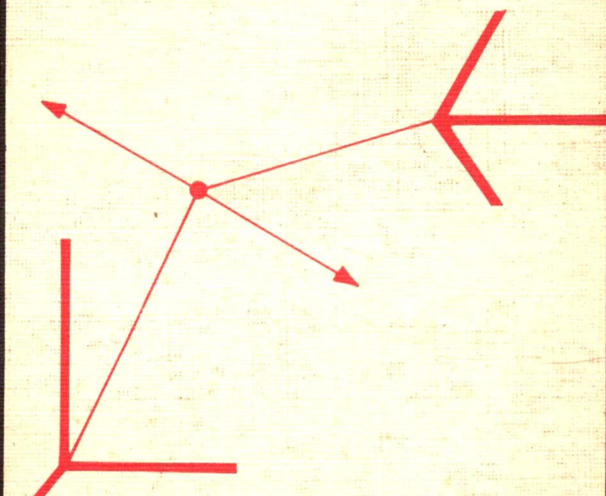
Selected Readings in Physics

kinetic theory

Volume 1. The Nature of Gases and of Heat



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KINETIC THEORY

Vol. I. The Nature of Gases and of Heat

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To Phyllis

Preface

THE study of the history of science is interesting and worthwhile for its own sake. Nevertheless, addiction to extensive reading in the original works of great scientists seems to be an acquired taste; and professional historians of science will probably always be greatly outnumbered by scientists. Yet it is often suggested that a scientist will be aided in his own study and research by occasional reading of the classics of science.

This volume—and subsequent ones on similar subjects—has been prepared expressly for the student and research worker in physics, on the premise that the best way to gain a deep understanding of the goals and methods of science is to study its historical development. At the same time it is not intended for the use of historians of science, who will prefer to study the original complete texts (most of which are fairly accessible). A thorough comprehension of the life, works, and historical environment of a single one of the scientists represented in this brief selection would require many years of study; clearly few scientists will be willing to expend those years, yet there is still something to be gained by reading a relatively short extract. We shall not go to the extreme degree of condensation adopted by many compilers of anthologies, who attempt to cover all of a large area of science with a single volume consisting of many two- or three-page selections. Instead we plan to devote at least five of these volumes to the area of kinetic theory, statistical mechanics, and thermodynamics. The selections will be long enough to enable the reader to follow the author's train of reasoning to its conclusion, although in some cases they may be only portions of longer works. The criterion for selection is not that the work necessarily represents an important original contribution, but rather that reading it enables one to understand more clearly the development of the subject. Thus, for example we present not only the theories that were "correct" from the modern viewpoint, but also some that seemed plausible at the time but were later rejected. If one wishes to understand the process by which scientific theories are developed, and accepted or rejected, one must be willing to look at the alternatives and objections to the theory that was ultimately successful. One's respect for the pioneer kinetic theorists cannot but be increased by the realization that they had to overcome another theory whose proponents could invoke the authority of such giants as Newton and Laplace.

Most writers of textbooks in physics seem to believe that the introduction of anecdotes from the history of physics enhances their exposition of the subject-matter itself. Unfortunately much of the "history" that one finds in textbooks or popularizations of physics is either false or misleading; and while the "human interest" angle may enliven the subject for those readers who would otherwise find it dull, it is doubtful whether this kind of history contributes anything to the understanding of physics itself. We suggest that it is not particularly important for a physicist to know who did what, where, and when, except insofar as that information provides the skeleton for science in its historical development, viewed as an organic whole. What must be grasped is the growth of scientific ideas and theories, the accumulation of experimental facts and techniques, and the interrelations thereof. We are not particularly concerned with questions of priority of discovery, although the fact that the same discovery was made independently by several scientists at about the same time can be a valuable indicator of the underlying currents of scientific thinking. Of course priority is important if it provides a motivation for scientists to expedite the publication of their discoveries. But most disputes about priority degenerate into squabbles about national glory. The two gas laws were known for many years as "Boyle's law" and "Charles's law"† by the British and Americans, and as "Mariotte's law" and "Gay-Lussac's law" by the French, despite the fact that almost all historians of science—including British and French—agree that the credit for the first should go to Boyle (with assists from Towneley and Hooke) while the credit for

† Or "Dalton's law".

the second should go mainly to Gay-Lussac, with some recognition of the work of Amontons. The claims of Mariotte and Charles are very weak indeed. The greatest scientists have always realized that there is no such thing as patriotism in science; it is unpleasant to observe the perversion of history of science by those who wish to assert the superiority of one country over others. (This does not, of course, imply that the investigation of the reasons why science developed more rapidly in some countries than in others cannot be a legitimate subject of research.)

A final word of caution: we hope that any teacher or textbook writer who wants to make a statement about the history of physics will not rely on our " Introduction " but will look at the original documents himself. Our remarks do not claim to constitute a definitive account of the history of the subject; while we have tried to avoid any gross errors, a certain amount of omission and over-simplification is inevitable. It should also be noted that the amount of space devoted to various works in the Introduction is not necessarily proportional to their importance. On the contrary, little need be said about the works actually reprinted in this volume, and therefore the Introduction tends to emphasize other works that had to be left out of the reprint section.

It is a pleasure to thank W. James King, J. Schwartz and R. Hahn for reading the manuscript and making valuable suggestions, and C. W. F. Everitt for providing useful information about Maxwell.

SELECTED READINGS IN PHYSICS

General Editor D. TER HAAR

KINETIC THEORY

Contents

Introduction

THE history of atomism goes back to the ancient Greek and Roman philosophers, but the history of the kinetic theory of gases does not really begin until the 17th century when Torricelli, Pascal, and Boyle first established the physical nature of the air. 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 many of 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 scientific attitudes which led to the " mechanico-corpuscular " view of nature, associated with the names of Galileo, Boyle, Newton, and others. 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 ft in a pump, although Galileo himself seems to have been the first to put this fact on record in 1638.† 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 fourteen times as dense as water, one might expect that it can be lifted only about 1/14 as far. This is indeed what is observed, and this fact tends to make plausible the

† *Dialogues concerning two new sciences*, English translation by Crew and de Salvio, pp. 12–17. Further details of this and other works mentioned in this Introduction may be found in the Bibliography.

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 in. 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 ".

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 the top of a mountain than at sea level. 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. 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. 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.

These early experiments in pneumatics were carried on at about the same time as the formation of the first scientific societies in Italy, England and France, and in many cases several scientists collaborated in the experiments. The Accademia del Cimento (Academy of Experiments) was founded in Florence in 1657; Torricelli himself had taught some of its charter members, and they in turn carried on his researches into the nature of air pressure. The Royal Society developed from an informal association of scientists in London; some of these men moved to Oxford and formed a separate group there about 1649, but after the Restoration the group again concentrated in London, and the Royal Society received its official charter in 1662. Several members of this group played important roles in the development of the theory of gases. Robert Boyle (1627–91), for example, was the seventh and last son of the Earl of Cork, a British nobleman who owned considerable property in Ireland; Boyle's fortune was put to good use in buying expensive scientific apparatus. The Oxford group met in his lodgings for a time. The best experimentalist of the group was Robert Hooke (1635–1703)—now remembered chiefly for his discovery of the relation between stress and strain—who constructed an improved air pump for Boyle about 1658. It was with this " pneumatical engine " that Boyle performed the experiments recorded in his book, *New Experiments Physico-Mechanicall, touching the Spring of the Air, and its effects* (Oxford, 1660). Boyle mentions that some of his experiments were done in the presence of such colleagues as Christopher Wren (1632–1723), the architect who designed St. Paul's Cathedral and many other buildings still standing in London and elsewhere, and John Wallis (1616–1703), mathematician and divine who made several important contributions to analytical geometry and algebraic analysis. It was Wallis, Wren, and Christian Huygens (1629–95), Dutch astronomer and physicist, who—in response to a request from the Royal Society in 1668—independently formulated the laws of impact. These laws are the basis of the kinetic theory of " billiard balls " (atoms represented by elastic spheres).

Isaac Newton (1642–1727) was elected to the Royal Society in 1671, after he had already invented the differential and integral calculus and discovered the unequal refrangibility of the rays of light and the binomial theorem (1665–66) and had become Lucasian Professor of Mathematics at Cambridge in 1669. His *Principia* was published in 1687, and he served as President of the Royal Society from 1703 until his death.

In all this illustrious company, perhaps we can even find a place for Richard Towneley (1628–1707), who though not a member of the Society was an active correspondent with many of its members; he performed a number of minor scientific experiments and meteorological observations at his estate in Towneley, Lancashire, but the chief reason for mentioning him here is that he was the person who first suggested Boyle's law.

Robert Boyle is generally credited with the discovery that the pressure exerted by a gas is inversely proportional to the volume of the space in which it is confined. From Boyle's point of view that discovery by itself was insignificant, and though he had provided the experimental evidence for it he readily admitted that he had not found any general quantitative relation between pressure and volume before Richard Towneley suggested his simple hypothesis. Robert Hooke also provided further experimental confirmation of the hypothesis. It was long known as " Mariotte's law " on the Continent, because Edmé Mariotte (1620–84), a French priest, proposed it in his *Essay de la nature de l'air* (1679). There are good reasons for believing that Mariotte was familiar with Boyle's work even though he does not mention it, so that he does not even deserve the credit for independent (much less simultaneous) discovery.†

Boyle's researches were carried out to illustrate not just a quantitative relation between pressure and volume, but rather the qualitative fact that *air has elasticity* ("spring ") and can exert a mechanical pressure of a magnitude sufficient to support a column of water or mercury. His achievement was to introduce a new variable—pressure—into physics; he could well afford to be generous about giving others the credit for perceiving the numerical relations between this variable and others. He considered that the crucial experiment 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 the air could be removed by means of his pump. 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.

Boyle also proposed a theoretical explanation for the elasticity of air—he likened it to " a heap of little bodies, lying one upon another " and attributed the elasticity of the whole to the elasticity of the parts (Selection 1 in this volume). The atoms are said to behave like springs which resist compression. To a modern reader this explanation does not seem very satisfactory, for it does no more than attribute to atoms the observable properties of macroscopic objects. It is interesting to note that Boyle also tried the " crucial experiment " which was to help overthrow his own theory in favor of the kinetic theory two centuries later, though he does not realize its significance;

† See for example W. S. James, *Science Progress* **23**, 261 (1928); **24**, 57 (1929).

‡ See Boyle's *Works*, p. 33.

in his Experiment No. 26 he places a pendulum in the evacuated chamber and discovers, 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. In 1859, James Clerk Maxwell deduced from the kinetic theory that the viscosity of a gas should be independent of its density (Selection 10)—a property which would be very hard to explain on the basis of Boyle's theory.

These criticisms are irrelevant in a sense, since Boyle's theory should be compared with other ideas current at the time, rather than with modern views. Soon after the publication of Boyle's *New Experiments*, attacks on the experiments and their interpretation were advanced by Thomas Hobbes (1588–1679), the writer on political philosophy, and Franciscus Linus, alias Francis Hall (1595–1675), Jesuit scientist and sometime Professor of Hebrew and Mathematics at Liège. Hobbes, though a participant in the new scientific movement, was engaged in a mathematical dispute with Wallis and also resented his exclusion from the Royal Society. He believed that a " subtle matter " exists, filling all space; this was a view that hampered the development of the kinetic theory right up to the beginning of the 20th century. Linus asserted that the Torricellian vacuum contained an invisible cord or membrane (Latin *funiculus*, diminutive of *funis*, rope). When air is stretched or rarefied, the *funiculus* exerts a violent attraction on all surrounding bodies, and it is this attraction which pulls the mercury up the tube. Indeed, if you put your finger over the end of the tube from a suction pump (or vacuum cleaner) you can actually feel the *funiculus* pulling in the flesh of your finger!

Laugh if you like at this fantastic idea, but remember that the funicular hypothesis was an example of the type of pseudo-mechanical explanation of physical phenomena that used to be quite popular in the early days of science. Moreover, the idea that a vacuum contains an entity that sucks things into it is much closer to " common sense " than the theory that the suction is merely due to the absence of normal atmospheric pressure inside the vacuum. It takes a considerable degree of sophistication to accept the idea that we are living at the bottom of a sea of air which exerts the tremendous pressure of 14·7 lb on every square inch of our bodies.

Boyle published in 1662 a *Defence* against the objections of Linus and Hobbes; in the course of refuting the funicular hypothesis, he provides some new experimental evidence on the compression and rarefaction of air. He presents this evidence as confirmation of Towneley's hypothesis (" Boyle's law "), which is mentioned here for the first time.

Newton discusses very briefly in his *Principia* (1687) the consequences of various hypotheses about the forces between atoms for the relation between pressure and volume (Selection 2). One particular hypothesis, a repulsive force inversely proportional to distance, leads to Boyle's law. It seems plausible that Newton was trying to put Boyle's theory in mathematical language, and that he thought of the repulsive forces as being due to the action of atomic springs in contact with each other, but there seems to be no direct evidence for this.

Neither Boyle nor Newton claimed that the hypothesis of repulsive forces between atoms is the only correct explanation for gas pressure; both were willing to leave the question open. Boyle mentions the Descartes theory of vortices (1644), for example, which is somewhat closer in spirit to the kinetic theory since it relies more heavily on the rapid motion of the parts of the atom as a cause of repulsion.† (Though Descartes did not believe in " atoms " in the classical sense.)

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† Incidentally, it is important to realize that there is more to the kinetic theory than just the statement that heat is atomic motion. That statement was frequently made, especially in the 17th century, but usually by scientists who did not make the important additional assumption that in gases the atoms move freely most of the time. It was quite possible to accept the " heat is motion " idea and still reject the kinetic theory of gases, as did Humphry Davy early in the 19th century.

Here is an example of a derivation of Boyle's law, which Tait (1885) mistakenly calls an " anticipation of the kinetic theory ", by Robert Hooke, in his *Lectures de Potentia Restitutiva* (1678) pp. 15–16: " 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