Einstein before 1905: The early papers on statistical mechanics

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(Received 14 September 1988; accepted for publication 6 June 1989)

Albert Einstein's work on the quantum and Brownian motion, which he began to publish in 1905, was preceded by three papers on kinetic theory and statistical mechanics published between 1902 and 1904. In these early papers, which give us considerable insight into Einstein's early education and development, Einstein independently derived many of Boltzmann's and Gibbs' results, including the canonical ensemble, an analysis of fluctuations, and the relation between entropy and probability. This article discusses those papers and their background in 19th-century physics.

I. INTRODUCTION

Between 1901 and the appearance of his ground-breaking work of 1905, Albert Einstein published five papers[1–5] and several book reviews[6] in the pages of the Annalen der Physik. The first two papers investigate a molecular force law; the last three concern the foundations of kinetic theory and thermodynamics.[7] To be sure, none of them matches Einstein's later work in scope or originality. Their chief value at the time perhaps lay in making Einstein known to the scientific world, in the spirit of Lord Rayleigh's tongue-in-cheek advice that "a young author who believes himself capable of great things would usually do well to secure the favorable recognition of the scientific world by work whose scope is limited, and whose value is easily judged, before embarking on greater flights."[8] But for us their value lies in what they say about Einstein himself—what he had been reading, what problems he found worth investigating, and what approaches he was taking. The kinetic theory papers in particular laid the foundations for Einstein's 1905 work on quanta[9] and Brownian motion.[10] For that reason alone they deserve to be better known.

In 1901, when the first of these five papers appeared, Einstein would have seemed an unlikely candidate to transform 20th-century physics. He had graduated the previous year from the Eidgenössische Technische Hochschule (ETH) in Zürich with adequate but by no means outstanding grades. Einstein had not found the atmosphere at the ETH congenial. He regularly cut classes and spent much of his time reading and working on his own in the laboratory. In the process, it seems, he thoroughly alienated his physics professor, Heinrich Weber. Thus, after graduating, he found himself without the assistantship or the recommendations that he otherwise might have expected. Moreover, his personal life was complicated by a partial estrangement from his parents, who thoroughly disapproved of his developing relationship with Mileva Marić, a fellow student at the ETH. His lack of a position prevented their marriage until 1903, after the birth of a daughter early in 1902. Not until June 1902 did he find stable employment in the Swiss Patent Office, having in the meantime precariously sustained himself by private tutoring and two temporary teaching positions.[11] Yet, in the midst of this uncertainty, through reading, reflection, and conversations with friends, Einstein made himself into a theoretical physicist.

II. NINETEENTH-CENTURY BACKGROUND: THE MOLECULAR HYPOTHESIS

It is striking to observe the disarray with which physics at the turn of the century presented itself to Einstein. The spectacular achievements of the 19th century in electromagnetic theory and thermodynamics had led, especially in the German-speaking countries of central Europe, to questioning of the long-dominant mechanical world view. For example, the notion of a mechanical aether (and hence a mechanical foundation for electrodynamics) was slowly dying away, and a new theoretical perspective—an electromagnetic basis for mass that would itself underlie mechanics—was fast gaining ground.[12]

Similarly, scientists as diverse as Planck and Ostwald defended thermodynamics as a branch of physics that could stand on its own, without the necessity—or the desirability—of a grounding in mechanics. The inability of the kinetic theory of gases to predict accurately the ratios of specific heats of gases or even by some accounts to explain irreversible processes remained a continuing source of difficulty.[13] Thus the atomic hypothesis itself, closely tied as it was to a mechanical description of nature, by no means enjoyed universal acceptance. The discovery of such new and poorly understood phenomena as x rays and radioactivity only added to the confusion and uncertainty. No wonder Boltzmann observed in an address to a scientific meeting in 1899 that "Everything remains...in a state of indecision and ferment."[14]

Einstein's early papers and correspondence reflect this tumult, and the memory remained fresh almost 50 years later when he wrote his "Autobiographical Notes." He was impressed by the ability of mechanics to explain a wide range of phenomena:

> What made the greatest impression upon the student, however, was less the technical construction of mechanics ...than the achievements of mechanics in areas which apparently had nothing to do with mechanics: the mechanical theory of light,...and above all the kinetic theory of gases:—the independence of the specific heat of monatomic gases of the atomic weight, the derivation of the equation of state of a gas and its relation to the specific heat, the kinetic theory of the dissociation of gases, and above all the quantitative connection of viscosity, heat-conduction, and diffusion of gases, which also furnished the absolute size of the atom. These results supported at the same time mechanics as the foundation of physics and of the atomic hypothesis...[15]

But he was also impressed by contemporary challenges to the mechanical world view, and by the competing claims of electromagnetic theory and thermodynamics:

> Reflections of this type made it clear to me as long ago as shortly after 1900, i.e., shortly after Planck's trailblazing work, that neither mechanics nor electrodynamics could

> (except in limiting cases) claim exact validity. By and by I despaired of the possibility of discovering the true laws by means of constructive efforts based on known facts. The longer and the more despairingly I tried, the more I came to the conviction that only the discovery of a universal formal principle could lead us to assured results. The example I saw before me was thermodynamics. The general principle was there given in the theorem: the laws of nature are such that it is impossible to construct a *perpetuum mobile* (of the first and second kind). How, then, could such a universal principle be found?[16]

What might have led Einstein to develop these views? In particular, what had he read on thermodynamics and kinetic theory, and how had his reading guided his approach to physics and his sense of what problems were important? Einstein's reflections on electromagnetic theory, culminating in the 1905 relativity paper, must also have influenced his thinking, especially as it led him to see the limitations of mechanics.[17] But in this article I will concentrate on thermodynamics and kinetic theory.

Einstein's reading included the leading figures in German physics in the latter half of the 19th century, physicists like Kirchhoff, Hertz, Mach, Planck, and Boltzmann. He read as well the physical chemists Ostwald and Nernst. Their works introduced Einstein in full measure to the perplexities facing physics at the turn of the century. And often these works discuss the broader aspects of physics—the status of the "mechanical world view" or the physical reality of atoms, for example—along with more limited, technical topics.

Perhaps the most intriguing connection is to the chemist Wilhelm Ostwald, whose "book on general chemistry" is the only work Einstein mentioned in his 1901 paper on molecular forces, the first paper he published. That book was the first volume of the *Textbook of General Chemistry*, subtitled *Stochiometry.*[18] To be sure, Einstein said only that he obtained the experimental parameters he needed from Ostwald. But, in addition, the *Stochiometry* contains extensive discussions of both capillarity and osmosis, topics Einstein addressed in the two molecular force papers. It also gives elementary treatments of kinetic theory and thermodynamics. Ostwald's name comes up several times in Einstein's correspondence from this period, in contexts that almost certainly refer to this work and that suggest he read it in some detail.[19]

In the *Stochiometry* Ostwald had given a conventional account of atoms and molecules. But 2 years later, when he published the first part of Vol. II of his *Textbook*, subtitled *Chemical Energy* (1893), Ostwald had explicitly rejected mechanical explanation in favor of "energetics," his idiosyncratic and none-too-rigorous physics of energy and its transformations.[20] Einstein almost certainly read in this volume as well. In one 1901 letter he used Ostwald's energetics terminology, and in another he spoke of reading Ostwald's treatment of electrochemistry, material he would have found useful for his second molecular force paper.[21]

Thus Einstein likely also encountered the sections on energetics, in which Ostwald included a vigorous attack on mechanical and atomic hypotheses. Ostwald spoke, for example, of the "dogmatic character" of the hypothesis that heat is motion and stated that a thermodynamics free of hypotheses is "not only more exact, but by far the more fruitful" approach.[22] Toward the end of the volume, Ostwald described the formation of mechanical hypotheses as a "childhood state of the intellect," as part of an extended discussion of radiant energy in which he also denied the necessity for a mechanical aether. He went on to suggest that the mechanical aether would go the way of kinetic theory, which, unlike thermodynamics,

> has led to progress only in few and relatively minor ways, in spite of the quite extraordinary expenditure of sagacity [Scharfsinn] and computational work that has been squandered on it...[23]

Einstein saw similar if better defended attacks on atomism and mechanism generally in other places, for example in Mach, whose *Science of Mechanics* and *Principles of the Theory of Heat* he had begun to read in 1897 or thereabouts.[24] Einstein recalled in his "Autobiographical Notes" that Mach had shaken his "dogmatic faith" in mechanics as the foundation of physics. He probably saw as well expressions of Mach's skeptical attitude toward atoms.[25]

Einstein had also read Gustav Kirchhoff's *Lectures on the Theory of Heat*. In the introductory sections, Kirchhoff remarked that the problem of reducing physical concepts to mechanics is closely linked to the indivisibility of matter, and that motion on a small scale could be imperceptible to the senses and still be responsible for macroscopic phenomena. For Kirchhoff, the reduction of physics to mechanics was a "goal worth striving for in the fullest measure." Nevertheless, he did not treat the theory of heat from an atomic standpoint because "At present such an approach must fail, since the mental picture [Vorstellung] that one until now could construct from thermal motion is still too unclear and cannot be subjected to satisfactory methods of calculation...The manner of these collisions is still very dark." He instead assumed that matter is distributed uniformly in space and argued that this assumption let him "start from mental pictures that are immediately connected to appearances and at the same time can be easily followed by calculation." His concluding lectures give a clear introduction to Maxwell's transport theory, but make no attempt to relate kinetic theory to thermodynamics.[26]

Similar reservations can be found in the introduction to Heinrich Hertz's *Principles of Mechanics*. Hertz, after rejecting the concept of force, suggested that a mechanics based on energy could avoid dubious atomic hypotheses:

> It is true that we are now convinced that ponderable matter consists of atoms...But the form of the atoms, their connection, their motion...are entirely hidden from us...although our conception of atoms is in itself an important and interesting object for further investigation, it is in no wise specially fit to serve as a known and secure foundation...Herein lies the advantage of the conception of energy...[27]

Nevertheless, Hertz rejected this approach as well, in part because of problems he saw in employing Hamilton's principle. He also saw a problem in defining energy rigorously: If energy is in some sense a "substance," and not derived from forces and Newton's laws, then the division of energy into kinetic and potential terms leads to difficulties—for example, in giving negative values to potential energy.[28]

Planck in his *Lectures on Thermodynamics* was equally cautious about the possibility of reducing thermodynamics to mechanics, stating of kinetic theory that

> Obstacles, at present unsurmountable...seem to stand in

> the way of its further progress...due...principally to essential difficulties...in the mechanical interpretation of the fundamental principles of thermodynamics.[29]

Planck much preferred the more fruitful approach of starting "from a few general empirical facts, mainly the two fundamental principles of thermodynamics." Unlike Ostwald or Mach, however, Planck thought these obstacles would likely prove temporary:

> Our aspiration after a uniform theory of nature, on a mechanical basis or otherwise, which has derived such powerful encouragement from the discovery of the principle of the conservation of energy, can never be permanently repressed.[30]

Einstein found still another expression of these attitudes in Henri Poincaré's *Science and Hypothesis*,[31] which the "Olympia Academy" read sometime between 1902 and 1905. Maurice Solovine recalled in 1956 that it "engrossed us and held us spellbound for weeks."[32] In Poincaré, Einstein would have found much to interest him: Chapter VI on classical mechanics argued for the problematic and conventional nature of mechanics. Chapter VIII on energy and thermodynamics spoke of the advantages of energetic theory, which "frees us from the hypothesis of atoms,...almost impossible to avoid with the classical theory," although "in passing from the classical system to the energetic...we have not advanced far enough." And in Chap. X, a discussion of the theories of modern physics, Poincaré remarked that the kinetic theory of gases had not on the whole been fruitful; but he also referred to the speculation that Brownian motion implied a violation of the second law: "One can almost see Maxwell's demon at work." Einstein may well have read this work too late for it to have been important in developing his point of view—a German translation did not appear until 1904. But at the least it would have reinforced lessons he had learned elsewhere.

This skeptical view of atomic theories by no means went unchallenged. By this time Einstein was reading Boltzmann, whose work is discussed below. He was also reading the physical chemist Walther Nernst, whose "theory of electric forces in dissociated electrolytes" he mentioned briefly in the second molecular force paper. The reference is probably to Nernst's *Theoretical Chemistry*, a work that in its treatment of physical and electrochemistry could have been very useful to Einstein. In a 1942 obituary of Nernst, he said it "offers, not only to the student but also to the scholar, an abundance of stimulating ideas; it is theoretically elementary, but clever, vivid, and full of intimations of manifold interrelations."[33] Nernst's book also contains a chapter on "The absolute size of molecules," as well as the following oblique criticism of Ostwald:

> Whether the molecular hypothesis can be squared with the actual facts, or...whether, perchance, the further building up of the doctrine of energy will lead to another and a clearer conception of matter, this is not the place nor the time to discuss...[The] molecular hypothesis, more than any other theoretical speculation, has given powerful and varied assistance to every branch of physical science...Therefore, in the following presentation of theoretical chemistry, the molecular hypothesis will receive special consideration...[34]

Einstein seems never to have seriously questioned the molecular hypothesis, in spite of his reading; but not surprisingly, he did find it a topic worthy of further investigation.

III. NINETEENTH-CENTURY BACKGROUND: THERMODYNAMICS

From many of these same authors, Einstein learned the thermodynamics that he later said gave him an example of a "universal formal principle" that alone could lead to "assured results."[35] Thermodynamics was not yet a settled discipline at the turn of the century. In spite of Clausius' maxim that "The entropy of the world tends toward a maximum," the entropy formulation of the second law was not universally understood, particularly as it applied to irreversible processes. And as we have seen, the extent to which thermodynamics could be grounded on molecular models was a matter of some controversy.

Einstein's earliest exposure to thermodynamics was probably his undergraduate introductory physics course taught by Heinrich Weber. Einstein's notes suggest a course strong in experimental detail but much weaker on the general features that later struck him as so important. The second law, for example, is discussed only in terms of a reversible Carnot cycle; irreversible processes and entropy go unmentioned.[36]

Nor is it surprising that the texts from which Einstein learned thermodynamics by no means spoke with one voice. Kirchhoff's *Lectures* give perhaps the most thorough treatment apart from Planck's that Einstein read in this period. Even so, Kirchhoff's treatment of the second law hinged on reversible heat engines. Entropy did not occupy the central position that Gibbs and Planck later gave it, and the discussion of irreversible processes was brief. Indeed, Kirchhoff stated repeatedly that the concept of entropy can properly be applied *only* to reversible processes. He added that entropy changes can be calculated for irreversible processes only if a reversible path connecting initial and final states could be found, a condition he implied would not always hold. (Planck, who edited the lectures, took vigorous exception in a footnote![37]) Einstein could have learned a great deal from Kirchhoff; he surely learned elsewhere to appreciate the central role of entropy and to think of thermodynamics as founded on the "universal formal principle" of which he spoke in his "Autobiographical Notes."

From Planck, Mach, and Ostwald, Einstein could have learned such a principle—that thermodynamics is properly grounded on the empirical absence of perpetual motion. All three used the Latin *perpetuum mobile* in this context, as did Einstein in his 1903 paper. Planck, for example, succinctly summarized the first law as follows: "it is in no way possible, either by mechanical, thermal, chemical, or other devices, to construct a *perpetuum mobile*." He argued that if the second law were not true, it would be possible to obtain virtually unlimited amounts of work from the heat contained in the earth. Consequently, "We shall..., according to the proposal of Ostwald, speak of a *perpetuum mobile* of the second kind, since it stands in the same relation to the second law as a *perpetuum mobile* of the first kind does to the first law."[38] Both Ostwald and Mach use similar language (although Mach did not adopt Planck's and Ostwald's distinction between two sorts of perpetual motion).[39] All three, moreover, emphasized what is today often called the zeroth law of thermodynamics: When two bodies are each in thermal equilibrium with a third, they are also in equilibrium with each other.[40] And all three insisted that thermodynamics can stand on its own, without the support of a mechanical underpinning.

In other respects the three were far apart. Mach in Chap. XV of his *Theory of Heat* introduced entropy following an historical discussion of the Carnot cycle and even showed how to calculate the increase in entropy for an (irreversible) adiabatic free expansion. But the entropy played no part in the following chapters, in which he analyzed the structure of thermodynamics. Instead, he treated the second law in terms of the "theorem of Carnot and Clausius," by which he meant the behavior of an ideal heat engine. He also developed mechanical and electrical analogies for reversible Carnot cycles, in which the limited convertibility of heat into work did not stand out. He by no means neglected irreversible processes, but he did not seem to look on them as central. He spoke, for example, of "special physical experiences which lie outside the scope of the theorem of Carnot and Clausius and from which results the difference in the behavior of heat and the other kinds of energy." Even the first law for Mach had a limited domain: "there is no meaning in attributing a work value to a quantity of heat which cannot be transformed into work...The principle of energy consists in a special form of viewing facts, but its domain of application is not unlimited."[41]

Unlike Mach, Ostwald believed that energy was the key to understanding nature: "*all* that we have until now been able to express by the ideas of Matter and Force—and much more besides—may actually be expressed by the idea of energy."[42] He thus proposed to reject mechanical models, and to reformulate both chemistry and physics in terms of energy and its transformations from one form to another. His laws of energetics attempted to describe those transformations. The first law was simply the conservation of energy. His "second law of energetics" was presented in two forms that he thought were equivalent. One involved the conditions for what he called "energy equilibrium" (and reads like an "energetics" version of the zeroth law). The other stated the impossibility of a *perpetuum mobile* of the second kind.

The second law of thermodynamics was for Ostwald subsidiary to his laws of energetics. To be sure, he did give a conventional derivation of the second law based on an analysis of reversible heat engines that included a definition of the entropy. But he went on to attempt an involved (and dubious) alternate derivation based on energetics principles. Thus he could look on the second law of thermodynamics as merely a special case of the second law of energetics. Both derivations are notable for their almost complete neglect of irreversible processes.[43]

In sharp contrast was Planck, whose early research had been devoted to clarifying and extending the second law, and who was preeminent in Germany in insisting on its central and fundamental nature. Planck prefaced the treatment of the second law in his *Thermodynamics* with a long general discussion of irreversible processes. He formulated the second law in terms of entropy changes, and applied it very generally to processes that need not involve the flow of heat and that need not be reversible.[44] Planck's text made a strong impression on Einstein; in his 1913 essay "Max Planck as a Scientist," he called it one of the

> ...masterworks of physical literature...that should be absent from the library of no physicist...The enjoyment with which one always takes this book to hand is due not least to the straightforward, truly artistic style characteristic of all Planck's work.[45]

Einstein also read, though we don't know when,[46] Planck's contribution to the energetics controversy that appeared in the Annalen early in 1896. That controversy, which included back-to-back articles by Boltzmann and Planck attacking the energeticists and the replies by Ostwald and Georg Helm,[47] was vigorously conducted. Planck, for example, described Ostwald's concept of volume energy as a "mathematical unthing." Planck's short, forceful article also made a strong impression on Einstein, who in the same 1913 essay said it "undoubtedly exerted an important influence" in this dispute, and described it as

> a masterfully written short piece showing that energetics as an heuristic method is worthless, indeed, that it even operates with untenable concepts. By reading this fresh short article, each friend of clean scientific thought can compensate himself for the annoyance that cannot be repressed in reading works of the kind attacked here.[48]

It is not at all clear when and in what order Einstein read these works. But we may suspect that he had for a time taken Ostwald's energetics seriously. Einstein had sent Ostwald a copy of his 1901 molecular force paper with a letter stating that the article had been inspired by Ostwald's book and asking if Ostwald "might have use for a mathematical physicist who is familiar with absolute measurements."[49] In addition, there are frequent references to Ostwald in his correspondence, including a reference to "radiant space energy," typical of Ostwald's energetics terminology.[50] It would be ironic if Ostwald's energetics, in eclipse after the attacks of Planck and Boltzmann, was nevertheless in part responsible for Einstein's willingness to question mechanical explanation and to employ energy methods as an alternative to classical mechanics in his second kinetic theory paper of 1903.

We can also see how Einstein's thinking on the second law evolved. In the introduction to his second molecular force paper, he had stated that the "second law of the mechanical theory of heat finds application to such physical systems as are able within arbitrary approximation to run through reversible cyclic processes" and suggested a generalization that might apply to the mixing of dissimilar gases.[51] It thus appears that in early 1902 he thought the second law itself, and not just the entropy principle, required reversible cycles. Further, he had begun to see for himself the limitations of those restrictions. But, by the beginning of 1903, any such restrictions had vanished: Without apparent hesitation he applied the second law to arbitrary processes in his second kinetic theory paper. By that time he had also read Planck's *Thermodynamics* carefully—an example borrowed from Planck figures prominently in the 1903 work.[52] It thus seems plausible that Planck's thermodynamics text and possibly his article attacking energetics led Einstein away from the excesses of the energeticists and toward a fuller understanding of thermodynamics.

IV. NINETEENTH-CENTURY BACKGROUND: BOLTZMANN AND KINETIC THEORY

In his final semester at the ETH, Einstein heard Hermann Minkowski lecture on capillarity in a course on "Applications of Analytical Mechanics." According to a fellow student, Einstein said it was the first lecture on mathematical physics he had heard at the Poly.[53] As an undergraduate, he had very likely read Kirchhoff's *Lectures on Mechanics,* which includes a chapter on capillary phenomena.[54] Ostwald too had treated this topic.[55] So it is perhaps not surprising that Einstein's first two published papers develop a thermodynamic description of capillary and electrolytic phenomena in order to investigate the possibility of a universal molecular potential.[56]

Einstein broke off his work on molecular potentials sometime after his second paper on that topic, which he submitted to the Annalen in April 1902. It may simply be that he found the approach unprofitable, although even in early 1903 he wrote in a letter to Michele Besso that he was at some pains over his work on molecular forces.[57] But Einstein had also been reading Boltzmann's *Lectures on Gas Theory* during this period.[58] In a letter to Mileva Marić in September 1900, he wrote, "Boltzmann is splendid...I am firmly convinced of the correctness of the principles of the theory..."[59] Einstein sent a copy of his first molecular force paper to Boltzmann[60] and by the spring of 1901 was hoping to extend his theory of molecular forces to the calculation of the transport properties of gases.[61] Those ideas may have formed the basis for his first, abortive Ph.D. dissertation of 1902, which by one account was critical of Boltzmann.[62]

From Boltzmann, Einstein would have gained a perspective on atoms and the mechanical world view very different from those of Mach, Ostwald, or Planck. Boltzmann presented mechanics as the foundation of physics and argued strongly for the fruitfulness of the kinetic–molecular theory that he had played so large a role in creating. His attitude toward the reality of atoms is complicated, and that complexity is only increased by the controversies his kinetic theory aroused.[63] But no one who read his work would have doubted his commitment to atomic models. Einstein would surely have noted Boltzmann's bitter complaint about contemporary attacks on kinetic theory that prefaced Pt. II of the *Gas Theory* and may well have seen his forceful polemics against energetics that had appeared in the Annalen in 1896.[64] He may also have read the first volume of Boltzmann's *Lectures on the Principles of Mechanics* (1897) and his two-volume *Lectures on Maxwell's Theory of Electricity and Light* (1891–1893), a work that made extensive use of mechanical models.[65]

Boltzmann had worked out his kinetic theory of gases in a series of papers in the 1860s and 1870s, in which he had taken three distinct approaches to the derivation and justification of the second law of thermodynamics.[66] First, in a series of papers in the late 1860s and early 1870s, Boltzmann used the methods of Hamiltonian dynamics, together with his generalization of Maxwell's velocity distribution function and an intuitive version of what later became known as the "ergodic hypothesis," to derive an expression for the entropy of a mechanical system. Boltzmann applied his expression for entropy not only to an ideal gas but also to a simple model for a solid, deriving the law of Dulong and Petit for the specific heat. But he did not treat irreversible processes; that is, he did not show that his expression necessarily implied entropy changes that are positive or, at best, zero for any arbitrary process.[67]

In 1872, Boltzmann developed his second approach to gas theory. Building on Maxwell's work of 1866,[68] he developed the H theorem and the well-known Boltzmann transport equation. This formulation required a detailed analysis of molecular collisions and hence was easily applicable only to gases. But the H function turns out to be a generalization of the entropy that can describe irreversible and nonequilibrium processes. And because the theory applies to transport processes, it allows a direct (if experimentally difficult) estimate of molecular dimensions.[69] Boltzmann also devoted most of Pt. I and some of Pt. II of the *Gas Theory* to transport processes and showed that they can, in principle, be used to calculate the size of a molecule.[70] Einstein referred to this work in his "Autobiographical Notes" when he wrote of "the quantitative connection of viscosity, heat-conduction, and diffusion of gases, which also furnished the absolute size of the atom."[71]

In his "Autobiographical Notes," Einstein said that his chief goal in his kinetic theory papers was "to find facts that would guarantee as much as possible the existence of atoms of definite finite size."[72] Yet neither the molecular potential nor the kinetic theory papers show an interest in molecular dimensions, or make any use of Boltzmann's transport theory. Einstein's molecular potential function does not depend on molecular size, and a 1901 letter suggests that at the time he preferred to think of molecules as point centers of force and looked on calculations of molecular dimensions with suspicion.[73] Nor does the topic come up in the kinetic theory papers, where there is only one passing reference to "point atoms." If Einstein had been consciously concerned in 1902 or 1903 to investigate molecular dimensions, he nevertheless chose not to follow the path that would have seemed to many of his contemporaries the most direct route.[74]

In 1877, Boltzmann developed a third approach to the second law, which Planck and Einstein later summarized in the famous relation between entropy and probability, $S = k \log W$. Boltzmann assumed that a fixed total energy is divided among the particles of a gas, and used combinatorials and the laws of large numbers to estimate the number of distinct microscopic states corresponding to a given molecular distribution of energies. He then argued that the logarithm of this "permutation number," which is proportional to the probability of the distribution, was a suitable measure of the entropy. This method also permitted treating irreversible processes: As a system evolves from a less probable to a more probable state, its probability, and hence its entropy, increases. Boltzmann recognized, of course, that his three approaches were not independent, and in 1877 he showed the connection between his new expression for entropy and the earlier results of 1871 and 1872.[75] But he did not make any significant use of combinatorials in later work, and the technique remained almost unknown until Planck employed it in his blackbody papers at the turn of the century.[76]

Einstein almost certainly had not read Boltzmann's papers in 1902.[77] And transport theory apart, the *Lectures on Gas Theory* is not a systematic presentation of this earlier research, but rather a collection of special topics.[78] In it, for example, Boltzmann developed the same formalism he had used in 1871 to derive an expression for the entropy. But in the *Gas Theory* he used that formalism to discuss the properties of compound molecules, with but an occasional brief reference to the wider possibilities. Similarly, he mentioned his combinatorial technique only briefly.[79] Einstein's treatment in his three kinetic theory papers is thus a complex mixture of what he took from the *Gas Theory*, his independent derivation of Boltzmann's earlier results, and additional work of his own. His achievement can be thought of as first recovering and then going beyond Boltzmann's first and third approaches to kinetic theory, based on the hints he found in the *Gas Theory* and Planck's 1901 blackbody papers. Even if the hints were sometimes strong ones, it was a remarkable achievement, the more so because Einstein increasingly found himself investigating not only kinetic theory and its relation to thermodynamics, but the status of classical mechanics as well. In the end, he also found the limits of thermodynamics.

V. EINSTEIN'S KINETIC THEORY PAPERS

By the fall of 1901, Einstein's thoughts were turning to the relation between kinetic theory and thermodynamics. He wrote Marcel Grossmann in September that he was reading Boltzmann's "works on the kinetic theory of gases" and "in recent days have written a short work that supplies the keystone to a chain of argument begun by him." This "short work" very likely became his 1902 kinetic theory paper. Einstein still may not have regarded this problem as central, for he went on to say that it was "too specialized" to be of interest to Grossman![80] Nevertheless, this new topic caught his interest and replaced molecular forces as a predominant theme in his work in 1902 and thereafter.

Einstein submitted this new work to the Annalen der Physik in June 1902, with the title "Kinetic Theory of Thermal Equilibrium and the Second Law of Thermodynamics." It was the same month in which he had been appointed a technical expert third class in the Swiss Patent Office in Bern, and only 2 months after he had submitted the second of the molecular force papers. Einstein's talent for short, vivid introductions that go quickly to the heart of a problem is as evident here as in the 1905 papers on relativity and the quantum:

> However great the achievements of the kinetic theory of heat in the province of gas theory have been, nevertheless, until now mechanics has not been able to supply an adequate foundation for the general theory of heat, because until now it has not succeeded in deducing the principles of thermal equilibrium and the second law...

In other words, Einstein was interested not in a kinetic theory of gases but a kinetic theory of heat. It is just this shift in perspective that is needed to develop a molecular foundation for the laws of thermodynamics. Although Boltzmann in 1871 had suggested by his choice of examples that his approach was not limited to gases, he did not—then or later—exploit its potential generality. He did state briefly in Sec. 35 of Pt. II of the *Gas Theory* that his mechanical approach "is not restricted to the theory of polyatomic gas molecules" and should apply to "an arbitrary warm body;" and in a footnote to Sec. 42 he sketched the application to solids and liquids.

Others had occasionally touched on this point. Maxwell, in a paper that was almost certainly unknown to Einstein in 1902, had remarked in 1878 that it was not easy to see in what ways Boltzmann's general approach is restricted to gases.[81] Gibbs in his *Elementary Principles in Statistical Mechanics*, which Einstein did not read until several years later, quietly gave a general treatment.[82] And Planck's work on blackbody radiation was one of the first applications of Boltzmann's methods to a specific system other than a gas.[83] But few others had discussed systems other than gases, and if Einstein was unaware of this aspect of Maxwell's and Boltzmann's work, it cannot be blamed on unfamiliarity with the contemporary research literature.

Einstein's mathematical tools in this first paper—chiefly Hamiltonian mechanics and Liouville's theorem—are taken almost entirely from Boltzmann's *Gas Theory*. Even the notation is similar: Both use p and q for coordinates and momenta, P and Q for initial values of p and q, and g for various infinitesimal domains in phase space.[84] It is the conceptual approach that is different: Einstein from the outset focused on general systems, with no restriction to gases, and used Boltzmann's Hamiltonian formalism to establish the molecular foundations of thermodynamics.

The first section of this paper, titled "Mechanical model for a physical system," began by considering "an arbitrary physical system representable by a mechanical system." The use of mechanical models and analogies was widespread among 19th-century physicists, and Einstein could have come across it in many places. Hertz's *Mechanics*, for example, includes a section on "dynamical models."[85] Another likely source is Boltzmann, who began the first volume of the *Gas Theory* with a section titled "Mechanical analogy for the behavior of a gas."

Boltzmann was even more explicit in his *Lectures on Maxwell's Theory of Electricity and Light*. That title would have aroused Einstein's interest, although whether he would have approved of Boltzmann's ingenious and complex mechanical models for electromagnetic phenomena is less certain; Klein has said of these models that "An unwary reader...might easily imagine that he had picked up a treatise on the design of engineering mechanisms by mistake." But surely Boltzmann's second and third lectures, which treat Helmholtz's mechanical analogy for the second law of thermodynamics, would have caught his eye. In these sections Boltzmann defended the use of mechanical analogies, remarking at one point that a mechanical model for a gas is as much an analogy as a mechanical theory of electromagnetism: "Perhaps the only difference is that we are more clearly aware of the symbolic [sinbildlichen] character of our theory."[86]

Einstein nowhere states that he read this work; and certainly his notion of a mechanical model did not entail the invention of intricate mechanisms. But his division of the forces that act on his system into two sorts, one slowly changing and derivable from a potential, the other rapidly varying and not derivable from a potential, is strongly reminiscent of Helmholtz's model. Helmholtz had used a rapidly varying cyclic coordinate in the Lagrangian (for example, the angle describing a disk rotating about an axis) to construct an analog to the kinetic energy of a gas molecule. Changes in that kinetic energy, regarded as heat, led to a function analogous to the entropy. And slow changes in the other, noncyclic, coordinates represented external work. Einstein's model, though more elaborate, used similar cyclic coordinates in the Lagrangian. Einstein could also have read of Helmholtz's model in Hertz's *Mechanics*. But Boltzmann's treatment shows the connection with heat and the second law much more clearly and explicitly.[87]

Einstein's first step in the construction of his own mechanical model was to establish a mechanical basis for the zeroth law (and hence for thermal equilibrium). In the process, almost as an aside, he introduced what Gibbs at about the same time called the canonical ensemble. Einstein first considered a collection of systems each of which has the same energy and, following Boltzmann,[88] used Liouville's theorem to show that the number of systems dN in an infinitesimal volume g of phase space is

$$dN = A\int_g dp_1...dq_n, \tag{1}$$

where A is a function of the energy and hence a constant for all systems in the ensemble. He then supposed that each system in the collection is divided into two subsystems, with momenta and positions $p_1\cdots q_n$ and $\pi_1\cdots\chi_n$. The interaction of the subsystems is negligible, so that the energy of the system can be regarded as the sum of the energies of the subsystems.

Einstein's derivation at this point has a touch of the mysterious about it: Since each member of the ensemble has the same energy, the constant A in Eq. (1) can be replaced with any function of the (constant) energy E and, in particular, with the function $A'e^{-2h\mathsf{E}}$, where h is an "arbitrary constant that we shall shortly have at our disposal." Equation (1) thus becomes

$$dN = A'\int e^{-2hE}dp_1\cdots d\chi_n. \tag{2}$$

At this point he needed only to divide his system into two subsystems, one much larger than the other, and to integrate over the variables of the larger, to obtain

$$dN = A'e^{-2hE}dp_1\cdots dq_n\int e^{-2hH}d\pi_1\cdots d\chi_n, \tag{3}$$

where H and E are the energies, respectively, of the larger and smaller subsystems, and where the total energy $\mathsf{E} = E + H$. By insisting that the integral not be a function of E, Einstein showed that h is a positive function of what he called $\omega(\mathsf{E})$, the volume of the phase space (in modern terminology) of the larger subsystem with E held fixed.

The odd character of this derivation—simply taking the constant A in Eq. (1) to be a Boltzmann factor, without anything in the way of motivation or explanation—may have its origin in Einstein's reading of Boltzmann's *Gas Theory*. In Sec. 37 of Pt. II, a section cited by Einstein, Boltzmann introduced the Boltzmann factor e^{-2hE} without explanation in a discussion of compound molecules. It is not clear that a reader unacquainted with his earlier work would have understood it. His brief discussion in Sec. 19 of Pt. I, unlike his derivation of 1871, is very closely tied to gases, so that its general character is not immediately evident. Einstein could have seen the importance of the Boltzmann factor without understanding fully how Boltzmann had arrived at it, and thus could have been led to his direct if not altogether enlightening derivation.

Having arrived at what I will continue for convenience to call the canonical ensemble, Einstein applied it (in Sec. 5) to a small system S that he called a thermometer, in equilibrium with a larger system Σ. He showed that the same value of h characterizes both S and Σ, and that h can therefore be considered a function of the absolute temperature. The zeroth law of thermodynamics follows directly.

Next came the absolute temperature. Again citing Boltzmann, Einstein derived the equipartition theorem, showing that each degree of freedom corresponds to an energy $1/4h$. Then, using an analogy with ideal gases, he defined the absolute temperature T as

$$1/4h = \kappa T, \tag{4}$$

where κ is briefly identified as a universal constant. In introducing this universal constant, Einstein may again have been following Boltzmann, who in a general discussion in Sec. 35 of Pt. II of the *Gas Theory* noted that the kinetic energy per degree of freedom of a system equals the absolute temperature "multiplied by a constant that is the same for all bodies and all temperatures." That statement is, as far as I know, the closest Boltzmann ever came to introducing what we today call Boltzmann's constant into physics.

Planck had found a numerical value for essentially the same constant, which he called k, in his 1901 papers on blackbody radiation. Einstein could easily have read them by this time; they had appeared in the Annalen within 30 pages of his own 1901 molecular force paper.[89] But as Eq. (4) suggests, Einstein's κ is just half Planck's k. Equation (4) is also consistent with Boltzmann, who likewise found the energy per degree of freedom to be $1/4h$. Furthermore, Einstein made no attempt in either the 1902 or 1903 papers to assign a numerical value to κ. One may therefore suspect that his introduction of κ owed more to Boltzmann and to his own recognition of the importance of this constant than to Planck.

Einstein ended the 1902 paper with a lengthy mechanical derivation of the second law. It is here that his mechanical *model* is most apparent. He had already introduced two sorts of forces, the one derivable from a potential and the other not. The latter, which caused "the addition of heat," correspond to cyclic coordinates in the Lagrangian and led him to an expression for the entropy equivalent to Boltzmann's 1871 result.[90] Like Boltzmann in 1871, Einstein did not treat irreversible processes. He had found a function of state that could plausibly be identified with the entropy. But he did not show that this function necessarily either increased or at best remained constant for any arbitrary process. He nevertheless concluded that "The second law thus appears as a necessary consequence of the mechanical world view."

Einstein's 1903 paper, "A Theory of the Foundations of Thermodynamics," arrived at the Annalen on 26 January 1903, only 6 months after its predecessor. As the title suggests, he was approaching the subject of his earlier effort from a more general point of view. There are two significant departures: He extended his treatment of the second law to include irreversible processes, and he attempted to divorce his theory as far as possible from a specific dependence on classical mechanics. Einstein had already broached the latter topic in 1902, when in Sec. 5 he observed that

> until now we have used the assumption that our system is mechanical only insofar as we have used Liouville's theorem and the energy principle. The fundamentals of the theory of heat can probably be developed for more generally defined systems.

And following the derivation of his expression for the entropy in Sec. 9, he noted

> The expression for the entropy ϵ is remarkable, because it depends solely on E and T, but no longer makes the special form of E as sum of potential energy and kinetic energy stand out. This fact lets us speculate that our results are more general than the mechanical description employed, particularly because the expression for h found in §3 exhibits the same character.

In these passages Einstein expressed for perhaps the first time the doubts that led him to seek alternatives to a mechanical description of nature. He may have been reflecting Hertz's remarks on the difficulties involved in a rigorous nonmechanical definition of potential energy (see above) and Hertz's program of doing away with forces—in a letter from this period Einstein spoke of "the elimination of the force concept" from physics.[91] He may also have been reflecting in a general way the notions he had absorbed from Ostwald. In any case, he began the 1903 paper in a similar vein[92]:

> The question naturally arises, whether kinetic theory is really necessary in order to derive these fundamentals of the theory of heat, or if perhaps hypotheses of a more general kind can suffice. That the latter is the case, and by what kinds of considerations one can arrive at the goal, will be shown in this essay.

Einstein began by supposing that the state of an isolated physical system is determined by a large set of scalar "state variables" $p_1 \cdots p_n$. The system evolves in time according to a set of first-order differential equations

$$\frac{dp_i}{dt} = \phi_i(p_1 \cdots p_n) \ (i = 1 \cdots i = n), \tag{5}$$

subject only to a unique constant integral that he called the "energy equation":

$$E(p_1 \cdots p_n) = \text{const.} \tag{6}$$

He next investigated the distribution in phase space of an ensemble of such systems. He first assumed that a macroscopic property of a system is determined by a time average over some function of the state variables and, further, that the time τ that a system spends in each arbitrary domain Γ of the state variables will, for very long times T, form a fixed limiting ratio τ/T. He then showed that for stationary distributions, the number of systems in the domain (or, alternatively, the probability that a single system is in the domain) is proportional to its volume in phase space. Einstein called this assumption a postulate and seemed to be using it as an alternative to Liouville's theorem. Combined with his earlier assumption that the only integral of Eqs. (5) is an energy integral, it allowed him to assume something like a postulate of equal *a priori* probabilities without explicitly invoking classical mechanics.[93]

And by now Einstein was some distance from classical mechanics. His state variables bear only the loosest relation to the positions and momenta of mechanics, and his first-order differential equations are no more than ghosts of Hamilton's equations. Thus his "energy" is simply a formal constant of the motion—it is not the energy of classical mechanics. Nor did Einstein propose a new and independent physical definition of energy, of the sort that the energeticists had attempted (and that Planck and Boltzmann had so heartily condemned). Instead, he had reduced mechanics to its barest mathematical bones. He could (and when convenient did) revert to classical mechanics as a special case. But he also had the freedom to explore, to see what might emerge from his very general assumptions. That he should have felt this program worth pursuing is persuasive evidence of the effect the debate on the foundations of physics and, in particular, the role of mechanics and the mechanical world view had on him. The molecular theory of heat had become for Einstein not simply an application of classical mechanics, but a tool for exploring its limits.

After restating the results of his 1902 paper in this new framework, Einstein extended his treatment to include arbitrary processes. Like Boltzmann in 1877, his approach involved combinatorials, which he could have seen described briefly both in Planck's papers and in Pt. I of the *Gas Theory*. There, as part of a discussion of the statistical nature of the H theorem in Secs. 6 and 8, Boltzmann had used the technique in a calculation of the entropy of an ideal gas and added that "this [probabilistic] conception of the entropy principle...strikes at the heart of the subject."

Einstein applied the combinatorial method to a discussion of the distribution in phase space of an ensemble of N systems all having the same energy (a microcanonical ensemble in Gibbs' terminology). Beginning in Sec. 7, he showed that for an equilibrium distribution, the probability dW that a system be in an infinitesimal region of phase space is proportional to the volume of phase space. If phase space is divided into ℓ equal infinitesimal domains $g_1 \cdots g_\ell$, then the probability W that at some arbitrary time t, ϵ_1 systems are in an infinitesimal domain g_1, ϵ_2 in a domain $g_2, \ldots, \epsilon_\ell$ in a domain g_ℓ is given by

$$W = \left(\frac{1}{\ell}\right)^N \frac{N!}{\epsilon_1! \epsilon_2! \cdots \epsilon_\ell!}. \tag{7}$$

Since N, ℓ, and all the ϵ are very large numbers, it follows that

$$\log W = \text{const.} - \int \epsilon \log \epsilon \, dp_1 \cdots dp_n, \tag{8}$$

where ϵ is now a function of the state variables p_i and the time, and "completely characterizes the distribution of states." Now Einstein could argue,

> If we follow the N systems for an arbitrary time, then the distribution of states, and thus also W, will change continuously with time, and we will have to assume that more and more probable distributions of states will follow from improbable ones, that is, that W always increases, until the distribution of states has become constant and W a maximum.

Einstein next had to find a connection between entropy and probability. He had derived his expressions for entropy and probability in the canonical and microcanonical ensembles, respectively, but he had neither defined those ensembles explicitly nor worked out the relation between them. Perhaps for that reason he did not derive the simple relation between entropy and probability, $S = k \log W$, that he may already have come across in Planck's work and that 2 years later, in the 1905 quantum paper, he himself named Boltzmann's principle. Instead, he argued indirectly (and at some length) that if "more and more probable distributions of states...follow from improbable ones," then his expression for the entropy of a system undergoing any arbitrary process would increase or at best remain the same.[94] Fluctuations aside, Einstein had recovered the full import of the second law.

Einstein concluded the 1903 paper by relating the entropy principle to the absence of perpetual motion—he had found his example of a "universal formal principle"! His proof, borrowed from Planck's thermodynamics text, suggests as well that he was now fully familiar with Planck's formulation of the second law. Einstein considered an isolated system consisting of a reservoir W, an engine M, and a group of adiabatic subsystems $\Sigma_1, \Sigma_2, \ldots$, on which the engine can do work. The engine goes through a complete cycle in which it receives a quantity of heat from the reservoir and does work on the subsystems Σ. The work is done reversibly, and so the entropy of the adiabatic subsystems does not change. But unlike most examples of this sort, the engine does *not* reject heat to a second, lower temperature reservoir. Accordingly, the only entropy change is that of the reservoir, $-Q/T$. Since by the second law this quantity must be positive, it follows that $Q \leqslant 0$—that is, the heat must be added to, and not extracted from, the reservoir W. In other words, work can be transformed entirely into heat, but not vice versa.[95] Hence, Einstein concluded, this condition "expresses the impossibility of a *perpetuum mobile* of the second kind."

Thus, by the beginning of 1903 when he submitted this paper to the Annalen, it is fair to say that Einstein had made himself the equal of anyone in Europe on the molecular foundations of thermodynamics. He had almost independently rederived many of Boltzmann's important results and had put those results together in a coherent whole, at a time when they were not widely understood or even widely known. He had independently arrived at Gibbs' canonical ensemble. And most important, he had taken the first steps in the development of Boltzmann's principle, his own "universal formal principle" that 2 years later was to lead him to the quantum.

Slightly over a year later, in March 1904, the third paper in this series, "Towards a General Molecular Theory of Heat," arrived at the Annalen. By this time Einstein had unquestionably read Planck's 1901 papers on blackbody radiation and was pondering their significance for his own work. His opening words echoed the title of Planck's second paper, "On the Elementary Units [Elementarquanta] of Matter and Electricity":

> First an expression for the entropy of a system will be derived, which is completely analogous to that found by Boltzmann for an ideal gas and assumed by Planck in his theory of radiation. Then a simple derivation of the second law will be given. After that the significance of a universal constant that plays an important role in the general molecular theory of heat will be investigated. Finally there follows an application of the theory to the radiation of a black body, in the course of which, without having recourse to special hypotheses, a highly interesting relationship results between the aforementioned universal constant specified by the size of the elementary units of matter and electricity and the order of magnitude of the radiation wavelengths.[96]

For Planck, one of the most important features of his blackbody work was the calculation of Boltzmann's constant and the electron charge. In spite of his puzzlement over Planck's results, that significance was surely not lost on Einstein, who in this paper calculated the value of his universal constant κ and, more important, sought out independent probes of its significance.

Before turning to these matters, Einstein first derived a considerably clearer version of the relation between entropy and probability. He first showed that his expression for the entropy of a system in equilibrium with a much larger reservoir at temperature T can be written

$$S = 2\kappa \log \omega(E), \tag{9}$$

where S is the entropy, κ is the universal constant, E is the energy of the system, and $\omega(E)$ is the volume of the shell of phase space between E and $E + \delta E$. He then replaced his combinatorial probability of 1903 with the canonical probability W that he had also found in 1903: In a unit energy interval,

$$W = Ce^{-E/2\kappa T}\omega(E). \tag{10}$$

Combining these two expressions yields

$$W = Ce^{(1/2\kappa)(S - E/T)}. \tag{11}$$

Thus Einstein had found a relation between entropy and probability very close to Boltzmann's principle. In the canonical ensemble, Einstein realized that for large systems the probability of finding energies significantly different from the peak or most probable value is small. Hence, E in Eq. (11) is essentially constant. And T in that equation is the constant temperature of the reservoir with which the system is in contact. Thus, to within an additive constant, Eq. (11) is equivalent to $S = k \log W$. Although Einstein did not explicitly make this last point, it is hard to imagine that he did not understand it.[97]

Einstein then turned to the calculation and significance of the constant κ. He first considered a system—a single point molecule—in contact with an infinite heat reservoir and, using his canonical formulation, calculated the average kinetic energy of the molecule to be $3\kappa T$. He noted that from the kinetic theory of gases and the ideal gas law, the kinetic energy per mole is equal to $\frac{3}{2}RT$. If N is the number of molecules in a mole, it follows that $\kappa = R/2N$. His numerical values of R and N were almost certainly taken from Planck's second Annalen paper.[98]

Einstein's work up to this point thus suggests more an understanding of the importance of his universal constant κ than an independent calculation of its value. But in the following section, titled "General Significance of the Constant κ," Einstein broke new ground in recognizing that κ is related to the stability of a system against fluctuations. Maxwell, with the introduction of his "demon," had already suggested the possibility of thermal fluctuations.[99] Boltzmann too, especially after the controversies of the 1890s, recognized that fluctuations were, in principle, possible. But neither one developed a formal procedure for calculating their magnitude. Even Gibbs, who made such a calculation, assumed that fluctuations would be undetectable.[100]

The canonical ensemble is conducive to a calculation of energy fluctuations, since it assumes a system that can exchange energy with a reservoir with which it is in equilibrium. Hence, it is no coincidence that both Einstein and Gibbs explicitly calculated expressions for energy fluctuations. Only Einstein, however, sought out instances in which those fluctuations would be significant. What led him to take this step is not clear. His introduction of the canonical ensemble to examine a small thermometer in equilibrium with a much larger system might possibly have led him to take seriously the possibility of significant fluctuations in small systems. And as we have seen, he had calculated κ by considering a very small system indeed: a single gas molecule in equilibrium with the rest of the gas. In both the 1902 (Sec. 7) and 1903 (Sec. 4) papers he had used the same technique to derive the Maxwell–Boltzmann velocity distribution law.[101] It is by no means impossible that Einstein might have looked on the Maxwell–Boltzmann distribution as an example of a small system that showed large fluctuations!

Einstein's derivation is straightforward. He first (in Sec. 4) found the average energy in the canonical ensemble and used it to calculate the now-standard result for the energy fluctuations:

$$\langle E^2 \rangle - \langle E \rangle^2 = \epsilon^2 = 2\kappa T^2 \frac{d\langle E \rangle}{dT}, \tag{12}$$

and went on to say,

> The absolute constant κ thus specifies the thermal stability of the system. This last relation is interesting because in it no quantity is found that suggests hypotheses lying at the foundation of the theory...
>
> The equation just found would permit an exact determination of the universal constant κ, if it were possible to determine the average value of the square of the energy fluctuation of a system; however, such is in the present state of our knowledge not the case. From experience we can in general imagine only a single class of physical systems in which an energy fluctuation might come to hand; it is that of empty space filled with thermal radiation.

He argued that if the linear dimensions of the space are on the order of a wavelength, then the energy fluctuations should be of the same order of magnitude as the energy itself. Equating the two, he found that the characteristic length that emerges from the calculation

$$2(\kappa/c)^{1/3}/T = 0.42/T, \tag{13}$$

where c is essentially the Stefan–Boltzmann constant, is of the same order of magnitude as the wavelength of the peak of the blackbody curve, $0.293/T$. Again, the numerical values were probably taken from Planck.[102] Einstein concluded that "because of the great generality of our hypotheses, this agreement should not be attributed to chance."

By his willingness to apply his kinetic theory to a decidedly nonmechanical system, Einstein showed the power of the approach he had begun in 1903. He was still far from a theory of blackbody radiation, although the agreement of his calculation with experiment was striking and must have seemed an encouraging confirmation of his approach. Einstein said of himself in the "Autobiographical Notes" that in physics he

> soon learned to scent out that which was able to lead to fundamentals and to turn aside from everything else, from the multitude of things which clutter up the mind and divert it from the essential.[103]

He had indeed found a fundamental path, which led him in the following years not only to the quantum, but to Brownian motion and critical opalescence as well. His molecular theory of heat—divorced from the classical mechanics, but grounded in a second law generalized to include Boltzmann's principle and fluctuations—was to provide a sure guide in the years ahead.

Note added in proof. The discrepancy between Einstein's $0.293/T$ and Planck's $0.294/T$ (Ref. 102) has been plausibly explained in the recently published second volume of Einstein's collected papers [Albert Einstein, *The Collected Papers of Albert Einstein*, edited by John Stachel *et al.* (Princeton U. P., Princeton, NJ, 1989), Vol. II, p. 108]. The editors have also uncovered evidence, based on turns of phrase, that suggests Einstein may have read two of Boltzmann's papers from the 1880s, both published in the Journal für die reine und angewandte Mathematik (see pp. 44 and 74). I do not think that the arguments I present here are significantly affected; but it is worth mentioning that in one of those papers, Boltzmann treats Helmholtz's mechanical analogy for the second law of thermodynamics, which I discuss in Sec. V. Einstein could conceivably have encountered it there as well.

ACKNOWLEDGMENTS

I am grateful to Roger Stuewer, Erwin Hiebert, Anne Lee Bain, and the anonymous referees for this Journal, who read earlier drafts of this essay and offered a number of helpful comments and suggestions. I have benefited greatly from several conversations with Martin J. Klein, who first called attention to Einstein's statistical mechanics and its importance for his later work; the many references in the notes to Professor Klein's published work, on which this essay builds, convey only a partial sense of my indebtedness. I am also grateful to Mark Thamert, OSB, and to Thomas Nichol for their help with Einstein's German. It is customary (and correct!) to add that I am solely responsible for any errors of fact or interpretation. I am also happy to acknowledge partial support for this work from the Bush Foundation and from a MacPherson grant from St. John's University.

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[12] See, for example, Arthur I. Miller, *Albert Einstein's Special Theory of Relativity* (Addison-Wesley, Reading, MA, 1981), Chap. 1.

[13] See, for example, Ref. 12, Chap. 1; Martin J. Klein, "The development of Boltzmann's statistical ideas," in *The Boltzmann Equation: Theory and Applications; Acta Physica Austraica Suppl. X*, edited by E. D. G. Cohen and W. Thirring (Springer-Verlag, Vienna, 1973), pp. 53–106; Kuhn, Ref. 7, Chap. II; and Stephen G. Brush, *The Kind of Motion We Call Heat* (North-Holland, New York, 1976), especially Chaps. 10 and 14.

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[15] Albert Einstein, "Autobiographical notes," in *Albert Einstein: Philosopher and Scientist*, edited by Paul A. Schlipp (Open Court, LaSalle, 1969), 3rd ed., p. 19. This work was written many years after the fact, and as Einstein himself warned, must be read with caution.

[16] Reference 15, p. 52.

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[18] Wilhelm Ostwald, *Lehrbuch der Allgemeinen Chemie*, Vol. I: *Stöchiometrie* (Engelmann, Leipzig, 1891), 2nd ed. Einstein's reference to the data of R. Schiff makes it clear that he was using the second edition (see pp. 354ff).

[19] CW I, Ref. 11, documents 92, 97, and 127, and possibly 79, 93, and 101.

[20] Wilhelm Ostwald, *Lehrbuch der Allgemeinen Chemie*, Vol. II, Pt. 1: *Chemische Energie* (Wilhelm Engelmann, Leipzig, 1893), 2nd ed. For discussions of the energetics movement, see Robert John Deltete, "The energetics controversy in late nineteenth-century Germany: Helm, Ostwald, and their critics," Ph.D. dissertation, Yale University, 1983; Erwin N. Hiebert, "The energetics controversy and the new thermodynamics," in *Perspectives in the History of Science and Technology*, edited by Duane H. D. Roller (University of Oklahoma, Norman, 1971), pp. 67–86; and Arie Leegwater, "The development of Wilhelm Ostwald's chemical energetics," Centaurus **29**, 314–337 (1986).

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[23] Reference 22, pp. 1012ff. See also the discussion in Holton, Ref. 17, pp. 219ff.

[24] Ernst Mach, *Die Mechanik in ihrer Entwicklung historisch-kritisch dargestellt* (Brockhaus, Leipzig, 1889), translated by Thomas J. McCormack, *The Science of Mechanics* (Open Court, LaSalle, 1960); Ernst Mach, *Die Principien der Wärmelehre* (Barth, Leipzig, 1896), translated in *Principles of the Theory of Heat*, edited by Brian McGuinness (Reidel, Boston, 1986). For the date, see a 1952 letter from Einstein to Carl Seelig, quoted in Holton, Ref. 17, p. 223.

[25] Reference 15, p. 21. For Mach on atoms, see, for example, Mach, *Mechanik*, Ref. 24, Chap. IV, Pt. IV, Sec. 9, and Chap. V, Pt. I, Sec. 2; and Mach, *Wärmelehre*, Ref. 24, Chap. XXI, Sec. 6; Chap. XXIV, Sec. 5; and Chap. 30, Sec. 7. For discussions of Mach's influence on Einstein, see Martin J. Klein's introduction to the English translation of Mach's *Wärmelehre*, Ref. 24, as well as Ref. 12, Chap. 2, and Ref. 17, Chap. 8.

[26] Gustav Kirchhoff, *Vorlesungen über die Theorie der Wärme* (Teubner, Leipzig, 1894), pp. 2ff. Einstein mentions this work in Einstein to Marić, April 1901, CW I, Ref. 11, Document 101. See also Christa Jungnickel and Russell McCormmach, *Intellectual Mastery of Nature* (University of Chicago, Chicago, 1986), Vol. 2, pp. 126–127.

[27] Heinrich Hertz, *Die Prinzipien der Mechanik* (Teubner, Leipzig, 1894); translated by D. E. Jones and J. T. Walley, *The Principles of Mechanics* (MacMillan, London, 1899; reprinted Dover, New York, 1956), p. 18 of the Dover edition.

[28] Reference 27, pp. 18–24 of the Dover edition.

[29] Max Planck, *Vorlesungen über Thermodynamik* (Von Veit, Leipzig, 1897), translated by Alexander Ogg, *Treatise on Thermodynamics* (Longmans, Green, London, 1927), p. viii.

[30] Reference 29, pp. viii and ix (Ogg translation).

[31] Henri Poincaré, *La Science et l'Hypothèse* (Flammarion, Paris, 1902), translated as *Science and Hypothesis* (Dover, New York, 1956).

[32] Albert Einstein, *Lettres à Maurice Solovine* (Gauthier-Villars, Paris, 1956), translated by Wade Baskin, *Letters to Solovine* (Philosophical Library, New York, 1987), p. 9 of the translation. The Olympia Academy was an informal reading and discussion group consisting of Einstein, Solovine, and Konrad Habicht.

[33] Albert Einstein, "The work and personality of Walther Nernst," Sci. Mon. **54**, 195–196 (1942), reprinted in Albert Einstein, *Out of My Later Years* (Citadel, Secaucus, 1956), pp. 233–235.

[34] Walther Nernst, *Theoretische Chemie vom Standpunkte der Avogadroschen Regel und der Thermodynamik* (Encke, Stuttgart, 1893), translated by Charles Palter, *Theoretical Chemistry* (MacMillan, London, 1895), p. 22 of the translation.

[35] Reference 15, p. 52. Note that Hermann von Helmholtz is not one of the authors I discuss in this section. Einstein did read his work during this period. But Helmholtz's *Vorlesungen über Theorie der Wärme* (Barth, Leipzig, 1903) was not published until 1903, probably in the latter part of the year; the editor's preface is dated Feb. 1903. Helmholtz is closer to Planck than Kirchhoff in his treatment of the second law, but he does not approach Planck's scope and generality, and his section on kinetic theory does not go beyond Maxwell. Thus Helmholtz is unlikely to have contributed directly to Einstein's education in thermodynamics or kinetic theory. But see also the discussion of Helmholtz's mechanical analogy to the second law in Sec. V, below.

[36] CW I, Ref. 11, document 37. For the discussion of Carnot cycles, see pp. 106ff (pp. 66ff of the translation).

[37] Kirchhoff, Ref. 26, especially lectures 5 and 6. Planck's note is on p. 69. Kirchhoff had criticized Planck's Ph.D. thesis on the same grounds, that the concept of entropy should not be applied to irreversible processes. See Planck, *Wissenschaftliche Selbstbiographie* (Barth, Leipzig, 1949), translated by Frank Gaynor, *Scientific Autobiography and Other Papers* (Philosophical Library, New York, 1949), p. 19 of the translation.

[38] Reference 29 (Ogg translation), Secs. 55 and 116.

[39] See, for example, Mach, *Wärmelehre*, Ref. 24, Chap. XIV, Sec. 10, Chap. XVI, Sec. 1, and Chap. XVIII; and Ostwald, Ref. 20, pp. 472–474.

[40] See Ref. 29, Sec. 2; Mach, *Wärmelehre*, Ref. 24, Chap. II, Sec. 3; Ostwald, Ref. 20, pp. 472 and 485 (Ostwald's discussion is in an energetics context). I could not find explicit statements of the law in either Kirchhoff, Ref. 26, or Einstein's undergraduate notes, CW I, Ref. 11, document 37. The term "zeroth law" is of course an anachronism, used here for convenience; it was first used in Ralph Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge U. P., Cambridge, England, 1939), Sec. 222.

[41] Mach, *Wärmelehre*, Ref. 24, Chap. XIX, Secs. 10, 14, and 18. For a detailed discussion of Mach's thermodynamics, see Erwin N. Hiebert, *The Conception of Thermodynamics in the Scientific Thought of Mach and Planck* (Bericht 5/68, Ernst Mach Institut, Freiburg i. Br., 1968).

[42] Wilhelm Ostwald, "Die Überwindung des wissenschaftlichen Materialismus," *Verhandlungen der Gesellschaft deutscher Naturforscher und Ärtze* (1895), pp. 155–168, translated by F. G. Donnan and F. B. Kenrick, Sci. Prog. **4**, 419–436 (1896), and reprinted in *The Question of the Atom*, edited by Mary Jo Nye (Tomash, Los Angeles, 1984), pp. 337–356.

[43] See Ostwald, Ref. 20, especially pp. 1–50 and pp. 471–499 for his second law of energetics. Later (pp. 1016ff), he argued that irreversible processes were a special consequence of radiant energy. See the work of Hiebert, Leegwater, and Deltete, Ref. 20, for more detailed discussions.

[44] Reference 29, especially Pt. III, Chaps. I and II. See also Hiebert, Ref. 41, Kuhn, Ref. 7, pp. 11ff, and Deltete, Ref. 20, Chaps. III and VIII.

[45] Albert Einstein, "Max Planck als Forscher," Naturwissenschaften **1**, 1076–1079 (1913).

[46] Einstein was reading the Annalen no later than 1899; see Einstein to Marić, September 1899, CW I, Ref. 11, document 57. The Annalen was found in the libraries of many gymnasia—see Jungnickel and McCormmach, Ref. 26, Vol. 2, p. 4. Thus Einstein might well have become acquainted with it at Aarau, or even before.

[47] Ludwig Boltzmann, "Ein Wort der Mathematik an die Energetik," Ann. Phys. **57**, 39–71 (1896), and also "Zur Energetik," Ann. Phys. **58**, 595–598 (1896); and "Nochmals über die Atomistik," Ann. Phys. **61**, 790–793 (1897); Max Planck, "Gegen die neuere Energetik," Ann. Phys. **57**, 72–78 (1896); Wilhelm Ostwald, "Zur Energetik," Ann. Phys. **58**, 154–167 (1896); and Georg Helm, "Zur Energetik," Ann. Phys. **57**, 646–659 (1896). See the sources cited in Ref. 20 for discussions of this controversy.

[48] Reference 45.

[49] Einstein to Ostwald, 19 March 1901, CW I, Ref. 11, document 92. One can make too much of this point. Boltzmann, for example, was also sent a copy (see document 85). See also Einstein to Marić, April 1901, document 96, in which Einstein said that he would soon "have honored all physicists from the North Sea to the southern tip of Italy" with job enquiries.

[50] See Ref. 21.

[51] Reference 2. Einstein postulated "mixtures on whose individual components arbitrary conservative forces act." For a brief discussion see Patrick H. Byrne, "Statistical and causal concepts in Einstein's early thought," Ann. Sci. **37**, 215–228 (1980). Einstein developed his ideas on conservative forces further in his first kinetic theory paper—see Sec. V, below.

[52] See Sec. V, below. For a probable earlier reference to Planck's text, see Marić to Einstein, November 1901, CW I, Ref. 11, document 123 in which she thanked him for the book of Planck's he had sent her.

[53] The source of the anecdote is Louis Kollros, "Erinnerungen-Souvenirs," Schweiz. Hochschulzeit. (Sonderheft) **28**, 169–173 (1955), reprinted in *Helle Zeit-dunkle Zeit*, edited by Carl Seelig (Europa Verlag, Zürich, 1956), p. 21. See also CW I, Ref. 11, pp. 265 and 399.

[54] Gustav Kirchhoff, *Vorlesungen über Mathematische Physik: Mechanik* (Teubner, Leipzig, 1876), lecture 13. This work is mentioned in CW I, Ref. 11, document 69; see also p. 369 for Minkowski's course. Capillarity was an important research topic for much of the 19th century; Minkowski himself wrote a review article in 1907. See Mehra, *Historical Development*, Ref. 7, p. 62, for a brief discussion and bibliography.

[55] Reference 18, Book 3, Chap. 12.

[56] References 1 and 2. See Pais, Ref. 7, pp. 56ff, and Klein, "Thought," Ref. 7, p. 510, for brief discussions.

[57] Speziali, Ref. 7, p. 14.

[58] Ludwig Boltzmann, *Vorlesungen über Gastheorie* (Barth, Leipzig, 1896–1898), reprinted in *Gesamtausgabe*, edited by Roman U. Sexl (Vieweg, Braunschweig/Wiesbaden, 1981), Vol. 1, translated by Stephen G. Brush, *Lectures on Gas Theory* (University of California, Berkeley, 1964).

[59] Einstein to Marić, CW I, Ref. 11, document 75; see also document 102. There is one earlier mention of Boltzmann (document 54), but the work is not specified, and might be Vol. I of his *Vorlesungen über die Prinzipe der Mechanik* (Barth, Liepzig, 1897–1904), or his *Vorlesungen über Maxwells Theorie der Electricität und des Lichtes* (Barth, Leipzig, 1891–1893), reprinted in *Gesamtausgabe*, edited by Roman U. Sexl (Vieweg, Braunschweig/Wiesbaden, 1982), Vol. 2.

[60] Marić to Helene Savić, 20 December 1900, CW I, Ref. 11, document 85.

[61] Einstein to Grossmann, 14 April 1901, CW I, Ref. 11, document 100; and Einstein to Marić, April 1901, documents 101 and 102.

[62] Anton Reiser, *Albert Einstein* (Boni, New York, 1930), p. 69. (Reiser was a pseudonym for Rudolph Kayser, Einstein's son-in-law.) The criticisms could have concerned Einstein's own efforts to use his molecular force law to calculate the transport coefficients of gases. (See Einstein to Marić, April 1901, CW I, Ref. 11, document 101.) If Kayser's account is correct, it seems likely that this work was separate from Einstein's 1902 kinetic theory paper, on which he was also working at this time.

[63] For Boltzmann's views on atomic models and mechanics, see Boltzmann, Ref. 14. See also Erwin N. Hiebert, "Boltzmann's conception of theory construction," in *Pisa Conference Proceedings*, edited by J. Hintikka, D. Gruender, and E. Agazzi (Reidel, Boston, 1980), Vol. II, pp. 175–198. See also Sec. V below.

[64] See Ref. 47.

[65] Boltzmann, Ref. 59, *Mechanik* and *Maxwells Theorie.*

[66] My brief summary follows Klein, Ref. 13, and Martin J. Klein, *Paul Ehrenfest*, Vol. 1: *The Making of a Theoretical Physicist* (North-Holland, New York, 1970), Chap. 6. See also Kuhn, Ref. 7, Chap. II; and Brush, *Heat*, Ref. 13, Chaps. 6, 10, and 14.

[67] Ludwig Boltzmann, "Über das Wärmegleichgewicht zwischen mehratomigen Gasmoleculen," Wien. Ber. **63**, 397 (1871), reprinted in *Wissenschaftliche Abhandlungen*, edited by Fritz Hasenöhrl (Barth, Leipzig, 1909), Vol. I, pp. 237–258 (hereafter cited as WA); "Einige allgemeine Sätze über Wärmegleichgewicht," Wien. Ber. **63**, 679 (1971), and WA I, pp. 259–287; "Analytischer Beweiss des zweiten hauptsatzes der mechanischen Wärmetheorie aus den Sätzen über das Gleichgewicht der lebendigen Kraft," Wien. Ber. **63**, 712 (1871), and WA I, pp. 288–308. The expression for the entropy appears on p. 303: If r is the number of molecules, χ the potential energy, h a function inversely proportional to the absolute temperature, and $d\sigma$ the infinitesimal volume $dx_1,...,dx_n$, then the entropy is given by the expression

$$-r\ln h+\frac{2h}{3}\langle\chi\rangle+\frac{2}{3}\ln\int\exp(-h\chi)d\sigma+\text{const.}$$

[68] James Clerk Maxwell, "On the dynamical theory of gases," Philos. Trans. **157**, 49–88 (1867), reprinted in *The Scientific Papers of James Clerk Maxwell*, edited by W. D. Niven (Cambridge U. P., Cambridge, England, 1890), reprinted Dover, New York, 1952, Vol. II, pp. 26–78 (hereafter cited as *Papers*). (Maxwell's kinetic theory papers were apparently never translated into German.)

[69] Ludwig Boltzmann, "Weiterer Studien über das Wärmgleichgewicht unter Gasmolecülen," Wien. Ber. **66**, 275 (1872) and WA I, pp. 316–402, translated in *Kinetic Theory*, edited by S. G. Brush, Vol. 2: *Irreversible Processes* (Pergamon, New York, 1966), pp. 88–175.

[70] Boltzmann, Ref. 58, Pt. I, Sec. 12 and Pt. II, Sec. 22. See the discussion in Klein, "Fluctuations," Ref. 7, p. 55.

[71] Reference 15, p. 19.

[72] Reference 15, p. 47; see also Ref. 16 above.

[73] Einstein to Marić, CW I, Ref. 11, document 102, in which he spoke sharply of "the mathematically unclear concept of the size of a molecule." In an earlier letter to Marić (document 75, September 1900), he referred ambiguously to "mass points of finite definite size."

[74] For "point atoms" see Ref. 5, Sec. 3. Even when his interests did turn to molecular dimensions in his 1905 Ph.D. dissertation, he made no direct use of his kinetic theory or Boltzmann's transport theory; see Pais, Ref. 7, pp. 88ff.

[75] Ludwig Boltzmann, "Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht," Wien. Ber. **76**, 373 (1877) and WA II, pp. 164–223; the comparison is on p. 222.

[76] Max Planck, "Ueber das Gesetz der Energieverteilung im Normalspectrum," Ann. Phys. **4**, 553–563 (1901) and "Ueber die Elementarquanta der Materie und der Electricität," Ann. Phys. **4**, 564–566 (1901). Translations of the versions that Planck gave in late 1900 to the German Physical Society are in *Planck's Original Papers in Quantum Physics*, edited by Hans Kangro (Taylor and Francis, London, 1972). See also the discussions by Martin J. Klein, in "Max Planck and the beginnings of quantum theory," AHES **1**, 459–479 (1962) and *Ehrenfest*, Ref. 66, Chap. 10, and by Kuhn, Ref. 7.

[77] See Ref. 80 below.

[78] See, for example, Klein, Ref. 13, pp. 92ff.

[79] Boltzmann, Ref. 58, Pt. II, Chaps. 3 and 4; combinatorials are used in Pt. I, Secs. 6 and 8. Boltzmann also made frequent references to his

earlier work.

[80] Einstein to Grossman, CW I, Ref. 11, document 122. The reference is probably to the two volumes of Boltzmann's *Gastheorie* and possibly also to his *Maxwells Theorie*, Ref. 59; see below. It is unlikely to refer to his Wiener Berichte papers. Einstein's correspondence makes no mention of journals apart from the Annalen during this period; and he wrote from Winterhur, where he was temporarily employed as a high-school teacher and where Boltzmann's papers were not likely to be available. Einstein's few citations include his direct borrowing of Liouville's theorem and the equipartition theorem from the *Gastheorie*, but not Boltzmann's 1871 expression for entropy (Ref. 67; compare Ref. 90); and his derivation is quite different from Boltzmann's, as is his use of combinatorials in 1903. Finally, Einstein says in his 1949 "Autobiographical notes" that at this time he was "not acquainted with the earlier investigations of Boltzmann and Gibbs," Ref. 15, p. 47.

[81] James Clerk Maxwell, "On Boltzmann's theorem on the average distribution of energy in a system of material points," Proc. Cambridge Philos. Soc. **12**, 547 (1879); Papers II, pp. 713–741.

[82] Josiah Willard Gibbs, *Elementary Principles in Statistical Mechanics* (Scribner's, New York, 1902). In a 1911 note in the Annalen, Einstein said that had he known of Gibbs' book in 1902, he would not have published his own work; see A. Einstein, "Bemerkungen zu den P. Hertzschen Arbeiten: 'Über die mechanischen Grundlagen der Thermodynamik'," Ann. Phys. **34**, 175–176 (1911). See also Ref. 80 above.

[83] Planck, "Normalspectrum" and "Elementarquanta," Ref. 76.

[84] Boltzmann, Ref. 58, Pt. II, Secs. 25 and 28.

[85] Hertz, *Mechanik*, Ref. 27, Secs. 418–428.

[86] Boltzmann, *Maxwells Theorie*, Ref. 65. The quotation is at the end of the second lecture. The description of Boltzmann's book is from Martin J. Klein, "Mechanical explanation at the end of the nineteenth century," Centaurus **17**, 58–82 (1972), p. 73, which also contains a detailed account of Boltzmann's approach to mechanical analogy.

[87] See Hertz, *Mechanik*, Ref. 27, Secs. 546–600. In 1902 Einstein was unlikely to have seen Helmholtz's papers or Boltzmann's discussions of them from the 1880s. Helmholtz's textbook discussion of his model in Helmholtz, Ref. 35, did not appear until 1903. I have not come across any other treatments of Helmholtz's model in the textbook literature. For bibliography and a full discussion of this model see Klein, Ref. 86, and Klein, *Ehrenfest*, Ref. 66, Chap. 4.

[88] Boltzmann, Ref. 58, Pt. II, Sec. 26. Such a collection is essentially what Gibbs called a microcanonical ensemble.

[89] For Planck's papers, see Ref. 76. Einstein referred to Planck's work on radiation and resonators in two letters from 1901: Einstein to Marić, April 1901, CW I, Ref. 11, documents 96 and 97. See Martin J. Klein, "The beginnings of quantum theory," in *History of Twentieth-Century Physics*, edited by C. Weiner (Academic, New York, 1977), pp. 1–39, for a discussion of Planck's treatment and the problems Einstein saw in it.

[90] Einstein's expression for entropy in Sec. 9 is

$$S=\frac{\langle E\rangle}{T}+\frac{2}{3}\ln\int\exp(-hE)\,dp_1\cdots dq_n+\text{const.}$$

For Boltzmann's equivalent result (which used velocities instead of momenta), see Ref. 67.

[91] Einstein to Besso, March 1903, in Speziali, Ref. 7, pp. 13ff. Einstein also makes this connection in his "Autobiographical notes," Ref. 15, p. 31.

[92] See the discussions of the 1902 and 1903 papers in Klein, "Thermodynamics," "Fluctuations," and "World View," Ref. 7, which first called attention to the importance of these passages. See also the discussions in Pais, Ref. 7, p. 67 and Kuhn, Ref. 7, pp. 170ff.

[93] Boltzmann had taken a similar approach in some of his early papers, but not in the *Gas Theory*; see, for example, Boltzmann, "Analytischer Beweiss," Ref. 67. See Klein, "World View," Ref. 7, pp. 190ff; Martin J. Klein, "Einstein's first paper on quanta," Nat. Philos. **2**, 59–86 (1963), pp. 71ff; and Pais, Ref. 7, pp. 73ff, for discussions of Einstein's later use of this concept to give a physical definition of probability.

[94] Boltzmann makes a similar statement in Sec. 8 of Pt. I of the *Gas Theory*, and more careful statements in Secs. 38, 40, and 88 of Pt. II.

[95] Planck, *Thermodynamik*, Ref. 29, Sec. 139, gave exactly the same argument. It appears that Planck was reading Einstein as well; in the third edition of his text published in 1911, Planck, apparently echoing Einstein's words cited below, added to Sec. 139 the statement that this example "formulates analytically the impossibility of a *perpetuum mobile* of the second kind."

[96] Reference 5. The reference to Boltzmann is probably to Sec. 8 of Pt. I of the *Gas Theory*. For discussions of this paper, see Klein, "Fluctuations," Ref. 7; Pais, Ref. 7, pp. 68ff; and Kuhn, Ref. 7, pp. 176ff.

[97] Nevertheless, it is instructive to compare his 1904 treatment with the far more general discussion of Boltzmann's principle he gave a year later, in the 1905 quantum paper; Einstein, "Gesichtspunkt," Ref. 9. See Klein, "First paper," Ref. 93 for a discussion of Einstein's use of Boltzmann's principle in 1905.

[98] Planck, "Elementarquanta," Ref. 76. For R Einstein used Planck's value 8.31×10^7 ergs/(mol K). [He could not have gotten it from Planck's thermodynamics text, where, because it is referred to the atomic weight of hydrogen rather than oxygen, R is given (Sec. 39) as 8.25×10^7.] The value for N, the number of molecules in a mole, is also taken from Planck, who compared his own result, 6.175×10^{23}, to Meyer's value, cited as 6.4×10^{23}. But as Kangro has pointed out, Planck had misread Meyer, whose value of 640 trillion hydrogen molecules per milligram corresponds (assuming a molecular weight of 2.016 for molecular hydrogen) to 1.29×10^{24} molecules/mol. See Oskar Emil Meyer, *Die kinetische Theorie der Gase* (Maruschke, Breslau, 1899), 2nd ed., Chap. 10, especially Secs. 120, 121, and Kangro, *Papers*, Ref. 76, pp. 44 and 59. (The estimates for Avogadro's number, as for most molecular magnitudes at the turn of the century, were not particularly accurate.) Significantly, Einstein cited not Planck's value but Meyer's, whose book on kinetic theory he knew of, but probably did not use directly.

[99] James Clerk Maxwell, *Theory of Heat* (Longmans, Green, London, 1872). A German translation was published in 1877 (Maruschke and Berendt, Breslau, 1877), but there is nothing to suggest Einstein read it during this period.

[100] See, for example, Boltzmann, Ref. 58, Secs. 38, 40, and 88 of Pt. II; and Gibbs, Ref. 82, p. 74. See also the discussion in Klein, "Fluctuations," Ref. 7, p. 44.

[101] In developing this now-standard textbook derivation, Einstein had again been anticipated by Boltzmann, who in Boltzmann, "Sätze," Ref. 67, after a long and complex argument, had arrived at something very like the canonical ensemble and had found the Maxwell–Boltzmann distribution by considering a single gas molecule in equilibrium with the rest of the gas. I am indebted to Martin J. Klein for calling this paper to my attention.

[102] The numerical value $0.293/T$ was probably taken from Planck's first blackbody paper [Planck, "Gesetz" (Ref. 76)], which cites the results of Lummer and Pringsheim. For Einstein's fluctuation-based estimate of $0.42/T$, he needed the Stefan–Boltzmann constant σ (more precisely, he used $c=4\sigma/C$, where C is the speed of light). He cited the value 7.06×10^{-15} ergs/(cm^3 K^4), which he probably also took from Planck's paper.

[103] Einstein, Ref. 15, p. 17.