The Development of the Kinetic Theory of Gases

VIII. Randomness and Irreversibility

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Contents

1. Introduction: the World-Machine and Cosmic History

"The most important question, perhaps, of contemporary scientific philosophy is that of the compatibility or incompatibility of thermodynamics and mechanism." That statement was made at the first international physics congress at Paris in 1900 by BERNARD BRUNHES, Director of the Puy-de-Dôme Observatory, in his discussion of GABRIEL LIPPMANN's paper on the conflict between CARNOT's principle and the kinetic theory of gases.[1] At issue was a problem that had been the subject of controversy during the preceding decade: how could one reconcile the basic laws of NEWTONIAN mechanics with the Second Law of Thermodynamics— in particular, how could the principle of irreversibility, apparently grounded quite firmly in experience, be explained by any mechanical model which had to be based on reversible equations of motion? HENRI POINCARÉ had again drawn attention to this difficulty in his opening address to the Paris congress.[2]

In spite of the supposed complacency of physicists at the end of the 19$^{\text{th}}$ century[3], it was clear to many sharp thinkers that this conflict between thermodynamics and mechanics cast serious doubt on the validity and internal consistency of the pre-

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[1] *Travaux Cong. Int. Phys., Paris, 1900*, **4**, 29 (Paris: Gauthier-Villars, 1901). For the text of LIPPMANN's paper see *Rapports Cong. Int. Phys., Paris, 1900*, **1**, 546 (Paris: Gauthier-Villars, 1900). (The fourth volume of the "Rapports" was published with the title "Travaux".)

[2] POINCARÉ, *Rapports Cong. Int. Phys., Paris, 1900*, **1**, 1.

[3] L. BADASH, *Isis* **63**, 48 (1972) has given a number of examples of English and American scientists who suggested in the 1880's and 1890's that all the basic principles of physics were known and only the details remained to be worked out. Dissatisfaction with foundations, and discoveries leading to new foundations, were found more frequently among German and French scientists. Thus BOLTZMANN wrote in 1898 that "today it is popular to look forward to the time when our view of nature will have been completely changed" (see below, end of § 7).

viously-accepted foundations of physical science. The feeling was reinforced by the publicity given to other difficulties confronting established theories, for example Lord KELVIN's two "clouds over the dynamical theory of heat and light" (the MICHELSON-MORLEY experiment and the apparent failure of the equipartition theorem for polyatomic gases).[4] For some, the way out was to reject the mechanistic philosophy and seek to base scientific theories on the principles of "energetics" or electromagnetism.[5] Others, like ERNST MACH, scorned their colleagues' search for theoretical foundations and urged a more empirical approach.[6]

As we know, KELVIN's clouds were soon to be dispersed by the new theories of PLANCK and EINSTEIN. But the problem of irreversibility was not so easily solved, and is still with us today though in a somewhat different form.[7] Nevertheless the attempt to solve it had already, before 1900, led to the introduction of a statistical viewpoint in molecular physics; or rather, had pushed the earlier statistical viewpoint in the direction of postulating randomness and indeterminacy at the atomic level. Thus the 19$^{\text{th}}$-century attempts to explain irreversibility did much to prepare the way for the stochastic[8] world-view that seems now to be an essential part of modern physics. In this paper I will discuss the concepts of randomness and irreversibility and their interactions in the development of the kinetic theory of gases before 1900.

[4] *Proc. Roy. Inst.* **16**, 363 (1900); *Phil. Mag.* [6] **2**, 1 (1901); *Baltimore Lectures on Molecular Dynamics and the Wave Theory of Light* (London: Clay, 1904) p. 486.

[5] A survey of writings on energetics has recently been given by E. N. HIEBERT in *Perspectives in the History of Science and Technology*, ed. D. H. D. ROLLER (Norman: University of Oklahoma Press, 1971) p. 67. Further references may be found in my notes to the English translation of BOLTZMANN's *Lectures on Gas Theory* (Berkeley: University of California Press, 1964), pp. 24, 215. On the electromagnetic view see R. MCCORMMACH, *Isis* **61**, 459 (1970); also A. M. BORK, *Science* **152**, 597 (1966). BORK concludes his account with the comment: "We cannot but be impressed with the great activity and restlessness which characterize the period before 1905. On all sides the physicist found his Newtonian universe floundering, not only in its details but even in its underlying mechanistic assumptions. The stage was set for the revolution to come."

[6] *Cf.* S. G. BRUSH, *Graduate Journal* **7**, 477 (1967), especially the works mentioned on pp. 533–34 and 564–65. The best general account of MACH's position is in the recent book by JOHN T. BLACKMORE, *Ernst Mach* (Berkeley: University of California Press, 1972).

[7] WOLFGANG BÜCHEL, *Philosophia Naturalis* **6**, 167 (1960). G. J. WHITROW, *The Natural Philosophy of Time* (London: Nelson, 1961), 10–12, 268–310. P. MORRISON, in *Preludes in Theoretical Physics in honor of V.F. Weisskopf* (New York: Interscience, 1966), 347. M. GARDNER, *Sci. Amer.* **216** (1), 98 (1967). T. GOLD, ed., *The Nature of Time* (Ithaca: Cornell University Press, 1967). E. M. HENLEY, *Ann. Rev. Nuclear Sci.* **19**, 367 (1969). M. DAKO, *Studium Generale* **22**, 965 (1969). R. E. PEIERLS, in *Methods and Problems of Theoretical Physics*, ed. J. E. BOWCOCK (New York: American Elsevier 1970), 3. P. C. W. DAVIES, *Physics Bull.* **22**, 211 (1971). J. BIEL & J. RAE, eds., *Irreversibility in the Many-Body Problem* (New York: Plenum Press, 1972). P. T. LANDSBERG, in *The Study of Time*, ed. J. T. FRASER, F. C. HABER & G. H. MÜLLER (New York: Springer, 1972), 59. B. GAL-OR, *Science* **176**, 11, **178**, 1119 (1972). R. G. SACHS, *Science* **176**, 587, **178**, 1119 (1972). S.-T. HWANG, *Found. Phys*, **2**, 315 (1972). J. MEHRA & E. C. G. SUDARSHAN, *Nuovo Cimento* [11] **11B**, 215 (1972).

[8] I do not want to use the word "statistical" here since a statistical theory may or may not assume that individual atomic behavior is deterministic. "Stochastic" means "random" but "stochastic theory" does not have quite the same connotations as "random theory"—it is the event or process that is said to be random, not the theory about it.

Since "randomness" is sometimes thought to be a characteristic 20th-century concept, it might be objected that one would be committing the sin of "present-mindedness" or writing "Whig history" by trying to extract its development from 19th-century physics. In defense of the approach followed here, I would point out that while deterministic ideas did dominate 19th-century physics, the older conception of the world as a "fortuitous concourse of atoms" had not been forgotten (certainly not by those who were aware of the origin of kinetic atomism in Greek antiquity) and was occasionally revived in a rather explicit way by 19th century philosophers[9]. On the other hand, a history of randomness would be of little value if it ignored the context of other scientific ideas and theories which were associated with it. In this case the emphasis will be on irreversibility and the problem of justifying thermal equilibrium in the kinetic theory of gases; if we attempted to extend our discussion into the 20th century it would be necessary to review several other areas of physics. The lack of a still wider consideration of the 19th-century context may perhaps be excused here since I have written at some length on this topic elsewhere.[10]

By now there is an abundance of secondary literature on randomness and irreversibility, so this paper will be in part a summary or critique of what has already been written on the subject[11]; but I will examine more closely certain important but neglected aspects.

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The introduction of statistical methods in 19th-century kinetic theory is often seen against the background of an orthodox viewpoint supposedly prevailing in the 18th century. This viewpoint could be characterized as the NEWTONIAN mechanical

[9] C. S. PEIRCE, *Monist* **1**, 162 (1891), **2**, 321 (1892). ANTOINE-AUGUSTIN COURNOT, *Essai sur les fondements de nos connaissances* (Paris, 1851); English trans. with introd. by M. H. MOORE, *An Essay on the Foundations of our Knowledge* (New York: Liberal Arts Press, 1956), *xxvii*, 41, *etc.* There was also DARWINIAN evolution with its postulate of random variation; *cf.* section 5, note 19.

[10] S. G. BRUSH, *Graduate Journal* 7, 477 (1967).

[11] H. BERNHARDT, *NTM, Z. Ges. Naturwiss. Tech. Med.* **4**, (10), 35 (1967), **6** (2), 27 (1969). B. BRUNHES, *La Dégradation de l'Énergie* (Paris: Flammarion, 1922). C. BRUNOLD, *L'Entropie* (Paris: Masson, 1930). E. DAUB, *Isis* **60**, 318 (1969); *Hist. Stud. Phys. Sci.* **2**, 321, 165 (1970); *Stud. Hist. Phil. Sci.* **1**, 213 (1970). R. DUGAS, *La Théorie Physique au sens de Boltzmann* (Neuchatel: Griffon, 1959). ADOLF GRÜNBAUM, *Archiv f. Philos.* **7** (1957). D. TER HAAR, *Elements of Statistical Mechanics* (New York: Rinehart, 1954), Appendix I. E. N. HIEBERT, *The Conception of Thermodynamics in the Scientific Thought of Mach and Planck* (Freiburg i. Br.: Ernst-Mach-Institut, 1968); in *Perspectives in the History of Science and Technology*, ed. D. H. D. ROLLER (Norman: University of Oklahoma Press, 1971), 67. L. JANOSSY, in *Max-Planck-Festschrift 1958* (Berlin: VEB Deutscher Verlag der Wissenschaften, 1959), 389. M. J. KLEIN, *Natural Philosopher* **1**, 83 (1963); *Amer. Scient.* **58**, 84 (1970); *Paul Ehrenfest*, **1** (New York: American Elsevier, 1970), Chap. 6; in *The Boltzmann Equation*, ed. E. G. D. COHEN & W. THIRRING (New York: Springer-Verlag, 1973), 53. w. KÖHLER, *Erkenntnis* **2**, 336 (1932). V. F. LENZEN, *Univ. Calif. Publ. Philos.* **10**, 119 (1928). H. REICHENBACH, *The Direction of Time* (Berkeley: University of California Press, 1956). A. REY, *La Théorie de la Physique chez les physiciens contemporains* (Paris: Alcan, 2. ed. 1923); *Le Retour Éternel et la Philosophie de la Physique* (Paris: Flammarion, 1927). L. ROSENFELD, *Acta Phys. Polon.* **14**, 3 (1955); in *Max-Planck-Festschrift 1958* (Berlin: VEB Deutscher Verlag der Wissenschaften, 1958), 203; in *Irreversibility in the Many Body Problem*, ed. J. BIEL & J. RAE (New York: Plenum Press, 1972), 1. R. SCHLEGEL, *Time and the Physical World* (New York: Dover Pubs., 1968 reprint of the 1961 ed.).

philosophy or "clockwork universe" picture, in which all motions are in principle determined by specifying them at some initial time, and all changes are cyclic; thus randomness and irreversibility are both completely absent from the main body of accepted physical laws. Unfortunately for the conventional accounts, things are not quite so simple: first because NEWTON himself had quite firmly rejected this view, second because geophysical speculations had already introduced the notion of irreversible heat flow by the end of the 18th century, and third because statistical considerations were by no means excluded from theories of natural phenomena in 1800. Thus the assertions of determinism and cyclic stability found in the writings of LAPLACE and his colleagues at the beginning of the 19th century must not be read as expressions of a monolithic world-view that had been accepted in all areas of science, but rather as admittedly hypothetical descriptions of an ideal world, of strictly limited value in dealing with the real world.

The clockwork universe of the 17th-century mechanical philosophers such as DESCARTES and BOYLE[12] was deeply repugnant to NEWTON on theological grounds, and moreover seemed to him inconsistent with certain obvious facts about the physical world. In the *Opticks* he pointed out that irreversible processes such as viscosity of fluids and imperfect elasticity of solids tend to make the world-machine run down: "motion is much more apt to be lost than got, and is always upon the decay."[13] In order to prevent the total quantity of motion in the world from decreasing to nothing, there must be "active principles" that operate to renew motion. Otherwise everything would freeze and life would cease; moreover, mutual gravitational perturbations of planets in the solar system would accumulate over long periods of time "till this system wants a reformation" which God perhaps accomplishes by feeding in comets with appropriately chosen masses and orbits.[14]

NEWTON's suggestion that the laws of physics by themselves are insufficient to ensure the proper functioning of the world over long periods of time without divine intervention was attacked by LEIBNIZ, and was one of the major issues in the famous LEIBNIZ-CLARKE debate of 1715–16.[15] As LEIBNIZ put it, NEWTON's view meant that "God almighty needs to wind up His watch from time to time; otherwise it would cease to move," implying that God was such a poor craftsman that He couldn't make a machine that would run forever without repairs.[16] LEIB-

[12] M. BOAS [HALL], *Osiris* **10**, 412 (1952); *Robert Boyle on Natural Philosophy* (Bloomington: Indiana University Press, 1965). E. A. BURTT, *The Metaphysical Foundations of Modern Physical Science* (Garden City, N. Y.: Doubleday, 1954, reprint of the 2. ed.). E. J. DIJKSTERHUIS, *The Mechanization of the World Picture* (New York: Oxford University Press, 1961, trans. of the Dutch ed., 1950).

[13] *Opticks* (4th London ed., 1730; New York: Dover Pubs., 1952), p. 398.

[14] See DAVID KUBRIN, *J. Hist. Ideas* **28**, 325 (1967). NEWTON's suggestion that perturbations might eventually cause the earth to fall into the sun was echoed in SWIFT's *Voyage to Laputa*; see MARJORIE NICOLSON, *Science and Imagination* (Ithaca: Cornell University Press, 1956), 123–27, reprinted from an article by M. NICOLSON & N. M. MOHLER, *Annals of Science* **2**, 299 (1937). (I thank Professor C. TRUESDELL for this reference.)

[15] See H. G. ALEXANDER, *The Leibniz-Clarke Correspondence* (Manchester, Eng.: Manchester University Press, 1956). For evidence that CLARKE was really expressing NEWTON's opinions see A. RUPERT HALL & MARIE BOAS HALL, *Isis* **52**, 583 (1961); A. KOYRÉ & I. B. COHEN, *Arch. Int. Hist. Sci.* **15**, 63 (1962).

[16] ALEXANDER, *op. cit.*, 11–12.

NIZ, on the contrary, believed that "the same force and vigour remains always in the world, and only passes from one part of matter to another, agreeably to the laws of nature and the beautiful pre-established order." It was LEIBNIZ's opinion that in processes such as the generation of heat by mechanical friction the total "force" (*i.e.*, some quantity equivalent to the *vis viva*, mv^2) would still be conserved, although it might be converted into the invisible motion of atoms.[17] Presumably such a process would not have to be irreversible, though LEIBNIZ did not explicitly address that point.

For anyone who accepted NEWTON's concept of atoms as being hard bodies that could never change their size or shape, it would seem that atomic collisions must be inelastic and hence irreversible; if two atoms meet head-on they would simply stop and not rebound. This theoretical difficulty seemed to make NEWTONIAN atomism incompatible with any kind of convervation law for motion (either momentum or energy). The debate on this point has been comprehensively analyzed by WILSON SCOTT.[18] Its significance for our story is that even though irreversibility in physical processes had been recognized by NEWTON, it was not yet possible to talk about irreversibility in the modern sense (*e.g.* as involving entropy increase) because a more basic kind of irreversibility—decrease of motion—had not yet been excluded by a conservation law. This dilemma corresponds to the circumstance that logically one cannot have a Second Law of Thermodynamics until after one has established a First Law, yet historically the Second Law (or something that looks like it) came earlier.

For NEWTON, as for many later scientists, the present state of the physical universe could not be explained as a result of "blind chance" because there were too many evidences of intelligent design.[19] Nor could it be attributed to the deterministic action of natural laws and initial conditions established by God, in the sense of the clockwork universe, for that would make it too easy to eliminate divine providence entirely.[20] Nevertheless by proposing a system of physical laws that could be successfully applied to the motions of planets and satellites, and to the shape of the earth, NEWTON had provided the essential basis for the idea that physical laws could in principle explain in a deterministic fashion the motions of all matter in the universe.

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NEWTON's assertion that the solar system might be unstable because of the accumulated effect of gravitational perturbations was taken up as a challenge to the ingenuity of the greatest mathematicians of the 18th and early 19th centuries. The "three-body problem" was attacked by EULER, LAPLACE, LAGRANGE, and POISSON, in the hope of getting at least a good approximation to the long-term effects of

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[17] ALEXANDER, *op. cit.*, 87–88.

[18] WILSON L. SCOTT, *The Conflict between Atomism and Conservation Theory* 1644–1860 (New York: Elsevier/London: Macdonald, 1970).

[19] *Opticks*, 402; for a general survey of NEWTON's opinions on this point see O. B. SHEYNIN, *Arch. Hist. Exact Sci.* 7, 217 (1971).

[20] ALEXANDER, *op. cit.*, 13–14. According to NEWTON's friend, the theologian RICHARD BENTLEY, there is really not much difference between randomness and determinism if one does not accept divine guidance in natural phenomena; randomness merely implies lack of knowledge of mechanical causes (see the passage quoted by SHEYNIN, *op. cit.*, 232).

perturbations. Their conclusion was that NEWTON had misconstrued the effects of planetary interactions, and that all deviations from the present orbits would oscillate cyclically between fixed limits, so that the solar system would be stable for an indefinitely long time.[21] Hence, just as NEWTON had feared, celestial mechanics could dispense with divine providence; in LAPLACE's celebrated phrase, "I have no need for that hypothesis."[22]

This conclusion did not imply that there are no irreversible processes in astronomy. Despite the success of NEWTON's law of gravity, treated as if it were pure action-at-a-distance with no need for propagation through a medium, the continental theorists could not entirely dispense with the hypothesis that interplanetary space is filled with an ethereal fluid, and it seemed improbable that the planets would not somehow be retarded as they moved through this fluid. LAPLACE concluded that the effect of such frictional action would be to make elliptical orbits more nearly circular,[23] without changing the mean distance of the planet from the sun. It also seemed likely that the tides of terrestrial oceans would have some effect on the rate of the earth's rotation, perhaps forcing it ultimately to present always the same face to the moon, as the moon does to the earth.[24] Thus, not for the last time, the aether was assigned the duty of irreversibly dragging ponderable matter toward a state of final equilibrium (*cf.* CULVERWELL's suggestion, section 6 below), in collaboration with other natural processes that seemed to have a similar effect.

Even if the present arrangement of the solar system should continue more or less the same for the indefinite future, as a stable equilibrium state, that did not mean that it had never changed in the past. Rather than postulate that God had created the planets in their present orbits (perhaps placed so that they would receive the right amount of the sun's heat in proportion to their density[25]) it seemed to at least a few philosophers—KANT, LAPLACE, and their followers—more reasonable to assume a gradual evolution of the solar system from a whirling chaos of primal matter, with the planets being formed as hot liquid balls.[26] As traditional theology loosened its grip on scientific speculation, such naturalistic schemes of cosmic evolution became more popular.

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[21] P. S. DE LAPLACE, *Traité de Mécanique Celeste*, **V** (Paris, 1825, reprinted by Chelsea Pub. Co., Bronx, N. Y., 1969, together with the BOWDITCH translation of the first four volumes), Livre XV, Chapitre I. See also LAPLACE's *Exposition du Système du Monde* (1796, 5th ed. 1824), English translation, *The System of the World* (Dublin, 1830), pp. 328–32; A. PANNEKOEK, *A History of Astronomy*, (New York: Interscience Pubs./London: Allen & Unwin, 1961, translated from Dutch edition of 1951), Chap. 30.

[22] AUGUSTUS DE MORGAN, *A Budget of Paradoxes* (Chicago; Open Court, 1915, reprint of 2. ed.), **II**, 1–2. The essence of this legend is supported by LAPLACE's published criticisms of NEWTON's theological assumptions, *e.g.* in *System of the World* (Dublin, 1830), 331–333.

[23] LAPLACE, *Mécanique Celeste*, **IV**, Livre X, Chap. VII.

[24] IMMANUEL KANT, *Wöchentliche Frag- und Anziehungs-Nachrichten* (1754), reprinted in *Allgemeine Naturgeschichte und Theorie des Himmels* (1755); partial English trans. by W. HASTIE (1900), reprinted with new introd. by M. K. MUNITZ, *Universal Natural History and Theory of the Heavens* (Ann Arbor, University of Michigan Press, 1969).

[25] See I. B. COHEN, in *Philosophy, Science, and Method*, ed. S. MORGENBESSER (New York: St. Martin's Press, 1969), 523.

[26] KANT, *op. cit.*; Laplace, *Exposition du Systeme du Monde* (1796).

But, granted that things do not always remain the same, how did it happen that during the 19th century "evolution"—an apparently neutral term but one loaded with optimistic connotations—had to compete with "dissipation" and "degeneration"? How could HUMPHRY DAVY say, as early as 1829, that "human science ... has discovered the principle of the decay of things"?[27]

2. The Cooling of the Earth

It is difficult to conceive of a time when people did not know that heat flows from hot bodies to cold bodies. Our problem is to understand how this apparently trivial example of irreversibility was translated into an illustration of a general law of nature, the Principle of Dissipation of Energy, and as such was seen to be in conflict with NEWTONIAN mechanics. The usual explanation is that this came about as a result of SADI CARNOT's analysis of steam engines, leading to the Second Law of Thermodynamics as a condition on the interconversion of heat and mechanical work; thus irreversibility was associated with the operation of *real* steam engines in which any flow of heat through a finite temperature-difference meant the loss of a possible transformation of some of that heat into useful mechanical work. Perhaps that is how irreversible heat flow acquired its unpleasant moral connotation—the term "dissipation" being a synonym for "intemperate, dissolute, or vicious mode of living ... squandering, waste ..."[1]—in the culture of industrialized Victorian Britain. But the idea that the natural behavior of heat entails a distinction between past and future time directions, and even the extrapolation to an ultimate "heat death" of the world, go back to the 18th century where they have nothing to do with steam engines. Instead we must look to the literature of geophysical or planetary science, where so many fundamental discoveries and theories of 19th-century physics originated.[2]

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[27] H. DAVY, *Consolations in Travel; or, the Last Days of a Philosopher* (Boston, 5th ed. 1870), 273. (The preface is dated 1829, the year of DAVY's death.)

[1] *Oxford English Dictionary* (London: Oxford University Press, 1933, reprinted 1961). For the association of energy-dissipation with "degeneration" see L. PFAUNDLER, *Die Physik des täglich Lebens* (Stuttgart, 1904), 268; W. S. FRANKLIN, *Phys. Rev.* **30**, 766 (1910). While it is generally assumed that dissipation of energy has pessimistic connotations, this is not necessarily the case. LUDVIG COLDING phrased it as the principle that "nature strives to realize an ever more perfect liberation of the forces of nature," and associated the scattering of matter and energy throughout infinite space with increasing freedom of the human soul. See *Oversigt over Det Kgl. Danske Videnskabernes Selskabs Forhandlinger*, No. 4–6, 136 (1856); English translation in PER F. DAHL, *Ludvig Colding and the Conservation of Energy Principle* (New York: Johnson Reprint Corp., 1972). HERBERT SPENCER, a decade later, saw dissipation as only one aspect of a general principle of Evolution, which "can end only in the establishment of the greatest perfection and the most complete happiness" (quoted in BRUSH, *Graduate J.* 7, 512 (1967).

[2] See S. G. BRUSH, "Relations between Planetary Science and 'Pure' Science in the 19th Century," to be published in the proceedings of the XIII International History of Science Congress, Moscow, 1971. Neglect of the geophysical literature accounts for statements such as that of BARNETT, that the concept of irreversibility was absent from "modern physical philosophy as it was developed in the seventeenth and eighteenth century" and was foreign to physical thought before 1850. M. K. BARNETT, *Osiris* **13**, 327 (1958).

Many speculators in earlier centuries had suggested that the earth was originally formed in a hot molten state and has subsequently cooled down. In the late 18th and early 19th centuries, this theory was most commonly attributed to LEIBNIZ, who advanced it in his *Protogaea*.[3] LEIBNIZ assumed that the outer surface of a molten proto-earth would solidify in a somewhat irregular manner, with bubbles bursting through at various places, while the inner part would still remain liquid. The evidence for this hypothesis consisted of familiar phenomena such as vitrified rocks, volcanos, hot springs, and the gradual increase in temperature noted as one goes down into the earth.[4]

Another argument for the central heat theory was provided by DORTOUS DE MAIRAN, who analyzed the seasonal variations of surface temperature in various parts of the world and concluded that the heat received from the sun is not sufficient to account for these temperatures. In particular, he estimated that the difference between summer and winter temperatures is so small compared to the average absolute temperature of the earth's surface that the latter must be maintained by a continual flow of heat from the inside of the earth.[5]

BUFFON incorporated the notion of gradual refrigeration of the earth into his grand theory of the Epochs of Nature. He conducted a series of laboratory experiments on the rate of cooling of heated spheres of iron and other substances of various diameters, and on the time required for molten iron to solidify; by extrapolating his results he estimated that it would take 1342 years for a globe of iron the size of the earth to solidify. Taking account of several other corrections he concluded that the time elapsed from the earth's molten state to the present must be about 74,000 years.[6] The recent discovery of ivory trunks of elephants in northern regions where these animals cannot now survive was taken as further evidence that these regions must formerly have been much warmer—one would expect that the earth's polar regions would cool down and become fit for organic life a little sooner

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[3] An extract was published in the *Acta Eruditorum* in 1693, and larger portions were available in various editions during the 18th century. The original complete work was first published in 1949 by W. E. PEUCKERT as Volume I of the new edition of LEIBNIZ' *Werke*. See C. C. BERINGER, *Geschichte der Geologie* (Stuttgart: Enke, 1954), pp. 25 ff; BERNHARD STICKER, *Sudhoffs Arch.* **51**, 244 (1967). A brief English extract may be found in K. F. MATHER & S. L. MASON, *A Source Book in Geology* (New York: McGraw-Hill, 1939, reprinted by Harvard University Press), 45–46.

[4] R. BOYLE, "Of the temperature of the subterraneal regions as to hot and cold," in *Tracts written by the Honourable Robert Boyle* (Oxford, 1671), reprinted in *The Works of the Honourable Robert Boyle*, ed. T. BIRCH (London, new ed. 1772), **3**, 326. E. C. BULLARD, in *Terrestrial Heat Flow*, ed. W. H. K. LEE (Washington: American Geophysical Union, 1965), 1.

[5] JEAN JACQUES DORTOUS DE MAIRAN (variously alphabetized as DORTOUS, DE, or MAIRAN), *Mem. Math. Phys. Acad. Roy. Sci.* 104 (1719); 143 (1765). See F. C. HABER, *The Age of the World* (Baltimore: Johns Hopkins Press, 1959) for a general discussion of MAIRAN's work and its relation to geophysical speculation in the 18th century.

[6] GEORGE-LOUIS LECLERC, Comte DE BUFFON, *Introduction à l'Histoire des Mineraux* (Paris, 1774); *Oeuvres Complètes de Buffon*, ed. M. FLOURENS, nouv. ed., **9**, 82, 89, 307, 308, 348–453 (Paris: Garnier Freres, n. d.); HABER, *op. cit.*, 116–122; JACQUES ROGER, *Dict. Sci. Biog.* **II**, 576 (New York: Charles Scribner's Sons, 1970); STEPHEN TOULMIN & JUNE GOODFIELD, *The Discovery of Time* (New York: Harper & Row, 1965), 143–149.

than the equatorial regions. Hence the hypothesis of a cooling earth seemed to gain support from paleontology.[7]

Although BUFFON is also known for his stochastic method for determining π (the "Buffon needle problem"), I am not aware that he attempted to make any connection between randomness and irreversibility.

From the theory of central heat and gradual refrigeration of the earth it was but a short step to the conjecture that all bodies in the universe are cooling off and will eventually become too cold to support life. This step seems to have been first taken by the French astronomer JEAN-SYLVAIN BAILLY (1736–1793) in his writings on the history of astronomy and the ensuing correspondence with VOLTAIRE. According to BAILLY, all the planets must have an internal heat and are now at some particular stage of cooling: Jupiter, for example, is still too hot for life to arise for several thousand more years; the moon, on the other hand, is already too cold. The final state is described as one of "equilibrium" where all motion has ceased. Thus the modern concept of the "heat death" of the universe, usually attributed to the 19th-century thermodynamic speculations of THOMSON, CLAUSIUS, and HELMHOLTZ, was actually published as early as 1777.[8]

The theory of cooling of the earth was attacked by a few writers in the 18th century,[9] the strongest opposition coming from the influential geologist JAMES HUTTON. While HUTTON accepted the concept of internal heat he did not like BUFFON's physical approach to the subject[10] and denied that there had been any substantial cooling of the earth's interior since its original formation. It is the debate on this particular aspect of HUTTON's theory that is of interest in connection with the development of the concept of irreversibility, and in fact it is HUTTON's critics (now forgotten) who used as a weapon the postulate that heat cannot stay concentrated in one place but must flow to cooler regions.

In reply to a criticism of RICHARD KIRWAN, who complained that there seemed to be no plausible means for continually generating heat inside the earth to replace that which diffused toward the surface, HUTTON disclaimed any obligation to explain the source of subterraneous fire but merely inferred its presence from the

[7] BUFFON, *Oeuvres*, **9**, 455–660.

[8] "Jupiter, où regne encore une chaleur brûlante, où les élémens travaillent pour atteindre l'équilibre; à la lune, déjà glacée, & où tout est équilibre, parce que tout est sans mouvement"—JEAN SYLVAIN BAILLY, *Lettres sur l'Origine des Sciences* (London & Paris, 1777), 342; see also his *Histoire de l'Astronomie Moderne* (Paris, nouv. ed. 1785), **II**, 726, 729. For further discussion of the BAILLY-VOLTAIRE correspondence see HABER, *Age of the World*, 132–135; EDWIN BURROWS SMITH, *Trans. Amer. Philos. Soc.* [n. s.] **44**, 427 (1954).

[9] J. B. L. ROMÉ DE L'ISLE, *L'Action du feu central bannie de la surface du globe, et le soleil retablie dans ses droits, contre les assertions de MM. le Comte de Buffon, Bailly, de Mairan, &c.* (Stockholm, 1779), cited by HABER, *Age of the World*, 135, who says that "Romé de l'Isle expressed the sentiments of a large number of the naturalists" in his critique. CONDORCET and D'ALEMBERT were also skeptical, according to SMITH, *op. cit.*

[10] HUTTON advises that we should not "suppose the wise system of this world to have arisen from the cooling of a lump of melted matter which had belonged to another body. When we consider the power and wisdom that must have been exerted, in the contriving, creating, and maintaining this living world which sustains such a variety of plants and animals, the revolution of a mass of dead matter according to the laws of projectiles, although in perfect wisdom, is but like a unit among an infinite series of ascending numbers"—JAMES HUTTON, *Theory of the Earth* (Edinburgh, 1795), 272.

general appearances of mineral bodies which "must necessarily have been in a state of fusion."[11] Yet HUTTON claimed not only that "subterraneous fire had existed previous to, and ever since, the formation of this earth," but also "that it exists in all its vigour at this day."[12] Indeed, as GORDON DAVIES has recently pointed out, HUTTON had a cyclic view of the earth's history in which denudation processes leading to the destruction of continents must be followed by consolidation of sediments and uplift of new continents (powered by the internal heat engine) in order to reconcile destruction with benign deity.[13] Thus a terrestrial version of the NEWTONIAN world-machine was confronted directly with the problem of irreversible heat flow, in the first round of a continuing debate on this theme.

HUTTON's disciple JOHN PLAYFAIR also felt the need to justify the assumption that the internal fire continues to burn with undiminished intensity throughout the geological ages, but failed to come up with more than a vague suggestion: nature may have "the means of producing heat, even in a very great degree, without the assistance of fuel or of vital air. Friction is a source of heat, unlimited, for what we know, in its extent, and so perhaps are other operations, both chemical and mechanical ..."[14] This passage reminds us again of the historical confusion between irreversible processes that conserve energy and those that supposedly do not; primitive ideas of energy conservation could still be invoked to counter apparent examples of irreversibility.

In another passage that was to become notorious in the 19th century, PLAYFAIR emphasized that the HUTTONIAN theory implies a cyclic view of the earth's history. As long as the central fires keep burning, new mineral strata can be formed and thrust upwards by volcanic action to replace those that are worn away by erosion; and there is nothing in the laws of nature to prevent this sequence from repeating itself indefinitely.[15] For PLAYFAIR there is a clear connection between this cyclic

[11] HUTTON, *Theory of the Earth*, 236. The opinions of HUTTON and KIRWAN have been reviewed by HABER, *op. cit.*, 164–171.

[12] *Ibid.*, 244. The only evidence he gives for this contention is that "the fires, which we see almost daily issuing with such force from volcanos, are a continuation of that active cause which has so evidently been exerted in all times, and in all places, so far as have been examined of this earth" (*ibid.* 246–247).

[13] *Ann. Sci.* **22**, 129 (1966); *The Earth in Decay* (London: Macdonald, 1969).

[14] *Illustrations of the Huttonian Theory of the Earth* (1802, reprinted by University of Illinois Press, 1956, and by Dover Pubs., New York, 1964), 185–186.

[15] "How often these vicissitudes of decay and renovation have been repeated, is not for us to determine; they constitute a series, of which, as the author of this theory has remarked, we neither see the beginning not the end; a circumstance that accords well with what is known concerning other parts of the economy of the world. In the continuation of the different species of animals and vegetables that inhabit the earth, we discern neither a beginning nor an end; and, in the planetary motions, where geometry has carried the eye so far both into the future and the past, we discover no mark, either of the commencement or the termination of the present order. It is unreasonable, indeed, to suppose, that such marks should any where exist. The Author of nature has not given laws to the universe, which, like the institutions of men, carry in themselves the elements of their own destruction. He has not permitted, in his works, any symptom of infancy or of old age, or any sign by which we may estimate either their future or their past duration. He may put an end, as he no doubt gave a beginning, to the present system, at some determinate period; but we may safely conclude, that this great *catastrophe* will not be brought about by any of the laws now existing, and that it is not indicated by any thing which we perceive." PLAYFAIR, *Illustrations*, 119–120.

terrestrial history (denying the possibility that the earth may be irreversibly cooling off) and the cyclic nature of the solar system. In a supplementary note he cites the mathematical investigations of LAGRANGE and LAPLACE which show that the effects of perturbations are confined within fixed limits, so that it can last forever in its present state as long as planetary motions are governed only by presently-known laws.[16] (Obviously the validity of the geological theory depends on the assumption that there are never any drastic changes in the mean earth-sun distance or sharp fluctuations in the amount of heat which the earth receives from the sun.)

For PLAYFAIR, both the HUTTONIAN system of the earth and the NEWTONIAN system of the world behave like intelligently designed machines. The possibility that the earth-machine might be more nearly comparable to the steam engines of HUTTON's friend JAMES WATT, as some later commentators have suggested, was probably only dimly realized at the time, and in any case the irreversible character of real heat engines had not yet been clearly pointed out.[17]

Contemplation of the significance of the earth's internal heat did lead some skeptics to formulate more or less explicitly the principle of irreversible heat flow. Thus JOHN HUNTER, in 1788, wrote that

> it is well known that heat in all bodies has a tendency to diffuse itself equally through every part of them, till they become of the same temperature.[18]

A few years later JOHN MURRAY asserted that

> The essential and characteristic property of the power producing heat, is its tendency to exist everywhere in a state of equilibrium, and it cannot hence be preserved without less or without diffusion, in an accumulated state ... If a heat, therefore, existed in the central regions of the earth, it must be diffused over the whole mass; nor can any arrangement effectually counteract this diffusion. It may take place slowly, but it must always continue progressive, and must be utterly subversive of that system of infinitely renewed operations which is represented as the grand excellence of the Huttonian theory.[19]

In reply to this, PLAYFAIR argued that if heat is "communicated to a solid mass, like the earth, from some source or reservoir in its interior," the equilibrium state will not be one of uniform temperature, if the heat can escape from the surface of the body into infinite space. Instead, there will be an equilibrium state in which the temperature is high near the center of the body but decreases going outward.[20]

MURRAY challenged PLAYFAIR's assumption that heat is "supplied" at the center, which he considered merely an arbitrary hypothesis dragged in to avoid his previous objection. On the other hand, MURRAY argued that the earth's heat would not be lost into space through its atmosphere but that the atmosphere would tend to retain the heat supplied by the sun. The temperature would gradually rise until the earth and its atmosphere are hot enough to produce a balance by re-radiation of heat; the final state would therefore be a stable one of constant temperature, in contrast to the opinions of certain writers (he cites BAILLY's *Histoire de*

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[16] *Ibid.*, 437–438.
[17] EDWARD BAILEY, *Charles Lyell* (London: Nelson, 1962), 18.
[18] JOHN HUNTER, *Phil. Trans. Roy. Soc. London*, **78**, 53 (1788).
[19] JOHN MURRAY, *System of Chemistry*, p. 49 (see also 51), as quoted by PLAYFAIR.
[20] *Trans. Roy. Soc. Edinburgh*, **6**, 353 (1812 [read 1809]).

l'Astronomie Moderne) who had claimed that planets are extinct suns and that all heavenly bodies are gradually cooling down, being destined to reach eventually a "state of Ice and Death."[21] Thus by 1814 the Heat Death was not only known in Britain but subject to attack.

The problem of terrestrial heat flow was obviously ripe for quantitative treatment by this time, and in fact PLAYFAIR proposed such a treatment in the last paper mentioned above. But he restricted himself to the very special case of a steady temperature distribution maintained by a heat source at the center of a sphere, which he computed on an *ad hoc* basis without attempting to formulate a general equation for heat flow.

The attempt to formulate that equation was apparently first made by J. B. BIOT in 1804, but BIOT failed to obtain a consistent differential equation.[22] He did at least recognize that a general law of heat conduction might be based on the fundamental assumption that the rate of heat flow between two bodies is proportional to their temperature difference, and he succeeded in deducing the exponential variation of equilibrium temperature with length on a long bar heated at one end.

The modern theory of heat conduction was established by JOSEPH FOURIER in a series of publications beginning in 1808.[23] Irreversibility was explicit from the beginning:

> When heat is unequally distributed among the different points [parts] of a solid body, it tends to come to equilibrium and pass successively from hottter to colder parts. At the same time the heat dissipates itself at the surface and loses itself in the surroundings or the vacuum. This tendency toward a uniform distribution, and this spontaneous cooling which takes place at the surface of the body, are the two causes which change at every instant the temperature of the different points.

In the later debates on irreversibility, it was often suggested that there is a basic contradiction between NEWTONIAN mechanics and any theory, such as FOURIER's, which is not symmetrical with respect to past and future time directions. It was pointed out that in NEWTON's second law, $F = ma$, the substitution of $-t$

[21] JOHN MURRAY, *Trans. Roy. Soc. Edinburgh*, **7**, 411 (1815 [read 1814]).

[22] J. B. BIOT, *J. Mines* **17**, 203 (1804); *Bibl. Brit.* **27**, 310 (1804). According to J. R. RAVETZ (as quoted by M. P. CROSLAND in the *Dict. Sci. Biog.* article on BIOT), BIOT, "was unable to present the differential equation corresponding to this physical model because of his inability to find plausible physical reasons for dividing a second difference of temperatures by the square of the infinitesimal element of length. Hence he could not convert his second difference into a second derivative." *Cf.* J. FOURIER, *The Analytical Theory of Heat*, trans. A. FREEMAN (1878, reprinted by Dover Pubs., New York, 1955), 59, 459–460. For a comprehensive discussion of the relation between BIOT's and FOURIER's formulations see I. GRATTAN-GUINNESS, *Joseph Fourier* 1768–1830 (Cambridge, Mass.: MIT Press, 1972), 83–87 and elsewhere.

[23] JOSEPH FOURIER, *Bull. Soc. Philomath.* **1**, 112 (1808) [summary by S. D. POISSON]; *Mem. Acad. Sci. Paris* **4**, 185 (1824 [submitted 1811]), published in somewhat different form as *Théorie Analytique de la Chaleur* (Paris, 1822); *Mem. Acad. Sci. Paris* **5**, 153 (1826 [submitted 1811]). These and other papers are reprinted in *Oeuvres de Fourier*, ed. G. DARBOUX (Paris: Gauthier-Villars, 1888, 1890). The original manuscript of the 1807 paper was first published in full with critical apparatus by GRATTAN-GUINNESS, *op. cit.*, 33, from which I have translated the quotation in the text; *cf.* FREEMAN trans., 14.

for t leaves the right-hand side invariant, whereas this is certainly not the case with FOURIER's heat conduction equation which contains a first derivative with respect to time. But the alleged contradiction rests on the assumption that NEWTONIAN mechanics deals only with *forces* that are time-reversible, *i.e.* with what are now called conservative systems. This seemed a natural assumption for those scientists who assumed that all macroscopic laws must ultimately be reducible to theories of atomic interactions, and that these interactions could not involve dissipation or velocity-dependent forces. Yet for many other scientists in the 18th and 19th centuries, there was no reason to impose such restrictions, and thus no contradiction. Far from perceiving a conflict between his theory and NEWTONIAN physics, FOURIER recognized that he was in a sense improving and generalizing NEWTON's "law of cooling," though the route from NEWTON's assumption about the heat lost from an object to the surrounding space, to FOURIER's assumption about the flow of heat among infinitesimal portions of matter within a body, was by no means an easy one, as BIOT had already discovered.[22, 24] Nevertheless the qualitative idea of irreversible heat flow was common to FOURIER and NEWTON.

While NEWTON's law of cooling, as it applied to finite temperature differences, was frequently challenged during the 18th century and finally rejected during the time FOURIER was developing his theory, FOURIER's equation became the basis for a successful and widely-used mathematical theory, and this theory in turn permeated the theoretical physics of the 19th and 20th centuries.[25] But at the same time, and especially after HELMHOLTZ formulated the principle of energy conservation in terms of forces between point particles, and CLAUSIUS and MAXWELL revived the kinetic theory of gases, the assumption that NEWTONIAN physics is fundamentally a time-reversible theory was becoming prevalent. The conflict between these two streams of theoretical physics became evident in the last quarter of the 19th century.

In understanding the development of FOURIER's theory it is essential to keep in mind his interest in its geophysical applications. This interest should not be a surprise to anyone who reads carefully the "Preliminary Discourse" but it is somewhat under-represented in the main body of the text of the *Théorie Analytique*. Unfortunately the standard English translation of this work[26] omits the supplement on the problem of terrestrial temperatures and heat flow inside a sphere which was published separately in a later volume of the *Mémoires* of the Paris Academy

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[24] ISAAC NEWTON, *Phil. Trans. Roy. Soc. London* **22**, 824 (1701); English trans. in the abridged ed. of *Phil. Trans.* (London, 1809), **4**, 572; both reprinted in I. B. COHEN (ed.), *Isaac Newton*'s *Papers & Letters on Natural Philosophy* (Cambridge, Mass.: Harvard University Press, 1958), 259–268; for further discussion and references see section 2 of the previous article in this series. FOURIER's acknowledgement of his debt to NEWTON may be found in the manuscript of the 1807 paper (footnote on p. 92 of the GRATTAN-GUINNESS edition, *op. cit.*) although it was omitted in later published versions. A somewhat vaguer reference to NEWTON did appear in Chap. IX, art. 429 of *Théorie Analytique de la Chaleur*: "Newton a considéré le premier la loi du refroidissement des corps dans l'air ... " as compared to "Newton a connu le premier le principe précédent et il en a fait usage pour déterminer la loi du refroidissement d'un corps exposé à un courant d'air," in the 1807 paper.

[25] The importance of FOURIER's theory as an inspiration for FRANZ NEUMANN and others involved in the development of the physics discipline in 19th-century Germany has recently been stressed by R. MCCORMMACH, *Hist. Stud.. Phys. Sci.* **3**, ix (1971).

[26] FREEMAN's translation cited in note 22, above.

for 1821–22. It is therefore worth noting that FOURIER himself stated that the geophysical problem had been a prime source of motivation.[27]

FOURIER's conclusions about the cooling of the earth have to be interpreted within the context of early 19th-century geophysical speculation. First, he showed that the periodic temperature variations at the surface due to solar heating would be washed out at a depth of less than 100 meters, and if there were no internal source of heat the temperature would be constant down to the center of the earth. Since existing data showed that there *is* an increase of temperature with depth below 100 meters, there must be an internal reservoir of heat, left over from the original formation of the earth. But the effect of this internal heat on the surface temperature is at present negligible, and it cannot have had any significant effect on the climatic variations during the past several thousand years, contrary to what had been assumed by BUFFON and other 18th century writers. FOURIER's results were viewed by some contemporary scientists as a *refutation* of the main features of the refrigeration theory; in any case they allowed the possibility that external causes might have produced much *lower* surface temperatures at some time in the past. (In this sense FOURIER had to come before AGASSIZ!)

FOURIER derived a theoretical formula for the time required for a sphere to cool down from an initial temperature b to its present temperature (taken as zero), in terms of the present temperature gradient at the surface, $\Delta = \partial T/\partial r$, and a ratio CD/K depending on the heat capacity and conductivity of the sphere:

$$t = \frac{b^2}{\pi \Delta^2} \frac{CD}{K}.$$

Curiously, though he suggested numerical values for all the quantities on the right-hand side of this equation, he did not actually work out an estimate for t. Perhaps he considered the value obtained by such a calculation—which could be as great as 200 million years—so absurdly large that it was not even worth writing down.[28] The outcome in any case was that while the earth does have an internal heat that has been diminishing slowly over a very long period of time, the actual amount of heat passing through the surface is so small as to have no significance on the time-scale of interest to geologists in the *early* 19th century, though with the greatly enlarged time-scales contemplated later in the century the same quantitative results took on an entirely different significance.

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[27] FOURIER, *Ann. Chim. Phys.* **27**, 136 (1824); *Mém. Acad. Roy. Sci. Paris* **7**, 570 (1827); see *Oeuvres*, **2**, 114, where the first person plural is changed to first person singular.

[28] " Quant au nombre T [number of centuries since beginning of cooling] il est évident qu'on ne peut l'assigner; mais on est du moins certain qu'il surpasse la durée des temps historiques, telle qu'on peut la connaître aujourd'hui par les annales authentiques les plus anciennes: ce nombre n'est donc moindre qui soixante ou quatre-vingts siècles. On en conclut, avec certitude, que l'abaissement de la temperature pendant un siècle est plus petit que 1/57600 d'un degré centesimal. Depuis l'École grecque d'Alexandrie jusqu'à nous, la déperdition de la chaleur centrale n'a pas occasionné un abaissement thermométrique d'un 288e de degré. Les températures de la superficie du globe ont diminué autrefois, et elles ont subi des changements très grandes et assez rapides; mais cette cause a, pour ainsi dire, cessé d'agir à la surface: la longue durée du phénomène en a rendu le progrès insensible, et le seul fait de cette durée suffit pour prouver la stabilité des temperatures." *Bull. Soc. Philomath.* **58**, (1820); quotation from *Oeuvres*, **2**, 286.

With the work of CHARLES LYELL we enter a new phase of geological speculation, in which—freed from many of the earlier theological restraints—scientists began to talk about periods of the order of millions or even hundreds of millions of years for the age of the earth.[29] LYELL's "Uniformitarian" geology was based on the assumption that all present features of the earth's surface should be explained by invoking only those physical causes now seen to be in operation. For many geologists such an assumption was essential if geology was to become a science in the same sense as physics and chemistry—for otherwise there would be no limit to the introduction of *ad hoc* catastrophic hypotheses to explain each special feature. But it was precisely in this attempt to become more scientific that the geologists collided head-on with the physicists, with both sides dissipating a considerable amount of energy.

In his *Principles of Geology* (1830), LYELL could not avoid discussing the still-popular theory of the cooling of the earth, but refused to give up the HUTTON-PLAYFAIR doctrine of a *constant* internal heat. In the absence of any evidence that the internal heat is variable in quantity, he thinks it is "more consistent with philosophical caution, to assume that there is no instability in this part of the solar system."[30] As MARTIN RUDWICK has recently noted, it was essential to LYELL's basic strategy in geological theory to deny any overall directional tendency or irreversibility in the history of the earth.[31] But other geologists could be Uniformitarians while at the same time claiming a gradual *progression* in the earth's history resulting from physical causes that might have been either constant or quantitatively more important in past epochs. (The term "progressive" was used in almost the same sense as "irreversible.")

LYELL's theory encountered the familiar criticism that internal heat simply could not remain constant. Thus GEORGE GREENOUGH (founder and first president of the Geological Society of London) declared in 1834:

> If there be heat in the centre of the globe, it must have the properties of heat and none other. I ask not how the Heat originally was lodged in that situation, for the origin of all things is obscure; but I ask why, in the countless succession of ages which the Huttonian requires, the Heat has not passed away by conduction, and if it has passed away, by what other heat it has been replaced.[32]

In the 1840's the situation changed somewhat, partly because of the researches of WILLIAM HOPKINS. HOPKINS (1793–1866) is now best known as the tutor of

[29] HABER, *Age of the World*; CHARLES C. GILLISPIE, *Genesis and Geology* (Cambridge, Mass.: Harvard University Press, 1951).

[30] CHARLES LYELL, *Principles of Geology*, **1** (2d ed., 1832), 162.

[31] M. J. S. RUDWICK, *Isis* **61**, 5 (1970); *Perspectives in the History of Science and Technology*, ed. D. H. D. ROLLER (Norman: University of Oklahoma Press, 1971), 209. M. BARTHOLOMEW, *Brit. J. Hist. Sci.* **6**, 261 (1973). LYELL himself cited HUMPHRY DAVY [*cf.* section 1, ref. 27] as a major exponent of the theory of "progressive development," in *Principles of Geology*, **1**, 145–46 (1830 ed.). LYELL's acceptance of the alternative cyclic theory is illustrated by the remark in his letter to GIDEON MANTELL, 12 February 1830: "All these changes are to happen in the future again, and iguanodons and their congeners must as assuredly live again in the latitude of Cuckfield as they have done so." [Quoted by SANDRA HERBERT, *The Logic of Darwin's Discovery* (Ph. D. Dissertation, Brandeis University, 1968), 11a, from *Life, Letters and Journals of Sir Charles Lyell, Bart.* (London, 1881).]

[32] GEORGE GREENOUGH, *Proc. Geol. Soc. London* **2**, 42 (1838) (quotation from p. 64).

WILLIAM THOMSON, JAMES CLERK MAXWELL, and other young mathematical physicists at Cambridge University—he is one of the few scientists to have acquired a reputation by teaching rather than research!—but was also one of the founders of British geophysics.[33] HOPKINS claimed that the precession and nutation of the earth-moon-sun system would be affected by the physical state of the earth's interior, and that the existing astronomical data could be accounted for only by assuming that the solid crust of the earth has a thickness at least one-fifth of its radius.[34] This was a rather impressive and unexpected argument, which convinced many scientists of the period that the liquid interior of the earth does not come nearly as close to the surface as had previously been thought. As a result, geological theories relying on the direct action of a molten interior in volcanic and other phenomena were less appealing. LYELL's argument that climatic changes have resulted from geographical changes rather than cooling of the earth as a whole gained favor, with the help of FOURIER's proof, mentioned above, that cooling could have little effect on the surface temperature even in a million years.[35] Considerable interest was shown in LOUIS AGASSIZ' theory of glacial epochs (*Étude sur les Glaciers*, 1840) which assumed that the surface temperature must have been rising rather than falling at some periods in the past.

HOPKINS was very much involved in these geological discussions of the 1840's and went along with the tendency to depreciate the importance of the earth's internal heat in accounting for most geological phenomena. But in an address to the Geological Society of London in 1852, after surveying recent research and speculation, he did assert very strongly the ultimate significance of terrestrial refrigeration in the "progressive development" of inorganic matter. On a long enough time scale, the cooling of the earth *is* important, and imposes an overall irreversibility on all processes. The unavoidable fact that heat flows from high temperatures to low means that no geological theory can legitimately be based on the assumption of a permanent or even cyclically changing high temperature inside the earth. Cyclic changes could be a result only of external action—of periodically changing irradiation from the sun or stars. But, if we may assume that heat has the same properties elsewhere in the universe as it does on earth, we may exclude such external causes since the sun and stars would also have to lose their heat eventually by radiation. Thus, contradicting the HUTTONIAN doctrine, HOPKINS announced that he was "unable in any manner to recognize the seal and impress of eternity stamped on the physical universe, regarded as subject to those laws alone by which we conceive it at present to be governed."[36]

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[33] See WALTER F. CANNON, *Isis* **51**, 38 (1960).

[34] WILLIAM HOPKINS, *Phil. Trans. Roy. Soc. London* **132**, 43 (1842). See also *Trans. Cambridge Phil. Soc.* **6**, 1 (1838) [read 1835]; *Phil. Trans. Roy. Soc. London* **129**, 381 (1839), **130**, 193 (1840). The calculation was later modified and extended by KELVIN and G. H. DARWIN, with additional arguments based on tidal phenomena, leading to the conclusion that the earth behaves as if it were almost completely solid.

[35] CHARLES LYELL, *Principles of Geology* (London, 1830–1833), **1**, Chap. VII.

[36] *Quart. J. Geol. Soc. London* **8**, pt. I, xxi (1852), quotation from p. lxxiv. This was HOPKINS' "Anniversary Address" as President of the Society, and it may be noted that LYELL had reiterated his non-progressionist views in a similar address the previous year; see *Quart. J. Geol. Soc. London* **7**, xxv (1851).

For HOPKINS, the physical properties of heat imply progressive geological change in the long run, but do not exclude uniformity in the short run, simply because the cooling of the earth takes place so slowly. Hence cosmic irreversibility is an axiom, not an hypothesis subject to test; no evidence of approximate uniformity during geological epochs can refute this idea of "progressive change towards an ultimate limit."[37]

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WILLIAM THOMSON's proficiency in the mathematical theory of heat conduction was a major factor in his rapid rise to eminence in British science in the middle of the 19th century. He first learned FOURIER's theory in 1840,[38] and soon became the leading British expert on it; in fact, just before his 17th birthday in 1841, he published a paper pointing out a mistake committed by Professor PHILIP KELLAND, of Edinburgh, who had criticized one of FOURIER's statements in his book on heat.[39] At about the same time (April 1841) THOMSON entered Peterhouse at Cambridge University. His father, JAMES THOMSON, had probably chosen Peterhouse so that WILLIAM could have the advantage of being tutored by HOPKINS, who was already famous for the number of successful "wranglers" he had coached for the mathematical examinations. During his years at Cambridge, THOMSON continued his original work in mathematical physics, going off in various directions from his original interest in the theory of heat conduction but always returning to that subject. Curiously enough there seems to be no record of any discussion between HOPKINS and THOMSON on the subject of heat conduction inside the earth; yet it seems hardly possible that this topic of mutual concern should not have figured in many of their conversations.

At the end of his fourth paper on FOURIER's theory, in 1842, THOMSON pointed out that when negative values of the time are substituted into the solution of the heat equation for a specified temperature distribution at $t=0$, there is in general no meaningful solution. In other words, an arbitrary initial distribution cannot in general be produced by evolution from some previous possible distribution.[40] Many years later, as Lord KELVIN, he referred to this result as a mathematical deduction that there must have been a creation.[41]

THOMSON was elected to the Chair of Natural Philosophy at the University of Glasgow in 1846, on the strength of testimonials from HOPKINS and many other distinguished scientists.[42] It was generally recognized that he had already embarked on a brilliant career in theoretical physics, although there was some doubt about whether he could effectively teach the practical side of science to ordinary students; it was partly to improve his experimental competence that THOMSON

[37] HOPKINS, *op. cit.*, p. lxxv.

[38] From Professor JOHN PRINGLE NICHOL at Glasgow University, where THOMSON studied before going up to Cambridge; see S. P. THOMPSON, *The Life of William Thomson, Baron Kelvin of Largs* (London: Macmillian, 1910), I, 14.

[39] PHILIP KELLAND, *Theory of Heat* (Cambridge, 1837), p. 64; P. Q. R. [WILLIAM THOMSON], *Cambridge Math. J.* **2**, 258 (1841), reprinted in his *Mathematical and Physical Papers* (Cambridge, 1882–1911), **I**, 1. This collection will be cited as THOMSON's *Papers*.

[40] *Cambridge Math. J.* **3**, 170 (1842); *Papers* **1**, 10.

[41] S. P. THOMPSON, *op. cit.*, 42, 111, 186.

[42] HOPKINS' testimonial is reprinted along with others, by THOMPSON, *op cit.*, 170–171.

spent some time working on the properties of steam in VICTOR REGNAULT's laboratory in Paris after his graduation from Cambridge. It was his understanding of the properties of steam that was to enable him to place the irreversibility of heat flow in a wider context (see next section).

THOMSON's inaugural dissertation at Glasgow dealt with the theory of distribution of heat inside the earth, and in particular the problem of the earliest time to which the solution of FOURIER's equation could be extended, going backwards from a specified temperature distribution.[43] He suggested "that a perfectly complete geothermic survey would give us data for determining an initial epoch in the problem of terrestrial conduction," and this proposal was later put into effect by a committee of the British Association for the Advancement of Science. As he noted in 1881, it was this dissertation "which, more fully developed afterwards, gave a very decisive limitation to the possible age of the earth as a habitation for living creatures; and proved the untenability of the enormous claims for TIME which, uncurbed by physical science, geologists and biologists had begun to make and to regard as unchallengable."[44] Thus THOMSON's work on heat conduction was the prelude to his attack on Uniformitarian Geology and (indirectly) DARWINIAN Evolution, "one of the best known of the fierce scientific battles that enlivened Victorian times"[45] which I have reviewed in another essay.[46]

The geological context of THOMSON's irreversibility principle, first published in 1852 in a short note entitled "On a Universal Tendency in Nature to the Dissipation of Mechanical Energy," should now be clear enough from his own words:

1. There is at present in the material world a universal tendency to the dissipation of mechanical energy.
2. Any *restoration* of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life, or subjected to the will of an animated creature.
3. Within a finite period of time past the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject.[47]

We must now examine the reasons why THOMSON's statement could become incorporated into the select company of "laws of physics" while HOPKINS' statement,

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[43] *Ibid.*, 188; see *Rept. Brit. Ass. Adv. Sci.* **25**, 18 (1855), **29**, 54 (1859); THOMSON's *Papers* **2**, 175, **3**, 291.

[44] *Papers*, **1**, 39.

[45] A. HOLMES, *The Age of the Earth* (London: Nelson, 2d. ed. 1937), 31.

[46] *Graduate J.*, **7**, 477 (1967). See also: J. W. GREGORY, *Trans. Geol. Soc. Glasgow* **13** (2), 170 (1908); H. I. SHARLIN, *Annals of Science* **29**, 271 (1972); JOE D. BURCHFIELD, *The Age of the Earth* (New York: Science History Pubs., 1973).

[47] *Proc. Roy. Soc. Edinburgh* **3**, 139 (1852).

along with earlier assertions about the irreversibility of natural processes,[48] never reached that status.

3. The Second Law of Thermodynamics and the Concept of Entropy

We now come to the area of science which is, according to almost all commentators, the sole source of the modern idea of irreversibility; the development of steam-engine theory from CARNOT through CLAPEYRON to CLAUSIUS, RANKINE, and THOMSON.[1] More recently, historians have explored the roots of SADI CARNOT's theory in the discussions of the efficiency of various kinds of machines by his father LAZARE CARNOT and other writers on engineering.[2] In these discussions there is

[48] In addition to the irreversibility statements mentioned in the text I have found the following:
(a) "The sort of retardation which fluids experience in gliding over the surface of a solid obstacle is, therefore, distinct from resistance on the one hand, and from friction on the other, though more allied to the former. But clearly to trace its origin and mode of operation, will require a careful analysis of those several means wherewith Nature speedily extinguishes every motion upon earth, and seems to diffuse a principle of silence and repose; which made the ancients ascribe to matter a sluggish inactivity, or rather an innate reluctance and inaptitude to change its place. [A footnote here refers to a note discussing the views of KEPLER and GALILEO on inertia.] We shall perhaps find, that this prejudice, like many others, has some semblence of truth." JOHN LESLIE, *An experimental inquiry into the nature and propagation of heat* (London, 1804), 298–299.
(b) "Without reference to any theory, I venture to propose the following as the simple experimental law: All bodies of *unequal* temperature tend to become of equal temperature." BADEN POWELL, *Rept. Brit. Ass. Adv. Sci.* **2**, 259 (1832) [this is in the context of a discussion of radiant heat].
(c) "Heat has a constant tendency to diffuse itself over all bodies, till they are brought to the same temperature." WILLIAM ENFIELD, *Institutes of Natural Philosophy* (London, 2d ed. 1799), 399.

[1] A typical statement is: "the narrow range of technical interests relative to the economy of heat engines, which constitutes the sole historical source of the Second Law, presents a sharp contrast to the wide variety of roots leading to the Energy Principle—a contrast in full conformity with the novel character of the ideas of restricted convertibility and irreversibility. At the same time, there follows, happily for the historian of thermodynamics, the result that, whereas, because of the great variety of interests involved, the chain of discoveries and enunciations constituting the history of the First Law is exceedingly difficult to expose, the development of the Second Law, on the contrary, takes a direct and relatively simple course which begins definitely and undisputedly with SADI CARNOT and culminates, twenty-five years later, in the systematic treatments of CLAUSIUS and THOMSON." M. K. BARNETT, *Osiris* **13**, 327 (1958) (quotation from p. 335). Other examples of the standard treatment of the history of the Second Law—generally well-written and accurate as far as they go—are V. V. RAMAN, *J. Chem. Ed.* **47**, 331 (1970); F. O. KOENIG, in *Men and Moments in the History of Science*, ed. H. M. EVANS (Seattle: University of Washington Press, 1959), p. 57; M. MOTT-SMITH, *The Concept of Energy Simply Explained* (New York: Dover Pubs., 1964, reprint of *The Story of Energy*, 1934); D. S. L. CARDWELL, *From Watt to Clausius* (Ithaca: Cornell University Press, 1971); ORAL BOYD MATHIAS, *An examination of the evolution of the first two laws of thermodynamics, being an attempt to discover the significance of conceptual changes accompanying their development* (Dissertation, University of Kansas City, Missouri, 1962).

[2] T. S. KUHN, *Arch. Int. Hist. Sci.* **13**, 251 (1960); *Isis* **52**, 567 (1961); MILTON KERKER, *Isis* **51**, 257 (1960); WILSON SCOTT, *The Conflict between Atomism and Conservation Theory 1644–1860* (London: Macdonald/New York: Elsevier, 1970); CARDWELL, *op. cit.*, Chapter 6.

always implicit or explicit the notion that in a poorly designed machine something is "lost" or "wasted" but until Sadi Carnot's 1824 memoir—or, strictly speaking, until Carnot wrote his later notes renouncing the caloric theory—it was not understood how this loss can be consistent with a conservation law.[3] This situation contrasts sharply with the geophysical speculations on heat flow, in which it was generally assumed that the total heat in the universe or in a closed system is conserved, so that if heat flows out through the surface of the earth the amount remaining inside must *therefore* decrease correspondingly.

Carnot posed the question:

> Is the motive power of heat invariable in quantity, or does it vary with the agent employed to realize it as the intermediary substance, selected as the subject of action of the heat?[4]

He had already stated that

> The production of motive power is then due in steam-engines not to an actual consumption of caloric, but *to its transportation from a warm body to a cold body*, that is, to its re-establishment of equilibrium ...[5]

Whenever there is a difference of temperature one has the *opportunity* of producing motive power in a steam engine; the question is whether this opportunity or potentiality depends only on the temperatures of the warm and cold bodies, or also on the working substance used in the engine. Carnot's celebrated answer is that it does depend only on the temperatures. Of more interest to us, however, are his sketchy remarks on *why* the theoretical opportunity is never realized in practice:

> Since every re-establishment of equilibrium in the caloric may be the cause of the production of motive power, every re-establishment of equilibrium which shall be accomplished without production of this power should be considered as an actual loss. Now, very little reflection would show that all change of temperature which is not due to a change of volume of the bodies can be only a useless re-establishment of equilibrium in the caloric.[6]

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[3] Wilson Scott, *op. cit.*

[4] *Reflections on the Motive Power of Fire by Sadi Carnot* ..., ed. E. Mendoza (New York: Dover Pubs., 1960), p. 9. In a footnote on this page Carnot states that he uses the terms "quantity of caloric" and "quantity of heat" indifferently, in the sense that should be familiar to the reader from elementary textbooks. This note seems to have been ignored by some later writers who claimed that Carnot was giving a new meaning to caloric, perhaps equivalent to that of entropy.

[5] *Ibid.*, p. 7. In the posthumous manuscript notes, translated in an appendix to the *Reflections* in Mendoza's edition. Carnot stated that heat is in fact consumed when motive power is produced (pp. 62–63, 68–69). He had already asked in the *Reflections*, "is it possible to conceive the phenomena of heat and electricity as due to anything else than some kind of motion of the body, and as such should they not be subjected to the general laws of mechanics?" (footnote on page 12). Later, he noted that to deny the conservation of heat in a cycle of operations involving production of motive power "would be to overthrow the whole theory of heat"—yet "the main principles on which the theory of heat rests require the most careful examination. Many experimental facts appear almost inexplicable in the present state of this theory" (footnote on page 19).

[6] *Ibid.* 12–13.

... Every change of temperature which is not due to a change of volume or to chemical action ... is necessarily due to the direct passage of the caloric from a more or less heated body to a colder body. This passage occurs mainly by the contact of bodies of different temperature; hence such contact should be avoided as much as possible. It cannot probably be avoided entirely ...[7]

This is the necessary condition for a *reversible* heat flow, but the term is not used yet. On the next page CARNOT refers again to the "loss of motive power" caused by contact between bodies at different temperatures, and says "This kind of loss is found in all steam-engines." Thus ordinary heat conduction, which previously seemed innocent enough by itself, has now been identified as the cause of inefficiency in steam engines.

In CLAPEYRON's reformulation of CARNOT's theory, "loss of motive power" became "loss of force" or "loss of *vis viva*" and was again attributed to the direct passage of heat which naturally occurs whenever two bodies at different temperatures are in contact; on order to obtain the maximum efficiency one must try to avoid such contact.[8]

According to MENDOZA, "as late as the 1830's the term "Carnot's theorem" denoted a statement that in any machine the accelerations and shocks of the moving parts all represented losses of ... useful work done," and even in 20th-century textbooks one occasionally finds this usage—the CARNOT in question being LAZARE rather than SADI.[9] But there are also scattered statements in the engineering literature before 1850 concerning the waste of motive power in steam engines, though there is usually no reference to SADI CARNOT in this connection.[10]

In 1848 WILLIAM THOMSON published his first paper on CARNOT's theory of the motive power of heat. At that time he had not been able to find a copy of CARNOT's original memoir, and was acquainted with the theory only through CLAPEYRON's paper which had been translated into English in the first volume of TAYLOR's *Scientific Memoirs*.[11] Moreover, he had not yet accepted the principle of convertibility of heat and mechanical work, and assumed with CARNOT and CLAPEYRON that the quantity of heat is conserved when motive power is produced. There is no mention of irreversibility here except indirectly when THOMSON alludes to engines "in which the economy is perfect" with the implication that for imperfect engines a smaller amount of mechanical effect would be obtained by the transmission of a given quantity of heat.[12]

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[7] *Ibid.* 13.

[8] *Ibid.* 75 (translated from CLAPEYRON's memoir in *J. École Polyt.* **14**, 153 (1834)).

[9] *Ibid.*, x. *Cf.* L. A. PARS, *A treatise on analytical dynamics* (London: Heinemann, 1965), p. 23: "Carnot's theorem. Loss of energy due to the imposition of an inert constraint. When an inert constraint is imposed there is a loss of energy which is equal in value to the energy of the relative motion."

[10] MARC SEGUIN, *De l'influence des chemins de fer* (Paris, 1839), xvi-xviii, 378–422 [or Bruxelles, 1839, pp. ix-x, 243–271]; HENRY DE LA BECHE & LYON PLAYFAIR, *Mem. Geol. Surv. Great Britain* **2** (II), 539 (1848).

[11] WILLIAM THOMSON, *Proc. Cambridge Phil. Soc.* **1**, 66 (1848); *Phil. Mag.* [3] **33**, 313 (1848); *Papers* **1**, 100. For his own version of the early history of the Second Law see KELVIN, *Popular Lectures and Addresses* (London, 1894), **2**, 451.

[12] *Papers*, 1, 103.

A few months after that paper was published, THOMSON finally obtained a copy of CARNOT's book from LEWIS GORDON, and on January 2, 1849, he read another "Account of Carnot's Theory of the Motive Power of Heat" to the Royal Society of Edinburgh. In this paper THOMSON was grappling with the crucial problem of whether to retain CARNOT's published assumption that heat is conserved in the steam-engine cycle, or to accept JOULE's proposal that it is actually converted into mechanical work; and this intellectual struggle seems to have blotted out the other problems such as irreversibility. He did state that "engines may be constructed in which the whole, or any portion of the thermal agency is wasted" when heat flows from one body to another by conduction, but a footnote attached to this sentence indicates that he was still unclear as to what is meant by "wasted":

> When "thermal agency" is thus spent in conducting heat through a solid, what becomes of the mechanical effect which it might produce? Nothing can be lost in the operations of nature—no energy can be destroyed. What effect then is produced in place of the mechanical effect which is lost? A perfect theory of heat imperatively demands an answer to this question; yet no answer can be given in the present state of science ...[13]

Here we see vividly how the Second Law of Thermodynamics, already born, cannot be christened until it has dragged its brother the First Law out of the womb.

The scene now shifts momentarily to Germany (THOMSON having missed his chance to be first in formulating the laws of thermodynamics) where RUDOLF CLAUSIUS has taken up the problem of the motive power of heat, stimulated by the papers of CLAPEYRON, THOMSON, and HOLTZMANN. Like THOMSON, CLAUSIUS considered CARNOT's work to be the most important even though so far he knew of it only through the writings of CLAPEYRON and THOMSON.

To CLAUSIUS in 1850 it was already clear that heat is not only interconvertible with mechanical work but in fact actually "consists in a motion of the least parts of bodies"[14]—and that this latter conclusion leads us to adopt the equivalence of heat and work, rather than the other way around. But he has not yet grasped the irreversibility implications of CARNOT's theory, for in reviewing THOMSON's position he says

> Heat can be transferred by simple conduction, and in all such cases, if the mere transfer of heat were the true equivalent of work, there would be a loss of working power in Nature, which is hardly conceivable.[15]

(In the context it appears that this is a report of THOMSON's opinion but CLAUSIUS at least does not dispute it.) Later in this paper, in order to demonstrate that one

[13] *Trans. Roy. Soc. Edinburgh* **16**, 541 (1849); *Papers* **1**, 113 (quotation from pp. 118–119).

[14] RUDOLF CLAUSIUS, *Ann. Physik* [2] **79**, 368, 500 (1850); English trans. by W. F. MAGIE, reprinted in *Reflections on the Motive Power*, etc., ed. MENDOZA (quotation from p. 110 of this edition).

[15] *Ibid.*, p. 111. MATHIAS [*op. cit.*, note 1] suggests that it is fortunate that CLAUSIUS didn't realize at this time the contradiction between this statement and the irreversibility implied by the Second Law because it might have hindered his development of the latter (p. 96).

substance cannot be used to produce more work with a given amount of heat than another, CLAUSIUS invokes the argument that if this were not true, one could transfer heat from a cold to a hot body, which "is not in accord with the other relations of heat, since it always shows a tendency to equalize temperature differences and therefore to pass from *hotter* to *colder* bodies."[16] While there is some justification for the usual view that this paper contains a complete formulation of the laws of thermodynamics, CLAUSIUS has not yet put together the pieces of the complete Second Law as we now know it.

Back to Scotland, where on February 4, 1850, W. J. M. RANKINE has read to the Royal Society of Edinburgh his paper "On the Mechanical Action of Heat, especially in Gases and Vapours." RANKINE's paper contains much of the content of the CLAUSIUS-THOMSON thermodynamics but gives the appearance of being restricted to deductions from a special molecular-vortex model. It contains two brief statements of irreversibility which, because they follow a recognition of the equivalence of heat and mechanical work, are more significant than earlier statements about the inefficiency of steam engines:

> ... the true mechanical equivalent of heat is considerably less than any of the values deduced from Mr. Joule's experiments; for in all of them there are causes of loss of power the effect of which it is impossible to calculate. In all machinery, a portion of the power which disappears is carried off by waves of condensation and expansion, along the supports of the machine, and through the surrounding air; this portion cannot be estimated, and is, of course, not operative in producing heat within the machine. ...[17]
>
> Dr. Lyon Playfair, in a memoir on the Evaporating Power of Fuel,[18] has taken notice of the great disproportion between the heat expended in the steam-engine and the work performed. It has now been shown that this waste of heat is, to a great extent, a necessary consequence of the nature of the machine ...[19]

There is a similar statement in another paper in 1851, but no attempt to generalize from the limitations of steam engines to a law of nature.[20] Indeed, at this point

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[16] *Ibid.*, p. 134. MATHIAS points out that in MAGIE's translation "other relations of heat" loses the anthropomorphic character of the original German (*Verhalten*, conduct). C. TRUESDELL has criticized several aspects of CLAUSIUS' formulation in this paper, in his recent book *The Tragicomedy of Classical Thermodynamics* (Vienna and New York: Springer-Verlag, 1973).

[17] W. J. M. RANKINE, *Trans. Roy. Soc. Edinburgh* **20**, 147 (1850); *Miscellaneous Scientific Papers* (London, 1881), 234 (quotation from p. 245).

[18] This may refer to the report by DE LA BECHE & PLAYFAIR cited in note 10 above.

[19] RANKINE, *Papers*, 278.

[20] *Papers*, 304. MAXWELL, in 1878, remarked that "In his earlier papers" RANKINE "appears as if battling with chaos, as he swims, or sinks, or wades, or creeps, or flies, 'And through the palpable obscure finds out/His uncouth way'" and followed this with similar jibes about particular thermodynamic statements which RANKINE had made [MAXWELL's *Scientific Papers*, **2**, 663]. On the other hand, KELVIN himself criticized RANKINE's molecular-votrex theory for not being concrete enough; this provided the occasion for his famous assertion, "I never satisfy myself until I can make a mechanical model of a thing. If I can make mechanical model I can understand it." *Notes of Lectures on Molecular Dynamics and the Wave Theory of Light* (Baltimore: Johns Hopkins University, 1884), 270.

RANKINE has not admitted that CARNOT's theorem is independent of the principle of equivalence of heat and work.[21]

By March 1851 THOMSON had been converted to convertibility of heat and work and hastened to catch up with CLAUSIUS and RANKINE by giving his own formulation of thermodynamics. The custom of calling CARNOT's principle the "Second Law" of thermodynamics probably originated in this paper; but the way THOMSON initially phrased it was not the same as what is now generally called the "KELVIN statement of the Second Law:"[22]

> PROP. II. (CARNOT and CLAUSIUS).—If an engine be such that when it is worked backwards, the physical and mechanical agencies in every part of its motion are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.[23]

This proportion was based on an "axiom" which is itself more nearly the usual version of the "KELVIN statement":

> It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.[24]

The second proposition follows from this axiom because of the postulated *reversibility* of the parts of the engine; this is one of the first uses of the *term* "reversibility" in thermodynamics, although the *concept* obviously goes back at least as far as SADI CARNOT.[25]

THOMSON then gave "the axiom on which Clausius' demonstration is founded," *i.e.* the "CLAUSIUS statement of the Second Law," in a somewhat more explicit form than CLAUSIUS himself had yet published:

> It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.[26]

THOMSON asserted that "it is easily shown" that either axiom is a consequence of the other.[27] In any case it is clear that both are negative statements and do not assert any tendency toward irreversibility. An explicit statement about irreversibility comes in only later on when THOMSON discusses a *perfect* CARNOT engine

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[21] *Papers*, 301.

[22] F. O. KOENIG, *op. cit.* (note 1), p. 76.

[23] WILLIAM THOMSON, *Trans. Roy. Soc. Edinburgh* **20**, 261 (1851); *Papers*, **1**, 174 (quotation from p. 178).

[24] *Ibid.*, p. 179. THOMSON adds a footnote: "If this axiom be denied for all temperatures, it would have to be admitted that a self-acting machine might be set to work and produce mechanical effect by cooling the sea or earth, with no limit but the total loss of heat from the earth and sea, or, in reality, from the whole material world." The use of the phrase "inanimate material agency" alludes to KELVIN's belief that the Second Law of Thermodynamics may not apply to living beings.

[25] *Reflections*, ed. MENDOZA, pp. 11, 15.

[26] *Papers*, **1**, 181.

[27] On the equivalence of the two forms see C. N. HAMTIL, *Amer. J. Phys.* **22**, 93 (1954); N. L. BALAZS, *Amer. J. Phys.* **22**, 495 (1954).

operating over an infinitesimal temperature range; in that case he states that the mechanical effect is the largest possible "although it is in reality only an infinitely small fraction of the whole mechanical equivalent of the heat supplied; the remainder being irrecoverably lost to man, and therefore "wasted," although not *annihilated.*"[28] Hence the paradox that even the completely reversible engine must include an irreversible process (except when the surroundings are at absolute zero temperature). But that process is not "wasting" energy since the maximum amout of mechanical effect has been extracted.

The lack of any general statement about irreversibility in this paper is puzzling. In fact, there had been one in an earlier draft dated March 1, 1851:

> Everything in the material world is progressive. The material world could not come back to any previous state without a violation of the laws which have been manifested to man; that is, without a creative act or an act possessing similar power ... I believe the tendency in the material world is for motion to become diffused ...[29]

The use of the term "progressive" where we might expect "irreversible" or even "degenerative" or "regressive" is another clear indication of the geological background of THOMSON's thinking; for it was HOPKINS and the other anti-LYELLIANS who proposed a "progressive" tendency, resulting from the gradual cooling of the earth, in opposition to the cyclic view.

THOMSON's paper of April 19, 1852, on the tendency toward dissipation of energy begins with the following statement clarifying the relation of this tendency to thermodynamics:

> The object of the present communication is to call attention to the remarkable consequences which follow from Carnot's proposition, that there is an absolute waste of mechanical energy available to man when heat is allowed to pass from one body to another at a lower temperature, by any means not fulfilling his criterion of a "perfect thermo-dynamic engine," established, on a new foundation, in the dynamical theory of heat. As it is most certain that Creative Power alone can either call into existence or annihilate mechanical energy, the "waste" referred to cannot be annihilation, but must be some transformation of energy.[30]

Unfortunately the arguments by which THOMSON proceeds from his axiom (the "KELVIN statement" quoted above) to this consequence are presented in an extremely obscure and incomplete manner. For example, there remains some confusion as to whether energy is indeed "dissipated" in a perfect CARNOT engine, or whether the dissipation is only a result of the friction of steam rushing through pipes. The only part of the exposition that seems at least qualitatively valid in the absence of detailed calculation is the assertion that some mechanical work could

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[28] *Papers*, **1**, 189.

[29] Quoted by HAROLD SHARLIN in Chapter 7 of his forthcoming biography of THOMSON; draft of paper on "Dynamical Theory of Heat" dated March 1, 1851, at Cambridge University.

[30] WILLIAM THOMSON, *Proc. Roy. Soc. Edinburgh* **3**, 139 (1857) [read 1852]; *Phil. Mag.* [4] **5**, 102 (1853); *Papers*, **1**, 554.

be obtained by using a perfect thermodynamic engine to equalize a non-uniform temperature distribution without allowing heat conduction; hence if the equalization is accomplished by heat conduction alone there must be a waste of mechanical effect.[31]

THOMSON listed four distinct processes, all involving heat, in this paper: (1) reversible creation of heat; (2) creation of heat by an "unreversible process (such as friction)" (3) diffusion of heat by conduction; and (4) absorption of radiant heat or light, except by vegetation or chemical action. The last three involve dissipation of energy. There is no mention of what was later to be seen as one of the most fundamental of all irreversible processes: *mixing* of two kinds of molecules at constant temperature. In this respect the "principle of dissipation of energy" is less general than the "principle of irreversibility."

So far THOMSON has not mentioned any *molecular* basis for the dissipation of energy except in the vague allusion to the tendency for motion to become diffused, in his draft of March 1, 1851. A somewhat more concrete presentation of his views appeared in a short note "On Mechanical Antecedents of Motion, Heat, and Light" read to the British Association meeting in 1854. Here THOMSON stated that gravitational potential energy[32] is continually being expended to produce motion and heat. If we trace these actions forwards in time,

> we find that the end of this world as a habitation for man, or for any living creature or plant at present existing in it, is *mechanically inevitable* ...[33]

There is a presumption (but not a very clear statement) that thermodynamics is reducible to mechanics.

CLAUSIUS did not comment immediately on THOMSON's statement of the dissipation principle; in fact, he did not refer to it in print until 1864.[34] But RANKINE, in a paper read to a meeting of the British Association at Belfast on September 2, 1852, challenged its universal validity. While admitting that the tendency for all other forms of energy to be converted into heat at uniform temperature "so that there will be an end of all physical phenomena ... appears to be soundly based on experimental data, and to represent truly the present condition of the universe, so far as we know it," RANKINE pointed out that *radiant* heat is the "ultimate form to which all physical energy tends." According to RANKINE, radiant heat is conducted by an "interstellar medium" which cannot convert radiant heat into the "fixed or conductible form" and therefore cannot have a "temperature." But if we assume that this interstellar medium "has bounds beyond which there is empty space," "then on reaching those bounds the radiant heat of the world will be totally reflected, and will ultimately be reconcentrated into foci." If a

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[31] Further details of the calculations for this case were given in a paper published the following year: *Phil. Mag.* [4] **5**, 102 (1853); *Papers*, **1**, 554.

[32] The term *potential energy* was introduced by RANKINE around this time and immediately adopted by THOMSON. W. J. M. RANKINE, *Proc. Glasgow Phil. Soc.* **3**, 276 (1853); *Papers*, 203; footnote on p. 554 of THOMSON's *Papers*, **1**.

[33] *Rept. Brit. Ass. Adv. Sci.* **24**, (II), 59 (1854); *Edinburgh New Phil. J.* **1**, 90 (1855); *Papers*, **2**, 34 (quotation from p. 37). In 1862, THOMSON stated that since the universe is infinite, the Second Law does *not* imply a state of universal death. *Popular Lectures and Addresses* (London, 1891), **1**, 356.

[34] R. CLAUSIUS, *Ann. Physik* [2] **121**, 1 (1864).

star (or lump of inert matter) happens to arrive at one of these foci, radiant heat can be converted into chemical power and thus "the world, as now created, may possibly be provided within itself with the means of reconcentrating its physical energies, and renewing its activity and life." Thus it is possible to imagine that in the distant future the mechanical energy of the universe could be reconcentrated and the world come to life again.[35]

* * *

The next major step in formulating the concept of irreversibility is found in a paper of CLAUSIUS, published in December 1854. CLAUSIUS introduced the concept of "equivalence of transformations" which he based on the principle:

> *Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time.* Everything we know concerning the interchange of heat between two bodies of different temperatures confirms this; for heat everywhere manifests a tendency to equalize existing differences of temperature, and therefore to pass in a contrary direction, *i.e.*, from warmer to colder bodies. Without further explanation, therefore, the truth of the principle will be granted.[36]

In a footnote he amplified the phrase "without some other change," explaining that it would of course be possible for heat to be transferred from a colder to a warmer body if this transfer were intimately associated with the passage of at least as much heat in the opposite direction. One example would be heat transfer by radiation; a body at any temperature is continually radiating heat, some of which may be observed by a *warmer* body, but it is necessary that the amount absorbed by the *cold* body from the warm body be even greater. CLAUSIUS also mentions that in addition to the simple transfer of heat, "another permanent change may occur which has the peculiarity of not being reversible" unless it is replaced by another similar permanent change or by a flow of heat from a warmer to a colder body. But CLAUSIUS did not indicate at this point the nature of these non-thermal irreversible processes.

In describing the various cyclic processes that may be undergone by a gas, returning it eventually to its initial state, CLAUSIUS distinguished between reversible ones that could be run backwards, and non-reversible ones.[37] He then defined the "equivalence-value of a transformation of work into the quantity of heat Q, of the temperature t," as $Q \cdot f(t)$, where $f(t)$ is a function of temperature. He selected the sign convention to be such that conversion of work into heat and passage of heat from a higher to a lower temperature will be *positive* transformations.

If heat is transferred from temperature t_1 to t_2, the equivalence-value of the transformation must depend on both t_1 and t_2, so CLAUSIUS writes it $Q \cdot F(t_1, t_2)$. If the two temperatures are interchanged the value must have opposite sign, by definition, hence $F(t_2, t_1) = -F(t_1, t_2)$. For a reversible cyclic process the total

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35 W. J. M. RANKINE, *Phil. Mag.* [4] 4, 358 (1852); *Papers*, 200. Some other suggestions along this line are cited by M. ČAPEK, *The Philosophical Impact of Contemporary Physics* (Princeton: Van Norstrand, 1961), 128.

36 R. CLAUSIUS, *Ann. Physik* [2] **93**, 481 (1854); *Phil. Mag.* [4] **12**, 81 (1856); *Mechanical Theory of Heat*, trans. HIRST (London, 1867), 111 (quotation from pp. 117–18).

37 *Mechanical Theory*, 121.

equivalence-values of all transformations must be zero; this implies that[38]

$$F(t, t') = f(t)' - f(t).$$

Then CLAUSIUS introduced the symbol T as "an unknown function of the temperature" defined as the reciprocal of f:

$$f(t) = 1/T.$$

Further, instead of placing the temperature t in parentheses he used subscripts to denote the values of T at particular values of t: T_1, T_2, etc. (This notation is psychologically preparing the reader to accept T as actually being equal to the absolute temperature, though CLAUSIUS doesn't want to commit himself to this yet.) Finally, he introduced the symbol N for the total value of all transformations in a cycle:

$$N = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \cdots = \sum \frac{Q}{T}$$

or, if the transfer takes place at continuously varying temperatures,

$$N = \int \frac{dQ}{T}.$$

He could then state the theorem: in a reversible cyclic process $N = 0$.

The proof of the theorem relied on the irreversibility principle: if N were negative, this would mean in effect that heat was passing from a colder body to a warmer body without compensation, contrary to the principle stated above. If N were positive and the cycle were reversible, then one could run it backwards and obtain a negative value of N, which is forbidden for the same reason.

This was now CLAUSIUS' way of stating the Second Law of Thermodynamics: for all reversible cyclic processes $\int dQ/T = 0$.[39] In the case of non-reversible cyclic processes, which he treated much more briefly at the end of the paper, the theorem was modified to read: "The algebraical sum of all transformations occurring in a cyclical process can only be positive", *i.e.* $N > 0$. Such a transformation he called an "uncompensated" one. He stated that there are numerous kinds of such transformations, although they do not differ essentially: the transmission of heat by mere conduction; production of heat by friction, or by the passage of an electric current against a resistance; and "all cases where a force, in doing mechanical work, has not to overcome an equal resistance, and therefore produces a perceptible external motion, with more or less velocity, the *vis viva* of which afterwards passes into heat."[40] The notable feature of this list is that every case involves the production of heat; this is a severe limitation on the concept of irreversibility as articulated by almost all writers up to and including CLAUSIUS. (The purely mechanical examples discussed earlier by NEWTON and others usually

[38] *Ibid.*, 123–125.

[39] *Ibid.*, 129. As anyone who has taken a course in thermodynamics is well aware, the mathematics used in proving CLAUSIUS' theorem is of a very special kind, having only the most tenuous relation to that known to mathematicians. "Six times have I tried to follow the argument of Clausius in the last quarter century, and six times has it gravelled me" (TRUESDELL, *Tragicomedy*, 30).

[40] *Ibid.*, 134–135.

involved violations of energy conservation unless one assumed that the "lost" *vis viva* was converted into molecular *vis viva* or heat.)

CLAUSIUS has practically reached the modern formulation of the entropy concept at this point, except that he cannot yet prove that his "unknown function" T is really the absolute temperature. For this, he points out, it is necessary to assume that "*a permanent gas, when it expands at a constant temperature, absorbs only so much heat as is consumed by the exterior work thereby performed.*" That would be true for an *ideal* gas obeying the laws of MARIOTTE and GAY-LUSSAC; in that case one could write simply $T = a + t$, where t is the centigrade temperature and $a = 273°$. CLAUSIUS believed that this assumption had been verified by REGNAULT's experiments and therefore could be adopted "without hesitation."[41]

It would seem that one should date the discovery or invention of the entropy concept from this 1854 paper, since the change in terminology from "equivalence-value of a transformation" to "entropy" can have no effect on the physical meaning of the concept itself. One might object that the physical definition of entropy has not yet been clearly established since T cannot rigorously be identified with absolute temperature except for ideal gases (CLAUSIUS has not yet adopted THOMSON's definition of absolute temperature based on CARNOT's theorem). Nevertheless it is certainly incorrect to ignore the 1854 paper entirely and so state, as is sometimes done, that CLAUSIUS first introduced the entropy concept in 1865.[42]

CLAUSIUS was able to provide a theoretical foundation for his assumption about T in his first paper on kinetic theory in 1857. There he explained that no interior work has to be performed to change the volume of a perfect gas since molecular attractions are assumed to be insignificant at large distances.[43]

Although CLAUSIUS did not want to put himself in the awkward position of basing his (macroscopic) mechanical theory of heat on microscopic assumptions, he continued in his later writings to state that T is simply the absolute temperature without providing a proof.[44] He did introduce in 1862 the concept of "disgregation," defined as a quantity dependent on molecular arrangements, but this quantity was never clearly related to actual positions and velocities of molecules, and it did not seem to imply any degree of randomness in those positions and velocities.[45] In stating that in nature there is "a general tendency, to transformations of a definite direction" he meant only that the equivalence-value of

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[41] *Ibid.*, 135.

[42] P. FONG, *Foundations of Thermodynamics* (New York: Oxford University Press, 1963), 17; E. O. HERCUS, *Elements of Thermodynamics and Statistical Mechanics* (Melbourne: University Press, 1950), 19; E. HOPPE, *Geschichte der Physik* (Braunschweig: Vieweg, 1926), 225; The opposite mistake is made by M. TRIBUS, who says CLAUSIUS coined the word entropy in 1850 [*Encyclopedia of Physics*, ed. R. BESANCON (New York: Reinhold, 1966), 239]. The confusion that can arise from reliance on secondary sources is well illustrated in the article by M. DUTTA, *Physics Today*, 75 (Jan. 1968).

[43] R. CLAUSIUS, *Ann. Physik* [2] **100**, 353 (1857), English trans. reprinted in S. G. BRUSH, *Kinetic Theory*, **1** (New York: Pergamon Press, 1965); see end of § 9.

[44] CLAUSIUS, *Ann. Physik* [2] **116**, 73 (1862); see *e.g.* p. 217 of the English trans., *Mechanical Theory of Heat* (1867).

[45] *Ibid.*, 220. See the discussions of "disgregation" by E. E. DAUB, *Isis* **58**, 293 (1967); M. J. KLEIN, *Hist. Stud. Phys. Sci.* **1**, 127 (1969); C. WEINER, "Clausius and the 'Internal' explanation of entropy" (unpublished).

uncompensated transformations is positive, with no further explanation of the physical significance of this tendency.[46]

By 1863 CLAUSIUS was finding that his "equivalence value of transformations," though still lacking a clear meaning, was a useful concept in describing various problems and in confounding objections to his theory. In particular, his principle that heat "incessantly strives to pass from warmer to colder bodies" and therefore cannot of itself pass from a colder to a warmer body had seemed obvious to him, but was doubted by G. A. HIRN and earlier by RANKINE in the paper mentioned above.[47] This criticism was valuable since it stimulated CLAUSIUS to clarify and refine his ideas and to show that the schemes proposed by HIRN and RANKINE could not in fact lead to violations of the Second Law.[48] Presumably it was this experience that encouraged him to replace the original clumsy phrase by a handy new one, and so in 1865 we see at last the famous term "entropy" introduced for the first time by the equation $dS = dQ/T$.[49] CLAUSIUS has at last recognized the signifance of THOMSON's dissipation principle,[50] and sees that his entropy concept provides a convenient way to state the directional character of cosmic processes. So the 1865 paper concludes with the celebrated statement of the "two fundamental theorems of the mechanical theory of heat":

1. The energy of the universe is constant.
2. The entropy of the universe tends to a maximum.

In a lecture in Frankfort in 1867, CLAUSIUS gave a more elementary discussion of disgregation and the equivalence-value of transformations. He noted that the Second Law contradicts the idea that (as "one hears it often said") the world is cyclic and may go on forever in the same way. On the contrary, the entropy of the universe tends toward a maximum, which has the consequence that:

> The more the universe approaches this limiting condition in which the entropy is a maximum, the more do the occasions of further changes diminish; and supposing this condition to be at last completely obtained, no further change could evermore take place, and the universe would be in a state of unchanging death.[51]

This was a definitive statement of the "heat death" concept which was so widely discussed in the late 19th century and afterwards.[52]

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[46] *Ibid.*, 247.

[47] G. A. HIRN, *Exposition analytique et experimentale de la Théorie Mécanique de la Chaleur* (Paris & Colmar, 1862). P. DE SAINT-ROBERT, *Cosmos, Revue Enc.* **22**, 200 (1863). G. A. HIRN, *Cosmos, Revue Enc.* **22**, 283, 413, 734 (1863). R. CLAUSIUS, *Cosmos, Revue Enc.* **22**, 560 (1863). RANKINE, paper cited in note 35; also RANKINE's article on "Heat" in *A Cyclopedia of the Physical Sciences* (London, 1857, 2. ed. 1860), esp. the statement of the Second Law on p. 413 (2d ed.).

[48] R. CLAUSIUS, *Ann. Physik* [2] **120**, 426 (1863) (*Mechanical Theory of Heat*, 267); *Ann. Physik* [2] **121**, 1 (1864) (*Mechanical Theory of Heat*, 290).

[49] R. CLAUSIUS, *Ann. Physik* [2] **125**, 353 (1865) (*Mechanical Theory of Heat*, 327; see p. 357 for definition of entropy, with change of sign from earlier definitions).

[50] See note 33; further brief mention in *Mechanical Theory of Heat*, 364.

[51] R. CLAUSIUS, *Phil. Mag.* [4] **35**, 405 (1868).

[52] See S. G. BRUSH, *Graduate Journal*, **7**, 477 (1967). In addition to the literature cited there, the following works may be of interest to anyone who wants to study the various ramifications and influences of the "heat death" concept. ADOLF FICK, *Die*

It has occasionally been noted[53] that RANKINE also introduced in 1854 a "thermodynamic function" equivalent to CLAUSIUS' "equivalence-value of a transformation." Unfortunately RANKINE's theory appeared to be so deeply entangled with his hypothesis of molecular vortices that he never received much credit for his contributions to thermodynamics, and that is certainly the case with his proto-entropy concept. His thermodynamic function was defined by the equation $\delta F = \delta H/Q$, where δH is the heat consumed in passing from one "curve of no transmission" (*i.e.*, adiabat) to another lying indefinitely close to it, and Q is the "actual heat" contained in the substance.[54] Thus F = constant could be used as the equation for a particular adiabatic change of state. RANKINE also gave an explicit formula for F for a perfect gas.[55] But the relation between Q and absolute temperature was obscured because at this time RANKINE was trying to maintain a distinction between the "absolute zero of gaseous tension" and the "point of absolute cold." He suggested that the difference between these two points might be determined from the JOULE-THOMSON experiment.[56] RANKINE did not use his thermodynamic

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Naturkräfte in ihrer Wechselbeziehung (Würzburg, 1869). H. F. WALLING, *Proc. Amer. Assoc. Adv. Sci.* **22**, 46 (1873); *Pop. Sci. Monthly* **4**, 430 (1874). AUGUST RITTER, *Anwendungen der mechanischen Wärmetheorie auf kosmologische Probleme* (Hannover, 1879) 64 and the lecture of E. DU BOIS-REYMOND which he cites. S. T. PRESTON, *Phil. Mag.* [5] **8**, 152 (1879), **10**, 338 (1880); *Nature* **19**, 460, 555 (1879), **20**, 28 (1879). WILLIAM MUIR, *Nature* **20**, 6 (1879). T. H. HUXLEY, "The struggle for existence in human society" (1888), reprinted in *Selections from the Essays of T. H. Huxley* (New York: Appleton-Century Crofts, 1948). ALEXANDER WILLIAM BICKERTON, *Trans. New Zealand Inst.* **27**, 538 (1895). GEORG HIRTH, *Entropie der Keimsysteme und erbliche Entlastung* (München, 1900). SVANTE ARRHENIUS, *Lehrbuch der kosmischen Physik* (Leipzig: Hirzel, 1903); *The Life of the Universe*, trans. H. BORNS (London & New York: Harper, 1909), 2, 230–241. KARL S. TRINCHER, *Biology and Information*, trans. from Russian (New York: Consultants Bureau, 1965), appendix by KUZNETSOV discussing writings of TIMIRYAZEV, UMOV and AUERBACH, 1901–1905. RONALD C. TOBEY, *The American Ideology of National Science*, 1919–1930 (Pittsburgh: University of Pittsburgh Press, 1971), on R. A. MILLIKAN's views. OLIVER LODGE, Nature **128**, 722 (1931). P. W. BRIDGMAN, in his *Reflections of a Physicist* (New York: Philosophical Library, 1950), 150 (reprinted from *Bull. Amer. Math. Soc.* 1932). E. A. MILNE, *Relativity, Gravitation and World Structure* (Oxford: Clarendon Press, 1935), 285–86. HENRY NORRIS RUSSELL, in *Time and its Mysteries*, Series III (New York: NYU Press, 1949), 1 (lecture given in 1940). JACQUES BARZUN, *Science the Glorious Entertainment* (New York: Harper & Row, 1964), 117. JEROME H. BUCKLEY, *The Triumph of Time* (Cambridge, Mass.: Harvard University Press, 1966), Chap. 5. NICHOLAS GEORGESCU-ROEGEN, *The Entropy Law and the Economic Process* (Cambridge: Harvard University Press, 1971).

[53] In his review of POINCARÉ's text on thermodynamics, P. G. TAIT wrote: "We look in vain for any mention of Rankine or his Thermodynamic Function; though we have enough, and to spare, of it under its later *alias* of Entropy"—*Nature* **45**, 245 (1892.) RANKINE is cited by J. T. MERZ, *A History of European Thought in the Nineteenth Century* (Edinburgh: Blackwood, 1904–1914), **1**, 316, **2**, 169; J. SWINBURNE, *Electrician* **50**, 442 (1903); V. V. RAMAN, *J. Chem. Educ.* **50**, 274 (1973).

[54] W. J. M. RANKINE, *Phil. Trans. Roy. Soc. London*, 115 (1854). *Papers*, 339 (see p. 351 for the definition of F).

[55] $F = \text{hyp. log}\, Q - \frac{Nh}{NQ+h} + N\, \text{hyp. log}\, V$, where h represents the deviation from the ideal gas law, $PV = NQ + h$. See *Papers*, 363–364.

[56] *Papers*, 376. See also p. 390 where he assumes that the difference ($\varkappa$) between the two zero points is 2.1° C, but says in a footnote that "it is probable that $\varkappa$ may be found to be inappreciably small."

function to give a formulation of the Second Law in the same way that CLAUSIUS did at this time. But in 1865, in a paper on "The Second Law of Thermodynamics", RANKINE did point out that his thermodynamic function was identical to the entropy of CLAUSIUS.[57] He did not perceive irreversibility as an essential aspect of the Second Law, and made no statement about a unidirectional change in his thermodynamic function. Moreover, he asserted that the Second Law could be *derived* from his hypothesis of molecular vortices, provided only that one assumes the molecular motion is *regular*.

It seems to me that both CLAUSIUS and RANKINE missed their opportunities to give a satisfactory theory of irreversibility based on the entropy concept. In his later papers CLAUSIUS concerned himself with the mechanical interpretation of the Second Law but never tried to give a mechanical explanation of irreversibility.[58] In the third edition of his treatise on the mechanical theory of heat he even eliminated the statement that the entropy of the world tends toward a maximum.[59]

4. The Introduction of Statistical Ideas in Kinetic Theory

The failure of CLAUSIUS to develop a statistical theory of irreversibility is all the more remarkable since, in addition to inventing entropy, he was the first to find an effective use for statistical methods in the kinetic theory of gases. But before we discuss that topic we must review the context of scientific thinking about molecular motion as it had developed up to the mid-19$^{\text{th}}$-century.

The suggestion of LUCRETIUS that atoms swerve randomly in their paths, thereby permitting the possibility of free will, was probably familiar to all educated men in the 17$^{\text{th}}$ and 18$^{\text{th}}$ centuries.[1] Randomness played some role in debates

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[57] RANKINE, *Phil. Mag.* [4] **30**, 241 (1865); *Papers*, 427. This appears to be one the first uses in print of the phrase "Second Law of Thermodynamics"—CLAUSIUS was still calling it the second theorem of the mechanical theory of heat.

[58] E. DAUB, *Dict. Sci. Biog.* **3**, 309, 310 (1971).

[59] R. CLAUSIUS, *Die Mechanische Wärmetheorie*, 3. Aufl. (Braunschweig, 1887). For further details on later thermodynamic discussions of entropy and irreversibility see E. E. DAUB, *Hist. Stud. Phys. Sci.* **2**, 321 (1970). Extensive bibliographies on thermodynamics may be found in J. R. PARTINGTON, *An Advanced Treatise on Physical Chemistry* (London: Longmans, Green and Co., 1949), **I**, 115–233.

[1] TITUS LUCRETIUS CARUS, *De Rerum Natura* (London, 1886), **1**, Bk. 2, ll. 216–224, 251–262, 292–293; English trans. by A. D. WINSPEAR (New York: S. A. Russell, The Harbor Press, 1956), 56. On the occasion of the Belfast meeting of the British Association in 1874, MAXWELL wrote a poem on "Molecular Evolution" which begins:

At quite uncertain times and places,
  The atoms left their heavenly path,
And by fortuitous embraces,
  Engendered all that being hath.
And though they seem to cling together,
  And form "associations" here,
Yet soon or late, they burst their tether,
  And through the depths of space career...

LEWIS CAMPBELL & WILLIAM GARNETT, *The Life of James Clerk Maxwell* (London, 1882, reprinted with a selection of letters from the second edition, 1884 by Johnson Reprint Corp., New York, 1969), 637.

about the nature of the world in the time of NEWTON, as well as in the development of probability theory.[2] For those who were deeply concerned about the place of God in the world, both randomness and determinism were distasteful. With the triumph of NEWTONIAN mechanics, it was recognized that molecular motions are "in principle" determined, so that a super-intelligence that could know all the positions and velocities of all molecules in the universe at one instant could know both the past and the future. This assertion is now generally referred to as "LAPLACEAN determinism" because LAPLACE popularized it in an especially vivid way in his essay on probability theory.[3] As has recently been noted by ROGER HAHN, similar statements can be found in earlier writings of LAPLACE, indicating the probable influence of CONDORCET.[4] Other scientists such as BOSCOVICH asserted the determinism of mechanical motions,[5] so that one should probably regard this

[2] O. B. SHEYNIN, *Arch. Hist. Exact Sci.* 7, 217 (1971).

[3] P. S. DE LAPLACE, *Essai Philosophique sur les Probabilités* (Paris, 1814, reprinted by Gauthier-Villars, Paris, 1921), 3: "Nous devons donc envisager l'état présent de l'universe comme l'effet de son état antérieur, et comme la cause de celui qui va suivre. Une intelligence qui pour un instant donné connaîtrait toutes les forces dont la nature est animée et la situation respective des êtres qui la composent, si d'ailleurs elle était assez vaste pour soumettre ces données à l'analyse, embrasserait dans la même formule les mouvements des plus grands corps de l'universe et ceux du plus léger atome: rien ne serait incertain pour elle, et l'avenir comme le passé serait présent a ses yeux." A similar statement, with a more astronomical flavor, may be found in *The System of the World* (Dublin, 1830), 24.

[4] R. HAHN, *Actes XI^e Cong. Int. Hist. Sci.*, Cracow, 1965 (pub. 1968), **2**, 167. HAHN quotes the following passage from LAPLACE's memoir of 1773, which may be set beside the quotation in the preceding note: "L'état présent du système de la Nature est évidemment une suite de ce qu'il étoit au moment précédent, & si nous concevons une Intelligence qui, pour un instant donné, embrasse tous les rapports des êtres de cet Univers, elle pourra déterminer pour un temps quelconque pris dans le passé ou dans l'avenir, la position respective, les mouvements, & généralement les affections de tous ces êtres." HAHN notes that in CONDORCET's *Lettre à d'Alembert* (1768) one finds a similar passage: "si la loi de la continuité n'etoit point violée dans l'univers, on pourroit regarder ce qu'il est à chaque instant, comme le résultat de ce qui devoit arriver à la matiere arrangée, une fois dans un certain ordre, & abandonnée ensuite à elle-memê.... Une intelligence qui connoîtroit alors l'état de tous les phénomenes dans un instant donné, les loix auxquelles la matiere est assujettie, & leur effet au bout d'un tempts quelconque, auroit une connoissance parfaite du Système du Monde."

HAHN has given a more extensive discussion of the development of LAPLACE's ideas on determinism and probability in a paper read at the XIII History of Science Congress in Moscow, 1971, to be published in its proceedings. I am indebted to Professor HAHN for sending me a preprint of this paper.

On the relation of LAPLACE's work in probability to various astronomical and political problems, see C. C. GILLISPIE, *Proc. Amer. Phil. Soc.* **116**, 1 (1972).

[5] R. J. BOSCOVICH, *Theoria Philosophiae Naturalis* (Vienna, 1758; Venice, 1763). English trans. by J. M. CHILD (from the first Venetian ed., 1763), *A Theory of Natural Philosophy* (Chicago: Open Court, 1922; reprinted by MIT Press, Cambridge, Mass., 1966), 141–142: "Any point of matter, setting aside free motions that arise from the action of arbitrary will, must describe some continuous curved line, the determination of which can be reduced to the following general problem. Given a number of points of matter, & given, for each of them, the point of space that it occupies at any given instant of time; also given the direction & velocity of the initial motion if they were projected, or the tangential velocity if they are already in motion; & given the law of forces expressed by some continuous curve, such as that of Fig. 1, which contains this theory of mine; it is required to find the path of each of the points. ... Now, although a

as an accepted position at the beginning of the 19th century; yet it by no means excluded the application of probability theory to all kinds of physical phenomena, and in fact it was just at the beginning of the 19th century that one notes a flowering of many branches of statistics.[6]

CASSIRER has claimed that little attention was paid to the broader implications of LAPLACE's statement on determinism until the "ignorabimus" speech of EMIL DU BOIS-REYMOND in 1872.[7] While one does find occasional discussions of LAPLACEAN determinism in a philosophical context between 1814 and 1872,[8] CASSIRER's view meshes with my interpretation that there was little serious debate on the issue of determinism until after the effectiveness of statistical methods had been demonstrated in kinetic theory. Even after the debate on the reversibility objection to the H-theorem had strongly suggested a need for assuming that molecular motions are "disordered" (see below), it was difficult for scientists to abandon the view of LAPLACE that one assumes phenomena to be random merely because of lack of knowledge rather than because of any inherent indeterminism.

An example of this view in midcentury Britain is furnished by a letter from R. L. ELLIS to J. D. FORBES, in connection with the debate on the application of statistical theory to observations of double stars. ELLIS says that "random" means nothing except with reference to the knowledge of the observer and his system of classifying the phenomena; "for everything which exists there is a definite reason why it is what it is" so the notion of *fundamental* randomness is meaningless.[9]

LAPLACEAN determinism has also been taken to imply the elimination of the

problem of such a kind surpasses all the powers of the human intellect, yet any geometer can easily see thus far, that the problem is determinate ... a mind which had the powers requisite to deal with such a problem in a proper manner & was brilliant enough to perceive the solutions of it (& such a mind might even be finite, provided the number of points were finite, & the notion of the curve representing the law of forces were given by a finite representation), such a mind, I say, could, from a continuous arc described in an interval of time, no matter how small, by all points of matter, derive the law of forces itself... Now, if the law of forces were known, & the position, velocity & direction of all the points at any given instant, it would be possible for a mind of this type to foresee all the necessary subsequent motions & states, & to predict all the phenomena that necessarily followed from them." This passage was pointed out by K. STIEGLER in a paper presented at the XIII History of Science Congress, Moscow, 1971. On the difference between LAPLACEAN and BOSCOVICHIAN determinism see O. B. SHEYNIN, *Arch. Hist. Exact Sci.* **9**, 306 (1973).

[6] JOHN THEODORE MERZ, *A History of European Thought in the Nineteenth Century*, **2** (Edinburgh & London: Blackwood, 2d ed. 1912), Chap. XII. C. C. GILLISPIE, *op. cit.* (note 4) and earlier paper in *Scientific Change*, ed. A. C. CROMBIE (New York: Basic Books, 1963), 431. HELEN M. WALKER, *Studies in the History of Statistical Method* (Baltimore: Williams & Wilkins, 1929), 19. HAROLD L. WESTERGAARD, *Contributions to the History of Statistics* (New York: Agathon Press, 1968, reprint of 1932 ed.), Chaps. XII & XIII. VINCENZ JOHN, *Geschichte der Statistik* (Wiesbaden: Sändig, 1968, reprint of 1884 ed.), 1. Teil, 314 ff.

[7] E. CASSIRER, *Göteborgs Högskolas Årsskrift* **42** (3) (1936); English trans. by O. T. BENFEY, *Determinism and Indeterminism in Modern Physics* (New Haven: Yale University Press, 1956), 4; E. DU BOIS-REYMOND, *Tageblatt* 1872 *Vers. Deutsch, Naturf. u. Aerzte*, 85, English trans. in *Pop. Sci. Monthly* **5**, 17 (1874).

[8] A. COURNOT, *Essai sur les fondements de nos connaissances* (Paris, 1851), **1**, 62. C. BABBAGE, *The Ninth Bridgewater Treatise* (London, 1837, 2d. ed. 1838), 111.

[9] R. L. ELLIS to J. D. FORBES, 10 October 1850, in *Life and Letters of James David Forbes* by J. C. SHAIRP *et al.* (London, 1873), 481.

concept of "time "(except as a mere mathematical parameter) in NEWTONIAN physics. Insofar as the equations of mechanics are time-reversible, there is no qualitative difference between past and future, only the difference between a plus and a minus sign.[10] This argument may be a source of confusion since it suggests a (false) converse; logically it would be quite possible to design an irreversible theory which is also deterministic (FOURIER's theory of heat conduction is an example).

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The published writings of scientists who identified heat with molecular motion before 1856 rarely state that this motion is in any way irregular or random. HERAPATH in 1821 postulated that gases consist "of atoms, or particles, moving about, and among one another, with perfect freedom" but also stated that different temperatures of the same body depend on the "velocity of vibration" of its particles.[11] As he noted, this was the usual definition proposed by "the advocates for the theory of heat by intestine motion" and indeed the "vibration" of atoms was often conceived as a regular back-and-forth motion.[12] The replacement of the caloric theory of heat by the wave theory[13] reinforced this idea by associating heat with vibrations of the ether, and those writers who talked about thermal molecular motion in the early 1850's often explicitly identified heat with vibrations of atoms.[14] JOULE, adopting HERAPATH's kinetic theory in 1847–48, emphasized that molecular motion is *rapid*, though he also remarked that the molecules are "constantly flying about in every direction". Only WATERSTON, in his 1845 paper that remained generally unknown until 1892, stressed the idea that the particles are "moving in all directions" and "encounter one another in every possible manner" during an infinitesimal time period. The earliest statements identifying heat with molecular motion by CLAUSIUS, THOMSON, and TYNDALL in the years 1852–53 are remarkably noncommittal about what kind of motion it is.[15]

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[10] M. CAPEK, *Philosophical Impact of Contemporary Physics* (Princeton: Van Nostrand, 1959), Chap. VIII. E. MEYERSON, *Identity and Reality* (New York: Dover Pubs. 1962, reprint of the English trans. by K. LOEWENBERG, 1930, of the 3rd French ed., 1926), Chap. VI.

[11] J. HERAPATH, *Ann. Phil.* [2] **1**, 273 (1821), esp. p. 281.

[12] R. HOOKE (1678), quoted in S. G. BRUSH, *Kinetic Theory*, **1** (Oxford & New York: Pergamon Press, 1965), 6; M. V. LOMONOSOV, *Nov. Comm. Acad. Sci. Imp. Petrop.* **1**, 230 (1750), English trans. in *Mikhail Vasil'evich Lomonosov on the Corpuscular Theory*, by H. M. LEICESTER (Cambridge, Mass.: Harvard University Press, 1970), 203. But LOMONOSOV also refers to "disordered motion" of atoms (*ibid.*, 215).

[13] See S. G. BRUSH, *Brit. J. Hist. Sci.* **5**, 145 (1970).

[14] L. WILHELMY, *Versuch einer mathematisch-physikalischen Wärme-Theorie* (Heidelberg, 1851), 16; N. DELLINGSHAUSEN, *Versuch einer speculativen Physik* (Leipzig, 1851), 57–58; ZACHARIAH ALLEN, *Philosophy of the Mechanics of Nature* (New York, 1852), 41, 344, 349, 355. L. COLDING, *Kgl. Danske Vid. Selsk. Skr.* [5] **3**, 1 (1852), English trans. in *Ludvig Colding and the Conservation of Energy Principle* by PER F. DAHL (New York: Johnson Reprint Corp., 1972) p. 80. See also C. F. MOHR, *Ann. Chem. Pharm.* **24**, 141 (1837); *Z. f. Phys.* [2] **5**, 419 (1837), English trans. in *Phil. Mag.* [5] **2**, 110 (1876); BABINET, *Compt. Rend. Acad. Sci. Paris* **7**, 781 (1838).

[15] J. P. JOULE, *Mem. Manchester Lit. Phil. Soc.* [2] **9**, 107 (1851), read 1848); see also his 1847 lecture reprinted in BRUSH, *Kinetic Theory*, **1**, 78. J. J. WATERSTON, *Phil. Trans. Roy. Soc. London* **183 A**, 5 (1893); the quoted phrases also appear in the abstract of his paper, published in *Proc. Roy. Soc. London* **5**, 604 (1846).

"*... heat consists in a motion of the ultimate particles of bodies, and is the measure of the vis viva of this motion*"—R. CLAUSIUS, *Ann. Physik* [2] **86**, 337 (1852), English trans.

According to KRÖNIG, who revived the kinetic theory of gases in 1856, the molecules of a gas move at constant speed until they strike another molecule or the side of the container. Since the smoothest wall is very rough on the molecular level, the resulting path of a molecule must be quite irregular, but according to the laws of probability this complete irregularity leads to complete regularity of behavior.[16] But in fact KRÖNIG makes no explicit use of probability concepts at all in this paper.

CLAUSIUS, sharing the same assumptions in his more substantial treatment in 1857, did not put any emphasis on the irregularity of molecular motion. He did invoke the "laws of probability" in arguing that "there are as many molecules whose angles of reflexion fall within a certain interval, e.g., between 60° and 61°, as there are molecules whose angles of incidence have the same limits, and that, on the whole, the velocities of the molecules are not changed by the side."[17] But here the stress is on the uniform distribution of directions of motion among all possible values, an idea that is not essentially connected with randomness.

As a result of the criticism of the Dutch meteorologist C. H. D. BUYS-BALLOT,[18] CLAUSIUS introduced his "mean-free-path" [*mittlere Weglänge*] concept. Rather than assume that a molecule can move several meters in a straight line before hitting a macroscopic object, CLAUSIUS preferred to attribute a finite size, or rather a finite sphere of action, to the molecules, so that intermolecular collisions would be frequent enough to cause each molecule to change its direction of motion before it can go more than a very short distance. In order to compute the relation between the average distance travelled by a molecule between successive collisions and the effective molecular diameter, CLAUSIUS suggested that we should "imagine a great number of molecules moving irregularly about amongst one another"[19] and then fix our attention on one particular molecule to see how often it collides with another one. The probability that a molecule will strike another one in passing through a layer of thickness x is asserted to be simply the ratio of the cross-

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in *Scientific Memoirs*, ed. J. TYNDALL & W. FRANCIS (London, 1853), 1, quotation from p. 342 and p. 5, resp.

"The work which any external forces do upon [a substance], the work done by its own molecular forces, and the amount by which the half *vis viva* of the thermal motions of all its part is diminished, must together be equal to the mechanical effect produced from it ..."—W. THOMSON, *Trans. Roy. Soc. Edinburgh* **20**, 261 (1851), *Phil. Mag.* [4] **4**, 8 (1852) (quotation from p. 12 of the latter).

"Assuming the hypothesis which is now gaining ground, that heat, instead of being an agent apart from ordinary matter, consists in a motion of the material particles ..." —JOHN TYNDALL, lecture Feb. 11, 1853 at the Royal Institution, London, reprinted in *The Royal Institution Library of Science, Physical Sciences*, **1**, 78 (New York: American Elsevier, 1970).

[16] A. K. KRÖNIG, *Ann. Physik* [2] **99**, 315 (1856); GRETE RONGE, *Gesnerus* **18**, 45 (1961); EDWARD E. DAUB, *Isis* **62**, 612 (1971).

[17] R. CLAUSIUS, *Ann. Physik* [2] **100**, 353 (1857); English trans. in *Phil. Mag.* [4] **14**, 108 (1857), reprinted in BRUSH, *Kinetic Theory*, **1**, 111. See the third article in this series, S. G. BRUSH, *Ann. Sci.* **14**, 185 (1958).

[18] C. H. D. BUYS-BALLOT, *Ann. Physik* [2] **103**, 240 (1858). There is some indication that CLAUSIUS had been thinking about mean-free-path ideas in an earlier paper on the scattering of light by water drops in the atmosphere, *Ann. Physik* [2] **76**, 161 (1849).

[19] R. CLAUSIUS, *Ann. Physik* [2] **105**, 239 (1858), English trans. in *Phil. Mag.* [4] **17**, 81 (1859), reprinted in BRUSH, *Kinetic Theory*, **1**, 135 (quotation from p. 139).

sectional area corresponding to the average number of molecules to be found in such a layer, to the total area of the layer.

Up to this point the reasoning is compatible with an "ignorance" concept of probability: if we know nothing about how the molecules are arranged in space it is reasonable to make such an assumption about the probability of a collision in the first infinitesimal layer, even if there is actually a regular lattice structure. But now, without any further discussion, CLAUSIUS assumes that if the molecule passes through the first such layer without suffering a collision, it must risk the same chance of a collision in the second layer; or, better, the probability that it does *not* suffer a collision in either the first or the second layer is the square of the probability that it does not suffer a collision in a single layer. CLAUSIUS did recognize that in order for this calculation to be valid one must at least exclude the possibility that the molecules are regularly arranged in space; but he didn't worry about any more subtle types of correlation.[20]

As was noted in the preceding paper (Part VII), CLAUSIUS used statistical methods in a rather limited and clumsy fashion in his theory of heat conduction in gases and was reluctant to take full advantage of MAXWELL's theory of the velocity distribution. The same is characteristic of his other writings on kinetic theory; he does not seem to want to recognize that any physically significant consequences might follow from the assumption of randomness,[21] and he is eager to replace molecular quantities by their average values in every calculation, sometimes prematurely.

We recall the remark of GIBBS, in his obituary of CLAUSIUS:

> In reading Clausius we seem to be reading mechanics; in reading Maxwell, and in much of Boltzmann's most valuable work, we seem rather to be reading in the theory of probabilities.[21a]

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With the entrance of JAMES CLERK MAXWELL, the kinetic theory finally draws on the mainstream of the development of probability theory; in fact, MAXWELL at first goes overboard in assuming what amounts to complete randomness of molecular motion, and later has to retreat to a more deterministic approach in order to comply with the accepted physical viewpoint.

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[20] He also stated that if the target molecules were not stationary but themselves moving with various velocities, then the mean free path would be different; but here he thought it was permissible to assume that each molecule is moving at the average velocity in order to do the calculation, and obtained the result that the mean free path would be $\frac{3}{4}$ as great as in the hypothetical case when all molecules but one are at rest. It was left for MAXWELL to generalize this calculation to the case where the molecules have a statistical distribution of velocities, and CLAUSIUS resisted for some time MAXWELL's replacement of the factor $\frac{3}{4}$ by $1/\sqrt{2}$. CLAUSIUS, *op. cit.*, p. 140; see S. G. BRUSH, *Am. J. Phys.* **30**, 271 (1962).

[21] The EHRENFESTS emphasized that CLAUSIUS did introduce in his treatment of mean free paths the assumption about the number of collisions, the "Stosszahlansatz," which was later to play an important role in BOLTZMANN's theory. PAUL & TATIANA EHRENFEST *Enc. math. Wiss.* **IV** (2, II, 6) (Leipzig: Teubner, 1912), English trans. by M. J. MORAVCSIK, *The Conceptual Foundations of the Statistical Approach in Mechanics* (Ithaca, N. Y.: Cornell University Press, 1959), 5.

[21a] J. W. GIBBS, *Proc. Amer. Acad.* (n.s.) **16**, 458 (1889); *The Scientific Papers of J. Willard Gibbs* (London & New York: Longmans, Green & Co., 1906), **2**, 261.

As CHARLES GILLISPIE has noted, MAXWELL probably was influenced by JOHN HERSCHEL's review of QUETELET's books in the *Edinburgh Review* (1850); here HERSCHEL provided a derivation of the normal law of errors quite similar to that which MAXWELL himself later used in presenting his velocity distribution.[22] MAXWELL's correspondence with LEWIS CAMPBELL in 1850, and with R. B. LITCHFIELD in 1858, indicates that he was probably familiar with HERSCHEL's article; he may also have discussed it with W. F. DONKIN and J. D. FORBES, who participated in a debate on this subject in the *Philosophical Magazine* in 1850–51.[23] In any case MAXWELL initially felt no need to justify his use of the law of errors for molecular velocities, and it was his failure to explain what this law had to do with the motions and collisions of molecules (assumed to obey NEWTONIAN laws) that prevented other kinetic theorists from appreciating the validity of his law when it was first published in 1860.

By analogy with HERSCHEL's assumption that deviations (for example of a ball dropped from a height, aimed at a mark) in perpendicular directions are independent, MAXWELL assumed in his 1860 paper that the probability of a molecule having a certain value of the x-component of velocity is not affected by knowledge of its y-component of velocity. He did not recognize that this assumption cannot be true in a finite system with fixed total energy (if one component of velocity is so large that it corresponds to nearly the entire kinetic energy of the system, then the other components cannot have similarly unrestricted values[24]). MAXWELL did give a generalized treatment that takes account of this situation in a much later paper, written near the end of his life.[25] But in his memoir "On the Dynamical Theory of Gases" published in 1867, he merely noted that "this assumption may appear precarious," and tried instead to derive the distribution law in a way explicitly involving molecular collisions.

MAXWELL's 1867 treatment avoids the use of terms suggesting randomness, asserting merely that in a gas there are a certain number of molecules having a specified value of the velocity vector. The number of encounters of molecules having two particular values of the velocity vector is then assumed to be proportional to $n_1 n_2$, the product of the numbers having those values separately; but MAXWELL does not explain why such an assumption of independence of the velocities of two molecules is any more acceptable than his previous assumption of the independence of

[22] JOHN HERSCHEL, *Edinburgh Rev.* **92**, 1 (1850), reprinted in his *Essays* (London, 1857), 365; C. C. GILLISPIE, in *Scientific Change*, ed. A. C. CROMBIE (New York: Basic Books, 1963), 431; ELIZABETH GARBER, *Centaurus* **17**, 11 (1972). For a discussion from the viewpoint of statistical theory, see O. B. SHEYNIN, *Biometrika* **58**, 234 (1971).

[23] J. D. FORBES, *Phil. Mag.* [3] **37**, 401 (1850); W. F. DONKIN, *Phil. Mag.* [4] **1**, 353, 458, **2**, 55 (1851); R. L. ELLIS, *Phil. Mag.* [3] **37**, 321, 462 (1850). For correspondence relating to this debate, including an "ignorance" definition of randomness by ELLIS, see J. C. SHAIRP *et al.*, *Life and Letters of James David Forbes* (London, 1873), Chap. XIV (by P. G. Tait).

[24] *Cf.* L. BOLTZMANN, *Phil. Mag.* [5] **23**, 305 (1887); *Wissenschaftliche Abhandlungen* (Leipzig: Barth, 1909), **III**, 255–256; J. L. F. BERTRAND, *Calcul des Probabilités* (Paris: Gauthier-Villars, 1889), 29–32; *Compt. Rend. Acad. Sci. Paris* **122**, 963, 1083, 1174, 1314 (1896); L. BOLTZMANN, *Compt. Rend. Acad. Sci. Paris* **122**, 1173, 1314 (1896); *Wissenschaftliche Abhandlungen* **III**, 564, 566.

[25] J. C. MAXWELL, *Trans. Cambridge Phil. Soc.* **12**, 547 (1879), reprinted in *The Scientific Papers of James Clerk Maxwell* (Cambridge University Press, 1890, reprinted by Dover Pubs., New York, 1952, 1965), **2**, 713.

different components of the velocity of the *same* molecule. There is one important difference which becomes clear only in BOLTZMANN's later work: MAXWELL's second assumption makes it possible to describe an irreversible time evolution of the velocity distribution function. Thus a connection between randomness and irreversibility emerged mathematically from MAXWELL's attempt to prove that his velocity distribution law represents a stable equilibrium in a gas of colliding molecules. The development of this connection will be our major concern in the rest of this paper, but there is only the barest hint of its significance in MAXWELL's conclusion that his distribution "is therefore a possible form of the final distribution of velocities" (because once attained it is not altered by further collisions); "it is also the only form" (because otherwise the direct and inverse collisions would not balance).[26]

The same memoir contains a discussion of another topic, seemingly unrelated to the problem of irreversibility, which was involved in the later LOSCHMIDT-BOLTZMANN discussion of the reversibility paradox. Under the heading "Final Equilibrium of Temperature" MAXWELL stated that, after some difficulty, he had managed to prove that a column of gas under gravitational forces must have the same temperature throughout. This result seemed to some scientists at the time contrary to common sense as well as to experience, since it was by then "well known" that the air gets colder as you go up in the earth's atmosphere.[27] If FOURIER's law of heat conduction were applicable here, one would expect this temperature gradient to be associated with a flow of heat from the earth out into space. But in many of the discussions of this problem, the temperature gradient was attributed *not* to thermal conditions alone, but rather (or mainly) to the action of the earth's gravity on air molecules at different heights. HERAPATH and WATERSTON had proposed explanations of the temperature gradient, based on kinetic theory, invoking such action, but their reasoning can now be seen as fallacious.[28] MAXWELL, after discussing the problem with WILLIAM THOMSON, decided that the Second Law of Thermodynamics requires a uniform temperature distribution. As justification for this conclusion, however, MAXWELL advanced only a much weaker principle: "if the temperature of any substance, when in thermic equilibrium, is a function of the height, that of any other substance must be the same function of the height" (otherwise it would be possible to rig up an engine that could take heat from the hotter substance and give it to the cooler substance at the same height). Then, having shown that the temperature is independent of height for gases, MAXWELL argues that it must also be independent of height for all other substances. Since he thought that the proof for gases depends on the precise form of the velocity distribution law, MAXWELL wrote: "we may regard this law of temperature,

[26] J. C. MAXWELL, *Phil. Trans. Roy. Soc. London* **157**, 49 (1867); *Papers*, **2**, 26; reprinted in S. G. BRUSH, *Kinetic Theory*, **2** (Oxford & New York: Pergamon Press, 1966) 23 (see p. 48).

[27] See, *e.g.*, JOHN HERSCHEL's article on "Meteorology" in the *Encyclopedia Britannica* (Edinburgh, 1861), or earlier reviews of the problem such as that by J. IVORY, *Phil. Mag.* **66**, 81, 241, (1825); *Phil. Trans. Roy. Soc. London* **113**, 409 (1823).

[28] J. HERAPATH, *Times*, 10 Jan. 1826, quoted in S. G. BRUSH, *Notes & Rec. Roy. Soc. London* **18**, 173 (1963); HERAPATH, *Railway Mag.* **1**, 109, 260 (1836); *Mathematical Physics* (London, 1847, reprinted by Johnson Reprint Corp., New York, 1972), **2**, 142–163. J. J. WATERSTON, *Phil. Trans. Roy. Soc. London* **183**, 1 (1892, submitted 1845), reprinted in *The Collected Scientific Papers of John James Waterston*, ed. J. S. HALDANE (Edinburgh: Oliver & Boyd, 1928) (see pp. 250 ff).

if true, as in some measure a confirmation of the law of distribution of velocities."[29] This is a rather curious statement since all observational evidence at that time indicated that the uniform-temperature law is *not* true. Of course the only experimental data available was for the atmosphere, where it was not evident how to disentangle the effects of differential heat input at the top and bottom of the imaginary column from the effect of gravity. Until the discovery of the isothermal layer (tropopause) by TEISSERENC DE BORT around 1900, it was generally thought that there is a uniformly linear decrease of temperature with height, and MAXWELL's theory (as reinforced by BOLTZMANN) provided the main support for the contention that this decrease is to be attributed entirely to the fact that more heat is supplied at the bottom of the atmosphere than at the top.

In 1867 began the correspondence with P. G. TAIT leading to the concept of "MAXWELL's Demon."[30] MAXWELL used this device to show that the Second Law of Thermodynamics cannot be an absolute law of nature, since one can conceive of violating it by sorting out individual molecules into fast and slow categories. Thus the Second Law, according to MAXWELL, "has only a statistical certainty"[31]—it is valid only as long as we consider very large numbers of molecules which we cannot deal with individually.

It must not be assumed that "statistical" here implies randomness at the molecular level, for it is crucial to the operation of the MAXWELL Demon that he be able to observe and predict the detailed course of motion of a single molecule. This point is made clear by MAXWELL in his *Theory of Heat*:

> ... in adopting this statistical method of considering the average number of groups of molecules selected according to their velocities, we have abandoned the strict kinetic method of tracing the exact circumstances of each individual molecule in all its encounters. It is therefore possible that we may arrive at results which, though they fairly represent the facts as long as we are supposed to deal with a gas in mass, would cease to be applicable if our facilities and instruments were so sharpened that we could detect and lay hold of each molecule and trace it through all its source.[32]

This statement comes near the beginning of the chapter in which the Demon makes his first public appearance, and is obviously intended to lay the groundwork for the discussion that follows. For MAXWELL it is our *knowledge* of the world that

[29] MAXWELL, 1867 paper reprinted in BRUSH, *Kinetic Theory*, **2** (see p. 85); further discussion in *Nature* **8**, 527, 753 (1873). For a direct proof without *assuming* a MAXWELL distribution see C. TRUESDELL, *Mathematical Aspects of the Kinetic Theory of Gases*, Notas de Matemática Fisica, Vol. 3, Instituto de Matemática, Univ. Federal do Rio de Janeiro, 1973 (see Chapter IX).

[30] TAIT to MAXWELL, 6/12/67 and subsequent correspondence, at Cambridge University. For those readers not familiar with the voluminous secondary literature on MAXWELL's Demon, the article by MARTIN J. KLEIN, *Amer. Sci.* **58**, 84 (1970) is especially recommended. Some interesting aspects of the subject are revealed in a paper by EDWARD E. DAUB, *Stud. Hist. Phil. Sci.* **1**, 213 (1970).

[31] MAXWELL's "Catechism on Demons," published in C. G. KNOTT, *Life and Scientific Work of Peter Guthrie Tait* (Cambridge, Eng.: Cambridge University Press, 1911), 214–215. According to KNOTT, this is in an "undated letter, which must have been written about this time," *i.e.* shortly after MAXWELL's letter to TAIT of 11 December 1867 in which the Demon idea is first introduced (*ibid.* 213–214).

[32] J. C. MAXWELL, *Theory of Heat* (London, 7th ed. 1883), 308–309.

is statistical, not the world itself; and in fact he flatly states that we should not suppose that the masses, for example, of hydrogen molecules have a statistical distribution of which we only observe the average; on the contrary he thinks that "the equality which we assert to exist between the molecules of hydrogen applies to each individual molecule, and not merely to the average of groups of millions of molecules."[33]

While MAXWELL's Demon is generally cited in connection with the possibility of violating the Second Law of Thermodynamics, it seems equally important to note that by making the *mixing* of different molecules the fundamental irreversible process, MAXWELL has really strengthened the concept of irreversibility, especially for those who seek molecular explanations for all phenomena. In this context it was only a short step (though not a trivial one) to BOLTZMANN's identification of entropy with disorder, and the idea that irreversibility is simply a tendency for things to get more chaotic.

MAXWELL's first explicit suggestion of a connection between irreversibility and randomness is found not in his discussion of the Demon but in a letter to the editor of the *Saturday Review*, 13 April 1868. In an earlier letter (7 April 1868) MAXWELL had commented on an article in the April 4 issue on "Science and Positivism" discussing CARO's treatment of "the doctrine of the gradual conversion of all kinds of energy into the form of heat, and the ultimate uniform distribution of temperature over all matter." In reply to a request for further information, MAXWELL wrote that the tendency for a gas to acquire a statistical distribution of velocities is an irreversible operation similar to process in which black and white balls are "jumbled together" in a box: "the operation of mixing is irreversible."[34] In contrast to the previous examples of "statistical" interpretations of the Second Law, the mixing is attributed not to the natural deterministic motions of the balls left to themselves, but to an external agent. From the viewpoint of an observer who sees the balls but not the external agent, their motion is random.

But are molecules in a gas really moving randomly? In his lecture on "Molecules" to the British Association meeting at Bradford in 1873, MAXWELL noted LUCRETIUS' hypothesis that the atoms "deviate from their courses at quite uncertain times and places, thus attributing to them a kind of irrational free will, which on his materialistic theory is the only explanation of that power of voluntary action of which we ourselves are conscious."[35] But MAXWELL rejected the materialistic view, which would make all motions cyclic if such randomness were not present, while maintaining that the motions of individual molecules are deterministic: "As long as we have to deal with only two molecules, and have all the data given us, we can calculate the result of their encounter." In our conception of molecules, "we leave the world of chance and change, and enter a region where everything is certain and immutable." It is only because we lack the necessary data that we must use the statistical method in dealing with a gas containing a large number of molecules.

[33] *Ibid.* 329.

[34] Letters held in the Pattison Collection, Bodleian Library, Oxford University; I thank Dr. THOMAS SIMPSON for providing copies.

[35] J. C. MAXWELL, *Nature* **8**, 437 (1873); *Phil. Mag.* [4] **46**, 453 (1873); *Pop. Sci. Monthly* **4**, 276 (1874); *Papers* **2**, 361 (quotations from p. 373). *Cf.* MAXWELL's poem cited above, note 1, this section.

Yet by the time he delivered the Bradford address MAXWELL was already beginning to move away from this position in expounding his ideas to nonscientists. In February 1873 he had read an essay to a faculty discussion club at Cambridge University on the question, "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?"[36] MAXWELL suggested that "recent developments of Molecular Science seem likely to have a powerful effect on the world of thought" by calling attention to the distinction between the Dynamical and the Statistical kinds of knowledge. While the emphasis is still on the epistemological side of this distinction, there is a significant shift in MAXWELL's conception of what really does happen at the molecular level when he writes: "Our free will at the best is like that of Lucretius's atoms—which at quite uncertain times and places deviate in an uncertain manner from their course." Here he stands against the "Determinist" who asserts that some cause other than the Ego determines the result of every action. In any case the doctrine that "from like antecedents follow like consequents" is of little use in a world where antecedents can never be established with sufficient precision, and we know that frequently a small error in the data leads to a large error in the result. Thus a pragmatist must renounce determinism.

In his correspondence with HERBERT SPENCER later the same year, MAXWELL stated that he had used the word "agitation" for the deviation of the actual velocity of an individual molecule from the mean velocity of the group in order to avoid the connotation of "rhythm." SPENCER was surprised that MAXWELL had rejected his notion that molecular motion is rhythmic, and was not much inclined to incorporate statistical notions into his own philosophy.[37]

Further evidence of the drift of MAXWELL's thinking may be found in his 1875 lecture to the Chemical Society of London, in which he remarked:

> The peculiarity of the motion called heat is that it 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.[38]

That this irregularity is essential to irreversibility was explicitly recognized in MAXWELL's article "Atom" for the *Britannica*:

> The constancy and uniformity of the properties of the gaseous medium is the direct result of the inconceivable irregularity of the motion of agitation of its molecules. Any cause which could introduce regularity into the motion of agitation, and marshal the molecules into order and method in their evolutions, might check or even reverse that tendency to diffusion of matter, motion, and energy, which is one of the most invariable phenomena of nature, and to which Thomson has given the name of the dissipation of energy.[39]

[36] CAMPBELL & GARNETT, *op. cit.* (note 1), 434. Similar views were expressed in MAXWELL's 1871 lecture on experimental physics, in his *Papers*, **2**, 241.

[37] DAVID DUNCAN, *Life and Letters of Herbert Spencer* (New York: Appleton, 1809), **2**, 161–163; letters from MAXWELL to SPENCER, 17 December 1873, and SPENCER to MAXWELL, 30 December 1873, at Cambridge University.

[38] MAXWELL, *Nature* II, 357 (1875); see *Papers* **2**, 436 for quotation.

[39] *Encyclopedia Britannica* (Edinburgh, 8th ed.) **3**, 36 (1875). See *Papers*, **2**, 462 for quotation.

This seems to me a stochastic as opposed to a statistical explanation of irreversibility, though MAXWELL himself does not point out the distinction.

In another article, "Diffusion," written for the *Britannica*, MAXWELL again emphasized that molecular motion is "irregular."[40] He also discussed the question of whether diffusion leads to an irreversible increase of entropy. This was a crucial point in the development of a general theory of irreversibility, going beyond the special case of heat flow. MAXWELL observed that the answer depends on whether the gases which interdiffuse are the same, or whether they are different and can be separated by a reversible process. In the first case there is no entropy increase, but in the second there is. But how can we be sure that two gases are really the same? This is the famous "GIBBS paradox" and MAXWELL's discussion is probably influenced by that of GIBBS though he does not mention him.[41] MAXWELL's conclusion goes beyond GIBBS, for he points out that it is quite possible that we might mix two gases which we *thought* were identical, and later discover that they could be separated by a reversible process; in this case we would have to correct the entropy-increase assigned to the original mixing from zero to a positive value. But this means that entropy is not an observable property of the system itself but depends on our knowledge about the system:

> Dissipated energy is energy which we cannot lay hold of and direct at pleasure, such as the energy of the confused agitation of molecules which we call heat. Now, confusion, like the correlative term order, is not a property of material things in themselves, but only in relation to the mind which perceives them.

So once again MAXWELL draws back from the position that molecular motions are random in themselves, giving in the process a remarkable anticipation of the modern "information theory" interpretation of entropy.

MAXWELL's critique of the attempts of BOLTZMANN, CLAUSIUS, SZILY and others to reduce the Second Law to a purely mechanical principle is well known and is cited here only for the sake of completeness, and to reiterate that his own interpretation of the Second Law in most of these remarks is statistical rather than stochastic.[42] While BOLTZMANN and HELMHOLTZ later revived the attempts to find mechanical analogies for thermodynamics in their papers on monocyclic systems in the 1880's, both recognized that the irreversibility aspect of the Second Law had to be based on statistical rather than purely mechanical foundations.[43]

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[40] *Encyclopedia Britannica*, 9th ed., **7**, 214 (1878); see *Papers*, **2**, 628 for quotation.

[41] J. W. GIBBS, *Elementary Principles in Statistical Mechanics* (New York: Scribner, 1902), 206–207; reprinted in *The Collected Works of J. Willard Gibbs* (New Haven: Yale University Press, 1948; New York: Dover Pubs., 1960), **2**. See also GIBBS, *Trans. Conn. Acad.* **3**, 108 (1875), *Works*, **1**, 55, esp. p. 167. (This paper is discussed in section 5, below.)

[42] KNOTT, *op. cit.* (note 31), 115–116; *Nature* **17**, 257, 278 (1878); *Papers*, **2**, 660 (see esp. 669–671).

[43] HELMHOLTZ published at least three statements (1882, 1885, and 1886) to the effect that heat is random molecular motion, that entropy is a measure of disorder, and that irreversibility is not an inherent property of nature but is due to our inability to reverse atomic motions. See his *Wissenschaftliche Abhandlungen* (Leipzig: Barth, 1895), **2**, 972, **3**, 209, 593.

5. Boltzmann's Statistical Theory of Entropy

LUDWIG BOLTZMANN is usually credited with establishing the connection between randomness and irreversibility, though much of BOLTZMANN's early work was anticipated or stimulated by the publications of MAXWELL.[1] In one of his first papers BOLTZMANN attempted to reduce the Second Law of Thermodynamics to the mechanical principle of least action, but did not pay special attention to the aspect of irreversibility.[2] However, this attempt did lead him in 1871 to introduce a statistical distribution function for molecular positions,[3] based on his own earlier generalization of MAXWELL's distribution to cases where forces are present.[4] Thus, as EDWARD DAUB has pointed out, BOLTZMANN successfully used probability concepts in the reduction of the Second Law to mechanics, but this reduction was not fruitful since "it failed to evoke ideas which were not contained in the laws which it explained"[5] and in particular it did not deal with the problem of irreversibility.

A major breakthrough came in 1872 with BOLTZMANN's paper "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen", which despite its bland title is one of the most important and influential works in the entire history of kinetic theory.[6] The introductory paragraph comes very close to postulating that molecular motions are random, arguing that the "most irregular" [*regellosesten*] events, "when they occur in the same proportions, give the same average value," hence we can observe "completely definite laws of behavior of warm bodies."[7] But when BOLTZMANN proceeds to his mathematical derivations involving the distribution function f, he always refers to this as giving the *number* of molecules having some specified velocity or other characteristic quantity.[8] The transition from a stochastic back to a statistical approach occurs in the following sentences:

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[1] S. G. BRUSH, *Amer. J. Phys.* **30**, 269 (1962); *Arch. Hist. Exact Sci.* **4**, 145 (1967); *Dict. Sci. Biog.* **2**, 260 (1970).

[2] BOLTZMANN, *Sitzungsberichte, K. Akademie der Wissenschaften, Wien, Mathematisch-Naturwissenschaftliche Klasse* [this journal will be cited as *Wien. Ber.* in the sequel] **53**, 195 (1866); reprinted in *Wissenschaftliche Abhandlungen von Ludwig Boltzmann*, hrsg. F. HASENÖHRL (Leipzig: Barth, 1909; reprint, New York: Chelsea Pub. Co., 1968), I, 9 [this collection will be cited as *Wiss. Abh.*].

[3] L. BOLTZMANN, *Wien. Ber.* **63**, 712 (1871); *Wiss. Abh.* **I**, 288.

[4] L. BOLTZMANN, *Wien. Ber.* **58**, 517 (1868), **63**, 397 (1871); *Wiss. Abh.* **I**, 49, 237.

[5] EDWARD E. DAUB, *Isis* **60**, 318 (1969).

[6] L. BOLTZMANN, *Wien. Ber.* **66**, 275 (1872); *Wiss. Abh.* **I**, 316; English trans. in S. G. BRUSH, *Kinetic Theory*, **2** (Oxford & New York: Pergamon Press, 1966), 88.

[7] Quoted from my translation, *op. cit.*, except that *regellos* has been translated as "irregular" instead of "random" so as not to prejudice the issue; BOLTZMANN presumably could have chosen the word *zufällig* if he had wanted to approximate the meaning that is conveyed in English by "random."

[8] For detailed discussion of the derivation of the H-theorem see BOLTZMANN's *Vorlesungen über Gastheorie*, I. Teil (Leipzig: Barth, 1896); English trans. by S. G. BRUSH, *Lectures on Gas Theory* (Berkeley: University of California Press, 1964), or RICHARD C. TOLMAN, *The Principles of Statistical Mechanics* (London & New York: Oxford University Press, 1938), Part One. Most of the abbreviated derivations given in modern textbooks are quite unsatisfactory, as I discovered some years ago in teaching a course covering this subject.

If one does not merely wish to guess a few occasional values of the quantities that occur in gas theory, but rather desires to work with an exact theory, then he must first of all determine the probabilities of the various states which a given molecule will have during a very long time, or which different molecules will have at the same time. In other words, one must find the number of molecules out of the total number whose states lie between any given limits.[9]

BOLTZMANN assumes that in the initial state, each direction of the molecular velocity is equally probable, and that the distribution function does not depend on the space coordinates. (Thus heat flow due to an externally imposed temperature gradient, the most important example of an irreversible processs in the earlier discussions reviewed in this paper, is excluded.) He then asserts that the number of collisions in time τ between pairs of molecules in which the two molecules have kinetic energies between x and $x+dx$, and between x' and $x'+dx'$, before the collision, and the first molecule has kinetic energy between ξ and $\xi+d\xi$ after the collision, is given by the expression[10]

$$dn = \tau f(x, t)\, dx \cdot f(x', t)\, dx'\, d\xi \cdot \psi(x, x', \xi)$$

where $\psi(x, x', \xi)$ depends on the nature of the collision and the force law. There are only three independent variables since conservation of total kinetic energy is assumed, $x+x' = \xi+\xi'$.

Thus, without any discussion BOLTZMANN assumes (as did MAXWELL in his 1867 paper) that there is no correlation between the two molecules before the collision so that the joint distribution can be written as a product of the single-molecule distributions.

Each such collision will reduce by one the number of molecules having kinetic energy x; thus the rate of change of $f(x, t)$ will depend on the integral of the above expression for dn over all permitted values of the other energies x' and ξ. A corresponding expression is then written down for the increase in $f(x,t)$ due to collisions in which one molecule acquires energy x after the collision, so that the net change in f is given by an equation of the form

$$F(x, t+\tau)\, dx = f(x, t)\, dx - \int dn + \int d\nu.$$

After some transformations, the expression for $\int d\nu$ is reduced to

$$\int d\nu = \tau\, dx \int_0^\infty \int_0^{x+x'} f(\xi, t)\, f(x+x'-\xi, t)\, \psi(\xi, x+x'-\xi, x)\, dx'\, d\xi$$

The function ψ must then be proved to satisfy certain properties corresponding to permutations of the variables x, x' and ξ for inverse collisions; BOLTZMANN has to assume at this point that the force between two point-particles is a function of their distance and acts in the direction of the line of centres, and that action and reaction are equal. The result is that f satisfies the integro-differential equation

$$\frac{\partial f(x, t)}{\partial t} = \int_0^\infty \int_0^{x+x'} \left[\frac{f(\xi, t)}{\sqrt{\xi}} \frac{f(x+x'-\xi, t)}{\sqrt{x+x'-\xi}} - \frac{f(x, t)}{\sqrt{x}} \frac{f(x', t)}{\sqrt{x'}}\right] \sqrt{x x'}\, \psi(x, x', \xi)\, dx'\, d\xi.$$

[9] My translation, in *Kinetic Theory*, **2**, 90.

[10] The factor τ was omitted by a misprint in Eq. (2), p. 96 of my translation.

This is in fact the famous "BOLTZMANN equation" which is widely used as the basis for solving problems of kinetic theory, plasma physics, and solid state physics— though it is derived originally here in a somewhat unfamiliar form because energies rather than velocities have been taken as the variables, and of course the terms corresponding to spatial non-uniformity and external forces are omitted.

From the BOLTZMANN equation it follows immediately that MAXWELL's distribution,

$$f(x,t) = C\sqrt{x}\,e^{-hx},$$

represents an equilibrium state in the sense that one gets $\partial f(x,t)/\partial t = 0$ by direct substitution. That is about as far as MAXWELL himself was able to go in justifying his distribution function: he could argue plausibly that once this state had been attained, subsequent collisions would not change it. But BOLTZMANN could now set himself a more ambitious task: suppose $f(x,t)$ is not initially MAXWELLIAN (but still, for the moment, subject to the conditions mentioned above); prove that it will inevitably tend toward the MAXWELL function.

For this purpose BOLTZMANN had the brilliant inspiration (probably the result of educated guesses based on his previous work with entropy formulae, combined with some trial-and-error work) to define a functional

$$E = \int_0^\infty f(x,t)\left\{\log\left[\frac{f(x,t)}{\sqrt{x}}\right] - 1\right\} dx.$$

This, believe it or not, is the BOLTZMANN "H-function," written in terms of energy rather than velocity; the actual use of the letter H was still two decades in the future.

By a procedure familiar to students of kinetic theory but of little interest to others, BOLTZMANN then computed the time-derivative of E using the expression derived earlier for $\partial f(x,t)/\partial t$, and found that

$$\frac{dE}{dt} \leqq 0$$

where the equality sign holds only when f is the Maxwell distribution.[11] This is Boltzmann's H-theorem.

The quantity E, when evaluated for the MAXWELL-BOLTZMANN form of the distribution function f, is the same (within a constant factor) as the expression BOLTZMANN had previously found for the "well-known integral $\int dQ/T$."[12] The proof

[11] *Ibid.*, 116. The last step in the derivation deserves to be recorded here because of its similarity to an equation used later by PLANCK: dE/dt is equal to an integral over the expression

$$\log\left(\frac{ss'}{\sigma\sigma'}\right)(\sigma\sigma' - ss').$$

If it is not the case that $ss' = \sigma\sigma'$ (corresponding to the Maxwell distribution) then either $ss' > \sigma\sigma'$ or $ss' < \sigma\sigma'$. "In the first case, $\log(ss'/\sigma\sigma')$ is positive but $\sigma\sigma' - ss'$ is negative, and in the second case the converse is true; in both cases the product $\log(ss'/\sigma\sigma')$ $(\sigma\sigma' - ss')$ is negative. ... Therefore E must necessarily decrease."

[12] L. BOLTZMANN, *Wien. Ber.* **63**, 712 (1871); *Wiss. Abh.* I, 288. It has been argued that under certain circumstances the H-theorem does not imply the entropy principle (*e.g.* in shearing flow): see C. TRUESDELL, *J. Rational Mech. Anal.* **5**, 55 (1956), § 50.

of the H-theorem has therefore "prepared the way for an analytical proof of the second law in a completely different way from those previously investigated" and in particular will allow a proof that this integral is negative for irreversible processes—previous work had only attempted to show that the integral is zero for reversible cyclic processes.

So far the H-theorem applies only to the special case of a dilute monatomic gas of point atoms interacting with central forces, in which only binary collisions need be considered, and for cases where external forces and spatial non-uniformities are absent. BOLTZMANN now has his work cut out for him: to remove these restrictions one by one, so as to establish the molecular basis of the Second Law for the most general case possible. He takes the first step in this direction in the last section of the same paper, by considering a system of polyatomic molecules (still assuming central forces between the molecules), but is able to complete the proof of the H-theorem only for the case of diatomic molecules which interact like elastic spheres. (He never did give a completely satisfactory treatment of polyatomic molecules.)

There was an interval of three years between BOLTZMANN's completion of his 1872 paper and the next one on this subject, read to the Vienna Academy in October 1875. During this interval BOLTZMANN was occupied with experimental work on electrical problems (stimulated in part by MAXWELL's electromagnetic theory) and developed a theory of elastic aftereffects. But he now returned to his unfinished business, and tackled the problems of generalizing the proof of thermal equilibrium to systems in which external forces are present. This involved first a detailed proof of the integro-differential equation for f, which had been written down without proof in the 1872 paper and used to compute transport coefficients, more or less by analogy with MAXWELL's 1867 theory. Then followed a proof of the H-theorem by routine manipulations similar to those of the 1872 paper. The conclusion was that in spite of the action of external forces, each direction of the molecular velocity is equally probable, and in each spatial element the velocity distribution is the same as it would be for a gas of the same density and temperature on which no external forces act. The effect of external forces consists only in causing the density of the gas to vary from one place to another in the manner already known from the laws of hydrostatics.[13]

BOLTZMANN's conclusion clearly implied the theorem, stated earlier by MAXWELL, that the temperature is the same throughout a vertical column of gas. It was this theorem that soon attracted the criticisms of BOLTZMANN's colleague JOSEF LOSCHMIDT, and led BOLTZMANN, in his defense of it, toward a clearer physical interpretation of the relation between molecular motion and irreversibility.

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[13] L. BOLTZMANN, *Wien. Ber.* **72,** 427 (1875); *Wiss. Abh.* **II,** 1.

In 1887, H. A. LORENTZ pointed out that there is a gap in BOLTZMANN's proof of the H-theorem for polyatomic molecules, due to the fact that in collisions between non-spherical molecules, inverse collisions may not exist. BOLTZMANN admitted the defect and showed that the damage could be repaired by constructing a cycle of collisions that would still produce the same effect; hence this objection was not a serious challenge to the validity of the theorem. See H. A. LORENTZ, *Wien. Ber.* **95,** 115 (1887), reprinted in his *Collected Papers* (The Hague: M. Nijhoff, 1934–39), **6,** 74; L. BOLTZMANN, *Wien. Ber.* **95,** 153 (1887); *Wiss. Abh.* **III,** 272. For further discussion and diagrams of the collisions in question see TOLMAN, *op. cit.* (note 8), 119–120.

The term "reversibility paradox" was invented by PAUL and TATIANA EHRENFEST in 1907 for an argument which they attributed to LOSCHMIDT.[14] But before LOSCHMIDT published his very brief remark on the reversal of molecular motions, subsequently elaborated on by BOLTZMANN, the paradox had been discussed extensively by MAXWELL with his friends TAIT and THOMSON. MAXWELL'S first letter to TAIT on how his Demon could violate the Second Law, dated 11 December 1867, has a pencilled addition which reads: "Very good. Another way is to reverse the motion of every particle of the Universe and to preside over the unstable motion thus produced." According to TAIT's biographer C. G. KNOTT, the addendum is by WILLIAM THOMSON, but to me it looks more like TAIT'S handwritting.[15]

In his letter to the editor of the *Saturday Review*, 7 April 1868, MAXWELL said that the materialist believes that if every motion in the world were accurately reversed, everything would run backwards, water would collect out of the sea and run up the rivers, all living things would regress from the grave to the cradle, and so forth—but that our experience of irreversible processes leads us to expect that no such thing would happen.[16] Similar thoughts were expressed in MAXWELL'S letter to STRUTT (later Lord RAYLEIGH) in 1870.[17]

The culmination of this discussion (of which only fragmentary records survive) was THOMSON'S paper "On the kinetic theory of the dissipation of energy," published in 1874.[18] THOMSON drew a distinction between "abstract dynamics" which is perfectly reversible, and "physical dynamics" which is not. Like MAXWELL, he associated the hypothesis that life processes are governed by abstract dynamics with materialism, which he of course rejected. While speculation about the reversal of life processes is "utterly unprofitable," THOMSON thought that consideration of the consequences of reversal of the motion of inanimate matter could clarify the theory of energy dissipation. For this purpose he invoked first an army of MAXWELL Demons, with instructions to turn back selected molecules as they reach an interface between hot and cold regions of a gas. He showed that without changing the pressure, the Demons can either maintain a temperature difference in the presence of diffusion, or create a temperature difference where none existed before.

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[14] P. & T. EHRENFEST, *Phys. Zeits.* **8**, 311 (1907), reprinted in PAUL EHRENFEST'S *Collected Scientific Papers*, ed. M. J. KLEIN (New York: Interscience/Amsterdam: North-Holland, 1959), 146: *Enc. math. Wiss.* **IV** (2 II, 6) (1912) reprinted in EHRENFEST'S *Papers*, 213; English trans. by M. J. MORAVCSIK, *The Conceptual Foundations of the Statistical Approach in Mechanics* (Ithaca, N. Y.: Cornell University Press, 1959). See also MARTIN J. KLEIN, *Paul Ehrenfest*, **1** (Amsterdam: North-Holland/New York: American Elsevier, 1970), Chap. 6; HANNELORE BERNHARDT, *NTM, Z. f. Gesch. Naturwiss., Tech. Med.* **4** (1) 35 (1967).

[15] C. G. KNOTT, *Life and Scientific Work of Peter Guthrie Tait* (Cambridge University Press, 1911), 213–214. I thank Dr. C. W. F. EVERITT for providing a photocopy of the original letter preserved at Cambridge University.

[16] Bodleian Library, Oxford, Pattison MSS (copy supplied by Dr. THOMAS SIMPSON).

[17] R. J. STRUTT, *Life of John William Strutt, Third Baron Rayleigh* (London: Arnold, 1924; reprint with additions by J. N. HOWARD, Madison, Wisc.: University of Wisconsin Press, 1968), 47.

[18] WILLIAM THOMSON, *Proc. Roy. Soc. Edinburgh* **8**, 325 (1874), reprinted in S. G. BRUSH, *Kinetic Theory*, **2**, 176.

But the most important part of THOMSON's discussion does not involve the MAXWELL Demon at all. He simply supposes that, starting from an initial unequal distribution of temperature, we allow diffusion to occcur until after a finite time interval the temperature is very nearly equal throughout the gas, and then instantaneously reverse the motion of each molecule.

> Each molecule will retrace its former path, and at the end of a second interval of time, equal to the former, every molecule will be in the same position, and moving with the same velocity, as at the beginning; so that the given unequal distribution of temperature will again be found, with only the difference that each particle is moving in the direction reverse to that of its initial motion.

While it might appear that this process is contrary to the principle of dissipation of energy, THOMSON points out, first, that if the reversed motion continues, there will be an "instantaneous subsequent commencement of equalization," so that the unequal distribution of temperature will be short-lived. Second, if we looked at a gas in thermal equilibrium, there would be no way to pick out the particular arrangement that could evolve into a nonequilibrium state if the velocities were reversed. It is true that if any gas be left for a sufficiently long time in a perfectly rigid vessel with no external influences, it will inevitably happen that, for example, more than 90% of the energy will be in one half of the vessel. But the probability of this happening at any particular time is enormously smaller than the probability of a more or less equal distribution. The odds against an unequal distribution become even greater if the gas interacts with an external heat reservoir.

To clinch the argument (and to give precise meaning to MAXWELL's statement that the validity of the Second Law is a "statistical certainty") THOMSON calculated the probability that in a jar containing 2×10^{12} molecules of oxygen and 8×10^{12} molecules of nitrogen, all of the oxygen molecules are found in a specified part of the jar whose volume is 1/5 of the whole: "The number expressing the answer in the Arabic notation has about 2,173,220,000,000 of places of whole numbers."

While THOMSON's explanation of irreversibility is statistical, it is not stochastic; there is no question of any fundamental randomness at the atomic level. In this connection it may be recalled that THOMSON's main objection to DARWIN's theory of evolution was that it was based on randomness rather than purposeful divine guidance.[19]

* * *

Before turning to the more famous discussion of the reversibility paradox by LOSCHMIDT and BOLTZMANN, we must mention a frequently-quoted remark of J. WILLARD GIBBS, first published in 1875. At the beginning of his memoir "On the equilibrium of heterogeneous substances," GIBBS placed CLAUSIUS' 1865 formula-

[19] WILLIAM THOMSON, *Rept. Brit. Ass. Adv. Sci.* **41**, lxxxiv (1871), reprinted in his *Popular Lectures and Addresses*, **2** (London: Macmillan, 1894), 132; see also G. BASALLA *et al.*, eds., *Victorian Science* (Garden City, N. Y.: Anchor Books, 1970), 128. THOMSON seems to have derived his objection from that of JOHN HERSCHEL, *Physical Geography of the Globe* (Edinburgh, 1861), 12. *Cf.* K. E. VON BAER, *Augsburger Allgemeine Zeitung*, **130**, 1986 (1873), English trans. in *Darwin and his Critics*, ed. D. L. HULL (Cambridge, Mass.: Harvard University Press, 1973), 416. On dislike for randomness as a source of neo-LAMARCKIAN hypotheses see E. F. GERSON, *Synthesis* **1** (2), 13 (1973).

tion of the two laws of thermodynamics ("Die Energie der Welt ist constant, Die Entropie der Welt strebt einem Maximum zu"), and based his own formulation of thermodynamics on energy and entropy as fundamental quantities.[20] But when he discussed the entropy increase associated with the mixing of two gases, GIBBS noted that this increase depends on the existence of a *difference* between the gases; for if they were identical in all respects, there would be no change in total entropy before and after mixing (the so-called "GIBBS paradox"). But, he speculated, it is conceivable that two gases might be "absolutely identical in all the properties (sensible and molecular)which come into play while they exist as gases either pure or mixed with each other, but which should differ in respect to the attractions between their atoms and the atoms of some other substances, and therefore in their tendency to combine with such substances." In this case their mixing *would* involve an entropy increase but there would be no way to distinguish this situation experimentally from the mixing of two identical gases. (As MAXWELL was to point out a little later in the passage already mentioned in the previous section, this means that entropy is not strictly an observable quantity but depends on knowledge or theories possessed by the observer.) So, GIBBS concluded,

> when such gases have been mixed, there is no more impossibility of the separation of the two kinds of molecules in virtue of their ordinary motions in the gaseous mass without any especial external influence, than there is of the separation of a homogeneous gas into the same two parts into which it has once been divided, after these have once been mixed. In other words, the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability.[21]

As can be seen from the preceding context (usually ignored when the last sentence is quoted[22]) GIBBS' suggestion that the Second Law has only statistical validity is not based on a specific atomic-kinetic model of matter, nor was it intended to apply to most situations in which energy is dissipated. His paper was entirely phenomenological in nature, and it is rather misleading to drag it into discussions of the statistical interpretation of irreversibility.

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According to textbook accounts, following the EHRENFESTS,[23] the reversibility paradox was first proposed by JOSEF LOSCHMIDT in discussions with BOLTZMANN

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[20] J. WILLARD GIBBS, *Trans. Conn. Acad.* 3, 108 (1875), reprinted in *The Collected Works of J. Williard Gibbs* (New Haven: Yale University Press, 1948), 1, 55; German trans. by W. OSTWALD, *Thermodynamische Studien* (Leipzig: Engelmann, 1892); French trans. by G. MATISSE, *L'Equilibre des substances hétérogènes* (Paris: Gauthier-Villars, 1919).

[21] GIBBS, *Collected Works*, 1, 167.

[22] L. BOLTZMANN, citation below, section 6, note 20; P. S. EPSTEIN, in *A Commentary on the Scientific Writings of J. Willard Gibbs*, ed. A. HAAS (New Haven: Yale University Press, 1936), 2, 59 (see p. 106, 112).

[23] *Op. cit.* (note 14), esp. *Conceptual Foundations*, 14–15; TOLMAN, *op. cit.* (note 8), 152; K. F. HERZFELD, *Kinetische Theorie der Wärme* (Braunschweig: Vieweg, 1925) (MÜLLER-POUILLETS Lehrbuch der Physik, Elfte Aufl., Dritter Band, Zweite Hälfte), 353–354; D. TER HAAR, *Elements of Statistical Mechanics* (New York: Rinehart, 1954), 340 f; M. J. KLEIN, *op. cit.* (note 14), 102; M. KAC, *Probability and Related Topics in Physical Sciences* (New York: Interscience, 1959), 61; H. BERNHARDT, *op. cit.* (note 14).

in Vienna, and was published in a series of papers in 1876–77.[24] There is also an embellishment of the story circulating among modern physicists, to the effect that when LOSCHMIDT told BOLTZMANN that his system would simply run backwards if all the molecular velocities were reversed, BOLTZMANN replied, "Well, *you* just try to reverse them!"[25] Actually LOSCHMIDT's published discussion of the paradox consists of only a single sentence in the context of a long discussion of the problem mentioned above in connection with the equilibrium under gravitational forces. LOSCHMIDT did not accept MAXWELL's conclusion[26] that a column of gas would have constant temperature throughout, but claimed instead that thermal equilibrium was possible without equality of temperature. In this way he hoped to demonstrate that the heat death of the universe is not inevitable. He claimed that the second law could be correctly formulated as a mechanical principle without reference to the sequence of events in time; he thought he could thus "destroy the terroristic nimbus of the second law, which has made it appear to be an annihilating principle for all living beings of the universe; and at the same time open up the comforting prospect that mankind is not dependent on mineral coal or the sun for transforming heat into work, but rather may have available forever an inexhaustible supply of transformable heat."[27]

After proposing a model which supposedly violated MAXWELL's constant-temperature theorem, LOSCHMIDT noted that in any system "the entire course of events will be retraced if at some instant the velocities of all its parts are reversed."[28] His application of this reversibility principle to the validity of the Second Law was somewhat obscurely stated, but BOLTZMANN (perhaps as a result of private discussions) quickly got the point and published a reply,[29] in which he gave a thorough discussion of the reversibility paradox, as well as a 50-page paper elaborating his theory of molecular motion in gases subject to external forces.[30]

BOLTZMANN conceded that it is impossible to prove that the entropy of a system always increases without taking account of the initial conditions. Moreover, such a

[24] J. LOSCHMIDT, *Wien. Ber.* **73**, 128, 366 (1876), **75**, 287, **76**, 209 (1877). RENÉ DUGAS. *La Théorie Physique au sens de Boltzmann* (Neuchatel: Griffon, 1959). 158–184. For LOSCHMIDT's earlier ideas on this subject see E. E. DAUB, *Stud. Hist. Phil. Sci.* **1**, 213 (1970).

[25] See *e.g.* J. E. MAYER, in *Isotopic and Cosmic Chemistry*, ed. H. CRAIG *et al.*, (Amsterdam: North-Holland, 1964), 10; KAC, *op. cit.* (note 23).

[26] See note 29, section 4. In the second paper of his series, LOSCHMIDT mentioned the continuing controversy about MAXWELL's conclusion in England, See R. C. NICHOLS, *Nature* **11**, 486 (1875); J. J. MURPHY, *Nature* **12**, 26 (1875); R. C. NICHOLS, *Nature* **12**, 67 (1875); S. H. BURBURY, *Nature* **12**, 107 (1875).

[27] LOSCHMIDT, *op. cit.* (note 24), first paper, p. 135; see also the third paper, p. 293.

[28] „Denn wenn wir im obigen Falle, nachdem eine zur Herstellung des stationären Zustandes vollkommen ausreichende Zeit τ verstrichen ist, plötzlich die Geschwindigkeiten aller Atome in entgegengesetzter Richtung annehmen, so würden wir damit am Beginne eines Zustandes stehen, dem ebenfalls der Charakter des Stationären zuzukommen scheinen würde." *Ibid.*, 139.

[29] L. BOLTZMANN, *Wien. Ber.* **75**, 67 (1877); *Wiss. Abh.* **II**, 116; English trans. in BRUSH, *Kinetic Theory*, **2**, 188.

[30] L. BOLTZMANN, *Wien. Ber.* **74**, 503 (1876); *Wiss. Abh.* **II**, 55. BOLTZMANN discussed the gravitational-equilibrium problem again in the second section of his paper in *Wien. Ber.* **78**, 7 (1878); *Wiss. Abh.* **II**, 250. Much later he dismissed the "ausgebreitete Literatur" on this problem in a few lines, with a footnote citing nine authors; see L. BOLTZMANN & J. NABL, *Enc. Math. Wiss.* **V**, (i) 516 (1905).

statement cannot be true for *all* initial conditions since it is certainly possible to find a special initial state (obtained by reversing all the molecular velocities of a system which has evolved from a non-uniform state toward a uniform one) for which succeeding states will have lower entropy. The crucial point, however, is that "since there are infinitely many more uniform than non-uniform distributions, the number of states which lead to uniform distributions after a certain time t_1 is much greater than the number that lead to non-uniform ones, and the latter are the ones that must be chosen, according to LOSCHMIDT, in order to obtain a non-uniform distribution at t_1."[31]

There follows the very important remark:

> One could even calculate, from the relative numbers of the different state distributions, their probabilities, which might lead to an interesting method for the calculation of thermal equilibrium.

Following up his own suggestion, BOLTZMANN developed soon afterward his statistical method for calculating equilibrium properties, based on the relation between entropy and probability articulated in this discussion of the reversibility paradox.[32] So it appears that LOSCHMIDT has followed the tradition of FRANCISCUS LINUS and C. H. D. BUYS-BALLOT by stimulating a major advance in gas theory through his criticism.[33]

It is curious that BOLTZMANN, who was apparently unaware of THOMSON's discussion published three years earlier,[34] chose exactly the same example to illustrate the statistical nature of irreversibility: he notes that a spontaneous decrease in entropy is "extraordinarily improbable and can be considered impossible for practical purposes; just as it may be considered impossible that if one starts with oxygen and nitrogen mixed in a container, after a month one will find chemically pure oxygen on the lower half and nitrogen in the upper half, although according to probability theory this is merely very improbable but not impossible."

Finally, BOLTZMANN mentioned

> a peculiar consequence of Loschmidt's theorem, namely that when we follow the state of the world into the infinitely distant past, we are actually just as correct in taking it to be very probable that we would reach a state in which all temperature differences have disappeared, as we would be in following the state of the world into the distant future ... If perhaps this reduction of the second law to the realm of probability makes its application to the entire universe appear dubious, yet the laws of probability theory are confirmed by all experiments carried out in the laboratory.

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[31] *Ibid.*, 192.

[32] L. BOLTZMANN, *Wien. Ber.* **76**, 373 (1877).

[33] LINUS criticized BOYLE's theory of gas pressure, forcing BOYLE to defend it and present quantitative evidence which he had not done earlier. BUYS-BALLOT criticized CLAUSIUS' kinetic theory (based on the assumption that the molecules have negligible size) by pointing out that the theory predicted diffusion at a rate much more rapid than is observed; this led CLAUSIUS to introduce his "mean free path" concept (attributing a finite but small diameter to his molecules). See BRUSH, *Kinetic Theory*, **1**, 4–5, 24–25.

[34] He did however cite it much later in his review article with NABL, *op. cit.*

If the world is to end in a Heat Death, it must have begun in a Heat Birth. Having got to this point BOLTZMANN, it would seem, is now prepared to give an interpretation of the "recurrence paradox" but in fact he did not do so until challenged by ZERMELO nearly 20 years later (see below).

BOLTZMANN was still unaware of another paradox: he has reached his conclusions by reasoning from what he calls "probability theory" while assuming that exact deterministic laws still apply to molecular motions and collisions.

* * *

In 1877 BOLTZMANN, inspired according to his own account by the reasoning involved in his reply to LOSCHMIDT's reversibility objection, proposed a new method for determining the state of thermal equilibrium of a system. This method, which is applicable to any system, not only gases, consists in enumerating all possible "complexions"—for example, all the ways in which a given total amount of energy can be distributed among a specified number of molecules—and assuming that the probability of a macroscopic state is proportional to the number of corresponding molecular complexions. (Each complexion is assigned equal probability.) The entropy of the system is directly related to this probabilty, and in the later forms of the theory is simply proportional to the logarithm of the probability, $S = k \log W$ in modern notation. The state of thermal equilibrium is then asserted to be the one that has the greatest probability.

Using this relation between entropy and probability, BOLTZMANN proposed the following interpretation of the physical significance of the Second Law:

> In most cases the initial state will be very improbable; the system passes from this through ever more probable states, reaching finally the most probable state, that is the state of thermal equilibrium.[35]

Thus irreversibility is simply a tendency to go from less probable to more probable states.

ERNEST NAGEL has suggested that "perhaps the greatest triumph of probability theory within the framework of nineteenth-century physics was BOLTZMANN's interpretation of the irreversibility of thermal processes."[36] Others might feel that this triumph was achieved only at the cost of muddying the concept of "probability." There has been considerable confusion about how one should interpret the quantity denoted by W, which PLANCK and others have called the "thermo-

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[35] L. BOLTZMANN, *Wien. Ber.* **76**, 373 (1877); *Wiss. Abh.* II, 164.

According to EDWARD DAUB, the success of BOLTZMANN's reduction of the Second Law to probability considerations rested on his application of the results to the thermodynamics of diffusion. However, it appears to me that in the paper in question, published in 1878, BOLTZMANN refers to his earlier statistical calculation of entropy only to justify his assumption that the entropy of a mixture is the sum of the entropies of its components, and that the rest of the argument does not involve probability in any essential way. See E. E. DAUB, *Isis* **60**, 318 (1969).

[36] E. NAGEL, in *International Encyclopedia of Unified Science*, ed. O. NEURATH, **1** (6) (Chicago: University of Chicago Press, 1939, 1955), 355 [=p. 13 in the separate edition of this number, *Principles of the Theory of Probability*].

dynamic probability" of a state of the system.[37] It cannot be determined by a routine combinatorial procedure as BOLTZMANN's remark seems to imply, for two reasons. First, in classical physics the particles of the system are permitted a continuous range of positions and velocities, so the actual "number" of complexions is infinite for any macroscopically defined state. If one tries to convert W into a proper fraction by dividing it by the *total* number of complexions, the result will be $W=0$ unless the "total" is limited in some special way. Second, since the entropy S is a function of temperature, either the number of complexions corresponding to a state, or the total number, or both, must depend on temperature. Yet temperature is a derived average property of the system from the viewpoint of kinetic theory, not part of its original specification, so it is not clear how this temperature-dependence can be consistently introduced into the model. If one takes too literally the frequently-made assertion that the equilibrium thermodynamic state of the system corresponds to the overwhelming majority of all microstates accessible at a given temperature (or fixed total energy), one would end up with the result $W=1$ for *all* temperatures. As J. R. PARTINGTON remarked, "thermodynamic states" are what FRANCIS BACON would have called "Idols of the Market Place."[38]

As this is an account of 19th-century theories, not a monograph on the foundations of statistical mechanics from the modern viewpoint, I shall not attempt to resolve these difficulties, but can only call attention to them. Within the framework of classical physics, it seems to have been generally agreed that one must retreat from the formula for "absolute entropy," $S=k \log W$, and talk only about the relative entropy of two states: $S-S'=k \log W/W'$. According to GIBBS and FOWLER, it is possible to justify such a formula by regarding the system under consideration as a random sample from a very large number of systems with certain hypothetical properties. Quantum physics, however, does give a procedure for computing absolute entropy, and does provide some justification for BOLTZMANN's postulated relation between entropy and probability.[39]

From this perspective it is of great interest that BOLTZMANN himself evaded the problem of counting a continuum of microstates by assuming first that each molecule can have only a finite number of energy-values,

$$0,\ \varepsilon,\ 2\varepsilon \quad \text{up to} \quad p\varepsilon$$

and then afterwards letting $\varepsilon \to 0$ and $p \to \infty$ in such a way that $p\varepsilon$ approaches a finite number, the specified total energy of the system. BOLTZMANN wrote that

[37] MAX PLANCK, *The Theory of Heat Radiation*, trans. by M. MASIUS from the 2d ed. (1913) of *Waermestrahlung* (New York: Dover Pubs., 1959), 120. A comprehensive discussion of the problem may be found in R. H. FOWLER, *Statistical Mechanics* (Cambridge, Eng.: Cambridge University Press, 2d ed. 1936), 189–207.

[38] J. R. PARTINGTON, *An Advanced Treatise on Physical Chemistry*, **1** (London: Longmans, Green and Co., 1949), 293. Despite his professions of skepticism PARTINGTON ends up by accepting BOLTZMANN's relation between entropy and probability.

[39] FOWLER, *op. cit.*, 203, 230. J. W. GIBBS, *Elementary Principles of Statistical Mechanics* (1902), Chapter XV; see *The Collected Works of J. Willard Gibbs* (New Haven: Yale University Press, 1948), **2**, 203. R. C. TOLMAN, *The Principles of Statistical Mechanics* (London: Oxford University Press, 1938), 562. A. I. KHINCHIN, *Mathematical Foundations of Statistical Mechanics*, trans. from Russian by G. GAMOW (New York: Dover Pubs., 1949), 139–145. P. G. WRIGHT, *Contemp. Phys.* **11**, 581 (1970).

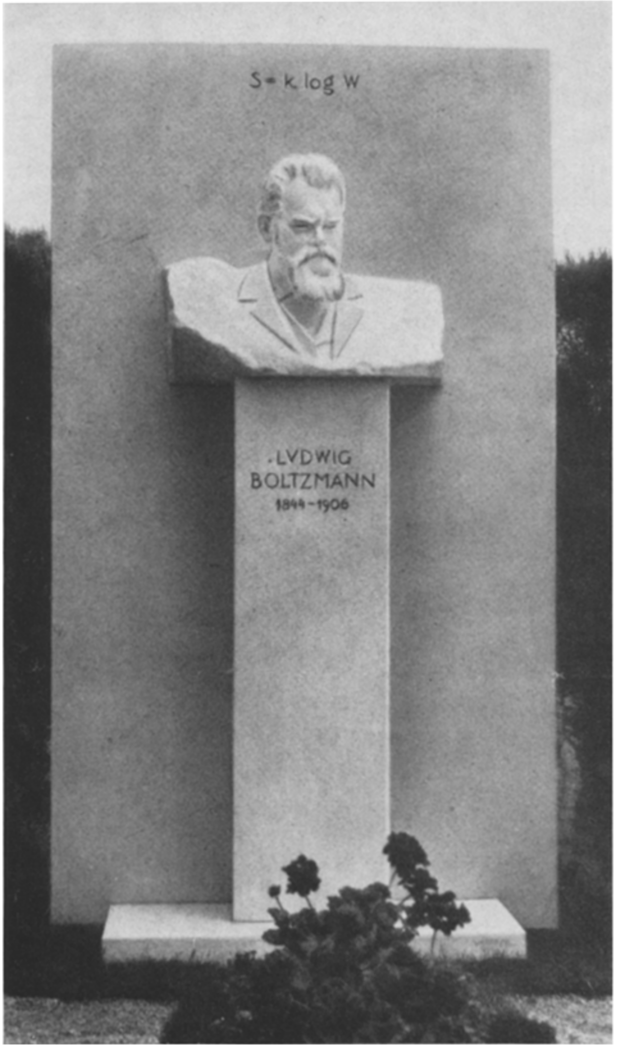

Fig. 1

"this fiction corresponds to no realizable mechanical problem, but rather a problem which is mathematically much easier to treat, and which reduces at once to the problem we have to solve" when the indicated limits are taken.[40] But it is evident from this why BOLTZMANN's method could so easily be taken over into quantum theory by MAX PLANCK in 1900.

While BOLTZMANN's relation between entropy and probability was invoked to account for irreversibility (a tendency to go from "less probable" to "more probable" states) and thus suggested a physical meaning for the qualitative direction-

[40] *Wien. Ber.* **76**, 376.

ality of time, it also had the effect of *eliminating* time as a variable in the description of the system. The process of seeking the most probable state becomes a mathematical exercise which may have no relation at all to the physical time-development of the system. It is also a process in which the deterministic dynamics of molecular collisions is replaced by random choice, for in carrying out the calculation of state probabilities, Boltzmann assumed "that the kinetic energy of each individual molecule is determined, as it were, by a lottery, which is selected completely impartially from a collection of lotteries which contains all the kinetic energies that can occur in equal numbers."[41] This is the key to the power of the new method: it is not restricted to special molecular models for which collision mechanisms can be worked out in detail; it can be used for any system, including (with slight modifications) those governed by quantum mechanics, for which the spectrum of possible energies is known.

In one sense Boltzmann has simply come back to Maxwell's 1860 viewpoint, in which a velocity distribution was derived directly from probabilistic arguments without regard to the particular molecular processes that might bring it about. That viewpoint was considered inadequate at the time by Maxwell and others, and it had to be justified by calculations based on special molecular models, culminating in Boltzmann's H-theorem of 1872. By 1877 Boltzmann was able to build on a solid foundation of molecular theory, so his method is not quite as simple-minded as the above summary makes it appear. For example, he is well aware that one cannot just postulate equal probabilities for all kinetic energies of a molecule (even though the postulate may be conditioned on fixed total energy for all molecules in the system) for that leads to the wrong answer in three-dimensional problems. Instead one has to insert a weighting factor, equivalent to the assumption that the distribution is uniform with respect to the momentum variable rather than the energy variable. The proof of this fact goes back to the theory of molecular collisions, reminding us that the emancipation from Newtonian dynamics is not yet complete.[42]

The extent of Boltzmann's acceptance of a probabilistic view of molecular behavior at this time is circumscribed by his comments on what is now known as the "ergodic hypothesis." As I have already discussed the history of this subject in some detail,[43] I need only summarize here the main point: the assumption that one can simply average over all possible states of a system in order to calculate its thermodynamic properties could be justified by proving that the system will eventually pass through all those states before returning to its initial condition. If that

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[41] *Wien. Ber.* **76**, 382.

[42] *Ibid.*, 404. For the proof of the required theorem Boltzmann referred to H. W. Watson's *Treatise on the Kinetic Theory of Gases* (Oxford: Clarendon Press, 1876), 12. A further indication that the use of the new method is a little tricky is provided by Boltzmann's reference to O. E. Meyer's attempt to apply it in his textbook on kinetic theory [*Die Kinetische Theorie der Gase* (Breslau, 1877), 262]. According to Boltzmann, Meyer made several mathematical errors that somehow cancel out in such a way that he gets the desired Maxwell distribution law as a result. For further discussion see Boltzmann, *Wien. Ber.* **78**, 7 (1878); Meyer, *Ann. Physik* [3] **10**, 296 (1884); Boltzmann, *Ann. Physik* [3] **11**, 529 (1880).

[43] S. G. Brush, *Arch. Hist. Exact Sci.* **4**, 145 (1967); *Transp. Theory and Stat. Phys.* **1**, 287 (1971). H. Bernhardt, *NTM, Z. Gesch. Naturwiss., Tech., Med.* **8**, (1) 13 (1971).

were the case, then it would be clearly understood that the use of probabilistic methods is only a matter of convenience, and does not contradict the belief that the behavior of the system is ultimately deterministic on the molecular level. The use of an "ensemble" of systems (as we now say, following the terminology of J. WILLARD GIBBS) is an equivalent but more abstract (and often more convenient way of applying statistical calculations to deterministic systems. Thus in his review of MAXWELL's paper "On Boltzmann's theorem on the average distribution of energy in a system of material points,"[44] BOLTZMANN wrote:

> There is a difference in method between Maxwell and Boltzmann, inasmuch as Boltzmann measures the probability of a condition by the time during which the system possesses this condition on the average, whereas Maxwell considers innumerably similarly constituted systems with all possible initial conditions. The ratio of the number of systems which are in that condition to the total number of systems determines the probability in question.[45]

(In 1894 BOLTZMANN repeated these two definitions of probability, but by this time he had made considerable use of the definition attributed to MAXWELL.[46])

In 1886 BOLTZMANN discussed his interpretation of the Second Law in less technical terms, in a lecture at the Vienna Academy. After stating that he would make no attempt to rescue the universe from the heat death, he said that the molecular interpretation of the Second Law depends on the law of large numbers, in the same way that the number of "so-called voluntary [*freiwilligen*] acts, marriages at a certain age, crimes, and suicides" remains constant in a sufficiently large population.[47] The implication of this statement is a little ambiguous, but it certainly suggests that molecular motions are individually at least unpredictable if not inherently random. But in any case BOLTZMANN's statistical interpretation of the Second Law has not yet reached its final stage, since toward the end of this lecture he remarks:

> Since a given system of bodies can never by itself pass into an absolutely equally probable state, but rather always into a more probable one, so it is not possible to construct a system of bodies which, after passing through different stages, periodically returns to its original state: a perpetuum mobile.[48]

6. Molecular Disorder

The problem of irreversibility was revived in England in the 1890's as part of a more general discussion of the conditions for validity of the equipartition theorem.

[44] J. C. MAXWELL, *Trans. Cambridge Phil. Soc.* **12**, 547 (1879); *Papers*, II, 713.

[45] L. BOLTZMANN, *Ann. Physik Beibl.* **5**, 403 (1881); *Wiss. Abh.*, **II**, 582; English trans. in *Phil. Mag.* [5] **14**, 299 (1882).

[46] L. BOLTZMANN, *Rept. Brit. Ass. Adv. Sci.* **64**, 102 (1894); *Wiss. Abh.* **III**, 521.

[47] L. BOLTZMANN, *Populäre Schriften* (Leipzig: Barth, 1905) 25 (quotation translated from p. 34).

[48] *Ibid.*, 48. *Cf.* BOLTZMANN's letter to ERNST MACH, 1893: "... Ich glaube, dass die Unmöglichkeit des perpetuum mobile ein reiner Erfahrungssatz ist, der in noch nicht geprüften Fällen jeden Augenblick durch die Erfahrung widerlegt werden kann. Dass ich dies bezüglich des s. g. 1. Hauptsatzes für enorm unwahrscheinlich, bezüglich des 2. Hauptsatzes für nicht einmal zu unwahrscheinlich halte, ist eine rein subjektive unbeweisbare Meinung." K. D. HELLER, *Ernst Mach* (Wien: Springer, 1964), 27.

Initially P. G. TAIT and others had tried simply to improve MAXWELL's proof of his velocity distribution law.[1] There were a few attempts to give quantitative descriptions of the approach to equilibrium for special models.[2] G. J. STONEY, in 1887, rediscovered the reversibility paradox and concluded that the Second Law of Thermodynamics is not a "true dynamical law," but also suggested that time itself does not exist apart from events in the universe,[3] thus anticipating in a rudimentary way BOLTZMANN's suggestion made a decade later. Also at this time there was published the interesting suggestion of L. GOUY that BROWNIAN movement may be considered as a visible violation of the Second Law, though this idea did not attract much attention until POINCARÉ mentioned it in 1900.[4]

Most of these scientists were either unaware of BOLTZMANN's earlier discussion of the same problems, or relcutant to plow through his lengthy memoirs. Instead, they preferred to discuss general principles on the basis of simple arguments and short calculations. Finally BOLTZMANN himself entered the debate, visiting a meeting of the British Association in 1894 and later replying to some of the letters in *Nature*. The outcome of BOLTZMANN's participation in this discussion was the concept of "molecular disorder," first pinpointed by S. H. BURBURY (1831–1911), a barrister who had turned to mathematics after becoming deaf; BURBURY was responding to a deceptively simple criticism of kinetic theory published by E. P. CULVERWELL (1855–1931) of Trinity College, Dublin. Another stimulus for BOLTZMANN was a brief exchange with MAX PLANCK concerning the assumptions involved in KIRCHHOFF's derivation of the state of thermal equilibrium in a gas. For some reason these penetrating discussions, which indicated a need for assuming randomness in mechanistic theories, have been overshadowed by the somewhat more exotic debate on the "recurrence paradox," although this involved some of the same issues. It is also of interest to follow the development of MAX PLANCK's ideas on randomness and irreversibility in radiation theory, in the years just before he arrived at the quantum theory. (These topics will be discussed in sections 7 & 8.)

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In 1890 E. P. CULVERWELL published a "Note on Boltzmann's Kinetic Theory of Gases, and on Sir W. Thomson's Address to Section A, British Association, 1884."[5] Using the example of a system of particles interacting with forces proportional to their distance, he claimed that (since in this case the motion is strictly periodic) it is impossible to prove *in general* that a set of particles will tend to the

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[1] P. G. TAIT, *Proc. Roy. Soc. Edinburgh*, **13**, 21 (1884); *Trans. Roy. Soc. Edinburgh* **33**, 65 (1886), reprinted in *Phil. Mag.* [5] **21**, 343 (1886) and in his *Scientific Papers* (Cambridge University Press, 1890–1900), **II**, 124.

[2] P. G. TAIT, *Trans. Royal Soc. Edinburgh* **33**, 65 (1887), Part V. RAYLEIGH, *Phil. Mag.* [5] **32**, 424 (1891), reprinted in his *Scientific Papers* (New York: Dover Pubs., 1964), **III**, 473. S. H. BURBURY, *Phil. Trans. Roy. Soc. London* **183 A**, 407 (1892).

[3] G. J. STONEY, *Proc. Roy. Soc. Dublin* **5**, 448 (1887); *Phil. Mag.* [5] **23**, 544 (1887).

[4] L. GOUY, *J. de Physique* [2] **7**, 561 (1889), quoted by BRUSH, *Arch. Hist. Exact Sci.* **5**, 1 (1968) (see p. 12); H. POINCARÉ, *Rapports Cong. Int. Phys., Paris*, 1900, **1**, 1 (Paris: Gauthier-Villars, 1900); *Congress of Arts and Science, Universal Exposition, St. Louis*, 1904 (Boston: Houghton, Mifflin & Co., 1905), **I**, 604. H. v. HELMHOLTZ, *Vorlesungen über Theorie der Wärme*, hrsg. F. RICHARZ (Leipzig: Barth, 1903), 260.

[5] E. P. CULVERWELL, *Phil. Mag.* [5] **30**, 95 (1890).

"Boltzmann configuration, in which the energy is equally distributed among all the degrees of freedom." Appealing to the reversibility principle, he asserted that "for every configuration which tends to an equal distribution of energy, there is another which tends to an unequal distribution." In order to explain the fact that temperature equilibrium does nevertheless occur, he suggested that there must be some kind of interaction of molecules with the aether. After all, "one of the most important purposes for which the existence of the aether is required," he wrote, is heat transfer leading to thermal equilibrium. Conversely, CULVERWELL asserted that if a system of particles in a vessel *not* containing aether did in fact attain equilibrium in all cases, "it would be to my mind a proof that the ultimate particles of matter did not individually obey those laws which they are known to obey when collected in the enormous numbers which compose the bodies for which the laws of motion have been experimentally proved." Explaining his views further at a British Association meeting the same year, he argued that molecular motions might be inherently irreversible, yet obey the NEWTONIAN laws of motion when taken *en masse*.[6] It is also conceivable, he thought, that there might be periodic deviations from NEWTON's laws, "the period being so short that no observations could detect it."

Responding to the widespread interest in such problems, the British Association appointed a committee, consisting of J. LARMOR and G. H. BRYAN, to investigate "the present state of our knowledge of Thermodynamics, specially with regard to the Second Law," and BRYAN gave the first report on this subject at the 1891 meeting.[7] This dealt primarily with the attempts of CLAUSIUS, SZILY, HELMHOLTZ and BOLTZMANN to reduce the Second Law to purely mechanical principles,[8] though even here BRYAN suggested that it might be necessary to introduce some kind of statistical element in order to justify certain assumptions in the proofs. He insisted that "A system which is irreversible will certainly not be monocyclic according to the definition of Helmholtz," so, to the extent that this viewpoint is valid, "it seems necessary to accept the principle of degradation of energy as a statistical property and not as a dynamical principle."[9] BRYAN discussed one of BOLTZMANN's mechanical models of a monocyclic system[10] but criticized BOLTZMANN's attempt to extend the dynamical analogy to irreversible processes, on the grounds that BOLTZMANN's argument holds only if friction is present, which is "not allowable in forming a purely dynamic analogue of the properties of heat."[11]

As for CULVERWELL's critique, BRYAN noted, first, that systems with forces directly proportional to the distance (what we now call the "harmonic oscillator") have special properties as regards periodicity, and conclusions based on such systems cannot be generalized to other systems. (This seems to miss the point,

[6] E. P. CULVERWELL, *Rept. Brit. Ass. Adv. Sci.* **60**, 744 (1890).

[7] G. H. BRYAN, *Rept. Brit. Ass. Adv. Sci.* **61**, 85 (1891).

[8] For further discussion and references on mechanical analogies for the Second Law of Thermodynamics see G. H. BRYAN, *Enc. Math. Wiss.* **5**, (1, 3), 73 (1903), § IV; L. DE BROGLIE, *La Thermodynamique de la particule isolée* (Paris: Gauthier-Villars, 1964); I. FENYES, Z. Physik **132**, 140 (1952). M. J. KLEIN, *Centaurus* **17**, 58 (1972).

[9] BRYAN, *op. cit.*, 107, 108.

[10] L. BOLTZMANN, *Vorlesungen über Maxwell's Theorie der Elektrizität und des Lichtes* (Leipzig: Barth, 1891), I, 8–23.

[11] BRYAN, *op. cit.*, 109.

that a *general* theorem can't be valid if it fails in a particular case.) Second, although it is true that a conservative dynamical system is always reversible, the reversed motion is often "dynamically unstable in the highest degree" as is readily discovered when one tries to ride a bicycle backwards. The slightest disturbance of the reversed motion leads to the MAXWELLIAN "special state" again, rather than to the original ordered state. (A similar argument has frequently been used in attempts to dispose of the reversibility paradox.[12] Yet it is not really a question of whether an exact reversal of molecular motions is *physically* possible, but rather whether in deriving the H-theorem one may group together direct and inverse collisions, making certain assumptions about their probability of occurrence. For this reason I will make a distinction, below, between the "reversibility paradox" and the "reversibility objection to the H-theorem.")

BRYAN's first report did not present any definite conclusions about the physical origin of irreversibility. He appealed to the example of mixing two different substances "in a minute state of subdivision"—after mixing them it is obviously impossible to separate them by simply stirring them up. For the same reason it is understandable how it *could* be proved on statistical grounds that heat cannot pass from a cold body to a hot one, but such an argument is admittedly not a proof. While BRYAN thought it possible that the presence of the aether will "facilitate the dissipation of energy" he defended the attempt to explain irreversibility *without* invoking the aether, on the grounds that such an attempt fulfills "what should be the highest object of scientific inquiry—namely, of helping us to 'judge the unknown from the known.'"[13]

The second part of BRYAN's report was presented at the Oxford meeting of the British Association in 1894, with an appendix by BOLTZMANN who attended this meeting. There is a review of the extensive literature on attempts to prove MAXWELL's distribution law for various systems, including the "test-cases" against the equipartition theorem proposed by WILLIAM THOMSON (now Lord KELVIN) in the 1890's. A short section on "BOLTZMANN's Minimum Theorem" is based on recent work of BURBURY (who introduced the letter H in 1890[14] for the functional which BOLTZMANN called E in 1872) and H. W. WATSON.[15] BURBURY was

[12] See BOREL's discussion quoted by R. DUGAS, *La Theorie Physique au sens de Boltzmann* (Neuchatel: Griffon, 1959), 186–87.

[13] BRYAN, *op. cit.*, 120. *Cf.* J. R. MAYER's opinion (1848), quoted by O. B. MATHIAS, *An Examination of the Evolution of the First Two Laws of Thermodynamics* (Dissertation, University of Kansas City, Kansas City, Missouri, 1962), from *Phil. Mag.* [4] **25**, 241 (1863)

[14] S. H. BURBURY, *Phil. Mag.* [5] **30**, 301 (1890). According to S. CHAPMAN [*Nature* **139**, 931 (1937)] this was the first use of the letter H instead of E. It has sometimes been suggested that H is intended as a capital Greek eta, but no definite evidence for this has ever come to my attention [see S. G. BRUSH, *Amer. J. Phys.* **35**, 892 (1967)].

In another paper in *Nature* **49**, 150 (1893), BURBURY calls this "Boltzmann's minimum function" and denotes it as B, but BRYAN, while retaining the phrase, went back to the letter H [G. H. BRYAN, *Rept. Brit. Ass. Adv. Sci.* **64**, 64 (1894); see p. 86]. BURBURY also calls it B in another paper, *Phil. Mag.* [5] **37**, 143 (1892).

Some further information about BURBURY is given by ROSS HESKETH, [London] *Times Higher Education Supplement*, 11 (20 April 1973). (I thank Professor E. A. MASON for this reference.)

[15] S. H. BURBURY **183**, 407 (1892); H. W. WATSON, *A Treatise on the Kinetic Theory of Gases* (Oxford: Clarendon Press, 2^d ed. 1893).

following the MAXWELLIAN 1860 tradition of using probability theory, explicitly treating the molecular coordinates as random variables, in contrast to the later MAXWELL-BOLTZMANN developments based on consideration of molecular collisions. But BURBURY also suggested that the process of redistribution of energy between the molecules may be effected by waves transmitted through the ether.

In conclusion, BRYAN wrote:

> The proof of the [Maxwell-Boltzmann distribution] law and the assumptions involved in it are fairly satisfactory for gases whose molecules collide with each other to a certain extent at random, but in a medium in which the molecules never escape from each other's influence the subject still presents very great difficulties.[16]

This is quite a fair summary of the state of the subject (even today) but it appears that BRYAN did not realize the full implications of his use of the word "random."

The discussion which followed the presentation of BRYAN's report was apparently concerned mainly with the problem of specific heats of gases. In response to various questions about the equipartition theorem, BOLTZMANN made a statement to the effect that he had primarily regarded the kinetic theory from the mathematical viewpoint, and while he had chosen his postulates in the light of the experimental data to be explained—for example, the specific heats of diatomic molecules, which could be accounted for by a model with five mechanical degrees of freedom—he did not feel obliged to prove that his theory was in agreement with *all* properties of gases.[17] In reply to G. F. FITZGERALD's objection that the equipartition theorem, if true, ought to apply to *everything* in the universe, including the aether, BRYAN indicated that BOLTZMANN thought this was still an open question, but BRYAN was willing to give his own opinion:

> In the absence of mutual action between the various solar systems, this would *not* be the only permanent distribution, nor would there be any tendency to assume such a distribution. If, however, the different solar systems were to collide with or encounter one another *at random* in such a way that transference of energy was liable to take place between any of the coordinates of any one system and any of the coordinates of any other system, the Boltzmann-Maxwell distribution *would* probably be unique and there would be a tendency to assume such a distribution as the ultimate result of a great number of encounters taking place.[18]

But BRYAN does not indicate that there is any conflict between the assumption of randomness and the assumption that one is dealing with a deterministic mechanical system.

The discussion in the columns of *Nature* soon turned to the problems of proving "BOLTZMANN's minimum theorem." CULVERWELL led off by criticizing a step in WATSON's proof, and then remarked: "I do not know Boltzmann's proof, but

[16] BRYAN, *op. cit.*, 98; this conclusion is quoted in the summary in *Nature*, **50**, 406 (1894).

[17] G. H. BRYAN, *Nature* **51**, 31, 152 (1894); E. P. CULVERWELL, *Nature* **51**, 78 (1894).

[18] G. H. BRYAN, *Nature* **51**, 152 (1894); G. F. FITZGERALD, *Nature* **51**, 221 (1895).

while I suppose it is all right, I find it very hard to understand how any proof can exist." Because of the reversibility of molecular motions, he thought it would be impossible to prove that dH/dt would be negative for all initial configurations, although possibly "by striking some kind of average" among configurations which approach the MAXWELLIAN state and those that recede from it (obtained by reversing velocities) the average value of dH/dt might be shown to be negative. He concluded by asking: "Will some one say exactly what the H-theorem proves?"[19]

CULVERWELL's modest inquiry seems to me to mark the transition from the "reversibility paradox" of the 1870's which—according to THOMSON's and BOLTZMANN's discussion—was resolved by a statistical but non-stochastic conception of molecular motions—and the more subtle "reversibility objection to the H-theorem." In the latter, but not in the former, attention is directed to identifying the stage in the proof of this particular theorem where irreversibility sneaks in. CULVERWELL isn't quite able to do this himself but he smells something.

BURBURY replied by stating that the proof of the H-theorem depends on the statement that

> If the collision coordinates be taken at random, then the following condition holds, viz.:—For any given direction of R [relative velocity vector of two colliding spheres] before collisions, all directions after collision are equally probable. Call that condition A.

But in the case of the reverse motion condition A is not fulfilled; hence the proof is not applicable. (In other words, MAXWELL's original assumption that the number of collisions is proportional to $n_1 n_2$ doesn't hold for reverse collisions.)

> Somebody may perhaps say that by this explanation I save the mathematics only by sacrificing the importance of the theorem, because I must (it will be said) admit that there are, after all, as many cases in which H increases as in which it diminishes. I think the answer to this would be that any actual material system receives disturbances from without, the effect of which, coming at haphazard, is to produce that very distribution of coordinates which is required to make H diminish. So there is a general tendency for H to diminish although it may conceivably increase in particular cases. Just as in matters political, change for the better is possible, but the tendency is for all change to be from bad to worse.[20]

It is this particular paper of BURBURY that BOLTZMANN himself cites as the origin of his "molecular disorder" assumption, before mentioning the earlier discussion with LOSCHMIDT; but it does of course throw some new light on the reversibility paradox too.[21] The need for a postulate of randomness did not clearly emerge from the *general* discussion of the statistical nature of the Second Law by MAXWELL, THOMSON, TAIT, LOSCHMIDT, and BOLTZMANN, but only in response to a detailed

[19] E. P. CULVERWELL, *Nature* **50**, 617 (1894).

[20] S. H. BURBURY, *Nature* **51**, 78 (1894).

[21] L. BOLTZMANN, *Vorlesungen über Gastheorie*, I. Teil (Leipzig: Barth, 1896); see English trans. by S. G. BRUSH, *Lectures on Gas Theory* (Berkeley: University of California Press, 1964), 40, 58.

technical criticism of the H-theorem by CULVERWELL, who must now be added to our list of worthy dissenters.[22, 23]

CULVERWELL did not quite get the point of BURBURY's new postulate, though he recognized that something new was being added to the theory which he characterized as "some amount of assumption as to an average state having been already attained."[24] BURBURY then restated his postulate that the coordinates are "taken at haphazard" with respect to each other even for molecules that have just collided (in analyzing the reversed collision). This assumption, he thought, was sufficient though perhaps not necessary for the proof and is "the most useful assumption, because the distribution of coordinates assumed to exist is that which would tend to be produced by any disturbances acting on the system from without."[25]

BRYAN, replying two weeks after BURBURY to CULVERWELL's question, missed the point in another way. He said that CULVERWELL's assumption about the reversed motion amounted to endowing his molecules "with the power of forethought and the prediction regarding their future state necessary to enable them to regulate their movements" whereas if the molecules "are allowed to take their own natural course, and nothing special is known about them," the only reasonable assumption to make is that which is conventionally made in proving the H-theorem, namely that the two molecules are uncorrelated before the inverse collision.[26] But in fact CULVERWELL's assumption had been nothing more than the validity of deterministic laws of motion, so that the implication of BRYAN's quoted phrase is either that the "natural course" of a molecule is random, or that it appears to be random because we don't know all its coordinates.

LARMOR's resolution of the problem was similar to the original discussion of THOMSON and BOLTZMANN:—the number of states which, on reversal, would return to an ordered state is small compared to the total number; and, moreover, if the reversed motion is continued the order will quickly disappear. But he was also willing to concede that "if the whole universe were thus reversed, the aberration would be permanent." However, he immediately ruled out this possibility by asserting that "the whole universe is a permanently dissipative system, and there is no question of a steady state being attained by it in measurable time."[27]

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[22] BOLTZMANN's closest approach to an independent discovery of the need for this hypothesis, which he cites in the same footnote in *Gastheorie*, is in the concluding pages of one of his replies to LOSCHMIDT, *Wien. Ber.* **78**, 7 (1878); *Wiss. Abh.* II, 250. The discussion there is more concerned with the relation between the excessively high kinetic energies of a single molecule and that of its neighbors as a source of statistical correlation, rather than with the correlation between two molecules in an inverse collision.

[23] To illustrate the technical nature of the objection it may be noted that WATSON, whose proof provoked CULVERWELL's original complaint, could not see why the value of H would necessarily be the same at the end of the reversed motion when the system has returned to its original state [but with reversed velocities], and argued instead that *because* the H-theorem is true, it could *not* have the same value. See H. W. WATSON, *Nature* **51**, 105 (1894).

[24] E. P. CULVERWELL, *Nature* **51**, 105 (1894).

[25] S. H. BURBURY, *Nature* **51**, 175 (1894).

[26] G. H. BRYAN, *Nature* **51**, 176 (1894), **52**, 29 (1895).

[27] J. LARMOR, *Nature* **51**, 152 (1894).

CULVERWELL, having digested the various responses to his challenge published by LARMOR, BURBURY, BRYAN, and WATSON,[20, 23, 26, 27] was now prepared to knock all the heads together. BRYAN's argument, as he pointed out, is no proof that H will decrease since it "depends on the previous assumption that the particles do 'naturally' tend to move in the desired way." WATSON, by stating that H decreases even when the system is *receding* from its equilibrium state, has given up the physical meaning of the H theorem. BURBURY still depends on an additional assumption which he has not yet stated very clearly (according to CULVERWELL) for the general case. CULVERWELL essentially agreed with LARMOR's interpretation, but improved it significantly with his own statement that if the proof of the H theorem "does not somewhere or other introduce some assumption about averages, probability, or irreversibility, it cannot be valid."[28]

Finally, on February 28, 1895, the British wranglers received an authoritative message from Vienna. BOLTZMANN, in a letter published in *Nature*, presented a discursive exposition of his answer to two questions: "(1) Is the Theory of Gases a true physical theory as valuable as any other physical theory? (2) What can we demand from any physical theory?" The second part of this letter[29] is a direct reply to CULVERWELL, in which BOLTZMANN reiterated his 1877 position that the Second Law is based on probability theory and can never be proved mathematically from dynamics alone. But while the casual reader might get the impression that BOLTZMANN is only repeating in simpler terms the view which he had already published before CULVERWELL raised his objections, there are some subtle changes. In particular, BOLTZMANN introduced a description of the "H-curve" (graph of H vs. time) in which he now asserted, contrary to what he had said in 1886,[30] that even if one starts from an initial state which "is not specially arranged for a certain purpose, but haphazard governs freely," the value of H must occasionally rise above its minimum value. While "the probability that H decreases is always greater than that it increases" it is also certain that H must *sometimes* increase. This does not disprove the H-theorem, he now says, but only illustrates its probabilistic nature. Unfortunately BOLTZMANN's use of the term "probability" is still ambiguous, and he does not state whether he agrees with BURBURY's interpretation.

BOLTZMANN concluded the letter with "an idea of my old assistant, Dr. Schuetz":

> We assume that the whole universe is, and rests for ever, in thermal equilibrium. The probability that one (only one) part of the universe is in a certain state, is the smaller the further this state is from thermal equilibrium; but this probability is greater, the greater is the universe itself. If we assume the universe great enough, we can make the probability of one relatively small part being in any given state (however far from the state of thermal equilibrium), as great as we please. We can also make the probability great that, though the whole universe is in thermal equilibrium, our world is in its present state....

[28] E. P. CULVERWELL, *Nature* **51**, 246 (1895).

[29] L. BOLTZMANN, *Nature* **51**, 413 (1895); *Wiss. Abh.* III, 535. (The first few paragraphs of the letter are quoted in my introduction to BOLTZMANN's *Lectures on Gas Theory*, English translation.)

[30] See note 44, section 5.

> If this assumption were correct, our world would return more and more to thermal equilibrium; but because the whole universe is so great, it might be probable that at some future time some other world might deviate as far from thermal equilibrium as our world does at present. Then the afore-mentioned H-curve would form a representation of what takes place in the universe. The summits of the curve would represent the world where visible motion and life exist.

In accordance with the "MATTHEW effect"[31] this idea was subsequently ascribed to BOLTZMANN rather than SCHUETZ.[32]

CULVERWELL, commenting on BOLTZMANN's letter, insisted that they were actually in agreement on the main point: a purely dynamical proof of the H-theorem is impossible, but it can be proved by making certain probabilistic assumptions. Though CULVERWELL is still somewhat vague on just what those assumptions are, he does give a helpful explanation of the paradox that "while there are as many configurations for which dH/dt is positive as there are for which it is negative" nevertheless H is much more likely to descend to its minimum value than to rise still higher. The point is that one should not "set off a configuration for which H increases against one for which it decreases, *although the values of H for each are different.*" He suggests the analogy of a tree turned upside down with an infinite number of branches passing through each point of the trunk. If you start from any point above the bottom, there are more paths leading down than up, since every upward branch finally turns downward; whereas if you start at the bottom you are more likely to choose a branch running upwards to the trunk. In this way it can be seen how, starting from any value of H above the minimum, dH/dt is more likely to be negative than positive.[33]

BURBURY developed his idea of random external disturbances a little more in two letters published in *Nature* in 1895. The thrust of these letters was to emphasize that his "condition A" (see above) is unlikely to be true for the reversed motion unless the gas is already in an equilibrium state, and that there is no particular reason that the condition will always be satisfied, even apart from reversals, in a system left to itself for an indefinite time free of external influences.[34] He did not specify the reason for his doubts, but in view of his later work in kinetic theory (or, anticipating BOLTZMANN's response) we might guess that he had in mind the possibility that two molecules cannot be completely uncorrelated before a collision if they have collided at some time in the past; and the magnitude of this effect would be greater in a dense gas. Thus the H-theorem, and perhaps other results of the kinetic theory, are valid only for rarified gases.[35]

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[31] ROBERT K. MERTON, *Science* **159**, 56 (1968).

[32] There is no reference to SCHUETZ in BOLTZMANN's later discussions of the idea; but he is mentioned by J. NABL, *Naturwiss. Runds.* **21**, 337 (1906).

[33] E. P. CULVERWELL, *Nature* **51**, 581 (1895). BOLTZMANN accepted the tree analogy in a somewhat different sense: see *Nature* **51**, 581 (1895); *Wiss. Abh.* **III**, 545.

[34] S. H. BURBURY, *Nature* **51**, 320, **52**, 104 (1895).

[35] S. H. BURBURY, *Nature* **52**, 316 (1895), *Proc. London Math. Soc.* **26**, 431 (1895); *Phil. Trans. Roy. Soc. London* **A 187**, 1 (1896); *Rept. Brit. Ass. Adv. Sci.* **66**, 716 (1896); *Proc. London Math. Soc.* **28**, 331 (1897), **29**, 225 (1898); *A Treatise on the Kinetic Theory of Gases* (Cambridge University Press, 1899), esp. p. 33: *Phil. Mag.* [5] **50**, 584 (1900).

BOLTZMANN conceded the force of this reasoning (which he was developing himself to some extent independently but obviously stimulated by the debate with the British) and admitted that the proof of the H-theorem is valid only if the mean free path of a molecule is very long compared to the average distance of two neighbouring molecules. In this case the assumption of external disturbances is not necessary.[36] BRYAN, enlarging on this suggestion, remarked that in the opposite case of liquids and solids where the molecules are crowded closely together, we know that the system can exist simultaneously in either of two states, hence the distribution cannot be unique, and it is just as well that we do not try to prove too much with the theorem. The same would be true for molecules immersed in a continuous ether. Yet we do know that solids and liquids obey the Second Law even if we don't know whether they obey the MAXWELL-BOLTZMANN distribution law; and this may simply be because BURBURY's "condition A" is always satisfied when we bring together a hot and a cold body which we can assume to have no initial statistical correlation.[37] BURBURY agreed with BRYAN that "contact with the refrigerator or with the reservoir, such as is supposed to take place in thermodynamics, is for this purpose a disturbance" which can bring about condition A.[38]

In the first volume of his *Vorlesungen über Gastheorie* BOLTZMANN adopted BURBURY's postulate, calling it the assumption that the state of the gas is "molecular disordered" [molekular-ungeordnet].[39] In addition to giving credit to BURBURY, he stated that KIRCHHOFF also made the assumption, although BOLTZMANN had criticized the way the assumption was used in the posthumous edition of KIRCHHOFF's lectures published by MAX PLANCK (see below). The following passage shows that BOLTZMANN recognized the importance of "condition A" as an *assumption* in gas theory, yet was not ready to go so far as to make it a *postulate* about molecular motions:

> That it is necessary to the rigor of the proof to specify this assumption in advance was first noticed in the discussion of my so-called H theorem or minimum theorem. However, it would be a great error to believe that this assumption is necessary only for the proof of this theorem. Because of the impossibility of calculating the positions of all the molecules at each time, as the astronomer calculates the positions of all the planets, it would be impossible without this assumption to prove the theorems of gas theory. The assumption is also made in the calculation of the viscosity, heat conductivity, etc. Also, the proof

[36] L. BOLTZMANN, *Nature* **52**, 221 (1895); *Wiss. Abh.* **III**, 546.

[37] G. H. BRYAN, *Nature* **52**, 244 (1895).

[38] BURBURY, *Nature* **52**, 316 (1895).

[39] BOLTZMANN, *Vorlesungen über Gastheorie*, I, 20–21 [the preface is dated September 1895]; see pp. 40–41 in the English translation. On the distinction between "molecular chaos" and the "*Stosszahlansatz*" assumption, see PAUL & TATIANA EHRENFEST, *The Conceptual Foundations of the Statistical Approach in Mechanics* (Ithaca: Cornell University Press, 1959), 40f; T. P. EGGARTER, *am. J. Phys.* **41**, 874 (1973). T. S. KUHN (private communication) has pointed out to me that BOLTZMANN's assumption is somewhat different from BURBURY's insofar as he wishes to *exclude* certain ordered states which would be expected to occur in a stochastic system. While this exclusion violates the meaning of a stochastic process, one could argue that it is consistent with the ordinary usage of the term "random" — "not ordered."

that the Maxwell velocity distribution is a possible one—i.e., that once established it persists for an infinite time—is not possible without this assumption. For one cannot prove that the distribution always remains molecular-disordered. In fact, when Maxwell's state has arisen from some other state, the exact recurrence of that other state will take place after a sufficiently long time.[40]

As can be seen from the last sentence of this quotation, BOLTZMANN is well prepared to meet the next attack on his H-theorem.

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7. The Recurrence Paradox

The notion that history repeats itself—that there is no progress or decay in the long run, but only a cycle of development that always returns to its starting point—has been inherited from ancient philosophy and primitive religion. It has been noted by some scholars that belief in recurrence, as opposed to unending progress, is intimately connected with man's view of his place in the universe, as well as with his concept of history. Starting, in some cases, from a pessimistic view of the present and immediate future, it denies the reality or validity of human actions and historical events by themselves; actions or events are real only insofar as they can be understood as the working out of timeless archetypal patterns of behavior in the mythology of the society. This attitude is said to be illustrated in classical Greek and Roman art and literature, where there is no consciousness of past or future, but only of eternal principles and values. By contrast the modern Western view, as a result of the influence of Christianity, is deeply conscious of history as progress toward a goal.[1] Nevertheless, the cyclical view has by no means died out, and its traces may have something to do with the persistent tendency to draw historical analogies and comparisons as well as the frequent revival of "oscillating universe" theories.[2]

[40] Quoted from my translation, *Lectures on Gas Theory*, 41–42; see also pp. 58–59 for a summary of the outcome of BOLTZMANN's discussion with the British physicists.

[1] E. MEYERSON, *Identity and Reality* (New York: Dover Pubs., 1962, trans. of the French ed. of 1926), Chap. VIII. A. REY, *Le Retour Éternel et la Philosophie de la Physique* (Paris: Flammarion, 1927). P. SOROKIN, *Social and Cultural Dynamics* (New York: American Book Co., 1937), **II**, Chap. 10. L. WHITE, *J. Hist. Ideas* **3**, 147 (1942). J. BAILLIE, *The Belief in Progress* (New York: Oxford University Press, 1950), § 10. M. ELIADE, *The Myth of the Eternal Return* (New York: Pantheon Books, 1954). M. CAPEK, *J. Phil.* **57**, 289 (1960) (discussion of 1896 MS. of C. S. PEIRCE). For evidence against the usual statement that the Greeks accepted ancient and Oriental cyclic views while Jews and Christians rejected them, see A. D. MOMIGLIANO, in *History and the Concept of Time*, ed. G. H. NADEL (Middletown, Conn.: Wesleyan University Press, 1966) [*History and Theory, Beiheft* 6], 1. Recent ideas are surveyed in the articles by G. J. WHITROW and others, in *The Study of Time*, ed. J. T. FRASER, F. C. HABER, & G. H. MÜLLER (New York: Springer, 1972).

[2] EDGAR ALLEN POE, *Eureka* (1848), reprinted in *Selected Prose, Poetry, and Eureka*, ed. W. H. AUDEN (New York: Holt, 1950), 483. J. DELEVSKY, in *Studies and Essays in the History of Science and Learning* (New York: Schuman, 1944), 375. E. J. ÖPIK, *The Oscillating Universe* (New York: New American Library, 1960). H. SCHMIDT, *J. Math. Phys.* **7**, 494 (1966). For the current cosmological literature see the compilations prepared by the Astronomisches Rechen-Institut Heidelberg, *Astronomy and Astrophysics Abstracts* (Berlin: Springer, 1969-), **1**-, subject category 162.

The suggestion that eternal recurrence might be proved as a theorem of physics, rather than as a religious or philosophical doctrine, seems to have occurred at about the same time to the German philosopher FRIEDRICH NIETZSCHE and the French mathematician HENRI POINCARÉ. NIETZSCHE encountered the idea of recurrence on his studies of classical philology, and again in a book by HEINE. It was not until 1881 that he began to take it seriously, however, and then he devoted several years to studying physics in order to find a scientific-sounding formulation of it.[3] POINCARÉ, on the other hand, was led to the subject by his attempts to complete POISSON's proof of the stability of the solar system, though he was also concerned with the difficulty of explaining irreversibility by mechanical models such as HELMHOLTZ's monocyclic systems.[4] POINCARÉ's theorem belongs to the history of theoretical physics, NIETZSCHE's speculations to the history of philosophical culture, and they are not usually discussed in the same context. Yet I find it necessary to consider them together since it was just at the end of the 19^{th} century that developments in science were strongly coupled to the philosophical-cultural background. Both NIETZSCHE and POINCARÉ were trying, though in very different ways, to attack the "materialist" or "mechanist" view of the universe.

NIETZSCHE's doctrine of the Eternal Return, as described in his book *Der Wille zur Macht* and elsewhere, has generally been treated by literary and philosophical commentators as a purely symbolic or metaphorical expression of his apocalyptic worldview. As ROSE PFEFFER wrote recently, "NIETZSCHE's theories and hypotheses have found no recognition and acceptance and have, on the whole, not been taken seriously by either scientists or philosophers."[5] Professor PFEFFER herself claims that the notion of eternal recurrence is of central importance in NIETZSCHE's philosophy, but she wishes to interpret the basic recurring units not as classical atoms but as quanta of energy: recurrence means only recurrence of "simultaneously occurring values of energy," not "configurations of simultaneously existing material, static, immutable elements." Thus NIETZSCHE is credited with having advanced a "dynamic world view" which "is in contrast to the mechanistic, materialistic principles of his time." I think a somewhat different conclusion will emerge if we interpret NIETZSCHE's effort as a qualitative anticipation of POINCARÉ's theorem.

NIETZSCHE's "proof" of the necessity of eternal recurrence (written during the period 1884–88 but not published until after his death in 1900) is as follows: "If the universe has a goal, that goal would have been reached by now" since the universe, he thinks, has always existed; the concept of a world "created" at some finite time in the past is considered a meaningless relic of the superstitious ages. He absolutely rejects the idea of a "final state" of the universe, and further remarks

[3] W. A. KAUFMAN, *Nietzsche: Philosopher, Psychologist, Antichrist* (Princeton: Princeton University Press, 1950), Chap. 11. C. ANDLER, *Nietzsche, sa Vie et sa Pensée* (Paris: Gallimard, 1958), **4**, Livre 2, Chap. I; Livre 3, Chap. I. O. BECKER, *Blättern für Deutsche Philosophie* **9**, 368 (1936), reprinted in his *Dasein und Dawesen: Gesammelte Philosophische Aufsätze* (Pfullingen: Verlag Neske, 1963), 41. J. STAMBAUGH, *Nietzsche's Thought of Eternal Return* (Baltimore: Johns Hopkins Press, 1972).

[4] H. POINCARÉ, *Compt. Rend. Acad. Sci. Paris* **108**, 550 (1889). According to G. H. BRYAN [*Rept. Brit. Ass. Adv. Sci.* **61**, 106 (1891)], POINCARÉ's critique is irrelevant because he assumed in effect that the temperature is equal to zero.

[5] R. PFEFFER, *Rev. Metaphysics* **19**, 276 (1965).

that "if, for instance, materialism cannot consistently escape the conclusion of a finite state, which WILLIAM THOMSON has traced out for it, then materialism is thereby refuted." He continues:

> If the universe may be conceived as a definite quantity of energy, as a definite number of centres of energy—and every other concept remains indefinite and therefore useless—it follows therefrom that the universe must go through a calculable number of combinations in the great game of chance which constitutes its existence. In infinity, at some moment or other, every possible combination must once have been realized; not only this, but it must have been realized an infinite number of times. And inasmuch as between every one of these combinations and its next recurrence every other possible combination would necessarily have been undergone, and since every one of these combinations would determine the whole series in the same order, a circular movement of absolutely identical series is thus demonstrated: the universe is thus shown to be a circular movement which has already repeated itself an infinite number of times, and which plays its game for all eternity.[6]

NIETZSCHE thought that his doctrine was not materialistic because materialism entailed the irreversible dissipation of energy and the ultimate heat death of the universe. But the discussion of POINCARÉ's theorem by POINCARÉ, ZERMELO, and BOLTZMANN showed that, on the contrary, it is precisely the mechanistic view of the universe that has recurrence as its inevitable consequence. Since ZERMELO and some other scientists believed that the second law must have absolute rather than merely statistical validity, they thought that the mechanistic theory was refuted by the "recurrence paradox."[7] The implication of NIETZSCHE's conclusion, as proved mathematically by POINCARÉ, is actually just the opposite of what he thought it should be: if there *is* eternal recurrence, so that the second law of thermodynamics cannot always be valid, then the materialist view (as represented by BOLTZMANN's interpretation) would be substantiated.

POINCARÉ's recurrence theorem was first published in his memoir "Sur le problème des trois corps et les équations de dynamique" which was awarded the prize of King Oscar II of Sweden on 21 January 1889.[8] POINCARÉ considered a mechanical system governed by a set of differential equations

$$\frac{dx_1}{dt} = X_1, \quad \frac{dx_2}{dt} = X_2, \ldots, \frac{dx_n}{dt} = X_n$$

where the $X_1 \ldots X_n$ are given functions of the variables $x_1 \ldots x_n$. For the case $n = 3$, (x_1, x_2, x_3) are the coordinates of a point P in space, and this point describes a cer-

[6] F. NIETZSCHE, *Der Wille zur Macht*, in his *Gesammelte Werke* (München: Musarion Verlag, 1926), **19**, Book 4, Part 3; English trans. by O. MANTHEY-ZORN in *Nietzsche, an Anthology of his Works* (New York: Washington Square Press, 1964), 90.

[7] See also F. WALD, *Die Energie und ihre Entwerthung* (Leipzig, 1889), 104. E. MACH, *Die Prinzipien der Wärmelehre* (Leipzig, 1896), 362. G. HELM, *Die Lehre von der Energie historisch-kritisch entwickelt* (Leipzig, 1887); *Grundzüge der mathematischen Chemie* (Leipzig, 1898). PIERRE DUHEM, *Traité d'Énergetique* (Paris: Gauthier-Villars, 1911). H. POINCARÉ, *Thermodynamique* (Paris, 1892); *Nature* **45**, 414, 485 (1892).

[8] *Acta Math.* **13**, 1 (1890), reprinted in *Oeuvres de Henri Poincaré* (Paris: Gauthier-Villars, 1952). **VII**, 262; English trans. of the section on the recurrence theorem in S. G. BRUSH, *Kinetic Theory*, **2** (Oxford & New York: Pergamon Press, 1966), 194.

tain curve (the "trajectory") as we vary the time t. In general, if the functions X_1, X_2, and X_3 are "uniform," we know that "one and only one trajectory will pass through every point in space" because of the determinism of NEWTONIAN mechanics. It is for this purely mechanistic system that POINCARÉ seeks to prove "stability" in the sense defined by POISSON[9]:

> the point P should return after a sufficiently long time, if not to its initial position, at least to a position as close as one wishes to this initial position.

POINCARÉ recognized that such a proof could not hold for *all* solutions, and in fact he noted that there will be an infinity of "asymptotic" solutions which are not stable in this sense; nevertheless he hoped to establish not only that there are also an infinity of solutions that *are* stable, but that the unstable ones are so much less numerous that they can be regarded as "exceptional." In the language of modern mathematics, the group of measure-preserving transformations of the phase space resulting from the dynamical equations of motion has the property that almost all points in a set of positive measure are carried back into that set infinitely many times. Thus while a completely rigorous proof of POINCARÉ's theorem had to wait for the development of the theory of measure of point sets, by LEBESGUE and others at the beginning of the 20th century,[10] POINCARÉ's own proof of the theorem was essentially correct; the finishing touches were added by CARATHÉODORY in 1919.[11]

In his proof POINCARÉ had to *assume* that the point P remains at a finite distance, *i.e.* that it does not leave a bounded region R having volume V. This restriction would appear to make it of less interest to the theory of stability of the solar system, but quite relevant to the problem of a gas in a finite container, provided the effect of the walls can be described in a non-singular way. But POINCARÉ did not give any indication in 1889 that he was going to be concerned with the latter application of his theorem.

In a brief paper in 1893 addressed to philosophers, POINCARÉ discussed the consequences of his theorem for the mechanistic conception of the universe.[12] Mech-

[9] S. D. POISSON, *Nouv. Bull. Sci. Soc. Philomath. Paris* **1**, 191 (1808); *Mém. Acad. Roy. Sci. Inst. France* **7**, 199 (1827).

[10] A comprehensive account of the history of this subject is given by T. HAWKINS, *Lebesgue's Theory of Integration* (Madison: University of Wisconsin Press, 1970).

[11] C. CARATHÉODORY, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 579 (1919); English trans. by S. G. BRUSH, *On Poincaré's Recurrence Theorem*, UCRL Trans.-871 (L), University of California, Lawrence Radiation Laboratory, Livermore, California. Professor TRUESDELL has persuaded me that my earlier statement in *Kinetic Theory*, **2**, 17, to the effect that POINCARÉ's proof was not much better than NIETZSCHE's, is unfair to POINCARÉ. He has shown me a proof which is essentially the same as POINCARÉ's but uses the concepts of measure theory (unpublished lecture notes).

[12] H. POINCARÉ, *Rev. Métaphys. Morale* **1**, 534 (1893), English trans. in BRUSH, *Kinetic Theory*, **2**, 203. This paper seems to be unknown to the physicists who have discussed the recurrence paradox. ZERMELO, in the paper cited below (note 15) explicitly stated that POINCARÉ "does not seem to have noticed [his theorem's] applicability to systems of molecules or atoms and thus to the mechanical theory of heat." While one does not expect scientists to read journals on metaphysics & morals, it is surprising that DUGAS omits this paper from his comprehensive account and bibliography in *La Théorie Physique au sens de Boltzmann* (Neuchatel: Griffon, 1959).

anism, he says, implies that all phenomena must be reversible, yet experience shows that many irreversible phenomena exist in nature.[13] To escape the contradiction, physicists have postulated "hidden movements": for example, if we didn't know that the earth rotates, we would regard the motion of the FOUCAULT pendulum as "irreversible" but having discovered that the earth does rotate, we can *imagine* that it might just as well be rotating in the opposite direction. Hence we don't consider this a contradiction of the principle of reversibility.[14] Similarly one might suppose that there are motions in the molecular world which account for macroscopic irreversibility, and which are "in principle" reversible.

POINCARÉ alluded briefly to MAXWELL's demon, and the argument that "the apparent irreversibility of natural phenomena is ... due to the fact that the molecules are too small and too numerous for our gross senses to deal with them." Yet, while the kinetic theory of gases based on this premise is, according to POINCARÉ, "up to now the most serious attempt to reconcile mechanism and experience," it still has not overcome the difficulties: his recurrence theorem, which would seem to apply to the entire world if the kinetic theory is valid, contradicts the "heat death" theory. If one attributed absolute validity to the Second Law, then the universe, instead of returning to its initial state, would tend toward a final state of uniform temperature.

One could reconcile the two theories by assuming that the heat death is not permanent but only lasts a very long time, so that the universe, after slumbering for millions of millions of centuries, will eventually reawaken. Then, as POINCARÉ puts it, "to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of MAXWELL's demon; it will suffice to have a little patience."

* * *

In 1896 the mathematician ERNST ZERMELO (at that time a student of MAX PLANCK) published a paper in the *Annalen der Physik* in which he claimed that POINCARÉ's theorem makes it impossible for the mechanical view of nature to explain irreversible processes.[15] While the recurrence paradox applies in the first instance to the kinetic theory of a system of mass-points interacting with conservative forces, ZERMELO argued that any other model within the framework of NEWTONIAN mechanics would be subject to the same objections. Thus one must

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[13] See the paper cited in note 4; this criticism was repeated in his textbook *Thermodynamique* (Paris, 1892), xviii, 414–423. See also POINCARÉ's exchange with TAIT, who criticized the book for ignoring the statistical basis of the Second Law [*Nature* **45**, 245, 414, 485 (1892)]. For POINCARÉ's later views on the relation between thermodynamics and kinetic theory see *La Valeur de la Science* (Paris: Flammarion, 1904), 180–185; *J. de Physique* [4] **5**, 369 (1906); *Compt. Rend. Acad. Sci. Paris* **143**, 989 (1906). POINCARÉ's view, that the apparent incompatibility of the principle of irreversibility and the reversibility of atomistic-mechanistic theories tended to undermine the accepted foundations of physics, was shared by some other scientists at the time; see the remarks of BRUNHES cited in note 1, section 1, and also his book *La Dégradation de l'Énergie* (Paris, Flammarion, 1922), quatrième partie.

[14] POINCARÉ attributes this example to HELMHOLTZ without giving a specific reference.

[15] E. ZERMELO, *Ann. Physik* [3] **57**, 485 (1896), English trans. in BRUSH, *Kinetic Theory*, **2**, 208.

either give up the validity of the Second Law of Thermodynamics or the mechanical theory of nature.

BOLTZMANN, who had apparently been unaware of POINCARÉ's earlier publications, replied that while the theorem is correct, it cannot be used as an objection to the molecular interpretation of the Second Law, since (as he had repeatedly emphasized) the validity of the Second Law is only statistical, not absolute.[16] As a result of the earlier discussion of the reversibility objection to his H-theorem, BOLTZMANN had already stated not only that entropy may sometimes decrease, but also that a system may eventually return to its initial state.[17] Thus the recurrence theorem seemed to be completely in harmony with his statistical viewpoint.

BOLTZMANN could decisively refute the contention that the mechanical viewpoint contradicts *experience* because the term "experience" had been improperly extended by ZERMELO (and POINCARÉ) to include *theoretical predictions* about what will happen to the universe in the remote future. The heat death is not a fact of experience but only an extrapolation from the observation that heat "always" flows from hot to cold. From the kinetic theory BOLTZMANN could estimate the time needed for an approximate recurrence of the positions and velocities of all the molecules in 1 cc of gas at ordinary density; it is a number so large that it would take trillions of digits even to write it down. Thus the recurrence paradox has nothing to do with the behavior of gases in the laboratory—

> when Zermelo concludes, from the theoretical fact that the initial states in a gas must recur,—without having calculated how long a time this will take—that the hypotheses of gas theory must be rejected or else fundamentally changed, he is just like a dice player who has calculated that the probability of a sequence of 1 000 one's is not zero, and then concludes that his dice must be loaded since he has not yet observed such a sequence!

It is interesting to note that BOLTZMANN is quite willing to jettison the "theory of central forces"—"the hypothesis that all natural phenomena can be explained by means of central forces between mass points"—while keeping the kinetic theory, which depends only on the assumption that the LAGRANGE equations of motion apply to the molecular collisions with sufficient accuracy for the explanation of thermal phenomena.[18] The difficulties about the equipartition theorem may be in BOLTZMANN's mind when he says here that "gas theory does not assume that either the properties of the aether or the internal constitution of molecules can be explained by centres of force," or perhaps he is simply indicating his allegiance to the mechanistic CARTESIAN as opposed to the dynamic KANT-BOSCOVICH tradition in natural philosophy.

In support of his statistical interpretation of the Second Law, BOLTZMANN cited "famous scientists, such as Helmholtz"[19] and quoted the remark of GIBBS,

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[16] L. BOLTZMANN, *Ann. Physik* [3] **57**, 773 (1896); *Wiss. Abh.* **III**, 567; English trans. in BRUSH, *Kinetic Theory*, **2**, 218.

[17] See the quotation at the end of section 6, above.

[18] See the translation in BRUSH, *Kinetic Theory*, **2**, 225; *cf.* BOLTZMANN's remarks in *Nature* **51**, 413 (1895) [*Wiss. Abh.* III, 535] where he claims that "this simple conception of Boscovich is refuted almost in every branch of science."

[19] *Sitzungsber. Akad. Wiss. Berlin* **17**, 172 (1884).

"The impossibility of an uncompensated decrease of entropy seems to be reduced to an improbability."[20] But his own theory of the H-curve is still only qualitative, and somewhat unsatisfactory from a mathematical viewpoint. BOLTZMANN asserted that the curve runs along very close to its minimum value most of the time, with occasional peaks corresponding to significant deviations from the equilibrium state. The probability of a peak decreases rapidly as the height of the peak decreases, and if the initial state lies on a very high peak, the state of the system will drop down toward the equilibrium state (minimum value of H) "with enormously large probability, and during an enormously long time it will deviate from it by only vanishingly small amounts." On the other hand if one waits an even longer time the initial state will eventually recur. Yet BOLTZMANN insisted that for any state with a value of H above the minimum, H is more likely to decrease than increase. No evidence was presented for any of these statements other than the original (qualitative) H-theorem.

In a second paper, ZERMELO protested that the properties attributed to the H-curve by BOLTZMANN are not only unproved, but incompatible with the laws of mechanics; and that probability theory cannot resolve this contradiction.[21] First, the overall periodicity of the system implies that every decrease in H must be balanced by an increase at some other time. Second, the probability of occurrence of a certain value of H should be measured by the volume in phase space of all states having this value; but from the equations of motion it can be shown that this volume is independent of time (this is called "LIOUVILLE's theorem" by physicists[22]). Hence there cannot be any tendency for H to increase or decrease. (The same argument was developed in more detail by GIBBS in 1902.[23]) While these objections might apply to an ensemble of systems over a long period of time, ZERMELO realized that BOLTZMANN had based his case for the H-theorem on more specific assumptions about the short-time behavior of the H curve for individual systems, and so he must also attack these assumptions.

If we assume that H has occasional peaks, and we choose the initial state to have a value of H ($=H_0$) greater than its minimum value, then it would seem that H_0 can just as well lie on a rising as a falling part of the curve and therefore can either increase or decrease. If we assume that the increasing branch occupies a smaller time interval, so that the probability of landing there is smaller, it would still

[20] See above, section 5, for the context of GIBBS' remark. BOLTZMANN cites both the original publication, *Trans. Conn. Acad.* **3**, 229 (1875), and OSTWALD's German edition, p. 198. The same quotation appears at the beginning of the second part of BOLTZMANN's *Vorlesungen über Gastheorie* (Leipzig: Barth, 1898) [English trans., *Lectures on Gas Theory*, 215]. According to ERWIN HIEBERT, both sides in the energetics controversy of 1895–96 tried to claim GIBBS' support [*The Conception of Thermodynamics in the Scientific Thought of Mach and Planck* (Freiburg i. Br.: Ernst-Mach-Institut, 1968), 53].

[21] E. ZERMELO, *Ann. Physik* [3] **59**, 793 (1896), English trans. in BRUSH, *Kinetic Theory*, **2**, 229.

[22] *Cf.* BRUSH, *Kinetic Theory*, **3** (Oxford & New York: Pergamon Press, 1972), 59; ZERMELO, though a mathematician, seems to have adopted the label from KIRCHHOFF, *Vorlesungen über die Theorie der Wärme* (Leipzig: Teubner, 1894), 144.

[23] J. WILLARD GIBBS, *Elementary Principles in Statistical Mechanics* (New York: Scribner, 1902), Chap. XII; *Collected Works*, **II**, 139–164. See also R. C. TOLMAN, *The Principles of Statistical Mechanics* (London: Oxford University Press, 1938), 165–179.

appear that the increase observed when one *does* land there is steeper and thus must be given a correspondingly greater weight. ZERMELO interpreted BOLTZMANN's argument as an attempt to avoid this objection by postulating that H_0 is always at a *maximum* of the H-curve, so that one only observes it to decrease. But ZERMELO says he "cannot conceive of such a curve" which consists only of maxima, nor can anyone else. As he says, it would only make sense if the maxima are not mathematical points but flat portions of the curve; but this again contradicts our experience of rapid dissipations of temperature inequalities or other ordered states.

ZERMELO also revived the reversibility argument, which he contended makes it impossible ever to derive irreversibility. Any alleged deduction must depend on errors or fallacious assumptions, in particular the "unprovable (because untrue) assumption that the molecular state of a gas is always, in BOLTZMANN's expression, 'disordered'." According to ZERMELO, only the initial state may be assumed to be disordered; the probability of a later state must depend on the initial state. It is not surprising that when ZERMELO refers to the "mechanical view of nature" he still has in mind a deterministic mechanical system in which randomness plays no role in the molecular motions themselves, but only in the observer's description of these motions. What is more remarkable is that BOLTZMANN, after having introduced the "molecular disorder" postulate, does not challenge this view; as we noted earlier, molecular disorder is for BOLTZMANN an assumption that may or may not be true—not a postulate.

BOLTZMANN's reply to ZERMELO's second paper is in one sense a reiteration of his earlier arguments, but it is at the same time a retreat from his contention that irreversibility follows *in general* from the kinetic theory.[24] We are concerned, he says, with what will happen in the present state of the world, which happens to be a state of low entropy; therefore we can say that H is a maximum in the initial state without having to claim (as ZERMELO suggested) that *all* points of the H-curve are maxima. If, however, we selected a completely arbitrary state of the universe, there are four possibilities. First, and most likely, the state is one of thermal equilibrium, so there will be no significant change of H at all from its minimum value. Second, H is above its minimum, and will "almost immediately" decrease if we follow it either forwards or backwards in time. Third, H is above its minimum, on an increasing branch, so the system passes to more improbable states as one goes forward in time. Fourth, H is above its minimum, on a decreasing branch, so the system passes to more improbable states as one goes backwards in time. The third and fourth cases have equal probability but both are "much rarer" than the second, which is in turn much rarer than the first.

From the description of the second case we can perhaps see why BOLTZMANN persists in saying that most parts of the H-curve above its minimum are maxima, even though he admits that this cannot be literally true. The key word is "almost" —if the peak is very narrow in time, then even if the initial state is slightly to the left of the actual maximum, one will quickly get over the top and further down the other side in a short time interval.[25] Thus it is a maximum with respect to finite

[24] L. BOLTZMANN, *Ann. Physik* [3] **60**, 392 (1897); *Wiss. Abh.* **III**, 579; English trans. in BRUSH, *Kinetic Theory*, **2**, 238.

[25] *Cf.* BOLTZMANN, *Math. Ann.* **50**, 325 (1898); *Wiss. Abh.* **III**, 629; PAUL & TATIANA EHRENFEST, *Conceptual Foundations*, 34.

differences but not with respect to infinitesimal differences. Some of the confusion might have been avoided if BOLTZMANN had stated this more explicitly.

But the second case cannot be taken as the "initial state" in laboratory experiments, for if we look at the value of H in 1896 and follow it backwards in time we expect it to increase, not decrease. Thus BOLTZMANN is really forced into accepting the fourth case as the typical one, which means that the third case is equally likely to be found somewhere, sometime, elsewhere in the universe. He therefore proposes that one should really *define the direction of time* as the direction in which one goes from less to more probable states. This would make the direction of time dependent on the individual observer, and would be different for different parts of the universe at different epochs:

> 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.[26]

It is ironic that BOLTZMANN has now adopted the viewpoint[27] of another of his critics, ERNST MACH, who in 1894 wrote:

> If we could really determine the entropy of the world it would represent a true, absolute measure of time. In this way is best seen the utter tautology of a statement that the entropy of the world increases with time. Time, and the fact that certain changes take place only in a definite sense, are one and the same thing.[28]

BOLTZMANN's conception of alternating time directions in the universe, and the idea that the direction of time is determined by human experience, has been revived in recent years by philosophers and cosmologists.[29] But from the viewpoint of this paper, it is more significant to note that the proposal was motivated by BOLTZMANN's desire to push the deterministic (though statistical) mechanical worldview to its furthest extreme, perhaps not entirely seriously. He chose *not* to make the alternative assumption that "molecular disorder" is continually main-

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[26] Quoted from the translation in BRUSH, *Kinetic Theory*, **2**, 242; the statement is repeated with some further discussion in *Gas Theory*, **II**, § 91.

[27] As noted above, the idea was to some extent anticipated by STONEY in 1887 (see note 3, section 6).

[28] ERNST MACH, *Monist* **5**, 22 (1894), reprinted in his *Popular Scientific Lectures* (LaSalle, Ill.: Open Court, 5th ed. 1943), quotation from p. 178. For further discussion of MACH's views see S. G. BRUSH, *Synthese* **18**, 192 (1968); E. N. HIEBERT, *op. cit.* (note 20).

[29] W. S. FRANKLIN, *Phys. Rev.* **30**, 766 (1910). A. S. EDDINGTON, *Nature* **127**, 447 (1931). M. BRONSTEIN & L. LANDAU, *Phys. Z. Sowjetunion* **4**, 114 (1933); English trans. in *Collected Papers of L. D. Landau*, ed. D. TER HAAR (Oxford & New York: Pergamon Press, 1965), 69. C. F. VON WEIZSÄCKER, *Ann. Physik* [5] **36**, 277 (1939). E. SCHRÖDINGER, *Proc. Royal Irish Acad.* **53** A, 189 (1950). K. G. DENBIGH. *Brit. J. Phil. Sci.* **4**, 183 (1953). HANS REICHENBACH, *The Direction of Time* (Berkeley: University of California Press, 1956). W. BÜCHEL, *Philosophia Naturalis* **6**, 108 (1960). H. SCHMIDT, *J. Math. Phys.* **7**, 494 (1966). W. J. COCKE, *Phys. Rev.* [2] **160**, 1165 (1967). H. ZANSTRA, *Vistas in Astronomy* **10**, 23 (1968). GEORGE K. BERGER, *Time and Thermodynamics* (Dissertation, Columbia University, 1971).

tained by random or external causes acting at the molecular level, as had been suggested by BURBURY.[30] While it is true that the statistical interpretation, like POINCARÉ's deterministic calculation, predicts recurrences, it is not hard to conceive of a postulate of continual or repeated randomization that would enforce irreversibility much more strongly; in fact this is just what WOLFGANG PAULI's proof of the quantum-mechanical H-theorem involves.[31] With such a postulate, recurrence is not impossible but neither is it certain. Here again we must stress the distinction between a statistical and a stochastic explanation of the Second Law.[32]

At the same time BOLTZMANN was willing to speculate in another direction, more in line with the "hidden variables" interpretation which would attribute randomness in molecular motion to determinism at a still lower level:

> Since today it is popular to look forward to the time when our view of nature will have been completely changed, I will mention the possibility that the fundamental equations for the motion of individual molecules will turn out to be only approximate formulas which give average values, resulting according to the probability calculus from the interactions of many independent moving entities forming the surrounding medium—as for example in meteorology the laws are valid only for average values obtained by long series of observations using the probability calculus. These entities must of course be so numerous and must act so rapidly that the correct average values are attained in millionths of a second.[33]

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I do not want to leave the impression that the hypothesis of randomness provides a logically satisfactory explanation for irreversibility in modern physics. In the context of the kinetic theory of gases and attempts to prove an H-theorem (either classical or quantal), it is not randomness itself but the way it is introduced into the equations that leads to irreversibility; one still has the choice of regarding irreversibility as an inherent property of the world or as a feature of our method of describing the world. The historical importance of the debates at the end of the 19th century was not that they led to a final solution of the problem, but that they popularized among scientists a new set of ideas, some of which were to assist the

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[30] For further discussion and reformulation of the "molecular disorder" hypothesis see J. H. JEANS, *Phil. Trans. Roy. Soc. London* **196** A, 397 (1901); *Phil. Mag.* [6] **5**, 597 (1903); P. & T. EHRENFEST, *Conceptual Foundations*, 40–42.

[31] W. PAULI, in *Probleme der modernen Physik, Arnold Sommerfeld zum 60. Geburtstage gewidmet von seinem Schülern* (Leipzig: Hirzel, 1928). R. C. TOLMAN. *op. cit.* (note 23), 455. D. TER HAAR, *Elements of Statistical Mechanics* (New York: Rinehart, 1954), 368; *Rev. Mod. Phys.* **27**, 289 (1955).

In their analysis, P. and T. EHRENFEST stress the need for making the assumption about the number of collisions ("Stosszahlansatz") after every short time interval Δt; see *Conceptual Foundations*, 16.

[32] *Cf.* W. KÖHLER, *Erkenntnis* **2**, 336 (1931).

[33] *Lectures on Gas Theory*, § 91. *Cf.* DAVID BOHM, *Causality and Chance in Modern Physics* (New York: Harper, 1961, reprint of 1957 ed.), 110–113; *Observation and Interpretation in the Philosophy of Physics*, ed. S. KÖRNER (New York: Dover Pubs., 1962, reprint of the 1957 ed.), 33.

transition from classical to quantum physics that took place in the following decades.

8. Toward Quantum Theory: Planck's Irreversible Radiation Processes

One of the best-known quotations about the nature of science is MAX PLANCK's remark,

> An important scientific innovation rarely makes its way by gradually winning over and converting its opponents ... What does happen is that its opponents gradually die out, and that the growing generation is familiarized with the ideas from the beginning.[1]

I suppose most people who read (or repeat) this quotation think PLANCK is referring to his quantum theory, but in fact he was talking about his struggle to convince scientists in the 1880's and 1890's that the Second Law of Thermodynamics involves a principle of irreversibility, and that the flow of energy from hot to cold is *not* analogous to the flow of water from a high level to a low one, as OSTWALD and the energetists claimed. He goes on to lament that his own efforts were fruitless, but the battle was eventually won because of advances from another direction: the statistical interpretation of entropy based on kinetic theory.

As is well known, PLANCK's quantum theory was developed with the help of BOLTZMANN's statistical theory of entropy; but it is only within the last few years that we have been reminded by historians of science such as MARTIN KLEIN and HANS KANGRO that PLANCK's work in radiation up to 1900 was done from a completely different viewpoint, and that considerations such as the RAYLEIGH "ultraviolet catastrophe" (posthumously baptized by PAUL EHRENFEST) played no significant role in his thinking during this period. Instead of approaching the problem of the frequency-distribution of black-body radiation by the methods of statistical mechanics (which leads to the difficulty of understanding why the aether does not take its proper share of energy as predicted by the equipartition theorem), PLANCK was attempting to develop a fundamental macroscopic theory based on thermodynamics and electromagnetic theory.[2] He hoped to establish the principle of irreversibility as part of this theory. We are concerned with PLANCK's development of radiation theory only insofar as it brought him into conflict with BOLTZMANN, and thereby led him to believe in a need for postulating randomness in order to explain irreversibility; but we shall not follow any of the subsequent development of quantum theory.

In his *Inauguraldissertation* (1879), PLANCK introduced a distinction between two kinds of processes: (1) those in which Nature has the same preference [*Vorliebe*] for the final state as for the initial state—such processes he calls *neutral*; (2) those in which Nature prefers the final state to the initial one—such are *natural*

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[1] MAX PLANCK, *A Scientific Autobiography and other Papers* (London: Williams & Norgate, 1950), 33–34; *Philosophy of Physics* (New York: Norton, 1936), 97. On one occasion the quotation has been attributed to KEYNES—see the query in the *New York Times Book Review*, Aug. 31, 1969, p. 23 and replies in the issue of October 5.

[2] MARTIN J. KLEIN, *Arch. Hist. Exact Sci.* **1**, 459 (1962); HANS KANGRO, *Vorgeschichte des Planckschen Strahlungsgesetzes* (Wiesbaden: Steiner, 1970).

processes.[3] The neutral processes include "reversible" processes but also others, such as the motion of a freely falling body. The neutral processes are not associated with entropy change; but entropy increases for natural processes. The former are only "ideal" since all actual processes occurring in nature are attended by heat conduction or friction or percussion, which are *natural* in the above sense; thus it appears that nature proceeds toward a certain goal, namely to maximize the total entropy, as CLAUSIUS has indicated in his statement of the Second Law.[4]

PLANCK's hostility to atomistic theories was evident as early as 1882 in a paper on evaporation, melting, and sublimation.[5] He emphasized that his results are independent of any molecular hypothesis, and argued that one should go as for as possible with thermodynamics before introducing assumptions about the interior constitution of bodies. At the end of the paper he wrote:

> The second law of thermodynamics, logically developed, is incompatible with the assumption of finite atoms.[6] Hence it is to be expected that in the course of the further development of the theory, there will be a battle between these two hypotheses, which will cost one of them its life. It would be premature to predict the result of this battle with certainty; yet there seem to be at present many kinds of indications that in spite of the great successes of atomic theory up to now, it will finally have to be given up and one will have to decide in favor of the assumption of a continuous matter.

The following year, in a paper on the thermodynamic equilibrium of gas mixtures, PLANCK showed that DALTON's law of partial pressures, which MAXWELL and STEFAN had deduced from kinetic theory, can be derived without the help of that theory.[7] In his conviction that the second law could be used as a research tool, and that the kinetic-atomic theory of matter was an erroneous or at best superfluous hypothesis, PLANCK might have seemed a likely recruit to the OSTWALD-DUHEM school of "Energetics," but in fact he eventually refused to follow that path.[8]

In a substantial three-part series, "Ueber das Princip der Verhaltung der Entropie" (1887), PLANCK announced at the beginning that he would abstain from special assumptions about the nature of molecular motions. He was interested only in developing methods for calculating the entropy function, which would deter-

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[3] MAX PLANCK, *Über den zweiten Hauptsatz der mechanischen Wärmetheorie* (München, 1879), reprinted in PLANCK's *Physikalische Abhandlungen und Vorträge* (Braunschweig: Vieweg, 1958), **I**, 1. For a general survey of PLANCK's views on thermodynamics see ERWIN N. HIEBERT, *The conception of thermodynamics in the scientific thought of Mach and Planck* (Freiburg: Ernst-Mach-Institut, 1968). An abbreviated version of this report has been published in *Perspectives in the History of Science and Technology*, ed. D. H. D. ROLLER (Norman: University of Oklahoma Press, 1971), 67.

[4] PLANCK, *Phys. Abh.* I, 42. *Cf.* E. BAUER's assertion [*Ann. Chim.* [8] **29**, 377 (1913)] that the word "irreversible" was *invented* for the case of luminescence.

[5] PLANCK, *Ann. Physik* [3] **15**, 446 (1882); *Phys. Abh.* **I**, 134.

[6] A footnote to the first sentence refers to MAXWELL's discussion of his "demon" in *Theory of Heat* (1871).

[7] PLANCK, *Ann. Physik* [3] **19**, 358 (1883); *Phys. Abh.* **I**, 164.

[8] See his recollections recorded in the "Scientific Autobiography" cited above in note 1, and HIEBERT's account, *op. cit.*, 41–50, 55–64.

mine what reactions actually occur, and in illustrating the fruitful applications of the second law to physical chemistry.[9]

It is surely not without significance that PLANCK served as co-editor of the third volume of the second edition of CLAUSIUS' treatise, *Die Mechanische Wärmetheorie*, dealing with the kinetic theory of gases, following CLAUSIUS' death in 1888.[10] This would have been a forceful reminder that the physicist whom PLANCK respected for his work in founding thermodynamics had also grappled with the problem of finding a molecular interpretation of the thermal properties of bodies.

When PLANCK became interested in the theory of solutions, he seemed quite willing to discuss molecular hypotheses and the analogy between solute molecules and gas molecules.[11] Yet the following year, at the meeting of German scientists at Halle (1891), he still insisted that kinetic theory was of little use, since this analogy had been discovered independently of kinetic theory and could not be explained or further developed with the aid of that theory.[12] PLANCK and OSTWALD joined in defending the macroscopic thermodynamic viewpoint in a discussion with BOLTZMANN at this meeting.[13]

Our earlier discussion of MAXWELL's ideas suggested that a crucial step in the development of an atomistic interpretation of irreversibility was the recognition that mixing of different kinds of molecules, rather than flow of heat, is the fundamental irreversible process. With this in mind we are interested to see that in 1892 PLANCK criticized "English physicists" for describing the Second Law too narrowly in terms of "dissipation of energy," pointing out that processes such as the interdiffusion of two ideal gases involve no dissipation of energy but rather a "dissipation of matter." This is for PLANCK another instance of the need for formulating the Second Law in terms of entropy rather than deriving it merely from energy considerations as OSTWALD and his Energetics group wished to do.[14] As ERWIN HIEBERT notes, this paper is soon followed by a more sympathetic view of atomism, and prepares the way for an open attack on Energetics.[15]

By this time PLANCK had become involved in another editing task touching on the atomistic interpretation of thermodynamics. In 1889, following the death of GUSTAV ROBERT KIRCHHOFF, PLANCK was called to Berlin to occupy KIRCHHOFF's chair. He was the logical person to edit KIRCHHOFF's lectures on heat for

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[9] PLANCK, *Ann. Physik* [3] **30**, 562, **31**, 189, **32**, 462 (1887); *Phys. Abh.* **I**, 196, 217, 232.

[10] *Die Mechanische Wärmetheorie* von R. Clausius, zweite umgearbeitete und vervollständigte Auflage des unter dem Titel „Abhandlungen über die mechanische Wärmetheorie" erschienenen Buches. Dritter Band. Entwickelung der besonderen Vorstellungen von der Natur der Wärme als einer Art der Bewegung. Herausgegeben von Dr. Max Planck und Dr. Carl Pulfrich (Braunschweig: Vieweg, 1889–1891). The second title page carries the title *Die Kinetische Theorie der Gase*.

[11] PLANCK, *Ann. Physik* [3] **39**, 161 (1890); *Phys. Abh.* **I**, 330 (see esp. p. 342).

[12] PLANCK, *Z. Physik. Chem.* **8**, 372 (1891); *Phys. Abh.* **I**, 372.

[13] W. OSTWALD, *Lebenslinien, Eine Selbstbiographie*, Zweiter Teil, *Leipzig, 1887–1905* (Berlin, 1927), 187–188, quoted by HIEBERT, *op. cit.* (note 3), 33–34.

[14] PLANCK, *Ann. Physik* [3] **46**, 162 (1892); *Phys. Abh.* **I**, 426; HIEBERT, *op. cit.*, 41–42. See also PLANCK's next paper on the Second Law, *Z. phys. Chem. Unterr.* **6**, 217 (1893); *Phys. Abh.* I, 437, in which he insists on the importance of irreversible processes in which there is no change of temperature (HIEBERT, p. 45).

[15] HIEBERT, *op. cit.*, 46.

publication as a volume in the *Vorlesungen über Mathematische Physik*. As it happened KIRCHHOFF, though not personally very enthusiastic about the kinetic theory of gases, had felt obliged to include a thorough treatment of this subject in his lectures, and as a result PLANCK was forced to become somewhat familiar with it.

Shortly after the publication of KIRCHHOFF's lectures on heat, edited by PLANCK, BOLTZMANN criticized the derivation of the collision integral given in the book, implying that it contained an error that might be the fault of the editor.[16] In particular, KIRCHHOFF seemed to be assuming that the probability of collision of two molecules could be calculated as if their coordinates before the collision were statistically independent, despite the fact that the variables have been defined in such a way that the molecules must have previously collided. This is almost exactly the same as CULVERWELL's reversibility objection against the proof of the H-theorem, and seems to require an additional postulate of "molecular disorder" for its justification. PLANCK recognized this problem in his reply, and argued that the same objection applied to any proof, not only KIRCHHOFF's. While as editor he had not felt it proper to criticize the validity of KIRCHHOFF's derivation, limiting himself to reproducing it accurately from the manuscript, he now suggested that the only way to avoid the difficulty was to assume that the MAXWELL distribution already is established, since it is only for this distribution that the probability that two molecules separate with certain velocities after a collision is the same as the probability that they have those velocities before the collision. Thus the proof of the MAXWELL distribution for thermal equilibrium might be based on the fact that it is the only one that satisfies the reversibility criterion.[17]

While BOLTZMANN did not accept PLANCK's conclusion,[18] the exchange of views reinforced the impact of the debate with the English physicists in the same period (1894–95) and must therefore be considered as one of the contributing factors leading to BOLTZMANN's "molecular disorder" assumption.

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Another consequence of PLANCK's move to Berlin was his contact with the experimental work being done there on black-body radiation by OTTO LUMMER and E. PRINGSHEIM at the Physikalisch-Technischen Reichsanstalt.[19] PLANCK's interest in demonstrating the manifold applications of thermodynamics, combined with this stimulus, led him to write a series of papers "Über irreversible Strahlungsvorgänge" in 1897–1900, culminating in the discovery of the quantum theory of radiation. These papers are relevant to our subject primarily because they led PLANCK to realize (as a result of BOLTZMANN's criticism) that the principle of irre-

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[16] LUDWIG BOLTZMANN, *Sitzungsber. k. Bayer. Akad. Wiss. München* **24** (3), 207 (1894); *Ann. Physik* [3] **53**, 955 (1894); BOLTZMANN's *Wiss. Abh.* **III**, 528.

[17] PLANCK, *Sitzungsber. k. Bayer. Akad. Wiss. München* **24** (4), 391 (1895); *Ann. Physik* [3] **55**, 220 (1895); PLANCK's *Phys. Abh.* **I**, 442.

[18] BOLTZMANN, *Ann. Physik* [3] 55, 223 (1895); *Sitzungsber. k. Bayer. Akad. Wiss. München* **25**, 25 (1896); Wiss. Abh. III, 532. See also *Gas Theory*, **I**, § 6; **II**, § 92.

[19] See the comprehensive discussion in KANGRO, *op. cit.* (note 2).

versibility could not be derived, as he had originally thought, from electromagnetic theory alone, but required an additional postulate of randomness.[20]

In the preface to his *Vorlesungen über Thermodynamik*, dated April 1897, PLANCK hinted that the Second Law might ultimately have to be based on electromagnetism, rather than on the kinetic theory.[21] He began the series on radiation with the statement that irreversible processes cannot be explained satisfactorily by the kinetic theory, assuming point-molecules interacting with conservative forces, because of the recurrence objection of ZERMELO.[22] But a resonator which can absorb and emit electromagnetic radiation can introduce irreversibility even though MAXWELL's equations themselves indicate that radiation in empty space or reflected from smooth walls behaves reversibly.[23]

Such a suggestion could hardly pass unchallenged by BOLTZMANN, who in addition to being the chief defender of kinetic theory was one of the leading authorities on MAXWELL's electromagnetic theory and its connection with thermodynamics. He immediately pointed out that any process of interaction between resonators and electromagnetic waves must be described by reversible equations, and that the apparent irreversibility in the process invoked by PLANCK was due only to the choice of special initial conditions. Just as in the case of a sphere fixed in space, bombarded by smaller spheres: if the latter are initially moving in parallel paths, they will be scattered in all directions; but if one then reverses their motions, the entire process will run backwards. Aside from the possibility of JOULE heating

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[20] KLEIN, *op. cit.* (note 2); *Natural Philosopher* 1, 83 (1963); KANGRO, *op. cit.*, 133–134. For PLANCK's own version of the exchange see his *Nobel-Vortrag* (1920), in *Phys. Abh.* III, 121; English trans. reprinted in *A Survey of Physical Theory* (New York: Dover Pubs., 1960), 102.

[21] In this preface, he distinguished three approaches to the development of the theory of heat. The first, the kinetic theory, "penetrates deepest into the nature of the processes considered, and, were it possible to carry it out exactly, would be characterized as the most perfect." But "Obstacles, at present unsurmountable, however, seem to stand in the way of its further progress. These are due not only to the highly complicated mathematical treatment, but principally to essential difficulties, not to be discussed here, in the mechanical interpretation of the fundamental principles of thermodynamics." The second method is that of HELMHOLTZ, based on the general principle that heat is due to motion but refusing to make special hypotheses as to the nature of this motion; PLANCK feels that this viewpoint, while "safer" than the first, "does not as yet offer a foundation of sufficient breadth." The third method, which he calls the most fruitful so far, proceeds directly from empirical facts and deduces physical and chemical laws of extensive application; while it is the best one available (and is to be used exclusively in this book) it "cannot be considered as final ... but may have in time to yield to a mechanical, or perhaps an electro-magnetic theory." *Treatise on Thermodynamics*, reprint of the third edition (1926), English trans. by A. OGG from the seventh German edition (1922) (New York: Dover Pubs., n. d.), viii. See HIEBERT, *op. cit.*, 66–67 for an extensive quotation from the original German version.

Lest someone be tempted to assume that PLANCK refers, in this quotation, to the BOLTZMANN-ZERMELO debate of 1896–97, it should be noted that he used almost the same words to characterize the status of kinetic theory in his introduction to CLAUSIUS' posthumous treatise on kinetic theory in 1889 (see p. viii of the book cited in note 10).

[22] For PLANCK's views on the ZERMELO-BOLTZMANN debate see his letter to LEO GRAETZ, 23 May 1897, quoted in KANGRO, *op. cit.*, 131.

[23] PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 57 (1897); *Phys. Abh.* I, 493.

there is no essential difference between purely mechanical and electrical processes. BOLTZMANN claimed to have satisfactorily answered the objections of LOSCHMIDT, CULVERWELL, POINCARÉ, and ZERMELO, thereby reinstating his molecular explanation of irreversibility, and argued that any explanation of irreversibility based on electromagnetic processes must rely on exactly the same kind of assumptions.[24]

In his second paper in this series, PLANCK stated that the reversibility theorem does not apply to the particular process he had in mind, since he assumed "that the intensity of the primary exciting wave at the location of the resonator (always assumed to be infinitely small) has at all times finite and continuous values." But the secondary spherical waves emitted by the resonator must necessarily have an unlimited intensity in the neighborhood of the resonator, if the resonator is infinitesimal in size. If the process is reversed, the primary wave (now a spherical wave converging on the resonator) no longer fulfills the condition. BOLTZMANN's objection therefore applies only to a singular case explicitly excluded in the theory.[25]

Since no process has yet been found in nature in which irreversible changes are produced by the action of conservative forces, according to PLANCK, it is important to investigate the laws of radiation which seem to offer such a possibility. There is a hint that the electromagnetic world-view, currently being advocated by LORENTZ and other physicists, may thereby gain an advantage over the mechanical world-view.[26]

BOLTZMANN was of course unable to accept the implication that his own attempts to explain irreversibility had failed; nor could he accept the special assumption about the resonator which PLANCK used to avoid BOLTZMANN's earlier objection. BOLTZMANN noted that if one adopted the physically-unrealistic assumption that the resonator has infinitesimal size, he would still have to postulate that it is surrounded by a region of very strong electric vibrations in order to get any scattering of the incoming wave at all; and then the process would still be reversible.[27]

As for the recurrence paradox against kinetic theory, BOLTZMANN insisted that this applies only to systems of a finite number of molecules, and that it is reasonable to expect agreement with the Second Law only in the limiting case of an infinite number of molecules, when the recurrence time also becomes infinite. The same relation between the finite and the infinite situation should hold if one replaces the differential equations of electromagnetism by finite-difference equations. Conversely, since the equations of electromagnetic theory have been derived from a purely mechanical model (even if an artificial one), it follows that if electric or even acoustic resonators can give rise to irreversible processes, then one would have a contradiction of POINCARÉ's statement[28] that irreversible processes cannot in principle be derived from the differential equations of pure mechanics.

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[24] BOLTZMANN, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 660 (1897); *Wiss. Abh.* **III**, 614.

[25] PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 715 (1897); *Phys. Abh.* **I**, 505.

[26] M. PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 641 (1894); *Phys. Abh.* **III**, 1. *Cf.* R. MCCORMMACH, *Isis* **61**, 459 (1970); S. GOLDBERG, *Arch. Hist. Exact Sci.* **7**, 7 (1970), § IIa.

[27] BOLTZMANN, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 1016 (1897); *Wiss. Abh.* **III**, 618.

[28] BOLTZMANN does not give a specific citation for this opinion of POINCARÉ; for the probable source see the publications cited in notes 4 and 13, section 7.

BOLTZMANN suggested that just as in gas theory, one can determine for radiation a "most probable state" or rather a general formula that includes all states in which the waves are not ordered but "run through each other" in all possible ways. This state would be expected to evolve in a space filled with resonators of sufficient multiplicity. It would happen only in relatively few cases that a disordered state changes back into an ordered one. But just as in the case of kinetic theory, one cannot prove that the latter process is impossible. Moreover, if one replaces the differential equations by finite difference equations (thinking of the aether as a large but finite number of vector atoms) then the recurrence theorem would also apply here.

In his next paper, without explicitly mentioning BOLTZMANN's criticism, PLANCK proposed to exclude those radiation processes which he called "synchronized with the system" ["auf das System abgestimmt"]—namely, those for which the intensity associated with one or more FOURIER components of the wave is comparable to the total intensity.[29] Such waves would have regularly-recurring gaps. The other (and more general) kind of wave would be associated with irreversible processes; and the distinction is clearly between "ordered" and "disordered" waves. PLANCK claimed to prove that his disordered waves cannot be reversed.[30] He admitted the possibility that the phase constants of the partial waves have values such that an initially disordered radiation process will appear to become ordered at a later time; whether such processes occur in nature or not depends on the conditions satisfied by the initial state.[31]

BOLTZMANN still was not satisfied, and claimed that PLANCK's proof that his disordered waves could not be reversed was incorrect.[32] PLANCK conceded an error in this proof, and proposed yet a further refinement of his theory, in which he introduced the concept of "natural" radiation and postulated that it was the only kind found in nature.[33] His definition of "natural" radiation depended somewhat on the details of his description of the resonator and the waves which it emits and absorbs, but, roughly speaking, may be seen as a generalization of his earlier concept of radiation processes "not synchronized with the system."[34]

PLANCK could then show that if the radiation is *always* "natural," a quantity analogous to entropy (defined in terms of the logarithm of the energy-density for each frequency) always decreases. The proof depended on the symmetry between ingoing and outgoing waves interacting with the resonator, *i.e.*, on the same kind of *microscopic* reversibility assumption that underlies the proof of BOLTZMANN's H-theorem. PLANCK was thus forced to recognize that in a deterministic system in which the radiation does not remain for an indefinitely long time (*e.g.* for a system of waves interacting with a resonator in a closed space) the property of irreversibility cannot be established without additional assumptions. Hence, he wrote,

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29 PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 1122 (1897); *Phys. Abh.* I, 508 (see esp. p. 518).

30 *Ibid.* 524–525.

31 *Ibid.* 531.

32 BOLTZMANN, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 182 (1898); *Wiss. Abh.* III, 622.

33 PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 449 (1898); *Phys. Abh.* I, 532.

34 See PLANCK's *Phys. Abh.* I, 550–552.

"this indeterminacy lies in the nature of the subject"—not perhaps in nature itself, but at least in any rational theory we can construct about nature.[35] In such a theory, "If a resonator is at any time stimulated by natural radiation of variable intensity, then the occurrence of the inverse process is absolutely excluded for all later times, provided that the exciting wave retains the properties of natural radiation."[36] But the door is still left open to a future theory in which more detailed information about the FOURIER components of the radiation, and the response of the resonator to these components, might be used to derive irreversibility.

By 1899, when he published the fifth paper in this series on irreversible radiation processes, PLANCK had molded his theory even more closely along the lines of BOLTZMANN's kinetic theory. He defined the entropy of a resonator with vibration frequency ν and energy U as

$$S = -(U/a\nu)\log(U/eb\nu)$$

and described the basic interaction between an incoming wave and a resonator in terms of two intensities rather than one—distinguishing between two directions of polarization of the incoming and outgoing waves. Thus the formula for entropy contained four terms, just like the Boltzmann H-function which has terms for the two colliding molecules before and after the collision; and the proof that $dS/dt \geqq 0$ turns on exactly the same property of logarithmic expressions of the form $\alpha \log \alpha + \beta \log \beta - \gamma \log \gamma - \delta \log \delta$.[37] The same kind of mathematics leads to exponential formulae for the radiation intensity in the stationary state, and to WIEN's formula for the energy distribution over frequencies.

In a lecture summarizing his theory at the Naturforscherversammlung in München later in 1899, PLANCK explained his hypothesis of natural radiation in somewhat clearer fashion. He appealed to the fact that it is not possible to find an absolutely sharp line in the spectrum. *i.e.*, there is no such thing as absolutely monochromatic radiation. Rather, even the most homogeneous ray is spread over a finite region of frequencies. But this "indeterminacy" [Unbestimmtheit] implies that for example in the visible spectrum an interval whose endpoints have frequencies in the ratio 1:1,000,001 would correspond to all vibration numbers between 510 billion and 510,000,510,000,000, *i.e.* a range of 510 million different frequency numbers. Thus in the FOURIER decomposition of the ray we have to deal with 510 million "unknown quantities." Moreover it is in principle impossible to determine these components experimentally, since the terms in the FOURIER series depend on the choice of a basic period. On the other hand, one can hardly believe that these details affect the measurable physical properties of the radiation. Hence one must add to MAXWELL's theory a new hypothesis, based on the concept of "natural radiation." This hypothesis states that the energy of the radiation is distributed completely *irregularly* [*unregelmässig*, italics in original] over the

[35] "Diese Unbestimmtheit liegt übrigens in der Natur der Sache" (*Ibid.* 557).

[36] "Wenn ein Resonator zu irgend einer Zeit durch natürliche Strahlung von veränderlicher Intensität erregt wird, so ist der Eintritt des umgekehrten Vorgangs für all späteren Zeiten absolut ausgeschlossen, so lange die erregende Welle der Eigenschaften der natürlichen Strahlung behält." (*Ibid.* 559).

[37] PLANCK, *Sitzungsber. Preuss. Akad. Wiss. Berlin* 440 (1899); *Phys. Abh.* **I**, 560 (see esp. pp. 585, 588 and compare BOLTZMANN's derivation as indicated above, section 5, note 11).

partial vibrations. It is this assumption that leads to the irreversibility of the Second Law of Thermodynamics. PLANCK now recognizes that this assumption of "natural radiation" is precisely analogous to BOLTZMANN's assumption of "molecular disorder" in the kinetic theory, and that the latter must also be added as a special hypothesis rather than derived from the original model of atoms bouncing around in a container with perfectly reflecting walls. (He adds that by modifying the assumption of perfectly reflecting walls, which seems physically unrealistic in any case, one could probably get over this difficulty and derive irreversibility.[38])

In view of the fact that PLANCK soon afterwards developed his quantum theory of radiation with the help of BOLTZMANN's statistical theory of entropy, one might be tempted to suggest that the concept of randomness was derived from BOLTZMANN by PLANCK and thence passed into the worldview of modern physics.[39] That things are not quite so simple is indicated by some remarks in PLANCK's 1932 lecture, "Causality in Nature":

> The determinists ... look for a rule behind every irregularity, and it is their task to formulate a theory of the laws of gases on the assumption that the collision between any two molecules is causally determined. The solution of this problem was the lifework of the great physicist, Ludwig Boltzmann, and it is one of the finest triumphs of theoretical investigation ... The new world image of quantum physics is due to the desire to carry through a rigid determinism in which there is room for quanta. For this purpose the material point which had hitherto been a fundamental part of the world image had to lose this supremacy. It has been analyzed into a system of material waves, and these material waves are the elements of the new world image. ... It is an essential fact, however, that the magnitude which is characteristic for the material waves is the wave function, by means of which the initial conditions and the final conditions are completely determined for all times and places. ... We see then that there is fully as rigid a determinism in the world image of quantum physics as in that of classical physics.[40]

* * *

We have now followed the discussion up to the eve of the invention of quantum theory. After 1900 we encounter a rapidly changing situation, in which many new factors appear: the phenomenon of radioactivity, in which an atom seems to explode at a time that is absolutely unpredictable on an individual basis though subject to statistical regularity when many atoms are involved; the EINSTEIN-SMOLUCHOWSKI theory of BROWNIAN movement, invoking observable statistical fluctuations of just the type that BOLTZMANN and his opponents had assumed would be extremely unlikely to occur during the lifetime of a human observer; and of course the develop-

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[38] M. PLANCK, *Ann. Physik* [4] **1**, 69 (1900); *Phys. Abh.* **I**, 614. *The Theory of Heat Radiation*, trans. from German ed. of 1913 (New York: Dover Pubs., 1959), 116–17.

[39] M. J. KLEIN, *Arch. Hist. Exact Sci.* **1**, 459 (1962); *Natural Philosopher* **1**, 83 (1963); L. ROSENFELD, in *Max-Planck-Festschrift* 1958, hrsg. B. KOCKEL *et al.* (Berlin: VEB Deutscher Verlag der Wissenschaften, 1959), 203.

[40] M. PLANCK, *The Philosophy of Physics* (New York: Norton, 1936, reprinted 1963), 58, 64–65, trans. from *Der Kausalbegriff in der Physik* (Leipzig: Barth, 1932). See also PLANCK's lecture in *Naturwissenschaften* **14**, 249 (1926); *Phys. Abh.* **III**, 159.

ment of quantum theory itself, leading to what some would call indeterministic laws of subatomic behavior.[41] The place to survey 20th-century ideas about randomness and irreversibility is certainly not this article, which attempts to cover (already at too great a length) only the role of such ideas in the classical kinetic theory of gases.[42] So we must conclude by mentioning only a handful of post-1900 contributions which do not seem to have been substantially affected by the abovementioned developments and thus still pertain to the 19th-century universe of discourse.

Boltzmann,[43] in his last major publication on kinetic theory (a survey written jointly with J. Nabl), started by stating the assumption that the smallest particles of bodies are in continuous irregular motion [steter unregelmässiger Bewegung].[44] But the word "irregular" cannot perhaps be taken too literally in view of his philosophical conviction, expressed a year earlier in a lecture at the St. Louis Congress, that "the regularity of the phenomena is the fundamental condition for all cognition."[45] Nevertheless, in order to prove the H-theorem Boltzmann must assume that the state of the gas is molecular-disordered not only initially but also remains so throughout the course of time; he knows that the latter does not necessarily follow from the former, though he does not put as much stress as did Planck on the fact that an extra assumption is needed.[46] The fact that Boltzmann still retains his concept of alternating time directions in the universe may indeed be an indication that he is willing to accept a world in which molecular disorder does not always prevail, but, on the contrary, recurrences of ordered states are to be expected.[47]

By this time Gibbs' *Statistical Mechanics*[48] had appeared and was beginning to attract attention among those scientists concerned with fundamental or mathematical aspects of gas theory. In his discussion of what later became known as the generalized H-theorem (or "Gibbs H-theorem"), Gibbs ascribed the approach

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[41] M. J. Klein, *Hist. Stud. Phys. Sci.* **2**, 1 (1970). M. Jammer, *The Conceptual Development of Quantum Mechanics* (New York: McGraw-Hill, 1966), 281–293, 323–345.

On Brownian movement, see my paper in *Arch. Hist. Exact Sci.* **5**, 1 (1968). The Ehrenfests' article, for example, which contains a fascinating (though sometimes historically misleading) discussion of Boltzmann's work, introduces ideas about the "determinancy of visible states" (pp. 36–37) based on Brownian movement, and thus belongs really to a later period than the one with which we are concerned.

[42] *Cf.* E. Cassirer, book cited in note 7, section 4; Alfred M. Bork, *Antioch Review* **27**, 40 (1967); Paul Forman, *Hist. Stud. Phys. Sci.* **3**, 1 (1971); John C. Greene, *Proc. Amer. Phil. Soc.* **103**, 716 (1959).

[43] According to Lise Meitner, Boltzmann in his Vienna lectures from 1902 to 1906 never mentioned Planck's quantum theory or Einstein's theory of Brownian movement. *Advancement of Science* **20**, (99), 39 (1964); *Bull. Atomic Sci.*, Nov. 1964, p. 2.

[44] L. Boltzmann & J. Nabl, *Enc. Math. Wiss.* **V** (I), 493 (1905).

[45] L. Boltzmann, *Congress of Arts and Sciences Universal Exposition, St. Louis*, 1904, ed. H. J. Rogers (Boston: Houghton, Mifflin & Co., 1905), **I**, 591 (quotation from p. 598); the original German text was published in Boltzmann's *Populäre Schriften* (Leipzig: Barth, 1905), 345.

[46] Boltzmann & Nabl, *op. cit.*, 513.

[47] *Ibid.* 521–522.

[48] J. Willard Gibbs, *Elementary Principles in Statistical Mechanics* (New York: Scribner, 1902), reprinted in *The Collected Works of J. Willard Gibbs* (New York: Dover Pubs., 1960), **II**.

of an ensemble to equilibrium not to any element of randomness in molecular behavior, but to the fact that the flow in phase space (determined by the equations of motion) produces a mixing which progressively deprives a macroscopic observer of information about the system. He suggested the analogy of a colored liquid or dye, initially separate from a body of water, which is then allowed to mix as the water is stirred. Assuming conservation of the amount of colored liquid and incompressibility (as well as mutual insolubility) of both liquids, one sees that the "average density" of colored liquid remains constant, as does the mean square density (which one might expect to provide a measure of the deviation from completely uniform mixing), *if* one defines density for sufficiently small spatial elements. On the other hand if one fixes the size of the spatial element and continues the mixing indefinitely long, then the mean square density does decrease to a minimum.[49] In order to sharpen this distinction the EHRENFESTS introduced the terms "fine-grained density" and "coarse-grained density" for these two conceptions.[50] One may then say that BOLTZMANN's H-function defined in terms of fine-grained density (which represents the "real behavior" of the systems on the microscopic level, as seen by a MAXWELL demon) is a constant of the motion; but the H-function defined in terms of the "coarse-grained density" (which is more like what a macroscopic observer could actually measure) does decrease as a result of the mixing process.[51] Of course this makes irreversibility an attribute of the interaction between nature and the observer, rather than an intrinsic property of nature itself—as indeed MAXWELL had observed in his remarks quoted in section 4.[52] In the same way we could complain that the word "random" is often used to characterize a limitation on our knowledge of nature rather than a property of nature itself.[53] These would be considered irrelevant objections by those who accept the "Copenhagen" philosophy, in which the observer is no longer, even in principle, considered separate from what he is observing.

It was S. H. BURBURY who again emphasized in 1903 the need for assuming randomness in order to derive irreversibility from the classical kinetic theory, and insisted that this is what BOLTZMANN's "molecular disorder" hypothesis must mean. Commenting on J. H. JEANS' reformulation of the problem in the language of GIBBSIAN statistical mechanics, BURBURY agreed with JEANS that any such assumption is "mathematically impossible if the motion is continuous, that is, if the state of the system at any instant is a necessary consequence of its past histo-

[49] GIBBS, *Works*, II, 144–151. *Cf.* E. ZERMELO, *Jahresber. Deutsch. Math.-Ver.* **15**, 232 (1906) for discussion of GIBBS' theory of irreversibility.

[50] P. & T. EHRENFEST, *Conceptual Foundations*, 52.

[51] A clear explanation may be found in TOLMAN, *Principles of Statistical Mechanics*, 165–179.

[52] „... der zweite Hauptsatz nur in bezug auf die Unvollkommenheit unserer technischen Mittel definiert ist"— M. v. SMOLUCHOWSKI, *Festschrift Ludwig Boltzmann* (Leipzig: Barth, 1904), 626, reprinted in *Pisma Marjana Smoluchowskiego* (Krakowie: Drukarnie Uniwersytetu Jagiellonskiego, 1924), **I**, 421 (quotations from p. 426).

[53] "We speak of chance in nature, when small variations in the initial data occasion considerable variations in the final elements, because we cannot observe those small variations"—A. PANNEKOEK, *Proc. Sect. Sci. K. Akad. Wet. Amsterdam* **6**, 42 (1903) (quotation from p. 48). According to J. D. VAN DER WAALS, Jr., adoption of the statistical view does not require us to abandon determinism or the mechanical view of nature. *Phys. Z.* **4**, 508 (1903).

ry."[54] It could only be made for a system "which is continually receiving disturbances at haphazard, which in fact takes a fresh start from chaos at every instant. It is fair to say that in nature disturbances are very frequently taking place. The isolated system, with its 6 N variables left to its own forces, hardly exists in practice."[55]

JEANS put the opposite interpretation on the same conclusion: the assumption favored by BURBURY, he said,

> merely amounts to a licence to misapply the calculus of probabilities. It is, if I was right, as illogical to base a kinetic theory on this assumption, coupled with the laws of dynamics, as it would be to base a system of dynamics on the asssumption that there is no causation in nature, coupling this assumptiion with the fundamental laws of dynamics.[56]

Just as illogical—but just as logical, perhaps, as what actually happened a few years later to the foundations of microscopic physics.

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[54] S. H. BURBURY, *Phil. Mag.* [6] **6**, 529 (1903). The same point was made by W. F. MAGIE: any state of the system is ordered in the sense that it is determined by the initial state, *Science* **23**, 161 (1906).

[55] BURBURY, *op. cit.*

[56] J. H. JEANS, *Phil. Mag.* [6] **6**, 720 (1903).

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