at the result that "the velocities of pulses propagated in an elastic fluid are proportional to the square root of the elastic force divided by the density, providing the elastic force of the fluid be supposed proportional to its condensation." Newton appears to have been working with his own version of Boyle's gas model, in which each particle is confined to the neighborhood of an equilibrium position by the repulsive forces of the surrounding particles;[3] it can execute simple harmonic motion around this position, with an elastic restoring force (proportional to displacement) which is the same force responsible for the resistance of the gas as a whole to compression. In other words, the "elastic force" is to be identified with what we now call the pressure of the gas. Thus we can now write Newton's formula for the speed of sound c as

$$c = \sqrt{p/\rho}$$

We might also say that Newton's formula assumes the acoustic motions of gas particles as isothermal, meaning that heat flows whenever necessary to preserve a uniform temperature in the gas despite changes in pressure and density. But we cannot claim that Newton himself assumed this, since he makes no mention of heat or temperature in his connection. In fact, as Truesdell[1] points out, Newton's statements about the variation in the speed of sound in summer and winter do not indicate that he has the modern conception of the relations between sound speed, pressure, density and temperature.

By the time he prepared the second edition of the *Principia* (1713), Newton had learned that the numerical value calculated from the above formula, 979 feet per second, is unmistakably lower than the experimental value, about 1142 feet per second. All he can do to explain the discrepancy is to suggest that solid particles or vapors in the air might speed up the transmission of pulses.

Leonhard Euler, in his first work on sound published in 1727, adopted a physical explanation for propagation essentially the same as Newton's; he stated somewhat more clearly that the speed of sound should increase with temperature though it is independent of pressure and density if the temperature remains constant; he dismissed rather scornfully Newton's explanation for the discrepancy between theoretical and experimental values, but could not do much better himself.[4] In what has been called the "first kinetic theory of gases," published two years later, Euler derived a formula relating pressure to the whirling speed of molecular vortices,

$$p = \tfrac{1}{3}\rho v^2$$

and stated that the whirling speed v should be "except for the numerical coefficient . . . the same . . . as the speed with which sound is carried through air." From experimental data he obtained the result $v = 477$ m/sec = 1590 feet/second.[5] This is the first calculation of molecular speeds, as well as the first indication of a direct connection between the speed of sound and the speed of a molecule, even though the latter is conceived as a rotational rather than a rectilinear speed.

The work of Bernoulli, Lagrange, and Euler during the 18th century established (though without a completely rigorous proof) that various kinds of sound waves, generated by different methods, propagated through different kinds of enclosures, all travel at the same speed in air, as long as the temperature is the same.[6] Moreover, the speed is independent of frequency at least within the range accessible to the ear (and to ordinary experimental apparatus available before 1900), a fact which is quite convenient to those sitting in the back rows of a concert hall. But it was all the more difficult to explain the discrepancy between the theoretical and experimental velocities. The first clue to an explanation was not even followed up by the person who discovered it: Lagrange, in 1760, showed that if the pressure of air is not simply proportional to the density but varies as ρ^m, then one can get the experimental value of the speed of sound by taking $m = \frac{4}{3}$, but he called this only a "fleeting conjecture" and did not suspect its physical significance.[7] It was not until the beginning of the 19th century that Laplace and Poisson suggested that the compressions and rarefactions that occur in a sound wave are adiabatic rather than isothermal, and that the speed of sound can be correctly calculated from a pressure-density relation of the form

$$p = k\rho^\gamma$$

where γ is the ratio of the specific heat at constant pressure to that at constant volume; the speed of sound is then

$$c = \sqrt{\frac{dp}{d\rho}} = \sqrt{\frac{\gamma p}{\rho}}$$

This explanation was quantitatively successful and, despite the fact that it had been developed within the context of the caloric theory of heat, was generally accepted after 1850.[8] (Unfortunately, physics textbooks still give the impression that the reason for using the adiabatic rather than the isothermal relation between pressure and density is that "sound vibrations are so rapid that the temperature inequalities do not have time enough for equalization" whereas, as Condon has pointed out, if one analyzes the effect of heat conduction the opposite situation is present: the vibrations of sound are ordinarily *too slow* for equilibration of energy.[9] At very high frequencies when heat conduction does become important, the isothermal assumption seems to be valid.)

When the early kinetic theorists first attempted to explain sound propagation, they could not accept Laplace's formula because it appeared to depend on a static conception of the nature of gases.

Herapath, who attacked the problem around 1830, arrived at a result similar to that which Euler had obtained a century before (see above); he identified the speed of sound with the average molecular speed in a particular direction, and showed how this speed could be computed from the pressure and density of a gas (§2.4). Aside from some confusion about the numerical constants,[10] Herapath's result was the first correct determination of molecular speeds from the modern kinetic theory of gases; it was subsequently adopted by J. P. Joule, who is usually credited with this accomplishment. As a calculation of the speed of sound it is open to criticism, since it does not take into account the thermal relations of a gas under rapid expansion and contraction. Waterston's first attempt to derive the speed of sound from kinetic theory in 1845 shared this defect; he argued that the speed of sound is equal to the average velocity of the molecules resolved in one direction, and that this is equal to one-half the average speed.[11] He did not realize that the ratio of specific heats (which he had been the first to compute, though incorrectly, from kinetic theory) was involved.

By 1858 the theory of sound propagation was in an embarrassing position. The Laplace–Poisson theory appeared to be physically sound as long as one considered only the macroscopic properties of gases, *i.e.* the concept of adiabatic compression allowed one to infer a correct relation between the ratio of specific heats and the speed of sound. But the theory appeared to depend on a conception of atomic structure and heat that had been completely rejected. On the other hand the kinetic theory was compatible with mid-century notions of atomic structure and heat but had not been as successful in explaining sound propagation as the Laplace–Poisson theory. It was just this anomaly that Waterston pointed out: "the theory of Laplace has in some instances been considered so perfect as to afford the means of deducing the specific heat of air from the velocity of sound, and this by zealous professors of the mechanical theory of heat." In particular, William Thomson seemed to be willing to accept the value $\gamma = 1.410$ on the basis of Laplace's theory, although the observations of Gay-Lussac and Welter and of Clément and Desormes gave significantly lower values (1.37 and 1.35, respectively).[12] "How," asked Waterston, "could Thomson have such confidence in deductions from the *caloric* theory of heat, as late as 1854?"

Waterston gives a detailed examination of the Newtonian theory of sound propagation based on the assumption of a static arrangement of repelling particles. Although he finds it possible to deduce a velocity formula, equivalent to

$$c = \sqrt{(4/3)p/\rho},$$

from this theory–thus in good agreement with experiment–Waterston presents three objections to the theory. First, "it does not take account of the condition of the front of a pulse when the particles from a condition of rest enter into the cycle of motion defined by the theory." (As far as I can see this type of difficulty is generally ignored in almost all theories of wave propagation: one is usually concerned only with the situation after the wave motion has been established.) Second, "The force of repulsion between two adjacent particles required by the theory is extravagantly large." Here Waterston is able to employ his earlier estimate of the spacing between atomic particles, and shows that the repulsive force needed in Newton's theory would have to be great enough to communicate a velocity equal to about 160000 times the velocity of light, acting during one second. Since this is implausible it is hard to accept such a theory.

The third objection to the static theory is that "the other physical properties of gases are not deducible from the hypothesis." This is one of the rare cases in the history of kinetic theory where the new theory is supported by an explicit criticism of the defects of the old theory[13] and is thus worth quoting at length:

> The deductive power of Newton's theory is confessedly limited to Mariotte's law and the velocity of sound. Laplace, by the invention of calorific atmosphere, is allowed to have added to these Dalton's and Gay-Lussac's theory of expansion; but it is a question whether the reciprocal action between heat-atmospheres and molecules, which he expresses by mathematical symbols, can be realised by the mind. . . . granting that Mariotte's law, Dalton and Gay-Lussac's law, and the velocity of sound are represented by the statical hypothesis, we have still Dalton and Graham's law of diffusion and diffusive velocity; Gay-Lussac's law of volumes; Dulong and Petit's law of specific heat, extended to the more simple gaseous bodies by Haycraft and the French physicists; the law of latent heat partially discovered by Gay-Lussac and Welter's experiments; also the diminution of temperature in ascending the atmosphere–all as yet undeduced from any statical theory of elastic fluids. It may be that additions to the mathematical hypotheses of Laplace will be attempted with the view of extending their capacity, as indeed there seems to be no limit to this artificial and barren system of procedure, which is

> as far removed from the simplicity of nature as the hideous epicycles of Ptolemy.

Waterston then turns to the kinetic theory, which he introduces "in a popular way" as follows:

> Suppose we range a number of ivory balls in a straight line upon a billiard table, and strike the first of the row upon the second, the initial velocity will be carried forward from one ball to the next adjacent, and so will make its appearance in the last. . . . These balls, confined to one line, are supposed to be in motion among themselves, so that those adjacent alternately strike against each other in opposite directions; the end ones being reflected from the cushions, and then back again after striking the next adjacent ball, the *vis viva* in one direction being at all times equal to the *vis viva* in the opposite.

One can then explain the propagation of sound by imagining that one cushion is moved forward with a comparatively slow velocity, so that "each time the adjacent ball strikes it, it will be reflected with a velocity greater than that with which it impinged" and the *increment* of velocity is then transferred down the line.

At this point Waterston reveals that "such a theory of elastic fluids was started by Mr. Herapath so far back as 1821" and that he has himself developed it in a paper now lying in the Archives of the Royal Society for 1845–46; and he reminds the readers of *Philosophical Magazine* that the same theory has independently been advanced by Krönig and Clausius.

Waterston then attempts to work out the kinetic theory of adiabatic compression based on his billiard-ball model. But, after such a promising start, he fails to accomplish any more than a heuristic justification of the Laplace formula; instead he turns to a discussion of the decrease in temperature found when ascending in the atmosphere, a phenomenon which he mistakenly thinks can be explained by his kinetic theory as a consequence of gravitational force alone. He concludes the paper with a plea for further investigation of the theory.

Waterston's paper on sound is such a beautiful illustration of the way one would like to think that science advances–the careful working out of consequences of hypotheses and comparison with experiments, judicious weighing of the merits and defects of the old theory before introducing the new one, etc.–and it was published at such a propitious time, just after the first Clausius paper but before Maxwell published his work on kinetic theory–that it is quite a letdown to realize that it had absolutely no effect on the development of the kinetic theory. Even when Tolver Preston called it to Maxwell's attention a few years later, it received no attention.[14] Its only consequence lay in the role it played in the subsequent rediscovery of Waterston's 1845 paper.

Notes for §3.3

1. On the early history of theories of sound propagation see C. Truesdell, *J. Rat. Mech. Anal.* **2**, 643 (1953); Part II of Editor's Introduction to vol. II13 of Euler's *Works* (Zurich: Fussli, 1956); Cherbuliez, *Mittheil. Naturforsch. Ges. Bern* (1870), p. 151, (1871), p. 1. Some remarks on the later developments will be found above in §1.8.
2. I. Newton, *Philosophiae naturalis principia mathematica* (London, 1687). Book II, §VII, props. XLI, XLII, XLIII, XLVII, XLIX; see Cajori's revision of Motte's translation of the third edition, *Sir Isaac Newton's Mathematical Principles of Natural Philosophy* (Berkeley: University of California Press, 1934); the quotation is from Truesdell, *op. cit.*, Editor's Introduction, p. XXII.
3. Newton, *op. cit.*, Book II, §V; see the reprint of the Motte–Cajori translation of this section, together with Boyle's ideas about gas structure, in Brush, *Kinetic Theory* **1**, 43–56.
4. L. Euler, *Dissertatio physica de sono* (Basel, 1727); *Opera Omnia* **III**.1, 182; Truesdell, *op. cit.*, Editor's Introduction, pp. XXIV–XXIX. Cf. R. S. Westfall, *Science* **179**, 751 (1973).
5. L. Euler, *Comm. acad. sci. Petrop.* **2** (1727), 347 (1729); Truesdell, *op. cit.*, p. LXXX; R. Hooykaas, *Arch. Int. Hist. Sci.* **2**, 180 (1948).
6. See works cited in note 1.
7. Lagrange, *Misc. Taur.* **2**, 11 (1760–61), reprinted in his *Oeuvres* **1**, 151. See Truesdell, *op. cit.*, p. LIII.
8. See J. B. Biot, *J. de physique* **55**, 173 (1802); T. S. Kuhn, *Isis* **49**, 132 (1958); B. S. Finn, *Isis* **55**, 7 (1964); J. Challis, *Brit. Assn. Rept.* **6**, 225 (1836); Truesdell, *op. cit.*, p. CIV.
9. See §1.8, note 18.
10. Finn (*op. cit.*, note 8) points out that Herapath introduced a factor $\sqrt{2}$ into his formula, which just happens to be rather close to the correct ratio of specific heats of air; thus he was able to get better agreement with the experimental value of the speed of sound than Laplace did.
11. Rayleigh, in a note added in 1901 to his 1892 introduction to Waterston's paper for the reprint in his own *Scientific Papers* (Cambridge, 1902), vol. **III**, p. 561, said: "It may be noted that Waterston's memoir contains the first calculation of the molecular velocity, and further that it points out the relation of this velocity to the velocity of sound." But he further states that the first publication of such a calculation is that of Joule, ignoring Herapath.
12. Waterston cites Thomson's paper "On the thermal effects of fluids in motion," *Phil. Trans.*, p. 361 (1854).
13. Another example is Gosiewski's review article, *Pamietnik Towarzystwa Nauk*

Scislych w Paryzu 5 (Art. 2) (1874) [English translation, "Various theories of pressure in gases," Lawrence Radiation Laboratory report UCRL-Trans-885(L), 1962].

14. S. Tolver Preston to J. C. Maxwell, 5/12/76, at Cambridge University. Preston enclosed a copy of Waterston's paper, with the comment: "It appears to me a somewhat remarkable fact that Mr. Waterston should already in 1845 (as appears from his paper) have investigated to some extent mathematically the kinetic theory of gases." (This letter was found by C. W. F. Everitt who provided me with a copy.)

3.4 Rayleigh's discovery of Waterston's paper

In 1891 Lord Rayleigh happened to come across Waterston's paper on the connection between molecular forces and the latent heat of evaporation.[1] This led him to the 1858 paper on the theory of sound, in which Waterston referred to his unpublished manuscript lying in the Royal Society Archives. Rayleigh was Secretary of the Royal Society in 1891, and had no difficulty in retrieving this manuscript. He arranged for the paper to be published in the *Philosophical Transactions* for 1892, with his own introductory remarks. Here is Rayleigh's explanation, or rather apology, for the refusal of the Royal Society to publish Waterston's paper when it was originally submitted:

> It is difficult to put oneself in imagination into the position of the reader of 1845, and one can understand that the circumstance of the memoir should have appeared speculative and that its mathematical style should have failed to attract. But it is startling to find a referee expressing the opinion that "the paper is nonsense, unfit even for reading before the Society." Another remarks "that the whole investigation is confessedly founded on a principle entirely hypothetical, from which it is the object to deduce a mathematical representation of the phenomena of elastic media. It exhibits much skill and many remarkable accordances with the general facts, as well as numberical values furnished by observation.... The original principle itself involves an assumption which seems to me very difficult to admit, and by no means a satisfactory basis for a mathematical theory...." The history of this paper suggests that highly speculative investigations, especially by an unknown author, are best brought before the world through some other channel than a scientific society, which naturally hesitates to admit into its printed records matter of

> uncertain value. Perhaps one can go further and say that a young author who believes himself capable of great things would usually do well to secure the favourable recognition of the scientific world by work those scope is limited, and whose value is easily judged, before embarking on greater flights.

These remarks of Lord Rayleigh do not justify the attitude of the Royal Society, but they hint at one of its failures as an organization for advancing scientific knowledge. By refusing to publish work by authors without established reputations, or theories which controvert accepted doctrines, a scientific society shirks one of its most important functions.[2] In the case of the kinetic theory of gases, the net result of the Royal Society's refusal to publish the works of Herapath and Waterston was to retard the progress of molecular physics by a decade or two, thus permitting the Germans Krönig and Clausius to gain the major share of credit as founders of the theory and in the long run damaging the Royal Society's own reputation.[3] Truesdell points out that American scientists have had an advantage over the Europeans in this one respect: they do not take their established scientific societies so seriously as arbiters of the value of new discoveries and theories.[4] But even in Britain it must have been evident by the latter part of the 19th century that most of the important work in physical science was making its first appearance in independent journals like the *Philosophical Magazine*, whereas most of the *Proceedings* and *Philosophical Transactions* of the Royal Society make rather dull reading. The British Association for the Advancement of Science had been founded in 1831 partly in order to break the monopoly of the Royal Society and provide a means for scientists outside the London establishment to communicate their results; and as we have seen, Herapath and Waterston did make some use of this channel to publicize their work though the *B. A. Report* could not publish full accounts of new theoretical developments.

Rayleigh's advice to young scientists is quite sensible, and has indeed been institutionalized in present-day graduate education: a student is expected to turn out a modest piece of conventional research in order to get his Ph.D. and his first publication; afterwards he may set his sights higher. But some of the greatest scientists have refused to fit into the mold, and have shown their brilliance in highly unorthodox initial attempts. As long as scientific societies control a large proportion of the journal literature, they bear a heavy responsibility for ensuring that fruitful new ideas are not suppressed.

Notes for §3.4

1. This is probably Waterston's paper "On Capillarity and its relation to Latent Heat," published in the *Philosophical Magazine* in 1858 (*Papers*, 407); it does not contain any reference to the paper on the theory of sound but may have been bound in the same volume in the set which Rayleigh was using. Rayleigh's Introduction was reprinted (with an additional note) in his *Scientific Papers* (Cambridge, 1902, reprinted by Dover Pubs., New York, 1964), III, 558–61; also in R. B. Lindsay, *Lord Rayleigh, The Man and His Work* (Oxford: Pergamon Press, 1970), pp. 164–68, and in Waterston's *Papers*, p. 206–13.
2. Recall also Humphry Davy's attitude: he was willing to communicate Herapath's experimental investigations to the Royal Society, but blocked the publication of the theory based on them. Even today many scientists would agree that experimental results are solid "facts" which deserve to be recorded in preference to theories, which are likely to be useless unless they dovetail with orthodox ideas or emanate from reputable scientists. In Herapath's case the experiments were wrong but the theory was mostly correct.
3. According to Haldane,

   "It is probable that in the long and honourable history of the Royal Society no mistake more disastrous in its actual consequences for the progress of science and the reputation of British science than the rejection of Waterston's papers was never made. The papers were foundation-stones of a new branch of scientific knowledge, molecular physics, as Waterston called it, or physical chemistry and thermodynamics as it is now called. There is every reason for believing that had the papers been published physical chemistry and thermodynamics would have developed mainly in this country, and along much simpler, more correct, and more intelligible lines than those of their actual development." [Haldane is here referring to Waterston's paper on vapour densities, rejected by the Royal Society, as well as to his paper on the kinetic theory.]

3.5 Later references

As a result of Rayleigh's efforts, Waterston has received some recognition as a founder of the kinetic theory, at least in Britain. Rayleigh emphasized Waterston's priority in stating the equipartition theorem when he wrote on this subject in 1900, and this priority was recognized in the textbooks by Jeans and Loeb which were widely circulated in the 1920's and 1930's.[1] Schuster and Shipley, writing on *Britain's Heritage of Science* in 1917, stated that "Waterston probably furnishes the most conspicuous example of a long-continued neglect of work which would have marked a great advance in knowledge had it been recognized at the time of its maturity."[2]

Like Herapath, Waterston usually makes the "long list" of founders of the kinetic theory but not the "short list" (cf. §2.6). But in more recent years he has edged ahead of his predecessor, since the number of authors who mention Waterston while omitting Herapath[3] is now greater than of those who do the opposite.[4]

Notes for §3.5

1. Rayleigh, *Phil. Mag.* [5] **49**, 98 (1900), reprinted in Rayleigh's *Scientific Papers* (Cambridge University Press, 1899–1920; New York: Dover Pubs., 1964), IV, 433. J. H. Jeans, *The Dynamical Theory of Gases* (Cambridge University Press, 1904, 4th ed., 1925; New York: Dover Pubs., 1954), pp. 12–13, 96. L. B. Loeb, *Kinetic Theory of Gases* (New York: McGraw-Hill, 1927), p. 81.
2. A. Schuster and A. Shipley, *Britain's Heritage of Science* (London: Constable, 1917).
3. W. C. Dampier, *A History of Science and its Relation to Philosophy and Religion* (London: Cambridge University Press, 1929, 4th ed., ed., 1948, rept. 1966), pp. 228–29. H. T. Pledge, *Science since 1500* (London: H.M.S.O., 1939; New York: Harper, 1959), 143. L. W. Taylor, *Physics the Pioneer Science* (Boston: Houghton Mifflin, 1941; New York: Dover Pubs., 1959), p. 213. W. Wilson, *A Hundred Years of Physics* (London: Duckworth, 1950). C. Singer, *A Short History of Scientific Ideas to 1900* (Oxford: Clarendon Press, 1959), p. 423. D. K. C. MacDonald, *Introductory Statistical Mechanics for Physicists* (New York: Wiley, 1963). L. Darmstaedter, *Handbuch zur Geschichte der Naturwissenschaften und der Technik* (Berlin: Springer, 2. Aufl. 1908), p. 565. H. Dingle, ed., *A Century of Science 1851–1951* (New York: Roy Publishers, n.d.), p. 19.
4. A. Klaus, *Über die Entwickelung der kinetischen Gastheorie* (Freiburg i. Br.: Henn, 1904), p. 6. J. T. Merz, *A History of European Thought in the Nineteenth Century* (Edinburgh: Blackwood, 2d ed., 1904–12), 1, 310, 434. D. ter Haar, *Elements of Statistical Mechanics* (New York: Rinehart, 1954), p. 26. H. I. Sharlin, *The Convergent Century* (New York: Abelard-Schuman, 1966). D. S. L. Cardwell, *From Watt to Clausius, the Rise of Thermodynamics in the early Industrial Age* (Ithaca, N.Y.: Cornell University Press, 1971). C. C. Gillispie, *The Edge of Objectivity* (Princeton, N.J.: Princeton University Press, 1960), pp. 480–481. H. Buckley, *A Short History of Physics* (New York: D. Van Nostrand Co., 1927), p. 153.

CHAPTER 4

Clausius

4.1 Joule's revival of Herapath's theory[1]

The scientists we discussed in the previous chapters, Herapath and Waterston, were more or less isolated workers and did not have any followers. We now come to the period when the kinetic theory became respectable and was intensively developed by several scientists, who read and criticized each other's work, so that we can no longer consider the work of a single one of them separately. Thus, although as the title of this chapter indicates, this period was at first dominated by the work of Clausius, we shall also consider the contributions of Joule and Krönig; on the other hand, detailed discussion of some of the later papers of Clausius will be postponed to Part C of the book.

It was the overthrow of the caloric theory, and its replacement by the wave or mechanical theory of heat, that created a situation favorable to the development of the kinetic theory of gases. It became widely accepted, during the period 1840–55, that heat is not an indestructible fluid but merely a particular form of energy which can be transformed into mechanical or electrical energy.[2] Consequently it was natural that the old idea, that heat is itself nothing but the motion of the component parts of a body, should be revived; and it was not surprising that two of the leaders in the thermodynamic revolution, the experimentalist Joule and the theoretician Clausius, should independently propose a kinetic theory.[3] However, some of their colleagues were not willing to accept the particular type of atomic motion implied by the kinetic theory, which in its earlier stages identified heat mainly with the *vis viva* or kinetic energy of translatory motion of elastic spheres. Rankine and Thomson preferred the vortex theory of the atom, which gave more importance to rotational motion, although it was not necessarily incompatible with the kinetic theory (see §5.4).

In 1847, when Joule gave his famous lecture "On Matter, Living Force, and Heat" in Manchester, he too seemed to be thinking primarily of rotation in his description of molecular motion.[4] On the basis of his experiments during the preceding five years on the equivalence of heat and mechanical work, he concluded that "the hypothesis of heat being a substance must fall to the ground" and that heat must either be the kinetic energy of molecular motion, or [what we would call the potential energy of] intermolecular attraction. He suggested that both possibilities are actually realized in nature, the latter one being the basis of the "latent heat" associated with phase changes.

The following year, after the publication of Herapath's *Mathematical Physics*, Joule was ready to accept the kinetic theory of gases based on linear motion.[5] While mentioning the hypothesis of rotatory motion of particles, which he attributed to Davy,[6] he thought that Herapath's theory was simpler. Without bothering to give any further justification of his assumptions he plunged immediately into the calculation:

> Let us suppose an envelope of the size and shape of a cubic foot to be filled with hydrogen gas, which, at 60° temperature and 30 inches barometrical pressure, will weigh 36.927 grs. Further, let us suppose the above quantity to be divided into three equal and indefinitely small elastic particles, each weighing 12.309 grs.; and further, that each of these particles vibrates between opposite sides of the cube, and maintains a uniform velocity except at the instant of impact; it is required to find the velocity at which each particle must move so as to produce the atmospherical pressure of 14831712 grs. on each of the square sides of the cube. In the first place, it is known that if a body moving with the velocity of $32\frac{1}{6}$ feet per second be opposed, during one second, by a pressure equal to its weight, its motion will be stopped, and that if the pressure be continued one second longer, the particle will acquire the velocity of $32\frac{1}{6}$ feet per second in the contrary direction. At this velocity there will be $32\frac{1}{6}$ collisions of a particle of 12.309 grs.

> against each side of the cubical vessel in every two seconds of time; and the pressure occasioned thereby will be $12.309 \times 32\frac{1}{6} = 395.938$ grs. Therefore, since it is manifest that the pressure will be proportional to the square of the velocity of the particles, we shall have for the velocity of the particles requisite to produce the pressure of 14831712 grs. on each side of the cubical vessel,
>
> $$v = \sqrt{\left(\frac{14831712}{395.938}\right)32\tfrac{1}{6}} = 6225 \text{ feet per second}$$
>
> The above velocity will be found equal to produce the atmospheric pressure, whether the particles strike each other before they arrive at the same sides of the cubical vessel, whether they strike the sides obliquely, and thirdly, into whatever number of particles the 36.927 grs. of hydrogen are divided.
>
> If only one-half the weight of hydrogen, or 18.4635 grs., be enclosed in the cubical vessel, and the velocity of the particles be as before, 6225 feet per second, the pressure will manifestly be only one-half of what it was previously, which shows that the law of Boyle and Mariotte flows naturally from the hypothesis.
>
> The velocity above named is that of hydrogen at the temperature of 60°; but we know that the pressure of an elastic fluid at 60° is to that at 32° as 519 is to 491. Therefore the velocity of the particles at 60° will be to that at 32° as $\sqrt{519}:\sqrt{491}$, which shows that the velocity at the freezing temperature of water is 6055 feet per second.[7]

Joule also attempted to derive the specific heat at constant volume by the following argument:

> . . . the absolute heat of the gas, or, in other words, its capacity, will be represented by the whole amount of *vis viva* at a given temperature. The specific heat may therefore be determined in the following simple manner:–
>
> The velocity of the particles of hydrogen, at the temperature of 60°, has been stated to be 6225 feet per second, a velocity equivalent to a fall from the perpendicular height of 602342 feet. The velocity at 61° will be $6225\sqrt{(520/519)} = 6230.93$ feet per second, which is equivalent to a fall of 603502 feet. The difference between the above falls is 1160 feet, which is therefore the space through which 1 pound of pressure must operate upon each pound of hydrogen, in order to elevate its temperature one degree. But

> our mechanical equivalent of heat shows that 770 feet is the altitude representing the force required to raise the temperature of water one degree; consequently the specific heat of hydrogen will be 1160/770 = 1.506, calling that of water unity.
>
> The specific heats of the gases will be easily deduced from that of hydrogen; for the whole *vis viva* and capacity of equal bulks of various gases will be equal to one another; and the velocity of the particles will be inversely as the square root of the specific gravity. Hence the specific heat will be inversely proportional to the specific gravity, a law which has been arrived at experimentally by De la Rive and Marcet.[8]

Joule later realized that this argument is not quite correct, and added the following note in 1851:

> If we assume that the particles of a gas are resisted uniformly until their motion is stopped, and that then their motion is renewed in the opposite direction, by the continued operation of the same cause, as in the projection upwards and subsequent fall of a heavy body; the maximum velocity of the particles will be to the uniform velocity required by the theory assumed in the text, as the square root of two is to one....[9]

This correction multiplies the calculated specific heats by a factor of two, giving much better agreement with experiment. In the following table we give, first the experimental specific heat quoted by Joule (taken from those of Delaroche and Bérard, reduced to constant volume), second, the values now accepted, and third, Joule's corrected theoretical values.[10]

Table 4.1-1. Specific heat at constant volume (cal/gr.)

Gas	Experimental (1848)	(modern)	Theoretical
Hydrogen	2.352	2.402	3.012
Oxygen	0.168	0.1554	0.188
Nitrogen	0.195	0.1765	0.214
Carbonic oxide	0.158	0.1525	0.136

Joule mentioned that other experimenters disagreed with the results of Delaroche and Bérard, and he proposed to wait until Regnault's results were published before deciding on the validity of the theory. He never published any other papers on the kinetic theory, presumably because later experiments failed to confirm his predictions, or perhaps because the later development of the theory by Clausius and Maxwell involved mathematical methods which were too difficult for him to follow.

Aside from the general encouragement given to the kinetic theory by the establishment of energy conservation, Joule's experiments with William Thomson on the free expansion of gases were sometimes cited as evidence that long-range intermolecular forces in gases are *not* repulsive (as the Boyle–Newton and caloric theories require) but, if anything, slightly attractive. This result was taken as support for the kinetic explanation of gas pressure.[11]

Notes for §4.1

1. This and the following three sections are reprinted with minor changes from my article in *Ann. Sci.* **14**, 185 (1958).
2. Brush, *Kinetic Theory* 1, 19–22 and works by Mayer and Helmholtz reprinted there. G. Sarton, *Isis* **13**, 18 (1929). A. E. Haas, *Die Entwicklungsgeschichte des Satzes von der Erhaltung der Kraft* (Wien: Hölder, 1909). M. Planck, *Das Prinzip der Erhaltung der Energie* (Leipzig, 1887). T. S. Kuhn, in *Critical Problems in the History of Science,* ed. M. Clagett (Madison: University of Wisconsin Press, 1959), p. 321. D. W. Theobald, *The Concept of Energy* (London: Spon, 1966), D. S. L. Cardwell, *From Watt to Clausius, The Rise of Thermodynamics in the early Industrial Age* (Ithaca: Cornell University Press, 1971). Y. Elkana, *Arch. Int. Hist. Sci.* **23**, 31 (1970). B. Hell, *Robert Mayer und das Gesetz von der Erhaltung der Energie* (Stuttgart: Frommans Klassiker der Philosophie, 1925). H. Timerding, *Robert Mayer und die Entdeckung des Energiegesetzes* (Leipzig: F. Deuticke, 1925). B. G. Kuznetsov and U. I. Frankfurt, *Tr. Inst. Ist. Est. Tekh.* **28**, 339 (1959). P. F. Dahl, *Ludvig Colding and the Conservation of Energy Principle* (New York: Johnson Reprint Corp., 1972).
3. In an Appendix added 20 February 1844 to a paper on electrolysis, Joule stated that in January 1843 he was "as strongly attached to the theory which regards heat as motion among the particles of matter as I am now." See Joule's *Scientific Papers* (London: Dawsons, 1963 reprint of 1887 ed.), **1**, 121 [cited by Y. Elkana, *Arch. Int. Hist. Sci.* **23**, 46]. Later, Joule attributed the theory to Herapath (see *Phil. Mag.* [4] **14**, 214 (1857); in his account of the origins of Joule's ideas on molecular motion, E. Mendoza notes that "the lavish phrases in Herapath's book for the experiments on the adiabatic compression of gases were almost the first nice things that Joule had ever had said about his work." *Manchester Mem.* **105** (2), 1 (1962–63). Clausius said that he had conceived the idea himself but did not publish it until after Krönig's paper had appeared (see *Ann. Phys.* [2] **100**, 353 (1857); *Phil. Mag.* [4] **14**, 108 (1857).
4. J. P. Joule, *Manchester Courier* (5 and 12 May, 1847), reprinted in Brush, *Kinetic Theory* 1, 78. Mendoza (*op. cit.*) has reproduced some diagrams from an earlier draft of this lecture and discusses the problems Joule might have encountered in trying to carry through the rotational theory.

5. J. P. Joule, paper read to a meeting of the Manchester Literary and Philosophical Society, 3 October 1848, and published in its *Memoirs*, November 1851; see also Joule's *Papers*, p. 290. It was reprinted in *Phil. Mag.* [4] **14**, 211 (1857), after Clausius complained that he had not been able to obtain a copy of this paper, and said "It is to be regretted that Joule did not publish his memoir in a more widely circulated periodical" (Clausius, *Ann. Phys.* [2] **100**, 353 (1857); *Phil. Mag.* [4] **14**, 108 (1857). Joule retorted that the *Memoirs* "are at present regularly forwarded to the principal scientific societies of Europe and America." While a German might feel that he should not be expected to search the publications of "literary and philosophical societies" for possible important contributions to physical science, it should be recalled that Dalton's papers on atomic theory had appeared in the same *Manchester Memoirs* a half-century earlier.
6. Davy, *Elements of Chemical Philosophy* (London, 1812), p. 95.
7. J. P. Joule, *Phil. Mag.* [4] **14**, 214 (1857); *Papers*, p. 294.
8. *Ibid.*, p. 215; *Papers*, p. 296.
9. *Ibid.*, p. 216; *Papers*, p. 297.
10. Joule's values were given for the ratio of the specific heat of the gas to that of water, and he did not consider the variation of the specific heat with temperature. The "modern values" have been taken from *Lange's Handbook of Chemistry*, ed. J. A. Dean (New York: McGraw-Hill, 11th ed., 1973), pp. 9-117–19, and are for 15°C, at which temperature the specific heat of water is 1.00040.
11. J. P. Joule and W. Thomson, *Phil. Trans.* **144**, 321 (1854), **152**, 579 (1862). For discussion and further references see J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949), **1**, 615–21.

4.2 Krönig's 1856 paper

August Karl Krönig (1822–79) is usually credited with reviving the kinetic theory after 1850 and stimulating the further developments of Clausius and Maxwell. His short paper, published in 1856, seems to have had an influence very much out of proportion to its actual substance.[1] This may perhaps be accounted for by the fact that Krönig was a fairly well-known scientist in Germany at the time; he was a Professor at the Realschule (technical high school) in Berlin, and was editor of *Fortschritte der Physik*, the annual survey of progress in physics, for several years. He was presumably influential in the Physikalische Gesellschaft of Berlin. Besides his paper on the kinetic theory in Poggendorff's *Annalen*, and a paper read at a meeting of the Gesellschaft in 1858 on gas diffusion, he wrote several papers on other subjects (mainly chemistry). He wrote a book on chemistry which was published in 1864.[2]

The paper itself represented no real advance over the work of Herapath and Joule though it seemed to be independent of them.[3] Its favorable reception was due primarily to the fact that the mechanical theory of heat had been experimentally established,[4] and also to the fact that Krönig was important enough for other scientists to pay attention to him. Even then it is doubtful whether anything would have come of his suggestions if Clausius, who had already conceived similar ideas but had not published them, had not developed them much further.

Krönig deduced the ideal-gas law from the simplest assumption of perfectly elastic spheres moving parallel to three perpendicular axes with a common velocity c. He set the pressure contributed by one molecule equal to mca, where a is the number of collisions per unit time, forgetting that the momentum of a molecule is reversed when it meets the wall, so the change of momentum is really $2mc$. From the context, it appears that this error is not merely a misprint. Immediately afterwards it becomes clear that Krönig is not interested in such trivial matters as factors of two, and he gives the final formula as $p = nmc^2/v$, having dropped another factor of one-third ("we . . . neglect the constant factors"); v is the volume of the system and n the number of molecules.

He then showed that his formula was equivalent to the laws of Mariotte and Gay-Lussac, assuming that the temperature measured from absolute zero was set equal to mc^2. Then he discussed the effect of gravity on the gas, and began by proving that the pressure of a gas molecule against the earth is $\frac{1}{2}mg$, where g is the acceleration of gravity. (One might have thought that this result, implying that the pressure of a gas is only one-half its weight, would have led him to discover the original error which introduced this spurious factor of one-half.) He showed that there should be a difference of pressure between the top and bottom of a container, which would be independent of temperature. He also gave a rather elementary discussion of molecular velocities and specific heats of gases, but did not make any calculations or comparisons with experiment except to note that light gases such as hydrogen would be expected to diffuse more rapidly than heavier gases such as oxygen. He explained that if a gas is allowed to expand into a vacuum there should be no change in temperature, but if it expands by pushing back a piston it will be cooled, while if it is compressed it will be warmed. No experiments on this point are mentioned.

For a chemist Krönig seemed remarkably uninterested in the consequences of his theory for such controversial problems as Avogadro's hypothesis and the number of atoms in gaseous molecules.

Here again he was to receive undeserved credit for the applications later made by Clausius to such questions.

Krönig's paper is sometimes regarded as the beginning of the "modern" kinetic theory. This is true only in the sense that it was the first such paper written after the first law of thermodynamics had been established (aside from Joule's paper, which was not widely read). On the other hand, it might more properly be regarded as the last example of a primitive phase of the theory, in which one could derive the ideal-gas law and identify absolute temperature with the *vis viva* of translatory motion of the molecules, but not much more. The theory provided a qualitative explanation for the results of Graham's experiments on diffusion, but its quantitative predictions of specific heats were not very successful (see Joule's paper, for example). Further progress depended on introducing definite assumptions about the nature of the molecules themselves, to replace the original assumption of infinitesimally small elastic spheres; it was also necessary to consider the statistical distribution of molecular velocities. From this point of view, Clausius and Maxwell were the real founders of the theory.

Notes for §4.2

1. A. K. Krönig, *Ann. Phys.* [2] **99**, 315 (1856). A generally favorable review in *Arch. Sci. Phys.* **33**, 137 (1856) concluded with the remark: "Cette theorie, comme on le voit, rend très-simplement compte de toutes les lois des gaz; mais il reste la grande difficulté de la relier à une theorie de la constitution des liquides et des solides: c'est là toujours le point difficile des différentes hypothèses que l'on a proposées dans la théorie mécanique de la chaleur."
2. See the biographical notice at the end of G. Ronge's survey of the history of kinetic theory [*Gesnerus* **18**, 45 (1961)] and E. Daub's article in the *DSB*. A summary of the chemistry textbook may be found in *Literarische Centralblatt für Deutschland* (Leipzig: Avenarius, 1864), p. 750.
3. E. E. Daub has argued that Krönig's paper is too similar to the abstract of Waterston's paper published in the *Fortschritte der Physik* to be considered completely original. *Isis* **62**, 512 (1971).
4. The first sentence of Krönig's paper is: "Die mechanische Wärmetheorie behauptet, dass die Wärme eines Körpers in nichts anderem besteht als in einer Bewegung seiner kleinsten Theile."

4.3 Clausius and the elementary kinetic theory

As the title of this book suggests, it was Rudolf Clausius (1822–88) who in his paper "Ueber die Art der Bewegung, welche wir Wärme nennen" (1857) defined the scope and viewpoint of most 19th-century work in the kinetic theory of gases. By 1857 it was no longer necessary to waste time proving that heat *is* motion (though that statement was to be challenged on a few occasions later in the century); the task of kinetic theory was to develop a particular hypothesis about the nature of this motion. Clausius, having been the first to formulate the equations of the mechanical theory of heat, now known as "thermodynamics," certainly had as much right as anyone to take for granted the general proposition that heat is *some* form of mechanical energy.[1]

Clausius' earliest publications, starting in 1847, were on topics in atmospheric physics: the theory of the reflection and refraction of sunlight by particles in the atmosphere. In some of this work he developed arguments and equations similar to those used later in his theory of the "mean free path" of gas molecules.[2] Two of these early papers were honored by selection for publication in Taylor's *Scientific Memoirs*, a collection of English translations of important foreign articles.[3]

Throughout his career Clausius profited from the wide dissemination of his works by translations: out of the first 105 articles listed in the *Royal Society Catalogue*, 41 were published in English translation shortly after their original publication in German, and three others were originally in English.[4] Both editions of his *Abhandlungen über die mechanische Wärmetheorie* (but not including the third volume on kinetic theory) appeared in English translation.[5] Much of the credit for this translating activity goes to John Tyndall, who first met Clausius when they were both working at the laboratory of Gustav Magnus in Berlin in 1851.

A paper on the theory of the elasticity of solids (1849) includes some brief remarks about free and bound heat which, according to Daub, "may mark the beginning of the line of thought which led to his rejection, in 1850, of the caloric theory in favor of the new principle of the equivalence of work and heat."[6] At least the paper indicates that he has been reading some of Victor Regnault's experimental papers. Of more direct relevance to his work in kinetic theory is his preference for replacing the real system of molecules in the solid by a "normal system" in which all quantities have their average values. The same trait is exhibited in the papers on the reflection of sunlight, in remarks

Fig. 4.3-1. Rudolf Clausius (1822–88). [Photo: Deutsches Museum, München.]

such as: "To simplify the investigation, let us for the present assume, not that the *average* number [of spheres of water] crossed by every ray is one, but that every ray cuts one sphere *exactly*."[7] While recognizing that molecular quantities must be conceived in principle as having irregular or fluctuating instantaneous values, Clausius always wants to simplify the calculation by replacing such values by averages whenever he can. Maxwell, on the contrary, likes to think in terms of statistical distributions, and some of his most interesting results such as the "Maxwell demon" critique of the Second Law depend explicitly on the existence of *deviations* from average values.

The difference between the approaches of Clausius and Maxwell was succinctly characterized by J. Willard Gibbs: "In reading Clausius, we seem to be reading mechanics; in reading Maxwell, and in much of Boltzmann's most valuable work, we seem rather to be reading in the theory of probabilities."[8] Another comparison might follow the one made recently between the Belgian statistician Adolphe Quetelet and the English statistician Francis Galton, both of whom applied the exponential distribution formula to a number of social and biological problems: for Quetelet it was a *law of errors*, since he was primarily interested in the *average man* and deviations from the average were of little real significance; whereas for Galton it was a *normal* law, since he was primarily interested in *individual differences* and in great deviations from the average, such as the genius.[9]

There are indications as soon as 1850, at the beginning of his memoir on thermodynamics, that Clausius assumes one can go beyond the mere *equivalence* of heat and work to a concrete representation of heat as a form of molecular motion. After mentioning the experiments of Joule on the production of heat by mechanical means he writes, rather mysteriously, "other facts have lately become known which support the view, that heat is not a substance, but consists in a motion of the least parts of bodies. If this view is correct, it is admissible to apply to heat the general mechanical principle that a motion may be transformed into work, and in such a manner that the loss of *vis viva* is proportional to the work accomplished."[10] Later in the same paper he argues that because permanent gases obey the laws of Mariotte and Gay-Lussac relating pressure, volume, and temperature, "we are naturally led to take the view that the mutual attraction of the particles, which acts within solid and liquid bodies, no longer acts in gases."[11] Here and elsewhere in his development of thermodynamic equations Clausius assumes that the heat added to a gas does no *internal* work because the effect of intermolecular forces is negligible.[12]

In 1852, following a discussion of the mechanical equivalent of electrical discharges, Clausius stated:

> To these propositions, which indeed are those of ordinary mechanics, but which it was necessary to premise here, let us now add, *that heat consists in a motion of the ultimate particles of bodies and is the measure of the vis viva of this motion.*[13]

But there were still numerous theoretical and practical problems to be resolved in the new science of thermodynamics, and Clausius postponed the detailed development of his ideas on molecular motion for a few more years.

As a result of his appointment as professor of physics at the new Eidgenössische Polytechnikum in Zurich in 1855, Clausius moved to a country which had been the homeland of several earlier writers on kinetic theory and related speculations: Leonhard Euler, Daniel Bernoulli, George-Louis LeSage, and Jean André Deluc. At the same time Switzerland was close enough to other European scientific centers so that there was no difficulty in keeping up with the latest discoveries and theories.

The publication of Krönig's paper in 1856 provided the occasion for Clausius to write up his own views on kinetic theory; the thorough and extensive treatment of the subject in Clausius' 1857 paper makes it quite plausible that he had in fact done most of the work before seeing Krönig's paper.[14] At about the same time as he was completing his technical exposition for the *Annalen der Physik*, Clausius gave a public lecture in Zürich on the nature of heat compared with light and sound.[15] The published text of this lecture gives a somewhat different view of the arguments for the kinetic theory, and shows that Clausius was aware of the relations between gas theory and other areas of physics. In particular it suggests that he could see the wave theory of heat as a possible route to the mechanical theory even though he does not seem to have followed that path himself. He gives an elementary yet perceptive discussion of the analogies between sound and light, noting that the wave theory of light was developed on the basis of these analogies; and he takes care to note that solid objects can be set into audible vibration by absorbing waves transmitted through the air. Then he discusses the experiments of Melloni and others on radiant heat, and the evidence for the view that radiant heat is not qualitatively different from light and therefore must be likewise conceived as a form of ether vibration. Since radiant heat can be absorbed by matter, making it warmer, it is natural to suppose that the temperature of matter is a measure of the molecular motions that can be excited by ether vibrations in the same way that audible vibrations of solids can be excited by the acoustic vibrations of air. On the other hand if heat were a substance it is very hard to understand how it could be created by the absorption of ether vibrations.

In his *Annalen* paper Clausius made no attempt to justify his assumption that heat is molecular motion but proceeded immediately to describe the kind of motion he had in mind. His first point was that real molecules must have more complicated motions that Krönig had assumed:

> Krönig assumes that the molecules of a gas do not oscillate about definite positions of equilibrium, but that they move with constant velocity in straight lines until they strike against other molecules, or against some surface which is to them impermeable. I share this view completely, and I also believe that the expansive force of the gas arises from this motion. On the other hand, I am of the opinion that this is not the only motion present.
>
> In the first place, the hypothesis of a rotatory as well as a progressive motion of the molecules at once suggests itself; for at every impact of two bodies, unless the same happens to be central and rectilineal, a rotatory as well as a translatory motion ensues.
>
> I am also of opinion that vibrations take place within the several masses in a state of progressive motion. Such vibrations are conceivable in several ways. Even if we limit ourselves to the consideration of the atomic masses solely, and regard these as absolutely rigid, it is still possible that a molecule, which consists of several atoms, may not also constitute an absolutely rigid mass, but that within it the several atoms are to a certain extent moveable, and thus capable of oscillating with respect to each other.

While Clausius could not provide a direct theoretical calculation of the amount of energy contained in these molecular vibrations and rotations, he argued that an equilibrium must be established, as a result of collisions among the molecules, so that eventually a fixed proportion of the total energy will be found in rotation and vibration, and the remainder in the translatory motion of the molecules as a whole.

Since the pressure depends only on the translational motion according to the kinetic theory, it might be thought that introducing other kinds of motion which contribute to the thermal energy but not to the pressure would destroy the simple relation between pressure, volume, and temperature embodied in the ideal gas law. In the theory as developed by Clausius, the *temperature* is first assumed proportional to the *translational* kinetic energy of the molecules, so that the equation of state is independent of the existence of other kinds of motion; but the total energy is also proportional to the temperature because of the conclusion that fixed fractions are always in the form of rotation and vibration. Thus the specific heat of the gas is independent of temperature.

Those conclusions, according to Clausius, hold only for "permanent gases" which obey the laws of Mariotte and Gay-Lussac. From the viewpoint of the theory this amounts to specifying the following conditions:

(1) The space actually filled by the molecules of the gas must be infinitesimal in comparison to the whole space occupied by the gas itself.
(2) The duration of an impact, that is to say, the time required to produce the actually occurring change in the motion of a molecule when it strikes another molecule or a fixed surface, must be infinitesimal in comparison to the interval of time between two successive collisions.
(3) The influence of the molecular forces must be infinitesimal. Two conditions are here involved. In the first place, it is requisite that the force with which all the molecules at their mean distance attract each other, vanish when compared with the expansive force due to the motion. But the molecules are not always at their mean distances asunder; on the contrary, during their motion a molecule is often brought into close proximity to another, or to a fixed surface consisting of active molecules, and in such moments the molecular forces will of course commence their activity. The second condition requires, therefore, that those parts of the path described by a molecule under the influence of the molecular forces, when the latter are capable of altering appreciably the direction or velocity of the molecule's motion, should vanish when compared with those parts of its path with respect to which the influence of those forces may be regarded as zero.

While his mathematical deductions applied only to the ideal gas model as defined above, Clausius also suggested a qualitative explanation for the mechanism and thermal aspects of changes of state, based on the idea that molecules in solids and liquids are held together by their mutual forces. In solids each molecule vibrates or rotates around a fixed equilibrium position, while in liquids there are no longer any equilibrium positions but the translational motions do not carry the molecules far enough apart to allow them to escape the influence of their forces. *Evaporation* of a liquid can be explained by assuming that even though the average motion of a molecule cannot overcome these attractive forces, "we must assume that the velocities of the several molecules deviate within wide limits on both side of the average value" and therefore a few molecules will be moving fast enough to escape from a liquid surface, even at temperatures below the boiling point. (This is one of the rare occasions when Clausius invoked *deviations* from an average to explain a physical process.)

The fact that a definite amount of heat must be supplied to change a solid to a liquid, or a liquid to a gas, without changing the temperature, the so-called "latent heat" of changes of state, could be explained by the need to supply energy so that the forces holding the molecules together could be overcome.

Turning to the comparison of different gases, Clausius noted that since the pressure is proportional to the product of the number of atoms and the kinetic energy of translational motion, equipartition of the latter follows from the hypothesis that "equal volumes contain the same number of atoms–a hypothesis which for other reasons [not specified] is very probable." In the case of compound gases the hypothesis is valid only for the number of *molecules* even though the molecules may contain different numbers of atoms. In order to explain all the data on combining volumes, Clausius proposes (as if it were a new idea) that also in simple gases there are two or more atoms in a molecule. Verdet and Marignac pointed out that similar suggestions had been made earlier by chemists such as Dumas, Gerhardt, and Laurent.[16] But Clausius does not make it clear in this paper how the Avogadro hypothesis can be *derived* from the kinetic theory.

In his derivation of the ideal gas law, Clausius took into account the fact that molecules will be striking the sides at all possible angles of incidence, and showed that the resulting total pressure will be the same as that found by Krönig (except for the missing factor of $\frac{1}{2}$) on the assumption that the molecules only move in directions parallel to the walls of a cubical container. But, while admitting that "there is no doubt that actually the greatest possible variety exists amongst the velocities of the several molecules" he assumed that all molecules move with the average velocity for the purposes of his derivations. He computed these mean velocities for oxygen, nitrogen, and hydrogen at 0°C: 461, 492, and 1844 meters per second, respectively.

Assuming that the total heat of the gas (*i.e.* the total energy of translational, rotational, and vibrational energy of the molecules) is always proportional to the energy of translatory motion, Clausius found that the ratio of translatory to total energy could be expressed in terms of the ratio of specific heats at constant pressure (c') and at constant volume (c)

$$\frac{K}{H}=\frac{3}{2}\left(\frac{c'}{c}-1\right)=\frac{3}{2}\frac{\gamma'-\gamma}{\gamma}$$

where γ and γ' are the specific heats calculated with respect to units of volume. He used experimental data (for which he did not give a specific reference) to conclude that the ratio of specific heats in ordinary gases is $c'/c = 1.421$, and hence $K/H = 0.6315$. It is clear from his formula, although he did not explicitly state it, that if there is no internal motion (*i.e.* $K = H$) then c'/c ought to be equal to $\frac{5}{3}$. (It will be recalled that Waterston obtained $\frac{4}{3}$ because of an arithmetic error.) Clausius was not willing to assert that each mode of motion ("degree of freedom" in modern terms) must have the same average energy; he would only say that the energies are in a constant ratio.

It may be noted that while Clausius did not use the term "kinetic energy" he did decide to change the definition of "*vis viva*" from mv^2 to $\frac{1}{2}mv^2$ "in accordance with a practice lately become general,... because it is only with this definition of the notion that we can, without the addition of a coefficient, equate the expressions representing a quantity of work and the increase or decrease of *vis viva* which corresponds to the same."[17]

* * *

One of the first responses to Clausius' paper was that of Stanislao Cannizzaro, the Italian chemist responsible for reviving the chemical atomic theory in its modern form based on Avogadro's hypothesis. In his famous "Sunto di un corso di Filosofia Chimica," published in 1858 and distributed to the participants at the Karlsruhe Congress in 1860, he wrote:

> In the third lecture I pass in review the various researches of physicists on gaseous bodies, and show that all the new researches from Gay-Lussac to Clausius confirm the hypothesis of Avogadro and of Ampère that the distances between the molecules, so long as they remain in the gaseous state, do not depend on their nature, nor on their mass, nor on the number of atoms they contain, but only on their temperature and on the pressure to which they are subjected.[18]

While Cannizzaro did not give much emphasis to the evidence from kinetic theory aside from this one statement, other chemists such as Lothar Meyer were glad to add this physical argument to the chemical debate.[19] (Cannizzaro's remarks on this subject in 1872 are quoted at the end of §5.4.)

Notes for §4.3

1. See E. E. Daub, *DSB* **3**, 303 (1971) and other biographical articles cited therein; articles cited in *Isis Cum. Bibl*; articles on the Second Law of Thermodynamics cited in §14.3, note 1; G. Ronge, *Urania* **19**, 321 (1956); E. W. Garber, *Maxwell, Clausius and Gibbs: Aspects of the Development of Kinetic Theory and Thermodynamics* (Ph.D. Dissertation, Case Institute of Technology, 1966) and *Hist. Stud. Phys. Sci.* **2**, 299 (1970).
2. R. Clausius, *Ann. Phys.* [2] **76**, 161 (1849). I. Schneider, *Arch. Hist. Exact Sci.* **14**, 143 (1974).
3. *Scientific Memoirs, selected from the transactions of foreign academies of science and learned societies, and from foreign journals*, ed. Richard Taylor (London, 1837–52; New York: Johnson Reprint Corp., 1966).
4. I have counted only the articles published through 1883, since the Fourth Series of the *Catalogue*, covering publications after 1883, does not list translations.
5. *The Mechanical Theory of Heat*, ed. T. Archer Hirst with introd. by J. Tyndall (London, 1867); *The Mechanical Theory of Heat*, trans. W. R. Browne (London, 1879).
6. Daub, *op. cit.* Max Planck, on the other hand, commented that in this paper Clausius used the assumption that heat is a conserved substance; see *Das Princip der Erhaltung der Energie* (Leipzig, 1887), p. 54.
7. *Taylor's Sci. Mem.*, p. 309 (1853), trans. from Clausius, *op. cit.* (note 2) by J. T[yndall].
8. J. W. Gibbs, *Proc. Am. Acad.* [n.s.] **16**, 458 (1889); *The Collected Works of J. Willard Gibbs* (New Haven: Yale University Press, 1948), **2**, Part Two, 261 (quoted from p. 265). Cf. I. Schneider, *Arch. Hist. Exact Sci.* **14**, 237 (1975).
9. Cf. V. L. Hilts, in *Foundations of Scientific Method: The Nineteenth Century*, eds. R. N. Giere and R. S. Westfall (Bloomington: Indiana University Press, 1973), p. 206.
10. *Ann. Phys.* [2] 79, 368, 500 (1850); Phil. Mag. [n.s.] **2**, 1, 102 (1851); tr. by W. F. Magie, reprinted in *Reflections on the Motive Power of Fire by Sadi Carnot and other papers on the Second Law of Thermodynamics by E. Clapeyron and R. Clausius*, ed. E. Mendoza (New York: Dover Pubs., 1960), p. 109 (quoted from p. 110).
11. *Ibid.*, p. 128.
12. R. Clausius, *Ann. Phys.* [2] **83**, 118 (1851); **93**, 481 (1854) [cf. discussion of this paper in §14.3]; Daub, *op. cit.*, p. 305.
13. *Ann. Phys.* [2] **86**, 337 (1852); *Scientific Memoirs*, eds. J. Tyndall and W. Francis: *Natural Philosophy* (London, 1853), p. 1 (quoted from p. 5).
14. "Before writing my first memoir on heat, which was published in 1850, and in which heat is assumed to be a motion, I had already formed for myself a distinct conception of the nature of this motion, and had even employed the same in several investigations and calculations. In my former memoirs I intentionally avoided mentioning this conception, because I wished to separate the conclusions which are deducible from certain general principles from those which presuppose a particular kind of motion, and because I hoped to be able at some future time to devote a separate memoir to my notion of this motion and to the special conclusions which flow therefrom. The execution of this project, however, has been retarded longer that I at first expected,

inasmuch as the difficulties of the subject, as well as other occupations, have hitherto prevented me from giving to its development that degree of completeness which I deemed necessary for publication." (First paragraph of the 1857 paper as translated in *Phil. Mag.*)

15. *Monatsschrift des Wissenschaftlichen Vereins in Zurich* **2**, 73 (1857). French trans. in *Rev. Sci.* **3**, 121 (1866).
16. R. Clausius, *Die Kinetische Theorie der Gase* (Braunschweig, 1889–91), p. 22. J. T. Merz, *History of European Thought* **1**, 435.
17. Quoted from the *Phil. Mag.* trans. in Brush, *Kinetic Theory* **1**, 129.
18. S. Cannizzaro, *N. Cim.* **7**, 321 (1858); *Sketch of a Course of Chemical Philosophy*, Alembic Club Reprints No. 18 (Edinburgh: The Alembic Club, Reissue edition 1961), quoted from p. 4.
19. L. Meyer, *Ber. D. Chem. Ges.* **4**, 25 (1871); *Die Modernen Theorien der Chemie* (Breslau, 1864, 2. Aufl. 1872), **25**, 356.

4.4 The mean free path

The ideal-gas theory was confronted with a very practical objection in 1858 by the Dutch meteorologist C. H. D. Buys-Ballot.[1] Buys-Ballot pointed out that if it were really true, as Joule, Krönig, and Clausius claimed, that the molecules of a gas move at speeds of the order of several hundred meters per second, one would expect gases to diffuse and mix with each other very rapidly. In fact, however, if hydrogen sulfide or chlorine is evolved in one corner of a room, it may be several minutes before it is noticed in another corner of the room, although according to the kinetic theory each of the molecules should have traversed the room hundreds of times by then. Other common phenomena also appear to contradict the assertion that molecules move at high velocities; for example, carbon dioxide may remain for a long time in an open vessel.

Clausius realized that this was a valid objection to the theory as thus far developed, and he attempted to answer it by showing that in real gases, where the intermolecular forces are not negligible, the molecules could not travel for great distances in a straight line. In order to prove this, he introduced the concept of "mean free path" (*normale mittlere Weglänge*), which he related to the range of influence of the repulsive forces exerted by a molecule.[2] There is some similarity between this theory and a discussion of the reflection of sunlight by various constituents of the atmosphere, which Clausius had published in 1849.[3]

If one assumes that the intermolecular forces are attractive at large separations and repulsive at small separations, then it is possible to define a distance ρ at which attraction and repulsion are balanced; *i.e.* if in an encounter the centers of gravity of two molecules pass within a distance not less than ρ, they will change their courses to some extent only through reciprocal attraction, whereas if they pass at a distance less than ρ the repulsive forces come into play and a "rebounding" of the molecules takes place.[4] The sphere of radius ρ around the molecule is called its "sphere of action." Clausius proposed the question: "How far on the average can a molecule move before its centre of gravity comes into the sphere of action of another molecule?" He asserted that this mean path would be greater if all the other molecules are at rest relative to the one considered, than it would be if they moved in all directions with the same speed, and, in particular, that the ratio of the paths in the two cases would be as $\frac{4}{3}$ to 1. Since only a rough estimate was required, Clausius assumed that all the other molecules were at rest, with mean distance between their centres denoted by λ.

At this point Clausius introduced an assumption which, if it is not the first use of statistical reasoning in kinetic theory, must certainly be called one of the most explicit treatments of molecular motion as a stochastic or random process. He imagines the entire space available to the gas to be divided into layers perpendicular to the direction of motion of a particular molecule, and seeks the probability that it will pass through a layer of thickness x without encountering the sphere of action of another molecule.

If the probability that the specified molecule will pass through a layer of thickness 1 is denoted by $e^{-\alpha}$, then the probability that it will pass through a layer of thickness x is $e^{-\alpha x}$. For a very thin layer of thickness $x = \delta$, the probability will be

$$W_\delta = e^{-\alpha\delta} \cong 1 - \alpha\delta \tag{1}$$

In order to find α in terms of the sphere of action, Clausius considered a layer of thickness λ containing n molecules. If these were arranged in a two-dimensional square array with spacing λ, then the total area of a plane bounding this layer would be $n\lambda^2$, of which the spheres of action would occupy an area $n\pi\rho^2$. The covered area would thus be a fraction $\pi\rho^2/\lambda^2$ of the total area seen by the molecule. If this fraction is small enough, one can add together several such layers of molecules randomly arranged, and the projections of their spheres of action on the boundary plane will not overlap appreciably, so that the fraction of the area covered, for a layer of thickness δ, will be

$$\frac{\pi\rho^2}{\lambda^2}\left(\frac{\delta}{\lambda}\right)$$

Since the probability W_δ that the molecule will pass through this layer without a collision is just the area which is not covered by these spheres of action, the constant α may be identified as

$$\alpha = \pi\rho^2/\lambda^3 \tag{2}$$

Going back to the original expression for W, we see that the probability of passing through a layer of finite thickness x is[5]

$$W = \exp\left(-\pi\rho^2 x/\lambda^3\right) \tag{3}$$

Using this expression, Clausius could then deduce the mean distance traveled between collisions. He considered a large number, N, of molecules traveling in one direction through the gas. A certain proportion would encounter the spheres of action of the molecules in each layer. The number of molecules that collide in the layer between x and $x + dx$ will be

$$N \exp\left[-\pi\rho^2(x + dx)/\lambda^3\right] \cong N \exp\left(-\pi\rho^2 x/\lambda^3\right)\left(1 - \frac{\pi\rho^2}{\lambda^3}\right) dx, \tag{4}$$

and the mean length of path will be the sum of the distances traveled by each molecule, divided by the number of molecules. In this way Clausius found that the mean free path is

$$l' = \frac{1}{N}\int_0^\infty N \exp\left(-\pi\rho^2 x/\lambda^3\right)\frac{\pi\rho^2}{\lambda^3} x\, dx = \frac{\lambda^3}{\pi\rho^2} \tag{5}$$

The primed letter, l', was used to denote the mean free path in the case where all the other molecules are at rest except the one considered. If all the other molecules moved at the same speed, the mean free path would be $\frac{3}{4}$ as great, as mentioned above, and in this case Clausius wrote it

$$l = \frac{3}{4}\frac{\lambda^3}{\pi\rho^2}$$

Now since $\frac{4}{3}\pi\rho^3$ is the total volume occupied by the sphere of action of a molecule, this equation simply means that the ratio of the mean free path to the radius of the sphere of action is equal to the ratio of the entire space occupied by the gas to that part of it which is actually filled by the spheres of action of the molecules.

Although this derivation was a valuable contribution to the theory, it did not completely answer the original objection, since Clausius had no way of estimating the size of the sphere of action. He could only guess that a value of 1000:1 for the ratio l/ρ might be within the bounds of possibility, and he thought that ρ itself was probably so small that this would still make l small compared with macroscopic dimensions.

The concept of mean free path which Clausius introduced turned out to be very useful in investigating many properties of gases, such as the conduction of heat, viscosity, and diffusion; indeed, it is still the basis for expositions of the kinetic theory given in most modern textbooks. It is not completely satisfactory, especially if one wishes to take account of the fact that not all molecules in the gas have the same velocity, but instead the velocities vary according to some statistical distribution law. The mean free path of a molecule will depend on its velocity, and the velocity-distribution law itself will vary from place to place in the gas if some process like heat conduction, viscosity, or diffusion is taking place. Some of these modified mean-free-path theories will be discussed in §12.2 in connection with the calculation of the viscosity coefficient. An alternative, more accurate, theory of transport phenomena was introduced by Maxwell (1866) (see §12.3); Maxwell's theory was reformulated by Boltzmann (1872) in terms of an integro-differential equation for the velocity-distribution function (§12.4). Methods for solving the Maxwell–Boltzmann transport equations were developed by Chapman and Enskog (1916–17); in most cases it was found that the mean-free-path theory predicted correctly the order of magnitude of the transport coefficients and their variation with density, and the variation with temperature for the special case of elastic spheres. However, the important phenomenon of thermal diffusion was not predicted by the mean-free-path theory at all; its discovery was one of the most important accomplishments of the Chapman–Enskog theory.

Notes for §4.4

1. *Ann. Phys.* [2] **103**, 240 (1858). On Buys-Ballot and his own atomic theory see H. A. M. Snelders, *Scientiarum Historia* **10**, 154 (1968); H. L. Burstyn, *DSB* **2**, 628 (1970). Buys-Ballot, *Verh. Ges. D. Naturf. Aerzte* **33**, 164 (1857).
2. R. Clausius, *Ann. Phys.* [2] **105**, 239 (1858); see bibliography for reprints and translations.
3. R. Clausius, *Ann. Phys.* [2] **76**, 161 (1849); Taylor's *Scientific Memoirs*, p. 303 (1853).
4. Note that this is equivalent to considering each molecule as a sphere with radius $\rho/2$.

5. This formula was tested experimentally for cathode ray absorption in gases by P. Lenard, *Ann. Phys.* [4] **12**, 714 (1903); see also C. Ramsauer, *Ann. Phys.* [4] **64**, 513, **66**, 546 (1921).

4.5 Later writings on kinetic theory

After 1860 Clausius published two major works on kinetic theory. The first was a long memoir on heat conduction (1862), stimulated by Maxwell's attempt to use the mean-free-path method to calculate the coefficients of viscosity, heat conduction, and diffusion (1860). This memoir is discussed in §13.4 in connection with the problem of heat conduction; my only comment here is that while the paper was of considerable value insofar as it forced Maxwell to improve his own theory of transport processes, and it did call attention to the predictions of kinetic theory at a time when experimental research in heat conduction was just beginning, the theoretical approach which Clausius himself adopted was very unsatisfactory. His attempt to extend the mean-free-path method was too complicated to be comprehensible to most readers, yet at the same time it failed to yield a result significantly more accurate than the most elementary treatment.

The other major work was a short paper in 1870 introducing the "virial theorem," by means of which the equation of state of imperfect gases could be systematically calculated from assumptions about intermolecular forces. Unfortunately Clausius himself did not succeed in using it effectively for this purpose; instead, he was primarily interested in finding a general mechanical foundation for the laws of thermodynamics. The virial theorem is discussed in §11.4.

Clausius conducted a rather ridiculous debate with Maxwell on the numerical value of the coefficient in the mean-free-path formula; he persisted in defending his value of $\frac{3}{4}$, based on the assumption that all molecules have the same speed, after Maxwell had deduced the value $\sqrt{\frac{1}{2}}$ from his own statistical velocity distribution. By the time Clausius accepted Maxwell's value, Maxwell had long since abandoned the mean-free-path theory itself (§12.2). Equally insignificant from the modern viewpoint, though perhaps necessary to ensure the general acceptance of the kinetic theory in the scientific community at the time, was the series of polemics and explications which Clausius published in response to various objections and misunderstandings.[1]

It is perhaps surprising that Clausius did not pursue the applications of his mean-free-path theory to transport phenomena; perhaps he realized that Boltzmann's and Maxwell's more sophisticated methods had superseded his own. He did attempt to improve the van der Waals' equation of state by taking account of the effect of temperature changes on the contribution of intermolecular forces to the pressure, using the qualitative idea that these forces would produce association of nearby molecules at low temperatures. But he did not make use of the Maxwell–Boltzmann distribution–now considered the proper tool for treating such problems–so his work degenerated into empirical curve-fitting.[2]

In assessing Clausius' contribution to the development of the kinetic theory, one has to recognize that while he failed to adopt the statistical methods introduced by Maxwell and Boltzmann and thus could not go beyond the elementary theory in calculating gas properties, his decision to focus on the formulation and interpretation of the Second Law of Thermodynamics had a strong indirect influence on the later discussions of randomness and irreversibility (ch. 14). It was Clausius' entropy concept, as interpreted statistically by Boltzmann, that provided the focus for these discussions, and thus determined the language of debates on the foundations of the kinetic theory of transport processes.

Notes for §4.5

1. See the following items in the Bibliography: Clausius 1863, 1872a, 1878, 1886; also *Ber. D. Chem. Ges.* **4**, 269 (1871).
2. R. Clausius, *Ann. Phys.* [3] **9**, 337 (1880), **14**, 279, 692 (1881).

   According to Elizabeth Garber, Clausius used the Maxwell distribution only once, in a calculation of a mechanical expression for the heat added to a gas [Clausius (1874c); Garber, *op. cit.*, §4.3, note 1, pp. 90–91].

CHAPTER 5

Maxwell

5.1 Possible source of the statistical approach

An essential property of a gas is the random motion of its constituent molecules; in fact the word "gas" itself implies chaos.[1] The early kinetic theorists paid lip service to this property but usually based their mathematical proofs on the assumption that all the molecules move with the same velocity, and sometimes in addition that they are all situated in a regular array in space, or move only in directions parallel to the walls of the container. In some cases plausible arguments were advanced to show that the results would be the same if the molecules moved randomly, but there was little interest in any effects that might be attributable specifically to *deviations* from the average behavior. It is to James Clerk Maxwell (1831–79) that we owe the introduction of the statistical approach in the kinetic theory; he and Ludwig Boltzmann (1844–1906) worked out a set of theorems and methods which have become a standard part of the training of all modern physicists and theoretical chemists, because they have been recognized to play an indispensable role in all atomic theories of matter.[2]

The origin of Maxwell's statistical methods has been the subject of recent historical investigations by C. C. Gillispie, C. W. F. Everitt, E. W. Garber, and others.[3] It seems quite possible that while Maxwell was indirectly influenced by earlier writers on statistics such as Laplace, Poisson, Cournot, and Quetelet, the most immediate stimulus for

Fig. 5.1-1. James Clerk Maxwell.

Maxwell's first derivation of his velocity-distribution law was a review of Quetelet's works on probability by Sir John Herschel in the *Edinburgh Review* of July 1850.[4] This is a typical Victorian book review, about a hundred pages long, in which the reviewer first gives his own analysis of the subject and does not mention the book until he is halfway through. Herschel believes that the law of errors is so important that it ought to be proved in a way that is both mathematically rigorous and intelligible to the general educated public. Since he thinks no such proof is available he decides to give his own, starting from the following three postulates:

(1) "The probability of a compound event, or of the concurrence of two or more independent single events, is the product of the probabilities of its constituents considered singly;

(2) that there exists a relation or numerical law of connexion (at present unknown) between the amount of error committed in any numerical determination and the probability of committing it, such that the greater the error the less its probability...;

(3) that the errors are equally probable if equal in numerical amount, whether in excess, or in defect of... the truth. This latter postulate necessitates our assuming the function of probability to be what is called in mathematical language *an even function*, or a function of the square of the error."

The form of the function, which is asserted to be generally valid, may be determined by considering a special case, namely "a ball dropped from a given height, with the intention that it shall fall on a given mark. Fall as it may, its deviation from the mark is *error*, and the probability of that error is the unknown function of its square, *i.e.* of the sum of the squares of its deviations in any two rectangular directions. Now, with the probability of any deviation depending solely on its magnitude, and not on its direction, it follows that the probability of each of these rectangular deviations must be the same function of *its* square. And since the observed oblique deviation is equivalent to the two rectangular ones, supposed concurrent, and which are essentially independent of one another,[5] and is, therefore, a compound event of which they are the simple independent constituents, therefore its probability will be the product of their separate probabilities. Thus, the form of our unknown function comes to be determined from this condition, *viz.* that the product of such functions of two independent elements is equal to the same function of their sum. But it is shown in every work on algebra that this property is the peculiar characteristic of, and belongs only to, the exponential or antilogarithmic function. This, then, is the function of the square of the error, which expresses the probability of committing that error."

What reason do we have for thinking that Maxwell (then age 19) read this review of Herschel's? Aside from the striking similarity to Maxwell's own derivation (see below) there is only a letter from Maxwell to Lewis Campbell, which is undated but thought to be written around June 1850 by Campbell and Garnett, who published it in their Life of Maxwell.[6] According to C. W. F. Everitt, who discusses this question in his forthcoming biography of Maxwell, the letter was probably written by Maxwell just after he read Herschel's review, since it repeats some of Herschel's remarks on probability theory in only slightly different words.

Maxwell's basic hypothesis in his 1860 paper was that the numerous collisions between molecules in a gas, instead of tending to equalize the velocities of all the molecules, as some scientists expected,[7] would instead produce a statistical distribution of velocities in which all velocities might occur, with a known probability. (The existence of a unique equilibrium distribution, to which any other distribution would tend, was not rigorously proved until later, and remained a subject of controversy for many years.) He began by pointing out that, if two elastic spheres collide, all directions of rebound are equally likely. He apparently believed that this fact would ensure, not only that all directions of motion are equally probable in the gas, but also that the probability distribution for each component of the velocity is independent of the values of the other components. His first proof of the distribution law depended on these two assumptions. (Maxwell later realized that the validity of the second assumption was not obvious, and in his 1867 memoir he therefore attempted an alternative demonstration, in which this property is deduced rather than assumed.)

He argues as follows:[8]

> Let N be the whole number of particles. Let x, y, x be the components of the velocity of each particle in three rectangular directions, and let the number of particles for which x lies between x and $x + dx$ be $Nf(x)\, dx$ where $f(x)$ is a function of x to be determined.
>
> The number of particles for which y lies between y and $y + dy$ will be $Nf(y)\, dy$; and the number for which z lies between z and $z + dz$ will be $Nf(z)\, dz$ where f always stands for the same function.
>
> Now the existence of the velocity x does not in any way affect that of the velocities y or z, since these are all at right angles to each other and independent, so that the number of particles whose velocity lies between x and $x + dx$ and also between y and $y + dy$ and also between z and $z + dz$ is
>
> $$Nf(x)f(y)f(z)\, dx\, dy\, dz$$
>
> If we suppose the N particles to start from the origin at the same instant, then this will be the number in the element of volume $(dx\, dy\, dz)$ after unit of time, and the number referred to unit of volume will be
>
> $$Nf(x)f(y)f(z)$$

But the directions of the coordinates are perfectly arbitrary, and therefore this number must depend on the distance from the origin alone, that is

$$f(x)f(y)f(z) = \phi(x^2 + y^2 + z^2)$$

Solving this functional equation, we find

$$f(x) = C\, e^{Ax^2}, \qquad \phi(r) = C^3\, e^{Ar^2}$$

If we make A positive, the number of particles will increase with the velocity, and we should find the whole number of particles infinite. We therefore make A negative and equal to $-1/\alpha^2$, so that the number between x and $x + dx$ is

$$NC\, e^{-x^2/\alpha^2}\, dx$$

Integrating from $x = -\infty$ to $x = +\infty$, we find the whole number of particles,

$$NC\alpha\sqrt{\pi} = N, \qquad \therefore C = \frac{1}{\alpha\sqrt{\pi}}$$

$f(x)$ is therefore

$$\frac{1}{\alpha\sqrt{\pi}}\, e^{-x^2/\alpha^2}$$

From this formula Maxwell then computes that the mean velocity of all the particles is $(2\alpha/\sqrt{\pi})$, and the mean-square velocity is $(3\alpha^2/2)$.

There have been many attempts to prove Maxwell's distribution law more rigorously. Without going into details, we may mention the types of proofs that have been given: (1) if the molecular velocities *already* have a Maxwell distribution, then collisions between molecules, because they conserve energy, will leave the distribution unchanged; hence Maxwell's distribution is the only one that is *stable*;[9] (2) one may define a quantity (now called Boltzmann's H-function) which depends on the velocity distribution, and show that the effect of molecular collisions is always to decrease H, unless the velocity distribution is Maxwellian, in which case H remains constant; thus any other distribution will tend to go over to the Maxwellian distribution, and then stay there;[10] (3) one may take the view that molecular velocities are random quantities, and apply the methods of probability theory to make the best possible estimate of their distribution given only the information that the total energy, mass, and momentum are fixed; it is possible to improve Maxwell's derivation here by taking account of the fact that the total energy and number of molecules are *finite,* and simply calculating all possible ways of dividing the energy among the molecules;[11] (4) one may simply treat the Maxwell distribution as a basic postulate of the theory, and use it to predict the results of experiments, especially those that ought to be sensitive to deviations from the Maxwell distribution.[12]

Notes for §5.1

1. A. C. Crombie, *Medieval and Early Modern Science* (New York: Doubleday, 1959) **2**, 259. E. O. von Lippmann, in *Beitrage zur Geschichte der Naturwissenschaften und Technik* (Weinhein/Bergstr.: Verlag Chemie, 1953), **2**, 73–76.
2. This chapter is based on my articles in *Ann. Sci.* **14**, 243 (1958) and *Am J. Phys.* **39**, 631 (1971), and on the article written jointly with C. W. F. Everitt in *Hist. Stud. Phys. Sci.* **1**, 105 (1969). The treatment of Maxwell's work here and elsewhere in the book owes much to continuing discussions and correspondence with Everitt over the last several years. His article in the *DSB* and his forthcoming book should be consulted for information about Maxwell's career and contributions to science.

   Other works dealing specifically with Maxwell's kinetic theory are: I. B. Hopley, *Clerk Maxwell's Contribution to Physics* (Thesis, University of London, 1957); J. Turner, *The Methodology of James Clerk Maxwell* (Thesis, Columbia University, 1953); E. W. Garber, *Maxwell, Clausius and Gibbs: Aspects of the Development of Kinetic Theory and Thermodynamics* (Dissertation, Case Institute of Technology, 1966); E. W. Garber, *Hist. Stud. Phys. Sci.* **2**, 299 (1970).
3. C. C. Gillispie, in *Scientific Change,* ed. A. C. Crombie (New York: Basic Books, 1963), p. 431, and comments on this paper by M. Hesse, p. 471. C. W. F. Everitt, private communication. E. W. Garber, *Centaurus* **17**, 11 (1972).
4. J. Herschel, *Edinburgh Review* **92**, 1 (1950); see §14.4 for further discussion and references to related works.
5. When he reprinted the review in his *Essays* (London, 1857), p. 365, Herschel added a footnote at this point: "That is, the increase or diminution in one of which may take place without increasing or diminishing the other. On this, the whole force of the proof turns." Note that this condition is not strictly true for the velocity components of a gas consisting of a finite number of molecules with fixed total energy. The generalization of Maxwell's velocity distribution to a finite system was accomplished by Boltzmann, *Wien Ber.* **76**, 373 (1877).
6. L. Campbell and W. Garnett, *The Life of James Clerk Maxwell* (London, 1882; New York: Johnson Reprint Corp., 1969), pp. 138–44. The letter is dated "June ? 1850" by Campbell and Garnett.
7. See for example E. Jochmann, *Ann. Phys.* [2] **108**, 153 (1859). Hirn's later attacks on the kinetic theory were partly due to his ignoring the spread of molecular velocities: see Bibliography, Gustav Adolph Hirn, 1884, 1886b, 1888 and Ladislaus Natanson, 1888a.
8. J. C. Maxwell, *Phil. Mag.* [4] **19**, 19, **20**, 21, 33 (1860); *The Scientific Papers of James Clerk Maxwell* (Cambridge University Press, 1890; New York: Dover Pubs., 1952,

1965), 1, 377; S. G. Brush, *Kinetic Theory* (New York: Pergamon Press, 1965), 1, 148 (quoted from pp. 153–54).

9. Maxwell, *Phil. Trans.* **157**, 49 (1867); *Papers* **2**, 26; Brush, *Kinetic Theory* **2**, 23 (see pp. 45–48).
10. L. Boltzmann, *Wien Ber.* **66**, 275 (1872); *Wissenschaftlichen Abhandlungen* (Leipzig: Barth, 1909; New York: Chelsea Pub. Co., 1968), 1, 316; S. G. Brush, *Kinetische Theorie* (Berlin: Akademie-Verlag/Oxford: Pergamon Press/Braunschweig: Vieweg & Sohn, 1970), **2**, 115. English trans. in Brush, *Kinetic Theory* 2, 88.
11. L. Boltzmann, *op. cit.* (note 5). J. C. Maxwell, *Trans. Camb. Phil. Soc.* **12**, 547 (1879); *Papers* **2**, 713.
12. These experiments are reviewed by J. P. Andrews, *Science Progress* **23**, 118 (1928).

5.2 Gas viscosity

One might naturally suppose that Maxwell, like his predecessors, was convinced of the validity of the kinetic theory from the start, and was motivated to work out its mathematical consequences in order to facilitate comparison with experimental data and thus persuade other scientists to adopt it. But the only evidence I have seen for Maxwell's opinions on gas theory before 1859 is an essay on the "Properties of Matter" which he wrote for William Hamilton's class at Edinburgh in 1848. It shows that at that time he had absorbed the prevalent non-kinetic views of gas structure, in which one assumes repulsive forces inversely as the distance between particles.[1]

It appears that Maxwell came to the kinetic theory as an exercise in theoretical mechanics involving the motions of systems of particles acting on each other only by impact. He had just finished a similar problem in his Adams Prize essay on the constitution of Saturn's rings, and some casual remarks in his correspondence suggest that he may have seen a connection between the interference of neighboring streams of particles in the rings and the viscosity of a gas composed of elastic spheres in motion.[2] In any case we know that after writing his first paper on kinetic theory, Maxwell returned to the problem of Saturn's rings and applied the velocity-distribution function to it, though this later work was never published.[3]

Maxwell's letter to Stokes, a few months after he saw Clausius' paper in the Philosophical Magazine (February 1859), suggests that he actually expected to be able to *disprove* the kinetic theory by showing that its predictions disagreed with known properties of gases. He explained his theory of gaseous "friction" (the term "viscosity" was used only in Maxwell's later papers) as follows:

> Divide the gas into layers on each side of the plane in which you measure the friction, and suppose the tangential motion uniform in each layer, but varying from one to another. Then particles from a layer on one side of the plane will always be darting about, and some of them will strike the particles belonging to a layer on the other side of the plane, moving with a different mean velocity of translation.
>
> Now though the velocities of these particles are very great and in all directions, their mean velocity, that of their centre of gravity, is that of the layer from which they started, so that the other layer will receive so many particles per second, having a different velocity from its own. . . .
>
> I do now know how far such speculations may be found to agree with facts, even if they do not it is well to know that Clausius' (or rather Herapath's) theory is wrong,[4] and at any rate as I found myself able and willing to deduce the laws of motion of systems of particles acting on each only by impact, I have done so as an exercise in mechanics. Now do you think there is any so complete a refutation of this theory of gases as would make it absurd to investigate it further so as to found arguments upon measurements of strictly "molecular" quantities before we know whether there be any molecules? One curious result is that μ is independent of the density. . . . This is certainly very unexpected, that the friction should be as great in a rare as in a dense gas. The reason is, that in the rare gas the mean path is greater, so that the frictional action extends to greater distances.
>
> Have you the means of refuting this result of the hypothesis?[5]

In his reply (which does not seem to have survived), Stokes apparently told Maxwell about an observation of Sabine (1829), which according to Stokes' own analysis indicated that the viscosity of a gas *does* vary with density.[6] Thus in his 1860 paper, referring to his theoretical prediction that viscosity should be independent of density, Maxwell wrote:

> Such a consequence of a mathematical theory is very startling, and the only experiment I have met with on the subject does not seem to confirm it.[7]

It turned out eventually that in computing the viscosity of air from Sabine's pendulum experiments, Stokes had implicitly *assumed* that the viscosity decreases in proportion to the density.[8] This was a natural assumption for anyone to make before 1859; it was only with the help of Maxwell's *theory* that one could correctly interpret the *experiments* designed to test the theory!

Evidently Maxwell did not consider the experiment reported by Stokes sufficiently conclusive, for he went to considerable effort to design and carry out his own experiments. He found that the viscosity of air, at a given temperature, remained constant when the pressure was varied between a half-inch and 30 inches.[9] This result was confirmed independently by O. E. Meyer.[10] Stokes and Meyer also realized that earlier experiments of Thomas Graham on the flow of gases through small tubes could be interpreted as measurements of viscosity, with similar results.[11] So the outcome was not a refutation of the theory but a rather convincing and surprising confirmation of it: the alternative static theory of gases would certainly lead one to expect that viscosity should increase with density, as it in fact does for a liquid. Rayleigh, 25 years later, wrote that "in the whole range of science there is no more beautiful or telling discovery than that gaseous viscosity is the same at all densities."[12]

Maxwell's first viscosity formula also implied that the viscosity coefficient should be proportional to the square root of the absolute temperature, provided that the molecules may be considered elastic spheres. His experiments, however, seemed to show that the viscosity was simply proportional to temperature. Maxwell's second theory of gas transport properties (1867), based on the assumption that the molecules repel each other with a force inversely as the fifth power of the distance between their centers, led to the same conclusion. (Maxwell had already done this calculation by the time he published his experimental results.[13]) While subsequent experiments by others indicated that the temperature exponent for most gases is somewhere between $\frac{1}{2}$ and 1, Maxwell retained the inverse fifth power model (now known as the "Maxwellian" molecule) because of its convenience for calculations. The development of this subject is reviewed in more detail in ch. 12.

* * *

Maxwell derived formulae for the coefficients of heat conduction and diffusion, the two other transport processes besides viscosity. We should not pass over too quickly the mere fact that these *are* the fundamental linear transport processes in a gas, and that they can all be conceptualized as special cases of a generalized transport process in which a physical quantity is carried by molecular motion and transferred from one molecule to another by collisions. No one before Maxwell had looked at gas properties in this way, and few scientists had even realized that all these properties can be subject to the same kind of systematic theoretical and experimental investigation. The publication of Maxwell's theory–both the elementary theory in 1860 and the comprehensive treatment in 1867–was responsible for stimulating much of the research on gas viscosity, heat conduction, and diffusion during the last part of the 19th century.[14]

As Clausius quickly pointed out and Maxwell soon conceded, the theoretical treatment of heat conduction in the 1860 paper contained a serious error and led to a patently absurd result; and it was left to Clausius to point out and explain the important consequence of the theory, that the heat conduction coefficient (like the viscosity coefficient) should be independent of density (§13.4). For some reason Maxwell was much less interested in heat conduction than in viscosity, yet his theory had a considerable impact on several aspects of heat transfer research. The natural assumption that the ability of a gas to conduct heat must depend on its density, and in particular should vanish gradually as the density goes to zero, had been the basis for interpreting all earlier experiments on heat transfer through gases, including those involving radiation. Since it is extremely difficult to disentangle *experimentally* the contributions of conduction, convection, and radiation to the total heat transfer through the gas, the kinetic-theory result that conduction is independent of density offered a new way of looking at the experimental data. It is no accident that Josef Stefan, who was one of the first to confirm experimentally the prediction of the kinetic theory, was also the person who reinterpreted the earlier radiation experiments of Dulong and Petit and others, and showed that they were compatible with his T^4 radiation formula (later known as the Stefan–Boltzmann law because Boltzmann derived it theoretically from thermodynamics and Maxwell's electromagnetic theory). (See §13.7.)

Maxwell's 1860 theory of diffusion was also criticized by Clausius, and an improved treatment was presented in the 1867 paper, for the special case of inverse fifth power forces. Maxwell gave the results of his theory for elastic spheres in 1873 and used the formula to compute molecular diameters, though he did not publish the details of the derivation of the formula.[15] According to Maxwell's theory and a similar one developed by Stefan, the diffusion coefficient should not depend on the concentration in a mixture of gases. A competing theory of O. E. Meyer predicted that the coefficient *does* depend on concentration. Experimental investigations toward the end of the century, and theoretical work culminating in the Chapman–Enskog theory of 1916–17, showed that Maxwell and Stefan were more nearly right: there is a very small concentration-dependence, much less than that given by Meyer's theory.[16]

Notes for §5.2

1. L. Campbell and W. Garnett, *The Life of James Clerk Maxwell* (London, 1882), p. 109.
2. Maxwell to P. G. Tait, 21 November 1857; Maxwell to G. G. Stokes, 7 September 1858. The second of these has been published in *Memoir and Scientific Correspondence of the late Sir George Gabriel Stokes,* ed. J. Larmor (Cambridge University Press, 1907), **II**, 7.
3. MS "Theory of Saturn's Rings" at Cambridge University; also MS "Mathematical Theory of Saturn's Rings."
4. "i.e., inadequate" (Maxwell's footnote).
5. Maxwell to G. G. Stokes, 30 May 1859, in *Memoir... of... Stokes* **II**, 8–10.
6. Stokes, *Trans. Camb. Phil. Soc.* **9**, [8] (1850); *Mathematical and Physical Papers* (New York: Johnson Reprint Corp., 1966, rept. of the 2nd ed. of 1880–1905 prepared by Stokes), **III**, 13.
7. Brush, *Kinetic Theory* **1**, 166.
8. O. E. Meyer, *Ann. Phys.* [2] **125**, 177, 401, 564 (1865); Stokes, material added to the reprint of his 1850 paper, in his *Mathematical and Physical Papers* **III**, 13, 76–77, 137–41.
9. *Phil. Trans.* **156**, 249 (1866); *The Scientific Papers of James Clerk Maxwell* **2**, 1.
10. O. E. Meyer, *Ann. Phys.* [2] **113**, 55 193, 383 (1861). For references to other research see J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949), **I**, 848–87.
11. "Stokes has been examining Graham's experiments on the rate of flow of gases through fine tubes, and he finds that the friction, if independent of density, accounts for Graham's results, but, if taken proportional to density, differs from those results very much. This seems rather a curious result, and an additional phenomenon, explained by the 'collision of particles' theory of gases."–Maxwell to H. R. Droop, 28 January 1862, in Campbell and Garnett, *op. cit.*, 332. Maxwell mentioned this conclusion in his experimental paper on gas viscosity (*Scientific Papers* **2**, 11); see also O. E. Meyer, *Ann. Phys.* [2] **127**, 253, 353 (1866). There is a recent discussion of this in the paper by E. A. Mason, *Philosophical Journal* **7**, 99 (1970).
12. Rayleigh, *Nature* **41**, 26 (1890). For an example of the presumption that (on the repulsive theory) viscosity must decrease with increasing temperature, see Thomas Webster, *The Principles of Hydrostatics* (Cambridge, 2nd ed. 1838), p. 2.
13. "If, as the experiments of Graham and those of this paper show, the viscosity is as the first power of the absolute temperature, then in the dynamical theory, which is framed to explain the facts, we must assume that the force between two molecules is

proportional inversely to the fifth power of the distance between them." Maxwell, *Scientific Papers* **2**, 11.

14. *Royal Society Catalogue*, Subject Index III, 69–70, 73–74, 231. J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949), I, 848–922.
15. J. C. Maxwell, *Nature* **8**, 298 (1873); *Scientific Papers* **2**, 343.
16. Brush, *Kinetic Theory* **3**, 17–18, 114–17, 184–90.

5.3 Specific heats and the hypothetico-deductive method

At the end of his 1860 paper Maxwell concluded that the principles of kinetic theory require complete equipartition of energy among all degrees of freedom in the "final state" of a mechanical system. His reasoning will be criticized in §10.4; here I am interested only in how the conclusion was related to his attitude about the physical validity of the kinetic theory. Maxwell was quite blunt about it:

> This result (which is true, however nearly the bodies approach the spherical form, provided the motion of rotation is at all affected by the collisions) seems decisive against the unqualified acception of the hypothesis that gases are such systems of hard elastic particles.

The paper ended with the sentence:

> Finally, by establishing a necessary relation between the motions of translation and rotation of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats of all gases.

Maxwell was even more emphatic about the failure of kinetic theory to predict the right values of specific heats in the summary of his paper delivered to the Oxford meeting of the British Association in 1860, published in its *Report* (but omitted from his *Scientific Papers*):

> This result of the dynamical theory, being at variance with experiment, overturns the whole hypothesis, however satisfactory the other results may be.[1]

At this point it would appear that Maxwell has been taken in by the naive version of the "hypothetico-deductive method" still advocated by some philosophers of science–if a single prediction from a hypothesis is falsified by experiment, you must reject the hypothesis.

But Maxwell soon realized that this method is inappropriate for most problems in physical science.[2]

In his unpublished paper on heat conduction written a few years later, Maxwell grappled with the specific heats problem again, and suggested at one point that "we must suppose .634 of the weight of air to consist of non-spherical particles and .366 of its weight to consist of perfectly spherical particles . . ."[3] But this rather implausible *ad hoc* assumption did not get into any of Maxwell's published papers.

Maxwell did not make any further attempts to resolve the difficulty, yet he did not let it stop him from developing other consequences of the theory. In 1876, when Boltzmann and Bosanquet proposed that diatomic molecules may have only five effective degrees of freedom–the sixth being unaffected by collisions and therefore not contributing to the specific heat–a solution of the specific heats problem seemed to have been found. But Maxwell, reviewing Watson's book on kinetic theory in 1877, refused to accept this solution on the grounds that it was not strictly deducible from any consistent mechanical model (§10.8). As far as Maxwell was concerned, none of the existing kinetic-theory models were wholly compatible with the properties of real gases. His view was that in theoretical physics one must maintain a high standard of mathematical rigor, even if this "leaves us no escape from the terrible generality" of the results; one can accept a theory as the best available at the time while at the same time recognizing oneself to be in a "state of thoroughly conscious ignorance which is the prelude to every real advance in knowledge."[4]

* * *

In a last-minute addition to his 1867 paper, Maxwell discussed the thermal equilibrium of a vertical column of gas. Herapath and Waterston had both believed that gravitational force alone would account for the observed fact that the temperature of the atmosphere decreases as one goes up, and this seemed to be one of the more important applications of the kinetic theory.[5] To Maxwell it was obvious that a situation in which "the temperature diminishes as the height increases at a greater rate than it does by expansion when air is carried up in mass" would lead to "a condition of instability, which is inconsistent with the second law of thermodynamics." Had he not made a mistake in calculation which led to this result, Maxwell might never have even raised the question at all. In any case he insisted that, according to the kinetic theory, the temperature should be the same at all heights, provided that a particular relation between average values of powers of the molecular velocity is valid; since this relation holds for the Maxwell velocity distribution he concluded that "this law of temperature, if true, [may be regarded as] in some measure a confirmation of the law of distribution of velocities."[6]

Maxwell's conclusion was confirmed and generalized by Boltzmann, who derived in 1868 the "Boltzmann factor" giving the effect of external forces on the velocity-distribution function (§6.1). Following a discussion with Guthrie in the columns of *Nature*, Maxwell published his own concise derivation of the generalized distribution law in 1873 (§10.6). The result that temperature is the same at all heights was challenged by Loschmidt in 1876 as part of his attempt to reinterpret the Sound Law of Thermodynamics (§14.5), and was not accepted by some later writers on meteorology.[7] There does not seem to have been any attempt to make a direct experimental test; in the earth's atmosphere the conditions of the theorem are violated since heat is continually being supplied in different amounts at the top and bottom of any vertical column because of radiation by the sun and earth, so this situation is not the same as the idealized one considered by Maxwell and Boltzmann.

In Maxwell's letter to Stokes, 30 May 1859, from which we have already quoted in §5.2, the supposedly unsatisfactory result that viscosity is independent of density is partially compensated by another conclusion deduced from the kinetic theory:

> If two sets of particles act on each other the mean *vis viva* of a particle will become the same for both, which implies, that equal volumes of gases at some press. and temp. have the same number of particles, that is, are chemical equivalents. This is one satisfactory result at least.

Maxwell was careful to note that this conclusion (he did not call it "Avogadro's hypothesis") followed from the equipartition theorem, in both his 1860 and 1867 papers.[8] Hence, he claimed that the kinetic theory gives an explanation of the "law of equivalent volumes" in gaseous reactions. He had the opportunity to make this point to British chemists at a meeting of the Chemical Society of London in June, 1867, when he participated in the discussion of Sir Benjamin Brodie's proposal to replace the atomic theory by a symbolic calculus of chemical operations.[9] Maxwell noted that the chemical atomic theory was based on an assumption which could now be deduced "from purely dynamical considerations" based on "the supposition advocated by Professor Clausius and others, that gases consist of molecules floating about in all directions, and producing pressure by their impact." That assumption (Maxwell called it a definition) was "that for every kind of substance the number of atoms, or molecules, in the gaseous state, occupying the space of a litre, at a temperature of 0 degrees, and of a pressure of 760 millimetres, must necessarily be the same." But actually finding that number was a step which "might be far off."[10] (Loschmidt's 1865 paper on molecular size apparently had not yet come to Maxwell's attention, though as early as 1861 he was eagerly awaiting the results of William Thomson's investigations on this subject.[11])

As noted at the end of §4.3, the fact that Avogadro's hypothesis was consistent with (and perhaps derivable from) the kinetic theory was of some assistance to the chemists who were trying to establish this hypothesis. A few years later the Chemical Society was given the following assessment of the connection between physical and chemical atomic theories by Cannizzaro, in his Faraday lecture:

> I have no hesitation in affirming that the solid base, the corner-stone of the modern theory of molecules and atoms, is the theory of Avogadro, Ampère, Kroenig, and Clausius, that is to say, the hypothesis that *these gases, at equal temperatures and pressures, contain in equal volumes equal numbers of molecules, whatever may be their nature and their weight*.... If any one amongst you, Gentlemen, still retain any doubt respecting the solidity of this foundation, I would invite him, not so much to examine the mathematical demonstrations of the constitutions of gases, and the discussion which has been raised in Germany as to their exactness, as to review the history of chemistry from the time when Gay-Lussac and Dumas introduced the practice of taking account of the weights and volumes of substances in the state of gas, down to our day.

While that last remark might seem like a put-down of the kinetic theory evidence for atomism, Cannizzaro again mentions the Krönig–Clausius theory and then says that we can avoid the various complications involved in the details of molecular structure if we

> start from the theory of the constitution of perfect gases, which is altogether independent of the notion of atoms and of chemical transformation.... I need scarcely remind you that the notion of a molecule, stripped of all the fantastic detail with which it has been encumbered, has acquired great credit amongst men devoted to mathematical and physical studies.[12]

In support of this statement he mentions Maxwell's "eloquent discourse" at the Liverpool meeting of the British Association,[13] and Tyndall's lecture on the "Scientific use of the imagination" delivered at the same meeting in 1870.[14]

Notes for §5.3

1. J. C. Maxwell, *B. A. Rep.* **30**, 15 (1860).
2. J. Dorling, *Stud. Hist. Phil. Sci.* **1**, 229 (1970). S. G. Brush, *Arch. Rat. Mech. Anal.* **39**, 1 (1970). A. F. Chalmers, *Br. J. Phil. Soc.* **24**, 164 (1973).
3. MS "On the Conduction of Heat in Gases" at Cambridge University.
4. *Nature* **16**, 242 (1877) (quotations from p. 245).
5. J. Herapath, *Mathematical Physics* **2**, 143. J. J. Waterston, *Collected Scientific Papers*, p. 253.
6. Brush, *Kinetic Theory* **2**, 85.
7. See the critical review by A. Schmidt, *Gerlands Beiträge zur Geophysik* **4**, 1 (1900) and other works cited therein.
8. Brush, *Kinetic Theory* **1**, 164, **2**, 32, 71.
9. See the historical articles by W. H. Brock, D. M. Knight, and D. M. Dallas in *The Atomic Debates* (Leicester: Leicester University Press, 1967).
10. J. C. Maxwell, *Chem. News* **15**, 303 (1867), reprinted in *Classical Scientific Papers: Chemistry* (New York: American Elsevier, 1968), p. 251.
11. Letter from Maxwell to W. Thomson, 17 December 1861, published in *Proc. Camb. Phil. Soc.* **32**, 733 (1936).
12. S. Cannizzaro, *J. Chem. Soc.* [2] **10**, 841 (1872) (quotations from pp. 946, 950). Nevertheless, more than 30 years later A. N. Meldrum complained against the common statement that Avogadro's hypothesis is supported by the kinetic theory, on the grounds that the latter is still only an hypothesis itself. See *Avogadro and Dalton* (Aberdeen: Printed for the University, 1904), p. 23.
13. J. C. Maxwell, *Scientific Papers* **2**, 215.
14. J. Tyndall, *Fragments of Science* (New York: Appleton, 6th ed., 1897), **2**, 101.

5.4 Reception of the kinetic theory in the 1860's

Having followed the major developments in the theory up to the point when it was radically revised by Maxwell and Boltzmann, we shall now examine the reaction of other scientists to it. The following quotations are from the period 1850–73, and show an increasingly more favorable attitude; as we shall see later on, the kinetic theory still had to undergo severe criticism before attaining its present established position.

We begin by introducing a rather interesting minor figure, George Johnstone Stoney (1826–1911). Stoney was Irish; his sister was the mother of George Francis Fitzgerald. He was educated at Trinity

College, Dublin, where he received his B.A. in 1848; in 1852 he was elected to the chair of Natural Philosophy at Queen's College, Galway (one of the unsuccessful rivals for this position was John Tyndall), but in 1857 he returned to Dublin as Secretary of the Queen's University, a position he held until 1882. He moved to London in 1893 so that his daughters could have a university education.[1]

In 1858 he published a short note in the *Proceedings of the Royal Irish Academy*, "demonstrating that the law of Boyle is contrary to the view that the particles of a gas are at rest, or that it can be a continuous substance." He discussed the static theories of Cauchy, Navier, Poisson, Haughton, and Jellett, and concluded:

> The examination which has been made above shows, no doubt, in the case of gases, as it does for either solids or liquids, that their constitution cannot be that of a stationary system, each molecule of which acts, but to a trifling extent, on each of those around it. But it does not show that it may not be such a system in a state of vivid molecular motion. The closer investigation of this hypothesis opens a new branch of the subject.

Stoney does not mention the work of Herapath, Joule, and Clausius in this paper, and he did not publish anything more on the kinetic theory until 1867. In that year he discussed the composition of atmospheres as influenced by gravity and varying temperatures, a subject to which he returned much later (1897, 1900, 1904, 1905). In 1868 he published one of the earliest estimates of atomic magnitude based on the kinetic theory.[2] He proposed the name "electron" for the smallest unit of electricity, and estimated its magnitude in 1874.[3] Other papers on the theory of the radiometer and specific heats of gases are listed in the Bibliography; they are the work of a scientist who was clearly aware of the direction in which science was going even though he did not himself make any discoveries of major importance.

The propagation of the kinetic theory in England was to some extent due to the popular lectures and books of John Tyndall, who was appointed Professor of Natural Philosophy at the Royal Institution of London in 1853 and succeeded Faraday as superintendent in 1867. Tyndall's efforts in getting the works of Clausius published in English translation have already been mentioned (§4.3). His experimental work on radiant heat will be discussed in §13.6. In a lecture in 1862, later published in his book *Heat as a Mode of Motion*, Tyndall gave a qualitative exposition of the kinetic theory, together with experiments illustrating the behavior of gases. Since the book went through several editions one may suppose that it had some influence in popularizing the kinetic concepts of heat and gases among scientists and educated laymen who were not able to understand the detailed mathematical theory.

Tyndall cannot be counted as an entirely faithful adherent of the theory himself, for in an article in *Philosophical Magazine* in 1863 he wrote

> ... a medium also embraces our atoms; within our atmosphere exists a second, and a finer atmosphere, in which the atoms of oxygen and nitrogen hang like suspended grains.... We must not only figure our atoms suspended in this medium, but we must figure them vibrating in it. In this motion of the atoms consists what we call their heat....[4]

In 1862, T. R. Birks published a book *On Matter and Aether*, which included the statements that heat is simple atomic or molecular kinetic energy, and that heat of vaporization is the energy spent in removing atoms to a distance beyond the range of their cohesive power. An anonymous reviewer in the *Philosophical Magazine* quoted these statements, and, despite their similarity to the doctrines of the kinetic theory and other atomic theories, all developed in the pages of *Phil. Mag.* in the preceding few years, said:

> Surely these numerous assertions can only be regarded as expressive of personal conceptions, the correspondence of which to physical realities is proved neither by immediate explanations of phenomena, nor by explanations deduced by mathematical reasoning.[5]

In 1863, Thomas Graham showed how the kinetic theory explained his experiments on diffusion, and wrote:

> According to the physical hypothesis now generally received, a gas is represented as consisting of solid and perfectly elastic spherical particles of atoms, which move in all directions, and are animated with different degrees of velocity in different gases.[6]

Two years later A. G. Girdlestone asserted:

> That gases are bodies whose particles are moving in straight lines is now no hypothesis, but a fact resting on empirical demonstrations, derived from the phenomena of diffusion, heat, etc.[7]

Balfour Stewart, in his textbook on heat (1866), also thought that the theory had been established, and referred to Maxwell's viscosity experiments.[8] Yet in 1868 Stoney was not satisfied with the reception of the kinetic theory:

> The dynamical theory of the molecular constitution of gases, which if I mistake not, may be ranked in point of importance and probability along with the wave-theory of light, does not appear to have yet met with that general attention and acceptance which it seems to deserve.[9]

> Rayleigh, in 1872, wrote that the kinetic theory

> has certainly great and increasing claims to be considered at least a truthful representation of the facts.[10]

W. K. Clifford, in popular lectures delivered the same year, was just as emphatic:

> We know that a gas consists of a vast number of separate molecules, rushing about in all directions with all manner of velocities... the manner in which the molecules interfere with each other proves that they repel one another inversely as the fifth power of the distance.[11]

Clifford noted that the kinetic theory is an example of describing the "unknown and unfamiliar as being made up of the known and the familiar; and this, it seems to me, is the true meaning of explanation."[12]

Maxwell's 1873 lecture on "Molecules" at the British Association meeting at Bradford–probably the most widely quoted of his writings, according to Campbell and Garnett[13]–presented a detailed though qualitative survey of the methods and results of the kinetic theory. His emphasis was on the "definite information" which had already been obtained about molecular properties, including the estimates of molecular sizes by Loschmidt, Stoney, and William Thomson; in spite of the need for using statistical techniques, Maxwell supported Sir John Herschel's view of the absolute identity of all molecules of the same chemical element. The overall impression conveyed by this lecture was that the kinetic theory of gases was now completely established, and was the most powerful tool available for probing the invisible world of atoms and molecules.[14]

In Germany, meanwhile, the kinetic theory had received the endorsement of Hermann von Helmholtz, in a lecture delivered in 1862:

> We must... conclude... that heat itself is a motion, an internal invisible motion of the smallest elementary particles of bodies. If, therefore, motion seems lost in friction and impact, it is not actually lost, but only passes from the great visible masses to their smallest particles....
>
> But what is the nature of this internal motion can only be asserted with any degree of probability in the case of gases. Their particles probably cross one another in rectilinear paths in all directions, until, striking another particle, or against the side of the vessel, they are reflected in another direction. A gas would thus be analogous to a swarm of gnats, consisting, however, of particles infinitely small and infinitely more closely packed. This hypothesis, which has been developed by Krönig, Clausius, and Maxwell, very well accounts for all the phenomena of gases.[15]

Gustav Fechner mentioned it without much enthusiasm in the second edition of his book on atomism, published in 1869.[16]

The contributions of O. E. Meyer, who was primarily an experimentalist but also developed the mean-free-path theory, reinforced those of Clausius in Germany. In 1867, A. Naumann used the kinetic theory to estimate the sizes and velocities of molecules and commented on the state of the theory:

> The uninterrupted development of the mechanical theory of heat has furnished continually increasing grounds of support for Clausius's view that the thermal content of a perfect gas... is represented by the progressive motion of the molecules, and by the motions of the constituent atoms of the molecules. In particular, the principle maintained by Clausius, according to which the *vis viva* of the progressive motion of the molecules is, in the case of all gases, proportional to the absolute temperature... has received a beautiful experimental confirmation from the recent researches of O. E. Meyer upon the internal friction of gases....[17]

In Vienna, Josef Stefan was using the kinetic theory to give an elementary discussion of the propagation of sound and heat in a gas as early as 1863, though his major work did not come until the following decade.[18] Josef Loschmidt, as mentioned in §1.8, used the mean-free-path formula to estimate the size of an atom in 1865. Ludwig

Boltzmann's first paper on kinetic theory appeared in 1868 (§6.1). Even Ernst Mach was sympathetic to the ideas of Krönig and Clausius in 1863 (§8.2).

In France there was not much interest in the kinetic theory; I have found a favorable reference by E. H. Amagat in 1869,[19] but there is also some evidence that the caloric and wave theories of heat had not been completely abandoned.[20] On the other hand the Académie des Sciences criticized a memoir by Ludvig Colding on the grounds that it rejected the Krönig–Clausius gas theory.[21]

In Italy, Luigi Magrini supported the kinetic view of matter, mentioning Graham's diffusion experiments, in a popular article that was translated in both France and America in 1867.[22] Five years later the famous chemist Cannizzaro told the Chemical Society of London, in a speech from which I have already quoted in §5.3, that he had "no hesitation in affirming" that the Krönig–Clausius gas theory based on Avogadro's hypothesis is the foundation of modern atomic theory.[23]

The kinetic theory received fairly early recognition in America: in 1861, Simon Newcomb reported at a meeting of the American Academy of Arts and Sciences in Boston:

> One of the most beautiful hypotheses ever propounded in physics is that which has lately been known as the Dynamical Theory of Gases.

He referred to Maxwell's papers and mentioned the discrepancy in the specific heats, then concluded:

> Considering the number and variety of the phenomena of gases which are accounted for on this theory, and especially the exactness with which it accounts for the hitherto inexplicable phenomena of diffusion, there seems to be a considerable probability in its favour. The small discrepancy between the observed and computed ratio of the specific heats (1.42 and 1.33) may be found to proceed from some property of the particles not taken account of in the mathematical analysis.[24]

John LeConte, another American, discussed various theories of the velocity of sound in a paper written in 1861 and published in the *Philosophical Magazine* in 1864. He referred to Herapath's formula for the velocity of sound, which "seems to have been a deduction from his ingenious speculations on molecular physics, the basis of which rests upon atomic considerations." He also said that "the fact that the development of the Dynamical Theory of Heat has cast so much light on the theory of the propagation of sound waves in the atmosphere, is one among many illustrations of the interconnexion of all branches of physical science."[25]

* * *

Although the identification of heat with molecular motion was fairly widely accepted after 1850, many scientists continued to pursue molecular theories which they considered in some way superior to the kinetic theory, though not necessarily denying its applicability for some purposes. The two principal alternatives were the "dynamic" view of the atom as a center of force, and the "atmospheric atom" which exchanged heat vibrations with other atoms through an intermediate ether; while these represented opposing world views, they were often mixed together.

In England, James Croll criticized Tyndall's theory of radiation based on "excursions" of the atom across centers of equilibrium external to itself. He argued instead that

> ... the ultimate atom itself is *essentially elastic.* For if heat-vibrations do not consist in excursions of the atom, then it must consist in alternate expansions and contractions of the atom itself. This again is opposed to the ordinary idea that the atom is essentially solid and impenetrable. But it favours the modern idea, that matter consists of a force of resistance acting from a centre.[26]

By 1867 Croll was completely converted to the notion that the atom is a center of force.[27] Arthur Ransome, too, thought that most phenomena could be explained by means of molecular forces rather than by postulating imponderable atmospheres with various properties.[28] But James Challis continued to develop his hydrodynamical theory:

> I suppose an elastic fluid to consist of inert spherical atoms of constant magnitude, each of which, by means of the reflexion of aetherial undulations from its surface, becomes a centre of repulsive force, the undulations being of necessity such that by their dynamical action they keep the atoms asunder.[29]

In another paper (1865), Challis discussed mathematically the possibility that the vibratory motions of the aether could produce "permanent motions of translation of atoms" and hinted that the forces of heat, aggregation, and gravity were due to this phenomenon.[30] In fundamental physics, he claimed, no other kind of force should be recognized than *pressure.*[31]

W. A. Norton, an American, published a long series of papers on a theory somewhat similar to that of Challis, but postulated that each atom of matter is surrounded by two atmospheres, one consisting of "electric ether," the other of "universal ether." Heat is due to "a series of repulsions, or outward acting impulses, imparted by the universal ether at the surface of the atom by the contractile force exerted by the atom upon its electric atmosphere."[32] As late as 1879 Norton rejected the kinetic theory and derived "Mariotte's law" from a static repulsive model of gases.[33]

In Germany the atmospheric atom was still popular, as shown in this report by Gustav Zeuner:

> That view of the constitution of bodies is the most widespread, which considers the body as made up of invariable particles, "atoms," whose distances apart are relatively very great.... These atoms attract each other.... The relatively large spaces between the molecules are filled with ether.... The ether surrounds the molecules and atoms in atmospheric fashion. These atmospheres, whose density diminishes from within outward, constitute with their kernel an individual whole. An atom with its envelope of ether Redtenbacher called a "Dynamide." ... Only in one point do the views diverge, namely, as to the question whether the so-called heat motion is caused by the motion of the atoms, *i.e.* of the material parts of the body, or by the motion of the ether particles collected in the body.... Redtenbacher assumed that the heat motion consisted in the radial motion of the ether envelopes surrounding the atoms or molecules of the body; these envelopes expand and contract....[34]

But Zeuner also notes that "Clausius defended another view with far-reaching consequences."

In France there was still skepticism. Achile Cazin hesitated to accept the kinetic theory because it was so speculative that a single contradictory experiment might overthrow it. (Apparently he was not familiar with Maxwell's later writings on this point.) He emphasized that the essential character of the mechanical theory of heat (*i.e.* macroscopic thermodynamics) is that it is independent of any hypothesis about the actual nature of heat; while that theory is obviously favorable to certain hypotheses, such as that heat *is* molecular motion, the best that can be said for such hypotheses is that "they disengage us from the old ideas, and certainly prepare for other, more complete hypotheses, which will be suggested by a more profound knowledge of the phenomena."[35] "For the savant", he said, "the cause of heat is of the same order with that of the fall of bodies which it is not his mission to fathom."[36]

The vortex atom theory, developed in different ways by Rankine and by William Thomson, was also quite popular during this period.[37] Rankine argued that the hypothesis of Herapath and Waterston is defective "inasmuch as it gives a fixed value, 5:3 or $1\frac{2}{3}$ for the ratio of the specific heat at constant volume; whereas that ratio is certainly known to be 1.408 for those gases in which it is the greatest." Rankine claimed that his own hypothesis of molecular vortices gives better agreement with experiment, though he avoids a detailed discussion on this point.[38]

William Thomson was enthusiastic about the vortex theory of Helmholtz and suggested that a mathematical development of the properties of vortex rings might show that they are the true atoms:

> Probably the beautiful investigations of D. Bernoulli, Herapath, Joule, Krönig, Clausius, and Maxwell on the various thermodynamic properties of gases, may have all the positive assumptions they have been obliged to make, as to mutual forces between two atoms and kinetic energy acquired by individual atoms or molecules, satisfied by vortex rings, without requiring any other property in the matter whose motion composes them than inertia and incompressible occupation of space. A full mathematical investigation of the mutual action between two vortex rings of any given magnitudes and velocities passing one another in any two lines, so directed that they never come nearer one another than a large multiple of the diameter of either, is a perfectly solvable mathematical problem; and the novelty of the circumstances contemplated presents difficulties of an exciting character. Its solution will become the foundation of the proposed new kinetic theory of gases.[39]

Thomson's attitude was favorable to the kinetic theory of gases during the 1860's and 1870's; by basing it on the vortex theory he thought it could be made *purely* kinetic, eliminating the need to postulate arbitrary intermolecular forces.

Maxwell was interested in the vortex theory for much the same reasons:

> If a theory of this kind should be found, after conquering the enormous mathematical difficulties of the subject, to represent in

> any degree the actual properties of molecules, it will stand in a very different scientific position from those theories of molecular action which are formed by investing the molecule with an arbitrary system of central forces invented expressly to account for the observed phenomena.
>
> In the vortex theory we have nothing arbitrary, no central forces or occult properties of any other kind. We have nothing but matter and motion, and when the vortex is once started its properties are all determined from the original impetus, and no further assumptions are possible.
>
> Even in the present undeveloped state of the theory, the contemplation of the individuality and indestructibility of a ring-vortex in a perfect fluid cannot fail to disturb the commonly received opinion that a molecule, in order to be permanent, must be a very hard body.[40]

At the same time Maxwell suggested that if we want "standards of length, time, and mass which shall be absolutely permanent, we must seek them not in the dimensions, or the motion, or the mass of our planet, but in the wavelength, the period of vibration, and the absolute mass of these imperishable and unalterable and perfectly similar molecules." He did not explain how, starting with nothing but a perfect fluid, unique fundamental units of length, time, and mass could be obtained.[41]

The vortex atom attracted considerable attention during the last part of the 19th century but the mathematical investigations suggested by Thomson never succeeded in deriving all the properties of real atoms and molecules from the theory. The fact that so much effort was devoted to these attempts is certainly striking evidence of the residual appeal of the Cartesian program, especially among scientists who presumably considered themselves followers of the Newtonian paradigm which called for a search for *forces* to account for phenomena (§11.2).

It is curious that once the kinetic theory had been established, the older static theory of gases was hardly ever mentioned, and there were very few attempts to compare the two theories in the light of recent experimental investigations. One article that does discuss both theories together is a review by W. Gosiewski (1844–1911), a Polish theoretical physicist living in Paris at the time (1874).[42] Gosiewski devotes nearly half of his article to a discussion of the static theories of Newton and Laplace, which he says must nevertheless be rejected because they are based on the discredited caloric theory. He then outlines the kinetic theory, mainly on the basis of the papers of Clausius. Although he gives an account of the virial theorem which Clausius had published in 1870, he ignores Maxwell's work on the velocity distribution of gas molecules and on the theory of transport processes. The omission of any reference to the papers of Boltzmann, Herapath, or Joule also suggests that Gosiewski had not studied the subject as thoroughly as one might wish. However, this defect is somewhat compensated by the account of the Newton and Laplace theories. His treatment of the problem of specific heats is rather disappointing; he seems to be willing to introduce the ratio of molecular to atomic kinetic energy as an adjustable parameter chosen to fit experimental results. There is a brief discussion of the mechanism of dispersion of sound waves in gases.

Notes for §5.4

1. On Stoney, see the obituary in *Proc. R.S. London* **86**, xx (1911) by "J. J."
2. G. J. Stoney, *Phil Mag.* [4] **36**, 132 (1868); see §1.8 for estimates by Loschmidt and others. See also his statements supporting the kinetic theory in *Proc. R.S.* **16**, 25 (1868), **17**, 1(1869).
3. G. J. Stoney, *B. A. Rep.* (1874); *Phil. Mag.* [5] **11**, 381 (1881); [5] **38**, 418 (1894). D. L. Anderson, *The Discovery of the Electron* (Princeton, N.J.: D. Van Nostrand Co., 1964), p. 75. J. G. O'Hara, *Notes and Records, R. S. London* **29**, 265 (1975).
4. J. Tyndall, *Phil. Mag.* [4] **25**, 200 (1863). In a popular article two years later, Tyndall suggested that vibrational but not translational motion of atoms should be considered heat: *Fortnightly Review* 3, 129 (1865), especially page 135. Even the later editions of *Heat as a Mode of Motion* state that while the kinetic theory is "very ably maintained," it is only "an hypothesis advocated by eminent men" which he himself neither accepts nor rejects (see page 59 of the 4th American edition, New York, 1873).
5. *Phil. Mag.* [4] **25**, 304 (1863); T. R. Birks, *On Matter and Aether, or the Secret Laws of Physical Change.*
6. T. Graham, *Phil. Mag.* [4] **26**, 409 (1863).
7. A. G. Girdlestone, *Phil. Mag.* [4] **29**, 108 (1865).
8. B. Stewart, *An Elementary Treatise on Heat* (Oxford, 1866), p. 367.
9. G. J. Stoney, *Phil. Mag.* [4] **36**, 132 (1868).
10. Rayleigh, *Phil. Mag.* [4] **44**, 219 (1872).
11. W. K. Clifford, *Lectures and Essays* (London: Macmillan, 1879), **1**, 138.
12. *Ibid.*; see also **1**, 158.
13. *Life of James Clerk Maxwell*, p. 358.
14. J. C. Maxwell, *Nature* **8**, 437 (1873); *Papers* **2**, 361.

    Clifford, commenting on Maxwell's Bradford address, remarked that because of the supposed similarity between the kinetic theory and Greek atomism, many people familiar with the latter think they are qualified to criticize the former, not realizing that it rests on much firmer evidence. He gave his own argument for atomism: "since compression of a gas within certain limits does not alter the rate of vibration which belongs to it, that rate of vibration cannot belong to the body of the gas as a whole, but it must belong to the individual parts of it. Now, by such reasoning as this it seems to me that the modern theory of the constitution of matter is put on a basis which is absolutely independent of hypothesis. The theory is simply an organized statement of the facts." But Clifford did not accept Maxwell's claim that all atoms of a substance are identical. See *Lectures and Essays* **1**, 222, 236.

15. H. von Helmholtz, "Ueber die Erhaltung der Kraft," *Vortrage und Reden* (Braunschweig, 5 Aufl. 1903), I, 187; English trans. in *Popular Scientific Lectures*, ed. M. Kline (New York: Dover Pubs., 1962), p. 186 (quotation from pp. 212–13). Helmholtz had previously reviewed the papers of Waterston, Joule, and Krönig in *Fortschr. 1850 und 1851*, p. 561 (1855), *Fortschr. 1856, p.* 352 (1859).
16. *Ueber die physikalische und philosophische Atomenlehre* (Leipzig, 2, Aufl. 1864), **96**, 219. "Insbesonder über die Wärme der Gase sind neurerdings (von Krönig und Clausius) eigenthunliche, mindestens von gewisser Seite her sehr probable, Ansichten aufgestellt worden, welche von vielen Physikern getheilt werden." (p. 96) "Mit der Ansicht von Krönig und Clausius über die Wärme der Gase, welche vieles gut erklärt, vertrüge sich dies allerdings nicht, sofern hier ein Bewungung der ganzen Gasmolecule als den Wärmezustand der Gase bedingend angeschen wird..." (p. 219). In the introduction to this edition he wrote: "Seit dem Erscheinen der vorigen Auflage dieser Schrift (1855) hat sich der Stand der physikalischen Atomistik nicht wesentlich geändert; sie hat sich nur fort weiter entwickelt und ist damit immer fester gewurzelt, wie ein Baum nach Massgabe, als er mehr Zweige treibt, auch fester wurzelt." See §8.2 for the possible influence of Fechner's writings on Mach.
17. A. Naumann, *Ann. Chem. Pharm.* **142**, 265, 284 (1867); *Phil. Mag.* [4] **34**, 205, 373 (1867). Naumann also cited as evidence for the kinetic theory "the recent microscopic observations [Fick, *Die Naturkräfte in ihrer Wechselbeziehung* (Würzeburg, 1869), p. 27] that fine particles floating in the air are animated by a tremulous motion..." [Naumann, *Ber. D. Chem. Ges.* **2**, 690 (1869): *Phil. Mag.* [4] **39**, 217 (1870)].
18. J. Stefan, *Wien Ber.* **47**, 81 (1863); *Ann. Phys.* [2] **118**, 492 (1863); see § 13.5 for his later work on heat conduction in gases, which was related to his discovery of the T^4 radiation law (§13.7).
19. E. H. Amagat, *C. R. Paris* **B8**, 1170 (1869); this is an experimental paper on the equation of state of gases, whose results he says are explicable by means of the "hypothesis of Bernoulli." In a later paper on compressibility of gases at high pressure, he claims to have adopted the kinetic theory but still invokes a caloric-ether to explain his results: *Ann. Chim. Phys.* [5] **22**, 353 (1881), English trans. in *The Laws of Gases*, ed. C. Barus (New York, 1899), p. 13.
20. See works cited in §9.6, note 4.
21. *Ludvig Colding and the Conservation of Energy Principle*, ed. Per F. Dahl (New York: Johnson Reprint Corp., 1972), pp. 140, 155.
22. L. Magrini, *Rev. Cours. Sci.* **4**, 769 (1867); *Smithsonian Report*, p. 281 (1868).
23. S. Cannizzaro, *J. Chem. Soc.* [2] **10**, 941 (1872).
24. S. Newcomb, *Proc. Am. Acad.* **5**, 112 (1862) (quotations from pp. 112 and 113).
25. J. LeConte, *Phil. Mag.* [4] **27**, 1 (1864); but see the skeptical remarks of Potter, *Phil. Mag.* [4] **27**, 107 (1864) on this subject.
26. J. Croll, *Phil. Mag.* [4] **27**, 346 (1864).
27. J. Croll, *Phil. Mag.* [4] **34**, 449 (1867).
28. A. Ransome, *Manchester Proc.* **6**, 121 (1867); *Phil. Mag.* [4] **33**, 360 (1967).

29. J. Challis, *Phil. Mag.* [4] **27**, 92 (1864).
30. J. Challis, *Phil. Mag.* [4] **10**, 207 (1865).
31. J. Challis, *Phil. Mag.* [4] **31**, 459 (1866).
32. W. A. Norton, *Phil. Mag.* [4] **10**, 95 (1865).
33. W. A. Norton, *Am. J. Sci.* [3] **3**, 327 (1872), **17**, 346, 433 (1879) (see p. 441 for his "comparison of the present with the kinetic theory of gases").
34. G. A. Zeuner, *Grundzüge der mechanischen Wärmetheorie* (Leipzig, 2, Aufl. 1866); English trans., *Technical Thermodynamics* (London, 1907), quoted from pp. 6 and 7. The work of Redtenbacher mentioned is *Dynamidensystem* (Mannheim, 1857).
35. A. Cazin, *C. R. Paris* **66**, 483 (1868); *Phil. Mag.* [4] **40**, 81, 197, 268 (1870).
36. A. Cazin, *Smithsonian Report*, p. 231 (1868), trans. from *Rev. Sci.* (1867).
37. *Royal Society Catalogue*, Subject Index III, 81–82, R. H. Silliman, *Isis* **54**, 461 (1963). P. J. Pauly, *Vortices and Vibrations: The Rise and Fall of a Scientific Research Program* (M.A. Thesis, Univ. of Maryland, College Park, 1975).
38. W. J. M. Rankine, *Trans. R. S. Edinburgh* **20**, 565 (1853); *Proc. Glasgow Phil. Soc.* **5**, 126 (1864).
39. W. Thomson, *Proc. R. S. Edinburgh* **6**, 94 (1869); *Phil. Mag.* [4] **34**, 15 (1867); *Mathematical and Physical Papers* (Cambridge University Press, 1910), **4**, 1.
40. J. C. Maxwell, *B. A. Rep.* **40**, 1 (1870); *Scientific Papers* **2**, 215 (quotation from p. 223).
41. On the contrary, for S. Tolver Preston it was the infinity of possible permutations of the vortex atom that made it so attractive, by giving scope for the infinite variety of thought. *Nature* **21**, 323 (1880).
42. W. Gosiewski, *Towarzystwo Nauk Scislych w Paryzu Pamietnik* **5**, no. 2, 1 (1874); English trans. by S. Shewchuck, University of California, Lawrence Radiation Laboratory, Livermore, report UCRL-Trans-885(L) (Oct. 1962).

5.5 Maxwell, Osborne Reynolds, and the radiometer*

Many window-shoppers are familiar with the radiometer, a sidewalk attention-getting device frequently displayed by jewellers. It is a simple instrument, consisting of a small glass bulb, partially evacuated, inside of which a set of vanes is mounted on a spike. Each vane is silvered on one side and blackened on the other. When the radiometer is placed in sunlight or near a source of heat, the vanes spin around.

Some rather involved physics is needed to explain completely how a radiometer works; we shall not attempt it here.[1] This section will recount how physicists sought an understanding of the phenomenon nearly a hundred years ago, and in so doing laid the foundations of the modern science of rarified gas dynamics. This account relies heavily on referees' reports preserved in the Royal Society Archives; they contain

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valuable evidence of the relations between the protagonists. Referees' reports in general are a useful primary source which has been too much neglected by historians of science.[2]

In 1873 the English chemist William Crookes was attempting to determine the atomic weight of thallium, an element he had discovered spectroscopically a few years before. Realizing that his delicate pan-balance might be disturbed by irregular air currents, he made his weighings in a vacuum. To his great surprise, he found that heat seems to diminish the weight of bodies in a vacuum. Further investigation showed that while the body moves up when the heat source is below it, it moves down when the source is above. Thus the effect is not simply a change of weight, but rather a directed force of repulsion associated with heat.[3] It was to illustrate this force more conveniently that Crookes constructed his radiometer (fig. 5.5-1).

Although "light-mills" similar to the radiometer had been made and studied in Germany (fig. 5.5-2), it was not until Crookes began to publicize his discovery that the radiometer attracted the attention of the scientific world at large. The intense, though short-lived, interest of contemporary scientists in the radiometer is indicated by the hundreds of publications in scientific and popular journals between 1875 and 1877. Anyone with a moderate degree of mechanical skill could construct his own radiometer, try variations in the size, shape, and color of the parts of the instrument, record the effects of temperature, pressure, humidity, and time of day, and have the satisfaction of publishing his results as a contribution to science. Those with a more theoretical bent could rush into print with their speculations about how the radiometer works, uninhibited by any established theory.

The radiometer caused a sensation, most probably because it seemed to prove a direct pressure or repulsive force of light or heat. It thus had a direct bearing on the fundamental problem of the nature of light and radiation. It had long been thought that light might exert a pressure, although there was no definite experimental proof until the work of Lebedev in Russia and Nichols and Hull in the United States around 1900. Proponents of the corpuscular theory of light in the 18th century believed that their theory would be confirmed if it could be shown that rays of light possess momentum. Several tried the experiment of directing powerful beams of light on delicately suspended bodies. These experiments were generally inconclusive–rather, varying conclusions were drawn from them. The issue was further confused by the lack of agreement as to whether or not light pressure would also be expected on the wave theory. If the waves are

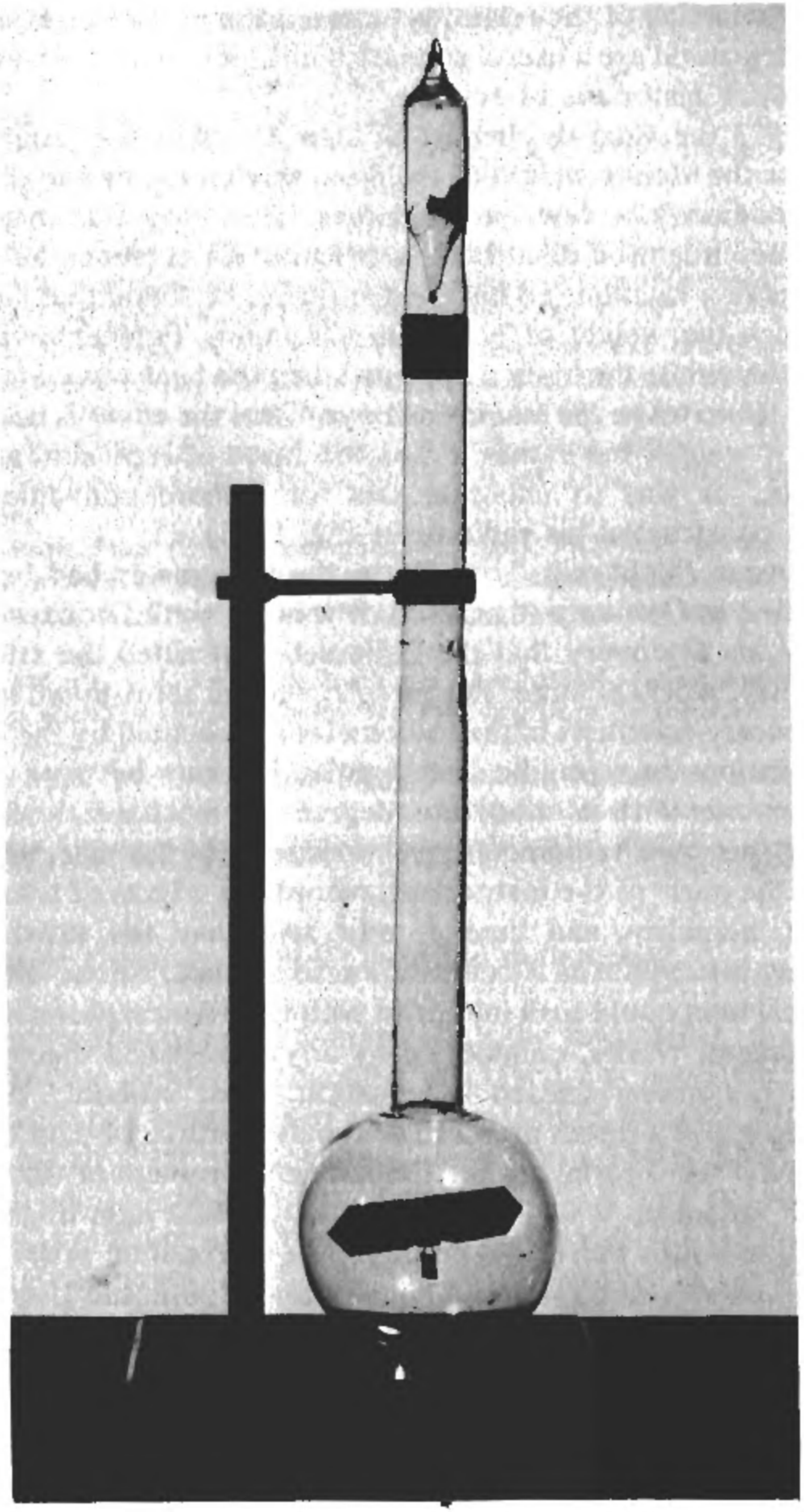


Fig. 5.5-1. Crookes' radiometer. [Photograph, Science Museum, London. Crown Copyright Reserved. Courtesy of Dr. F. Greenaway.]

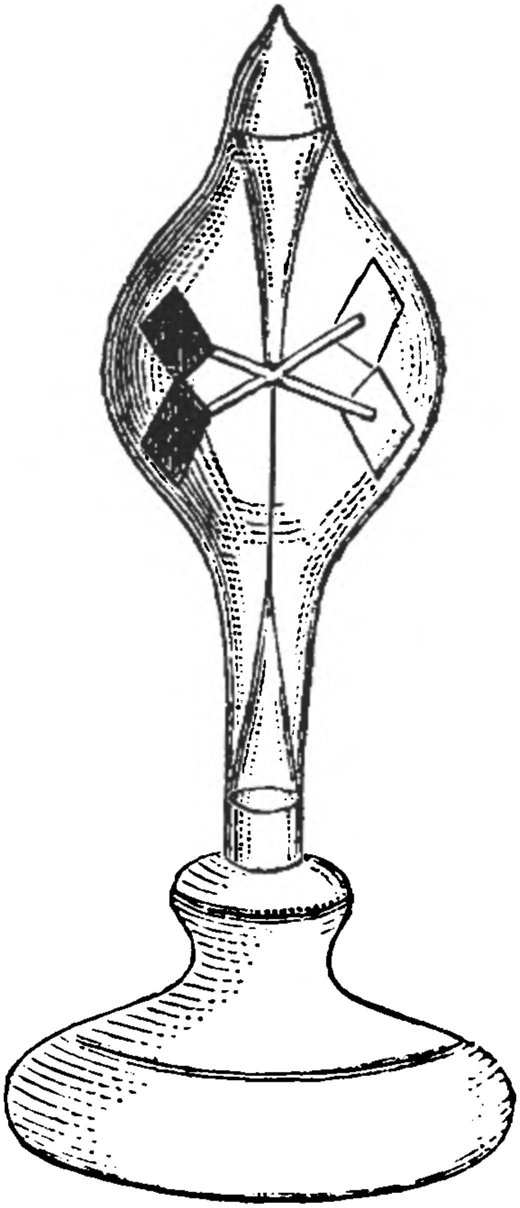


Fig. 5.5-2. Radiometer or light-mill constructed by Dr. Geissler of Bonn, as shown in Reynolds's paper in the *Phil. Trans.* **166**, 425 (1876).

longitudinal, there should be a pressure; but if they are transverse, as proposed by Young and Fresnel at the beginning of the 19th century, it is less certain, at least without Maxwell's electromagnetic theory.

A somewhat skeptical observer, the physician W. B. Carpenter, reported the initial reaction of British scientists in 1873: when the radiometer "was first exhibited at the soirée of the Royal Society, there was probably not one who was not ready to believe with its inventor that the driving round of its vanes was effected by the direct mechanical energy of that mode of radiant force which we call Light."[4] Carpenter criticized this "readiness to admit a novelty" as evidence of an unscientific attitude, and compared it with the gullibility of scientists who accepted accounts of supernatural phenomena.[5] This was an unkind dig at Crookes himself, who had been involved in investigations of spiritualism in the years immediately preceding.

According to Carpenter, "two of the most distinguished among British mathematical physicists" agreed with Crookes that the motion of the vanes was a direct effect of radiant energy. One of these may have been James Clerk Maxwell; in any case, Maxwell's first impressions of the radiometer are significant since he played an important role in the later development of its theory. In a letter to his friend William Thomson (later Lord Kelvin), Maxwell gave the following account of Crookes' demonstration at the Royal Society soirée:

> They whip spirits all to pieces. A candle at 3 inches acts on a pith disk as promptly as a magnet does on a compass needle. No time for air currents and the force is far greater than the weight of all the air left in the vessel. Attraction by a bit of ice very lively. All this at the best attainable vacuum. . . .[6]

Maxwell had made two major contributions to theoretical physics by this time, both relevant to the radiometer problem. First, in his 1867 paper on kinetic theory, he had developed a powerful method for dealing with viscosity, heat conduction, and diffusion in gases, based on transport equations for the flow of momentum, energy, and matter. Second, on the basis of his electromagnetic theory of light, Maxwell produced a quantitative estimate of the pressure of light. In his *Treatise on Electricity and Magnetism* (1873), Maxwell wrote that concentrated radiation from an electric lamp, "falling on a thin metallic disk, delicately suspended in a vacuum, might perhaps produce an observable mechanical effect," although he estimated that the force due to ordinary sunlight would be only about a tenth of the horizontal magnetic force in Britain (§793). Thus he would certainly be interested in the results of Crookes' experiments.

When Crookes submitted a written account of his work to the Royal Society, it was sent to Maxwell to review for publication in the *Philosophical Transactions.* Maxwell made his report on 24 February 1874. Fortunately the referees' reports on this and other papers on the radiometer (except for the ones published by Larmor in 1907 in the *Memoir and Scientific Correspondence* of G. G. Stokes) have been preserved at the Royal Society; they give a valuable insight into the development of the theory.

Maxwell wrote that Crookes "has made a great discovery with respect to the mode in which a body placed in air of different densities is acted on when bodies of different temperatures are placed near it. . . ." He agreed that the observed "repulsion from a heat-emitting body" is "due to radiation." Although, as he notes, he had suggested "a probable repulsive action of radiation" in his treatise on electricity, "the effects observed by Mr. Crookes seem to indicate forces of much larger value." Maxwell seems willing to accept this quantitative refutation of his own theory, and recommends publication of the paper.[7]

In the summer of 1874, Coggia's comet made a spectacular appearance in the skies of Europe. Its tail, visible for several weeks, showed the familiar behavior of pointing away from the sun. In the past, observations of comets had stimulated astronomers to suggest that some kind of repulsive action of the sun, perhaps light pressure, acts on the volatile matter of the comet and pushes it out on the opposite side. The new comet of 1874 must have reopened the discussion of light pressure in many European scientific circles, and helped to prepare the way for the radiometer fad of 1875–77.

Crookes himself suggested in his first paper that experiments on the radiometer might help to reveal something about the nature of the sun's repulsive action on comets. Maxwell had discussed comets' tails in earlier correspondence with astronomers, but had not adopted the light-pressure explanation. That comets' tails were a subject of conversation in Maxwell's house during the visit of the comet in 1874 is evident from an anecdote of Garnett: the frequent repetition of the word "tail" caused Maxwell's terrier to run round in circles chasing his own.[8]

One of the first scientists to challenge the light-pressure theory of the radiometer was Osborne Reynolds, Professor of Engineering at Owens College, Manchester. Reynolds thought comets' tails were either an electrical effect or a "negative shadow."[9] In 1873 he had published a paper on the steam engine where he discussed the condensation of a mixture of steam and air on cold surfaces; this study may have inspired his suggestion, a year later, that the radiometer effect depends on the condensation and evaporation of gas molecules at the surface of the vanes. Although his radiometer theory in its original form did not prove successful, it did prefigure in a general way later explanations based on gas-surface interactions. More important at the time, however, was the work of a young physicist, Arthur Schuster, who came to Manchester in 1875. Schuster, with Reynolds' encouragement, carried out what was subsequently regarded as the "crucial experiment" on the radiometer: the observation of the rotation of the radiometer case in a direction opposite to that of the vanes.[10] This was taken to mean that no momentum is brought into the system by the radiation, only energy; the actual turning of the vanes must then depend on some internal mechanism, presumably associated with the residual gas in the bulb.

By this time it had also been pointed out by several observers that light ought to produce a greater force on the reflecting, silvered side of the vanes than on the blackened side where it is absorbed; in fact they soon noted that the vanes move in just the opposite way.

By 1876, the British scientists who were actively working on the radiometer problem–Crookes, Schuster, Reynolds, Stoney, Dewar, and Tait–agreed that the rotation was not a direct effect of radiation striking the vanes, but that it depended in some way on the residual gas and the temperature difference between the two sides of the vanes. They thought that gas molecules striking the hot, black side would somehow exert more pressure than those striking the cold, silvered side. However, they disagreed about the precise reason for this pressure difference. They recognized that the ordinary methods of the kinetic theory of gases based on the Clausius mean-free-path concept were inadequate to deal with rarefied gases. The mean free path of a molecule might be larger than the distance a molecule travels between successive collisions with solid surfaces; in this case equilibration of temperature, which usually takes place rapidly as a result of intermolecular collisions, would be ineffective, and it might be possible for an unequally heated vane to establish a large temperature gradient in the surrounding gas. However, no one was able to calculate accurately the net force on the vanes due to this temperature gradient without arbitrary assumptions.

This was clearly a problem for an expert in kinetic theory, and Maxwell was frequently asked for his opinion. Realizing that the radiometer problem was very difficult, he did not want to commit himself in public until he had considered it carefully. His reports to the Royal Society on the papers of Crookes, Reynolds, and Schuster show him skeptical of the existing theories and, indeed, more concerned with the details of experimental apparatus than with theoretical explanations. However, on one occasion his reputation as an authority on physics forced him to appear before an imperious audience; in May of 1876 Maxwell wrote to his uncle, Robert Cay:

> . . . I was sent for to London, to be ready to explain to the Queen why Otto von Guericke devoted himself to the discovery of nothing, and to show her the two hemispheres in which he kept it,

> and the pictures of the 16 horses who could not separate the hemispheres, and how after 200 years W. Crookes has come much nearer to nothing and has sealed it up in a glass globe for public inspection. Her Majesty however let us off very easily and did not make much ado about nothing, as she had much heavy work cut out for her all the rest of the day....[11]

For the next year and a half there is little evidence of Maxwell's thinking about the radiometer problem. However, his official Cambridge University report reveals that the Cavendish Laboratory had acquired four radiometers by May 1877.[12] It was also during this period that Arthur Schuster came to Cambridge from Manchester. While the flurry of excitement about radiometers was generally dying down, since light pressure seemed not to be directly involved after all, Maxwell was just beginning to define the real problem for himself and to set to work on it seriously.

It was not until just before his death in 1879 that Maxwell's paper "On stresses in rarefied gases arising from inequalities in temperature" was completed: it was worth waiting for.[13] The main part of the paper was devoted to calculating the force resulting from temperature inequalities in the interior of a gas. Maxwell found that the stress in gases is proportional to the second spatial derivative of the temperature. Thus, contrary to the results of the earlier theories of Fitzgerald and Stoney, a constant temperature gradient (constant first spatial derivative) would not by itself produce an inequality of pressure. However, a small object in the gas, acting as a heat-source, could produce a changing temperature gradient and a resulting stress which might be sufficient to account for the motion of the radiometer vanes. If the vane itself is the source of the heat flow, the stress will be found only near the edges of the vane.

As Maxwell was careful to point out, his kinetic theory gives only the *normal* stress on the surface of the vane. The theory cannot be used to compute tangential stresses without further assumptions; in fact, the usual assumption in kinetic theory is that the physical state of the gas next to a surface is the same as that of the surface itself, in which case there can never be a tangential stress. This in turn involves two assumptions, one being that there is no "slipping" (discontinuous velocity change) of the gas relative to the surface, the other that there is no temperature-discontinuity. Both are of dubious validity in rarefied gases in view of the discovery of slip phenomena by Kundt and Warburg.[14]

Maxwell now recognized a fatal defect in his original theory: when any number of solid spheres are maintained at various temperatures in a gas, a state of equilibrium will eventually be reached in which there is a steady flow of heat, and in this case there can be no forces on any of the spheres as long as only normal stresses are considered. Nevertheless, Crookes' experiments showed that forces do act "between solid bodies immersed in rarefied gases, and this, apparently, as long as inequalities of temperature are maintained." (§§11–12)

Maxwell proposed to attribute the effect to "the phenomenon discovered in the case of liquids by Helmholtz and Piotrowski[15] and for gases by Kundt and Warburg, that the fluid in contact with the surface of a solid must slide over it with finite velocity in order to produce a finite tangential stress." Kundt and Warburg had found that the velocity of sliding of a gas over the surface due to a given tangential stress varies inversely as the pressure, so that this effect should be stronger in rarefied gases. The existence of such currents sweeping along the surfaces of solid bodies immersed in a rarefied gas would completely destroy the simplicity of the kinetic-theory solution of the problem.

In an Appendix added to his paper in May, 1879, Maxwell said that while he had previously been reluctant to give any quantitative treatment of the effect of slipping, one of the referees of the paper had encouraged him to do so and had even suggested various possible hypotheses about the gas-surface interaction. Maxwell now proposed a set of equations which "express both the fact that the gas may slide over the surface with a finite velocity . . . and the fact that this velocity and the corresponding tangential stress are affected by inequalities of temperature at the surface of the solid which give rise to a force tending to make the gas slide along the surface from colder to hotter places."[16]

Here is the basis of the modern theory of the radiometer effect, and of many other phenomena that take place in rarefied gases. Maxwell does not claim the credit for discovering the tendency of a gas to creep along the surface from colder to hotter places. Instead, he states that the phenomenon was discovered by Osborne Reynolds, who called it "thermal transpiration," and who showed that it is a necessary consequence of the kinetic theory of gases. Maxwell reveals that "it was not till after I had read Professor Reynolds' paper that I began to reconsider the surface conditions of gas, so that what I have done is simply to extend to the surface phenomena the method which I think most suitable for treating the interior of the gas. I think that this method is, in some respects, better than that adopted by Professor

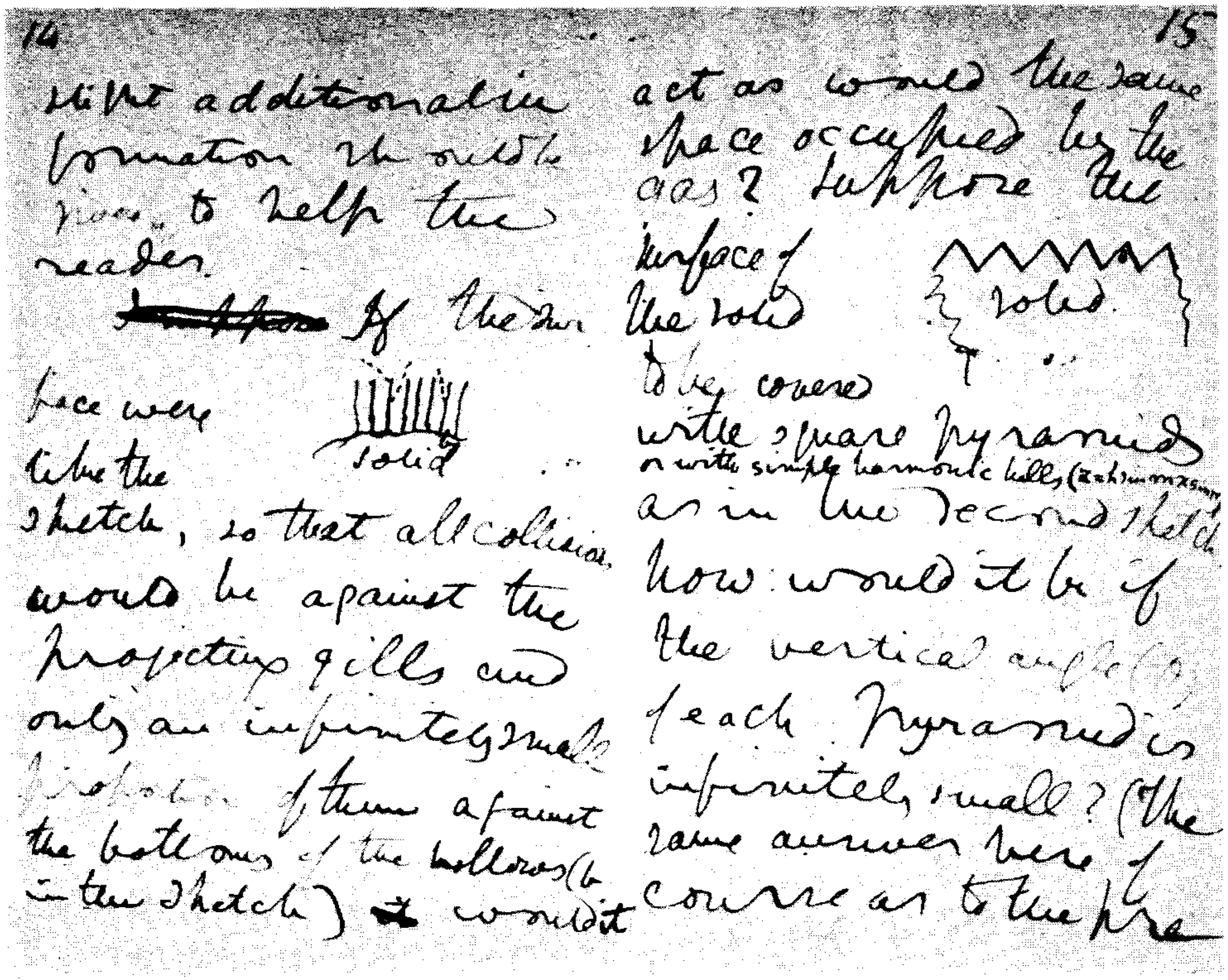
Reynolds, while I admit that his method is sufficient to establish the existence of the phenomena, though not to afford an estimate of their amount."

Thus the most important part of Maxwell's paper, the treatment of gas-surface interactions, owes its origin to the suggestion of an unnamed referee, and its success to Maxwell's acquaintance with a paper by Osborne Reynolds–a paper which had not yet been published! The crucial importance of the referees' reports for disentangling the history of the radiometer begins to emerge.

Maxwell's paper was sent to the Royal Society in the middle of March 1878. It was referred to William Thomson, who submitted his report on 15 June 1878. Thomson had received a summary of the theory in a letter from Maxwell on 7 March 1878,[17] and he says in his report that he has already discussed the paper with its author. It seems probable that Maxwell knew that Thomson was the refereee; he could hardly have failed to recognize the literary style of Thomson, with whom he frequently corresponded (there might have been some pretense of anonymity since the Secretary of the Royal Society, Stokes, had sent a typewritten copy of portions of the report to Maxwell rather than the original). The most important part of Thomson's report (fig. 5.5-3) reads:

> If the surface were like the sketch, so that all collisions would be against the projecting gills and only an infinitely small proportion of them against the bottoms of the hollows (*b* in the sketch) would it act as would the same space occupied by the gas? Suppose the surface of the solid to be covered with square pyramids or with simple harmonic hills ($z = h \sin mx \sin ny$) as in the second sketch. How would it be if the vertical angle (θ) of each pyramid is infinitely small? (The same answer here of course as to the preceding question.) If $\theta = 180°$ and the surface of the solid is supposed to be frictionless (that is to say if we have simply a smooth frictionless solid) how will it be in this case? (I suppose in this, as in the other extreme, the resultant action on the solid will be equilibrant.)[18]

It was apparently this problem proposed by Thomson that induced Maxwell to throw caution to the winds and formulate a theory of gas-surface interactions. Some insight into the early stages of this theory can be gleaned from Maxwell's report,[19] dated 23 October 1878, on the sixth of Crookes' series of papers "On repulsion resulting from radiation." Crookes submitted the paper to the Royal Society on 27



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as in the second sketch
how would it be if
the vertical angle (θ)
of each pyramid is
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Fig. 5.5-3. A page of William Thomson's report on Maxwell's paper (1878).

June 1878, so Maxwell presumably received it only a few weeks after seeing Thomson's report on his own paper. Maxwell is interested mainly in a new instrument constructed by Crookes, "a small fly with clear mica vanes which can be placed in different parts of the radiometer bulb to detect differences of pressure on its vanes." Explorations with this device would permit a direct test of Maxwell's prediction that if the isothermal surface adjacent to the surface of the solid is not parallel to that surface, there will be a tangential stress of the gas on the solid. (The force would be directed from places where consecutive isothermal surfaces are close together to places where they are further apart.) "At the surface of the solid," Maxwell writes in his report, "the gas cannot support this stress but must yield to it. This causes a current sweeping over the surface." The theory is confirmed qualitatively by Crookes' observations.

Three months later, in January 1879, Osborne Reynolds submitted his paper "On certain dimensional properties of matter in the gaseous state" to the Royal Society. It contains a general theory of the flow of rarefied gases, with applications to the radiometer and to the new phenomenon of "thermal transpiration," one of the first major discoveries stimulated by the radiometer. Maxwell was asked to report on Reynolds' paper; he made good use of the information contained in it in extending his own theory.

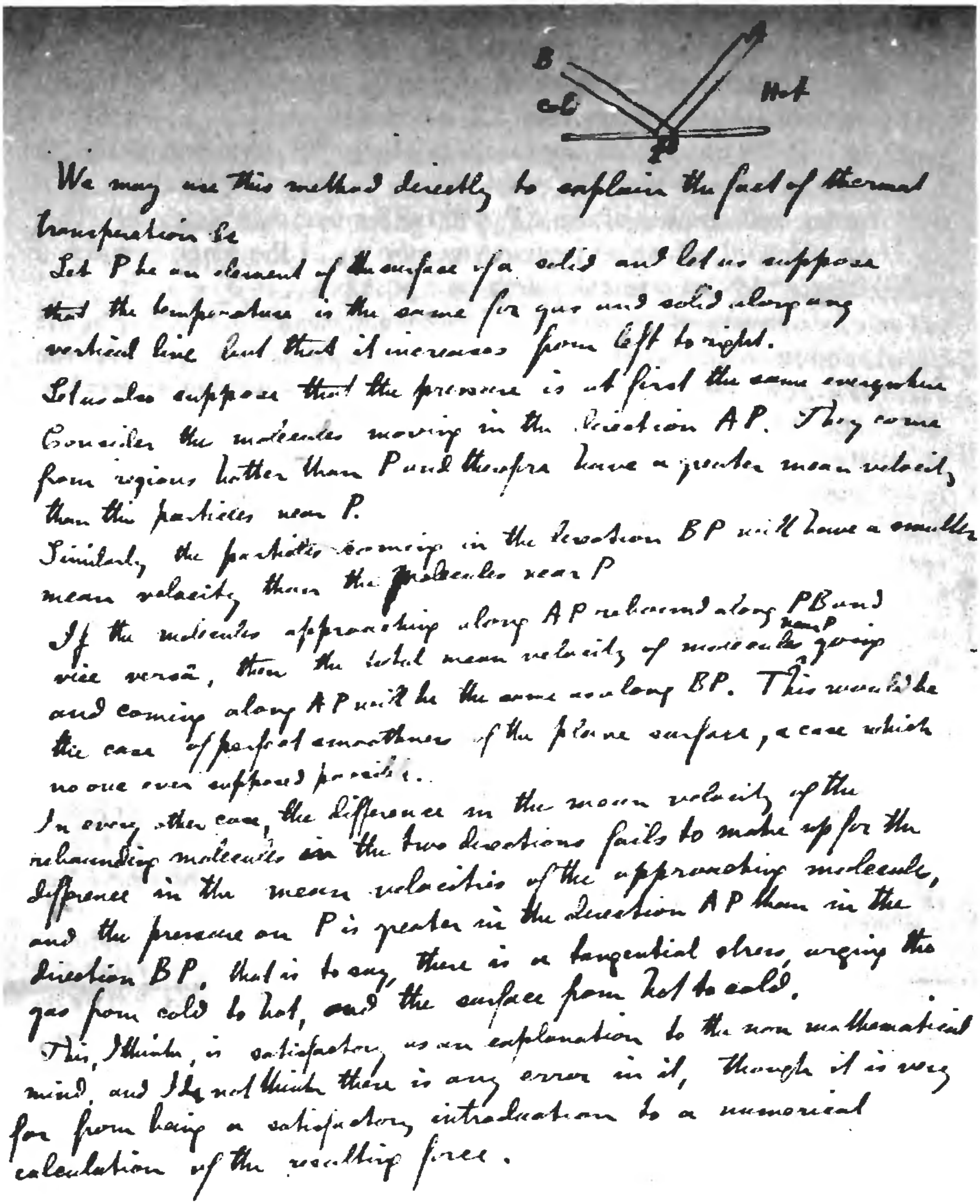
Thermal transpiration, as Reynolds defines it, is the flow of gas through porous plates caused by a temperature difference on the two sides of the plate. To illustrate the magnitude of the effect, Reynolds stated that a temperature difference of 160°F between two sides of a porous plate, with hydrogen gas maintained at atmospheric pressure on one side, would sustain a permanent pressure difference of one inch of mercury, the higher pressure being on the hotter side. The rate of transpiration depends on the porosity of the plate and the density of the gas in such a way that similar results are obtained "so long as the density of the gas is inversely proportional to the lateral dimensions of the passages through the plates." In other words, similar effects could be observed in rarefied gases with channels of larger diameter. Now it was just this "scaling" property of the phenomenon which led Reynolds to discover it in the first place, according to his own account. He had recognized that the radiometer effect depends on the ratio of the size of the vanes to the mean free path of the molecules in the gas: there would be no effect for very large vanes, or for very small mean free paths. Since the mean free path decreases as the pressure (or density) increases,

> it appeared that by using vanes of comparatively small size the force should be perceived at comparatively greater pressures of gas. . . . On considering how this might be experimentally tested, it appeared that to obtain any result at measurable pressures the vanes would have to be very small indeed; too small almost to admit of experiment. And it was while thinking of some means to obviate this difficulty that I came to perceive that if the vanes were fixed, then instead of the movement of the vanes we should have the gas moving past the vanes–a sort of inverse phenomenon–and then instead of having small vanes, small spaces might be allowed for the gas to pass. Whence it was at once obvious that in porous plugs I should have the means of verifying these conclusions. . . .[20]

In his first report on Reynolds' paper, Maxwell approved heartily of the experiments described, but was less satisfied with the theoretical deductions.[21] He felt that Reynolds had not clearly stated what happens at the surface, and suggested the hypothesis "that the surface has on it small prominences of various shapes from which the molecules rebound, with a velocity which is greater or less than the impinging molecules, accordingly as the temperature of the solid is greater or less than that of the gas." Maxwell even worked out the beginnings of a quantitative theory based on this idea, remarking that "conditions of this kind might perhaps assist Prof. Reynolds in forming a theory about the rebounding molecules." Reynolds did make some use of this suggestion–he says in his published paper that §VII "was revised and somewhat enlarged in August, 1879, in accordance with a suggestion made by one of the referees," but he does not adopt the particular formulation given by Maxwell. Nevertheless there is a clear train of influence running through the referees' reports from Thomson to Maxwell to Reynolds, leading eventually to the modern theory of gas-surface interactions in rarefied gases.[22]

Maxwell's report concludes (fig. 5.5-4) with his own explanation of the mechanism of thermal transpiration (and incidentally of the radiometer effect):

> We may use this method directly to explain the fact of thermal transpiration, etc.
>
> Let P be an element of the surface of a solid and let us suppose that the temperature is the same for gas and solid along any vertical line but that it increases from left to right.
>
> Let us also suppose that the pressure is at first the same everywhere. Consider the molecules moving in the direction AP.



We may use this method directly to explain the fact of thermal transpiration &c

Let P be an element of the surface of a solid and let us suppose that the temperature is the same for gas and solid along any vertical line but that it increases from left to right.

Let us also suppose that the pressure is at first the same everywhere

Consider the molecules moving in the direction AP. They come from regions hotter than P and therefore have a greater mean velocity than the particles near P.

Similarly, the particles coming in the direction BP will have a smaller mean velocity than the molecules near P

If the molecules approaching along AP rebound along PB and vice versa, then the total mean velocity of molecules near P going and coming along AP will be the same as along BP. This would be the case of perfect smoothness of the plane surface, a case which no one ever supposed possible.

In every other case, the difference in the mean velocity of the rebounding molecules in the two directions fails to make up for the difference in the mean velocities of the approaching molecules, and the pressure on P is greater in the direction AP than in the direction BP, that is to say, there is a tangential stress, urging the gas from cold to hot, and the surface from hot to cold.

This, I think, is satisfactory as an explanation to the non mathematical mind, and I do not think there is any error in it, though it is very far from being a satisfactory introduction to a numerical calculation of the resulting force.

Fig. 5.5-4. A page from Maxwell's report on Reynold's paper (1879).

> They come from regions hotter than *P* and therefore have a greater mean velocity than the particles near *P*.
>
> Similarly the particles coming in the direction *BP* will have a smaller mean velocity than the molecules near *P*.
>
> If the molecules approaching along *AP* returned along *PB* and vice versa, then the total mean velocity of molecules near *P* going and coming along *AP* will be the same as along *BP*. This would be the case of perfect smoothness of the plane surface, a case which no one ever supposed possible.
>
> In every other case, the difference in the mean velocity of the rebounding molecules in the two directions fails to make up for the difference in the mean velocities of the approaching molecules, and the pressure on *P* is greater in the direction *AP* than in the direction *BP*, that is to say, there is a tangential stress, urging the gas from cold to hot and the surface from hot to cold.
>
> This, I think, is satisfactory as an explanation to the non-mathematical mind, and I do not think there is any error in it, though it is very far from being a satisfactory introduction to a numerical calculation of the resulting force.[23]

Unfortunately, this beautifully simple argument did not appear in print at the time when the scientific world was interested in knowing how the radiometer works.

The relations between Maxwell and Reynolds deteriorated rapidly after this report was written. Several more letters about Reynolds' paper passed between Reynolds, Maxwell, Stokes, and William Thomson (acting as the other referee). One of these should be quoted at length (Maxwell to Stokes, 2 September 1879):

> Of course I cannot profess to follow with minute attention the course of an acrobat [Reynolds] who drives 24 in hand, but as on more than one occasion he throws up the reins and starts a new team, it is probable that the results will be sufficiently flexible to adapt themselves to the facts, whatever the facts may be. But O. R. says he has improved all this, and I hope he has. . . .
>
> But to criticize Stoney when he comes to the Radiometer, and the Stoney Stratum which he calls the Crookes' Layer required hermeneutic powers of an order considerably above *dp*/*dt* [*i.e.* Maxwell] or even O. R. and this fact is a powerful temptation to the feebleminded to pass the whole thing over in silence, though to the eagle eye of Thomson a happy expression, even though in the midst of erroneous words, may illuminate the whole conglomera-

> tion of blunders with a meaning which the author himself could never be made to recognize.
>
> With respect to Graham's experiments, O. R. is right and Thomson wrong, for there is considerable difficulty, perceived by Graham himself, in getting any simple law out of them. The result was that Graham was driven to the excessively fine pores of graphite plate, whereby he approximated to the law of effusion and got rid of transpiration almost entirely. On the other hand, O. R. is impervious to Thomson's lucid statement of the difference between effusion and transpiration, namely that what restrains the flow of gas is collisions but that in effusion the collisions between two molecules of gas are very few compared with those between a molecule and a solid surface whereas in transpiration the collisions between two molecules mostly preponderate, so that in effusion the velocity of the molecules governs the velocity of effusion, whereas in transpiration viscosity is the ruling consideration. I am afraid I have not answered your letter at all, except about O. R. being the discoverer of dimensional properties in gases. I have always felt inclined to give him leave to practise at his "mean range" till he has qualified himself to go in among the all comers for the R. S. meetings.[24]

This is the letter which Horace Lamb referred to when he wrote to Larmor in 1905 regarding the latter's edition of the Stokes letters: "Maxwell's letter is certainly amazing and characteristic, and hits off very happily and good-naturedly some of O. R.'s peculiarities. The gaiety of the world will lose by its omission, but I cannot urge its publication at present. I remember that O. R. long bore a grudge against Maxwell on account of this paper, and he might still be sensitive to the brilliant raillery."[25]

We must now say something about the reasons for Reynolds' "grudge against Maxwell on account of this paper." There is more to it than the normal resentment of authors against the referees who criticize and delay the publication of their papers. In this case Maxwell had made use of Reynolds' discovery of thermal transpiration (with proper acknowledgment) in his own paper, which was published before Reynolds'. Here Maxwell had cast doubts in public on the value of Reynolds' work before Reynolds was in a position to defend himself. The situation was further aggravated by the fact that any criticism of Maxwell's rôle in the affair was soon impossible because of the sympathy called forth by his painful illness (cancer of the abdomen) and death. This illness may also account for Maxwell's erratic behavior during this period. Tait, writing to Stokes in December 1879, suggested that "Maxwell's hereditary malady [his mother had died of the same cause] had begun to affect him some months before his death," as shown by his conflicting recommendations of Chrystal and Garnett for the Edinburgh chair of mathematics:

> I began to fear [Tait continued] that his mind was affected; but, happily, this phase was very transient. I had full details of his malady from my colleague Sandars, who attended him and who was an old fellow-student of his in Edinburgh, but I considered it much too painful and delicate a subject to be even hinted at in public. No man could have behaved more tenderly or nobly than Maxwell did under long trials of the most overwhelming nature. How he could manage to do splendid mathematical work all the time is inconceivable.[26]

Here was a trap waiting for Reynolds–the circle of Maxwell's powerful friends (Tait, Thomson, Stokes, and many others) would rush to his defense if anyone should dare criticize the dead hero.

On 23 October 1879, just two weeks before Maxwell's death, Reynolds sent a letter to Stokes to be communicated to the Royal Society. He protested the slur on his work in Maxwell's paper, and ventured "to request those interested in the subject to withhold their opinion until they have an opportunity of reading my paper. In the meantime I can only express my opinion that Professor Maxwell is mistaken in supposing that the results which are obtained from his method are more definite than those to be obtained by mine."[27] Apparently Reynolds wanted the letter to be read to the Royal Society immediately, but Stokes was reluctant to do so. In a letter to Reynolds on 5 November 1879, just after Maxwell had died, Stokes demanded that Reynolds should either rewrite his letter or allow Stokes to add his own comments after presenting it.[28] Reynolds chose the second alternative, and his letter was read the following April with a note by Stokes appended. In this note, Stokes mentioned that Maxwell's work had been partly based on a suggestion of William Thomson.

In the meantime, Thomson was working to undermine the originality of Reynolds' discovery of thermal transpiration. He wrote to Stokes about a paper by W. Feddersen on the subject, based on a theoretical prediction of Carl Neumann in 1872.[29] Stokes passed on the reference to Reynolds, who added a note to his own paper in December 1879, in which he stated that M. J. Violle[30] had attributed Feddersen's results to the presence of water vapor. But in attempting to repel the threatened German invasion of his priority, Reynolds had hastily grasped at a French straw; he seems to have misunderstood Violle's remarks. To discuss the work of Feddersen, Neumann, Dufour, and others would be out of place here; we mention this incident only because it throws another sidelight on the relations between Reynolds and Maxwell's friends.

FitzGerald, in a note in the *Philosophical Magazine* for February 1881, recalled Maxwell's criticism of Reynolds' work, and further complained that "Prof. Reynolds' paper is very elaborate, and necessarily somewhat difficult, not only from the nature of the subject, but also, in parts, owing to the inelegant method that Prof. Reynolds has pursued." Reynolds replied:

> With regard to Professor Maxwell's remarks on my paper, and his own work on the same problem, of course, the sad circumstance of his death occurring, so that this was about the last work he did, renders it very difficult to approach the subject; but with reference to what I have already said, and in explanation of the apparently imperfect idea at which he arrived as to the scope and purpose of my method, it may be stated that, before writing his own paper, Professor Maxwell had only seen my paper in manuscript in the condition in which it was first sent in to the Royal Society, when the preliminary part was very much compressed, and, as I fear, somewhat vaguely stated, besides being founded on different assumptions from the present.[31]

* * *

By now scientists were no longer concerned primarily with the radiometer itself. The radiometer had served to direct attention to the phenomena of rarified gases; this subject could now develop independently without being tied to a particular instrument. Crookes moved on to study electrical discharges in rarified gases, opening a path to experimental atomic physics; Reynolds turned to other topics in fluid dynamics, such as the problem of the onset of turbulence.

As often happens in science, a phenomenon which can be reproduced experimentally fairly easily, such as the radiometer effect, turns out to be complicated from a theoretical viewpoint; and then a very refined experimental technique is needed to isolate individual aspects which can be analyzed theoretically. Almost no research on the radiometer itself was done for about forty years after Maxwell's death. G. D. West, in 1920, was probably correct in attributing this to the fact that "the majority of physicists felt that the matter had been placed beyond their grasp, rather than because some well-understood explanation had been given which rendered further research superfluous."[32] William Sutherland, attempting to revive interest in the subject in 1896 on the grounds that Reynolds' theory was unsatisfactory, gave a vivid retrospective account:

> The comparative neglect into which the radiometer has fallen is probably the natural compensation for the exalted interest of its two or three years' reign over the scientific imagination twenty years ago. In reading amongst the papers about it published at that time, one gets an impression of the laboratory of Crookes as of an arsenal where night and day the equipment of a great expedition into the unknown was being pushed on under the sleepless eye of a patriot leader; but in the answering bustle outside, Stokes, Schuster, Stoney, FitzGerald, Pringsheim, Reynolds and others soon showed that the new conquest was simply an outlying part of the Kinetic Theory of Gases. Or, to vary the figure, Crookes appears as a friendly counsel subjecting Nature to a passionate and eloquent cross-examination with his fellow physicists as judge and jury bringing in a verdict for the Kinetic Theory. And then the interest died rapidly away, perhaps mostly on account of Reynolds' great paper . . . which was probably held to settle consequences of the kinetic theory of gases, especially as the same train of reasoning had led him to his discovery of Thermal Transpiration with the beautiful establishment of its simple quantitative laws, simple in the illumination of his theory, but complex enough without it.[33]

That, in outline, was the "public history" of the radiometer; we have attempted in this section to give some indication of the private history of the interactions between the major participants.

Notes for §5.5

1. See for example L. Loeb, *Kinetic Theory of Gases* (New York: McGraw-Hill, 2nd ed. 1934); E. Kennard, *Kinetic Theory of Gases with an Introduction to Statistical Mechanics* (New York: McGraw-Hill, 1938); A. E. Woodruff, *Phys. Teacher* **6**, 358 (1968).

2. We wish to acknowledge the generous cooperation of the staffs of the Royal Society of London and the Cambridge University Library in providing us with copies of the relevant documents. We also thank Brigadier Wedderburn-Maxwell, the Royal Society, and Cambridge University for permission to quote. We intend to publish the complete texts of these and other letters and manuscripts of Maxwell relating to kinetic theory at a later time (S. G. Brush, C. W. F. Everitt and E. W. Garber, *Maxwell on Kinetic Theory*, in press).
3. For a comprehensive account of the work of Crookes, see A. E. Woodruff, *Isis* **58**, 188 (1966). Earlier discussions of "light pressure" are surveyed by M. L. Schagrin, *Am. J. Phys.* **42**, 927 (1974).
4. W. B. Carpenter, *Nineteenth Century* **1**, 242 (1877). Cf. Galton's letter to Darwin, quoted by M. J. Kottler in *Isis* **65**, 171 (1974).
5. W. B. Carpenter, *Mesmerism, Spiritualism, Etc. Historically and Scientifically Considered* (New York, 1877), p. 7.
6. Letter No. 108 in the Maxwell Collection at Cambridge University.
7. Royal Society Archives, 1874, No. 295.
8. Reported by A. Ferguson, *Nature* **128**, 604 (1931).
9. O. Reynolds, *Papers on Mechanical and Physical Subjects* (Cambridge, 1900–3), **1**, 8. Most of the other papers by Reynolds mentioned in this section may be found here. Some of Reynolds' scientific work is discussed in a commemorative volume, *Osborne Reynolds and Engineering Science Today*, eds. D. M. McDowell and J. D. Jackson (Manchester, Eng.: Manchester University Press, 1969).
10. A. Schuster, *Proc. R. S. London* **24**, 391 (1876); *Phil. Trans.* **166**, 715 (1877). See also his *Biographical Fragments* (London: Macmillan, 1932), pp. 230–32: Schuster says he first proposed the experiment to Reynolds and others during the winter of 1873–74 but was reluctant to do it himself for fear of "cutting into what I consider to be other people's work." Finally Reynolds set up the apparatus and they did it together.
11. Maxwell to Robert Cay, 15 May 1876, letter at Peterhouse Library, Cambridge University.
12. J. C. Maxwell, *Cambridge University Reporter*, 15 May 1877, p. 434. There are no radiometers in the list of apparatus for the previous year (*ibid.*, 20 May 1876, p. 496).
13. J. C. Maxwell, *Phil. Trans.* **170**, 231 (1879); reprinted in Maxwell's *Scientific Papers* **2**, 681. The paper is marked "Received March 19–Read April 11, 1878," but additional notes were added, dated May and June 1879. Abstracts appeared in *Proc. R. S. London* **27**, 304 (1878) and *Nature* **18**, 54 (1878).
14. A. Kundt and E. Warburg, *Ann. Phys.* [2] **155**, 337, **156**, 177 (1875); English trans. in *Phil. Mag.* [4] **50**, 53 (1875).
15. H. Helmholtz and G. von Piotrowski, *Wien Ber.* **4**, 607 (1860).
16. Maxwell assumed that "of every unit of area [of the surface] a portion f absorbs all the incident molecules, and afterwards allows them to evaporate with velocities corresponding to those in still gas at the temperature of the solid, while a portion $1-f$ perfectly reflects all the molecules incident upon it." He derived, as a first approximation, the following equation, relating the velocity of the gas near a flat surface in the yz plane to the temperature θ, to its gradients, and to the viscosity μ and the density ρ of the gas:

$$v - G\left(\frac{dv}{dx} - \frac{3}{2}\frac{\mu}{\rho\theta}\frac{d^2\theta}{dx\,dy}\right) - \frac{3}{4}\frac{\mu}{\rho\theta}\frac{d\theta}{dy} = 0$$

where G is the "Gleitungs-coefficient" (slip coefficient) previously introduced by

Helmholtz and Piotrowski. G is related to the mean free path l of a molecule by the equation

$$G=\frac{2}{3}\left(\frac{2}{f}-1\right)$$

Kundt and Warburg found that for air at different pressures p flowing through glass capillary tubes from 17°C to 27°C, $G = 8/p$ centimeters. (Appendix, added May 1879, to the paper cited in note 13.)

A rough qualitative explanation of the origin of the radiometer force based on the surface flow set up by a temperature gradient was given by Maxwell in a referee's report (pp. 222–224).

17. Published by J. Larmor in *Proc. Camb. Phil. Soc.* **32**, 743 (1936).
18. Royal Society Archives, 1878, Maxwell (70) Thomson's Report (marked "123" in the upper right-hand corner of the first page).
19. Royal Society Archives, 1878, No. 88.
20. O. Reynolds, *Phil. Trans.* **170**, 727 (1879) (recd. 17 January, read 6 February 1879, with an Appendix added December 1879).
21. Royal Society Archives, 1879, No. 188 (28 March 1879).
22. Not much has been added to the theory since the work of these men. Although the concept of "accommodation coefficient" was introduced in the 20th century by Knudsen and others as a further development of Maxwell's ideas, it remains for the most part an empirical parameter representing the probability that a molecule will be absorbed temporarily by the surface to acquire an average energy corresponding to the surface temperature before bounding off again. Attempts to calculate it from molecular theory have not been particularly successful. As recently as 1961, L. Waldmann remarked in a symposium that "for the calculation of the slip coefficients, at present only Maxwell's theory of 1879 is available." [*Rarefied Gas Dynamics*, ed. L. Talbot (New York: Academic Press, 1961), p. 323.]
23. Maxwell, *op. cit.* (note 21).
24. Royal Society Archives, 1879, No. 57.
25. See J. Larmor, *Memoir and Scientific Correspondence of the late Sir George Gabriel Stokes* (Cambridge University Press, 1907); letter from Lamb to Larmor, 1 October 1905, in Stokes papers, Add. 7618, Box 3, Cambridge University.
26. Stokes Papers, Box 13, Cambridge University.
27. O. Reynolds, *Proc. R. S. London* **30**, 300 (1880), reprinted in his *Papers* **1**, 391.
28. Letter from Stokes to Reynolds, 5 November 1879, in Stokes–Kelvin papers, Add. MS. 7618, Box 1, Cambridge University.
29. Thomson to Stokes, 11 April 1880, in Stokes–Kelvin letters, Add. MS. 7618, Box 1, Cambridge University; see W. Feddersen, *Ann. Phys.* [2] **148**, 302 (1873); C. Neumann, *Leipzig. Ber.* **28**, 49 (1872).
30. J. Violle, *J. Phys.* **4**, 97 (1875).
31. O. Reynolds, *Phil. Mag* [5] **11**, 335 (1881); *Papers* **1**, 384. In later years Reynolds seemed reluctant to credit Maxwell's contributions to kinetic theory by name even when citing his papers: see *Phil. Trans.* **186**, 123 (1894); note in *Papers* **2**, 538.
32. G. D. West, *Proc. Phys. Soc. London* **32**, 222 (1920).
33. W. Sutherland, *Phil. Mag* [5] **42**, 373, 476 (1896); see also Reynolds, *Phil. Mag.* [5] **43**, 142 (1896).

CHAPTER 6

Boltzmann*

6.1 The distribution law

Ludwig Boltzmann (1844–1906) was educated at Linz and Vienna, receiving his doctorate in 1867 from the University of Vienna, where he had studied with Josef Stefan. Boltzmann held professorships at the universities of Graz, Vienna, Munich, and Leipzig. In 1876 he married Henrietta von Aigentler, who bore him four children.

The first stimulus for Boltzmann's researches came from teachers and colleagues at the University of Vienna, especially Stefan and Joseph Loschmidt. In a lecture Stefan suggested the problem in electrical theory whose solution constituted Boltzmann's first published paper (1865);[1] he also published a few papers on kinetic theory and did important experimental work on gases and radiation that provided the basis for some of Boltzmann's theories. Loschmidt (also in 1865) accomplished the first reliable estimate of molecular sizes with the help of the Clausius–Maxwell kinetic theory. Although Loschmidt was later to dispute Boltzmann's interpretation of the Second Law of Thermodynamics, the problem of finding quantitative relations between

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Fig. 6.1-1. Ludwig Boltzmann (1844–1906).

atomic magnitudes and observable physical quantities was a common interest of both men.

Boltzmann began his lifelong study of the atomic theory of matter by seeking to establish a direct connection between the Second Law of Thermodynamics and the mechanical principle of least action (1866). Although Clausius, Szily, and others later worked along similar lines, and Boltzmann himself returned to the subject in his elaboration of

Helmholtz' theory of monocyclic systems (1884), the analogy with purely mechanical principles seemed insufficient for a complete interpretation of the second law. The missing element was the statistical approach to atomic motion that had already been introduced by the British physicist James Clerk Maxwell.[2] Boltzmann's first acquaintance with Maxwell's writings on kinetic theory is indicated by his paper on thermal equilibrium (1868). In this paper, he extended Maxwell's theory of the distribution of energy among colliding gas molecules, treating the case when external forces are present. The result was a new exponential formula for molecular distribution, now known as the "Boltzmann factor" and basic to all modern calculations in statistical mechanics. To understand how Boltzmann arrived at this result, we must first review the work of Maxwell on which it is based.

Maxwell, in his first paper on kinetic theory (1859), had pointed out that the collisions of gas molecules would not simply tend to equalize all their speeds but, on the contrary, would produce a range of different speeds. Most of the observable properties of a gas could be calculated if one knew, instead of the positions and velocities of all the molecules at any given time, only the average number of molecules having various positions and velocities. In many cases it seems reasonable to assume that the gas is spatially uniform, that is, the average number of molecules is the same at different places in the gas. The problem is then to determine the velocity distribution function $f(v)$, defined so that $f(v)\,dv$ is the average number of molecules having speeds between v and $v+dv$.

Maxwell argued that $f(v)$ should be a function that depends only on the magnitude of v, and that the velocity components resolved along the three coordinate axes should be statistically independent. Hence, he inferred that

$$f(v) = (N/\alpha^3\pi^{3/2})e^{-(v^2/\alpha^2)}, \tag{1}$$

where N is the total number of molecules, and α^2 is inversely proportional to the absolute temperature.

In his long memoir of 1866, Maxwell admitted that the assumptions used in his previous derivation of the distribution law "may appear precarious"; he offered another derivation in which the velocities of two colliding molecules, rather than the velocity components of a single molecule, were assumed to be statistically independent. This means that one can express the joint distribution function for the probability that molecule 1 has velocity v_1, while at the same time molecule 2 has velocity v_2, as the product of the probabilities of these two separate events

$$F(v_1, v_2) = f(v_1)f(v_2) \tag{2}$$

To derive the distribution function itself, Maxwell argued that the equilibrium state would be reached when the number of collisions in which two molecules with initial velocities (v_1, v_2) rebound with final velocities (v_1', v_2') is equal to the number of collisions in which two molecules with initial velocities (v_1', v_2') rebound with final velocities (v_1, v_2); from this condition it follows that

$$F(v_1, v_2) = F(v_1', v_2') \tag{3}$$

By combining this equation with that for the conservation of energy (in the case when no forces act),

$$\tfrac{1}{2}m_1v_1^2 + \tfrac{1}{2}m_2v_2^2 = \tfrac{1}{2}m_1v_1'^2 + \tfrac{1}{2}m_2v_2'^2, \tag{4}$$

Maxwell deduced (as before) that

$$f(v_1) = (N/\alpha^3\pi^{3/2})e^{-(v^2/\alpha^2)} \tag{5}$$

This type of reasoning about velocity distribution functions was repeatedly used and generalized by Boltzmann in his own works on kinetic theory. He began, in his 1868 paper, by considering the case in which one of the particles of a system is acted on by a force with a corresponding potential function, $V(x)$. The condition of conservation of energy would then be

$$\tfrac{1}{2}M_1v_1^2 + V(x_1) + \tfrac{1}{2}m_2v_2^2 = \tfrac{1}{2}m_1v_1'^2 + V(x_1') + \tfrac{1}{2}m_2v_2'^2, \tag{6}$$

and Boltzmann could then apply Maxwell's procedure to deduce the distribution function

$$f(v) = (\text{const.}) \exp\left[-h(\tfrac{1}{2}mv^2 + V[x])\right] \tag{7}$$

The constant factor h could be related to the absolute temperature of the gas, as Maxwell and Clausius had done, by comparing the theoretical pressure of the gas with the experimental relation between pressure and temperature (Gay-Lussac's law). In modern notation, h is equivalent to $1/kT$, where k is a constant, now called Boltzmann's constant, and T is the absolute temperature on the Kelvin scale.

The physical meaning of the Maxwell–Boltzmann distribution law is that the energy ($E = mv^2/2 + V[x]$) of a molecule is most likely to be roughly equal to kT; much larger or much smaller energies occur with small but finite probability.

In the same paper of 1868, Boltzmann presented another derivation of the Maxwell distribution law that was independent of any assumptions about collisions between molecules. He simply assumed that there is a fixed total amount of energy to be distributed among a finite number of molecules, in such a way that all combinations of energies are equally probable. (More precisely, he assumed uniform distribution in momentum space on the energy surface.) By regarding the total energy as being divided into small but finite quanta, he could treat this as a problem of combinatorial analysis, and obtained a rather complicated formula that reduced to the Maxwell velocity-distribution law in the limit of an infinite number of molecules and infinitesimal energy quanta.

The device of starting with finite energy quanta and then letting them become infinitesimal is not essential to such a derivation, but it reveals an interesting feature of Boltzmann's mathematical approach. Boltzmann asserted on several occasions that a derivation based on infinite or infinitesimal quantities is not really rigorous unless it can also be carried through with finite quantities. While this prejudice kept him from appreciating and using some of the developments in pure mathematics that appeared toward the end of the 19th century, it also had the curious effect of making some of his equations for energy distribution and transfer look similar to those of modern quantum theory. (This is perhaps not quite accidental, since Planck and other early quantum theorists were familiar with Boltzmann's works and used many of his techniques.)

Notes for §6.1

1. All of Boltzmann's publications for which only the year is given may be found in his *Wissenschaftliche Abhandlungen.* (There is a general bibliography for this chapter at the end of §6.6)
2. See *The Scientific Papers of James Clerk Maxwell* (Cambridge, 1890). The 1859 and 1866 papers of Maxwell, together with other papers by Clausius, Boltzmann, Kelvin, Poincaré, and Zermelo (cited by year in this article) may be found in S. G. Brush, ed., *Kinetic Theory*, 2 vols. (Oxford, 1965–66).

6.2 Transport equation and H-theorem

Although Maxwell and Boltzmann had succeeded in finding the correct distribution laws by assuming that the gas is in an equilibrium state, they thought that the kinetic theory should also be able to show that a gas will actually tend toward an equilibrium state if it is not there already. Maxwell had made only fragmentary attempts to solve this problem; Boltzmann devoted several long papers to establishing a general solution.

Approach to equilibrium is a special case of a general phenomenon: dissipation of energy and increase of entropy. It was Boltzmann's achievement to show in detail how thermodynamic entropy is related to the statistical distribution of molecular configurations, and how increasing entropy corresponds to increasing randomness on the molecular level. This was a peculiar and unexpected relationship, for macroscopic irreversibility seemed to contradict the fundamental reversibility of Newtonian mechanics, which was still assumed to apply to molecular collisions. Boltzmann's attempts to resolve this contradiction formed part of the debate on the validity of the atomic theory in the 1890's. Seen in this context, the proof of the distribution law has even more significance than the law itself.

Boltzmann's major work on the approach to equilibrium (and on transport processes in gases in general) was published in 1872. This paper, like that of 1868, took Maxwell's theory as the starting point. Boltzmann first derived an equation for the rate of change in the number of molecules having a given energy, x, resulting from collisions between molecules. He considered a typical collision between two molecules with energies x and x' before the collision, and energies ξ and $x + x' - \xi$ after the collision. Such a collision reduces by one the number of molecules with energy x; the number of such collisions is assumed to be proportional to the number of molecules with energy x, and also to the number of molecules with energy x'. Boltzmann used here, without any comment, Maxwell's assumption of statistical independence of the velocities of two colliding molecules (eq. 2); later it was recognized that there might be valid grounds for objecting to this assumption.[1] With this assumption, the decrease in $f(x)$ will be equal to the product, $f(x)f(x')$, multiplied by an appropriate factor for the collision probability and integrated over all values of x'. Similarly, the increase in $f(x)$ may be attributed to inverse collisions in which the molecules have energies ξ and $x + x' - \xi$ before the collision, and x and x' after the collision. By such arguments Boltzmann arrived at the equation

$$\frac{\partial f}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi, t) f(x + x' - \xi, t)}{\sqrt{\xi}\sqrt{x + x' - \xi}} - \frac{f(x, t) f(x', t)}{\sqrt{x}\sqrt{x'}} \right] \times \sqrt{xx'}\, \psi(x, x', \xi)\, dx'\, d\xi \tag{8}$$

(This is a special case of the general Boltzmann transport equation [eq. 9]; terms describing the effect of external forces and nonuniformities on the change of f are here omitted. The square root expressions in the denominators, which do not appear in the form of the equation generally used, result from the fact that energy rather than velocity is the variable.)

One additional assumption involved in this derivation should be mentioned: The collision probability function $\psi(x, x', \xi)$, is the same for both the direct and inverse collisions; that is, the collision is perfectly reversible.

Following Maxwell's 1866 development of the transport equations, Boltzmann showed the diffusion, viscosity, and heat conduction coefficients of a gas could be calculated by solving the general transport equation

$$\frac{\partial f}{\partial t}+\xi\frac{\partial f}{\partial x}+\eta\frac{\partial f}{\partial y}+\xi\frac{\partial f}{\partial z}+X\frac{\partial f}{\partial \xi}+Y\frac{\partial f}{\partial \eta}+Z\frac{\partial f}{\partial \zeta} + \int d\omega_1 \int b\,db \int d\phi\, V(ff_1-f'f_1')=0 \qquad (9)$$

where (ξ, η, ζ) are components of the velocity of a particle and (X, Y, Z) are components of the force acting on it, and V, ϕ, b and ω_1 are variables characterizing the relative motion of the two molecules during a collision. (Values of the function f for velocities of the two molecules before and after the collision are indicated by f, f_1, f' and f_1'.)

An exact solution of Boltzmann's transport equation is possible only when the molecules interact with inverse fifth power forces, and in this case the results are the same as those already found by Maxwell.[2] Boltzmann made several attempts to develop accurate approximations for other force laws, but this problem was not satisfactorily solved until the work of S. Chapman and D. Enskog in 1916–17.[3] Boltzmann's equation is now frequently used in modern research on fluids, plasmas, and neutron transport.

If the velocity-distribution function is Maxwellian, then the integral on the right-hand side of eq. 8 vanishes identically for all values of the variables, and we find $\partial f/\partial t=0$. In other words, once the Maxwellian state has been reached, no further change in the velocity-distribution function can occur.

So far this is simply an elaboration of the previous arguments of Maxwell and of Boltzmann himself, but now, with an explicit formula for $\partial f/\partial t$, Boltzmann was able to go further and show that $f(x)$ always tends toward the Maxwell form. He did this by introducing a function,

E, depending on $f(x)$

$$E = \int_0^\infty f(x,t)\left\{\log\left[\frac{f(x,t)}{\sqrt{x}}\right] - 1\right\} dx \tag{10}$$

and showing that E always decreases until f reaches the Maxwellian form:

$$\begin{aligned} \frac{DE}{dt} &< 0 \qquad \text{if} \quad f \neq (\text{const.})x\ e^{-hx} \\ \frac{dE}{dt} &= 0 \qquad \text{if} \quad f = (\text{const.})x\ e^{-hx} \end{aligned} \tag{11}$$

(The proof is straightforward and relies simply on the fact that the quantity $(a-b)\log(b/a)$ is always negative if a and b are real positive numbers.[4]) Boltzmann also noted that in the Maxwellian state, E is essentially the same as the thermodynamic entropy (aside from a constant factor). Thus Boltzmann's "H-function" (the notation was changed from E to H in the 1890's) provides an extension of the definition of entropy to non-equilibrium states not covered by the thermodynamic definition.

The theorem that H always decreases for non-equilibrium systems was called "Boltzmann's minimum theorem" in the 19th century, and now goes by the name "Boltzmann's H-theorem."

Notes for §6.2

1. See Boltzmann, *Vorlesungen über Gastheorie* I, §3; P. and T. Ehrenfest, "Begriffliche Grundlagen der Statistischen Aufassung in der Mechanik." [Cf. §14.6.]
2. It was in reference to this result of Maxwell's that Boltzmann wrote his oft-quoted comparison of styles in theoretical physics and styles in music, dramatizing the almost magical disappearance of V from the integrand of eq. 9 when the words "let $n = 5$" were pronounced (*Populäre Schriften*, p. 51).
3. See §§12.6, 12.7; Brush, *Kinetic Theory* 3.
4. See §14.5, note 11.

6.3 Reversibility and recurrence paradoxes[1]

The H-theorem raised some difficult questions about the nature of irreversibility in physical systems, in particular the so-called "reversibility paradox" and "recurrence paradox." (The modern terminology goes back only to the Ehrenfests' 1911 article, in which the words

Umkehreinwand and *Wiederkehreinwand* were introduced.) The reversibility paradox, first discussed by Lord Kelvin (1874) and brought to Boltzmann's attention by Loschmidt, is based on the apparent contradiction between one of the basic premises of Boltzmann's derivation–the reversibility of individual collisions–and the irreversibility predicted by the theorem itself for a system of many molecules. Of course there must be such a contradiction between any molecular theory based on Newtonian mechanics and the general principle of dissipation of energy, but Boltzmann's work was the first to reveal this inconsistency explicitly.

Boltzmann's initial response (1877) to the reversibility paradox was the suggestion that the irreversibility of processes in the real world is not a consequence of the equations of motion and the form of the intermolecular force law but, rather, seems to be a result of the initial conditions. For some unusual initial conditions the system might in fact decrease its entropy (increase the value of H) as time progresses; such initial conditions could be constructed simply by reversing all the velocities of the molecules in an equilibrium state known to have evolved from a non-equilibrium state. But, Boltzmann asserts, there are infinitely many more initial states that evolve with increasing entropy, simply because the great majority of all possible states are equilibrium states. Moreover, the entropy would also be almost certain to increase if one picked an initial state at random and followed it backward in time instead of forward.

The recurrence paradox arises from a theorem in mechanics first published by Poincaré in 1890. According to this theorem, any mechanical system constrained to move in a finite volume with fixed total energy must eventually return to the neighborhood of any specified initial configuration. If a certain value of the entropy is associated with every configuration of the system (a disputable assumption) then the entropy cannot continually increase with time, but must eventually decrease in order to return to its initial value. Therefore the H-theorem cannot always be valid.

Poincaré, and later Zermelo (1896) argued that the recurrence theorem makes any mechanical model, such as the kinetic theory, incompatible with the Second Law of Thermodynamics; and since, it was asserted, the second law is a strictly valid induction from experience, one must reject the mechanistic viewpoint.

Boltzmann replied that the recurrence theorem does not contradict the H-theorem, but is completely in harmony with it. The equilibrium state is not a single configuration but, rather, a collection of the overwhelming majority of possible configurations, characterized by the Maxwell–Boltzmann distribution. From the statistical viewpoint, the recurrence of some particular initial state is a fluctuation that is almost certain to occur if one waits long enough; the point is that the probability of such a fluctuation is so small that one would have to wait an immensely long time before observing a recurrence of the initial state. Thus the mechanical viewpoint does not lead to any consequences that are actually in disagreement with experience. For those who are concerned about the cosmological consequences of the second law–the so-called "heat death" corresponding to the final attainment of a state of maximum disorder when all irreversible processes have run their course–Boltzmann suggested the following idea. The universe as a whole is in a state of thermal equilibrium, and there is no distinction between forward and backward directions of time. However, within small regions, such as individual galaxies, there will be noticeable fluctuations that include ordered states corresponding to the existence of life. A living being in such a galaxy will distinguish the direction of time for which entropy increases (processes going from ordered to disordered states) from the opposite direction; in other words, the concept of "direction of time" is statistical or even subjective, and is determined by the direction in which entropy happens to be increasing. Thus, the statement "entropy increases with time" is a tautology, and yet the subjective time directions in different parts of the universe may be different. In this way local irreversible processes would be compatible with cosmic reversibility and recurrence. (Boltzmann's concept of alternating time directions has recently been revived in connection with theories of oscillating universes.)

Note for §6.3

1. These paradoxes are discussed in more detail in ch. 14.

6.4 Statistical mechanics and ergodic hypothesis

Having followed Boltzmann's work on irreversible processes into some of the controversies of the 1890's, let us now return to his contributions to the theory of systems in thermal equilibrium (for which the term "statistical mechanics" was introduced by J. Willard Gibbs).

It would be possible (as is in fact done in many modern texts) to take the Maxwell–Boltzmann distribution function (eq. 7) as the basic postulate for calculating all the equilibrium properties of a system. Boltzmann, however, preferred another approach that seemed to rest on more general grounds than the dynamics of bimolecular collisions in low-density gases. The new method was in part a by-product of his discussion of the reversibility paradox, and is first hinted at in connection with the relative frequency of equilibrium, as opposed to non-equilibrium configurations of molecules: "One could even calculate, from the relative numbers of the different distributions, their probabilities, which might lead to an interesting method for the calculation of thermal equilibrium."[1] This remark was quickly followed up in the same year (1877) in a paper in which the famous relation between entropy and probability,

$$S = k \log W,$$

was developed and applied. In this equation, W is the number of possible molecular configurations ("microstates" in modern terminology) corresponding to a given macroscopic state of the system.[2]

The new formula for entropy–from which formulas for all other thermodynamic quantities could be deduced–was based on the assumption of equal *a priori* probability of all microstates of the system (that is, all microstates that have the same total energy). As noted above, Boltzmann had already proved in 1868 that such an assumption implies the Maxwell velocity distribution for an ideal gas of non-interacting particles; it also implies the Maxwell–Boltzmann distribution for certain special cases in which external forces are present. But the assumption itself demanded some justification beyond its inherent plausibility. For this purpose, Boltzmann and Maxwell introduced what is now called the "ergodic hypothesis," the assumption that a single system will eventually pass through all possible microstates. (See §10.10.)

There has been considerable confusion about what Maxwell and Boltzmann really meant by ergodic systems. It appears that they did not have in mind completely deterministic mechanical systems following a single trajectory unaffected by external conditions; the ergodic property was to be attributed to some random element or at least to collisions with a boundary. In fact, when Boltzmann first introduced the words *Ergoden* and *ergodische*, he used them not for single systems but for collections of similar systems with the same energy but different initial conditions. In these papers of 1884 and 1887, Boltzmann was continuing his earlier analysis of mechanical analogies for the Second Law of Thermodynamics, and, also developing what is now (since Gibbs) known as ensemble theory. Here again, Boltzmann was following a trail blazed by Maxwell, who had introduced the ensemble concept in his 1879 paper. But while Maxwell never got past the restriction that all systems in the ensemble must have the same energy, Boltzmann suggested more general possibilities and Gibbs ultimately showed that it is most useful to consider ensembles in which not only the energy but also the number of particles can have any value, with a specified probability.

The Maxwell–Boltzmann ergodic hypothesis led to considerable controversy on the mathematical question of the possible existence of dynamical systems that pass through all possible configurations. The controversy came to a head with the publication of the Ehrenfests' article in 1911, in which it was suggested that while ergodic systems are probably nonexistent, "quasi-ergodic" systems that pass "as close as one likes" to every possible state might still be found. Shortly after this, two mathematicians, Rosenthal and Plancherel, used some recent results of Cantor and Brouwer on the dimensionality of sets of points to prove that strictly ergodic systems are indeed impossible (§10.12). Since then, there have been many attempts to discover whether physical systems can be ergodic; "ergodic theory" has become a lively branch of modern mathematics, although it now seems to be of little interest to physicists.

After expending a large amount of effort in the 1880's on elaborate but mostly fruitless attempts to determine transport properties of gases, Boltzmann returned to the calculation of equilibrium properties in the 1890's. He was encouraged by the progress made by Dutch researchers–J. D. van der Waals, H. A. Lorentz, J. H. van't Hoff, and others–in applying kinetic methods to dense gases and osmotic solutions. He felt obliged to correct and extend their calculations, as in the case of virial coefficients of gases of elastic spheres. The success of these applications of kinetic theory also gave him more ammunition for his battle with the energeticists (see below).

Notes for §6.4

1. Brush, *Kinetic Theory* 2, 192.
2. This formula for S is clearly related to Boltzmann's earlier expression for the H-function (eq. 9). If we know that the system has probability W_i of being in

macrostate i, with given values of W_i for all i, then the expectation value of the entropy can be calculated from

$$S = k\Sigma W \log W$$

with an appropriate interpretation of the summation or integration. See §14.5 for further discussion.

6.5 Other contributions

Although Boltzmann's contributions to kinetic theory were the fruits of an effort sustained over a period of 40 years, and are mainly responsible for his reputation as a theoretical physicist, they account, numerically, for only about half of his publications. The rest are so diverse in nature–ranging over the fields of physics, chemistry, mathematics, and philosophy–that it would be useless to try to describe or even list them here. Only one common characteristic seems evident: most of what Boltzmann wrote in science represents some kind of interaction with other scientists or with his students. All of his books originated as lecture notes; in attempting to explain a subject on the elementary level, Boltzmann frequently developed valuable new insights, although he often succumbed to unnecessary verbosity. He scrutinized the major physics journals and frequently found articles that inspired him to dash off a correction, design a new experiment, or rework a theoretical calculation to account for new data.

Soon after he started to follow Maxwell's work on kinetic theory, Boltzmann began to study the electromagnetic theory of his British colleague. In 1872, he published the first report of a comprehensive experimental study of dielectrics, conducted in the laboratories of Helmholtz in Berlin and of Töpler in Graz. A primary aim of this research was to test Maxwell's prediction that the index of refraction of a substance should be the geometric mean of its dielectric constant and its magnetic permeability ($i = \sqrt{\epsilon\mu}$). Boltzmann confirmed this prediction for solid insulators and (more accurately) for gases. He also confirmed the further prediction that if the speed of light (and hence the index of refraction) varies with direction in an anisotropic crystal, then the dielectric constant must also vary with direction.

During the next few years, Boltzmann began experimental work in diamagnetism while continuing his theoretical research in kinetic theory. He proposed a new theory of elastic aftereffects, in which the stress on a material at a given time depends on its previous deformation history.

In 1883, as a result of preparing an abstract of H. T. Eddy's paper (on radiant heat as a possible exception to the Second Law of Thermodynamics) for Wiedemann's *Beiblätter*, Boltzmann learned of a work by the Italian physicist Adolfo Bartoli on radiation pressure. Bartoli's reasoning stimulated Boltzmann to work out a theoretical derivation, based on the Second Law of Thermodynamics and Maxwell's electromagnetic theory, of the fourth power law previously found experimentally by Stefan (§13.7):

$$(\text{radiation energy}) \propto (\text{absolute temperature})^4$$

Although at the time the "Stefan–Boltzmann law" for radiation seemed to be an isolated result with no further consequences, it did at least show a possible connection between thermodynamics and electromagnetism that was exploited in the later quantum theory. In the 1920's it was applied by Eddington and others in explaining the equilibrium of stellar atmospheres.

In the 1890's Boltzmann again revived his interest in electromagnetic theory perhaps as a result of Hertz's experiments, which he repeated before a large audience in Graz. He published his *Vorlesungen über Maxwell's Theorie*... in 1891 and 1893, along with the same papers in which he suggested new mechanical models to illustrate the field equations. In 1895 he published an annotated German edition of Maxwell's paper "On Faraday's Lines of Force" in Ostwald's *Klassiker der exakten Wissenschaften.* Boltzmann was partly responsible for the eventual acceptance of Maxwell's theory on the Continent, although he did not advance the theory itself as much as did Lorentz, nor did he grapple with the difficult problems that ultimately led to Einstein's theory of relativity.

6.6 Defense of the atomic viewpoint

Throughout his career, even in his works on subjects other than kinetic theory, Boltzmann was concerned with the mathematical problems arising from the atomic nature of matter. Thus an early paper with the title "Über die Integrale linearer Differentialgleichungen mit periodischen Koeffizienten" (1868) turned out to be an investigation of the validity of Cauchy's theorem on this subject, which is needed to justify the application of the equations for an elastic continuum to a crystalline solid in which the local properties vary periodically from one atom to the next. Every time someone published new data on the specific heats of gases, Boltzmann felt obliged to worry again about the distribution of energy among the internal motions of polyatomic molecules.[1]

Until the 1890's, it seemed to be generally agreed among physicists that matter *is* composed of atoms, and Boltzmann's concern about the consistency of atomic theories may have seemed excessive. But toward the end of the century, the various paradoxes–specific heats, reversibility, and recurrence–were taken more seriously as defects of atomism and Boltzmann found himself cast in the role of principal defender of the kinetic theory and of the atomistic-mechanical viewpoint in general. Previously he had not been much involved in controversy–with the exception of a short dispute with O. E. Meyer, who ironically had accused Boltzmann of proposing a theory of elasticity that was inconsistent with the atomic nature of matter. But now Boltzmann found himself almost completely deserted by Continental scientists; his principal supporters were in England.

In retrospect it seems clear that the criticisms of kinetic theory in this period were motivated not primarily by technical problems, such as specific heats of polyatomic molecules but, rather, by a general philosophical reaction against mechanistic or "materialistic" science and a preference for empirical or phenomenological theories, as opposed to atomic models. The leaders of this reaction, in the physical sciences, were Ernest Mach, Wilhelm Ostwald, Pierre Duhem, and Georg Helm. Mach recognized that atomic hypotheses could be useful in science but insisted, even as late as 1912, that atoms must not be considered to have a real existence (§8.7). Ostwald, Duhem, and Helm, on the other hand, wanted to replace atomic theories by "Energetics" (a generalized thermodynamics); they denied that kinetic theories had any value at all, even as hypotheses.

In the first volume of his *Vorlesungen über Gastheorie* (1896), Boltzmann presented a vigorous argument for the kinetic theory:

> Experience teaches that one will be led to new discoveries almost exclusively by means of special mechanical models.... Indeed, since the history of science shows how often epistemological generalizations have turned out to be false, may it not turn out that the present "modern" distaste for special representations, as well as the distinction between qualitatively different forms of energy, will have been a retrogression? Who sees the future? Let us have free scope for all directions of research; away with all dogmatism, either atomistic or antiatomistic! In describing the theory of gases

> as a mechanical *analogy*, we have already indicated, by the choice of this word, how far removed we are from that viewpoint which would see in visible matter the true properties of the smallest particles of the body.

In the foreword to the second volume of this book (1898), Boltzmann seemed rather more conscious of his failure to convert other scientists to acceptance of the kinetic theory. He noted that attacks on the theory had been increasing, but added:

> I am convinced that these attacks are merely based on a misunderstanding, and that the role of gas theory in science has not yet been played out. The abundance of results agreeing with experiment which van der Waals has derived from it purely deductively, I have tried to make clear in this book. More recently, gas theory has also provided suggestions that one could not obtain in any other ways. From the theory of the ratio of specific heats, Ramsay inferred the atomic weight of argon and thereby its place in the system of chemical elements–which he subsequently proved, by the discovery of neon, was in fact correct....
>
> In my opinion it would be a great tragedy for science if the theory of gases were temporarily thrown into oblivion because of a momentary hostile attitude toward it, as was for example the wave theory because of Newton's authority.
>
> I am conscious of being only an individual struggling weakly against the stream of time. But it still remains in my power to contribute in such a way that, when the theory of gases is again revived, not too much will have to be rediscovered....

Boltzmann and Ostwald although on good personal terms, engaged in bitter scientific debates during this period; at one point even Mach thought the argument was becoming too violent, and proposed a reconciliation of mechanistic and phenomenological physics.[2] While teaching at Leipzig with Ostwald during the period 1900–02, Boltzmann was undergoing periods of mental depression and made one attempt at suicide. He returned to Vienna in 1902, where he succeeded himself as professor of theoretical physics and also lectured on the philosophy of science, replacing Ernst Mach, who had to retire for reasons of health. In 1904 he went to the United States to attend the World's Fair at St. Louis, where he lectured on applied mathematics, and also visited Berkeley and Stanford. He later described his experiences on this trip in a satirical article, "Reise eines deutschen Professors ins Eldorado." But despite his travels and discussions with scientific colleagues, he somehow failed to realize that the new discoveries in radiation and atomic physics occurring at the turn of the century were going to vindicate his own theories, even if in somewhat altered form. The real cause of Boltzmann's suicide in 1906 will never be known;[3] but insofar as despair over the rejection of his lifework by the scientific community may have been a contributing factor (as has sometimes been suggested without much evidence), it is certainly one of the most tragic ironies in the history of science that Boltzmann ended his life just before the existence of atoms was finally established (to the satisfaction of most scientists) by experiments on Brownian motion guided by a kinetic-statistical theory of molecular motion.

Notes for §6.6

1. According to E. Cassirer (*Determinism and Indeterminism in Modern Physics*, p. 176), Boltzmann's arguments for atomism based on the epistemology of differential equations have been generally ignored except for an article by R. Hönigswald in *Festschrift für Paul Natorp* (Berlin: De Gruyter, 1924), p. 178 (see pp. 184–85).
2. *Die Principien der Wärmelehre, historisch-kritisch entwickelt* (Leipzig, 1896), p. 362ff. (See §8.5.)
3. A recent suggestion is that Boltzmann suffered infection of the facial nerves; for this and references to other views see Karl F. Herzfeld, *Questions in Statistical Mechanics. Some Reactionary Viewpoints* (Coral Gables, Florida: Center for Theoretical Studies, report CTS-HS-71-1), p. 1. The story that the suicide was a response to criticisms of atomic theory continues to appear in the literature: see Lewis S. Feuer, *Einstein and the Generations of Science* (New York: Basic Books, 1974), pp. 335–41.

6.7 Bibliography

I. *Original Works*. The technical papers that originally appeared in various periodicals have been reprinted in Boltzmann's *Wissenschaftliche Abhandlungen*, ed. F. Hasenöhrl, 3 vols. (Leipzig, 1909). Lectures and articles of general interest are collected in *Populäre Schriften* (Leipzig, 1905); some of these are translated, with extracts from other works, in *Theoretical Physics and Philosophical Problems*, ed. B. McGuinness (Dordrecht and Boston: Reidel, 1974). A review article written with J. Nabl, "Kinetische Theorie der Materie," was published in *Encyklopädie der mathematischen Wissenschaften* (Leipzig, 1905), V, pt. 1, art. V8. Other works are *Vorlesungen über Maxwells Theorie der Elektrizität und des Lichtes*, 2 vols. (Leipzig, 1891–93); his ed. of Maxwell's "On Faraday's Lines of Force," *Ueber Faraday's Kraftlinien* (Leipzig, 1895), with 31 pages of notes by Boltzmann; *Vorlesungen über Gastheorie*, 2 vols. (Leipzig, 1896–98), trans. by S. G. Brush, with introduction, notes, and bibliography, as *Lectures on Gas Theory* (Berkeley: University of California Press, 1964); *Vorlesungen über die Principe der Mechanik*, 3 vols. (Leipzig, 1897–1920); and *Über die Prinzipien der Mechanik, Zwei akademische Antrittsreden* (Leipzig, 1903). Books based on Boltzmann's lectures are Charles Emerson Curry, *Theory of Electricity and Magnetism* (London, 1897), with a preface by Boltzmann; and Hugo Buchholz, *Das mechanische Potential*, published with *Die Theorie der Figur der Erde* (Leipzig, 1908).

II. *Secondary Literature.* Works on Boltzmann are Engelbert Broda, *Ludwig Boltzmann: Mensch, Physiker, Philosoph* (Berlin, 1955); S. G. Brush, "Foundations of Statistical Mechanics 1845–1915," in *Archive for History of Exact Sciences* 4 145–83, (1967) [ch. 10 in this book]; E. G. D. Cohen and W. Thirring, eds., *The Boltzmann Equation* (Wien and New York: Springer-Verlag, 1973) (articles by Broda, Flamm, Klein, and others); René Dugas, *La théorie physique au sens de Boltzmann et ses prolongements modernes* (Neuchâtel, 1959); P. and T. Ehrenfest, "Begriffliche Grundlagen der statistischen Aufassung in der Mechanik," in *Encyklopädie der mathematischen Wissenschaften* (Leipzig, 1911), IV, pt. 32, trans. by M. J. Moravcsik as *The Conceptual Foundations of the Statistical Approach in Mechanics* (Ithaca, N.Y., 1959); Y. Elkana, "Boltzmann's scientific research programme and the alternative to it," in *The Interaction between Science and Philosophy*, ed. Y. Elkana (New York, 1974); M. Grunwald, "Boltzmanns Verteidigung des Materialismus in der anbrechenden 'Krise der Physik'" *Naturwissenschaft Tradition Fortschritt* (Berlin, 1963), pp. 119–38 [= Beiheft zu *Zeitschrift für Geschichte der Naturwissenschaften, Technik und Medizin*]; G. Jaeger, "Ludwig Boltzmann," in *Neue Österreichische Biographie 1815–1918*, §1, *Biographien* (Vienna, 1925), II, 117–37; Martin J. Klein, "The Maxwell–Boltzmann relationship," in *Transport Phenomena – 1973*, ed. J. Kestin (New York: American Institute of Physics Conference Proceedings No. 11, 1973), pp. 297–308.

CHAPTER 7

*Van der Waals**

7.1 The states of matter

What kinds of substances is the world made of? Earth, water, air, and fire, replied the ancients.

Today's student of elementary chemistry quickly learns that these four are *not* the basic elements of which everything is composed. Instead, matter comes in over a hundred varieties: hydrogen, helium, . . ., hahnium, and an indefinite number of other elements that probably can exist but have not yet been named. When he studies physics, the student learns that these elements are not really different kinds of matter after all, but are compounded of a smaller number of "elementary particles": electrons, protons, neutrons, and a host of more transitory pieces of matter and energy. So we seem to have gone far beyond the old naive conception of four basic elements such as earth, water, air, and fire: each of these is an arbitrarily-defined mixture of the basic building blocks of the universe.

But perhaps the question has been misunderstood. In the realm of everyday experience, as well as in the physical chemistry laboratory, we do encounter three distinctly different kinds of substances: solid, liquid,

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and gas. Only we recognize nowadays that an elementary substance such as hydrogen is in some sense the *same* even as it changes its *form* or *physical state* from solid to liquid or gas. We also have a fourth element corresponding to fire: we call it *plasma*, and we can find it in stars, in interstellar space, or in terrestrial laboratories devoted to research on thermonuclear energy. We can even find a little of it in ordinary "fire."

Although plasma has been called the "fourth state of matter," because its properties are so different from those of ordinary solids, liquids, and gases, there is really a continuous transition from ordinary gases to plasmas. As a gas is heated, the violence of a few intermolecular collisions knocks loose some of the electrons from their stable orbits inside the atoms, and gradually the gas becomes more and more ionized. When it consists of electrically charged particles, it has the properties of a plasma; but there is no definite temperature at which a sudden transition occurs. In contrast, if one heats an ordinary crystalline solid, it remains definitely solid until a particular temperature (melting point) is reached; at higher temperatures it is unmistakably liquid. (There are, of course, certain solids that have a gradual transition to the liquid state, but they are unimportant exceptions to the general rule as far as we are concerned.) Similarly, if one heats a liquid, it remains liquid (although part of it evaporates) up to a definite temperature (the boiling point), and becomes entirely gaseous at higher temperatures.

Ordinary experience teaches us that solids, liquids, and gases are distinct forms of matter, and that discontinuous transitions can take place from one form to another at particular temperatures. Scientific experiments, on the other hand, have shown that the gaseous and liquid states are only two extremes of a continuum, and that it is possible to go from one to the other without ever encountering a discontinuous change in properties. It was in 1873 that the Dutch physicist Johannes Diderik van der Waals first gave a comprehensive explanation of this fact; and in 1910 he received the Nobel Prize in Physics for his work on the continuity and physical properties of gases and liquids.

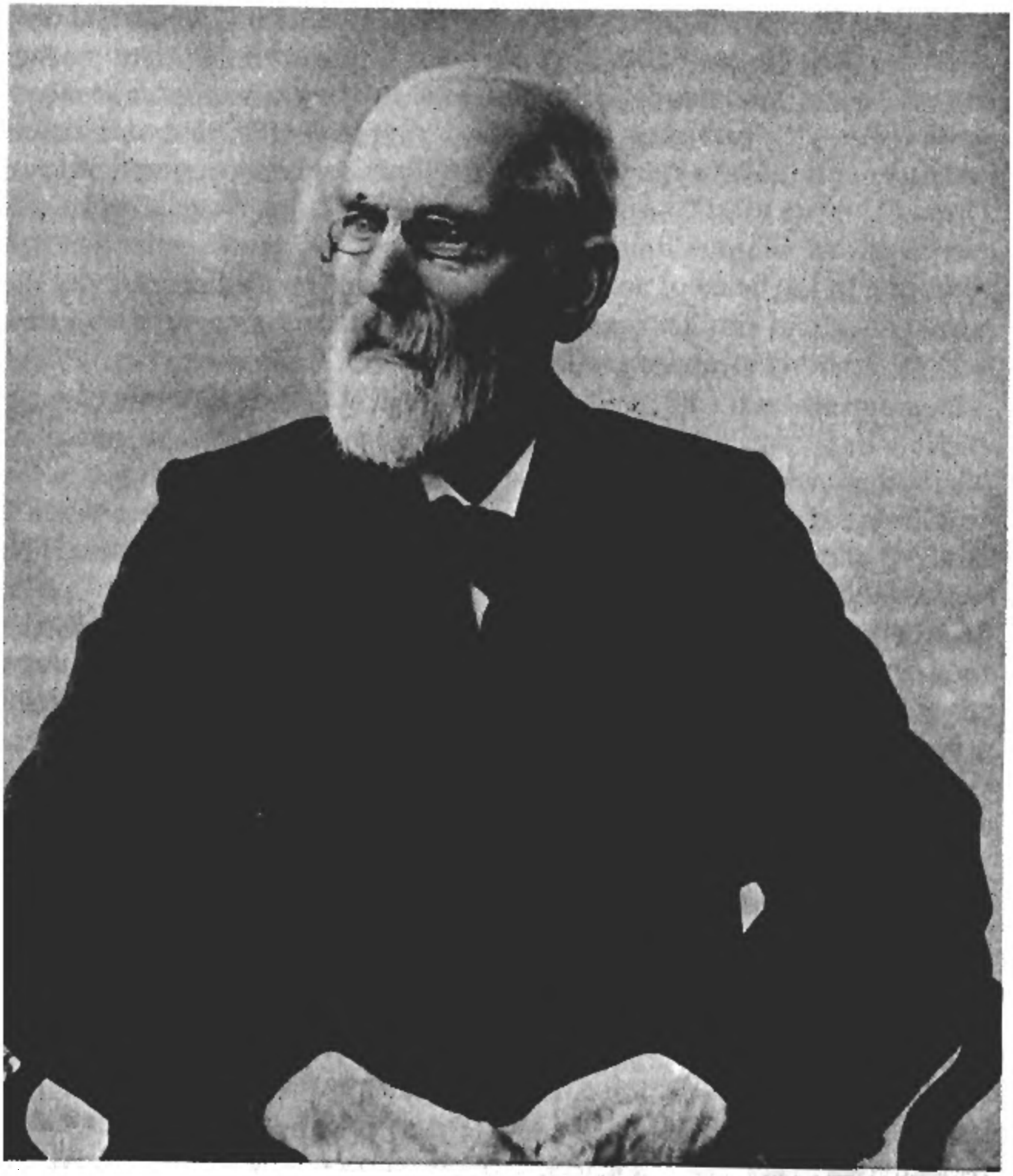
As a basis for his explanation of the continuity of the gaseous and liquid states, van der Waals proposed a particular conception of the molecule: he regarded it as an impenetrable sphere (having a small but definite diameter) that can exert long-range attractive forces on other molecules. In the light of sophisticated 20th-century ideas about atomic and molecular structure, this simple "model" of van der Waals might appear to be obsolete. On the contrary: theoretical calculations performed during the last 15 years with the help of high-speed electronic computers have shown that if one wants a fundamental understanding of some of the basic qualitative properties of the liquid state of matter, van der Waals' model is probably more useful than any other, because it emphasizes the *essential* features of the molecule that determine liquidity without introducing "realistic" but irrelevant complications. Thus, 100 years after its original publication, van der Waals' theory still serves as an illuminating example of how an astute scientist can penetrate to the heart of an important but complex phenomenon by the proper choice of simplifying approximations, thereby opening up a new field of theoretical and experimental research.

7.2 Biographical note[1]

First of all, who was van der Waals? He was born in Leiden, The Netherlands, on 23 November 1837, the son of Jacobus van der Waals; Elisabeth van den Burg was his mother's maiden name. Apparently the economic position of his family (about which not much is known) was not such as to permit him to attend a secondary school where he could prepare for a university education. Instead, after completing elementary school he went to work as a schoolteacher. He continued studying mathematics and physics part-time at Leiden University during the years 1862–65, but while he could obtain teaching certificates in those subjects, he was not permitted to take the regular university examinations because he had not learned Latin and Greek.

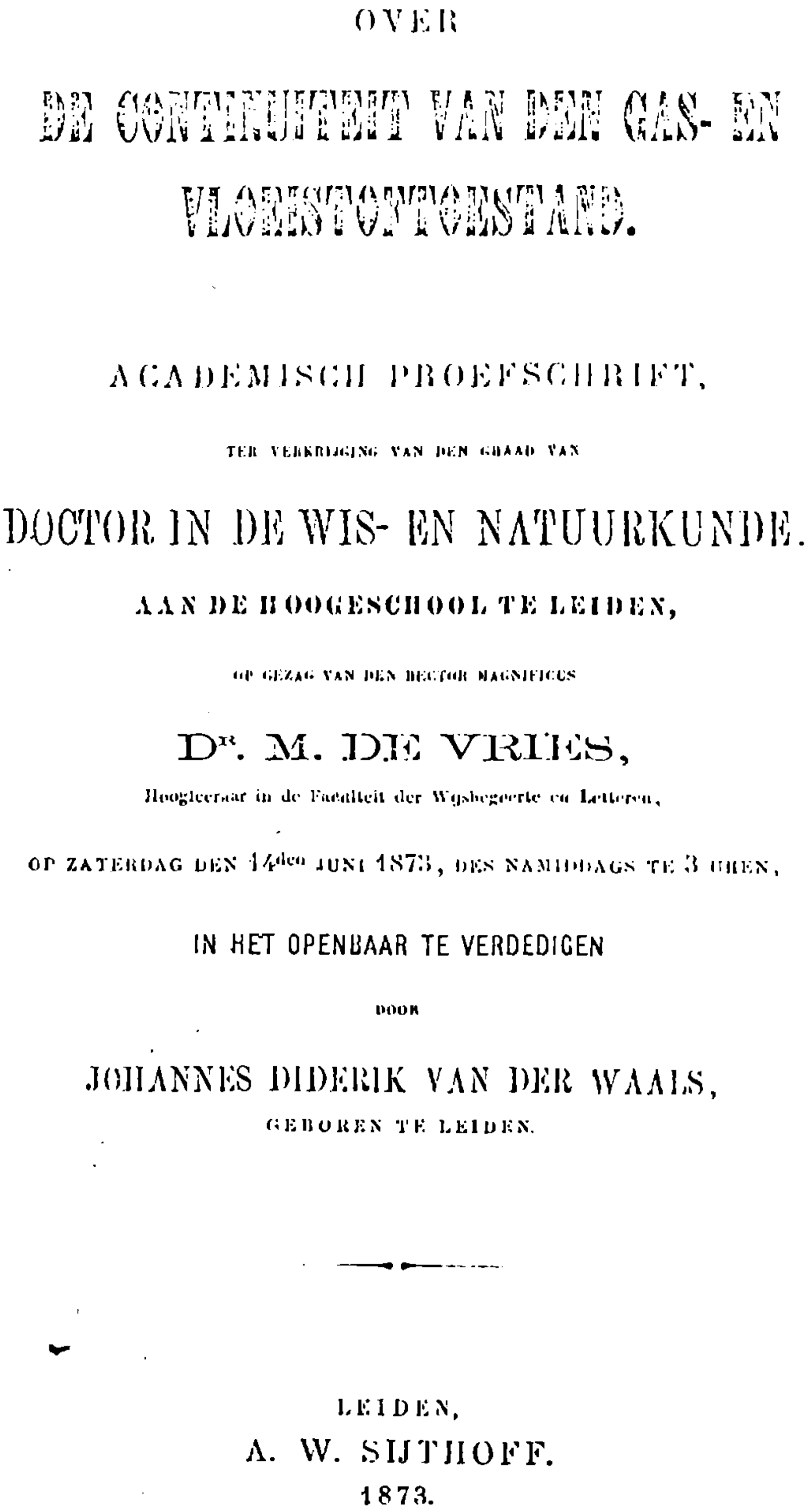
In 1864 he found a teaching position at a secondary school in Deventer, and in the same year married Anna Magdalena Smit. She died a few years later, after giving birth to three daughters and a son; the latter, Johannes Diderik Jr., followed his father into a career in physics, and was still living in Amsterdam at the time I began writing this chapter. (He died in 1971.)

Thanks to new legislation van der Waals was eventually able to obtain an exemption from the classical language requirements so in 1873 he completed his doctoral dissertation and received his degree from Leiden University. Lest anyone be tempted to draw the moral that science students should not be burdened with language requirements, I should point out that van der Waals' own work was first published in Dutch, and would not have become so rapidly known in England and other countries except for the fact that the Scottish physicist James Clerk Maxwell published an enthusiastic review of it in *Nature* in 1874. As Maxwell remarked in a lecture the following year,



JDvdWaals

Fig. 7.2-1. J. D. van der Waals.



OVER

DE CONTINUITEIT VAN DEN GAS- EN VLOEISTOFTOESTAND.

ACADEMISCH PROEFSCHRIFT,

TER VERKRIJGING VAN DEN GRAAD VAN

DOCTOR IN DE WIS- EN NATUURKUNDE.

AAN DE HOOGESCHOOL TE LEIDEN,

OP GEZAG VAN DEN RECTOR MAGNIFICUS

Dr. M. DE VRIES,

Hoogleeraar in de Faculteit der Wijsbegeerte en Letteren,

OP ZATERDAG DEN 14den JUNI 1873, DES NAMIDDAGS TE 3 UREN,

IN HET OPENBAAR TE VERDEDIGEN

DOOR

JOHANNES DIDERIK VAN DER WAALS,

GEBOREN TE LEIDEN.

LEIDEN,
A. W. SIJTHOFF.
1873.

Fig. 7.2-2. Title page of thesis (1873).

van der Waals' thesis "has certainly directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written."

Van der Waals was now properly launched on his career in research, at what is considered a fairly advanced age for physicists. In 1876, already known as one of Holland's leading scientists, he was appointed the first Professor of Physics at the new University of Amsterdam. The faculty included other scientists of international reputation such as J. H. van't Hoff (physical chemistry) and Hugo de Vries (genetics), but for 20 years van der Waals was the only teacher of physics. This meant that he was responsible not only for teaching mathematical physics to the physics and chemistry students, but also experimental physics to the medical and philosophy students; he was also in charge of the teaching laboratory. Despite this heavy load he continued to publish important scientific papers extending his theories in various directions; modern research workers still regard as fundamental his Principle of Corresponding States (see below), his theory of the equation of state of mixtures, and his theory of capillarity.

In addition to his own work, van der Waals was a stimulating influence on the development of physical science in the Netherlands in the last part of the 19th century. A significant part of the progress in such fields as molecular theory, physics of fluids, and low temperature physics was accomplished by Dutch scientists during the period 1870–1915, partly because of the leadership of van der Waals and partly because these fields were temporarily in a state of decline in other countries. As secretary of the mathematics and physics branch of the Royal Academy of Sciences at Amsterdam from 1896 to 1912, van der Waals was responsible for the publication of an English-language edition of the Proceedings of the Section of Sciences, an innovation which greatly facilitated the knowledge of Dutch scientific work in other countries. In 1898, on the 25th anniversary of his dissertation, a group of his students established a "Van der Waals Fund" to be used to sponsor experiments related to the theories of van der Waals; this fund has nourished a strong tradition of research at Amsterdam up to the present time.

Van der Waals was of small stature and had clear blue eyes. It is said that while he had a religious turn of mind, he did not join any established church; and he only voted once in his life. He lived a simple, rather monotonous life, keeping to a regular schedule; his recreations were walking, reading, playing billiards (like several other pioneers of the kinetic theory of gases) and solitaire card games. He died in Amsterdam on 8 March 1923.


PROF DR J D VAN DER WAALS


NED VEREENIGING DER PENNINGVRIENDEN
NOBELPRIJS 1910
P
T

Note for §7.2

1. I thank Professors S. R. de Groot, A. Michels, J. V. Sengers, and J. D. van der Waals, Jr. for helping me to obtain biographical information for this chapter. The following sources have been consulted: J. H. Jeans, *Memorial Lectures delivered before the Chemical Society, 1914–1932* (London: The Chemical Society, 1933), 3, 75; H. Kamerlingh Onnes, in *Great Chemists*, ed. E. Farber (New York: Interscience, 1961), ch. 54; W. Leendertz, *De Gids* **87** (2), 151 (1923); T. P. Levensma, *Nederlandsche Helden der Wetenschap* (Amsterdam: N. V. Kosmos, 1946), p. 162; J. J. van Laar, *J. D. van der Waals, Ein Lebensabriss* (Leipzig: Barth, 1900).

7.3 Earlier research on the gas–liquid transition

The origin of the scientific problem on which van der Waals worked is to be found in experiments on steam engines conducted in the late 17th and 18th centuries, followed by more fundamental laboratory investigations in the 19th century. The operation of the early steam engines often involved the behavior of water at high temperatures and high pressures. The French physicist Denis Papin (1647–1712) found that when water is heated in a strong closed container, it remains liquid at temperatures much higher than its normal boiling point.[1] It was in connection with these experiments that Papin invented in 1681 his "Digester" for cooking food, now known in a somewhat different form (but employing the same principle) as the "pressure cooker."

Such experiments were difficult and dangerous to perform, since the metal containers that could be fabricated at that time could not withstand high temperatures and pressures; and to make containers of glass, so that one could see what was happening inside, was even more risky. Eighteenth-century builders of steam engines (such as Newcomen and Watt, in Britain) abandoned high-pressure systems because of the difficulty of finding suitable materials, and operated their engines at atmospheric pressure or below. Nevertheless, scientific curiosity about what *would* happen to water, if it could be contained at high pressures and high temperatures, still lingered.

The first definite indication of what might happen to the liquid–gas transition at high pressures was uncovered by James Watt in 1783. Watt and the chemist Joseph Black had earlier found, independently, that after water is heated up to its boiling point, a substantial amount of heat must be added to change it to steam at the same temperature. Black proposed to call this the "latent heat of fusion," for the heat needed to convert a solid to a liquid at its melting point. But Watt found, by analyzing his steam data, that the latent heat of vaporization varies with pressure; at high pressures, as the boiling point of water increases, the latent heat of vaporization decreases and apparently goes to zero. Moreover, extrapolation of other data suggested that the densities of water and steam enclosed together would become equal at sufficiently high pressures and temperatures.[2]

In 1822 a French scientist, Baron Cagniard de la Tour (1777–1859), proposed to demonstrate that there must be a limiting temperature above which a liquid becomes gaseous in spite of being compressed in a small space. Illustrating, perhaps, the difference between the engineering and the scientific viewpoint, Cagniard de la Tour tried other liquids for which this limiting temperature might be more easily attained than for water, since he wanted to establish a *general* phenomenon. He was successful with alcohol: when a glass tube was purged of air, filled to about two-fifths its capacity with alcohol, sealed and then heated, the liquid could be seen to expand to about twice its original volume; then it suddenly disappeared, *i.e.* no meniscus (boundary between liquid and gas) was visible. According to Cagniard de la Tour, this meant that the liquid had changed to gas–though, logically speaking, he might just as well have concluded that the gas had all been liquified by the high pressure.[3]

Having worked out a practical technique for observing this peculiar behavior, Cagniard de la Tour was able to apply it to other liquids such as sulfuric ether, and finally, with much difficulty, to water. He concluded that *for every substance there is a particular pressure, volume, and temperature called the "critical point"* at which the liquid appears to change to a gas. (For water, $p_c = 218$ atm, $v_c = 3.2$ cc/g, $T_c = 374$°C.)

During the next 40 years, many other scientists repeated Cagniard de la Tour's experiments with various substances. Almost all of these scientists[4] seem to have accepted the idea that the liquid is actually changed to a gas at the critical point, until 1863. In that year the Irish physical chemist Thomas Andrews (1813–85) published his experiments on carbon dioxide, stating that after the liquid–gas surface vanished, "the space was then occupied by a homogeneous fluid" which could not be called either liquid or gas but is somehow continuous with both. His theory was presented to the Royal Society of London in 1869 under the title "On the continuity of the gaseous and liquid states of matter," and gave what is now considered an essentially correct qualitative description of the variations of pressure, volume, and temperature around the critical point.[5]

Andrews' results for carbon dioxide are shown in fig. 7.3-1, where pressure is plotted against volume for samples kept at various fixed temperatures (isotherms). The pressure was not measured directly but could be estimated from the volume of a sample of air maintained in equilibrium at the same pressure, assuming Boyle's law was valid for the air. At high temperatures (*e.g.* the curve labeled 48.1° [Celsius temperature]) carbon dioxide, like air, obeys Boyle's law, but at lower temperatures an inflection in the curve becomes noticeable. What happens next is indicated more clearly in fig. 7.3-2: the isotherm at 31.3°C has a point of inflection at *C*, the critical point. (More recent experiments give the critical temperature as 31.0°C; the critical pressure is 73 atmospheres, and the critical volume is 2.23 cc/gm.) At lower temperatures a typical isotherm looks like the curve *ABDE*: starting out from the rarefied gas (*E*) and increasing the pressure, one finds that there is a sudden condensation at point *D*, so that the volume changes

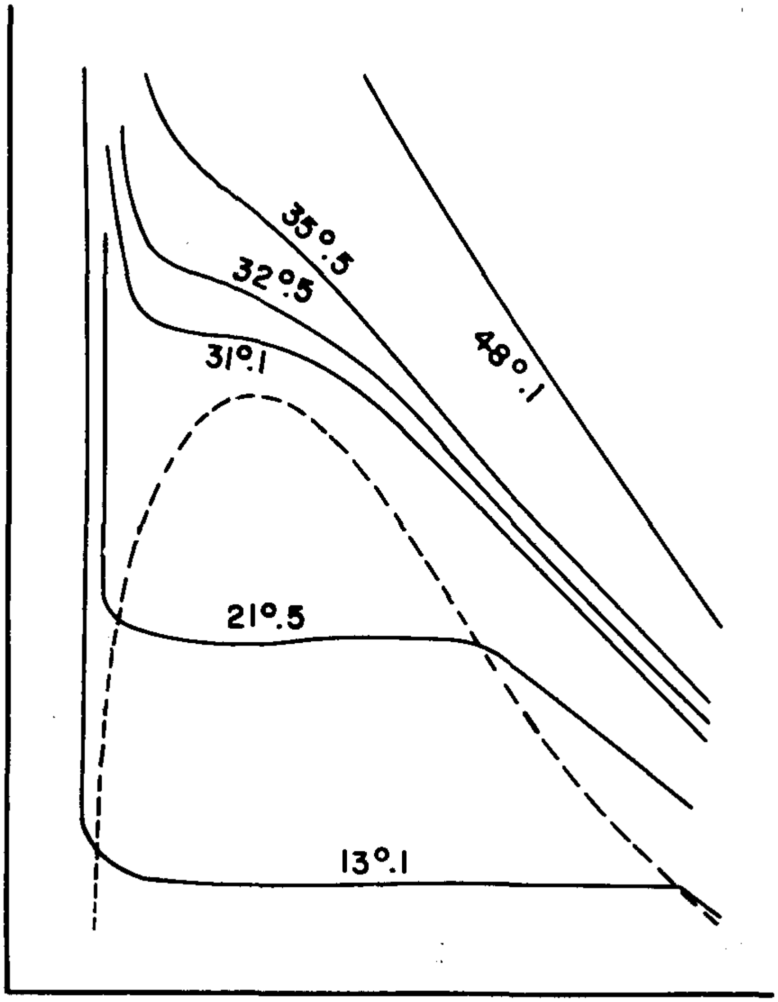


Fig. 7.3-1. Thomas Andrews' isotherms for carbon dioxide, based on Andrews' data (after J.R. Partington, *An Advanced Treatise on Physical Chemistry*, vol. I).

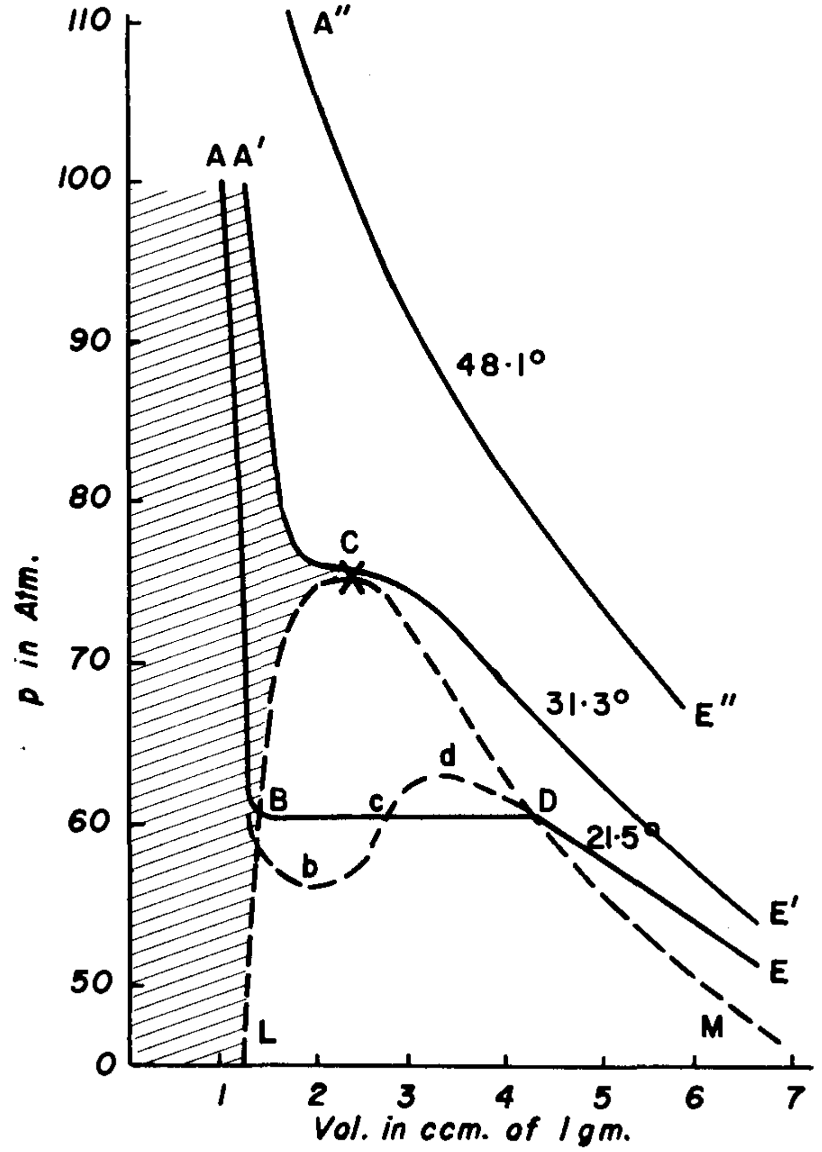


Fig. 7.3-2.

from about 4.5 cc to only 1.5 cc. This is just the normal condensation of a gas to a liquid, except that one is accustomed to thinking of reducing the temperature at constant pressure rather than increasing the pressure at constant temperature. The remaining portion of the isotherm, from *B* to *A*, represents the compression of the liquid, and is much steeper than *DE* since it takes a much greater change in pressure to produce the same change in volume for a liquid as compared to a gas.

For isotherms at temperatures above 21.5°C, as shown in fig. 7.3-2, the flat portion of the curve (*BD*) extends only between the two sides of the dotted curve and thus becomes shorter and shorter, going to zero at the critical point *C*. This corresponds to the discovery of Watt, mentioned above, that the densities of liquid and gas become more nearly equal at higher temperatures and pressures.

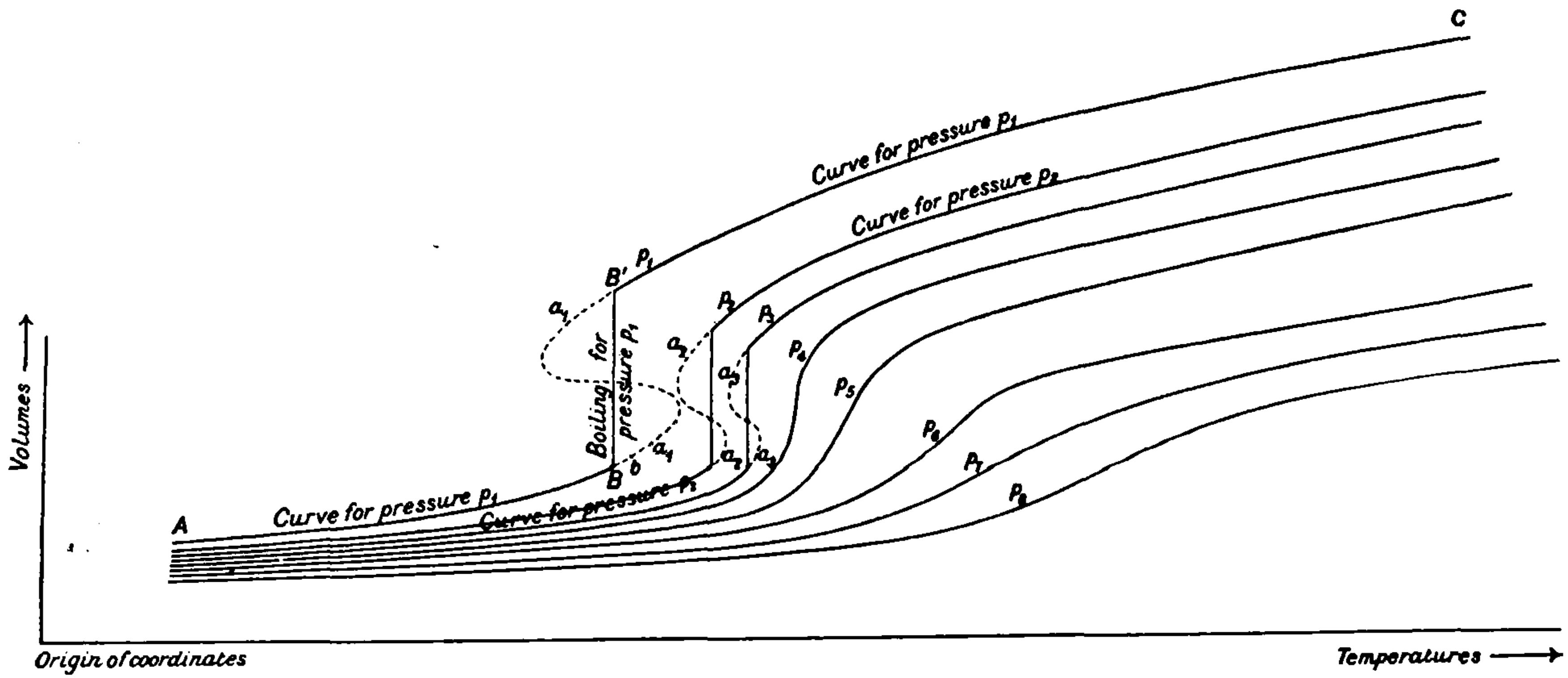
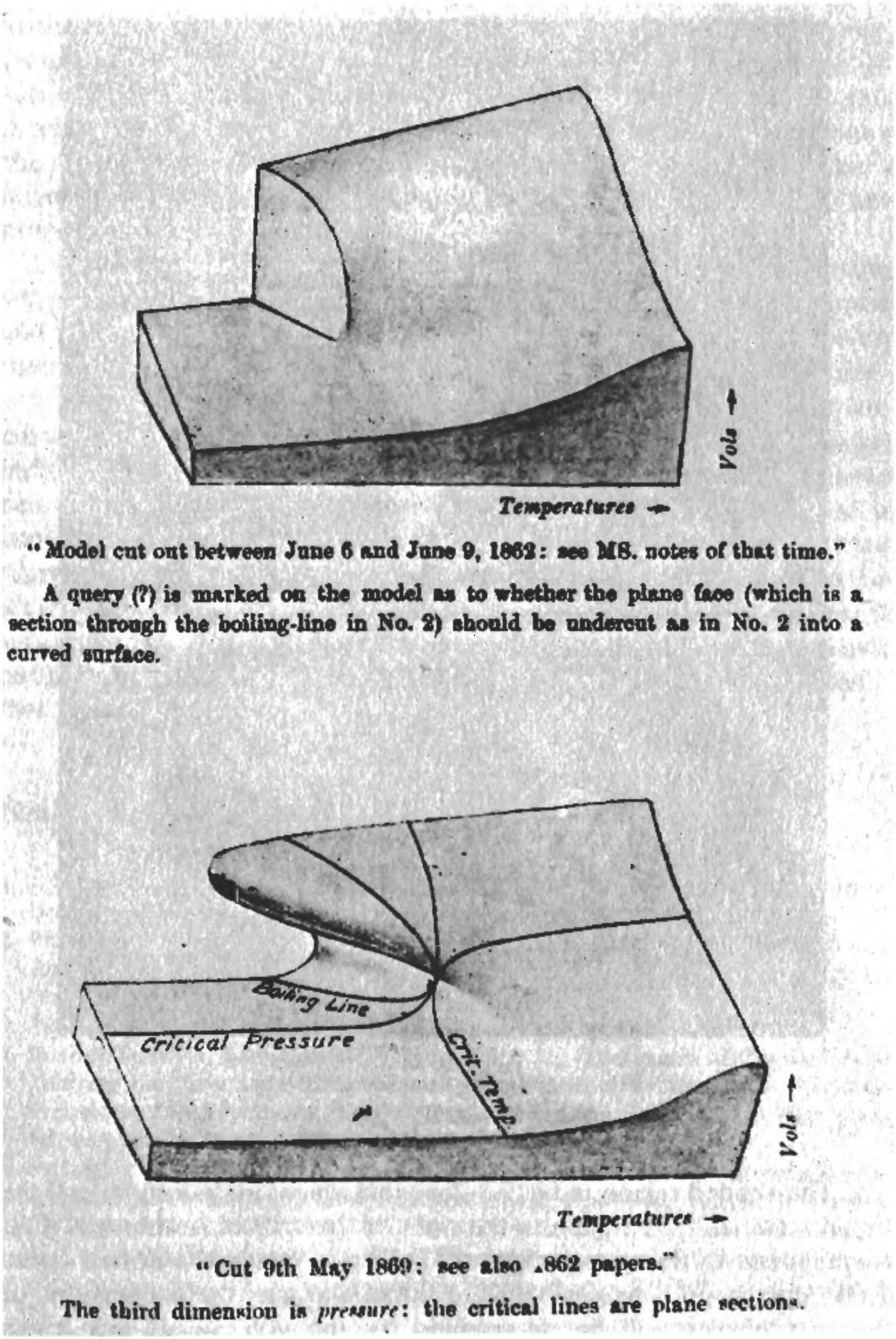


Fig. 7.3-3. James Thomson's diagram showing temperature-dependence of volume, at a series of different fixed pressures (from manuscript notes dated 1862, in *Collected Papers*, p. 322). He wrote: "If the dotted curves a_1a_1, etc. have a real existence, I suppose they will represent possible but unstable states of the fluid-states which perhaps men cannot bring into occurrence: unles perhaps in some extreme or special circumstances."



"Model cut out between June 6 and June 9, 1862: see MS. notes of that time."

A query (?) is marked on the model as to whether the plane face (which is a section through the boiling-line in No. 2) should be undercut as in No. 2 into a curved surface.

"Cut 9th May 1869: see also 1862 papers."

The third dimension is *pressure*: the critical lines are plane sections.

Fig. 7.3-4. James Thomson's solid models giving curves of change of state, based on Andrews' data (from Thomson's *Collected Papers*, p. 277).

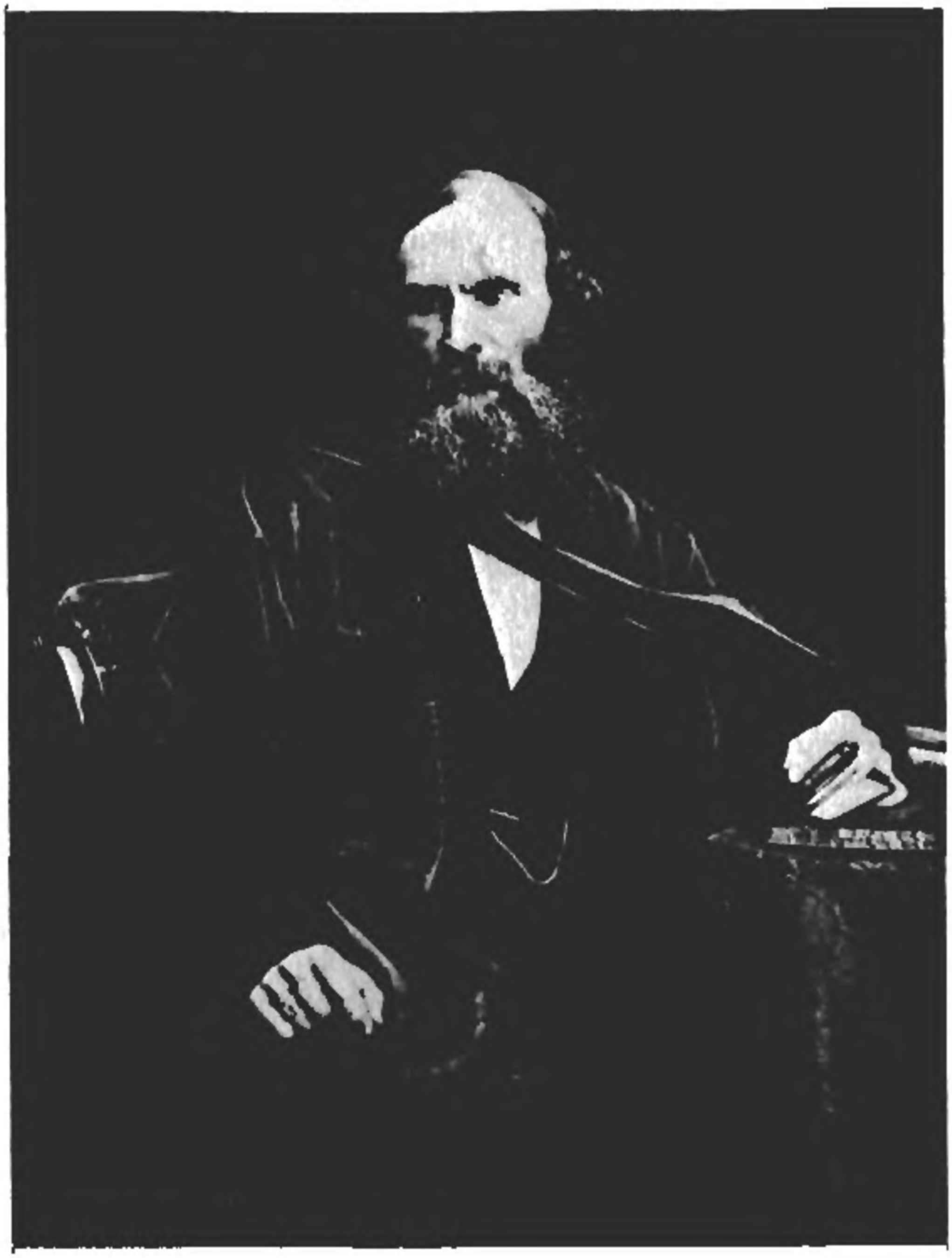


Fig. 7.3-5. James Thomson (1822–92).

The shaded region in fig. 7.3-2 is what we would normally call the liquid state, and the region to the right of the critical isotherm $A'CE'$ corresponds to the gaseous state. The region inside the dotted curve LCM corresponds to a mixture of liquid and gas; the proportions of the two phases will be determined by the volume, at any given temperature or pressure. (Note that one cannot control the pressure and temperature independently, since at the boiling point one determines the other.) But it is evident from the graph that one can pass from gas to liquid states without ever going through a definite "condensation" and one can convert a liquid to a gas without "boiling" it–this is what is meant by the continuity of states. As soon as one gets above the critical temperature and pressure, it is impossible to make a meaningful distinction between liquid and gas; the resulting "fluid" has properties that merge into both.

In 1871, James Thomson (1822–92), brother of William Thomson, suggested that there might be a continuous transition between liquid and gaseous states *below* the critical point as well as above it, even though Andrews' experiments indicated discontinuous change in density along the horizontal line *BD*. Thomson proposed an alternate curve, an S-shaped isotherm which would avoid this discontinuity, indicated by the dotted line *bcd* in fig. 7.3-2.The portions of this curve near *B* and *D* would correspond to a supercooled liquid and a superheated gas, respectively, but most of the curve would not represent stable states of the system. Thomson's theory might be viewed as a plea for *continuity* in the face of apparent *discontinuity*; it anticipated in a curious way the qualitative results of van der Waals published two years later, but without giving the molecular rationale that was essential.[6]

Notes for §7.3

1. J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1951), **II**, 276.
2. Partington, *op. cit.* **I**, 623 (1949). *Partners in Science: Letters of James Watt and Joseph Black*, eds. E. Robinson and D. McKie (Cambridge, Mass.: Harvard University Press, 1970), pp 117–18.
3. Partington **I**, 623.
4. In 1830, however, John Herschel suggested that the experiments of Cagniard de la Tour are the "first step" toward proving the continuity of the states of matter. *Preliminary Discourse on the Study of Natural Philosophy* (London, 1830, New York: Johnson Reprint Corp., 1966), p. 234.
5. Partington **I**, 625–29. Andrews' paper in *Phil. Trans.* **159**, 575 (1869) has recently been reprinted in *Cooperative Phenomena near Phase Transitions*, ed. H. E. Stanley (Cambridge, Mass.: MIT Press, 1973). See also the account of Andrews' contributions by J. S. Rowlinson, *Nature* **224**, 541 (1969) and the survey of the history of critical point phenomena by E. S. R. Gopal and B. Viswanathan, *J. Sci. Ind. Res. (New Delhi)* **28**, 204 (1969).
6. Partington **I**, 675.

   "The continuity of the gaseous and liquid states furnishes a strong experimental presumption against any kind of constitution of matter, corpuscular or otherwise.

The atomic conception of definite proportions is therefore not only not absolutely necessary, but doubly improbable." E. J. Mills, *Phil. Mag.* [4] **42**, 112 (1871), reprinted in *Classical Scientific Papers*: *Chemistry*, ed. D. M. Knight (New York: American Elsevier, 1968), p. 302 (quoted from p. 310).

7.4 Kinetic theory of non-ideal gases

Daniel Bernoulli and John Herapath had attempted to modify the ideal-gas equation of state ($PV = RT$) by taking account of the finite size of the molecules; later Elie Ritter introduced a correction for attractive forces within the context of the caloric theory of gas pressure (§11.3). The particular forms of the corrections introduced by these authors have not survived in modern kinetic theory, but they do indicate the desire to take some account of short-range intermolecular forces.

In 1858 Clausius invoked a finite molecular size in order to explain the fact that diffusion and intermixing of gases is much slower than one would expect from the computed velocities of individual molecules (§4.4). His concept of "mean free path" was then used by Maxwell to develop the elementary theory of viscosity, heat conduction, and diffusion (§5.2). According to Maxwell's theory, a measurement of the viscosity coefficient of a gas, for example, should give direct information about the effective molecular diameter (d) and the number of molecules in a given volume (N); or rather, it gives the value of the product Nd^2. Loschmidt in 1865 pointed out that if such a gas could be condensed to a regular arrangement of touching spheres, its volume would then be approximately Nd^3. With this second relation between N, d, and an experimentally measurable quantity it was possible to estimate both N and d for several substances, the results being within 20% of those presently accepted (§1.8). Thus by the time van der Waals completed his theory, fairly definite information about molecular sizes was available.

In addition to the finite size of molecules, it was also known before 1873 that there must be some kind of attractive forces between molecules. For van der Waals the best evidence of these forces was Laplace's successful theory of capillarity and surface tension in liquids, based on a definite hypothesis of intermolecular attractive forces. But Laplace's theory had been developed at the beginning of the 19th century at a time when most scientists (including Laplace) had not accepted the kinetic theory of gases; the pressure of a gas was attributed to intermolecular *repulsive* forces rather than to the impacts of rapidly moving molecules against the sides of the container. Laplace's force law (short-range attractive combined with long-range repulsive forces) could no longer be taken as the basis for a molecular theory after the kinetic theory of gases had been established. More reliable evidence about the intermolecular force law came from the experiments of J. P. Joule and William Thomson in the 1850's, showing that when a gas is allowed to expand into a vacuum there is in general a small cooling effect. If the forces had been repulsive at the average distance between molecules in a gas, one would have expected an increase in average molecular speed in this situation–the forces would have been acting to push the molecules apart, thereby accelerating them. Since, according to the kinetic theory, increase in average molecular speed means a higher temperature, repulsive forces would lead to a heating effect while attractive forces would lead to a cooling effect, and the latter is what was actually observed.

Thus by the time van der Waals started his work on the theory of the gas–liquid transition, there was reasonably good evidence at hand for a molecular model qualitatively similar to the one we now accept: short-range repulsive forces, which can be represented by ascribing a finite diameter d to the molecule; and long-range attractive forces, probably decreasing fairly rapidly with increasing distance. There was also, thanks to Clausius and Maxwell, a mathematical framework for kinetic theory into which such a model might be incorporated.

Van der Waals started by deriving a general "equation of state" for a system of molecules with short-range repulsive and long-range attractive forces. He showed that the total pressure of the system could be regarded as the sum of the external and the internal pressure. The external pressure P is what one actually measures in an experiment; the internal pressure results from intermolecular attractive forces. (For example, a molecule attempting to leave the surface will be repelled by the pressure of whatever is *outside* the system, and will also be dragged back by the attractive forces of other molecules *inside* the system.) Without proposing a specific mathematical form for the attractive force law, van der Waals argued that its effect on the pressure should be inversely proportional to the square of the volume of the system (or directly as the square of the density). Thus the term P in the ideal-gas equation of state is to be replaced by $P + a/V^2$

$$P + \frac{a}{V^2} = RT$$

This is, of course, equivalent to saying that the external pressure, which is the quantity one can measure directly, is *less* than the ideal-gas pressure by an amount inversely proportional to the square of the volume.[1]

The effect of short-range repulsive forces was also taken into account in a very simple way: van der Waals assumed that the volume available for molecular motion is not the total volume V but an amount somewhat smaller, the correction term being proportional to the number of molecules and to the volume each one occupies. Thus if there are N molecules with diameter d, the volume correction term, usually called b, will be proportional to Nd^3. (For reasons discussed in §11.5, the actual correction is *four* times the volume occupied by the molecules; this fact, first realized by van der Waals, is proved in all texts on kinetic theory.)

Putting together these two corrections for attractive and repulsive forces, van der Waals obtained as his final equation of state

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

Notice that this is a *cubic equation* in the variable V. It is therefore possible for certain combinations of the values of P, T, a, and b, to find three values of V that satisfy the equation. This might seem at first to be a disadvantage for an equation that is supposed to represent the physical properties of gases, but in fact it is just this peculiarity that accounts for its greatest success. Van der Waals found that by plotting P against V for various fixed values of T he obtained isothermal curves that were remarkably similar to those found experimentally by Andrews for carbon dioxide (fig. 7.4-1). The additional values of V are just the parts of the S-shaped curve postulated by James Thomson to represent unstable states of the fluid by which one might make a continuous transition from liquid to gas even at temperatures below the critical point. At temperatures above the critical point there is only one real root of the cubic equation, that is, only one value of V for a given P; these are the curves in the upper right-hand corner of fig. 7.4-1, which approach a hyperbola corresponding to Boyle's law at higher temperatures.

Mathematical analysis of van der Waals' equation shows that at the critical point the pressure, volume, and temperature of the fluid must be related to the constants a, b, and R by the following equations

$$v_c = 3b; \qquad p_c = a/27b^2; \qquad T_c = 8a/27bR$$

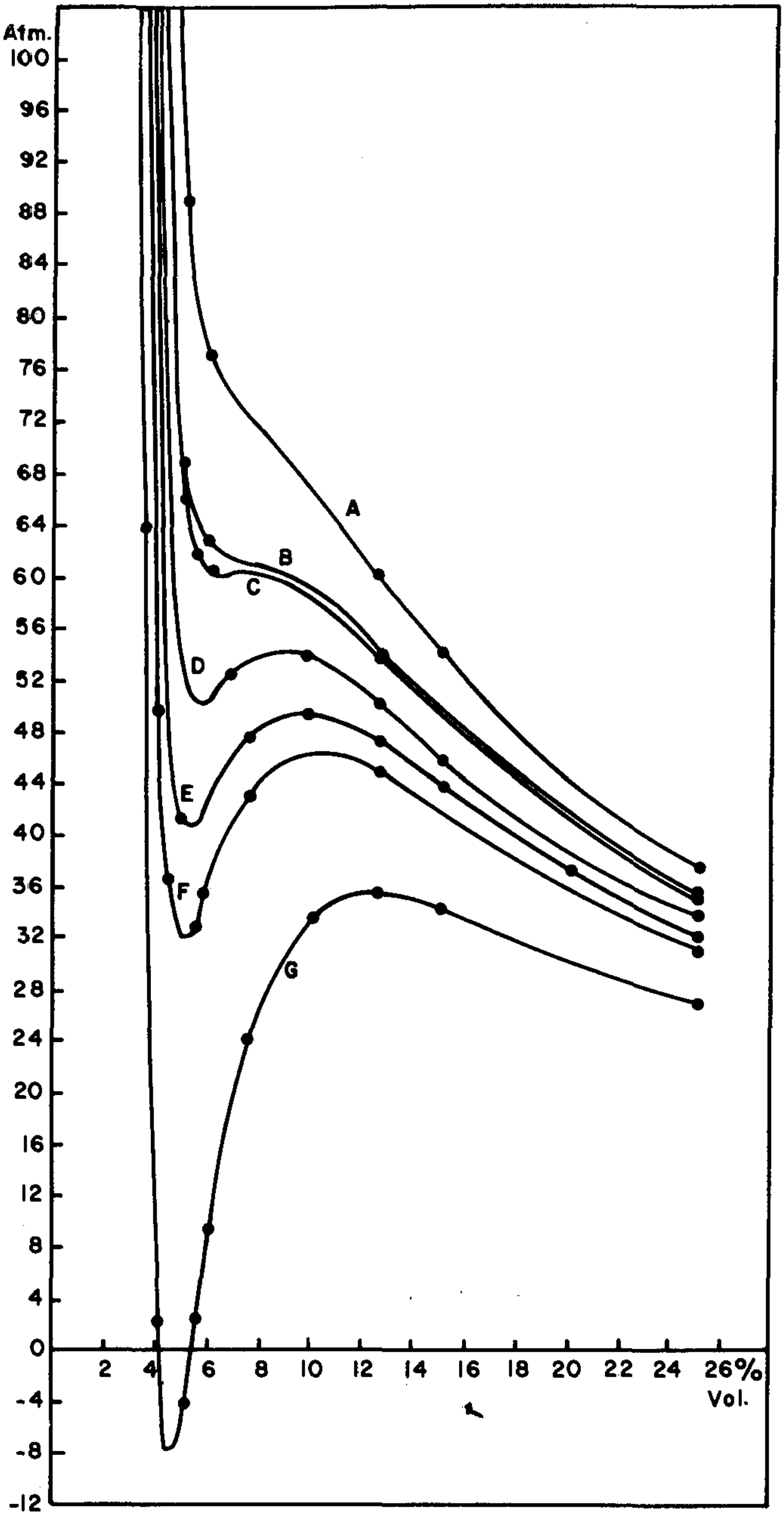


Fig. 7.4-1. Plots of isotherms of carbon dioxide from van der Waals' equation of state (after Partington). A: 48.1°C (321.1°K); B: 32.5°C (305.5°K); C: 31.4°C (304.4°K); D: 21.5°C (294.5°K); E: 13.1°C (286.1°K); F: 6.5°C (279.5°K); G: −20°C (253°K).

Conversely if the critical pressure, volume, and temperature of any fluid satisfying van der Waals' equation are known, these equations can be inverted to determine the constants a, b, and R. Different substances will, of course, have different values of these constants (except for R which should be the same for all substances that behave like ideal gases at high temperatures and low densities).

In 1881, van der Waals proposed a general relation between the properties of all fluids based on his equation; this is known as the "Law of Corresponding States."[2] He pointed out that if the pressure, volume, and temperature of any substance are expressed as ratios of the critical values of these variables,

$$\Pi = p/p_c, \qquad \phi = v/v_c, \qquad \vartheta = T/T_c,$$

then his equation of state becomes

$$(\Pi + 3/\phi^2)(3\phi - 1) = 8\vartheta$$

This equation is known as the "reduced van der Waals equation," and the variables Π, ϕ, and ϑ are called the reduced pressure, volume, and temperature. If the reduced van der Waals equation was correct for all substances, then the Law of Corresponding States would be valid, since two substances would be in corresponding states if they had the same reduced pressure, volume, and temperature. But the law does not depend on the validity of any particular equation of state such as van der Waals'; it requires only that all substances have the same relation between the reduced variables, whatever that relation may be. (The mathematical requirement for an equation of state to be compatible with the Law of Corresponding States is that it must contain two independent constants aside from the gas constant R.) Subsequent experimental work stimulated by the proposed Law of Corresponding States has shown that it is not accurate for all conditions; nevertheless it provides a good approximate rule for estimating the properties of fluids if they have not yet been measured.[3] For example, the law was used as a guide in some of the early successful attempts to liquefy hydrogen and helium.

In view of the fact that van der Waals' dissertation was first published in Dutch, and a German translation was not available until 1881, it seems that his work became known to scientists in other countries remarkably quickly. British scientists learned of it almost immediately through a review by Maxwell in *Nature* (1874).[4] Maxwell judged that many of van der Waals' investigations "are conducted in an extremely original and clear manner; and he is continually throwing out new and suggestive ideas; so that there can be no doubt that his name will soon be among the foremost in molecular science." Maxwell, Clausius, and later the Austrian physicist Ludwig Boltzmann tried to "improve" on van der Waals' equation by more elaborate calculations of the effects of intermolecular forces, but while these attempts served to publicize the subject they did not result in more useful equations (§§11.6, 11.7). Indeed, it has always been something of a mystery why van der Waals' equation works as well as it does, considering the very primitive assumptions from which it was derived. Most equations of state proposed later on, though more complicated in form, do not fit the experimental data much better. With his shrewd physical insight, van der Waals managed to extract the most important qualitative results from his model; his followers could only refine the calculations and test the theory on other substances. (The physicist G. E. Uhlenbeck recently complained that the successes of the van der Waals equation "were so remarkable that they practically killed the subject for more than fifty years!"[5])

Notes for §7.4

1. J. D. van der Waals, *Over die continuiteit van de Gas- en Vloeistoftoestand* (Leiden, 1873), 55. English trans. by R. Threlfall and J. F. Adair, in *Physical Memoirs* (London, 1890), **1**, Part 3, see p. 389. A useful analysis of van der Waals' reasoning and its relation to earlier and later research is given by J. S. Rowlinson, *Nature* **244**, 414 (1973). On the origin of the equation see M. J. Klein, *Physica* **73**, 28 (1974). On the cohesion term see E. R. Tuttle, *Am. J. Phys.* **43**, 644 (1975).
2. J. D. van der Waals, *Amsterdam Verh.* **20**, 5–6 (1880); abstracted in *Ann. Phys. Beibl.* **5**, 27, 250 (1881); English trans., chs. XII and XIII in *Physical Memoirs* (London, 1890), **1**, Part 3.
3. J. R. Partington, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949), **1**, 688–96, 702–3.
4. J. C. Maxwell, *Nature* **10**, 477 (1874). In his widely read lecture to the Chemical Society of London, "On the Dynamical Evidence of the Molecular Constitution of Bodies" (1875, see Bibliography) Maxwell gave a further discussion of the van der Waals equation, including his proof of the "equal areas" rule for the equilibrium state in the two-phase region.
5. G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (Providence: American Mathematical Society, 1963), p. 34.

7.5 The van der Waals force

As we mentioned earlier, van der Waals did not specify the precise nature of the long-range attractive force which enters into his pressure-correction term (a/V^2). Ludwig Boltzmann developed a method for calculating the pressure correction for any hypothetical force law (§11.7) and Maxwell also showed how properties such as gas viscosity could be expressed in terms of the intermolecular force law. There was thus the possibility that by computing the theoretical equation of state and viscosity coefficients for a number of possible force laws, and comparing the results with experimental data, one could determine the actual force law for particular molecules. This research program was undertaken by W. H. Keesom in Holland, and later by J. E. Lennard-Jones in England, in the early decades of the 20th century. At the same time, the development of the quantum theory of the atom gave some hope of calculating a theoretical force law from the electrical structure of the molecule. By 1931 Lennard-Jones was able to establish a force law consistent with experimental data and theoretical calculations for a number of simple molecules: the long-range attractive forces between *neutral nonpolar molecules* (with no net electric charge or dipole moment) vary *inversely as the seventh power of the distance.*[1] These forces are quite appropriately known as "van der Waals" forces. However, this term should not be taken to imply that the a/V^2 term in the van der Waals equation follows directly from inverse seventh power attractive forces, as one occasionally reads in textbooks (see §11.7). In the modern theory of the equation of state, both attractive and repulsive forces enter in a more complicated way into an infinite series of corrections to the pressure.

Note for §7.5

1. For detailed discussion see S. G. Brush, *Arch. Rat. Mech. Anal.* **39**, 1 (1970).

7.6 Recent speculations about states of matter

During the past 15 years, theoretical and experimental research has concentrated on a rather close analysis of the behavior of fluids near the critical point. It has been found that the gas–liquid critical point is in many ways similar to certain kinds of transitions of magnetic materials (such as the disappearance of ferromagnetism when a magnet is heated above the "Curie point"). Very accurate experiments have shown quantitative discrepancies from the results predicted by the van der Waals equation; for example, it has been found that whereas the equation predicts that the difference in density between liquid and gaseous phases should go to zero as the square root of the difference between the temperature and the critical temperature, in reality this difference varies nearly as the cube root.[1] This might seem rather an unimportant defect; yet the new theories suggest that by taking seriously such discrepancies one may be led to a significantly better understanding of the microscopic structure of fluids. The modern workers in this field can be called followers of van der Waals not because they accept all of his conclusions, but because they adopt his general approach, drawing on analogies between different physical phenomena and selecting relevant models that can be worked out mathematically to suggest new insights.

In developing the theory of liquids physicists are still far from being able to demand the degree of mathematical accuracy that has been achieved in the theory of gases and of the critical point. The difficulty seems to lie in finding an "ideal" liquid, that is, a simple model comparable to the "ideal gas" (in which intermolecular forces are negligible and the molecules move freely through space) and the "ideal solid" (in which the forces are so strong that they impose a regular "lattice" arrangement on the molecules). It has recently been proposed by B. Alder and W. G. Hoover (Lawrence Livermore Laboratory) that the van der Waals model could be the basis of such an ideal liquid, although its properties would have to be established by numerical computation.[2] Once the properties of the ideal liquid are known, scientists would have a "reference point" against which to test the properties of real liquids. (In addition, the model probably has the desirable property of solidification at high pressures and low temperatures, so that it can represent all three states of matter.)

Another question raised by van der Waals' work is still unanswered: is there a critical point for the transition from solid to liquid? If so, it is at a pressure so high that laboratory experiments are extremely difficult. While some physicists have stated flatly that there cannot be such a critical point,[3] it is generally believed that at the pressures found within stars, all matter becomes an ionized plasma even at the lowest temperatures, so there can no longer be a sharp distinction between solid, liquid, and gas. To take the extreme case, if a solid is compressed at absolute zero, it eventually succumbs to the effect known as "quantum degeneracy" in which the "zero-point energy" of all constituent particles becomes greater than the potential energy of the forces holding them in a definite lattice arrangement. Either there is a discontinuous breakdown of the solid structure at a particular pressure, with a transition to a fluid state, or a continuous change to a fluid state which would imply the existence of a liquid–solid critical point (see the two alternatives sketched in fig. 7.6-1). This is a question of current interest to astrophysicists in connection with the collapse of dense stars.[4]

The success of the van der Waals theory and of more recent theories of phase transitions has interesting implications for a problem often discussed by philosophers of science. Much has been made of the concept of "level of organization" or "level of complexity" in the phenomena of nature. For a long time it was customary to say that whenever we try to go from theories of simple entities to theories of more complex entities, we must expect to introduce new basic princi-

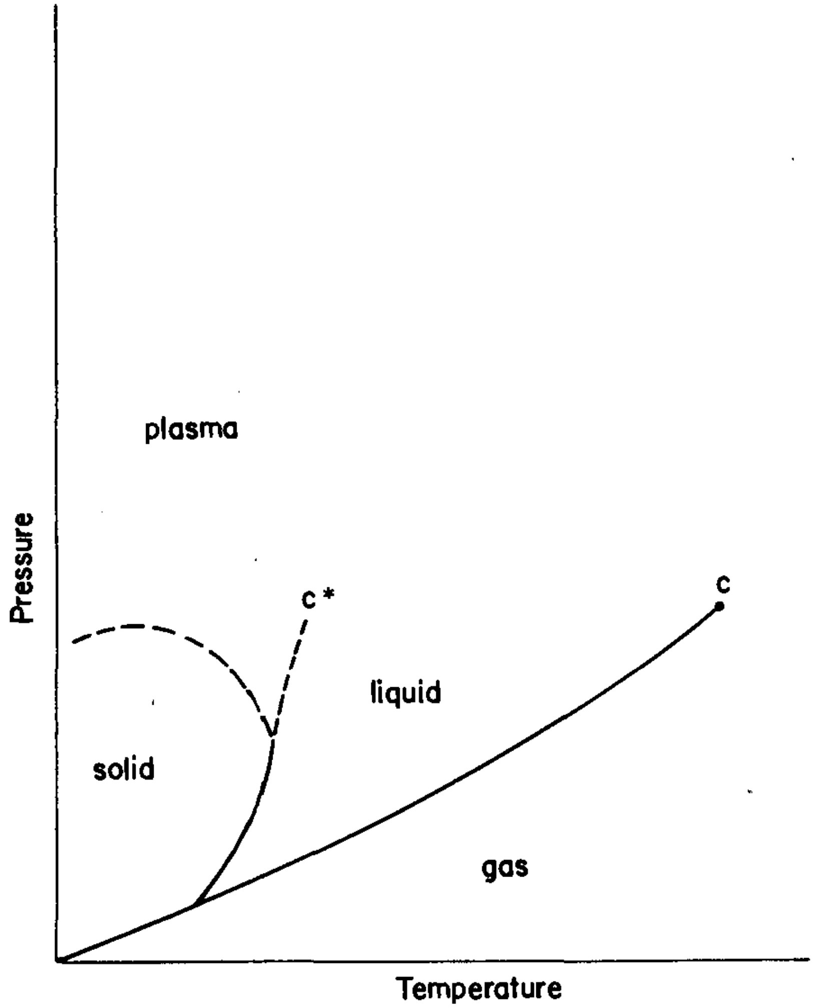


Fig. 7.6-1. General phase diagram of states of matter, showing two possible paths of the solid–liquid transition line ("melting curve") at high pressures. For most substances (water is an exception) the melting point initially increases with increasing pressure; thus compression of a liquid may solidify it. Yet at sufficiently high pressures solids must change to the plasma state even at zero temperature; thus the transition line must either end in a critical point (C^*) or bend back toward the zero-temperature axis.

ples. Thus, sociology cannot be completely explained in terms of individual psychology; biology cannot be reduced to chemistry; and the properties of macroscopic objects cannot be understood on the basis of the properties of atoms. After all, an individual atom cannot be liquid, or gaseous, or solid[5]; that type of property pertains only to very large numbers of interacting atoms. In view of this preconception (one might almost say, a negative attitude about the prospects of science) it was a milestone in the history of science when van der Waals showed that a single general atomic theory, which did not incorporate any assumption about when a fluid is gaseous and when it is liquid, could be used to derive the states of gas and liquid and to explain the transition (either discontinuous or continuous) from one to the other. It was now possible to jump from one level of complexity to a higher level without introducing new laws of nature; van der Waals had pointed out an exciting path for the scientists of the next century to follow.

Notes for §7.6

1. E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945). J. S. Rowlinson, in *Critical Phenomena*, eds. M. S. Green and J. V. Sengers (Washington, D.C.: National Bureau of Standards, 1966), p. 9.
2. B. J. Alder and W. G. Hoover, in *Physics of Simple Liquids* (Amsterdam: North-Holland Pub. Co., 1968), p. 81.
3. M. E. Fisher, in *Essays in Physics*, eds. Conn and Fowler (London: Academic Press, 1972), **4**, 43.
4. S. G. Brush, in *Progress in High Temperature Physics and Chemistry*, ed. C. A. Rouse (New York: Pergamon Press, 1967), **1**, 1.
5. For an example of earlier speculations about differences between sizes of liquid and gaseous particles see J. Jeffreys, *Phil. Mag.* [3] **16**, 10 (1840).

CHAPTER 8

*Mach**

The place of Ernst Mach (1838–1916) in the history and philosophy of science is ambiguous. As a critic of Newtonian views on space and time, he played an important role in preparing the way for Einstein's theory of relativity; and his views on scientific method and the interpretation of physical theories make him an influential ancestor of modern logical positivism. Yet his persistent opposition to atomic theories, and his ultimate refusal to accept relativity, raise the suspicion that Mach's viewpoint provides a basis only for destructive criticism, and tends to discourage the development of hypotheses that may turn out to be fruitful.

Leon Rosenfeld offered the following judgment on Mach's position:

> When Mach criticized the atomic theory he of course bet upon the wrong horse and he has to bear the blame for it. But apart from that his paper on the *Erhaltung der Arbeit* was just a very sound warning against the danger of introducing arbitrary elements into atomic theory. His whole point was that one has no right to introduce and to apply to atoms the mechanical concepts which have been derived from experiences about macroscopic

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* Reprinted, with some additional notes and minor changes, from my article in *Synthese* **18**, 192 (1968), by permission of D. Reidel Publishing Company, Dordrecht, Holland.

bodies, unless one has cogent experimental reasons for doing so. I therefore think that it is unfair to criticize Mach just because he happened to draw the wrong conclusion, as his criticisms were completely sound.[1]

On the other hand, one cannot ignore the comment of Einstein about Ostwald and Mach:

> The antipathy of these scholars towards atomic theory can indubitably be traced back to their positivistic philosophical attitude. This is an interesting example of the fact that even scholars of audacious spirit and fine instinct can be obstructed in the interpretation of facts by philosophical prejudices.[2]

Max Planck, earlier in the century, felt it necessary to combat the influence of Mach's views on the younger generation of physicists (just as Lenin felt it necessary to rescue his fellow-Marxists from Machist corruption[3]). Lecturing at Leiden in 1909, Planck asserted that Mach's viewpoint, which denied reality to anything but human sensations, tended to divert the attention of scientists from the true goal of scientific endeavour, which was to establish the nature of the external world independent of the human observer. Judged by the fruits of his method, Mach was a false prophet.[4] Again, at a lecture in Berlin 1913, Planck attacked the anti-atomist position:

> Whoever rejects faith in the reality of atoms and electrons, or the electromagnetic nature of light-waves, or the identity of heat and motion, can never be found guilty of a logical or empirical contradiction, but he will find it difficult from his standpoint to advance physical knowledge.[5]

If we are to judge a scientific method or philosophy such as Mach's by its "results," we must be much more careful than heretofore in describing what those results actually were. In particular, we cannot be content to say that Mach was simply "right" or "wrong" on a certain point, judged by accepted modern views. Instead, we must examine physical theories as they stood in the late 19th century when Mach was criticizing them, and see what he actually said about them. When Mach's statements on atomic theory are put into their historical context, it turns out that Mach's position is much more complex than is generally reported. Moreover, some of the scientific questions discussed by Mach are by no means settled even today, to say nothing of the philosophical or methodological ones. Thus, while we maintain that the philosophy of science cannot usefully be studied apart from the history of science, we find that history by itself cannot be used to justify the exclusive validity of any one scientific method.

In recent publications Lewis Feuer has suggested that Mach's rejection of atomism can be explained psychologically: because of his hostility to his father and other dominant males, going back to his childhood, he sought to replace masculine descriptions of nature by feminine ones. As evidence Feuer cites the passage from Mach's 1882 address on "The Economical Nature of Physical Inquiry," predicting that "physical science will give up its mosaic play with stones and will seek out the boundaries and forms of the bed in which the living stream of phenomena flows." According to Feuer, in this metaphor "atoms" = "stones" = "testicles."[6] While interesting as an example of Freudian-style explanation, Feuer's suggestion does not seem to me to contribute much to our present subject since it does not attempt to account for the *changes* in Mach's position during his career.

Notes for §8.0

1. Discussion remark at the Ninth Symposium of the Colston Research Society (1957), in *Observation and Interpretation in the Philosophy of Physics*, ed. S. Körner (New York: Dover Pubs., 1962), pp. 54–55.
2. *Albert Einstein Philosopher-Scientist*, ed. P. A. Schilpp (New York: Library of Living Philosophers, 1949; Harper Torchbook reprint, 1959), p. 49, translated by Schilpp from Einstein's "Autobiographisches" written at age 67. Einstein said that while Mach's epistemological position influenced him in his younger years he now considered it "essentially untenable" as illustrated by the fact that it led Mach to oppose the kinetic atomic theory (*ibid.*, p. 21).
3. V. I. Lenin, *Materializm i Empiriokrititsizm* (1909); English trans., *Materialism and Empiriocriticism: Critical Comments on a Reactionary Philosophy* (Moscow: Foreign Languages Publishing House, 1947).
4. M. Planck, *Phys. Z.* **10**, 62 (1909); reprinted in his *Physikalische Abhandlungen und Vorträge* (Braunschweig: F. Vieweg & Sohn, 1958), III, 6. English trans. in Planck's *A Survey of Physical Theory* (New York: Dover Pubs., 1960, reprint of the trans. by R. Jones and D. H. Williams). New English trans. by Ann Toulmin in *Physical Reality*, ed. S. Toulmin (New York: Harper, 1970), p. 3.
5. M. Planck, *Neue Bahnen der Physikalischen Erkenntnis* (Berlin: Norddt. Buchdr., 1913/Leipzig: Barth, 1914); reprinted in *Phys. Abh.* III, 65. English trans. in *Phil. Mag.* [6] **28**, 60 (1914); also in *A Survey of Physical Theory*–the quoted passage is slightly different, on p. 54.
6. L. S. Feuer, *American Imago* **27**, 12 (1970); *Einstein and the Generations of Science* (New York: Basic Books, 1974), p. 26f. For the context of the quotation see below, §8.4.

8.1 The background for Mach's opinions on atomism

I shall summarize here the various theories and schools in the late 19th century which were concerned with atomism in one way or another, making only those distinctions that seem necessary in order to understand where Mach placed himself:

(1) The *Atmospheric Atom Model* of the late 18th and early 19th centuries. As the model was usually described, there are two kinds of atoms: matter-atoms and ether-atoms. Matter-atoms attract each other, the attractive force being inversely as the square of the distance, at least at large distances; ether-atoms repel each other, and matter-atoms attract ether-atoms.[1] Each matter-atom is therefore surrounded by an atmosphere of ether-atoms. Other atmospheres, composed of caloric for example, may be added. The model provides the basis for explaining electrical, magnetic, thermal, mechanical, and gravitational properties by postulating imponderable particulate fluids. This model, with various modifications, can be found in most physics textbooks published between 1780 and 1860; of particular interest to us is *Anfangsgründe der Physik* (Wien 1844; 4th ed. 1860) by Andreas Ritter von Ettingshausen, one of Mach's teachers at Vienna.

(2) *Dynamism*, the belief that the ultimate basis for the properties of matter is to be found in forces acting through space. Boscovich had shown how the atom could be reduced to a point-center of force, and Kant had advocated the construction of a system of physics based on attractive and repulsive forces. This suggestion of Kant had been taken up by the German school of *Naturphilosophie*, and, according to some historians of science, exerted considerable influence on the development of electromagnetism (Oersted and Faraday) and the discovery of the Law of Conservation of Energy.[2] In the 19th century, Dynamism split into two distinct theories:

(2a) *Physical Dynamism* became a respectable part of physics, as another version of atomism; it was usually treated as a hypothesis subject to modification in the light of experimental discoveries, and used by such scientists as Hamilton, Helmholtz, Maxwell, Lord Kelvin, van der Waals, and Sutherland. Maxwell and Kelvin emphasized the artificial nature of the assumption that atoms exerted forces on each other proportional to some inverse power of their distance, and, but for the mathematical difficulties involved, would really have preferred something like the vortex theory of the atom, which involved nothing but matter and motion with no need for postulating occult "action at a distance" forces.[3] Boltzmann, in the 1890's tried to divert criticism of atomic theory against this one version of it, so as to leave unimpaired the atomic concept itself.[4] In the 20th century the model of atoms or molecules exerting a combination of attractive and repulsive forces on each other has been used extensively (by Lennard-Jones and many others) though it is no longer taken as a fundamental model, but rather one that can be derived as an approximation from quantum theory.[5]

(2b) *Philosophical Dynamism*, in the non-mathematical form used by the *Naturphilosophen*, developed into anti-atomism by accepting the reasoning that if all the properties of matter depend only on the forces exerted by atoms, then the atom itself is superfluous. This view was maintained by Immanual Hermann von Fichte (son of the better-known philosopher Johann Gottlieb Fichte), who attacked atomism—both the Atmospheric Atom Model and Physical Dynamism—in a series of articles starting in 1854.[6] Gustav Fechner (soon to be the founder of psychophysics) defended atomism,[7] though most physicists paid no attention to Fichte. The views of both sides in the Fichte–Fechner debate were already becoming obsolete, and Ernst Mach was one of the few working scientists who had any interest in this controversy.

(3) *The Kinetic Theory of Gases*, revised in the 1850's by Joule, Krönig, and Clausius, and further developed and applied by Maxwell, O. E. Meyer, van der Waals, and (in Vienna) Stefan and Boltzmann. It may be regarded as the leading example of a mechanistic[8] physical theory; it claimed to reduce the observable macroscopic properties of gases to the motions and collisions of atoms, calculated according to the principles of Newtonian mechanics. The strength of the Kinetic Theory was its success in explaining and predicting transport properties such as viscosity and diffusion; its weakness was the failure to account for specific heat capacities of polyatomic gases. While the Kinetic Theory was based directly on an atomic hypothesis, it did not rely directly on a detailed atomic theory such as the Atmospheric Atom Model or Physical Dynamism. Instead, it required little more information about atoms than their sizes, and conversely it greatly strengthened belief in the reality of atoms by providing the first reliable estimates of atomic dimensions (§1.8).

(4) *Chemical Atomic Theory*, based on Cannizarro's revival of Dalton's theory in 1860. This theory was concerned mainly with the atomic constitution of molecules, the interpretation of chemical reactions, and the determination of relative atomic weights. The conclusions of Chemical Atomic Theory, unlike those of Kinetic Theory,

were independent of the absolute sizes and weights of the atoms, and anti-atomists therefore tried to reformulate these conclusions in terms of relative combining weights without reference to atoms.[9]

(5) *Physical Atomism*, the common ground of all scientists who believed in the reality of atoms, and/or their usefulness in constructing scientific theories. Physical Atomism was no longer a single coherent theory after about 1850, since different models had to be used to explain different properties of matter. Although Physical Atomism was highly vulnerable to criticism for this reason, it was those theorists who did not retreat into phenomenology but continued to explore, unsuccessfully, all the possible atomic models consistent with classical physics, who must be given some share of the credit for the downfall of classical physics. In saying this we are in effect shifting the burden of proof from those who want "to apply to atoms the mechanical concepts which have been derived from experiments about macroscopic bodies" (Mach's view as stated above by Rosenfeld) to those who wish to deny that the realm of the invisible can be interpreted with the help of the same laws that apply to the realm of the visible. In other words, we consider the oft-ridiculed preoccupation with mechanical models in 19th-century physics as a perfectly reasonable attempt to push a successful technique as far as possible.

(6) The tradition of *Pure Thermodynamics*, uncontaminated by atomism. Many scientists thought it worthwhile to preserve Thermodynamics as a set of laws based directly on experiment, whose validity would not depend on the acceptance of any theory about the internal structure of matter. Note that these scientists–Clausius, Kelvin, Rankine, Helmholtz, Gibbs, and Max Born–were not anti-atomists. They all contributed to atomic theory in separate publications.

(7) Attempts to find *Mechanical Analogies for Thermodynamics* (Hamilton's Principle, principle of least action, etc.). Only a few physicists–Clausius, Szily, Boltzmann, and Helmholtz–did any serious work along this line, but the subject aroused enough interest for the British Association to request a special report on it.[10]

(8) Attempts to establish a *Statistical Interpretation of the Second Law of Thermodynamics.* Maxwell, who ridiculed the German attempts to find mechanical analogies for the Second Law,[11] maintained that the Second Law is essentially statistical in nature, and proposed the celebrated "Maxwell Demon" to illustrate this thesis.[12] Boltzmann put the statistical interpretation on a more quantitative basis with his H-theorem, and the subject was later discussed at length by Kelvin,

Tait, Jeans, and Paul and Tatiana Ehrenfest.[13] Gibbs and Tolman emphasized the view that the statistical aspect of irreversibility (ordered motions becoming disordered) stems more from the limitations of human observations of phenomena than from the nature of the phenomena themselves.[14] It should be noted that such statistical interpretations, though often presented in conjunction with the Kinetic Theory of Gases, are not a logical consequence of that theory; one can accept the results of Kinetic Theory without committing himself to a fundamental explanation of irreversibility. The reversibility and recurrence paradoxes, popularized by the Ehrenfests, were used by the anti-atomists to attach not only the Statistical Interpretation of the Second Law but also the Kinetic Theory and Physical Atomism in general.[15] Atomism was said to be defective because a system of atoms governed by Newtonian mechanics could not exhibit the irreversible behavior which is a fact of experience.

(9) *Energetics*, a generalization of thermodynamics which claimed to provide a unified phenomenological description of all physical phenomena. The proponents of Energetics–Ostwald, Duhem, Helm, and others–were active anti-atomists. The name "Energetics" came from an earlier paper of Rankine, who in fact does not belong to this school at all but rather to Pure Thermodynamics and Physical Atomism. It is important to observe the distinction between Pure Thermodynamics–which claims validity only within a limited region and is mainly concerned with axiomatizing results already known, while conceding the usefulness of atomism in finding new results–and Energetics, which claims to be the only legitimate scientific theory, sufficient unto itself.[16]

(10) *Empiriocriticism*, a critical view toward all scientific hypotheses not directly induced from experiment. The term was originally associated with the work of Avenarius, but since the publication of Lenin's book[17] it has been applied to Mach, Stallo, Pearson, and others who hold similar views. Empiriocriticism claims to stand above all theories (1)–(9), being more concerned with the method than the content of science. The detailed criticism of Kinetic Theory and Physical Atomism by Stallo[18] presumably was consonant with the views of other members of the group; Mach, in particular, praised Stallo's book, and dedicated the second edition of his own treatise on heat to Stallo.[19]

Let us now see how Mach traced his own path through this maze of positions, starting from the first one and ending up at the last one, without ever completely accepting any of the intermediate ones.[20]

Notes for §8.1

1. This model has obvious similarities to the ordinary theory of positive and negative electric charges, and in fact both theories developed together in the 18th century from a common origin in Newton's theory of gas pressure. See I. B. Cohen, *Franklin and Newton* (Philadelphia: American Philosophical Society, 1956). On the later version of this model developed by Mossotti, see note 5 to §3.1.
2. See R. C. Stauffer, *Isis* **48**, 33 (1957) and other works discussed in §1.7.
3. See §5.4.
4. L. Boltzmann, *Nature* **51**, 413, 581 (1895).
5. See for example the review by C. A. Coulson, *Nature* **195**, 744 (1962); S. G. Brush, *Arch. Rat. Mech. Anal.* **39**, 1 (1970).
6. I. H. von Fichte, *Zeitschrift für Philosophie und philosophische Kritik* **24**, 24, **25**, 58, 169 (1854) and other articles in this journal.
7. G. Fechner, *ibid.* **25**, 25 (1854); *Über die physikalische und philosophische Atomenlehre* (Leipzig, 1855, 2nd ed., 1864). See H. A. M. Snelders, *Janus* **58**, 194 (1971).
8. As explained in §1.6, a more accurate term might be "kineticist" since the term "mechanistic" does not, in ordinary usage, exclude action at a distance.
9. F. Wald, *Z. phys. Chem.* **22**, 253, **34**, 78 (1897); Ostwald, *Nature* **70**, 15 (1904). D. M. Knight, *Atoms and Elements* (London: Hutchinson, 1967); *Classical Scientific Papers: Chemistry* (New York: American Elsevier, 1968), §V. W. H. Brock, ed., *The Atomic Debates* (Leicester: Leicester University Press, 1967). M. Tanaka, *Jap. Stud. Hist. Sci.* **5**, 87 (1966).
10. G. H. Bryan, *B.A. Rep.* **61**, 85 (1891), **64**, 64 (1894). See M. J. Klein's article on mechanical explanation, *Centaurus* **17**, 58 (1972).
11. See letters to P. G. Tait, December 1, 1873 and October 13, 1876, in C. G. Knott, *Life and Scientific Work of Peter Guthrie Tait* (Cambridge: At the University Press, 1911), pp. 115, 222.
12. Letter to P. G. Tait, December 11, 1867, published on pp. 213–14 of Knott's biography, *op. cit.*; *Theory of Heat* (London, 1871), ch. XXII.
13. Brush, *Kinetic Theory* **2** (Oxford: Pergamon Press, 1966); P. and T. Ehrenfest, *The Conceptual Foundations of the Statistical Approach in Mechanics*, English trans. by M. J. Moravcsik from the German encylopedia article of 1911 (Ithaca: Cornell University Press, 1959); further references given in notes to ch. 14.
14. J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (New York: Scribner, 1902); R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford: Clarendon Press, 1938). For recent opinions on this subject see S. Watanabe, *Prog. Theoret. Phys., Yukawa Commemoration Number*, p. 135 (1965); F. C. Andrews, *Proc. Nat. Acad. Sci. USA* **54**, 13 (1965); P. Morrison, in *Preludes in Theoretical Physics in honor of V. F. Weisskopf* (New York: Interscience, 1966), p. 347. I. Prigogine, in *A Critical Review of Thermodynamics*, eds. E. B. Stuart et al. (Baltimore: Mono, 1970), p. 1
15. §14.7; S. G. Brush, *Grad. J.* **7**, 477 (1967).
16. E. N. Hiebert, in *Perspectives in the History of Science and Technology*, ed. D. H. D. Roller (Norman: University of Oklahoma Press, 1971), p. 67.
17. See note 3 of the introductory section of this chapter.
18. See §1.7.
19. "Vorwort zur zweiten Auflage" of Mach's *Die Principien der Wärmelehre* (Leipzig, 1896); see also the note on page 430 of the 4th ed.
20. The major works of Mach in which his views on atomism are expressed are the

following:

(a) *Compendium der Physik für Mediciner*, (Wien, 1863). I am indebted to Professor Erwin Hiebert for showing me a copy of this rare book, and pointing out its significance.

(b) *Die Geschichte und die Wurzel des Satzes von der Erhaltung der Arbeit*, Vortrag gehalten in der K. böhm. Gesellschaft der Wissenschaften am 15 Nov. 1871 (Prag, 1872; 2nd ed., 1909). English trans., *The History and Root of the Principle of Conservation of Energy* (Chicago, The Open Court Publishing Company, 1911); some of the same material also appears in the article "On the Principle of the Conservation of Energy" in Mach's *Popular Scientific Lectures* (Chicago: Open Court, 1895); 5th ed., 1943, p. 137.

(c) *Die Mechanik in ihrer Entwickelung historisch-kritisch dargestellt* (Leipzig, 1883; 9th ed., 1933); English trans., *The Science of Mechanics*; *A Critical and Historical Account of its Development* (Chicago: Open Court Publishing Company, 1883; 6th ed., with new introduction by Karl Menger, 1960).

(d) *Beiträge zu Analyse der Empfindungen* (Jena, 1886; 9th ed., 1922); English trans., *Contributions to the Analysis of the Sensations* (Chicago: Open Court Publishing Company, 1897); Dover reprint 1959.

(e) *Die Principien der Wärmelehre, historisch-kritisch entwickelt* (Leipzig, 1896; 4th ed., 1923).

(f) *Die Leitgedanken meiner naturwissenschaftlichen Erkentnisslehre und ihre Aufnahme durch die Zeitgenossen* (Leipzig: Barth, 1919) (reprinted from *Physikalische Zeitschrift* **11** (1910) 599, and *Scientia* **7** (1910), nr. 14). English trans. by Ann Toulmin, in *Physical Reality*, ed. S. Toulmin (New York: Harper & Row, 1970), p. 28.

For a more complete list of works by and about Mach, see J. Thiele, *Centaurus* **8**, 189 (1963).

8.2 Mach's early pro-atomism (1862)

At the age of 24, Mach wrote a *Compendium der Physik für Mediciner* (1863) which he dedicated to "seinem hochverehrten Lehrer, Herrn Andreas Ritter von Ettinghausen . . . aus Hochachtung und Dankbarkeit." In this rare and seldom-cited work, Mach wrote that it is no longer possible to treat such phenomena as heat and light separately in a textbook of physics; they should rather be discussed systematically as various kinds of molecular processes which happen to give rise to light, heat, or sound. "Indeed, the customary division is not physical but rather physiological." He uses the atomic theory in this book,

> not because it is the most recent and advanced, and requires no further support, but rather because it brings together the phenomena in a simple and perspicuous [*anschaulich*] connection. One can, if he wishes so to express himself, consider that the

> atomic theory is a formula that has already led to many results, and will lead to many others. In fact, whatever may be the metaphysical view of matter in the future, one can always transcribe into this view the results obtained by atomic theory, just as one can express formulae by polar or rectangular coordinates.[1]

"The goal of physics," says Mach in this *Compendium*, "is to extract a small number of principles from the phenomena. Since these ultimate principles frequently have not yet been found, we must be content with a hypothesis, the so-called atomistic theory." Citing Fechner's *Atomenlehre*,[2] he says that we have to choose between the Dynamic and Atomic Theories; in other words, does matter fill space continuously, or should we imagine that there are empty places between the occupied parts of space?

> According to the atomistic theory one attributes the essential properties of matter to particles or atoms, separated by empty space; one assumes that they are impenetrable and inert, and moreover that they can interact with each other by means of any kind of force.... The atomic theory agrees with physical phenomena much better than the dynamic theory, yet frequently it is subjected to critical examination.[3]

Mach then quotes nearly a page of pro-atomistic arguments from Fechner's book.

"Certain physical phenomena can only be explained by the atomistic theory," according to the young Mach. "First is the polarization of light. Light depends on aether-vibrations . . . ."[4] "In favor of the atomic theory is the fact that it explains all physical phenomena from a single viewpoint. Under certain assumptions about the nature of the forces acting on the atoms, it is possible to reduce all phenomena, at least in the most general features, to the equilibrium and motion of atoms."[5] Then follows an exposition of the Atmospheric Atom Model which we have described above.

Mach also gives a qualitative exposition of the Kinetic Theory of Gases,[6] citing the papers of Krönig and Clausius, and discusses the relation between the spectra of gases and molecular structure.[7] In a paper "Molecular Forces in Fluids," published in 1862 when he had just finished writing his *Compendium*, he indicates that he has also applied the Kinetic Theory to capillary phenomena.[8]

There are three obvious sources for Mach's atomic theory: first, Fechner's *Atomenlehre*; second, the papers of Krönig and Clausius on Kinetic Theory; and third, Ettingshausen's textbook *Anfangsgründe der Physik*, which he does not cite but was presumably quite familiar with. These and other sources exposed him to four of the theories listed above, and three of them he accepted: the Atmospheric Atom Model, the Kinetic Theory of Gases, and Physical Atomism. We know that he was aware of the existence of the other one, Dynamism; since Fechner cited his own articles in the *Zeitschrift für Philosophie* replying to Fichte's criticisms of atomic theory, it is reasonable to suppose that Mach also read Fichte's articles.

Fichte's attack on atomism provides an interesting sidelight on 19th-century philosophy of science which I hope to discuss in more detail elsewhere. Here I must merely note its significance in the development of Mach's views; Fichte proposed an anti-atomic position which Mach explicitly rejected early in his career, and did not return to even when he himself turned against atomism. The notion that matter is space-filling force was no more attractive to Mach than the notion that matter is composed of discrete particles; both went beyond the limits of sense-experience and therefore could not have any scientific foundation.

A more detailed analysis of Mach's early views on atomism may be found in a paper by Erwin Hiebert.[9] According to John Blackmore, Mach never believed in the *reality* of atoms but in the period 1860–63 he thought that the *atomic theory* had "provisional value."[10]

Notes for §8.2

1. *Compendium*, p. vi (trans. by S.G.B.).
2. See note 7, §8.1.
3. *Compendium*, pp. 12–13.
4. *Ibid.*, pp. 13–14.
5. *Ibid.*, p. 15.
6. *Ibid.*, pp. 92–94.
7. *Ibid.*, p. 179.
8. E. Mach, *Wien Ber.* **46**, 125 (1862).
9. E. N. Hiebert, in *Ernst Mach Physicist and Philosopher*, eds. R. S. Cohen and R. J. Seeger (*Boston Studies in the Philosophy of Science* VI) (Dordrecht: D. Reidel Pub. Co., 1970), p. 79.
10. J. T. Blackmore, *Ernst Mach* (Berkeley: University of California Press, 1972), pp. 33–34.

8.3 Mach turns against atomism (1872)

According to Mach's own account,[1] it was the composition of his *Compendium* that "first made me conscious of the insufficiency of [the atomic] theory." In his lectures on psychophysics in 1864,[2] "I already stated clearly that we are not justified in thinking of atoms spatially."[1] "My attempts to explain mechanically the spectra of the chemical elements and the divergence of the theory with experience strengthened my view that we must not represent to ourselves the chemical elements in a space of three dimensions. I did not venture, however, to speak of this candidly before orthodox physicists."[1]

Mach's first outright public rejection of atomism came in his monograph on the history of the principle of conservation of energy, published in 1872.[3] He observed that the conclusion that, if heat can be transformed into mechanical work, it must consist in mechanical processes–in motion–has

> spread over the whole cultivated world like wildfire . . . now people are everywhere eagerly bent on explaining heat by means of motions; they determine the velocities, the average distances, and the paths of molecules, and there is hardly a single problem which could not, people say, be completely solved in this way by means of sufficiently long calculations and of different hypotheses. No wonder that in all this clamour the voice of one of the most eminent, that of the great founder of the mechanical theory of heat, J. R. Mayer, is unheard–
>
> > "Just as little as, from the connexion between the tendency to fall and motion, we can conclude that the essence of this tendency is motion, just so little does this conclusion hold for heat. Rather might we conclude the opposite, that, in order to become heat, motion–whether simple or vibrating, like light or radiant heat–must cease to become motion (*Mechanik der Wärme*, Stuttgart, 1867, p. 9)."[4]

Mach denies that the discovery of conservation of energy proves that heat is not a substance:

> If anyone today should still wish to think of heat as a substance, we might allow that person this liberty with little ado. . . . If, then we are astonished at the discovery that heat is motion, we are astonished at something which has never been discovered. It is quite irrelevant for scientific purposes whether we think of heat as a substance or not.[5]

The connection between Mach's philosophy of science and his anti-atomism is brought out clearly a little later in the same work:

> ...in the investigation of nature, we have to deal only with knowledge of the connexion of appearances with one another. What we represent to ourselves behind the appearances exists *only* in our understanding, and has for us only the value of a *memoria technica* or formula, whose form, because it is arbitrary and irrelevant, varies very easily with the standpoint of our culture.... But let us suppose for a moment that all physical events can be reduced to spatial motions of material particles (molecules). What can we do with that supposition? Thereby we suppose that things which can never be seen or touched and only exist in our imagination and understanding can have the properties and relations only of things which can be touched. We impose on the creations of thought the limitations of the visible and tangible.... In a complete theory to all details of the phenomenon details of the hypothesis must correspond, and all rules for these hypothetical things must also be directly transferable to the phenonenon. But then molecules are merely a valueless image.[6]

While Mach seems to grant no value at all to Physical Atomism, regarding it as a useless hypothesis, he attacks Chemical Atomic Theory from just the opposite viewpoint: it places too severe a restriction on imagination by forcing us to visualize molecules as arrangements of atoms in a space of only three dimensions. Since the space in which molecules exist has nothing to do with the real physical world accessible to our sensations, why should we not permit ourselves to use as many dimensions as we like in arranging hypothetical atoms?[7]

Before dismissing this suggestion as facetious, we should recall that modern physicists, who know scarcely more about elementary particles than 19th-century physicists and chemists knew about molecules, have generously endowed these particles with "charm" and other properties which have no simple mechanical interpretation in three-dimensional space but may be interpreted with the help of extra dimensions. The justification for doing this is the same as that given by Mach: since we cannot "see" these particles anyway, we have no reason to require that they may have only those spatial or mechanical properties that belong to macroscopic objects.

Mach rejected the notion of the heat death of the universe (Lord Kelvin's extrapolation of the Second Law of Thermodynamics), claiming that "time" is only an abstraction from the causal relations between objects and has no meaning for the universe as a whole, so that it is nonsense to say that "the entropy of the universe increases with time."[8] Here he sets himself apart from Boltzmann's position (first published in the same year, 1872) that molecular collisions lead to a secular increase in entropy, and also from the Energetics position of later years, which maintained that this entropy increase is a fundamental law of nature standing above mechanistic physics. Later, Mach was to move closer to Energetics on this point (see below).

Summarizing Mach's position in 1872, we may say that he has repudiated his earlier acceptance of Kinetic Theory and Physical Atomism, without however going over to the Dynamism which he had previously seen as the alternative to Atomism; he feels that the Chemical Atomic Theory is hypothetical, but could be more useful if the prejudice in favor of visualizable molecular models were abandoned. His sympathies lie with Pure Thermodynamics, and he disagrees with almost all his colleagues in stating that the problem of the irreversible time-evolution of the universe is "not a scientific question."[8]

Notes for §8.3

1. E. Mach *Die Geschichte und die Wurzel* (cited in §8.1, note 22(b)), note added to the 2nd ed., p. 86 in the English trans.
2. *Österrechische Zeitschrift für praktische Heilkunde* **9**, 146, 202, 225, 242, 260, 277, 294, 316, 335, 352, 362 (1863).
3. *Die Geschichte und die Wurzel* (op. cit.).
4. *Ibid.*, p. 37 of the English trans.
5. *Ibid.*, p. 47.
6. *Ibid.*, p. 49.
7. *Ibid.*, pp. 51–53.
8. *Ibid.*, p. 63.

8.4 Miscellaneous remarks (1882–95)

Mach carried on the battle against atomism in conjunction with propaganda for his scientific method, without stopping long for detailed criticism or evaluation of the status of atomic theory. In his lecture at Vienna in 1882 on "The Economical Nature of Physical

Enquiry,"[1] he said:

> When a geometer wishes to understand the form of a curve, he first resolves it into small rectilinear elements. In doing this, however, he is fully aware that these elements are only provisional and arbitrary devices for comprehending in parts what he cannot comprehend as a whole. When the law of the curve is found he no longer thinks of the elements. Similarly, it would not become physical science to see in its self-created, changeable, economical tools, molecules and atoms, realities behind phenomena, forgetful of the lately acquired sapience of her older sister, philosophy, in substituting a mechanical mythology for the old animistic or metaphysical scheme, and thus creating no end of suppositious problems. The atom must remain a tool for representing phenomena, like the functions of mathematics. Gradually, however, as the intellect, by contact with its subject-matter, grows in discipline, physical science will give up its mosaic play with stones and will seek out the boundaries and forms of the bed in which the living stream of phenomena flows. The goal which it has set itself is the *simplest* and most *economical* abstract expression of facts.

In his *Science of Mechanics*, first published in 1883,[2] Mach quoted without comment Hero's argument for atomism (p. 132), attributed Newton's confusion about the concept of mass to his preoccupation with atomism (pp. 239, 265), reverted uncritically to his own earlier interest in "molecular forces" in connection with the forms of liquids[3] (p. 479), and finally stated again the hypothetical character of atomism (pp. 588–89):

> . . . chemical, electrical, and optical phenomena are explained by atoms. But the mental artifice atom was not formed by the principle of continuity; on the contrary, it is a product especially devised for the purpose in view. Atoms cannot be perceived by the senses; like all substances, they are things of thought. Furthermore, the atoms are invested with properties that absolutely contradict the attributes hitherto observed in bodies. However well fitted atomic theories may be to reproduce certain groups of facts, the physical inquirer who has laid to heart Newton's rules will only admit those theories as *provisional* helps, and will strive to attain, in some more natural way, a satisfactory substitute.
>
> The atomic theory plays a part in physics similar to that of certain auxiliary concepts in mathematics; it is a mathematical

> model for facilitating the mental reproduction of facts... As mathematical helps of this kind, spaces of more than three dimensions may be used, as I have elsewhere shown. But it is not necessary to regard these, on this account, as anything more than mental artivices. [A footnote refers to the work of Lobachevski, Bolyai, Gauss, and Riemann on generalized multidimensional spaces.]

In *The Analysis of Sensations* (1886),[4] Mach asserted that "the artificial hypothetical atoms and molecules of physics and chemistry" are only mental symbols for "a relatively stable complex of sensational elements" (p. 311) and chided scientists for taking refuge in atomism in order to retain the idea of "constancy" of a body (p. 357). In an article published in English under the same title in 1890,[5] Mach said:

> I make no pretensions to the title of philosopher. I only wish to adopt in physics a point of view that need not be instantly changed the moment our glance is carried into the domain of another science; since, indeed, all must form one whole. The molecular physics of today does certainly not meet this demand.

Mach rewrote parts of his book on the history of the principle of conservation of energy for publication in English in 1894.[6] He repeated his contention that the existence of a mechanical equivalent for heat does not prove that heat is motion rather than substance. But he now has a different opinion about the relation between time and entropy:

> If we could really determine the entropy of the world it would represent a true, absolute measure of time. In this way is best seen the utter tautology of a statement that the entropy of the world increases with the time. Time, and the fact that certain changes take place only in a definite sense, are one and the same thing.

This is exactly the suggestion made by Boltzmann in 1897 in his reply to Zermelo's criticism of the H-theorem,[7] although Boltzmann uses it for a different reason. A bounded mechanical system must, according to Poincaré's recurrence theorem, return eventually to its original configuration, so that its time-evolution will be cyclic. Hence the entropy of the universe, regarded as a mechanical system of particles restricted to a finite space with fixed total energy, cannot continually increase but must eventually decrease in order to return to its original value. Boltzmann suggested that the human sense of time-direction is determined by the direction of increasing entropy through the irreversibility of natural processes, and therefore any organisms living during a period in which entropy is (from our viewpoint) decreasing with time would not experience "time going backwards" but would simply define time in a sense opposite to ours. (Boltzmann probably did not take this idea any more seriously than did Mach, but Hans Reichenbach thought highly of it.[8])

Notes for §8.4

1. E. Mach, *Die ökonomische Natur der physikalischen Forschung* (Wien, 1882); English trans. in Mach's *Popular Scientific Lectures.*
2. *Die Mechanik* (cited in §8.1, note 20(c)).
3. E. Mach, *Wien Ber.* **46**, 125 (1862).
4. *Analyse der Empfindungen* (cited in §8.1, note 20(d)).
5. E. Mach, *Monist* **1**, 48 (1890).
6. E. Mach, *Monist* **5**, 22 (1894), reprinted in *Popular Scientific Lectures.*
7. §14.7, note 26.
8. §14.7, note 29.

8.5 Reconciliation of mechanistic and phenomenological physics (1896–1900)

By 1895, Mach had acquired a number of allies in his battle against atomism, including especially the adherents of Energetics. The dispute came to a head in the bitter debate between Ostwald and Boltzmann at Lübeck in 1895, and was continued for a few years thereafter in the pages of the *Annalen der Physik* and other journals.[1] Although Mach took no part in this debate, it seems to be generally believed that he supported the position of Ostwald.[2] It therefore came as a surprise to me when I read the section in Mach's *Wärmelehre* (1896) in which Mach comments on the dispute and suggests that a reconciliation of mechanistic and phenomenological physics should be possible. Having already pointed out earlier the defects of the mechanistic viewpoint, he feels that something should now be said in its favor, lest the extreme phenomenology of Energetics carry the day. He mentions now with approval the Kinetic Theory, which, by representing the properties of gases and solutions in terms of statistical mass motions of molecules, has stimulated experimental investigations of the temperature-dependence of diffusion velocity, viscosity, etc., and has thereby led to the acquisition of new knowledge about these properties. "The freedom that one permits himself in assuming invisible secret motions is basically no greater than in the case of Black's assumption of a latent heat."[3]

At the same time Mach carefully distinguished between attempts to find Mechanical Analogies for Thermodynamics and attempts to establish a Statistical Interpretation of the Second Law of Thermodynamics. He recognized the value of Boltzmann's discovery that the Second Law corresponds to a principle of least action,[4] and said that we should not, after all, be surprised, having once found that heat behaves like kinetic energy, to find also that it satisfies some other mechanical principles. The occurrence of the expression

$$\delta \cdot \Sigma \int mv^2\, dt$$

in Boltzmann's derivation need not be considered strange, and certainly need not be taken as a new proof of the mechanical nature of heat.[5] On the other hand, Mach did not like Boltzmann's idea of explaining the Second Law by distinguishing between ordered and disordered motion, making a parallel between entropy increase and increase of disordered motion at the expense of ordered motion,[6] this seemed too artificial to Mach.

> If one realizes that an actual analogy of entropy increase in a purely mechanical system of absolutely elastic atoms does not exist, then one can hardly resist the conclusion that a violation of the Second Law–without the help of a demon–must be possible if such a mechanical system were the actual basis of heat processes. I agree completely with F. Wald, when he says: "In my judgment the root of this [entropy] principle lies much deeper, and if it is possible to bring the molecular hypothesis and the entropy principle into harmony, then it is lucky for the hypothesis but not lucky for the entropy theorem."[7]

Although Mach does not mention the recurrence and reversibility paradoxes specifically, he seems to be siding with the critics of kinetic theory who would be willing to throw out mechanical models if they permitted any deviations from the absolute validity of the Second Law.

When Mach wrote his *Wärmelehre* he must not have understood all the ramifications of Boltzmann's theory of irreversibility, for a few pages after the criticism just mentioned, he quotes approvingly Boltzmann's idea that a physical system when left to itself passes to a more probable state, in connection with the tendency toward stability in natural processes discussed by Fechner, Hering, Avenarius, and

Petzoldt.[8] Mach does not seem to realize that he is thereby conceding the validity of an important part of the Statistical Interpretation of the Second Law.

Mach's earlier judgment on atomism was elaborated, with special reference to the Chemical Atomic Theory, in the same book.[9]

> Modern atomistics is an attempt to make the substance concept in its naivest and rawest form–that the body is absolutely permanent–the basis of physics. The *heuristic* and *didactic* value of atomistics, which lies in its perspicuousness [*Anschaulichkeit*] setting into motion the simplest, easiest, most concrete elementary and instinctive functions of fantasy and the intellect, should certainly not be denied. It is significant that Dalton, who was a schoolmaster by trade, revived atomistics. But atomistics, with its childish and superfluous accompanying pictures, stands in sharp contrast to the other philosophical developments of modern physics. It would undoubtedly be possible, just as with the Black substance-picture, to extract from atomistics the essential factual kernel and get rid of the superfluous accompanying pictures. Among these realities belong the concept of definite combining weights, and of multiple proportions. Only with some effort could the simple volume relations of compounds also be represented [without atomic theory]. Above all other things, however, atomism represents the principle that the elements emerge *unchanged* from their compounds. How little this "invariability" of a body corresponds to the original raw substance concept, will become clear. Through the progress of "Stereochemistry" atomistics has again gained ground.

The attempt to eliminate atomism from Chemical Atomic Theory was made by Wald,[10] the year after the publication of Mach's book, and Mach quoted it in a footnote added to the second edition in 1900.[11] At the same time he amplified his remark about stereochemistry, and praised Stallo's book *The Concepts and Theories of Modern Physics* (1882), which he had just learned of through a reference in Bertrand Russell's book *The Foundations of Geometry.*[12] He also replied to Boltzmann's article in favor of atomism, and denied that he advocated a continuous space-filling matter.[13]

Mach and Boltzmann were both teaching in Vienna at this time, and Boltzmann took over Mach's lectures on philosophy of science when Mach retired. It would be of great interest to know something about the personal relations of the two men at this time, since their views on atomism have usually been considered to be irreconcilable. Some evidence on this point is provided by the recollections of Philipp Frank:[14]

> There was always this interesting point: what was the relation between Mach and Boltzmann? This is a point which of course plays a great role in the history of modern physics, and has become rather a political issue in the Russian literature. In the Russian literature we find it sometimes said that Mach was responsible for the suicide of Boltzmann. It is said that Boltzmann was so desperate about the rejection of atomic theory by physicists, resulting from Mach's attacks on it, that he took his life. As a matter of fact this could hardly be true, since Boltzmann was himself, philosophically speaking, rather a follower of Mach. Boltzmann once said to me, "You see, it doesn't make any difference to me if I say that the atomic model is only a picture. I don't mind this. I don't require that they have absolute, real existence. I don't say this. 'An economic description,' Mach said. Maybe the atoms are an economic description. This doesn't hurt me very much. From the viewpoint of the physicist this doesn't make a difference." Boltzmann had a philosophical viewpoint which did not require that you believe in the real existence of atoms. And there wasn't, I would say, any opposition to Boltzmann's physics from the viewpoint of Mach. This opposition existed only, so to speak, in the philosophical realm. Also, strange as it was, in Vienna the physicists were all followers of Mach *and* followers of Boltzmann. It wasn't the case that people would hold any antipathy against Boltzmann's theory of atoms because of Mach. And I don't even think that Mach had any antipathy. At least it did not play as important a role as is often thought. I was always interested in the problem, but it never occurred to me that because of the theories of Mach one shouldn't pursue the theories of Boltzmann.
>
> I wouldn't say, either, that Mach was against the statistical interpretation of thermodynamics. The views of Mach agreed with those of the American, Stallo. He believed that there are no sufficient experimental proofs for assuming the existence of atoms. From the philosophical viewpoint, he rejected them, for reasons which are really similar to those of Stallo. His chief argument, I think, was always that if the atom were a mechanical object, then you could not explain, for instance, the great com-

plexity of spectral lines. Therefore there must be something else there. Schrödinger has always been, throughout his whole life, influenced in a certain way by Mach. And I always had the idea that the atom of Schrödinger is not the atom in the sense of the atomistic theory.

Individually and privately there might have been cases in which people were somehow diverted from the study of atomistic theory because they believed in the phenomenalistic theory, but I don't think that it played a great role among the productive physicists. All were more or less followers of Mach in the philosophical sense: Einstein, Heisenberg, and probably also Bohr.

Notes for §8.5

1. Blackmore, *Ernst Mach*, ch. 14.
2. See for example the statement of A. Sommerfeld, quoted in the translator's introduction to Boltzmann's *Lectures on Gas Theory*.
3. *Die Principien der Wärmelehre* (Leipzig, 1896), p. 362.
4. L. Boltzmann, *Wien Ber.* **53**, 195 (1866).
5. Mach, *Wärmelehre*, p. 364.
6. L. Boltzmann, *Wien Ber.* **76**, 373 (1877); see discussion in §14.5.
7. Mach, *Wärmelehre*, p. 364, citing F. Wald, *Die Energie und ihre Entwerthung* (Leipzig, 1899), p. 104.
8. Mach, *Wärmelehre*, p. 381.
9. Mach, *Wärmelehre*, pp. 428–29.
10. See note 9, §8.1.
11. *Wärmelehre*, 4th ed., p. 357.
12. See note 19, §8.1.
13. *Wärmelehre*, 4th ed., p. 431; Boltzmann, *Wien Ber.* **105**, 807 (1896), English trans. in *Monist* **12**, 65 (1901).
14. Interview with T. S. Kuhn, deposited in the archives of the Sources for History of Quantum Physics project (July 16, 1962).

8.6 Mach "sees" an atom (1903)

Stefan Meyer has reported the following incident, which occurred around 1903.[1] The apparatus invented by Elster and Geitel, and by Crookes, had made it possible to display the flashes made by individual alpha particles on a screen. Of course this does not mean that one actually sees individual atoms, but, as Meyer points out, when we say that we "see" the sun we are actually reporting only our observation of light rays, and the trail back from this observation to a glowing sphere of mass 2×10^{30} kg around which planets revolve is complicated indeed. Be that as it may, there was naturally great curiosity in Vienna to see what impression the new device would make on Ernst Mach. Whenever any of the atomists would speak of atoms to him, he would always say: "Have you seen one?" Up to then, the atomists had to admit that they had not. But now the tables were turned. Though already sick and partially lame, Mach came to the laboratory to look at the spinthariscope. When he saw the flashes, he made no hair-splitting qualifications, but said simply: "Now I believe in the existence of the atom." An entire world picture had changed for him in a few minutes (according to Stefan Meyer).

Note for §8.6

1. S. Meyer, *Wien Ber.* **159**, 1 (1950). The story is confirmed by Karl Przibram in a letter written 12 December 1967 to John Blackmore, though Przibram thinks that "Meyer's words about 'ein ganzes Weltbild' being changed is not to be taken too literally. I do not think that Mach will have given up his positivistic views, but only conceded that atoms now fitted into them." Blackmore, *Ernst Mach*, p. 320. Blackmore also cites an article mentioning a similar story told by Mach's student Anton Lampa: F. Chmelka, *Universum* **21**, 79 (1966).

8.7 The unrepentant sinner (1910)

That should have been the end of the story, except that in real life things never turn out quite as neatly. Whether Mach later had second thoughts and withdrew his rash surrender to the atomists, or whether Stefan Meyer's memory has retrospectively changed the importance or the date of the incident, we do not know.[1] In any case, Mach's last published statements give no indication that he has changed his mind about the existence of atoms.

In 1909, Planck attacked Mach in the lecture mentioned at the beginning of this article.[2] In his reply, Mach reiterated his opinion that atomism is a "hypothetical-fictive physics" and repeated his objection to Boltzmann's statistical interpretation of the Second Law of Thermodynamics.[3] He associated himself with Ostwald as a follower of Rankine's views on the superiority of descriptive to explanatory science, ignoring the fact that Rankine himself devoted considerable effort to developing a molecular-vortex theory of heat. In this essay, written at the age of 72, Mach gives the impression of being a sinner on his deathbed, refusing to be converted by Father Planck to the faith which all his colleagues have accepted; rather than join the company of believers in the reality of atoms, he prefers to maintain to the end his freedom of thought. He reiterated this disbelief in the preface to his book *Physical Optics* in 1913.

At about the same time, Einstein talked to Mach about atomism, and asked him whether he would not accept the atomic theory if (as now seemed likely) it turned out to be the only one that could account for the experimental facts. There are at least three extant accounts of this meeting,[4] all of which agree in essentials: Mach said that he would agree that the atomic theory was the best and most useful hypothesis for physics, without necessarily accepting the "real existence" of atoms.

Notes for §8.7

1. In the opinion of Otto Blüh, the Meyer story "reads like one of the pious fabrications about a life-long disbeliever's return to the faith, *in extremis*.... Since Mach did not mention his 'conversion' anywhere after 1903, it is hard to believe that he was serious when he spoke the words. Was he supposed to give up a founded scientific attitude in one moment of 'inspiration'?" *Ernst Mach Physicist and Philosopher,* eds. R. S. Cohen and R. J. Seeger (Dordrecht-Holland: D. Reidel Pub. Co., 1970), p. 1 (see note 25). John Blackmore has reviewed all the evidence and concludes that the spinthariscope episode did occur, but that it did not change Mach's views on the *reality* of atoms; "The only change was that Mach now accepted the existence of extremely small complexes of microsensations, which some phenomenalists such as Joseph Petzoldt and Anton Lampa, but not Mach, identified with 'atoms'." Blackmore, *Ernst Mach,* p. 322.
2. Note 4, introductory section of this chapter. E. N. Hiebert, *The Conception of Thermodynamics in the Scientific Thought of Mach and Planck* (Freiburg i. Br.: Ernst-Mach-Institut, 1968).
3. E. Mach, *Die Leitgedanken* (cited in note 20(f), §8.1).
4. C. B. Weimberg, *Mach's Empirio-Pragmatism in Physical Science* (New York: Albee Press, 1937), p. 104. I. B. Cohen, *Sci. Am.* **193** (1), 68 (1955). P. Frank, *Einstein: His Life and Times* (New York: A. Knopf, 1947), p. 105. (I am indebted to Lewis Auerbach for the last two references.)

8.8 Summary and concluding remarks

Atomism, as Mach knew it, took several forms in the late 19th century. First was the Atmospheric Atom Model, defended by Fechner and

Mach's teacher Ettingshausen. After initially accepting this model, Mach rejected it, as did almost all his contemporaries. Second was Dynamism, which Mach rejected initially and never mentioned again, except obliquely when he denied that he advocated a continuum theory of matter. Third was the Kinetic Theory, which Mach regarded as a hypothesis which led to some useful results but had been accorded too much attention by physicists because of their confusion about the logical implications of the equivalence of heat and work. Fourth was the Chemical Atomic Theory; Mach thought that its successful results did not depend on the existence of atoms and could be formulated also in a non-atomistic system. Fifth was Physical Atomism, which Mach would grant no more than heuristic value.

The sixth theory on our list, Pure Thermodynamics, was separate from atomism but not hostile to it. Mach tacitly approved of this theory though he contributed nothing to it himself. The tradition of Pure Thermodynamics has continued down to the present, as may be seen by looking at the recent papers on Caratheodory's method in the *American Journal of Physics*; yet, ironically, this is the theory which is now recognized by its practitioners as mainly heuristic, whereas Mach apparently thought it could be developed as a research method; while atomic theory, which Mach considered heuristic, remains at the frontiers of new knowledge.

The only part of mechanistic physics to which Mach gave his unqualified approval (though only in a few words), the attempts to find Mechanical Analogies for Thermodynamics, has completely dropped out of sight in the 20th century. Attempts to find a Statistical Interpretation of the Second Law of Thermodynamics, on the other hand, have been vigorously pursued despite Mach's skepticism; Boltzmann's H-theorem and Maxwell's demon still find a prominent place in modern textbooks. Some of the vehemence of Planck's attack on Mach may be explained by the fact that Planck himself was only a recent convert to Boltzmann's statistical theory of entropy, having previously opposed it.[1] Planck had reluctantly forced himself to use Boltzmann's methods in order to provide a theoretical justification for his radiation formula, and apparently he thought that everyone who still believed that the principle of increasing entropy is absolutely rather than statistically true must be counted as an enemy of modern quantum physics.

Energetics, as a theory of physics, is dead, despite periodic attempts at reviving it. Mach, though sympathetic to many of its goals, did not give his full support to it. Empiriocriticism, Mach's own scientific methodology, has been acknowledged as the forerunner of modern logical positivism and operationalism, and has sometimes been credited with stimulating the theories of relativity and quantum mechanics. It has survived as one possible basis for scientific method, though certainly not the only one.

Having discussed in some detail Mach's views on atomism in relation to 19th-century atomic theories, I would like to conclude by pointing out what seems to be a *lack* of relationship that one might expect. While Mach was not alone in expressing a distaste for crude mechanistic models in physics, his critique of atomism seems to issue from a philosophical viewpoint that is less in touch with the contemporary state of science than were the objections raised by the other anti-atomists. Mach seemed to have little interest in such problems as the paradox of specific heats, or in the detailed comparison of theory and experiment, or even in the logical consistency of atomic models. He left this sort of criticism to writers such as Stallo, whose book *The Concepts and Theories of Modern Physics* (1881) contains a devastating indictment of the kinetic theory of gases. (Mach's endorsement of Stallo has already been noted.) For Mach the unreality of atoms, or rather of any entity that was not subject to sense observation, was a basic axiom; the validity of the axiom could not be affected by the fact that certain phenomena could only be explained, at a particular time, by an atomic theory. On the other hand, Mach was perfectly willing to admit the utility of atomism as a hypothesis. In this respect, Mach's anti-atomism was both more and less strong than Ostwald's. Ostwald, in the 1890's, wanted to eject atomism from science on scientific grounds and replace it by other hypotheses such as Energetics; this was too extreme a position for Mach to follow, as we have seen in the section in *Wärmelehre*. But later, after the work of Einstein, Smoluchowski, and Perrin on Brownian movement had provided new scientific evidence for atomism–evidence which made no impression at all on Mach's views–Ostwald changed his mind and was willing to rehabilitate atomic theory.[2] Mach, as we have seen, still refused to be converted, and rejected atomism as late as 1913 in the preface to his *Physical Optics*.

It is just because of this dogmatic character of Mach's anti-atomism–his refusal to take account of scientific evidence–that I think the final verdict has to go against Mach's methodology, even with the many historical factors taken into account. While I have only considered atomic theory in this article, a similar case can be made on the basis of Mach's views on mechanics.[3] It must be emphasized that while Mach's writings may well have prepared other scientists to accept the revolution in the conception of the nature of matter that occurred in the 20th century, Mach himself was not prepared for that revolution, and he played essentially no constructive role in bringing it about. The path to quantum mechanics did not lead through Pure Thermodynamics or Energetics or Empiriocriticism, but rather through just the kind of naive juggling of mechanistic hypotheses about atoms and molecules which Mach himself deplored. Similarly, the debt of Einstein's relativity to Mach has been overestimated, even by Einstein himself (perhaps intentionally). If Planck, Einstein, Bohr, De Broglie, Heisenberg, Schrödinger, and Dirac had followed Mach's rules for constructing scientific theories, they would hardly have been able to arrive at the results they did.

Notes for §8.8

1. M. Planck, *A Scientific Autobiography and other Papers,* trans. from German essays of 1947/48 (London: Williams & Norgate, 1950).
2. W. Ostwald, *Grundriss der allgemeninen Chemie* (Leipzig: Engelmann, 4th ed., 1909), Vorbericht. English trans., *Outlines of General Chemistry* (London, 1912). In a letter to Ramsay, 17 November 1908, Ostwald wrote that "J. J. Thomson has convinced me concerning atoms, molecules, and Brownian movement, though I have not become an enthusiast, for I cannot turn my brain around so easily. Arrhenius, with whom I spent a cheery week-end in Salsburg, has also influenced me." M. W. Travers, *A Life of Sir William Ramsay, K.C.B., F.R.S.* (London: Arnold, 1956), p. 252.
3. See for example M. Bunge, *Am. J. Phys.* **34**, 585 (1966). In a previous article Bunge reached similar conclusions about Mach's views on atomism: *Boletin del Quimico Peruano* 3, 12 (1951). Blackmore's conclusion is that "Mach the phenomenalist and ally of David Hume doomed the understanding of Mach the scientist" (*Ernst Mach,* p. 323).

Index to Books 1 and 2[*]

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[*] *The Kind of Motion We Call Heat* is published in two books: page numbers 1–300 in the index refer to Book 1 and page numbers 301–770 refer to Book 2.

*Index to Books 1 and 2**

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STUDIES IN STATISTICAL MECHANICS

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