History of the Kinetic Theory of Gases*

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1. EARLY THEORIES OF GASES

The kinetic theory of gases originated in the ancient idea that matter consists of tiny invisible atoms in rapid motion. In the 17th century this idea was revived and used to explain, among other phenomena, the properties of gases.

The British chemist and physicist Robert Boyle (1627-1691), building on the work of several other 17th-century scientists, showed that air is "elastic": it resists compression and expands to fill the available space. The mechanical pressure P exerted by a given amount of gas at a particular temperature is inversely proportional to the volume V of its container, a relation now known as "Boyle's Law."

Boyle mentioned two alternative atomistic explanations for air pressure: (1) air is composed of particles that repel each other, like coiled-up pieces of wool or springs; (2) air is composed of whirling particles that push each other away by impacts. The first hypothesis was taken up by Isaac Newton, who proved mathematically that if air pressure is due to the repulsion of neighboring particles, then the repulsive force must be inversely proportional to their distances. The second hypothesis, which Boyle associated with Descartes' etherial vortices, lacked a quantitative foundation in the 17th century, though it gained qualitative support from the common idea that heat is related to atomic motion and the observation that air pressure increases with temperature.

The Swiss mathematical physicist Daniel Bernoulli (1700-1782) formulated a quantitative kinetic theory in his book on hydrodynamics. He derived Boyle's law for gas pressure by computing the force exerted on a movable piston by the impacts of n particles moving with speed v, in a closed space of total volume V. If V is smaller the pressure will be greater because the particles strike the piston more frequently. If the space occupied by the particles themselves is small compared to the volume V, the pressure P should be inversely proportional to V; so, as stated by Boyle's law, the product PV is constant (see Bernoulli, 1738).

Bernoulli also showed that the pressure will be proportional to the kinetic energy of the particles ($\frac{1}{2}nmv^2$, where m is the mass of a single particle) since the frequency of impacts is proportional to the speed v and the force of each impact is proportional to the momentum mv. This, he remarked, explained the observed fact that increases of pressure arising from equal

increases of temperature are proportional to the density, and suggested that temperature itself could be defined in terms of the pressure of air at a standard density. Although other scientists had not yet accepted the concept of an absolute temperature scale, Bernoulli's theory introduced the idea that heat or temperature could be identified with the kinetic energy of particles in an ideal gas.

Experimental work on gases around 1800 confirmed the simple relation between pressure, volume and temperature assumed by Bernoulli. The French chemist Joseph Gay-Lussac (1778-1850) and others showed that pressure increases in proportion to temperature if the

volume is held constant, or volume increases in proportion to temperature if pressure is held constant; these relations can be summarized in the equation $PV = NR(t+273)$, where N is proportional to the total mass of gas present, t is the temperature in degrees Celsius (centigrade) and R is a universal constant. But it was not yet known whether the equation would be valid down to temperatures so low that $(t + 273)$ is zero, or whether all gases would condense before that point of "absolute cold" is reached so the equation would no longer apply.

The kinetic theory was not widely accepted in the 18th century; most scientists preferred the Newtonian repulsion theory, which was compatible with the idea that heat is a fluid, "caloric," rather than the energy of atomic motion. Caloric was sometimes thought to be composed of particles that repel each other and are attracted to the atoms of ordinary matter. Thus gas pressure increases with temperature because the gas acquires more of the self-repelling caloric fluid. Temperature itself could be defined as the density of caloric (amount of the caloric fluid divided by volume).

With this definition of temperature, the caloric theory could explain why compression can increase the temperature of a gas even though no heat is added from outside (the same amount of caloric is concentrated in a smaller volume), or expansion can decrease the temperature even though no heat is lost (the same amount of caloric is spread over a larger volume). But there was one anomalous observation, whose significance was not appreciated until much later: Gay-Lussac found that in the free expansion of a gas (into a vacuum rather than pushing back a piston) there is practically no change in temperature.

The caloric theory could also explain phenomena such as the latent heat of phase transitions (solid to liquid or liquid to gas) and the heat absorbed or released in chemical reactions, by postulating that some caloric is "bound" to the individual atoms or compounds. The ordinary pressure-volume relations of gases are determined by the unbound or "free" caloric that fills the space between particles. The kinetic theory seemed to offer no plausible account of these phenomena, and moreover its hypothesis that the atoms move at constant speed between collisions seemed incompatible with the generally-accepted idea that all space is filled with an ethereal fluid.

Finally, the caloric theory gained credibility in the early 19th century from Laplace's use of it to calculate the speed of sound in gases, resolving a long-standing discrepancy between theory and observation; and it was indirectly supported by the acceptance of the particle theory of light, since light and heat were widely viewed as qualitatively identical phenomena.

2. CHEMICAL ATOMIC THEORY

An essential feature of the modern kinetic theory of gases is that the particles (atoms or molecules) of a gas occupy a relatively small part of the total volume, and are thus able to move most of the time in straight lines through empty space, unaffected by the presence of other particles or by any resisting ethereal fluid. This model is radically different from the one

proposed at the beginning of the 19th century by the English chemist John Dalton (1766-1844), founder of the modern chemical atomic theory. Dalton explicitly adopted Newton's hypothesis that gas pressure is due to short-range repulsive forces between particles, and envisioned these particles as being surrounded by caloric atmospheres in contact with those of their neighbors. Moreover, particles of different elements should have different sizes, so an equal number would occupy different amounts of space.

Dalton also adopted a supplement to Newton's hypothesis, perhaps inspired by 18th-century electrostatic theories: atoms of different elements do not repel each other, they may even attract. He used this idea to explain why air, now known to be a mixture of oxygen and nitrogen, did not separate into its components under the influence of gravity (so that the denser oxygen would sink to the bottom). Self-repulsion of each kind of atom would tend to disperse each among the others rather clustering with their own kind. Another consequence of this idea is Dalton's "law of partial pressures": the total pressure of a gas mixture is simply the sum of the pressures each kind of gas would exert if it were occupying the entire space by itself. (This law can also be derived from kinetic theory without invoking differential forces between like and unlike atoms.)

When Dalton prepared his famous table of "atomic weights" he assumed the simplest possible formula for each chemical compound. Thus a water molecule was assumed to contain one atom of oxygen and one of hydrogen. If that were true, then (using modern data) since one gram of hydrogen reacts with 8 grams of oxygen to form 9 grams of water, the atomic weight of oxygen relative to hydrogen would be 8.

Gay-Lussac's discovery of the "Law of Combining Volumes" did not fit comfortably with Dalton's ideas. The Law states that in gaseous reactions the volumes of the reactants and products are related to each other by ratios of small integers; thus for example two liters of hydrogen combine with one liter of oxygen to form two liters of water. The most plausible atomistic interpretation of this Law is that the volume of each gas is proportional to the number of particles it contains. Then two particles of hydrogen would combine with one of oxygen to form two particles of water. That would imply that a "particle" of oxygen can split into two parts, one for each of the resulting water particles; thus gases may be composed of particles each of which is made of two or more atoms. It would also imply that the atomic weight of oxygen is 16, not 8.

Dalton rejected Gay-Lussac's conclusions; while he criticized the accuracy of Gay-Lussac's measurements, it appears that his major objection was that the results contradicted his own theory. As noted above, the volume of a gas cannot be proportional to the number of Daltonian particles since they have different sizes and are in contact; worse, the idea of a molecule composed of two oxygen atoms violates the principle that atoms of the same kind repel each other.

The Italian physicist Amedeo Avogadro (1776-1856) was the first to fully articulate and explore the consequences of Gay-Lussac's results and put the chemical atomic theory into its

modern form. The ultimate particles with which kinetic theory deals are not atoms but molecules, each of which may contain one or more atoms of the same or different kinds. "Avogadro's hypothesis" asserts that every kind of gas contains the same number of molecules in a given volume under the same conditions. The hypothesis, when generally adopted by chemists after 1860, allowed the definitive calculation of atomic weights of elements if they formed gaseous compounds. The gaseous forms of many common elements such as hydrogen, nitrogen, oxygen, and chlorine are composed of diatomic molecules, though others like mercury were later found to be monatomic.

Avogadro's hypothesis is favorable to the kinetic theory of of gases insofar as it implies that the volume occupied by a certain number of molecules is independent of their size and shape, which suggests they are not ordinarily in contact. But it was not until 1859 that Maxwell showed that the hypothesis could be derived from the kinetic theory; the earlier version of kinetic theory we are now doing to consider is actually inconsistent with it. That proves nothing except perhaps that the relation between physics and chemistry in the 19th century was not as close as it might have been.

3 NEGLECTED PIONEERS: HERAPATH AND WATERSTON

John Herapath (1790-1868) was an Englishman who might be called an amateur scientist except that the distinction between amateur and professional was not very significant at the time. But he was definitely an outsider, a clever eccentric who never enjoyed any recognition from the scientific community but lived to see his ideas vindicated.

Herapath was initially interested in developing an explanation of gravity in terms of the impacts of particles of an ethereal fluid, somewhat along the lines of the "kinetic theory of gravity" proposed by G. S. LeSage and many others. Herapath's version was somewhat different: he proposed to take account of the effect on the gravific particles of the high temperatures in the space near the Sun. In this way he came to consider the relation between temperature and particle velocity.

Herapath was puzzled by the old paradox of collisions between atoms: if they meet head-on they must stop at least for an instant before rebounding.   Is the collision elastic or inelastic? It can't be elastic, since an atom by definition has no smaller parts and cannot change its size, so how can it store its kinetic energy during that instant? But if it were inelastic, both atoms would have to stop; then what happens to their energy?

To avoid the paradox, Herapath decided to adopt momentum instead of energy as the fundamental measure of motion, since momentum is always conserved whether collisions are elastic or inelastic. Herapath simply assumed that the scalar momentum mv of a particle is a measure of its absolute temperature and that the total momentum of a system is conserved in collisions while individual momenta tend to be equalized. (One consequence of this unorthodox

definition was that temperature of a mixture of hot and cold fluids should be somewhat lower than one would expect using the ordinary definition of temperature.)

Herapath arrived at the same relation between pressure, volume, and particle velocity that Bernoulli had derived (he apparently did not know of Bernoulli's work). But he expressed it somewhat differently: PV is proportional to T_H^2, since T_H, which he called "true temperature," is proportional to mv rather than to mv².
(I have added the subscript "H" to avoid confusion with the absolute temperature T used elsewhere in this chapter.)

Herapath submitted his first paper on kinetic theory to the Royal Society of London in 1820, hoping to get it published in the Philosophical Transactions. That would have given his views wide circulation in the international scientific community; moreover, as Herapath himself frankly admitted, it would have enhanced his personal reputation so that he could embark on a career of teaching and scientific research.

Humphry Davy (1778-1829), a well-known chemist, became president of the Royal Society shortly after the submission of Herapath's paper and was mainly responsible for its fate. Davy had earlier supported the general idea that heat is molecular motion rather than a substance, and thus he might have been expected to be receptive to a theory that gave this idea a precise mathematical formulation. But his reaction was negative, for several reasons. The only one he made explicit to Herapath was his reluctance to consider heat as a simple quantity that could be completely extracted from a body by annihilating the motion of its molecules, thus implying the existence of a lowest temperature ("absolute zero"). It is also evident that he found Herapath's derivations difficult to follow and would have preferred a less abstract, less mathematical approach emphasizing instead the correspondence between concepts and observations at each step: that seems to be a persistent difference in the attitudes of chemists and physicists.

Finally, we may conjecture that Davy had a metaphysical repugnance for the basic assumption of kinetic theory -- that particles move through empty space with no interactions except when they collide. By this time Davy had adopted some of the sentiments of Romantic nature philosophy; for example, seeing the world as an interconnected system dominated by all-pervading forces rather than by push-pull mechanisms.

Herapath was told that his paper would not be published in the Philosophical Transactions and he was advised to withdraw it, since according to the custom of the Royal Society once a paper was "read" (formally presented, if only by title or abstract, at a meeting) it became the property of the Society and could not be returned to its author. Herapath complied with this advice and sent his paper to an independent scientific journal, the Annals of Philosophy, where it was published in 1821. Later he attacked Davy and the Royal Society in a series of letters in the Times of London.

Denied recognition by the scientific establishment, Herapath nevertheless did have an opportunity to present his ideas to a larger public. The Annals of Philosophy, though now

forgotten, was not by any means an obscure journal in the early 19th century. Michael Faraday and other reputable scientists published there. It was similar in content and circulation to the major physical science journals Philosophical Magazine (with which it merged in 1826), the Annalen der Physik und der Chemie, or the American Journal of Science. So if Herapath's theory was ignored by most scientists in the 182Os, we cannot simply blame Davy and the Roval Society but must recognize that the theory was out of harmony with prevailing ideas about the nature of gases and heat, and failed to convince its readers that those ideas should be revised.

Herapath later became editor of the Railway Magazine, a position that give him an opportunity to publish his scientific work though to a limited and perhaps unappreciative audience. In 1836 he presented a calculation of the speed of sound, which he had completed four years earlier. This was in fact the first calculation of the average speed of a molecule from the kinetic theory of gases. (J. P. Joule, was is usually credited with this accomplishment, was simply following Herapath's method.) Herapath found that the speed of sound in air at 32°F should be about 1090 feet per second, in good agreement with the experimental results available at that time.

In the 1840s, stimulated by the publications of Thomas Graham on gas diffusion and of Regnault on compressibility, Herapath revised and elaborated his kinetic theory and published the two-volume treatise Mathematical Physics (1847). He claimed that he had calculated from his theory in 1844 a formula for the time required for a given volume of gas to pass through a small hole into a vacuum, and that this formula was subsequently confirmed by the experimental results of Graham.

Herapath also claimed to have predicted in advance Regnault's result (1846) that the pressure of very dense gases is greater than that given by Boyle's law. This is indeed what the model of atoms as impenetrable spheres would lead one to expect if one ignores short-range attractive forces. However, earlier experiments had indicated deviations in the opposite direction, suggesting that attractive forces are more important than repulsive. (Later kinetic theories managed to account for the fact that attractive forces dominate at low temperatures, repulsive at high.)

The British physicist James Prescott Joule (1818-1889), one of the founders of the law of energy conservation, is the only scientist known to have read Herapath's Mathematical Physics during the first few years after its publication. Joule presented a short paper on kinetic theory, based on Herapath's work, at scientific meetings in 1848, but very few scientists learned about it.

Herapath lived long enough to see the kinetic theory revived by others. In 1860, after Maxwell's first paper was reported in a British magazine, Herapath published a letter calling attention to his own earlier work, and thus helped to ensure that he would be remembered as one of the pioneers of kinetic theory -- though by this time he could not be credited with the first kinetic theory, since Daniel Bernoulli's chapter in Hydrodynamica had also been rediscovered.

As I mentioned at the beginning of this section, Herapath's version of kinetic theory is inconsistent with Avogadro's hypothesis, a fact that passed unnoticed in the 1820s but would have called for revision if anyone had tried to integrate it with chemical atomic theory after 1860.

The other neglected pioneer was the Scottish scientist John James Waterston (1811-1883); his theory was more nearly correct than Herapath's but had no influence at all because it remained unknown until long after the modern kinetic theory had been established by Clausius and Maxwell.

Like Herapath, Waterston was interested in the problem of explaining gravity by impacts of particles, and his efforts on this problem led him to develop a kinetic theory of gases. Waterston was employed as a Naval Instructor to the East India Company's cadets at Bombay, India. In 1843 he published a book that included some of his early results on the kinetic theory of gases. His most significant conclusion was that "equilibrium of temperature depends on molecules, however different in size" having the same kinetic energy. This was a special case of what later became known as the "equipartition theorem." There is no evidence that any physical scientist read the book; perhaps it was overlooked because of its misleading title, *Thoughts on the Mental Functions.*

Two years later Waterston submitted a long manuscript, presenting a detailed account of the kinetic theory of gases, to the Royal Society of London. Two members of the Society, asked to review the paper, recommended that it should not be published -- primarily because they disagreed with its fundamental premises. But no one had told Waterston, still far away in India, that once his paper had been officially "read" to the Society (i.e. presented by title or abstract, not read word for word) it would not be returned to him; and Waterston had not retained a copy for himself. Thus he could not easily follow Herapath's course of publishing the original paper in an independent journal, although he did try to call attention to his theory by circulating shorter versions, and by mentioning it when he published papers on related subjects.

In 1851 Waterston presented a short paper on his kinetic theory at the annual meeting of the British Association for the Advancement of Science. The published abstract of that paper clearly states that in gas mixtures, the average kinetic energy of each kind of molecule is the same; thus he established his priority for the first statement of the equipartition theorem. He also indicated in this abstract that Avogadro's hypothesis follows from the kinetic theory.

The German chemist and physicist August Karl Krönig (1822-1879), who published a short paper proposing a kinetic theory of gases in 1856, was probably familiar with the published abstract of Waterston's 1851 paper and may have been influenced by it (see Daub, 1971).

Waterston also attempted to calculate the ratio of the two specific heats (c_p, at constant pressure, and c_v, at constant volume). Because of a numerical mistake he obtained the value $c_p/c_v = 4/3$ for a monatomic gas instead of the correct theoretical value 5/3. Since his value was fairly close to the observed ratios for air and other gases he didn't realize his error.

In 1858 Waterston published a paper arguing that Laplace's calculation of the speed of sound from the caloric theory of adiabatic compression and expansion could be based equally well on Waterston's own kinetic theory of gases and thus did not provide evidence for the caloric theory of heat.

In 1891 the British physicist Lord Rayleigh, surveying the literature on acoustics for his comprehensive treatise on that subject, came across Waterston's 1858 paper on the theory of sound, which referred to his unpublished manuscript lying in the Royal Society Archives. Rayleigh was Secretary of the Royal Society at that time, and had no difficulty in retrieving the manuscript and arranging for its belated publication in the *Philosophical Transactions*. In his introduction to the paper, Rayleigh remarked: "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 record 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 whose scope is limited, and whose value is easily judged, before embarking on greater flights" (see Waterston 1892).

These remarks of Lord Rayleigh do not justify the original refusal of the Royal Society to publish Waterston's brilliant paper, but they hint at one of its failures as an organization for advancing scientific knowledge. By rejecting work by authors without established reputations, or theories that contradict established doctrines, a scientific society shirks one of its most important functions. 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, this permitting the German scientists August Krönig and Rudolf Clausius to gain the major share of credit as founders of the theory and damaging the Society's own reputation.

4. REVIVAL OF THE KINETIC THEORY BY CLAUSIUS

The "kinetic theory of heat" -- the old idea that heat is directly related to the kinetic energy of atomic motion -- had to be given serious consideration as soon as energy conservation and thermodynamics had been introduced in the middle of the 19th century (see Chapter 14). Additional evidence that gas pressure is not caused by repulsive intermolecular forces (previously associated with the caloric fluid) came from experiments on the free expansion of gases by J. P. Joule and William Thomson; they confirmed that (as Gay-Lussac had found earlier) there is essentially no temperature change; more accurate measurements suggested that long-range forces are attractive, not repulsive.
Another reason for favoring a kinetic theory of heat was the general adoption of the wave theory of light which -- combined with the view that heat and light are qualitatively the same phenomenon -- suggested that heat, like light, is a form of motion rather than a substance.

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It was still logically possible to reject the kinetic theory of heat, as did J. R. Mayer and later Ernst Mach, by denying the need to reduce heat to any other form of energy. This antireductionist or positivist stance was the basis for the "energetics" movement at the end of the 19th century, but it was uncongenial to most scientists.

Having accepted the kinetic theory of heat, one still had several possible hypotheses to choose from. The molecular motion might be translational, rotational, or vibrational, or a combination of all three; the molecules might be small relative to the space in which they move, or large and thus crowded together; the motion might be similar for each molecule in the system or differ according to a definite pattern. Physicists still believed that an ether is needed to transmit energy between bodies in the form of light or radiant heat; if the ether also fills the space between molecules inside a body, it should have some effect on their motion. The old idea that molecules "swim" in the ether, or are suspended by it at definite equilibrium points around which they may vibrate, was not yet dead.

Among these possibilities the kinetic theory of gases was perhaps the simplest but by no means the most plausible. In fact, it seemed too simple to be true. It required that one ignore the ether and assert that molecules move through space at constant velocity, encountering no resistance except when they collide with each other or a boundary surface. The first scientist who was able to overcome the general reluctance to give serious consideration to this idea was the German physicist Rudolf Clausius (1822-1888).

In his first paper on kinetic theory, published in 1857, Clausius stated that he had been thinking about molecular motion even before writing his first article on thermodynamics in 1850, but had abstained from publishing his ideas because he wanted to establish the empirical laws of heat without making them appear to depend on any molecular hypothesis. Now that Krönig had taken the lead with his 1856 paper, there was no question of priority, but the time seemed auspicious to attempt a unified description of several phenomena from the kinetic viewpoint. Krönig had assumed that the molecules have only translatory motion (and, as Clausius was perhaps too polite to point out, had not even given the correct numerical factor in the pressure equation for that simple case). Clausius concluded that one must also include other kinds of molecular motion, such as rotation, and showed how one could estimate the fraction of the total energy which is translational by using heat data.

By including rotational motion in his kinetic theory, Clausius was compromising not with alternative theories but with empirical knowledge of gas properties. But the result of this compromise was damaging to the kinetic theory all the same: the ratio of translational energy to total energy came to be 0.6315 for the common gases whose ratio of specific heats is 1.421. Now 0.6315, as Maxwell and others intuitively realized, is not a very nice number. It is unlikely (though not impossible) that a direct calculation based on a plausible molecular model would lead to such a number. Perhaps the best that can be said for 0.6315 is that, despite the accuracy implied by its four significant figures, it is not too far away from 3/5, and we will see later there is some hope of making sense out of 3/5.

Clausius did take one step in this direction by reviving Avogadro's proposal that gaseous molecules may contain two or more atoms of the same kind. Some chemists had already come to the same conclusion, but Clausius was probably the first to introduce the idea into mid-19th century physics.

Another assumption dictated by experimental data was the extremely small size of molecules: Clausius stipulated that "the space actually filled by the molecules of the gas must be infinitesimal in comparison to the whole space occupied by the gas itself." Moreover, "the influence of the molecular forces must be infinitesimal" [Clausius 1857/1965, p. 116]. This means not only that the forces between molecules at their *average* distances are negligible but also that the short-range repulsive forces that cause molecules to rebound at collisions must act over a very small portion of the path of the molecule. If these conditions were not satisfied the gas would not obey the ideal gas laws. By this time it was well known from Regnauit's experiments that real gases do *not* obey the ideal gas laws, but Clausius was unable in 1857 to carry out the complex calculations needed to compute the deviations using a molecular model, so he limited his theory to ideal gases.

While the strict mathematical deductions of his theory were thus limited to crases obeying the laws of Boyle and Gay-Lussac - - that is, temperatures and pressures not too far from those of the atmosphere -- Clausius did not hesitate to propose a qualitative description of molecular motion in other states of matter. In solids, the molecules vibrate about fixed equilibrium positions, while their constituent atoms vibrate and rotate within the molecule. In liquids the molecules no longer vibrate around fixed positions but may move around, yet without completing separating themselves from their neighbors. In the gaseous state the molecules move in straight lines, going beyond the reach of the attractive forces of other molecules but occasionally undergoing elastic collisions with them.

From this qualitative picture Clausius was able to develop a theory of changes of state. Thus, the *evaporation* of a liquid can be explained by assuming that even though the average motion of its molecules may not be sufficient to carry them beyond the range of the attractive forces of their neighbors, "we must assume that the velocities of the several molecules deviate within wide limits on both sides of this average value" (Clausius 1857/1965, p. 118) and therefore a few molecules will be moving fast enough to escape from a liquid surface even at temperatures below the boiling point.

The phenomena of *latent heat* could also be explained by the kinetic theory, if one adopted Clausius' description of the three states of aggregation:

> In the passage from the solid to the liquid state the molecules do not, indeed, recede beyond the spheres of their mutual action; but, according to the above hypothesis, they pass from a definite and, with respect to the molecular forces, suitable [ordered] position, to other irregular positions, in doing which the forces which tend to retain the molecules in the former position have to be overcome.

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[Clausius 1857/1965: 121]

Whenever a body is moved against the action of a force, mechanical work must be done, and therefore, according to the law of conservation of energy, heat must be supplied.

"In evaporation, the complete separation which takes place between the several molecules and the remaining mass evidently again necessitates the overcoming of opposing forces."

[Clausius 1857/1965, p. 121]

and so heat must again be provided (latent heat of vaporization).

Near the end of his 1857 paper Clausius calculated the average speeds of molecules of oxygen, nitrogen, and hydrogen at the temperature of melting ice and found them to be 461 m/sec, 492 m/sec, and 1,844 m/sec respectively. A Dutch meteorologist, C.H.D. Buys-Ballot, looked at these numbers and realized a consequence that had escaped the notice of Herapath, Joule, Waterston, and Clausius: if the molecules of gases really move that fast, the mixing of gases by diffusion should be much more rapid than we observe it to be. For example, if you release an odorous gas like ammonia or hydrogen sulfide at one end of a room it may take a minute or so before it is noticed at the other end; yet according to the kinetic theory all the molecules should have traversed the length of the room several times by then.

Buys-Ballot apparently thought he had refuted the new theory by pointing out an obvious contradiction between its predictions and the real world.   To meet this objection, Clausius had to make an important change in the theory. Abandoning his earlier postulate that the gas molecules have infinitesimal size, he now assumed that they have a large enough diameter or "sphere of action" so that a molecule cannot move very far without hitting another one.

Clausius now defined a new parameter: the <u>mean free path</u> (L) of a gas molecule, to be computed as the average distance a molecule may travel before interacting with another molecule. He argued that L may be large enough compared with molecular diameters so that the basic concepts of kinetic theory used in deriving the ideal gas law are unimpaired, yet small enough so that a molecule must change its direction many times every second, and may take a fairly long time to escape from a given macroscopic region of space. In this way the *slowness* of ordinary gas diffusion, compared with molecular speeds, could be explained.

The mean free path is inversely proportional to the probability that a molecule will collide with another molecule as it moves through the gas. For spheres of diameter d this probability is proportional to the collision cross section (πd^2) and to the number of molecules per unit volume (N/V). Thus the mean free path is determined by the formula

$$L = k \ V/Nd^2$$

where k is a numerical constant of order of magnitude 1 (its precise value was a matter of dispute

for some time).

When Clausius introduced the mean free path in 1858 it may have looked like only an ad hoc hypothesis invented to save the theory, since he did not have any independent method for estimating the parameters N and d in the above formula. But before anyone had a chance to criticize it on those grounds, Maxwell incorporated the mean free path into his own kinetic theory and showed that it could be related to gas properties such as viscosity (see next section). As a result it soon became a valuable concept, not only for interpreting experimental data, but also for determining the size of molecules and thus justifying its own existence.

5. MAXWELL'S TRANSPORT THEORY AND THE SIZE OF ATOMS

The kinetic theory of Clausius was quickly taken up and developed into a powerful mathematical research instrument by the Scottish physicist James Clerk Maxwell (1831-1879).

Clausius had used probability concepts in his derivation of the mean-free-path formula, but it was Maxwell who converted the kinetic theory of gases into a fully statistical doctrine.
Clausius and earlier kinetic theorists had assumed that all molecules in a a homogeneous gas at a given temperature have the same speed, but Maxwell asserted that the collisions among molecules will instead produce a statistical distribution of speeds. To describe this distribution he borrowed a mathematical formula from the social sciences. The crucial step was his translation of the "normal distribution law" or "law of errors," discovered by Adrain and Gauss and extensively applied by Quetelet, into a distribution law for molecular velocities. Maxwell's velocity distribution law, and its extension by Boltzmann to include the effects of forces, will be discussed in Chapter 15.2. Here we need note only that according to Maxwell's law, the average speed is proportional to $\sqrt{T}$ as in earlier kinetic theories, but a gas at a high temperature contains molecules moving at all speeds, including very low speeds, and a gas at a low temperature also contains (in different proportions) molecules moving at very high speeds.

Maxwell greatly extended the scope of the kinetic theory by showing how it could be used to calculate not only the thermal and mechanical properties of gases in equilibrium, but also their "transport properties": diffusion, viscosity, and heat conduction.
In his first paper, published in 1860, he used the Clausius mean-free-path idea to obtain unexpected results for the viscosity of a gas; and he analyzed the collisions of systems of spherical or nonspherical bodies, attempting to find a theoretical model that could account for the observed ratios of specific heats of gases.

Maxwell calculated the viscosity of a gas by estimating on the mutual friction of neighbouring layers of gas moving at different speeds. One might expect, on the basis of experience with liquids, that a fluid will have higher viscosity (will flow less freely) at lower temperatures, and that a denser fluid will be more viscous than a rarer fluid, since in both cases the motion will be more strongly obstructed by intermolecular forces. Maxwell showed that if the kinetic theory of gases is correct, both expectations will be wrong, because the mechanism

that produces viscosity is different. In a gas, viscous force originates not in the forces between neighboring molecules but in the transfer of momentum that occurs when a molecule from a faster-moving stream wanders over to a slower-moving stream and collides with a molecule there. The rate of momentum transfer increases with the average molecular speed, so (1) the viscosity increases with temperature.

The momentum transferred by each collision is also proportional to the difference in each speeds of the two layers, and if we assume that this difference is simply proportional to the distance between the layers (linear velocity gradient) then it is proportional to the mean free path between collisions. The rate of collisions is proportional to the density, but the mean free path is inversely proportional to the density according to Clausius' formula (see above), hence the density term cancels out and (2) the viscosity is independent of density. It is, like the mean free path, inversely proportional to the molecular diameter.

At that time the only experimental data on gas viscosity appeared to indicate that it increases with density. Maxwell therefore expected, when he published his theoretical calculation in 1859, that it would lead to a refutation of the kinetic theory.

Maxwell also obtained disappointing results from his analysis of the distribution of energy in systems of colliding nonspherical particles. In such systems he found that a generalized equipartition theorem should apply: the average kinetic energy of translational motion of the particles should be equal to the average kinetic energy of rotation around each of the three principal axes of the particle. This led to a ratio of specific heats equal to 4/3, clearly different from the observed value of about 1.4 for common gases. Hence, he concluded, "a system of such particles could not possibly satisfy the known relation between the two specific heats of all gases" (Maxwell 1860, p. 318).

According to the kinetic theory, assuming equipartition of energy, the ratio of specific heats should be $c_p/c_v = (2+n)/n$, where n is the number of mechanical "degrees of freedom." Thus a point-mass has 3 degrees of freedom because it can move in any of the 3 spatial dimensions, so its specific heat ratio should be 5/3; the ratios for monatomic gases such as mercury and argon actually have this value. A nonspherical body, or a diatomic molecule composed of two point-masses bound together by conservative forces, has an additional 3 degrees of freedom, so its ratio should be 4/3, whereas diatomic molecules such as hydrogen and oxygen have the ratio 1.4 or 1.41.

Boltzmann later suggested that a diatomic molecule may really have only 5 effective degrees of freedom because rotation around the axis of symmetry (the line joining the two atoms) is not changed by collisions between molecules and therefore does not contribute to the specific heat. This would make the ratio 1.4. Maxwell did not accept this hypothesis and continued to regard the problem as unsolved; fortunately the refutation of his initial predictions about specific heats and viscosity did not discourage him from pursuing the kinetic theory. (The specific heat problem was not satisfactorily resolved until the 20th century, when it was found to be a quantum effect.)

Maxwell himself initiated the experimental test of his predictions for the effect of temperature and density on viscosity. He found that the viscosity coefficient of air is indeed constant over a wide range of densities, contrary to the alleged experimental facts mentioned above. Later it was pointed out by 0. E. Meyer and others that the analysis of the pendulum data had been based on the assumption -- natural enough before Maxwell's theory was known -- that the viscosity coefficient does go smoothly to zero as the density goes to zero. While it is true that its value must be zero *at* zero density (if there is no gas left, it can't exert any viscous resistance to the swing of the pendulum), the drop occurs quite suddenly at a density lower than that reached in most experiments before 1850.

Crudely speaking, the theory refuted the experiment in this case. One might argue that it was not the experiment itself but only its *interpretation* that was refuted. But in ordinary scientific discourse the term "experimental fact" is commonly applied to data inferred from experiments with the help of some kind of interpretation or theoretical assumption. As Einstein observed (quoted by Heisenberg 1971, p. 63), our theories determine what we observe; hence experiments can never furnish a completely impartial test of a theory.

The investigation of the temperature dependence of viscosity did not yield such a clear-cut result. According to the original "billiard ball" model (elastic spheres with no forces except at contact) the viscosity coefficient μ ought to be proportional to the square root of the absolute temperature. But Maxwell and others found a stronger temperature variation, $\mu \propto T^x$, where x ranges from about .75 to 1.O.

At about the same time (early 1860s) Maxwell developed a much better formulation of transport theory, which avoided the mean-free-path approximation. All the results of the new theory depended on the velocity distribution function for a gas not in thermal equilibrium -- a function that Maxwell was unable to determine -- except in the special case of repulsive forces inversely proportional to the 5th power of the distance between two particles. For this case the velocity-distribution function did not have to be known, and Maxwell found that the viscosity coefficient is directly proportional to the absolute temperature, $\mu \propto T$. Maxwell's own experimental results agreed with this, and so he concluded by 1866 that the kinetic theory gave completely accurate predictions for gas viscosity. The viscosity coefficient is still independent of density for the inverse 5th-power force law, as long as the density is not so high or so low that the gas properties do not depend mainly on binary collisions of particles; at very low densities interactions with the surface of the container dominate the flow behavior, whereas at very high densities simultaneous interactions of three or more particles must be taken into account.

A few years later, the Austrian physicist Ludwig Boltzmann (1844-1906) developed a different version of transport theory, equivalent to Maxwell's theory insofar as it leads to the same formulas for the coefficients of diffusion, viscosity and heat conduction, but more convenient for some other applications. Rather than trying to eliminate the non-equilibrium velocity distribution function by choosing a special form of the force law, Boltzmann used that function as the primary object of study. We will write it f(x,v,t) to indicate that it depends not only on the molecular velocity (v) but also on spatial position (x) and time (t). Boltzmann

computed the change in f(x,v,t) resulting from all relevant physical parameters, including especially the collisions that changed the numbers of particles having specified velocities. The result, published in 1872, was an integrodifferential equation for f(x,v,t), now called "Boltzmann's transport equation" or simply "the Boltzmann equation." It plays a major role in 20th century kinetic theory, including theories of ionized gases (plasma physics) and in calculations of neutron flow in nuclear reactors.

In the 1910s, the Swedish physicist David Enskog (1884-1947) developed a general solution of Boltzmann's transport equation, while the British geophysicist Sydney Chapman (1880-1970) worked out an equivalent general solution for Maxwell's transport equations. Enskog and Chapman could then derive formulae for the transport coefficients for a wide variety of force laws; they also uncovered a new transport process, "thermal diffusion," predicted by kinetic theory and later used as one of the processes for separating isotopes in the development of the atomic bomb. The experimentally-determined temperature dependence of transport coefficients can now be used to draw conclusions about which law most nearly represents the actual force between atoms.

But in the 1860s, when the mere existence of an atomic structure of matter was no more than a plausible hypothesis, Maxwell's theory was used to accomplish a major advance: the first reliable estimate of the *size* of an atom. For this purpose the earlier result relating μ to the particle diameter d was most useful:

$$\mu \propto L \propto V/Nd^2$$

(L = Clausius' mean free path, N = number of molecules in volume V.) Josef Loschmidt (1821-1895), an Austrian physicist and chemist, pointed out in 1865 that this relation could be used to determine d if one other equation for N and d were known. In particular, he suggested that the volume occupied by the gas molecules themselves, if they were closely packed, should be approximately the volume of the substance condensed to the liquid state,

$$V_{liq} \approx Nd^3.$$

If the density of a substance is known in both the liquid and gaseous states, the ratio or "condensation coefficient" $V/V_{liq} = V/Nd^3$ could be combined with the mean free path ($L \approx V/Nd^2$) to obtain a value for d.

In this way Loschmidt concluded that the diameter of an "air molecule" is about $d \approx 10^{-7}$ cm. This value is about four times too large according to modern data, but considerably better than any other well-founded estimate available at the time.

The corresponding value of the number of molecules in a cubic centimeter of an ideal gas at standard conditions (O°C, 1 atm pressure) would be

$$N_L \approx 2 \times 10^{18}.$$

Although Loschmidt himself did not give this result explicitly in his 1865 paper, it can easily be deduced from his formula, and so this number is now sometimes called "Loschmidt's number." Its modern value is 2.687×10^{19}. It should not be confused with the related constant, "Avogadro's number," defined as the number of molecules per gram-mole, equal to

$$N_A = N_L/V_0 \ = \ 6.02 \times 10_{23},$$

where ($V_0 = 22420.7$ cm^3 atm mole^{-1}. Avogadro himself did not give any estimate of this number, but only postulated that it should have the same value for all gases.

During the next few years, other scientists (the most influential being William Thomson, Lord Kelvin) made similar estimates of atomic sizes and other parameters with the help of the kinetic theory of gases. As a result, the atom came to be regarded as no longer a merely hypothetical concept but a real physical entity, subject to quantitative measurement, even though it could not be "seen." This was one of the most important contributions of the kinetic theory to 19th-century science; yet it was carelessly brushed aside by skeptics like Ernst Mach and Wilhelm Ostwald, who argued at the end of the century that we still have no convincing evidence for the existence of the atom and should therefore banish it from the elite company of established physical theories (Chapters 16.3, 16.5).

6. THE VAN DER WAALS EQUATION AND
THE CRITICAL POINT

Most of the quantitative results of the kinetic theory mentioned so far are valid only for gases that are approximately "ideal" -- that is, the density is low enough so that the size of each molecule is small compared with the space between molecules. In this case the laws of Boyle and Gay-Lussac, usually combined in the "ideal gas equation of state" PV = RT, will be valid. Moreover, in deriving the Maxwell-Boltzmann transport equations and the formula for transport coefficients, one needs to include only binary collisions.

Daniel Bernoulli (1738) did realize that modifications to the ideal gas law would be expected if the space occupied by the particles themselves is not infinitesimally small compared to the total volume in which the gas is contained. But it was not until 1873 that the Dutch physicist Johannes Diderik van der Waals (1837-1923) accurately estimated the theoretical correction involved, and showed how, by including as well an estimate of the effects of long-range attractive forces, one could account for some of the peculiar properties of gases at high densities.

Van der Waals argued that when the molecules occupy a finite space, the volume V in the equation of state should be replaced by V - b, where b is a small multipled of the space occupied by spheres of diameter d.

Interatomic attractive forces had previously been postulated by Laplace and others to

explain capillarity and surface tension in liquids, but before 1850 it was assumed that such forces were effective primarily at short distances; it was thought that in gases there must be long-range <u>repulsive</u> forces (associated with the caloric fluid) to account for the resistance of the gas to the external pressure. In the van der Waals theory, the attractive forces were supposed to dominate at large distances between molecules, whereas repulsive forces were effective only at distances where the atoms are nearly in contact. Van der Waals did not specify a particular form for this force law, but argued that the net effect of the attraction would be to increase the external pressure in the equation of state by an amount inversely proportional to the square of the density (i.e., inversely as the square of the volume).

Combining these two corrections, van der Waals arrived at the equation of state

$$[P + (a/V^2)](V - b) = RT,$$

where a and b are constants characteristic of each gas.

The most interesting feature of the van der Waals equation is not its ability to fit small deviations from the ideal gas law, but the fact that it gives a remarkably good qualitative description of the behavior of the system near the gas-liquid critical point. The critical point had been discovered in 1822 by a French scientist, Cagniard de la Tour. He found that when liquid alcohol was sealed in a glass tube with its own vapor (no air present) and heated, the liquid-gas meniscus eventually disappears. Cagniard de la Tour and others showed that for every substance there is a particular pressure, volume, and temperature, called the critical point, at which the distinction between liquid and gas vanishes. (For water, $P_c = 218$ atm; $V_c = 3.2$ cc/g; $T_c = 374'C$.) It was initially assumed that the liquid simply changes to a gas above the critical point, but in 1863 the Irish physical chemist Thomas Andrews demonstrated that the supercritical substance can be changed continuously into either gas or liquid by appropriate variations of temperature and pressure.

As the first successful explanation of phase transitions, van der Waals' theory demonstrated the fertility of the atomistic approach and stimulated much research on liquid-gas critical phenomena in the last quarter of the 19th century, especially in Holland. It was a major breakthrough to show that the same model could be used to explain two different states of matter, for some scientists had previously attributed different properties to "gas molecules" and "liquid molecules" (see Levelt Sengers 1979). Even though the van der Waals theory was eventually replaced by more sophisticated theories of the critical point in the 20th century, it played an important role by demonstrating that qualitative changes on the macroscopic level, such as changes from the liquid to the gaseous state, might be explained by quantitative changes on the microscopic level.

1.7 MAXWELL AND BOLTZMANN ON IRREVERSIBILITY AND INDETERMINISM

Having provided a satisfactory molecular interpretation of the First Law of Thermodynamics, kinetic theorists soon turned their attention to the Second. As formulated by Clausius, the Second Law of Thermodynamics implied that useful mechanical work cannot be obtained from heat except when heat flows from a high temperature to a low temperature in the special way described by Sadi Carnot; that heat spontaneously flows from hot to cold but not the reverse; and that a mysterious quantity called "entropy" tends to increase to a maximum. For the universe as a whole this state of maximum entropy was called by Clausius the "Heat Death": all energy is uniformly diffused throughout space at a low temperature, so that no mechanical work can be done and life cannot exist.

Along with puzzling about the meaning of entropy, some physicists also wondered about the implications of the statistical approach in kinetic theory. It is often stated that this approach was used only as a matter of convenience in dealing with large numbers of particles whose precise positions and velocities at any instant are unknown, or, even if known, could not be used in practice to calculate the gross behavior of the gas. It appears that, up until the time of Maxwell, 19th-century physicists always assumed that a gas is really a deterministic mechanical system. Thus if the superintelligence imagined by the French astronomer P. S. de Laplace (1749-1827) were supplied with complete information about all the individual atoms at one time he could compute their positions and motions at any other time as well as the macroscopic properties of the gas. This situation is to be sharply distinguished, according to the usual accounts of the history of modern physics, from the postulate of atomic randomness or indeterminism which was adopted only in the 1920s in connection with the development of quantum mechanics. Thus, part of the "scientific revolution" that occurred in the early 20th century is supposed to have been a discontinuous change from classical determinism to quantum indeterminism. But, as we will see, discussions about irreversibility in connection with the kinetic theory of gases led to doubts about determinism several decades before Heisenberg's Principle was announced.

Late in 1867, the same year Clausius forecast the Heat Death of the Universe, the P. G. Tait wrote to his old friend J. C. Maxwell asking for help in explaining thermodynamics in a textbook he was preparing. Maxwell responded by imagining a tiny gatekeeper who could produce violations of the Second Law. Maxwell's "Demon," as he came to be known, is stationed at a frictionless sliding door between two chambers, one containing a hot gas, the other a cold one. According to Maxwell's distribution law, the molecules of the hot gas will have higher speeds on the average than those in the cold gas (assuming each has the same chemical constitution), but a few molecules in the hot gas will move more slowly than the average for the cold gas, while a few in the cold aas will travel faster than the average for the hot gas. The Demon identifies these exceptional molecules as they approach the door and lets them pass through to the other side, while blocking all others. In this way he gradually *increases* the average speed of molecules in the hot gas and *decreases that* in the cold, thereby in effect causing heat to flow from cold to hot.

In addition to reversing the irreversible, Maxwell's Demon offered a new model for the fundamental irreversible process: he translated heat flow into molecular mixing. The ordinary phenomenon, heat passing from a hot body to a cold one, was now seen to be equivalent (though not always identical) to the transition from a partly ordered state (most fast molecules in one place, most slow molecules in another place) to a less ordered state. The concept of molecular order and disorder was henceforth to be associated with heat flow and entropy, though Maxwell himself didn't make the connection explicit.

Maxwell's conclusion was that the validity of the Second Law is not absolute but depends on the nonexistence of a Demon who can sort out molecules; hence it is a statistical law appropriate only to macroscopic phenomena.

To call the Second Law a "statistical law" does not of course imply logically that it is based on random events -- to the contrary. If Maxwell's Demon could not predict the future behavior of the molecules from the observations he makes as they approach the door, he could not do his job effectively. And in some of the later discussions it appeared that a relaxation of strict molecular determinism would make complete irreversibility more rather than less likely. (This was indeed the effect of the Burbury-Boltzmann "molecular disorder" hypothesis mentioned below.) Nevertheless at a more superficial level of discourse the characterization "statistical" conveyed the impression that an element of randomness or disorder is somehow involved.

Boltzmann then provided a quantitative version of Maxwell's argument with the help of his transport equation for the non-equilibrium velocity distribution function. He showed that collisions always push $f(x,v,t)$ toward the equilibrium Maxwell distribution. In particular, the quantity $H = \int f(x,v,t) \log f(x,v,t)$ always decreases with time unless f is the Maxwell distribution, in which case H maintains a fixed minimum value. This statement is now known as Boltzmann's H-theorem.

For a gas in thermal equilibrium, Boltzmann's H is proportional to minus the entropy as defined by Clausius in 1865. While the entropy in thermodynamics is defined only for equilibrium states, Boltzmann suggested that his H-function could be considered a generalized entropy having a value for any state. Then the H-theorem is equivalent to the statement that the entropy always increases or remains constant, which is one version of the second law of thermodynamics. The justification for Maxwell's distribution law is then based on the assertion of a general tendency for systems to pass irreversibly toward thermal equilibrium.

Boltzmann's Viennese colleague Josef Loschmidt pointed out in 1876 that according to Newton's laws one should be able to return to any initial state by merely reversing the molecular velocities. There seems to be a fundamental contradiction between the reversibility of Newton's laws and the irreversibility we see in nature. This contradiction became known as the "Reversibility Paradox"; it had already been discussed two years earlier by William Thomson, in a paper that attracted little notice.

Boltzmann replied by proposing that entropy is really a measure of the probability of a state, defined macroscopically. While each *microscopic* state (specified by giving all molecular positions and velocities) can be assumed to have equal probability, macroscopic states corresponding to "thermal equilibrium" are really collections of large numbers of microscopic states and thus have high probability, whereas macroscopic states that deviate siqnificantly from equilibrium consist of only a few microscopic states and have very low probability. In a typical irreversible process the system passes from a nonequilibrium state (for example high temperature in one place, low in another) to an equilibrium state (uniform temperature); that is, from less probable (lower entropy) to more probable (higher entropy). To reverse this process it is not sufficient to start with an equilibrium state and reverse the velocities, for that will almost certainly lead only to another equilibrium state; one must pick one of the handful of very special microscopic states (out of the immense number corresponding to macroscopic equilibrium) which has evolved from a nonequilibrium state, and reverse its velocities. Thus it is possible that entropy may decrease, but extremely improbable.

The distinction between macro- and microstates is crucial in Boltzmann's theory. Like Maxwell's Demon, an observer who could deal directly with microstates would not perceive irreversibility as an invariable property of natural phenomena. It is only when we decide to group together certain microstates and call them, collectively, "disordered" or "equilibrium" macrostates, that we can talk about going from "less probable" to "more probable" states.

This is an irreversible process in the same sense that shuffling the deck after dealing a grand-slam hand in bridge is an irreversible process; the rules of the game single out certain distributions of cards as "ordered" (all the same suit or all aces, kings and queens in the same hand), and we call these "rare" distributions although in fact each of the possible distributions of 52 cards among four hands of 13 each has exactly the same probability.

If you play bridge long enough you will eventually get that grand-slam hand, not once but several times. The same is true with mechanical systems governed by Newton's laws, as the French mathematician Henri Poincaré (1854-1912) showed with his recurrence theorem in 1890: if the system has fixed total energy and is restricted to a finite volume, it will eventually return as closely as you like to any given initial set of molecular positions and velocities. If the entropy is determined by these variables, then it must also return to its original value, so if it increases during one period of time it must decrease during another.

This apparent contradiction between the behavior of a deterministic mechanical system of particles and the Second Law of Thermodynamics became known as the "Recurrence Paradox." It was used by the German mathematician Ernst Zermelo in 1896 to attack the mechanistic worldview. He argued that the Second Law is an absolute truth, so any theory that leads to predictions inconsistent with it must be false. This refutation would apply not only to the kinetic theory of gases but to any theory based on the assumption that matter is composed of particles moving in accordance with the laws of mechanics.

Boltzmann had previously denied the possibility of such recurrences and might have

continued to deny their certainty by rejecting the determinism postulated in the Poincaré-Zermelo argument.   Instead, he admitted quite frankly that recurrences are completely consistent with the statistical viewpoint, as the card-game analogy suggests; they are fluctuations, which are almost certain to occur if you wait long enough. So determinism leads to the same qualitative consequence that would be expected from a random sequence of states! In either case the recurrence time is so inconceivably long that our failure to observe it cannot constitute an objection to the theory.

While Boltzmann sidestepped the issue of determinism in the debate on the recurrence paradox, maintaining a somewhat ambiguous "statistical" viewpoint, he had to face the issue more squarely in another debate that came to a head at almost the same time. E. P. Culverwell in Dublin had raised, in 1890, what might be called the "reversibility objection to the H theorem," not to be confused with the "reversibility paradox" discussed by William Thomson, Loschmidt, and Boltzmann in the 1870s. Culverwell asked how the H-theorem could possibly be valid as long as it was based on the assumption that molecular motions and collisions are themselves reversible, and suggested that irreversibility might enter at the molecular level, perhaps as a result of interactions with the ether.

The ether was always available as a hypothetical source and sink for properties of matter and energy that didn't quite fit into the framework of Newtonian physics, although some physicists were by this time quite suspicious of the tendency of their colleagues to resolve theoretical difficulties this way.

Culverwell's objection was discussed at meetings of the British Association and in the columns of Nature during the next few years. It was S. H. Burbury in London who pointed out, in 1894, that the proof of the H-theorem depends on the Maxwell-Boltzmann assumption that colliding molecules are uncorrelated. While this would seem a plausible assumption to make before the collision, one might suppose that the collision itself introduces a correlation between the molecules that have just collided, so that the assumption would not be valid for later collisions. Burbury suggested that the assumption might be justified by invoking some kind of "disturbance from without [the system], coming at haphazard" [Burbury 1894, p. 78].

Boltzmann, who participated in the British discussions of the H theorem, accepted Burbury's conclusion that an additional assumption was needed, and called it the hypothesis of "molecular disorder." He argued that it could be justified by assuming that the mean free path in a gas is large compared with the mean distance of two neighboring molecules, so that a given molecule would rarely encounter again a specific molecule with which it had collided, and thus become correlated (see Boltzmann 1896-1898, pp. 40-41).

"Molecular disorder" is not merely the hypothesis that states of individual molecules occur completely at random; rather it amounts to an exclusion of special ordered states of the gas that would lead to violations of the Second Law. In fact such ordered states would be generated by a random process, as Boltzmann noted in his discussion of the recurrence paradox.

In modern terminology, one makes a distinction between "random numbers" and "numbers generated by a random process" -- in preparing a table of random numbers for use in statistical studies, one rejects certain subsets, for example pages on which the frequencies of digits depart too greatly from 10%, because they are inconveniently-nonrandom products of a random process.

Boltzmann recognized that the hypothesis of molecular disorder was needed to derive irreversibility, yet at the same time he admitted that the hypothesis itself may not always be valid in real gases, especially at high densities, and that recurrence may actually occur.

In view of Boltzmann's partial abandonment of determinism on the molecular level, we must reconsider the view that 19th-century physicists always assumed determinism and used statistical methods only for convenience.

There is no doubt that some 19th-century thinkers did see determinism as the essence of science. Thus W. Stanley Jevons, a philosopher of science, wrote in 1877:

> We may safely accept as a satisfactory scientific hypothesis the doctrine so grandly put forth by Laplace, who asserted that a perfect knowledge of the universe, as it existed at any given moment, would give a perfect knowledge of what was to happen thenceforth and for ever after. Scientific inference is impossible, unless we may regard the present as the outcome of what is past, and the cause of what is to come. To the view of perfect intelligence nothing is uncertain.
> [Jevons 1877, pp. 738-39]

Hence, as Laplace himself had remarked in 1783 (see Gillispie 1972, p. 10), there is really no such thing as "chance" in nature, regarded as a *cause* of events; it is merely an expression of our own ignorance, and *"probability belongs wholly to the mind"* (Jevons 1877, p. 198).

But was this view really held by scientists themselves? By the time Jevons wrote the words quoted above, support for absolute determinism was already beginning to collapse. In arguing for some degree of continuity between the 19th and 20th centuries, I do not want to overstate the case; 20th-century events (including the discovery of radioactive decay, though it actually occurred just before 19OO) accounted for most of the impetus toward atomic randomness, while the 19th-century background accounted for a significantly smaller amount. Nevertheless the discussion of randomness and irreversibility in connection with kinetic theory and the Second Law of Thermodynamics was quite familiar to physicists in the early decades of the 20th century.

The claim that 19th-century kinetic theory was based on molecular determinism must rely heavily on the evidence of the writings of James Clerk Maxwell and Ludwig Boltzmann; though in the absence of any explicit statements one might legitimately infer that they tacitly accepted the view of their contemporaries. In fact as we have already seen in the case of Boltzmann, the situation is a little more complicated: the words were ambiguous but the equations pushed

physical theory very definitely in the direction of indeterminism. As in other transformations of physical science -- the cases of Kepler, Fresnel, Planck, and Heisenberg might be adduced here -- mathematical calculation led to results that forced the acceptance of qualitatively different concepts.

Maxwell's earliest work in kinetic theory, in particular his introduction of the velocity-distribution law, seems to derive from the tradition of general probability theory and social statistics (as developed by Adolphe Quetelet) rather than from the mechanistic analysis of molecular motions. Maxwell's law asserts that each component of the velocity of each molecule is a random variable, which is statistically independent of every other component of the same and every other molecule. Only in his later papers did Maxwell attempt to justify the law by relating it to molecular collisions, and even then he needed to assume that the velocities of two colliding molecules are statistically independent. On the other hand, the computation of gas properties such as viscosity and thermal conductivity, whose comparison with experimental data provided the essential confirmation of the theory, did involve the precise dynamical analysis of collisions of particles with specified velocities, positions, and force laws. Without determinism in this part of the theory Maxwell could not have achieved his most striking successes in relating macroscopic properties to molecular parameters.

Maxwell did not consistently maintain the assumption of determinism at the molecular level, though he occasionally supported that position, for example, in his lecture on "Molecules" at the British Association meeting in 1873. Yet in the same year, in private discussions and correspondence, he began to repudiate determinism as a philosophical doctrine. A detailed exposition of his views may be found in a paper titled "Does the progress of physical science tend to give any advantage to the opinion of necessity (or Determinism) over that of the contingency of events and the Freedom of the Will?" presented to an informal group at Cambridge University. The answer was no -- based on arguments such as the existence of singular points in the trajectory of dynamical systems, where an infinitesimal force can produce a finite effect. (These arguments have led some contemporary scientists to list Maxwell as one of the precursors of "chaos theory.") The conclusion was that "the promotion of natural knowledge may tend to remove that prejudice in favor of determinism which seems to arise from assuming that the physical science of the future is a mere magnified image of that of the past" [Campbell & Garnett 1882, p. 434].

By 1875 Maxwell was asserting that molecular motion is "perfectly irregular; that is to say, that the direction and magnitude of the velocity of a molecule at a given time cannot be expressed as depending on the present position of the molecule and the time" (Maxwell 1875a, p. 235). He also stated that this irregularity must be present in order for the system to behave irreversibly (Maxwell 1875b).

Two decades later, as noted above, Boltzmann seemed to have reached a similar conclusion. But he was not quite satisfied that his hypothesis of molecular disorder resolved the reversibility and recurrence paradoxes; in response to further criticisms by Zermelo he proposed a new hypothesis. Suppose we consider the curve of H as a function of time for the entire

universe, or for a part of the universe isolated from the rest. A high value of H will correspond to a low-entropy highly-ordered state, where life can exist. If the recurrence theorem is correct then such a state can be regarded as one of an infinite number of maxima of an oscillating curve. If we follow H forward in time from one of these peaks, it will decrease in accordance with the H theorem; but it must eventually increase again to get to the next peak. Such an epoch of increasing H (decreasing entropy) would seem to violate the Second Law. But, Boltzmann suggested, if the irreversible processes in our environment and in our own bodies are "running backwards" then our own sense of the direction of time must also be reversed. Thus for any conscious beings who exist during this epoch, H must decrease when measured with respect to the time-changes of those beings, so for them the Second Law still holds.

Although Boltzmann did not regard this proposal as any more than a speculative hypothesis, he justified it as follows:

> One has the choice of two kinds of pictures. One can assume that the entire universe finds itself at present in a vry improbable state. However, one may suppose that the eons during which this improbable state lasts, and the distance from here to Sirius, are minute compared to the age and size of the universe. There must then be in the universe, which is in thermal equilibrium as a whole and therefore dead, here and there relatively small regions of the size of our galaxy (which we call worlds), which during the relatively short time of eons deviate significantly from thermal equilibrium. Among these worlds the state probability increases as often as it decreases. For the universe as a whole the two directions of time are indistinguishable, just as in space there is no up or down. However, just as at a certain place on the Earth's surface we can call "down" the direction toward the centre of the Earth, so a living being that finds itself in such a world at a certain period of time can define the time direction as going from less probable to more probable states (the former will be the "past" and the latter the "future") and by virtue of this definition he will find that this small region, isolated from the rest of the universe, is "initially" always in an improbable state. This viewpoint seems to me to be the only way in which one can understand the validity of the Second Law and the Heat Death of each individual world without invoking a unidirectional change of the entire universe from a definite initial state to a final state.

[Boltzmnn 1897, p. 242]

Boltzmann's hypothesis asserts that irreversibility -- the statement that "entropy increases with time" is not a law of nature but a <u>tautology</u>: the direction of time is determined by the direction of entropy increase. (Curiously this idea had recently been advanced by Ernst Mach, the most famous critic of Boltzmann's kinetic-atomic theories.) Alternatively it could be seen as foreshadowing Einstein's idea that time is not absolute but is somehow relative to the observer.

During the 19th century the kinetic theory of gases solved some old problems, predicted some unexpected new facts, and generated some puzzling paradoxes. It left to 20th century science a rich legacy of useful knowledge about molecules and gases and provocative conjectures

about irreversibility and indeterminism.

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