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Jürgen Renn

Einstein's Controversy with Drude and the Origin of Statistical Mechanics: A New Glimpse from the "Love Letters"

# EINSTEIN'S CONTROVERSY WITH DRUDE AND THE ORIGIN OF STATISTICAL MECHANICS: A NEW GLIMPSE FROM THE "LOVE LETTERS"

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# 1. Introduction: Statistical Mechanics as a Conduit from Classical to Modern Physics

In this paper I argue that statistical mechanics, at least in the version published by Einstein in 1902,<sup>1</sup> was the result of a reinterpretation of already existing results by Boltzmann. I will show that, for this reinterpretation, a certain perspective on these results was decisive which was shaped by Einstein's occupation with specific problems of the constitution of matter and radiation, as well as with atomism as a general foundation of physics. Using newly available evidence, I will identify the electron theory of metals as the key problem triggering the elaboration of statistical mechanics. In this way, a conjecture by the Ehrenfests on the role of electron theory for a renewal of statistical physics, as well as a hypothesis by the editors of volume 2 of Einstein's *Collected Papers* concerning its role for Einstein's work, receive an unexpected confirmation. In addition, I will argue that a controversy between Einstein and Drude in 1901 was, in effect, not so much a dispute about the latter's electron theory of metals, as has been assumed so far, but a controversy in which Einstein's real opponent was, at least in part, Boltzmann and whose issue was the foundation of an atomistic theory of matter. It was this controversy which became the starting point of Einstein's elaboration of his approach to statistical mechanics.

The development of statistical physics in the 19th century was closely associated with the hope to extend the mechanical principles to the range of thermal phenomena and to establish atomism as a conceptual foundation of physics. The work of Maxwell and Boltzmann on the kinetic theory of gas provided a solid foundation for this hope. It was based on an idealized but nevertheless rather concrete model of a gas as a collection of particles moving freely through an essentially empty space and occasionally interacting with each other. By way of these interactions the kinetic energy could be shown to become equally distributed within the physical system resulting in a statistical "equipartition of energy," characteristic for the state of thermal

<sup>1</sup> Einstein 1902b.

equilibrium. Many features of macroscopic systems described by phenomenological thermodynamics could be reconstructed within the kinetic theory of gas. In addition, the kinetic theory allows for a number of rather surprising statistical assertions about the atomistic constituents of a gas, such as that about the statistical distribution of the energies of the single particles known under the designation "Maxwell-Boltzmann distribution."<sup>2</sup>

While 19th century kinetic theory was a means to extend the range of the mechanical foundation of physics, 20th century statistical mechanics became a means to question and to eventually overcome just this foundation. Arguments based on statistical mechanics (concerning, in particular, the equipartition of energy) made it indeed possible to show that classical electrodynamics was unable to cope with the thermal equilibrium of heat radiation. Among the first to attain this insight into the limits of classical radiation theory was Albert Einstein in 1905.<sup>3</sup> Two years later he applied methods of statistical mechanics in a first attempt at a quantum theory of solid bodies.<sup>4</sup> Since statistical mechanics does not require an analysis of the interaction between single atomistic constituents of a macroscopic system it is much more generally applicable than the kinetic theory of gas. Statistical mechanics rather considers the statistical properties of a "virtual" ensemble of macroscopic systems, all of which are characterized by the same dynamics but vary in the initial values of their atomistic constituents. Different thermodynamical systems in equilibrium are represented by different such statistical ensembles - an isolated thermodynamic system by a "microcanonical ensemble" in which all members have the same (or approximately the same) energy, a system which is not isolated but in contact with a heat reservoir and held at a fixed temperature by a "canonical ensemble" in which the energies of the members obey a certain statistical distribution (characterized by an exponential function) allowing them to take all possible values. Due to its generality statistical mechanics can be employed in classical and, with appropriate modifications, also in quantum physics. It is for this reason that it could play a key role in the transition from classical to modern quantum physics.

Building blocks of statistical mechanics can be found already in the numerous publications of the eminent protagonists of the 19th century kinetic theory of heat, James Clerk Maxwell and Ludwig Boltzmann. It was, however, only in the book which Josiah Williard Gibbs published in 1902, entitled *Elementary Principles in Statistical Mechanics*,<sup>5</sup> that statistical mechanics found, for the first time, a coherent and autonomous formulation. The now standard terminology "microcanonical ensemble" and "canonical ensemble" for two essential concepts of statistical mechanics is due to him. In the same year 1902 Einstein published the first of a series of three papers on statistical physics, entitled *Kinetic Theory of Thermal Equilibrium and of the* 

3 Einstein 1905a.

<sup>2</sup> For a history of the Maxwell-Boltzmann distribution, see Brush 1976, Chapter 10.

<sup>4</sup> Einstein 1907.

<sup>5</sup> Gibbs 1902.

Second Law of Thermodynamics (1902), A Theory of the Foundations of Thermodynamics (1903), and On the General Molecular Theory of Heat (1904).<sup>6</sup> These three papers are based on Boltzmann's major book on the kinetic theory of heat, entitled Vorlesungen über Gastheorie.<sup>7</sup> But they established, independently of Gibbs, statistical mechanics and provided the basis for Einstein's exploration of the consequences of the quantum hypothesis for a revision of the foundations of classical physics, and also for his analysis of Brownian motion and other fluctuation phenomena as evidence for the existence of atoms.<sup>8</sup>

There can be little doubt that statistical mechanics, with its important impact on the further development of 20th century physics, represents a conceptual innovation in the history of science. The fact that so many of its building blocks are found in the work of Maxwell and Boltzmann and hence actually predate its creation suggests that this innovation was largely due to a change of perspective, to a reinterpretation of preexisting results in a new light. In Einstein's case, this new light was, as I will show in detail, provided by a new context of application of statistical physics.

That a certain revitalization of statistical physics at the beginning of the new century was caused by a new context of application is a conjecture that was first expressed by Paul and Tatiana Ehrenfest in 1911. They point, in particular, also to the electron theory of metals as one such new context:<sup>9</sup>

"In particular, the last few years have seen a sudden and wide dissemination of Boltzmann's ideas (the *H*-theorem, the Maxwell-Boltzmann distribution, the equipartition of energy, the relationship between entropy and probability, etc.). However, one cannot point at a corresponding progress in the conceptual clarification of Boltzmann's system to which one can ascribe this turn of affairs.

It is much more likely that the study of electrons and the investigation of colloidal solutions with the ultramicroscope have been responsible. In general, both of these have had the effect o reviving and deepening the concept that all bodies can be pictured as aggregates of a finite number of very small and identical elementary components, and that correspondingly every process in a physical or chemical problem which can be observed by normal methods is a complex of an enormously large number of individual processes. The opportunity arose to apply the methods of the kinetic theory of gases to completely different branches of physics. Above all, the theory was applied to the motion of electrons in metals (V 14, Section 40, by H.A. Lorentz), to the Brownian motion of microscopically small particles in suspensions (Section 25), and to the theory of black-body radiation (V 23, by W. Wien)."

<sup>6</sup> Einstein 1902b, Einstein 1903, and Einstein 1904.

<sup>7</sup> Boltzmann 1896, 1898.

<sup>8</sup> Einstein 1905c; for an historical discussion, see Stachel et al. 1989, hereafter Vol. 2, the editorial note "Einstein on Brownian Motion," pp. 206-222.

<sup>9</sup> Ehrenfest and Ehrenfest 1959/1990, p. 68. The references are to other sections of the Encyclopädie.

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The impact of novel applications on a conceptual system is, however, not necessarily limited to such a revitalization. New circumstances of application can change the meaning of concepts, and attempts to solve new problems by traditional conceptual means may lead to shifts of emphasis within the conceptual system.<sup>10</sup> What was a marginal and problematic result from one point of view, that is, as interpreted within one conceptual system, may come to constitute the core of another, new conceptual system. For example, the result, established by Michelson, Morley and others towards the end of the 19th century, that no effect of the earth's motion with respect to the hypothetical ether can be found was, in this way, transformed from a stumbling stone of Lorentz's ether-based electrodynamics into the corner stone of Einstein's special theory of relativity, in the form of the principle of relativity.<sup>11</sup> Such a continuous transition from one conceptual system to another, different one is possible in a science like physics because its conceptual systems are formulated in a controlled technical language which displays characteristics of both a formal system and a natural language. While such a conceptual system is flexible enough to cope with a wide range of experience, it is also rigid enough occasionally to display inconsistencies when separate legitimate applications of a concept lead to extensions of meaning which turn out to be incompatible. The representation of physical results in terms of language and mathematical formalism provides an important instance of mediation between the old and the new system. A new conceptual system can emerge from interpreting a mathematical representation of physical concepts and their relation, such as the Lorentz transformations for example, no longer as depending, albeit in a problematic way, on the old conceptual system, but rather as defining the relation between fundamental concepts of the new system, such as the relativistic concepts of space and time in this example.

In this paper I will argue that a similar process of reinterpretation explains the emergence of statistical mechanics in the hands of Einstein. In other words, Boltzmann's work on the kinetic theory of heat played an analogous role for Einstein's creation of statistical mechanics as Lorentz's work on the electrodynamics of moving bodies did for his creation of special relativity. To take one example that I will consider in some detail below, the equipartition of energy for arbitrary material bodies in thermal equilibrium was only a marginal topic in Boltzmann's work. He did assemble the mathematical tools necessary for its derivation in the sense of the later statistical mechanics but actually considered such a demonstration to be problematic because of its dependence on a far-going hypothesis about the dynamical properties of arbitrary bodies.<sup>12</sup> To Boltzmann such a derivation had to be strictly grounded in the principles of mechanics, with the consequence that he placed those physical systems in the center of his research

<sup>10</sup> See the introduction to Damerow et al. 1992.

<sup>11</sup> This example is discussed in more detail in Renn 1993.

<sup>12</sup> In this paper I will not discuss the role of the ergodic hypothesis which is usually in the focus of the history of statistical mechanics; for an excellent survey, see Brush 1976, Chapter 10; for a recent discussion of its role for Boltzmann, see Gallavotti 1974.

which he considered tractable under this condition, in particular gases. He did introduce also the virtual statistical ensembles which later became core concepts of statistical mechanics but never systematically analyzed their relation to each other, although he had developed the means even for such an analysis.

New contexts of application, in particular the electron theory of metals and the theory of heat radiation, shifted the emphasis within the kinetic theory of heat, as it was perceived by Einstein, from Boltzmann's questions concerning the mechanical foundations of the theory of heat to the problem of the derivation of the equipartition law for general physical systems in thermal equilibrium, as well as to related problems.<sup>13</sup> This shift of emphasis brought him to identify, as I will show in detail below, a "gap" in Boltzmann's work. Instead of solving the questions left by Boltzmann, e.g. concerning the dynamical properties of general physical systems, Einstein introduced new ones and reassembled Boltzmann's results in order to fill the "gap" he perceived. This change of perspective had the consequence that these results now assumed a new meaning as corner stones of a new approach, statistical mechanics. The relation between canonical and microcanonical ensemble, for instance, which Boltzmann had touched upon only in passing, became a key relation representing the relation between a physical system at a fixed temperature and a heat reservoir. On the basis of this relation, Einstein was able to derive not only the equipartition theorem for more general physical systems at a given temperature but also genuinely novel results as for instance a formula for energy fluctuations of such systems. One can indeed characterize Einstein's turn of perspective with similar words as those used by Martin Klein in order to explain Gibbs' indifference with regard to the discussion about irreversibility so important to Boltzmann's work; commenting on a pertinent observation by Ehrenfest. Klein remarked:<sup>14</sup>

"[...] he was quite correct in saying that Gibbs had largely ignored almost all issues over which this battle had raged. But Gibbs took a very different view of the structure of the subject from Ehrenfest, or Boltzmann, and he was not trying to solve the same problem."

In Einstein's case we are in the position to analyze in detail how such a very different view emerged out of his concerns with specific problems related to an atomistic theory of matter and to the theory of radiation. In order to reconstruct the emergence his perspective, I will first discuss the evidence that has until now been available on his early scientific interests. This evidence suggests that Einstein's interest in the electron theory of metals may have been one of several research topics motivating his search for a generalization of the kinetic theory of gas

<sup>13</sup> The present treatment is focussed on the equipartition theorem. For an extensive discussion of this as well as of other aspects of Einstein's approach to statistical mechanics, see Vol. 2, the editorial note "Einstein on the Foundations of Statistical Physics," pp. 41-55.

<sup>14</sup> Klein 1970, p. 129

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(section 2). A reconstruction of a controversy he had with Drude concerning the electron theory of metals will not only confirm this influence but also show that this controversy directly triggered the elaboration of statistical mechanics. In the light of newly available contemporary evidence, I will show in particular that this controversy, whose content was so far unknown, concerned, at least in part, Boltzmann's statistical physics and also affected an early attempt by Einstein to obtain a doctorate (section 3). The conceptual bond connecting Einstein's various early scientific interests, such as that in the electron theory of metals, is then characterized as a kind of "interdisciplinary atomism" that was implicit in turn-of-the century-physics but that was not generally pursued as a systematic research program. As an illustration for the impact on Einstein's thinking of the links between his different research interests, I will offer a tentative reconstruction of his decision to reject his own approach to an electron theory of metals (section 4). Einstein's quest for an interdisciplinary atomism is shown to be the presupposition also of his identification of the "gap" in Boltzmann's work on the kinetic theory of heat, a gap whose very existence was denied both by Boltzmann and Drude. Einstein's atomism is then shown as constituting the perspective from which he could reinterpret elements of Boltzmann's work as building blocks of statistical mechanics, the new approach capable of filling this gap (section 5). Finally, in an epilogue the contrast between the original intentions behind Einstein's work on statistical mechanics and its eventual consequences is discussed with the aim to remove the teleological aura surrounding this work, which is evoked by its later, revolutionary consequences for 20th century physics (section 6).

# 2. Einstein's Early Scientific Activities according to the "Love Letters"

Until a few years ago very little was known about Einstein's scientific interests and activities prior to his pathbreaking papers of 1905 on the light quantum hypothesis, on Brownian motion, and on the electrodynamics of moving bodies. The prehistory of these papers could only be reconstructed on the basis of Einstein's few earlier publications and on that of his later recollections, apart from a handful of contemporary letters. The situation changed considerably when his correspondence with Mileva Mari¶, beginning in 1897, (the so-called "love letters") was published in the first volume of the *Collected Papers of Albert Einstein*.<sup>15</sup> In addition to insights into the dramatic relation between Mileva Mari¶ and Albert Einstein, these letters indeed revealed several hitherto unknown and rather diverse scientific interests of the young Einstein, e.g. in radiation experiments and in the electron theory of metals; they show him as an abident

<sup>15</sup> Stachel et al. 1987, hereafter: Vol. 1. For an English translation of the "love letters," see Renn and Schulmann 1992.

reader of textbooks and of contemporary physics journals; they bear evidence to early contacts with leading physicists such as Boltzmann, Drude, and Wien; and last but not least, they contain important hints as to the prehistory of his 1905 papers.

Elsewhere I have claimed, on the basis of an analysis of Einstein's letters, that one can recognize a close relation between these hints and Einstein's other, seemingly unrelated scientific interests in this period, such as the electron theory of metals.<sup>16</sup> According to this reconstruction, key ideas of the papers of his *annus mirabilis* 1905 had first been developed under the different horizon of these seemingly unrelated physical interests. This horizon was above all characterized, according to this interpretation, by Einstein's search for a conceptual unity of physical phenomena on an atomistic foundation. It was this search that gave intellectual coherence to his early scientific endeavors, ranging from thermoelectricity, via radiation theory, to the electrodynamics of moving bodies, long before it turned out that the outcome of the search would shake the conceptual foundation of classical physics.

But in spite of the availability of Einstein's "love letters" as a new source for reconstructing his early intellectual development, the evidence remains slim. Many of the letters merely contain allusions to conversations about scientific subjects with Mileva or brief sketches of Einstein's ideas, from which their content can hardly be reconstructed; other letters only mention an argument, without giving it. The years 1901 and 1902, for instance, are a period characterized by controversies, but each controversy represents a riddle. In this time, Einstein unsuccessfully attempted to obtain a doctorate, first under one supervisor, with whom he had a falling-out for unknown reasons, then with another one who rejected, for unknown reasons, a dissertation by Einstein whose precise content has also remained obscure.<sup>17</sup> In-between these two controversies he had, in mid-1901, a dispute with Paul Drude concerning the electron theory of metals, one of the previously unknown research interests revealed by the "love letters." In analogy to the freely moving molecules of a gas, Drude's theory assumes freely moving charge carriers inside a metal, accounting both for its electric and its thermal conductivity, as well as for the connection between these conductivities described by the Wiedemann-Franz law. The nature of Einstein's objections to Drude's theory, which was published in 1900,<sup>18</sup> has remained just as unknown to us as the character of Drude's response to a letter we know Einstein had written to him in June 1901.<sup>19</sup> There is a puzzling hint at a possible connection between Einstein's disser-

<sup>16</sup> Renn 1993. See also the introduction to Renn and Schulmann 1992, and in Vol. 2, the editorial notes "Einstein's Dissertation on the Determination of Molecular Dimensions," pp. 170-182, and "Einstein on Brownian Motion," pp. 206-222.

<sup>17</sup> Einstein retracted the dissertation, probably on Kleiner's advice on 1 February 1902, see the Receipt for the Return of Doctoral Fees, Vol. 1, Doc. 132, p. 331, and also the discussion below.

<sup>18</sup> Drude 1900a and b; see also Drude 1902.

<sup>19</sup> See Einstein to Mileva Mari¶, 4 June 1901, Vol. 1, Doc. 112, p. 306.

tation and his controversy with Drude, but it has remained unclear whether this connection was one of content or just established by Einstein's spirit of rebellion pervading all of these controversies.<sup>20</sup> I will later come back to this riddle.

The obscurity surrounding Einstein's controversy with Drude is particularly unfortunate given its potential interest for understanding Einstein's development, both intellectual and personal. What is known about the controversy provides some insights into the way in which he took on the role of a rebel against scientific authorities, as well as into what appears to have been, at the time, a central focus of his scientific interests. The correspondence with Mileva suggests, in fact, that Einstein had developed, independently from Drude, his own approach to an electron theory of metals.<sup>21</sup> Hints at a relation between Einstein's interests in electron theory and in statistical physics have given rise to an interesting suggestion concerning the role of the electron theory of metals for the emergence of his statistical mechanics, as one among several of his contemporary research interests:<sup>22</sup>

"Aside from his reading of material directly concerned with kinetic theory, Einstein was studying at least three other topic in 1901 and 1902 that may have suggested the need to extend the foundations of thermodynamics and kinetic theory. First, since at least the spring of 1901, Einstein had been reading Planck's papers on irreversible radiation processes, in which Planck sought to extend the concept of entropy to radiation. Second, Einstein was studying the work of Drude and others on the electron theory of metals, in which the apparatus of kinetic theory is employed to explain such phenomena as electric and thermal conductivity. ... Third and most important, Einstein was working on a theory of molecular forces."

The surmised link between Einstein's interest in the electron theory of metals and his elaboration of statistical mechanics becomes particularly plausible in view of evidence for his recognition of the central role of the equipartition of energy in such a theory, as we will discuss in detail below. But on the basis of the historical sources so far available, there was nevertheless little possibility to come to definite conclusions about the complex relations between Einstein's interest in electron theory, his controversy with Drude, his failed dissertation, and his creation of statistical mechanics.

Under these circumstances it deserves attention that a previously unknown passage from a letter by Mileva Mari¶ to Albert Einstein, concerning Drude's response to Einstein's objections, has now come to light. The passage is contained in a letter of which only a partial copy was available to the editors of Vol. 1 of the *Collected Papers of Albert Einstein*. The complete letter has now become accessible, as a result of an auction of the "love letters."<sup>23</sup> In the following this

<sup>20</sup> See Einstein to Mileva Mari¶, 17 December 1901, Vol. 1, Doc. 128, p. 326.

<sup>21</sup> See Einstein to Mileva Mari¶, 4 April 1901, Vol. 1, Doc. 96, pp. 284-285.

<sup>22</sup> See the editorial note in Vol. 2, "Einstein on the Foundations of Statistical Physics," pp. 45-46; see also the discussion in Renn 1993, pp. 332-334.

passage will be set into the context of Einstein's early scientific interests and that of his attempt to obtain a doctorate in 1901. Although many aspects of this story have been discussed before, it is here recounted in its entirety in order to display for the first time all available contemporary evidence in favor of the role of Einstein's interest in electron theory for the emergence of his approach to statistical mechanics.

# 3. Einstein's Early Controversies and his Failure to obtain a Doctorate in 1901

#### A First Controversy: Einstein's Attempted Doctorate with H.F. Weber

In October 1900 Einstein was working on a doctorate in physics, under the supervision of his ETH physics professor H.F. Weber.<sup>24</sup> The original choice of topic of the dissertation, which Einstein hoped to complete by Eastern of 1901,<sup>25</sup> is not known. It may have been related to thermoelectricity, a subject on which several other students of Weber were doing research and on which Einstein himself had written his diploma thesis under Weber.<sup>26</sup> This first attempt at a doctorate failed, however, rather quickly. Einstein's correspondence with Mileva testifies to a falling-out he had had with Weber by the beginning of spring 1901.<sup>27</sup> As I have mentioned above, the background for this conflict is not known. A possible reason for it is that Weber expected his students to primarily engage in first-hand experimental work, whereas Einstein may have hoped that he could base theoretical conclusions on experimental work done by others.<sup>28</sup> In this case, Einstein's theoretical research for his dissertation may have been related not to thermoelectricity but to molecular forces in liquids, a subject on which he wrote his first paper, submitted in December 1900.<sup>29</sup> It is indeed difficult to imagine that Einstein's theoretical study

<sup>23</sup> I gratefully acknowledge the kindness of Mr. Felix de Marez Oyens, from Christie's, who pointed my attention to the missing page of the letter by Einstein to Mileva Mari¶, ca. 8 July 1901, Vol. 1, Doc. 116. As, unfortunately, no copy of the page is available to me, my interpretation had to be based on a raw transcription of the passage in question.

<sup>24</sup> See the Questionnaire for Municipal Citizenship Applicants, 11-26 October 1900, Vol. 1, Doc. 82, p. 270, and the editorial note in Vol. 2, "Einstein's Dissertation on the Determination of Molecular Dimensions," pp. 170-182.

<sup>25</sup> See Mileva Mari¶ to Helene Savi¶, 20 December 1900, Vol. 1, Doc. 85, pp. 272-273.

<sup>26</sup> See Einstein to Carl Seelig, 8 April 1952, and the editorial note in Vol. 1, "Einstein on Thermal, Electrical, and Radiation Phenomena," pp. 235-237.

<sup>27</sup> See, in particular, Einstein to Mileva Mari¶, 23 March 1901, Vol. 1, Doc. 93, pp. 279-280, and Einstein to Mileva Mari¶, 27 March 1901, Vol. 1, Doc. 94, pp. 281-283.

<sup>28</sup> For further discussion, see the editorial note in Vol. 2, "Einstein's Dissertation on the Determination of Molecular Dimensions," pp. 170-182.

<sup>29</sup> Einstein 1901.

of molecular forces as it is pursued in this paper could have been much to Weber's liking. But, in spite of the falling-out with Weber, Einstein continued to be interested in thermoelectricity as well and even developed a theory of his own on this subject.<sup>30</sup>

The topic of molecular forces is mentioned as the subject of Einstein's doctoral work in a letter to his friend Marcel Grossmann in April 1901.<sup>31</sup> It is, however, likely that by that time Einstein was no longer working under Weber but under a new supervisor, Alfred Kleiner, professor at the University of Zurich. Definitely, Einstein attempted to obtain a doctorate under Kleiner in the fall of 1901, as I will discuss in detail below.

# A Second Controversy: Einstein's Criticism of Drude and Boltzmann

Einstein's controversy with Drude took place in the middle of 1901, in the period of transition from his first supervisor Weber to Alfred Kleiner, and possibly after a shift of his dissertation topic in spring 1901 from thermoelectricity to molecular forces. Einstein nevertheless continued to follow the literature in thermoelectricity. He studied, in April 1901, Drude's electron theory of metals, finding it similar to his own approach to the subject.<sup>32</sup> Drude's theory explains the empirically known connection between electric and thermal conduction, treating the assumed freely moving charged particles inside the metal on the basis of a specific, very simple gas model.<sup>33</sup> At the end of May, Einstein read with enthusiasm a paper by Max Reinganum who had shown that the explanation of this connection does in fact not depend on the details of the atomistic model assumed.<sup>34</sup> Reinganum rather argued that this explanation only depends on quite general statistical properties of the freely moving charge carriers, in particular on the validity of the equipartition theorem, that is, on the assumption that the mean kinetic energies of the charge carriers and of the atoms of the metal are equal. At the time he became familiar with Reinganum's work, Einstein decided not to publish this own theory but rather considered to write, between late May and early June, a personal letter to Drude.<sup>35</sup> The reasons for Einstein's abandonment of his own theory have so far remained obscure; in section 4 I will argue that they are closely related to his reading of Reinganum.

<sup>30</sup> See Einstein to Mileva Mari¶, second-half of May 1901, Vol. 1, Doc. 110, p. 303.

<sup>31</sup> See Einstein to Marcel Grossmann, 14 April 1901, Vol. 1, Doc. 100, pp. 290-291.

<sup>32</sup> See Einstein to Mileva Mari¶, 4 April 1901, Vol. 1, Doc. 96, pp. 284-285.

<sup>33</sup> For an historical review of the electron theory of metals, see Kaiser 1987.

<sup>34</sup> See Einstein to Mileva Mari¶, 28 May 1901, Vol. 1, Doc. 111, p. 304, and Reinganum 1900.

<sup>35</sup> See Einstein to Mileva Mari¶, second-half of May 1901, Vol. 1, Doc. 110, p. 303, and also Einstein to Mileva Mari¶, 4 June 1901, Vol. 1, Doc. 112, p. 306.

As Einstein's letter to Drude is unknown, conclusions about its content have to exclusively rely on allusions to it in Einstein's other contemporary correspondence. What is clear from these allusions is only that he had formulated "two factual objections" to Drude's theory and that he had informed Drude that he was looking for a position.<sup>36</sup> Einstein received Drude's response in early July and forwarded it to Mileva.<sup>37</sup> It was apparently very disappointing to him, probably both with regard to its scientific content and with regard to his hopes for a position. To Mileva and to his fatherly friend Jost Winteler he announced that he would soon publish a polemic rejoinder to Drude.<sup>38</sup> This is virtually all that so far was known about Drude's response, apart from the fact that, in his letter to Winteler, Einstein also referred to Drude's claim that an "unfallible" colleague of his, whose name is not mentioned, was of the same opinion as Drude himself concerning the issue of Einstein's objections.<sup>39</sup>

The newly found passage stems from a letter by Mileva written in early July, just after she had seen Drude's response.<sup>40</sup> Her letter to Einstein makes it clear how desperately they both must have waited for this response. She reacts with irony to the fact that that splendid fellow Drude has now finally sent a word. In the bohemian spirit of rebellion which is documented by many letters of this period and which united the young couple against the rest of the world, and in particular against the scientific establishment, she mocked herself about the court-like behavior of the masters of physics. Her remark about this behavior was occasioned by the way in which, in his response, Drude referred to another great master of classical physics, Ludwig Boltzmann. Drude's response must have been aimed, so Mileva's sarcastic interpretation, at making it clear to a scientific novice such as Einstein that, of course, a great master like Boltzmann cannot have been wrong.

At first glance it is quite surprising that Drude should have mentioned Boltzmann in his response. It seems that Drude had felt the need to defend Boltzmann against Einstein's objections, rather than his own electron theory. But this single piece of additional information about Drude's response makes it, all of a sudden, understandable why Einstein, immediately after this exchange, thoroughly reread Boltzmann's major work on gas theory and developed his approach to statistical mechanics: in order to substantiate his criticism of Drude which, in fact,

<sup>36</sup> See Einstein to Mileva Mari¶, 4 June 1901, Vol. 1, Doc. 112, p. 306, and Einstein to Jost Winteler, 8 July 1901, Vol. 1, Doc. 115, p. 310.

<sup>37</sup> See Einstein to Mileva Mari¶, 7 July 1901, Vol. 1, Doc. 114, p. 308.

<sup>38</sup> See Einstein to Mileva Mari¶, 7 July 1901, Vol. 1, Doc. 114, p. 308, and Einstein to Jost Winteler, 8 July 1901, Vol. 1, Doc. 115, p. 310.

<sup>39</sup> See Einstein to Jost Winteler, 8 July 1901, Vol. 1, Doc. 115, p. 310.

<sup>40</sup> For an incomplete publication of this letter, see Einstein to Mileva Mari¶, ca. 8 July 1901, Vol. 1, Doc. 116, pp. 310-311. The following paraphrase is based on a raw transcription of the missing page.

must have been a criticism of Boltzmann as well. In turn, Einstein's subsequent scientific activities thus explain why Drude's reaction to Einstein's criticism contained a reference to Boltzmann.

Indeed, in early September 1901, Einstein communicated to his friend Marcel Grossmann that he had succeeded in filling a "gap" in Boltzmann's theory and that he was preparing a small publication about his findings.<sup>41</sup> The reference is most probably to an early draft of Einstein's first paper on statistical mechanics, which he eventually submitted in June 1902.<sup>42</sup> Although the meaning of the gap Einstein perceived is not clear from the letter to Grossmann, it can be reconstructed from this paper as well as from other documents concerning Einstein's statistical mechanics.<sup>43</sup> In his 1902 paper on the kinetic theory of thermal equilibrium, Einstein pointed to the achievements of the kinetic theory in the field of gas theory but also to its failure to derive, from mechanics and probability theory alone, theorems on thermal equilibrium and the second law of thermodynamics for more general systems.<sup>44</sup> He acknowledged that Maxwell and Boltzmann had come close to this goal but also made it clear that this was the gap he intended to fill with his own paper. His paper suggests that he viewed Boltzmann's theory as lacking in particular a proof of the equipartition theorem for general physical systems in thermal equilibrium, that is, a proof that does not depend on the specific dynamic assumptions of the systems at hand.

The newly found passage makes it clear that Einstein's identification of this gap must have been closely related to his criticism of Drude's electron theory. From what we now know about Drude's response it follows that at least one of Einstein's objections must have been directed at the statistical assumptions introduced by Drude and their justification by a kinetic theory of matter. This would indeed explain the reference to Boltzmann in Drude's reply. Drude apparently disputed the very existence of the gap which Einstein intended to fill not only in the statistical foundation of Drude's electron theory but also, more generally, in statistical physics as it had been developed by Boltzmann. After all, a master such as Boltzmann will surely have done it right, as Mileva reported about Drude's response.

<sup>41</sup> See Einstein to Marcel Grossmann, 6 September 1901, Vol. 1, Doc. 122, p. 315.

<sup>42</sup> Einstein 1902b.

<sup>43</sup> See the editorial note in Vol. 2, "Einstein on the Foundations of Statistical Physics," pp. 41-55.

<sup>44</sup> See Einstein 1902b, p. 417.

#### A Third Controversy: Einstein's Attempted Doctorate with A. Kleiner

My claim that Einstein's criticism of Drude was, at least in an essential part, directed against Boltzmann receives additional support from a reconstruction of Einstein's third controversy in the years 1901 and 1902. As I have mentioned before, he had turned, after his conflict with Weber, to Alfred Kleiner as the supervisor of his planned doctoral thesis. But although Einstein never had any personal falling-out with Kleiner as he did with Weber, this project also failed for reasons that have not been entirely clear. Here I will show that all available evidence points to the conclusion that Einstein included his approach to statistical mechanics in his dissertation, along with applications of statistical physics to specific problems, and that the inclusion of this new approach may have been one of the reasons for Kleiner's advice to withdraw the dissertation.

In the period between mid-September and mid-November 1901, Einstein attempted to combine the various aspects of his research on the kinetic theory for a doctoral thesis.<sup>45</sup> Did this thesis indeed comprise his work on statistical mechanics? This question can only be answered by a careful analysis of the rather indirect evidence that is available concerning this second early attempt by Einstein to attain a doctorate. By mid-November he gave a draft of this thesis to Alfred Kleiner, along with an early draft paper dealing with the electrodynamics of moving bodies.<sup>46</sup> He submitted this dissertation officially to the University of Zurich on 23 November of this year.<sup>47</sup> A contemporary letter by Mileva describes the subject of the dissertation as a treatment of molecular forces in gases from several known phenomena.<sup>48</sup> In another contemporary letter Einstein discussed a problem he had discovered in applying his theory of molecular forces to liquids, which is another aspect of the kinetic theory possibly treated in his dissertation.<sup>49</sup> From these references alone it is only clear that the dissertation was intended to cover a wide range of topics related to the kinetic theory but not whether it also included Einstein's work on statistical mechanics.

It is at this point that the puzzling remark in one of his contemporary letters mentioned in section 2 adds an important piece to the puzzle, suggesting that statistical mechanics was indeed part of the dissertation. In mid-December Einstein wrote to Mileva that he wondered which stance Drude would take once Kleinert accepts the dissertation.<sup>50</sup> This reference to Drude in the

<sup>45</sup> See Einstein to Swiss Patent Office, 18 December 1901, Vol. 1, Doc. 129, p. 327; see also Mileva Mari¶ to Helene Savi¶, 23 November - mid-December 1901, Vol. 1, Doc. 125, p. 320.

<sup>46</sup> See Einstein to Mileva Mari¶, early November 1901, Vol. 1, Doc. 123, p. 316, and Einstein to Mileva Mari¶, 13 November 1901, Vol. 1, Doc. 124, p. 318.

<sup>47</sup> See Receipt for the Return of Doctoral Fees, Vol. 1, Doc. 132, p. 331.

<sup>48</sup> See Mileva Mari¶ to Helene Savi¶, 23 November - mid-December 1901, Vol. 1, Doc. 125, p. 320.

<sup>49</sup> See Einstein to Mileva Mari¶, 12 December 1901, Vol. 1, Doc. 127, p. 324; see also Einstein to Grossmann, 14 April 1901, Vol. 1, Doc. 100, pp. 290-291.

<sup>50</sup> See Einstein to Mileva Mari¶, 17 December 1901, Vol. 1, Doc. 128, p. 326.

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context of Einstein's dissertation is, at first glance, just as surprising as the remark in the newly available passage, mentioning Boltzmann in the context of Einstein's criticism of Drude's electron theory. It is difficult to account for this reference to Drude if the dissertation only dealt with molecular forces, as the direct references to its content seem to indicate. There are, in fact, no references to Einstein's dissertation (apart perhaps from this one) that point to a relation with thermoelectricity or electron theory, a relation that would, of course, explain Einstein's remark about the reaction he expected from Drude. But in light of the new evidence Einstein's curiosity concerning this reaction does not need to be interpreted as implying that the dissertation also dealt with the latter's electron theory. It seems more likely that Einstein hoped to impress Drude by the way in which he had filled the gap in Boltzmann's approach to the kinetic theory, a gap whose very existence Drude apparently had denied.

In mid-December 1901 Kleinert had yet to read Einstein's dissertation.<sup>51</sup> The earliest available evidence for his reaction to it is dated February 1902 and stands for a dramatic turn of events. On February 1, 1902 Einstein officially retracted his dissertation from the University of Zurich.<sup>52</sup> A later biographer wrote, probably on the basis of a recollection by Einstein himself, that Kleiner had rejected the dissertation because of Einstein's sharp criticism of Ludwig Boltzmann.<sup>53</sup> This report fits well with the hypothesis that Einstein's dissertation combined his attempt to fill a gap in Boltzmann's approach to kinetic theory with a study of molecular forces in various applications, and – this cannot be excluded – perhaps even with allusions to the electron theory of metals and other generalizations of the kinetic theory. The hypothesis that the dissertation comprised an early version of Einstein's statistical mechanics receives support also from another contemporary letter in which he reports to Mileva that a friend recommended him to send to Boltzmann that part of his dissertation which refers to the latter's book, i.e. to Boltzmann's *Gastheorie*, which is the only work to which Einstein's 1902 paper on statistical mechanics makes reference.<sup>54</sup>

References to Einstein's Controversy with Drude in his Later Publications

In mid-December Einstein had written Mileva that, in case Kleiner would reject the dissertation, he would make that fact public, together with his work.<sup>55</sup> To Mileva and Jost Winteler he had earlier announced a polemic reply to Drude. The conflict with Weber, the controversy with Drude, and the failure of his dissertation project with Kleiner served to strengthen Einstein's

<sup>51</sup> See Einstein to Mileva Mari¶, 19 December 1901, Vol. 1, Doc. 130, p. 328.

<sup>52</sup> See Receipt for the Return of Doctoral Fees, Vol. 1, Doc. 132, p. 331.

<sup>53</sup> See Kayser 1930, p. 69.

<sup>54</sup> Boltzmann 1896 and 1898. Boltzmann 1898 is quoted in Einstein 1902b on pp. 420 and 427.

<sup>55</sup> See Einstein to Mileva Mari¶, 17 December 1901, Vol. 1, Doc. 128, p. 326.

perception that, in his early scientific endeavors, he was struggling against the established scientific authorities. It also confirmed and enhanced his aversion against authorities in general.<sup>56</sup> To Winteler he wrote that he saw the blind belief in authority as the greatest enemy of truth. But Einstein also appears to have been somewhat discouraged by the reaction of the scientific establishment to his efforts. A direct rejoinder to Drude's negative response to his criticism could, in any case, not be identified among his publications. That no open attack on Drude exists is understandable. Apart from the fact that such an attack might have spoiled Einstein's ambitious plans for his career, it might have been not easy to publish in view of the fact that Drude was the editor of the *Annalen der Physik* and a big shot in contemporary German physics.<sup>57</sup> But it is, of course, quite possible that at least some of Einstein's scientific arguments against Drude were not sacrified to such strategic considerations.

The newly found passage makes it now easier to scrutinize Einstein's publications of this period for traces of his failed dissertation and of his rejoinder to Drude. Some of his early papers apparently cover indeed facets of this dissertation, first of all the paper on molecular forces in liquids,<sup>58</sup> then according to the interpretation given here at least the first of the three papers on statistical mechanics.<sup>59</sup> But neither of these papers contains any reference to Drude or to the electron theory of metals. The only explicit mentioning of Drude's electron theory in Einstein's early publications is found in his 1905 paper on the light quantum.<sup>60</sup> There he describes a physical system composed of gas particles, freely moving electrons, resonators, and radiation in thermal equilibrium, a system for which he assumes the validity of the equipartition theorem. In a footnote to the introduction of this assumption Einstein refers to Drude's electron theory with the remark that this theory also depends on the assumption of the equipartition theorem. Although the footnote itself contains no criticism of Drude's theory, it is located in a section of Einstein's paper in which he discusses the catastrophic implications of an application of the equipartition theorem to classical radiation in thermal equilibrium, motivating the revolutionary proposal of the light quantum. Implicitly, the context of this reference to Drude makes it thus clear how highly problematic the application of the equipartition theorem to other systems than a gas could be and hence also how much this application was in need of justification. It is ironical, and perhaps was meant to be so, that, instead of providing such a justification at this point (Einstein's papers on statistical physics are not quoted), he merely referred to the example of Drude's electron theory in order to justify his own application of the equipartition theorem to a

<sup>56</sup> See the introduction to Renn and Schulmann 1992.

<sup>57</sup> See the discussion in Jungnickel and McCormmach 1986, Vol. 2, p. 309.

<sup>58</sup> Einstein 1902a.

<sup>59</sup> Einstein 1902b, 1903, and 1904. Einstein had announced his intention to publish his results on statistical mechanics in the *Annalen* as early as September 1901, see Einstein to Marcel Grossmann, 6 September 1901, Vol. 1, Doc. 122, p. 315.

<sup>60</sup> See Einstein 1905a, Doc. 14, p. 133.

system composed of gas particles, radiation, and electrons. It is indeed unlikely that Einstein was not aware of this crucial gap in his argument, which, at the same time, was also the missing part in Drude's theory.

The dissertation which Einstein finally submitted in 1905 also dealt with a facet of the kinetic theory, the determination of the dimensions of molecules in solution.<sup>61</sup> It treats the general question of establishing absolute molecular dimensions, but now in the context of a single, highly specialized problem;<sup>62</sup> it thus no longer bears direct evidence to Einstein's overarching ambitions in the years 1900 to 1902. The established authorities of physics, in this case represented by Alfred Kleiner, had in fact made it impossible for him to publish the diverse aspects of his exploration of the kinetic theory of matter under a single, unifying umbrella. The history of Einstein's first attempt to attain a doctorate in 1901 thus also explains the remarkable splitting of his early publications into those dealing with the theoretical core and those dealing with the concrete implications of statistical mechanics.

In addition to splitting up the results of his 1901 dissertation into his various publications, Einstein may have sent privately to Boltzmann the part of the dissertation that was directly related to the *Gastheorie*, as his friend had advised him to do.<sup>63</sup> If he did so, his work on statistical mechanics failed to make any impression on Boltzmann, at least if the treatment in the last grand review of the kinetic theory Boltzmann wrote together with Nabl for Sommerfeld's *Encyclopädie* is taken as a gauge.<sup>64</sup> There Einstein's first two papers on statistical mechanics appear hidden, among several other papers by Boltzmann himself, in a footnote to a passage dealing with applications of the statistical method. Certainly Boltzmann and Nabl did not consider Einstein's contribution as filling an important gap in the kinetic theory but rather saw it as one specialized contribution among many others. Therefore, the question remains as to how Einstein could have identified (or only believed to have identified) a gap that remained obscure to masters of classical physics such as Drude and Boltzmann. In order to attempt an answer to this question we have to take another look not only at Einstein's perspective on the kinetic theory but also at the scientific context of this theory around the turn of the century.

<sup>61</sup> Einstein 1905b.

<sup>62</sup> This aspect is often overlooked; it is extensively discussed in the editorial note in Vol. 2, "Einstein's Dissertation on the Determination of Molecular Dimensions," pp. 170-182.

<sup>63</sup> See Einstein to Mileva Mari¶, 8 February 1902, Vol. 1, Doc. 136, pp. 334-335.

<sup>64</sup> See Boltzmann and Nabl 1905, p. 549.

# 4. The Interdisciplinary Potential of 19th Century Atomism and Einstein's Perspective

# Atomism at the Turn of the Century: Growing Evidence and Growing Problems

Drude's electron theory and Boltzmann's kinetic theory of gas not just happen to be two arbitrary subjects of interest to Einstein, but rather share an important common property also with several other of his early research topics: they are two examples of the application of atomistic ideas to physical and chemical problems around the turn of the century.<sup>65</sup> Other prominent examples are Lorentz's atomistic version of Maxwell's electromagnetism, also often referred to as electron theory, the ion theory of electrolytic conduction, the kinetic theory of solutions, and the use of atomistic models in anorganic and organic chemistry. Whereas in antiquity and in early modern science atomism had served as a universal theory of nature, the scientific atomism of the late 19th century had become a specific and versified conceptual tool in various branches of physics and chemistry

Nevertheless, the different species of atomism clearly showed traces of their common ancestry. In fact, they all operated with the transposition of the concept of body, familiar from our macroscopic experience, into an invisible microworld. Like bodies, atoms were thought to be distinguishable entities with a position in space and time, moveable independently from each other unless they are bound together. In addition they were ascribed other properties also familiar from the bodies of macroscopic experience, such as shape, rigidity, or electric charge. Which of these properties were ascribed to them in each single case depended on the specific context in which an atomistic microworld was introduced. In Lorentz's electromagnetism, for instance, the atomistic constituents of electricity were, of course, imagined to carry electric charge, whereas in the kinetic theory of gas, atoms were sometimes imagined as small elastic billiard balls. In chemistry, the complexity of the quantitative relations in chemical reactions was reduced to simple assumptions on the constellation of atoms in molecules. In summary, late 19th century physics and chemistry atomism was widely considered as a flexible working hypothesis useful for specific scientific explanations, while the question of the reality of atoms was open to debate.

In addition to the disputed issue of the reality of atoms, scientists at the end of the 19th century were confronted with the problem of the compatibility of atomistic ideas elaborated in different contexts. In fact, as a consequence of the adaption of the atomistic idea to the specific explanatory purposes of different branches of science, the atomism of the kinetic theory of gas was

<sup>65</sup> For a review, see Brush 1976, § 1.9; see also the editorial note in Vol. 2, "Einstein on Brownian Motion," pp. 206-222, and the literature cited there.

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not obviously compatible with the atomism employed in theories of electromagnetism, let alone with that developed in chemistry. An example of such problems of compatibility is the clash between the chemical insights into the internal complexity of molecules and the failure of physical theories of atomism to account for this complexity. It was not only a matter of explaining the complex composition of molecules, but, more basically, of demonstrating that theories such as the kinetic theory of heat were not incompatible with the available chemical knowledge. It was in fact a well known problem for the kinetic theory that the thermal behavior of matter did, in many cases, not show evidence of this complex internal constitution. According to the equipartition theorem, every internal degree of freedom of an atomistic constituent of a gas should equally contribute to the mean energy and hence to the specific heat of the gas, thus implying the so-called Dulong-Petit law on specific heats, but the empirical knowledge on specific heats suggested that this was not the case, given what was known about the internal degrees of freedom from the chemical composition of some gases and in particular from spectral analysis.<sup>66</sup>

In spite of such problems of compatibility between the different branches of atomism in the 19th century, problems which contributed to the skepticism with respect to the atomistic hypothesis, the number of indications grew that it would continue to play a role in the conceptional foundations of physics. Around the turn of the century, this growth consisted, on the one hand, in the sometimes surprising multiplication of ways in which Avogadro's number, a fundamental characteristics of the atomistic scale, could be established<sup>67</sup> and, on the other hand, in novel opportunities for applications of the age-old atomistic idea. Naturally, such novel opportunities offered themselves, in particular, at the frontiers of experimental research, where new empirical knowledge was produced.<sup>68</sup> Examples are the new kinds of radiation for which attempts were made to decide whether they were waves or elementary particles, studies of the interaction between matter and radiation, such as the Zeeman and the photoelectric effects, which confirmed atomistic models of matter or gave rise to new ones, the study of solutions with the newly developed ultramicroscope which revealed several of them as being not homogeneous but suspensions of colloidal particles, etc.. Evidence for the magnitude of Avogadro's number could be gained from such different sources as the study of the capillarity of liquids, the kinetic theory of gas, experiments with thin layers and, surprisingly, also from the theory of black body radiation. The agreement, at least in order of magnitude, between conclusions based on this diverse

<sup>66</sup> See Einstein 1907, pp. 184-185, and, for historical discussions, Brush 1976, § 10.8, Harman 1982, pp. 134-139. The Dulong-Petit law states that the product of the atomic specific heat and atomic weight is – at least for a number of solid monoatomic elements – constant.

<sup>67</sup> Avogadro's number is defined as the number of molecules per gram-mole; for an historical review of methods for its determination, see Brush 1976, pp. 75-78.

<sup>68</sup> For a brief review, see the editorial note in Vol. 2, "Einstein's Dissertation on the Determination of Molecular Dimensions," pp. 170-173.

evidence about the size of the microworld not only confirmed the atomistic hypothesis but also made it more and more urgent to relate its different fields of application to each other and to establish a single atomistic model compatible with all of them.

Einstein's Atomism, his Perception of Contemporary Physics, and the Second Objection to Drude

The growing significance of atomism, and of the conceptual problems that came with its growth, was, of course, differently perceived by different contemporary scientists. Some scientists at the turn of the century preferred to deal only with the local application of atomism relevant to their specific field of interest, disregarding the implications for the rest of physics and chemistry. For the young Einstein, on the other hand, atomism was a bond between different fields of contemporary science that allowed him not only cherish the hope for conceptual unification<sup>69</sup> but also to perceive the conceptual clashes between different theories that to others appeared as being separated by disciplinary or subdisciplinary boundaries. Building up such an "interdisciplinary" vision of atomism, he could thus benefit from an unexploited potential of 19th century physics.

As I have pointed out elsewhere, he probably took up his studies of physics at the ETH already with a bias in favor of atomism, a bias that was probably stimulated by his reading of popular scientific literature and that was strongly confirmed by his reading of Boltzmann.<sup>70</sup> In September 1900 he showed himself, in a letter to Mileva, firmly convinced of Boltzmann's atomistic principles.<sup>71</sup> Earlier he had already considered atomistic explanations of capillarity and of thermoelectricity.<sup>72</sup> In the fall of 1900 he studied the theory of ions,<sup>73</sup> in early spring 1901 he developed a model of matter in which it is composed of atomistic electromagnetic resonators.<sup>74</sup> In addition, he pondered in these years about an atomistic theory of light, performed radiation experiments, followed with enthusiasm the literature on the photoelectric effect and on electron theory, and worked on a theory of molecular forces applicable to gases as well as to liquids, comparing these forces to gravitation.<sup>75</sup>

<sup>69</sup> See Einstein to Marcel Grossmann, 14 April 1901, Vol. 1, Doc. 100, pp. 290-291.

<sup>70</sup> See Renn 1993.

<sup>71</sup> See Einstein to Mileva Mari¶, 13 September 1900, Vol. 1, Doc. 75, pp. 260-261.

<sup>72</sup> See the editorial notes in Vol. 1, "Einstein on Thermal, Electrical, and Radiation Phenomena," pp. 235-237, and "Einstein on Molecular Forces," pp. 264-266.

<sup>73</sup> See Einstein to Mileva Mari¶, 3 October 1899, Vol. 1, Doc. 79, p. 267.

<sup>74</sup> See, e.g., Einstein to Mileva Mari¶, 23 March 1901, Vol. 1, Doc. 93, pp. 279-280.

<sup>75</sup> See the discussion of these interests in Renn 1993. For Einstein's adherence to a corpuscular theory of light, see also the editorial notes in Vol. 2, "Einstein on the Theory of Relativity," p. 263.

Einstein also closely followed Planck's publications on black body radiation, one of them including a determination of Avogadro's number.<sup>76</sup> Just around the time when Einstein developed his criticism of Drude, in spring 1901, he raised doubts on Planck's justification for the equipartition of energy in his treatment of black body radiation.<sup>77</sup> The fact that the equipartition theorem plays a key role both for the theory of heat radiation and for the electron theory of metals certainly contributed to placing it into the focus of Einstein's attention. As I have indicated, a derivation of this theorem from the most general principles possible was one of the problems he must have had on his mind when he identified a "gap" in Boltzmann's *Gastheorie* later in 1901; how exactly he saw this gap and attempted to fill it will be discussed in the next section. But the broad range of Einstein's interests not only had an impact on his choice of problems to study, it also alerted him, as I have claimed above, to the "non-local" consequences of a model, i.e. to its implications beyond the narrow range of a specific application. His criticism of Drude may well be a case in point. In the following I will argue that Einstein's second "factual objection" to Drude was probably related to the latter's lack of concern with such implications.

The above mentioned problem of compatibility between the kinetic theory of heat and what was known about the behavior of matter from other contexts arises also for Drude's electron theory. In fact, Drude's explanation of electric and thermal conduction by an internal gas of charge carriers freely moving inside a metal is incompatible with the interpretation of the thermal behavior of metals by the classical kinetic theory. The freely moving charge carriers contribute many more degrees of freedom to the entire system than this interpretation admits, which rather suggests the model of a crystal-like rigid body with elastically bound atoms. This objection to the electron theory of metals was raised by several authors – but is not mentioned in Drude's papers – and was eventually resolved only in the context of the quantum theory of the solid state.<sup>78</sup> For reasons that I will discuss in the following, it seems not unlikely that it represents the second "factual" objection Einstein had made to Drude.

First of all, this hypothesis would explain why Einstein himself had earlier given up his own electron theory of metals, a problem that was left open in the reconstruction presented in section 3. Indeed, this decision cannot be related to his other objection, which we have discussed in that section and which was directed against the lack of justification for the application of the equipartition theorem in Drude's theory. On the contrary, when Einstein read, in late May 1901, Reinganum's paper on the central role of the equipartition theorem for the electron theory of

<sup>76</sup> See, e.g., Einstein to Mileva Mari¶, 10 April 1901, Vol. 1, Doc. 97, pp. 286-287; see Planck 1900.

<sup>77</sup> See Einstein to Mileva Mari¶, 10 April 1901, Vol. 1, Doc. 97, pp. 286-287.

<sup>78</sup> See the discussion in Kaiser 1987; for a contemporary review, see Seeliger 1921.

metals he showed himself completely convinced of its fundamental principles.<sup>79</sup> Why then should he have given up his pursuit of such a theory shortly after he became acquainted with this paper?<sup>80</sup>

The clue for Einstein's decision seems to lie in Reinganum's paper. In this paper Reinganum emphasizes the good agreement between Drude's theory and empirical knowledge and argues, as was mentioned earlier, that this agreement depends not so much on the details of Drude's atomistic model but on the assumption of the validity of the equipartition theorem lying behind this and similar models. But he also hints at a fundamental problem of an electron theory based on the hypothesis of free electrons, albeit only in a passing remark. Reinganum points to the incompatibility between Drude's electron theory of metals and a kinetic theory of specific heats which is based on Boltzmann's principles as a difficulty for either one of the two theories:<sup>81</sup>

"Because of the experiments of Mr. Kaufmann on cathode rays, and because of Lorentz's theory, brilliantly confirmed by Zeeman's experiments, which ascribes to the bound electrons of luminiscent gases a number of degrees of freedom, the assumption of completely free electrons in metals does not appear too daring; never-theless also the extended theory by Giese [which does not assume free electrons, JR] merits a consideration since, if one does assume free electrons, the theory of the Dulong-Petit law of specific heats, as it has been built up by Richarz according to Boltzmann's principles without so far leading to contradictions, would have to be replaced by a completely different theory of this law, at least if the number of electrons is comparable to that of the metal atoms."

The way in which this passage connects Drude's theory to cathode ray experiments, to Zeeman's experiments and to Lorentz's electron theory could have only been to Einstein's liking. But its upshot, the incompatibility of the assumption of free electrons in metals with the theory of specific heats following from the equipartition theorem, must have shattered his firm conviction in the principles of the electron theory of metals, once the significance of Reinganum's remark had dawned upon him. The close temporal relation between Einstein's reading of Reinganum's paper, of which at first he only noted the aspects favorable to electron theory, and the decision to abandon his own approach argues in favor of this incompatibility being the reason for his decision and also the substance of his second objection against Drude.<sup>82</sup>

<sup>79</sup> See Einstein to Mileva Mari¶, 28 May 1901, Vol. 1, Doc. 111, p. 304.

<sup>80</sup> In his letter to Mileva Mari¶, second half of May 1901 (Vol. 1, Doc. 110, pp. 303-304), Einstein mentioned his dissatisfaction with his theory of thermoelectricity and announced his intention to write to Drude. In his letter to Mileva Mari¶, 28 May 1901 (Vol. 1, Doc. 111, p. 304), he mentioned the paper by Reinganum. Both letters carry no date but are dated on the basis of circumstantial evidence. Their sequence as given in Vol. 1 of the *Collected Papers* should be reversed and the correct date of Doc. 110 is probably 30 May 1901. This is suggested both by Einstein's treatment of the issue of a position at an insurance society and by his attitude to thermoelectricity in the two letters. Concerning Einstein's intention to search for a position at an insurance society, it is rather clear that Doc. 111 introduces the subject and Doc. 110 comes back to it. Concerning thermoelectricity it also appears more likely that Einstein's enthusiasm for the electron theory (Doc. 111) is followed by a disappointment with his own approach (Doc. 110) than vice versa.

<sup>81</sup> Reinganum 1900, p. 401. Where no English source is given, the translation is mine.

There are, in addition, indications in the "love letters" that Einstein himself had been on the track of this problem in the atomistic explanation of thermoelectricity. In a letter to Mileva from October 1899, one of the earliest letters in which he reported on his ponderings about the laws of thermoelectricity, he mentioned his intention to explore the contribution of the charge carriers to the thermal behavior of a metal.<sup>83</sup> Pursuing this line of thought Einstein may well have arrived at the conclusion that the contribution of the charge carriers to the specific heat was much too large for admitting the explanation of thermoelectricity by an electron gas. His reading of Reinganum may have thus struck a familiar chord, in particular as in spring 1901 Einstein also attempted to explain deviations from the Dulong-Petit law of specific heats, i.e. from the implications of the equipartition theorem for the thermal behavior of solid bodies.<sup>84</sup> In his famous 1907 publication about the explanation of such deviations by the quantum hypothesis, Einstein came back to the assumption of moveable electrons inside a solid body and again referred to a paper by Drude in support of this assumption.<sup>85</sup> But in view of the quantum hypothesis, the assumption of free electrons now had become acceptable since their contribution to the specific heat of a solid body no longer leads to such dramatic consequences as in the classical theory. In summary, this problem was central to Einstein's thinking about the atomistic constitution of matter and is hence a likely candidate for his second objection to Drude.

Given the decisive role of the quantum hypothesis for avoiding the conflict between the electron theory of metals and the theory of specific heats, it does not come as a surprise to find the first unambiguous reference to Einstein's continued interest in the electron theory of metals only after his 1907 paper on a quantum theory of specific heats. This reference is contained in a paper by Paul Gruner on the electron theory of metals which acknowledges Einstein's advice.<sup>86</sup> As the paper suggests, this advice pointed into a similar direction as Reinganum's and probably also Einstein's observations on Drude's theory discussed in section 3: towards a generalization of the basic assumptions, away from the specifics of a particular atomistic dynamics. In spite of this tendency towards generalization, Einstein's enthusiasm for a concrete atomistic model of metals was, however, neither defeated by his controversy with Drude nor by the advent of statistical mechanics. In fact, in 1911, Einstein became interested in exploiting the quantum hypothesis for an atomistic theory of metals and even conceived of experiments to test his ideas.<sup>87</sup>

<sup>82</sup> Drude later published a note of correction to his earlier papers where he did cite Reinganum (Drude 1902, p. 689), without, however, discussing this fundamental objection.

<sup>83</sup> See Einstein to Mileva Mari¶, 10 October 1899, Vol. 1, Doc. 58, p. 238.

<sup>84</sup> See Einstein to Mileva Mari¶, 23 March 1901, Vol. 1, Doc. 93, pp. 279-280.

<sup>85</sup> See Einstein 1907, p. 185. Drude's paper (Drude 1904) deals with the interpretation of dispersion measurements, a topic also considered by Einstein as early as spring 1901, see Einstein to Mileva Mari¶, 27 March 1901, Vol. 1, Doc. 94, p. 283.

<sup>86</sup> See Gruner 1909, p. 48.

#### 5. Einstein's Statistical Mechanics and the Gap in Boltzmann's Theory

#### The Gastheorie from the Perspective of an Interdisciplinary Atomist

The wealth of contemporary applications of the atomistic described in the previous section is hardly reflected in Boltzmann's *Gastheorie*, from which Einstein mainly drew his knowledge about the kinetic theory.<sup>88</sup> No wonder then that he observed, in a letter to Mileva from April 1901, that he found in Boltzmann's *Gastheorie* too little emphasis on a comparison with reality.<sup>89</sup> Einstein's rich knowledge about the contemporary applications of atomism provided him indeed with peculiar glasses through which he read this book, noticing shortcomings that easily escaped the attention of less broadly informed readers. But he also was, on the other hand, less well prepared than other readers of the *Gastheorie*, in the sense that he was not familiar with Boltzmann's earlier achievements and in that of the goals which had motivated the latter's research. Einstein rather brough this own interests to bear on the results as they were presented in the *Gastheorie*, thus developing a new interpretation of these results by placing them into a new context.

In reading Boltzmann, Einstein must have naturally concentrated on the introduction of a statistical ensemble of systems since such an ensemble is most suited for a generalization to systems other than gases.<sup>91</sup> Boltzmann's use of a virtual ensemble was intended to circumvent the practically impossible determination of the time development of a system with many degrees of freedom. The analysis of its development in time is replaced by the analysis of a statistical ensemble of copies of the system, all sharing the same dynamics but distributed over the possible initial values compatible with the given constraints on the system:<sup>92</sup>

<sup>87</sup> See Einstein to Michele Besso, 11 September 1911, Klein et al. 1993, hereafter: Vol. 5, Doc. 283, p. 321, Einstein to Michele Besso, 21 October 1911, Vol. 5, Doc. 296, p. 321, and Michele Besso to, 23 October 1911, Vol. 5, Doc. 299, p. 342. See also Einstein 1922 where another objection to Drude's theory, related to the temperature dependence of electric conductivity, is discussed. This objection represents a further possible candidate for Einstein's criticism of Drude; it seems, however, more closely related to Einstein's concerns with electron theory around 1911 than with those around 1901.

<sup>88</sup> For evidence, see the recollection in Einstein 1979, p. 44, and, for a historical review, the editorial note in Vol. 2, "Einstein on the Foundations of Statistical Physics," pp. 41-55.

<sup>89</sup> See Einstein to Mileva Mari¶, 30 April 1901, Vol. 1, Doc. 102, p. 294.

<sup>90</sup> In his papers laying the foundations of statistical mechanics Einstein only quoted Boltzmann's *Gastheorie*; only in 1909 he also referred to an earlier work by Boltzmann, see the editorial note in Vol. 2, "Einstein on the Foundations of Statistical Physics," in particular, p. 44.

<sup>91</sup> The ergodic ensemble introduced by Boltzmann later became the starting point for Einstein's paper on statistical mechanics, see Einstein 1902b, § 2.

<sup>92</sup> Boltzmann 1898, § 35, pp. 102-103.

"The mathematically most perfect method would now consist in taking into account, for each state of a given warm body, the arbitrary initial conditions starting from which it arrives just this time to the thermal state which it now possesses for a long time without change. But since the same mean values result in any case, whatever the initial state might have been, they cannot be different from the mean values which we obtain when we conceive, instead of a single warm body, infinitely many of them which are completely independent from each other and which start, with equal heat content and equal external conditions, from all possible initial states."

In his *Gastheorie* Boltzmann analyzed one particular kind of ensemble in great detail which he called "Ergoden" and which is now called, following Gibbs, a "microcanonical ensemble:"<sup>93</sup>

"We now conceive again of an enormously great number of mechanical systems which all have the same constitution we have earlier described. The total energy E shall have again the same value. But for the rest, the coordinates and moments of the various systems shall have, at the beginning of the time, the most diverse values."

For such a system Boltzmann demonstrated the equipartition of the "lebendige Kraft" (*vis viva*, i.e. kinetic energy) over the various "Momentoiden" (momentoids, a generalization of the concept of momentum to generalized coordinates; their number corresponds to that of the degrees of freedom of an atomistic constituent of the system) and concluded:<sup>94</sup>

"Of course, this equality of the mean value of the *vis viva* corresponding to each momentoid is only proven for the presupposed (ergodic) distribution of states. This distribution of states is certainly a stationary one. There can be, however, and in general there will be other stationary distributions of states for which these theorems are not valid."

Einstein probably found it difficult to see how Boltzmann's derivation of the equipartition theorem from the assumption of such an ergodic or microcanonical ensemble could be put to practical use in treating radiation in thermal equilibrium or an electron gas inside a metal. In order to justify his application of the equipartition theorem to the electrons inside a metal Drude had referred to a paper by Boltzmann on the theory of gas molecules.<sup>95</sup> Given how little was known about the dynamics of electrons inside a metal this certainly was a problematic step. But also the representation of the charge carriers in thermal equilibrium by an ergodic ensemble could not have appealed to Einstein as an unproblematic alternative, since an ergodic ensemble presupposes a constant value of the energy rather than of the temperature as Drude had assumed.

<sup>93</sup> Boltzmann 1898, § 32, p. 89.

<sup>94</sup> See Boltzmann 1898, § 34, p. 101.

<sup>95</sup> See Drude 1900a, p. 570; the paper by Boltzmann is Boltzmann 1868 (*Wissenschaftliche Abhandlungen*, Vol. 1, pp. 49-96).

In the passage quoted above Boltzmann left it indeed open whether or not the equipartition of energy could be proven also for other stationary ensembles, e.g. an ensemble characterized by a constant value of the temperature.

Boltzmann's own admission of the difficulty to extend his results beyond gas theory may have confirmed Einstein's impression that there is indeed a gap in the *Gastheorie*. Boltzmann's attempt to apply his conclusions concerning the validity of the equipartition theorem also to solid and liquid bodies is essentially contained in the brief paragraph § 35, devoid of any formulas, and in a footnote.<sup>96</sup> The paragraph in question is announced by the following cautious remark:<sup>97</sup>

"Before I proceed to the application of the theorems presented until now to the theory of gases with polyatomic molecules, I will first add a completely general consideration which, however, does not rigorously remain on the mathematical standpoint but from the very beginning makes use of certain facts of experience. It nevertheless perhaps justifies the conjecture that the meaning of these theorems is not restricted to the theory of polyatomic gas molecules."

The most important "fact of experience" which Boltzmann then uses as the starting point of his argument is that a body, whatever its initial state may have been, will appear to come to a stationary final state in which the observable mean values of its microscopic parameters always take on the same values. He continues with the justification of the usage of mean values taken over the statistical ensemble that I have quoted above:<sup>98</sup>

"But since the same mean values result in any case, whatever the initial state might have been, they cannot be different from the mean values which we obtain when we conceive, instead of a single warm body, infinitely many of them which are completely independent from each other and which start, with equal heat content and equal external conditions, from all possible initial states."

He then comes to a preliminary conclusion, again expressed in a very prudent tone:<sup>99</sup>

"It therefore has a certain probability that the mean values found in § 34 are not only valid for the set of systems there defined but also for the stationary final state of any single warm body, [and] that, in particular, the equality of the mean *vis viva* corresponding to each momentoid [i.e. the validity of the equipartition theorem] is also in this case the condition for the temperature equilibrium between the different parts of a warm body."

<sup>96</sup> See Boltzmann 1898, § 35 and p. 126, note 1.

<sup>97</sup> Boltzmann 1898, p. 101.

<sup>98</sup> Boltzmann 1898, p. 103.

<sup>99</sup> Boltzmann 1898, p. 103.

In order to add plausibility to his argument, Boltzmann then briefly turns to the case of two physical systems in thermal equilibrium with each other. He justifies his assertion that the validity of the equipartition theorem is the characteristic property of their thermal equilibrium by considering a gas being divided by a thermally conductive membrane, thus effectively making two systems out of one. His conclusion is that for each molecule of one of the two gases the mean kinetic energy of its center of gravity must be equal. Boltzmann finally extends his argument to the case in which one of the physical systems is an arbitrary body, by simply adding:<sup>100</sup>

"This mean *vis viva* should also be equal to the mean *vis viva* corresponding to an arbitrary momentoid which determines the molecular motion of an arbitrary body in thermal equilibrium with the gas."

In a footnote to a later passage Boltzmann elaborates just a little bit more the idea of an arbitrary body in thermal equilibrium with a gas. He there justifies the extension of his theorems to such a body by considering it as representing a single gas molecule surrounded by the much larger mass of gas:<sup>101</sup>

"We want to conceive a certain given solid or liquid [tropfbar flüssigen] body under the picture of an aggregation of n material points, which hence has 3n degrees of freedom, for instance the 3n orthogonal coordinates. If it is surrounded by a much larger mass of gas, it can, so to say, be considered as a single gas molecule and the laws found in the text can be applied to it."

These extremely brief and isolated remarks do, however, not constitute a rigorous derivation of the validity of the equipartition theorem for general physical systems in thermal equilibrium but rather mark even more vividly a weak spot in Boltzmann's exposition in the *Gastheorie*. The book does, in particular, not treat the canonical ensemble as a representation of a system in thermal equilibrium, let alone the equipartition of energy based on this representation. Since Einstein was quite aware of how precarious and central the validity of the equipartition theorem was in some of the applications of the kinetic theory of heat, in particular for the cases of electron theory and heat radiation, he must have identified this weak spot in Boltzmann's *Gastheorie* as a crucial gap. Boltzmann's line of argument, as I have sketched it, could have appeared to Einstein, on the other hand, almost like a blueprint of an approach to be worked out. In fact, Boltzmann's argument not only comprises essential ideas on which Einstein's statistical mechanics is based but also offers itself for a further mathematical elaboration because of its predominantly qualitative character. When Einstein took up this challenge, he did not know that such an elaboration had already been accomplished to a large extent by Boltzmann himself, albeit from a different perspective.

<sup>100</sup>Boltzmann 1898, p. 104.

<sup>101</sup>Boltzmann 1898, p. 126, note 1.

Statistical Mechanics from the Perspective of a Mechanical Atomist

It is impossible here to exhaustively review the numerous building blocks of statistical mechanics that can be traced back to various publications by Boltzmann.<sup>102</sup> Nevertheless, a few examples may suffice in order to indicate that the gap Einstein meant to have identified in Boltzmann was really no gap at all, at least as far as the crucial definitions and technical results taken by themselves are concerned. Under the name of "holode" Boltzmann introduced, for example, the canonical ensemble in a paper of 1885:<sup>103</sup>

"Let an arbitrary system be given whose state is characterized by the arbitrary coordinates  $p_1, p_2...p_g$ ; the corresponding momenta be  $r_1, r_2...r_g$ . We want to briefly call them the coordinates  $p_g$  and the moments  $r_g$ . The system shall be exposed to arbitrary internal and external forces; the former ones shall be conservative. Let be the *vis viva* [i.e. the kinetic energy], the potential energy of the system.

•••

Case 1: We now conceive of very many N such systems, exactly equally constituted; each system completely independent of every other one. The number of all these systems for which the coordinates and momenta lie between the limits

$$p_1$$
 and  $p_1 + dp_1$ ,  $p_2$  and  $p_2 + dp_2$ , ...,  $r_g$  and  $r_g + dr_g$ 

shall be:

$$dN = N e^{-h(+)} - \frac{\sqrt{d} d}{e^{-h(+)} \sqrt{d} d}$$

where

$$\mathbf{d} = {}^{-1/2} \mathbf{d} \mathbf{p}_1 \mathbf{d} \mathbf{p}_2 \qquad \dots \qquad \mathbf{d} \mathbf{p}_g, \, \mathbf{d} = \mathbf{d} \mathbf{r}_1 \mathbf{d} \mathbf{r}_2 \qquad \dots \qquad \mathbf{d} \mathbf{r}_g.$$

Clearly, if one takes h = 1 / kT where k is Boltzmann's constant and T the absolute temperature, Boltzmann's expression corresponds to the modern definition of a canonical ensemble. In his paper, Boltzmann then determines the kinetic energy L and the potential energy of the ensemble:

$$L = \frac{Ng}{2h}$$

and

$$= N \frac{e^{-h} d}{e^{-h} d}$$

<sup>102</sup>For such reviews, see Ehrenfest and Ehrenfest 1911 and Gallavotti 1994.

<sup>103</sup>Boltzmann 1885 (*Wissenschaftliche Abhandlungen*, Vol. 3, pp. 131-132); see also Boltzmann 1872 (*Wissen schaftliche Abhandlungen*, Vol. 1, pp. 401-402) and Boltzmann 1884, an earlier version of Boltzmann 1885.

He has thus established key properties of a canonical ensemble, and proceeds to show that it represents an equilibrium ensemble and a mechanical model of thermodynamics. Boltzmann's second example ("Case 2") is the ergodic or microcanonical ensemble for which he demonstrates similar properties.

The principal aim of Boltzmann's introduction of a canonical ensemble (or of a "holode," as he called it) was, however, not to establish a statistical mechanics applicable to a given physical system and suitable to derive its thermodynamic properties, let alone to explore its atomistic constitution. His intention was rather *vice versa* to find a class of mechanical systems which show an analogy with the behavior of warm bodies. He thus elaborated a line of thought initiated by Helmholtz with the aim to study the foundational question of the relation between mechanics and thermodynamics. In the introduction to his paper Boltzmann explains:<sup>104</sup>

"The most complete mechanical proof of the second law would obviously consist in showing that for each arbitrary mechanical process there are equations which are analogous to those of the theory of heat. But since this theorem does, on the one hand, not seem to be correct in this generality and since it is not possible, on the other hand, due to our ignorance of the essence of the so-called atoms, to exactly determine the mechanical conditions under which the thermal motion proceeds, the task emerges to study in which cases and to what extent the mechanical equations are analogous to those of the theory of heat. This cannot be a matter of postulating mechanical systems which are completely congruent to warm bodies but of finding all systems which more or less show an analogy with the behavior of warm bodies. In this way the question was first raised by Mr. von Helmholtz, and I intend to pursue in the following the analogy he discovered between the systems which he designates as monocyclic and the theorems of the mechanical theory of heat in the case of some systems I will discuss some very special examples."

The special examples which Boltzmann discusses in the sequel merely serve to illustrate his theoretical program; they deal with very special mechanical arrangements, such as a ring of continuous matter rotating around a central body, none of which is directly relevant to concrete problems of statistical physics. Boltzmann's exclusive subject was indeed the relation between mechanics and the theory of heat. It therefore does not come as a surprise that he did not find it necessary to take up the canonical ensemble in the *Gastheorie*, in particular as this line of enquiry could just as well be illustrated by the example of an ergodic or microcanonical ensemble.<sup>105</sup>

<sup>104</sup>Boltzmann 1885 (*Wissenschaftliche Abhandlungen*, Vol. 3, p. 122). For a discussion of Helmholtz's approach and its relation to that of Boltzmann, see Klein 1972.

<sup>105</sup>It was hence not any "obscurity" that was responsible for the neglection of this particular contribution of Boltzmann's, as Gallavotti suggests (Gallavotti 1994, p. 1572), but his different outlook on what today are problems of statistical mechanics. Obscurity in hindsight is often a side-effect of historical development, see the discussion in Damerow et al. 1992, p. 5.

This brings me to my second example of Boltzmann's anticipation of results of statistical mechanics in disguise, this time taken directly from the *Gastheorie*. While, in the *Gastheorie*, the only virtual ensemble considered is the ergodic one, Boltzmann did introduce there the mathematical expression for a canonical ensemble. But its physical interpretation does not refer to a virtual ensemble but rather to a real physical system – a gas – which is characterized by a probability distribution for its atomistic components. In his treatment of gases with polyatomic molecules Boltzmann began by assuming that, at a given initial time, the number of molecules of a certain kind whose center of gravity lies in a particular, infinitesimally small region of phasespace, is given by:<sup>106</sup>

$$A_1 e^{-2hE_1} dp_1 \qquad dq_{\mu}.$$

Here the position and state of a molecule (not of a member of a virtual ensemble!) are given by the generalized coordinates  $p_1$ ,  $p_2$ , ...,  $p_{\mu}$  and the generalized momenta  $q_1$ ,  $q_2$ , ...,  $q_{\mu}$  of its components; *h* is a constant depending on the temperature and  $A_1$  a constant characteristic for the different species of molecules; finally,  $E_1$  is the value of the sum of the total kinetic energy of a molecule and the potential energies due to the intramolecular and the external forces acting on the molecule at the given time.<sup>107</sup> That the above expression does not characterize a virtual ensemble is clear from the way it is introduced; it becomes entirely evident from the sequel of Boltzmann's argument. He considers in fact collisions between molecules in order to make plausible the stationary character of the assumed probability distribution. We have hence encountered a second case in which a mathematical expression given by Boltzmann is equivalent to one of statistical mechanics but is embedded in a different physical context.

A third example of the same kind will make it clear that Boltzmann was not only familiar with the mathematical properties of the canonical ensemble but was also aware of its relation to the ergodic or microcanonical ensemble, even if again under a somewhat different disguise. In a paper published in 1871 he considered an arbitrary body in thermal equilibrium with a gas.<sup>108</sup> But unlike the extremely brief remarks in the *Gastheorie*, which we have discussed in the preceding subsection, he there proceeded with a detailed quantitative analysis of the motion of the atoms of this body. He presupposed that the energy of the entire system is a constant of motion and that the coordinates and velocities of its atomistic constituents take on all possible values compatible with this restriction. This system can thus be described by an ergodic or microcanonical ensemble, which is, however, not what he explicitly does in the section in question. For the sake of this particular argument Boltzmann rather focuses on the consideration of time av-

<sup>106</sup>Boltzmann 1898, § 37, p. 108.

<sup>107</sup>The analogy with the Maxwell-Boltzmann distribution for monoatomic gases is discussed in Boltzmann 1898, pp. 121-122.

<sup>108</sup>Boltzmann 1871b (Wissenschaftliche Abhandlungen, Vol. 1, pp. 259-287).

erages. He assumes that the entire system consists of atoms, of which r belong to the body immersed in the mass of gas. In addition, both and r are taken to be large – with r, however, vanishingly small with respect to atoms. The potential energy takes on the form:

$$=$$
 1 + 2

where  $_1$  is a function of the r atoms of the body and  $_2$  a function of the remaining -r atoms of the gas.

Boltzmann first determines, using a theorem of mechanics by Jacobi, the average time during which the coordinates of the r atoms of the body lie between  $x_1$  and  $x_1 + dx_1$ , etc., which he writes as:

$$dt = C e^{-h_{1}} dx_{1} dy_{1} \dots dz_{r}$$

where h depends on the temperature as before and C is a constant. By taking into account also the velocities (or rather the momenta), an expression analoguous to the probability distribution for a canonical ensemble can be derived by the same argument. In the same paper – albeit not in the same context – Boltzmann argues that time averages can, for systems such as the one considered here, be interchanged with ensemble averages.<sup>109</sup> If hence the expression for the average time is reinterpreted as an expression concerning the number of systems in a virtual ensemble, it can be claimed that Boltzmann thus effectively demonstrated that a canonical ensemble represents a body in contact with a heat reservoir, which in turn can be represented by a microcanonical ensemble.

Such a reinterpretation of Boltzmann's result is in fact at the core of its discussion in the 1911 review paper by the Ehrenfests, where it is treated as an achievement with pioneering significance for statistical mechanics:<sup>110</sup>

"It is actually the origin of the idea of representing the behavior of a body in thermal equilibrium by the average behavior of a canonical ensemble. In an ergodic system consisting of N molecules, let us consider a group of N' molecules, where N' may be a large number but still very small compared to N. Boltzmann obtains an expression for the relative length of time during which the state of these N' molecules lies in the region  $dq_1^{1}$  ...  $dp_r^{N}$ . This expression is

(78)  $dW = e^{-E' \ell} dq_1^{1} \dots dp_r^{N'}$ 

where E' is the total energy of the group of molecules in this state and /2 the time average of the kinetic energy per degree of freedom of the ergodic system. If we consider instead the corresponding stationarily distributed ergodic ensemble (Eq.

<sup>109</sup>See Boltzmann 1871b (*Wissenschaftliche Abhandlungen*, Vol. 1, pp. 277-278). 110Ehrenfest and Ehrenfest 1959/1990, p. 65.

31a), the Eq. (78) will be proportional to the number of such individuals in the group for which the state of the N' molecules under consideration lies in the region  $dq_1$  dp<sub>r</sub>. This is the form in which one finds the theorem in Maxwell's work (1878 [3]). Gibbs expresses it in the following way (op. cit., p. 183): 'If a system of a great number of degrees of freedom is microcanonically distributed in phase, any very small part of it may be regarded as canonically distributed.' The part of the system of N' molecules in whose behavior we are interested is the body, while the whole ergodic system is this body together with a very large temperature bath. This is the way in which Einstein also uses the ergodic hypothesis and the microcanonical and canonical ensembles in two papers on the 'kinetic theory of thermal equilibrium and the second law of thermodynamics' (1902, 1903) [1, 2]."

The significance that the Ehrenfests attribute to Boltzmann's result is, however, only a projection from the hindsight of statistical mechanics. First of all, the described reinterpretation in terms of a virtual ensemble, which is necessary in order to transform this result into a building block of statistical mechanics, was, although a plausible step, actually not carried out by Boltzmann himself, as we have seen. Secondly, his result only played a marginal role in his own work. It was merely conceived as supplementing the treatment of polyatomic gas molecules presented in an earlier paper.<sup>111</sup> Concerning the relationship between the two approaches, Boltzmann remarked in the concluding paragraph of his paper:<sup>112</sup>

"We thus arrive in a much easier way to what we have found there. Since, however, the demonstration that the hypothesis made in the present section is satisfied for warm bodies has not yet been given [i.e. that the coordinates and velocities of their atomistic constituents take on all possible values compatible with the energy equation, J.R.], yes, that it is even possible [for this hypothesis] to be satisfied, I therefore have chosen in that treatise the path that is more complicated but free of any hypothesis."

This attitude corresponds to that which Boltzmann also took in the *Gastheorie*. There he extensively discussed the other, more complicated approach to polyatomic gas molecules, which involves a detailed analysis of molecular dynamics and which I have mentioned in the second example of this subsection. In the *Gastheorie*, he restricted himself to merely allude to the approach of his 1871 paper, in the context of the qualitative considerations of § 35, omitting the quantitative aspects discussed in the paper. By presenting the generalization to arbitrary bodies as being merely a "conjecture," Boltzmann indeed provoked, as we have seen, in his reader Einstein the impression that there was actually a gap in the *Gastheorie*.<sup>113</sup>

<sup>111</sup>Boltzmann 1871a (Wissenschaftliche Abhandlungen, Vol. 1, pp. 237-258).

<sup>112</sup>Boltzmann 1871b (Wissenschaftliche Abhandlungen, Vol. 1, p. 287).

<sup>113</sup>See Boltzmann 1898, § 34, p. 101.

The few examples presented here illustrate that essential results of statistical mechanics have been anticipated in the work of Boltzmann where they are found, however, embedded in conceptual contexts different from that of statistical mechanics. That not the technical details but the perspective on them was new in statistical mechanics is a view that was explicitly stated by Gibbs. In the preface to his 1902 *Elementary Principles of Statistical Mechanics*, he writes:<sup>114</sup>

"The matter of the present volume consists in large measure of results which have been obtained by the investigators mentioned above [i.e. Maxwell and Boltzmann, J.R.], although the point of view and the arrangement may be different."

and in an earlier passage he notes:<sup>115</sup>

"But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics."

When Boltzmann, on the other hand, looked back on his own research in 1899 he felt that his motives and his perspective had been different from those prevailing at the turn of the century:<sup>116</sup>

"Each of these substances [caloric substance, electric and magnetic fluids, etc., J.R.] was conceived of as consisting of atoms, and the task of physics seemed confined for ever to ascertaining the law of action of the force acting at a distance between any two atoms and then to integrating the equations that followed from all these interactions under appropriate initial conditions.

This was the stage of development of theoretical physics when I began my studies. How many things have changed since then! Indeed, when I look back on all these developments and revolutions I feel like a monument of ancient scientific memories. I would go further and say that I am the only one left who still grasped the old doctrines with unreserved enthusiasm – at any rate I am the only one who still fights for them as far as he can.

•••

I therefore present myself to you as a reactionary, one who has stayed behind and remains enthusiastic for the old classical doctrines as against the men of today; but I do not believe that I am narrow-minded or blind to the advantages of the new doctrines. ....."

<sup>114</sup>Gibbs 1902, p. x.

<sup>115</sup>Gibbs 1902, p. viii.

<sup>116</sup>Boltzmann 1974, p. 82.

Indeed, narrow-minded he was not: when Boltzmann commented in 1904 on the work of Gibbs he understood quite well that the latter's statistical mechanics, although based on a systematization of familiar results, nevertheless represents a novel approach with a scope much wider than that of "ascertaining the law of action of the force acting at a distance between any two atoms" and wider also than that of the kinetic theory of heat:<sup>117</sup>

"The merit of having systematized this system, described in a sizable book and given it a characteristic name belongs to one of the greatest of American scientists, perhaps the greatest as regards pure abstract thought and theoretical research, namely Willard Gibbs, until his recent death professor at Yale College.

•••

The wide perspective opening up if we think of applying this science to the statistics of living beings, human society, sociology and so on, instead of only to mechanical bodies, can here only be hinted at in a few words."

The significance of a particular perspective for interpreting or reinterpreting physical results is hence not a matter of narrow- or open-mindedness but rather of the scientific context in which these results are immersed and which lends them a particular meaning. This scientific context was, as we have seen, different in Boltzmann's and in Einstein's case. In the following subsection I will reconstruct how Einstein succeeded, from his particular perspective, to reinterpret some of Boltzmann's results and to lay, independently from Gibbs, the foundations of statistical mechanics. As Einstein's work on statistical mechanics has been extensively discussed in volume 2 of the *Collected Papers*, I can confine myself here to a few remarks illustrating my point.

Einstein's Statistical Mechanics as a Reinterpretation of Boltzmann's Gastheorie

Einstein certainly was in a more difficult position than Gibbs when he set out to fill the gap he perceived in Boltzmann. Whereas Gibbs was thoroughly familiar with Boltzmann's work, e.g. with the crucial 1871 paper discussed above,<sup>118</sup> Einstein essentially only knew the *Gastheorie*. Apart from the qualitative considerations of § 35, his starting points for a quantitative treatment of the statistical properties of general mechanical systems were Boltzmann's introduction of the ensemble idea and the probability distribution for polyatomic molecules introduced as the second example in the previous subsection. But Einstein's engagement with virtually all aspects of turn-of-the century atomism did not only enable him to identify a gap in Boltzmann, it also helped him to fill it. First of all, it must have been clear to Einstein that the validity of the probability distribution found in Boltzmann could not depend on the peculiar features of a gas, e.g.

<sup>117</sup>Boltzmann 1974, p. 171.

<sup>118</sup>See Gibbs 1902, p. viii.

on the collisions between its molecules. In early 1901, Einstein had even speculated about an analogy between the energy distribution over the molecules of a gas and the energy distribution over the frequencies of radiation in thermal equilibrium.<sup>119</sup> Drude, on the other hand, did not take into account such an energy distribution for the free electrons inside a metal; indeed, its derivation from the dynamics of the electron motion inside the metal would have been purely speculative.<sup>120</sup>

It was therefore plausible for Einstein to reinterpret the probability distribution for the number of compounded molecules in a gas with a given range of values for the coordinates and momenta of their components, quoted in the preceding subsection, as the probability distribution for the number of copies of a given physical system in a virtual ensemble under analogous conditions. In fact, Einstein's first paper on statistical mechanics contains the following expression characterizing a "canonical ensemble:"<sup>121</sup>

$$dN' = A''e^{-2hE}dp_1 \qquad dq_n$$

This expression is interpreted as giving the probability that the state variables of a system in thermal equilibrium with a system of infinitely large energy (the heat reservoir) lie in an infinitely small volume of phase space. The claim that Einstein first found the canonical ensemble by transferring the idea of an exponential distribution of the energies in a gas with polyatomic molecules from the kinetic theory to the theory of statistical ensembles receives further support from the close similarity between Boltzmann's and Einstein's expressions for these two cases.

Although the reinterpretation of Boltzmann's probability distribution as defining a canonical ensemble disposes with the necessity of a detailed consideration of the interactions between the atomistic constituents of a system, it did not, however, *per se* provide a physical justification for the assumption that this ensemble represents indeed a physical system in thermal equilibrium. The approach by which Einstein attempts, in his first paper, to provide such a justification again closely follows Boltzmann, or rather, Einstein's reinterpretation of Boltzmann's arguments. In the *Gastheorie*, Boltzmann had, as we have seen, argued that his results could be extended to an arbitrary body by considering it as a single gas molecule in thermal equilibrium with a surrounding mass of gas. If now this relation between the body as a large molecule and the surrounding gas is mapped into a relation between ensembles one arrives at Einstein's justification for the claim that the canonical ensemble represents a physical system in thermal equilibrium. In fact, the reinterpretation of Boltzmann's image suggests to represent both the entire

<sup>119</sup>See Einstein to Mileva Mari¶, 30 April 1901, Vol. 1, Doc. 102, pp. 294-295.

<sup>120</sup>See the discussion of this weakness in Seeliger 1921, pp. 788-789, and in Kaiser 1987, p. 278. Einstein's criticism of Drude may have also included this aspect, closely related to the derivation of the equipartition law.

<sup>121</sup>Einstein 1902b, p. 422. Einstein did not use this terminology.

system and the body by such virtual ensembles and to study their relation. Clearly the entire system could be represented by an ergodic or microcanonical ensemble and the body, at least tentatively, by a canonical ensemble. As the next and conclusive step, one then had to show, just as Gibbs put it, that "[i]f a system of a great number of degrees of freedom is microcanonically distributed in phase, any very small part of it may be regarded as canonically distributed."<sup>122</sup>

Probably starting from Boltzmann's image, as I have suggested, Einstein thus transferred the idea of a small thermodynamic system in contact with a large heat reservoir, familiar from macroscopic thermodynamics, to the relation between two ensembles. In his paper he indeed treated the canonical ensemble as a small thermodynamic system in contact with a large heat reservoir, represented by the microcanonical ensemble.<sup>123</sup> The complex line of argumentation that Einstein followed in his paper in order to derive the probability distribution of a system in thermal equilibrium is guided and rendered plausible, in spite of several short-comings, by this fundamental idea.<sup>124</sup> His argument can be described as another successful transfer of properties familiar from the macroscopic world into a microworld, in this case described by statistical ensembles.

This line of attack was well prepared by his earlier research experience: When Einstein approached the task of filling the gap in Boltzmann's work, he was already experienced in modifying, in various ways, the basic atomistic idea by additional assumptions that either transposed macroscopic properties into the microworld or that transferred properties assumed in one kind of atomistic theory to another one. An example for the first case is his (or rather Planck's) resonator model of matter which makes the concept of a resonator, familiar from macroscopic electrodynamics, the constituent of an atomistic theory that promised to explain the interaction between matter and radiation.<sup>125</sup> An example for the second case is Einstein's (and, of course, Drude's) combination of the kinetic theory of matter with the atomistic theory of electricity in their electron theories of metal. By ascribing electrical charge to the atomistic constituents assumed in the kinetic theory of heat, these theories attempted, as was discussed, to explain the thermal properties of matter by the motion of these particles and its electrical properties by their charge. Einstein's reinterpretation of Boltzmann's results in his approach to statistical mechanics was hence indeed facilitated by this experience with the transfer of properties from the macro- to the microworld.

<sup>122</sup>Gibbs 1902, p. 183.

<sup>123</sup>See Einstein 1902b, in particular, § 3 and § 5.

<sup>124</sup>See, e.g., Einstein's exchange with Paul Hertz on certain difficulties of Einstein's argumentation, which is briefly summarized in note 20 to Einstein 1902b, Vol. 2, p. 74.

<sup>125</sup>See Einstein to Mileva Mari¶, 23 March 1901, Vol. 1, Doc. 93, pp. 279-280.

It is remarkable that, when Boltzmann and Nabl briefly commented on Einstein's approach in their 1905 review, they identified Boltzmann's image of a body as a large molecule as its core idea. Their comment is implicit in a brief passage found in a section on the application of Liouville's theorem to the calculation of specific heats. The context of the passage is a discussion of the thermal equilibrium of polyatomic gases; in a footnote to the passage Einstein's first two papers on statistical mechanics are cited alongside with several papers by Boltzmann:<sup>126</sup>

"By application of the statistical method to arbitrary bodies (their treatment, so to say, as gas molecules with very many atoms) one can find mechanical systems which show full mechanical analogy with warm bodies,<sup>127</sup> not only a partial one as the cyclic systems of Helmholtz."

In other words, Boltzmann and Nabl apparently considered Einstein's approach as nothing but an elaboration of Boltzmann's image, just as I have claimed in my reconstruction. In their brief comment they do not discuss, however, Einstein's reinterpretation of this image in terms of statistical ensembles. If at all, they allude to this aspect only by their phrase "application of the statistical method." What is more important, they present Einstein's approach in the same light in which Boltzmann had set his introduction of the canonical ensemble in his 1884 paper, which in fact is cited in Boltzmann's and Nabl's footnote, that is, as the elaboration of a mechanical analogy with warm bodies, in extension of Helmholtz's monocyclic systems. Nothing in their remark hints at a novel approach; Einstein's two papers rather appear as merely supplementing, at best, Boltzmann's own earlier publications which in fact they are, at least from a technical point of view.<sup>128</sup> I take Boltzmann's and Nabl's reaction to Einstein's work as another confirmation of how much the creation of statistical mechanics was a matter of perspective.

# 6. Epilogue: the Ambivalent Success of Einstein's Atomism

Einstein had developed his statistical mechanics with the aim to cover a wider range of atomistic phenomena than those accessible to the kinetic theory of Maxwell and Boltzmann, and he wanted to contribute what he could to establish the existence of atoms beyond the doubt of the skeptics.<sup>129</sup> In this he was eminently successful, at least initially. Statistical mechanics helped him and others to augment the available evidence in favor of the atomistic constitution of matter

<sup>126</sup>Boltzmann and Nabl 1905, p. 549.

<sup>127</sup>The footnote to this passage contains the following references: Boltzmann 1871a, 1877, 1884, 1887; Einstein 1902b, 1903. Boltzmann 1885, discussed above, is an extended version of Boltzmann 1884.

<sup>128</sup>The similarity of Einstein's formalism with that of Boltzmann, together with the fact that Einstein designated his own approach just as filling a gap, may account for the remarkable difference between Boltzmann's reaction to Gibbs, on the one hand, and to Einstein, on the other. The greater prominence of Gibbs may, of course, also have played a role.

<sup>129</sup>See Einstein 1979, p. 44.

and even provided hints at a discrete structure of radiation. Einstein's explanation of Brownian motion in 1905, together with its experimental confirmation by Perrin, was perhaps his most influential contribution in this regard, and it also was a consequence of his occupation with statistical mechanics.<sup>130</sup> Of course, not all of Einstein's youthful extrapolations of atomistic ideas had turned out to be as fortunate; his attempt at an electrodynamics of moving bodies based on a corpuscular theory of light, for instance, had to give way to the introduction of a new framework of space and time that was essentially indifferent to the question of whether light was a wave or consisted of particles. But the accumulated evidence in favor of atomism that became available by the 1910s and that was masterly exposed in Perrin's comprehensive reviews seemed to dispell with any reasonable doubt about the existence of atoms and thus represented a fulfillment of Einstein's original goals.<sup>131</sup>

This evidence was taken, as described in section 4, from quite different physical or chemical, and otherwise unrelated contexts of research and yet points to more or less the same value for Avogadro's number and other general features of a corpuscular structure of matter. I take this as an indication for the integrative, cross-disciplinary significance of atomism at this time, linking chunks of physical and chemical knowledge to each other in new ways, and thus constituting a scientific reality of the material microworld independently from any single theory or discipline. Atomism had, as we have seen, played this role for Einstein's youthful endeavors, but it had now taken on this role also for the scientific community at large.

At the same time, however, the wealth of evidence in favor of a discrete structure of matter had increased, as I have also pointed out above, the challenge for a coherent description of this microworld. Since the properties of atoms were obtained by a transfer of properties from the macroworld into the microworld, there could be no *a priori* guarantee that the resulting combination of atomistic properties would yield a coherent picture. Atoms had to carry charge in order to account for electrical phenomena, they had to move rapidly in order to account for thermal phenomena, they had to move rapidly in order to be capable of explaining complex spectra, and yet not too many in order to give rise to the observed specific heats, they had to be able to combine in complicated ways to molecules in order to explain chemical compositions, but they had to do all of this, if possible, on the basis of the known physical laws.<sup>132</sup> In a word, the concept of an atom gradually came into the position of the concept of the ether at the end of the 19th century, when it was overburdened with the tasks it had to fulfill and the properties it had to possess, in particular being an immoveable carrier of electromagnetic waves and yet to show no trace of the motion of masses passing through it.<sup>133</sup>

<sup>130</sup> See the editorial note in Vol. 2, "Einstein on Brownian Motion," pp. 206-222 and the literature cited there. 131 See Nye 1972.

<sup>132</sup>See Harman 1982, pp. 133-139 for an overview.

<sup>133</sup>See Einstein 1920 for a discussion of the ether as a concept overloaded with requirements.

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Einstein encountered the dilemma of finding a coherent picture of the microworld when he applied, in his 1905 light quantum paper, concepts of statistical physics to the problem of black body radiation. This application did disclose a surprising and novel aspect of the structure of radiation in thermal equilibrium, its particle-like behavior for low energy densities within the range of validity of Wien's radiation formula.<sup>134</sup> But Einstein's insight could not be brought into harmony with the ordinary way in which the microworld was furnished, following our macroscopic experience, that is, consisting of either particles or states of a continuum.<sup>135</sup> With more success Einstein employed statistical mechanics to unravel new aspects of the atomistic constitution of matter, in particular in his 1907 analysis of specific heats of solids.<sup>136</sup> Eventually, however, it turned out that the same dilemma which Einstein had discovered in the theory of radiation also plagued the atomistic conception of matter. The history of quantum theory makes it clear that the traditional elements of the conceptual furniture of the microworld, particles and states of a continuous medium, were equally insufficient in accounting for the growing wealth of empirical knowledge about the microstructure of matter. Statistical mechanics played a key role in the analysis of this knowledge and hence for the development of quantum theory. In this way, statistical mechanics was no longer an instrument for extracting from this empirical knowledge the evidence for a microworld made up of atoms as they were envisaged by the young Einstein, but rather became a tool for assembling insights into a new conceptual foundation of physics, beyond the classical dichotomy of particles and fields, and beyond any possibility of transferring properties from the macroworld to the microworld. Reminding the reader that Einstein never quite accepted this foundation of physics and that he had his problems in particular with its intrinsically statistical character may provide a suitable but somewhat ironical ending to this reconstruction of the origins of statistical mechanics in the atomistic world picture of his youth.

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<sup>134</sup>See Einstein 1905a. The dependence of Einstein's paper on the light quantum on his earlier work on statistical physics is analyzed in Klein 1963.

<sup>135</sup>For a reconstruction of this conflict and its empirical roots, see Wheaton 1983. 136Einstein 1907.

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