

Insuperable difficulties: Einstein's statistical road to molecular physics

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January 6, 2006

Abstract

In this essay I analyze Einstein's statistical papers from 1902–1904. In these papers, Einstein developed the foundations of a theoretical program that he applied to concrete problems in 1905 and in subsequent years. It combined skepticism about classical mechanics, a firm belief in molecules, and absolute confidence in statistical principles. However, Einstein's dissertation does not follow his statistical program. I conjecture that Einstein avoided his own theoretical ideas to win the approval of his Ph. D. advisor, Alfred Kleiner.

Keywords: Einstein; Boltzmann; Kleiner; Statistical physics; Molecules; Entropy

1 Introduction

Two papers in the extraordinary sequence Einstein wrote in his miraculous year 1905 are devoted to molecules: his Ph.D. dissertation of April 30 (Einstein 1905b), and the paper on

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Brownian motion of May 11 (Einstein 1905c). Einstein's interest in molecular physics did not come out of the blue. He had published three papers on the foundations of thermodynamics and statistical mechanics in 1902, 1903, and 1904—apart from his early papers on molecular forces, the *only* issue he published on during those formative years.

The three papers just mentioned, sometimes called the *statistical trilogy*, are usually regarded as less important than the 1905 papers. To be sure, they did not “change the face of physics,” to use Stachel's (1998) phrase, in the way his 1905 papers did. Boltzmann and Nabl (1904) mention Einstein's work in a footnote, but did not devote any substantial comment on it. Neither did the influential Encyclopedia article of the Ehrenfests (1912). Authors who did discuss Einstein's papers in some detail, such as Ornstein (1910) and P. Hertz (1910), were critical. Einstein's admission in his (1911) reply to Hertz, that he would never have published the first papers of the trilogy if he had known Gibbs' (1902) book, likewise did not help him gain recognition for his approach.

Even so, these papers are important for understanding the development of Einstein's thinking before the outburst of creativity in 1905, in particular in the two papers on molecules. Kuhn (1978) in particular has stressed that the statistical trilogy is also important in its own right, as the start of a general theory of statistical thermodynamics (developed, e.g., in Tisza 1966).

This essay will sketch how these three papers laid the groundwork for a theoretical statistical program that Einstein came to execute in 1905 (and indeed in many later works as well). Many scholars have already reviewed and analyzed the statistical trilogy from various perspectives.¹ Although this paper necessarily overlaps with what other commentators have written, there will be some differences in emphasis. First, I will concentrate on conceptual issues connected with the statistical aspects of Einstein's approach. Thus, from a historical perspective, I will focus mainly on the relation of his work to Boltzmann's.² However, I will not limit myself to a historical discussion, but on occasion offer critical comments from today's vantage point.

¹(See Klein 1967, Ezawa 1979, Pais 1982, Mehra & Rechenberg 1982, Gearhart 1990, von Plato 1994, Navarro 1998, Renn 1998) and the editorial note, “Einstein on the Foundations of Statistical Physics,” in (CPAE, Vol. 2, pp. 41-55).

²I refer to Gearhart (1990) for a careful analysis of the thermodynamical background to Einstein's trilogy, the development of his thinking, and his indebtedness to Planck, Nernst, Ostwald and others.

As I will show in section 2, Einstein gradually developed an approach in his trilogy that might be characterized as a unique blend of a firm belief in the reality of molecules, skepticism about the validity of classical mechanics, and absolute trust in statistical methods, the centerpiece of which became his “Boltzmann principle”. Moreover, from 1904 onwards, he showed a keen interest in finding experimental tests for the numerical value of Boltzmann’s constant or Avogadro’s number.

Section 3 discusses how this program was applied both in his light quantum paper (Einstein 1905a) and in his paper on Brownian motion (Einstein 1905c). However, as I will argue, Einstein’s dissertation (1905b) does not fit easily within this overarching program, and appears as a curious anomaly. In that paper, providing a method to determine the size of molecules, he ignored his own statistical framework and relied on classical hydrodynamics instead. His approach is all the more curious given that in his Brownian motion paper, written almost simultaneously, and dealing with an intimately related issue, Einstein adopted a very different approach and had a very different aim. In effect, that paper points out that the hydrodynamical point of view is untenable for phenomena predicted by the statistical approach. I conjecture that his advisor, Alfred Kleiner, might have had reservations about Einstein’s statistical theory. To obtain a doctorate, Einstein obviously depended on his approval, which was not automatic—as may be inferred from Einstein’s retraction of an earlier dissertation submitted to Kleiner in 1901.

In section 4, I will discuss evidence for a contrast in outlook between Einstein and Kleiner, and argue that it might have induced Einstein to choose a less ambitious topic for his dissertation, and leave his more controversial ideas for the Brownian motion paper.

2 The statistical trilogy

2.1 1902: Kinetic theory of thermal equilibrium and the second law of thermodynamics

The first paper of the statistical trilogy focuses on the “kinetic theory of heat” (Einstein 1902). This phrase, or the term “molecular-kinetic theory” that Einstein started using three years later, is roughly identical to what today we call “statistical mechanics”. This last

name had, unbeknownst to Einstein, been coined by Gibbs (1902) to emphasize that the only ingredients of the theory are mechanics and probability theory. Einstein similarly states that his approach uses no more than the mechanical equations and probability calculus.

The more traditional name “kinetic theory” or “kinetic-molecular theory” suggests a different emphasis—that physical systems are composed of molecules, and that their thermal properties, such as temperature and pressure, are explained in terms of molecular motion. “Kinetic theory” thus describes older versions of the theory, developed by Maxwell and Boltzmann in the 1860s and early 1870s. Only gradually did it emerge from their works that the statistical assumptions employed could not themselves be derived from mechanics, or even expressed in mechanical terms, and had to be introduced as conceptually independent elements.

Einstein notes that kinetic theory, although successful for gases, has not yet been able to provide a general theory of heat. Boltzmann and Maxwell came close to this goal, he says, but his paper aims to fill a gap still left in their work.

He considers an arbitrary physical system, represented as a mechanical system with n coordinates q_i and velocities \dot{q}_i described by a Lagrangian $\mathcal{L}(q_1, \dots, q_n, \dot{q}_1, \dots, \dot{q}_n)$.³ As customary, he proceeds to a Hamiltonian framework by introducing the conjugate momenta $p_i = \partial\mathcal{L}/\partial\dot{q}_i$. The equations of motion (which he does not actually write down) then take the Hamiltonian form:

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}, \quad \frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad i = 1, \dots, n, \quad (1)$$

where $H(p_1, \dots, q_n)$ is the Hamiltonian of the system. The solution of these equations from an arbitrary set of initial values at time $t = 0$ determines a trajectory $(p_1(t), \dots, q_n(t))$ in phase space. The Hamiltonian is an integral of the equations of motion, i.e., its value does not change as the state evolves along a trajectory:

$$H(p_1(t), \dots, q_n(t)) = E, \quad (2)$$

where the constant E is determined by the initial values. Einstein assumes that, apart

³Here and in the sequel, I have adapted some of Einstein’s notations to modern conventions.

from the Hamiltonian H , or functions of H , no other function of the microscopic variables $(p_1 \dots, q_n)$ has this property. This assumption is a version of Boltzmann's *ergodic hypothesis* (a name coined by the Ehrenfests in 1912).⁴

Next, he considers an ensemble of “infinitely many (N)” systems of the same kind with their energy between E and $E + \delta E$. The number of systems in that ensemble with their momenta and coordinates lying between p_i and $p_i + dp_i$ and between q_i and $q_i + dq_i$ is denoted as “ dN ”. This number is characterized by the expression:⁵

$$dN = \rho(p_1, \dots, q_n) dp_1 \cdots dq_n. \quad (3)$$

In general, the distribution function ρ will change in time. For a system in thermal equilibrium, ρ is assumed to be stationary. He derives the well-known fact (Boltzmann 1868a, Maxwell 1879) that, under the ergodic hypothesis, the only stationary distribution function ρ is the microcanonical one, or more accurately, the uniform distribution over the energy shell:⁶

$$dN = A dp_1 \cdots dq_n, \quad E \leq H \leq E + \delta E \quad (4)$$

where A is a normalization constant, depending on E and δE .

This result is applied to an ensemble of systems composed of two subsystems: σ and Σ . Let system σ be characterized by the variables (p_1, \dots, q_ℓ) , and Σ by $(\pi_1, \dots, \chi_\lambda)$.⁷ System Σ (which is meant to model the environment) is assumed to be “infinitely bigger” than σ , i.e., $H_\sigma \ll H_\Sigma$, and the total Hamiltonian is, in first approximation, of the form

$$H_{\text{tot}}(p_1, \dots, q_\ell, \pi_1, \dots, \chi_\lambda) = H_\sigma(p_1, \dots, q_\ell) + H_\Sigma(\pi_1, \dots, \chi_\lambda), \quad (5)$$

⁴Boltzmann's original 1868 version of the hypothesis is that the system will eventually pass through every state compatible with the condition (2). The equivalent version that the Hamiltonian is the only independent integral is given in his (1871b) (Boltzmann 1909, p. 281–2).

⁵Einstein actually put $dN = \psi(p_1, \dots, q_n) \int_g dp_1 \cdots dq_1$, where g is the entire ‘thickened energy hyper-surface’, i.e., the region of phase space with $E \leq H \leq E + \delta E$. This expression is probably taken, almost verbatim, from (Boltzmann 1898, sec. 32, eq. (82)), while failing to note that Boltzmann extends his integral over an $(2n - 1)$ th infinitesimal subregion of a proper energy hypersurface. Einstein's mistake is corrected in (Einstein 1903).

⁶It seems Einstein is the first author to employ a shell of finite thickness rather than the proper energy hyper-surface. He thus avoids the tedious transformation from volume to surface integrals.

⁷Einstein (1902) puts $\ell = \lambda$. He removes this unnecessary restriction in his (1903).

i.e., the interaction between the two systems is neglected. Assume that this ensemble is microcanonical, so that

$$dN = A dp_1 \cdots d\chi_\lambda, \quad E_{\text{tot}} \leq H_{\text{tot}} \leq E_{\text{tot}} + \delta E. \quad (6)$$

The question is now to find the subensemble (dN') for which the momenta and coordinates of subsystem σ have prescribed values between p_1 and $p_1 + dp_1$, etc., while the momenta and coordinates of Σ may have any values whatsoever. In other words, we have to trace out the variables of the environment:

$$dN' = A dp_1 \cdots dq_\ell \int_{E_{\text{tot}} \leq H_{\text{tot}} \leq E_{\text{tot}} + \delta E} d\pi_1 \cdots d\chi_\lambda. \quad (7)$$

Versions of this problem had been discussed many times before (e.g. Boltzmann 1868, 1871b, 1898; Maxwell 1879). The answer, at least approximately, is the canonical distribution,

$$dN' = A' e^{-2hH_\sigma(p_1, \dots, q_\ell)} dp_1 \cdots dq_\ell, \quad (8)$$

for some constants A' and h .

But in contrast to Boltzmann, who nearly always⁸ approached this question by assuming that the environmental system Σ was an ideal gas (so that H_Σ is a sum of quadratic terms: $H_\Sigma = \sum_{i=1}^\lambda \pi_i^2/2m_i$) and proceeded to evaluate the integration in (7) explicitly as the surface area of a hyper-sphere in λ dimensions, finally taking a limit $\lambda \rightarrow \infty$, Einstein uses a clever formal trick to obtain the desired result more generally and easily. He first notes that nothing prevents us from rewriting the constant A in (6) as $A = A' e^{-2hH_{\text{tot}}}$, since H_{tot} is a constant in the integral (7), if we neglect variations of order δE . It follows from (5) that

$$dN' = A' e^{-2hH_\sigma} dp_1 \cdots dq_\ell \int_{E_{\text{tot}} - H_\sigma \leq H_\Sigma \leq E_{\text{tot}} - H_\sigma + \delta E} e^{-2hH_\Sigma} d\pi_1 \cdots d\chi_\lambda. \quad (9)$$

He then shows that there is one and only one value of h that makes the integral independent of H_σ .

⁸The exception is Boltzmann (1871b), where he used an argument similar to Einstein's.

Indeed, with $H_\sigma(p_1, \dots, q_\ell) = E_1$, the integral in (9) may be written as

$$\chi(E_{\text{tot}} - E_1) := \int_{E_{\text{tot}} - E_1 \leq H_\Sigma \leq E_{\text{tot}} - E_1 + \delta E} e^{-2hH_\Sigma(\pi_1, \dots, \chi_\lambda)} d\pi_1 \cdots d\chi_\lambda. \quad (10)$$

Since E_1 is assumed to be infinitely small compared to E_{tot} , one may approximate: $\chi(E_{\text{tot}} - E_1) = \chi(E_{\text{tot}}) - E_1 \chi'(E_{\text{tot}})$. Thus, the necessary and sufficient condition that the integral is independent of E_1 is

$$\chi'(E_{\text{tot}}) = 0 \quad (11)$$

Introducing what is nowadays called the ‘structure function’⁹ of system Σ ,

$$\omega(E) := \int_{E \leq H_\Sigma \leq E + \delta E} d\pi_1 \cdots d\chi_\lambda, \quad (12)$$

one can reexpress condition (11) as

$$h = \frac{\omega'(E_{\text{tot}})}{2\omega(E_{\text{tot}})}. \quad (13)$$

If a value for h is chosen accordingly, the integral in (9) becomes independent of E_1 ; it may thus simply be absorbed into the constant A' , and we obtain (8). For a given form of H_Σ and value of E_{tot} , that value of h is unique.

At this point in the paper Einstein stops talking about ensembles. He identifies the relative number of systems in the canonical ensemble dN' in any region g of phase space with the relative probability that the state of a single system lies in that region, and replaces dN' by a probability element dW .

The next investigations in this paper are all related to the parameter h in the canonical distribution (8). We have already seen that (i) h is uniquely determined by the structure function of the environmental system Σ . He continues by showing that (ii) h is positive,¹⁰ and that (iii) if the system σ is a thermometer with an empirical temperature scale θ , the value of θ must be determined by h . He argues that (iv) two systems, each described by a

⁹Strictly speaking, (12) is δE times the structure function. Cf. Einstein’s 1904 redefinition (39).

¹⁰Actually, this proof assumes that the Hamiltonian H_Σ is a sum of unbounded quadratic terms, i.e., it is valid for the ideal gas. It is now known that h can be negative when H has an upper bound.

canonical ensemble, will be in thermal equilibrium if and only if their h 's are equal. This, he notes, implies the transitivity of thermal equilibrium (nowadays often called the zeroth law of thermodynamics).

Next, in a section called “The mechanical meaning of h ,” he demonstrates (v) the equipartition theorem: If the kinetic part L of the Hamiltonian $H = L + V$ is a sum of quadratic terms (Boltzmann’s (1892) “Momentoiden”), i.e., if

$$L = \frac{1}{2} \sum_i^n \alpha_i r_i^2, \quad (14)$$

then the expected value of each term becomes

$$\frac{1}{2} \langle \alpha_i r_i^2 \rangle = \frac{1}{4h} = \frac{\langle L \rangle}{n}, \quad (15)$$

where $\langle f \rangle \equiv (A'/N) \int f e^{-2hH_\sigma} dp_1 \cdots dq_\ell$. He then (vi) applies the equipartition theorem to the case where the system σ is an ideal gas, to obtain

$$\frac{1}{4h} = \kappa T, \quad (16)$$

where T is the absolute temperature (or rather the ideal gas temperature) and κ a universal constant (today, 2κ is called the Boltzmann constant k).

The final sections are devoted to a derivation of the second law. Einstein considers only the first part of that law, i.e., the proposition that the inexact heat differential δQ has an integrating denominator: $\delta Q/T = dS$. He uses an argument, originally due to Helmholtz (1884) for so-called monocyclic mechanical systems (also discussed by Hertz (1894)), that had been transposed to canonical ensembles by Boltzmann (1884,1887).

It assumes that the system is acted upon by two different kinds of external forces: conservative forces (gradients of a potential energy) and non-conservative “rapidly changing” forces,¹¹ responsible for heat exchange. He obtains an expression for entropy, however, that had not been presented in this setting before, although it is similar to a result obtained by

¹¹In other versions of the argument, the term ‘rapidly changing’ is used only for coordinates, not forces.

Boltzmann (1871c) by a different argument. Einstein's result is ¹²

$$S = \frac{\langle H \rangle}{T} + 2\kappa \log \int e^{-2hH} dq_1 \cdots dp_n + \text{const.} \quad (17)$$

He emphasizes that this expression depends only on H and T . In particular, it does not refer to the circumstance that the Hamiltonian is a sum of a kinetic and potential energy. Hence he suggests that the result is not restricted to mechanical systems, as long as h has the property (13).

Comments. Einstein opened his paper with the aim of filling a gap in Boltzmann's work. What was that gap? In the editorial note, "Einstein on the Foundations of Statistical Physics," in (CPAE, Vol. 2), it is argued that it was the proof of the equipartition theorem for canonical ensembles. According to that editorial note, Boltzmann had only succeeded in proving the theorem for the microcanonical case, and for a "real canonical ensemble" but never for a "virtual canonical ensemble" (CPAE, Vol. 2, p. 49). This distinction between real and virtual ensembles presumably coincides with what I will call a many-body-system and a proper ensemble, respectively.

This suggestion sounds implausible to me. It is true that Boltzmann rarely distinguished carefully between an N -body system, in the case that the subsystems do not interact, and a proper ensemble consisting of an infinite number of imagined systems. (In fact, the phrase "an infinite number (N)" is vintage Boltzmann.) Boltzmann was sloppy in these matters, considered ensembles to be artificial, and changed his choice of methods repeatedly. (See Uffink (2004) for a closer look at Boltzmann's work.) But I do not think Einstein was pre-occupied with mathematical and formal niceties, particularly since he similarly interchanged analyses in terms of an N -body system of non-interacting subsystems and in terms of an ensemble in his next paper of 1903. Moreover, he said in 1903 that the distinction between an isolated system and one in contact with a heat bath is only of "formal significance." Einstein

¹²Boltzmann (1871c) presented his result as

$$-r \log \mathfrak{h} + \frac{2\mathfrak{h}}{3} \frac{\int \chi e^{-\mathfrak{h}\chi} d\sigma}{\int e^{-\mathfrak{h}\chi} d\sigma} + \frac{2}{3} \log \int e^{-\mathfrak{h}\chi} d\sigma + \text{const}$$

where $\mathfrak{h} = 2h$, r is the number of particles ($3r = \ell$), $d\sigma$ stands for $dp_1 \cdots dq_{3r}$, χ denotes the potential energy, and Boltzmann works in units such that $\kappa = \frac{1}{3}$.

showed no qualms about applying the canonical distribution to the former case, where the microcanonical one would have been appropriate.

Renn (1998) argues that the ‘gap’ lies in the fact that in Boltzmann’s *Gastheorie* of 1896 and 1898, the only work to which Einstein explicitly refers, the equipartition theorem is obtained only for gases, whereas Einstein derived it for arbitrary mechanical systems. This suggestion is much more plausible. As we have seen, Einstein opened the paper by referring to kinetic theory’s lack of success for systems other than gases.

Nevertheless, Boltzmann did derive the equipartition theorem from the assumption of an exponential distribution (8) for dN in the *Gastheorie* Vol. II, sec. 42. As Renn notes, Boltzmann interprets this derivation as a description of a gas of non-interacting, poly-atomic molecules, rather than an ensemble. Thus, in this context, dN denotes the relative number of molecules, not members of an ensemble, and ℓ numbers the degrees of freedom of a single molecule, rather than a complete gas system. But in a footnote to sec. 42, Boltzmann explains how the same methods and results can be extended to an ensemble of arbitrary thermal bodies (like solids or fluids). All that is needed is to regard such a body as a large poly-atomic molecule. Thus, Einstein could easily have seen how the result may be applied to the latter case, since the mathematics is exactly the same.

I would therefore locate the ‘gap’ in a slightly different spot. In his *Gastheorie* Boltzmann emphasized that it had not been proven whether the canonical distribution is in all circumstances the *unique* stationary distribution for an arbitrary system in contact with a heat bath (1898, sec. 41). This limitation, of course, also restricts the equipartition theorem, because it might not hold for other stationary distributions. Einstein’s treatment does not allow for such exceptions, and might thus be seen as an attempt to answer this open problem.

Nevertheless, I agree with Renn that the perceived gap was actually non-existent. Boltzmann (1871b) had already obtained the canonical distribution as a unique stationary distribution for an arbitrary thermal system (gas, liquid or solid) under the same conditions as Einstein (1902). One might ask why Boltzmann left this issue open in 1898, when he had obtained a definite answer 27 year earlier. The answer is that Boltzmann (1868, 1871b) relied on the ergodic hypothesis. Perfectly aware of its dubious validity, however, he avoided it in his later work (except for the brief period 1881–1885). In the *Gastheorie* he likewise

avoids the assumption and leaves open the possibility that there are several independent integrals. Thus, the microcanonical distribution (4), which he had derived as the *only* stationary distribution in Boltzmann (1868, 1871a, 1871b) is now presented as the *simplest* stationary distribution. Leaving open the possibility of such additional integrals undercuts the proof that an arbitrary mechanical system in contact with the heat reservoir must be characterized by a canonical distribution.

It is not certain with how much of Boltzmann's work Einstein was familiar.¹³ There is much in (Einstein 1902) that reminds one of assumptions, methods and results of Boltzmann that were not mentioned in the *Gastheorie*. His assumption of the ergodic hypothesis (cf. Boltzmann 1871b), his use of the canonical entropy (17) (cf. Boltzmann 1871c), etc. suggest that he knew, perhaps indirectly, more of Boltzmann's work than just the *Gastheorie*. On the other hand, that he rederived some of Boltzmann's pre-*Gastheorie* work can also be interpreted as evidence that he did not know of its existence. For example, it is quite possible that Einstein independently reinvented the ergodic hypothesis to streamline Boltzmann's (1898) argument—without realizing Boltzmann's doubts about the hypothesis.

Another place where Einstein diverged from Boltzmann and hence another candidate for the 'gap', is Einstein's avoidance of the assumption that the environment is an ideal gas. Of course, this generality is achieved at the price of an additional assumption: The integral in (9) should not depend on E_1 . Yet, I do not think Einstein valued this point particularly.¹⁴

Einstein's presentation is more systematic than most of Boltzmann's writing, and is consistently presented from the ensemble point of view. But again, it seems implausible to me that Einstein would criticize Boltzmann's sometimes wavering approach. An identification of probabilities with relative time spent in a given state is mentioned in passing in (Einstein 1902). In (Einstein 1903), which devotes more space to the interpretation of probability, Einstein shows himself a follower of Boltzmann and interprets probability in terms of relative time. (He later became quite insistent on this point, as can be seen in (Einstein 1905a,

¹³Although Einstein only cites the *Gastheorie*, the editorial note in (CPAE, Vol. 2, p. 44) suggests that Einstein may have read several papers by Boltzmann. Gearhart (1990) argues that he might have known Boltzmann's papers published in *Crelle's Journal* but not those in the *Wiener Berichte*.

¹⁴Perhaps he might have had second thoughts about it. It is curious to note that in his lecture notes from 1913, a course that roughly follows his own papers from 1902-1904, he falls back on Boltzmann's approach by assuming the environment to consist of (or at least contain) an ideal gas, points out that this assumption is troublesome, but does not mention his own 1902 argument to avoid it.

1909a, 1909b, 1916) Clearly, Einstein would agree with Boltzmann in the identification of probability, relative numbers in ensembles, and relative times—certainly for stationary distributions and under the assumption of the ergodic hypothesis.

Regardless of what gap Einstein might have perceived, it seems to me that the real merit of the paper, as compared to Boltzmann’s work, lies in the effort Einstein devoted to an elucidation of the properties and meaning of h , thus showing that it can be interpreted as the inverse temperature for any system described by the canonical ensemble, i.e., in his treatment of the issues (i)–(vi) above.¹⁵ This point also has a bearing on the equipartition theorem, of course: not in *proving* that theorem but in establishing its empirical meaning. Some of these points were also treated by Gibbs (1902).

My final comment on this paper concerns a striking side remark. Right before the start of the section on “The *mechanical* meaning of h ,” Einstein notes:

I would like to note here that until now we have made use of the assumption that our systems are mechanical only inasmuch as we applied Liouville’s theorem and the energy principle. Probably the basic laws of the theory of heat can be developed for systems that are defined in a much more general way. We will not attempt to do this here, but will rely on the equations of mechanics. We will not deal here with the important question as to how far the train of thought can be separated from the model employed and generalized. (Einstein 1902, p. 427).

Insofar as he claims that his results thus far rely only on the energy principle and Liouville’s theorem, this quote indicates (with hindsight) a remarkable underestimation of the logical dependence of his approach on the ergodic hypothesis. But much more important, historically speaking, is his comment on the problem not treated. Evidently, in 1902, Einstein already considered it an important and desirable goal to go far beyond a merely *mechanical* underpinning of the theory of heat. No other author I know of in the kinetic theory of heat or

¹⁵Boltzmann emphasized the relation between h and temperature too (cf. *Gastheorie*, sec. 35), but he never spent much time arguing why or how that view is justified (e.g., by deriving the zeroth law). In fact, he never bothered to introduce, let alone discuss the value of the constant of proportionality that we now honor with his name. In most of his writings, he assumes temperature units are chosen such that $k = 2/3$, thus detracting from the possibility of experimental checks of this constant. Perhaps it was for this reason that Einstein felt Boltzmann did not pay enough attention to “the comparison to reality” (Einstein to Mileva Maric, 30 April 1901, CPAE, Vol. 1, Doc. 102).

statistical mechanics had ever voiced such an opinion before. It shows that, in 1902, Einstein already distrusted the validity of classical mechanics.

2.2 1903: A theory of the foundations of thermodynamics

To the casual reader, Einstein's next paper may at first sight look like a rehash of the previous one: It goes over the same calculations at great length, with only a few changes and a host of minor corrections. The changes, however, provide clues about how his ideas were developing. Einstein's aim is now to see in what sense the "kinetic" part of the kinetic theory of heat is really essential to the results obtained before. This aim, of course, is linked to his earlier remark that the entropy expression (17) does not require that the Hamiltonian is a sum of kinetic and potential energy, and to his desire to go beyond classical mechanics. Two other main issues not discussed in his earlier paper are the explicit interpretation of probability as a time average and an extension of the discussion of the second law to its 'second part', i.e., the non-decrease of entropy for all adiabatic processes that begin and end in an equilibrium state. Also, the paper provides Einstein's first steps in forging a link between entropy and probability.

In order to go beyond mechanics, Einstein replaces the coordinates and momenta of his earlier paper with abstract "state variables" $p_1 \dots p_n$, and assumes they obey some general, not necessarily Hamiltonian, dynamical equations:

$$\frac{dp_i}{dt} = \phi_i(p_1, \dots, p_n), \quad (i = 1, \dots, n). \quad (18)$$

The ergodic hypothesis is introduced as the condition that there is only one independent integral of these equations, the "energy function" $E(p_1, \dots, p_n)$.

He introduces the empirical assumption that every isolated physical system, with an energy between E^* and $E^* + \delta E^*$, eventually attains a stationary state. (This has been called the "minus first law" of thermodynamics by Brown and Uffink (2001).) In that situation, the values of all observables¹⁶ can be equated with their average over time. The probability of a region g of the thickened energy surface in phase space should therefore be defined as the

¹⁶Pace John Bell. "*Wahrnehmbare GröÙe*" were not invented in Copenhagen.

relative time that the system's state spends in that region during a very long period. In other words, if τ is the total time that the state lies in g during a long period \mathcal{T} , that probability is

$$\lim_{\mathcal{T} \rightarrow \infty} \frac{\tau}{\mathcal{T}}. \quad (19)$$

He then proceeds to consider an ensemble of systems with energy between E^* and $E^* + \delta E^*$, such that the number of systems dN in any subregion g of the thickened energy shell is equal to these relative time averages. In other words,

$$dN = N \lim_{\mathcal{T} \rightarrow \infty} \frac{\tau}{\mathcal{T}}. \quad (20)$$

Since the right hand side does not depend on time, the ensemble must be stationary. But, under the ergodic hypothesis, there is only one stationary state distribution over the energy shell, i.e., the microcanonical one:

$$dN = A \int_g dp_1 \cdots dp_n. \quad (21)$$

This ensemble therefore yields the physically meaningful probabilities for an isolated system in a stationary state with an energy between E^* and $E^* + \delta E^*$.

Actually, Einstein overlooked a crucial issue at this point. The claim that (21) is stationary—i.e., that volume integrals are conserved under the time evolution—is a version of Liouville's theorem. In the Hamiltonian setting of (Einstein 1902), the validity of this claim is a theorem. But for the more general equations of motions (18), an extra condition is needed to ensure stationarity of the microcanonical distribution (21), i.e.,

$$\sum_{i=1}^n \frac{\partial \phi_i}{\partial p_i} = 0. \quad (22)$$

Einstein's correspondence with Besso (see the comments below) shows that he was aware of this oversight even before the paper was published.¹⁷

He then presents a discussion of the same issues as before (prudently omitting the claim

¹⁷Later papers, such as (Einstein 1905c, 1907a) explicitly mention (22) as an additional assumption.

that h is positive). In particular, he re-obtains the canonical expression for entropy,

$$S = \frac{\langle E \rangle}{T} + 2\kappa \log \int e^{-2hE} dp_1 \cdots dp_n + \text{const.}, \quad (23)$$

thereby showing that this result does not depend on a distinction between coordinates and momenta, or between kinetic and potential energy.

There are two points where the argument differs from his earlier paper. First, the relation (16), previously shown to hold only for the ideal gas (when T is the ideal-gas temperature), is now postulated to hold for an arbitrary system. Einstein simply *defines* the absolute temperature T of the environment Σ by this relation. In this way, he was able to circumvent the use of the equipartition theorem with its implicit distinction between kinetic and potential energy terms. Second, Einstein introduces a strong assumption: he argues that in the canonical distribution the energy E will never deviate appreciably from a fixed mean value (Einstein 1903, p. 182). This assumption allows him to drop the distinction between the constant E^* , the function $E(p_1, \dots, p_n)$, and its expected value $\langle E \rangle$. In view of (16), this simplification leads him to write (23) in an alternative form

$$S = 2\kappa(2hE - c), \quad (24)$$

where

$$c = -\log \int e^{-2hE} dp_1 \cdots dp_n. \quad (25)$$

The canonical distribution can then be written as

$$dN = \text{const.} e^{-2hE} dp_1 \cdots dp_n = e^{c-2hE} dp_1 \cdots dp_n. \quad (26)$$

Compared with (24), there thus appears a proportionality between entropy and the logarithm of the probability density of the canonical ensemble.

To obtain the desired extension of the second law, Einstein considers an arbitrary *non-stationary* ensemble of isolated systems with energy between E and $E + \delta E$. Let that ensemble be characterized by:

$$dN = \rho_t(p_1, \dots, p_n) dp_1 \cdots dp_n. \quad (27)$$

He divides the energy shell into regions g_i , ($i = 1, \dots, \ell$) of equal size, i.e., such that

$$\int_{g_1} dp_1 \cdots dp_n = \dots = \int_{g_\ell} dp_1 \cdots dp_n \quad (28)$$

and considers the “probability”¹⁸ of the state distribution by counting the number of ways in which one can distribute N systems over these regions g_i , so as to obtain n_i systems in each region g_i . The answer, of course, is

$$\mathcal{W} = \frac{1}{l^N} \frac{N!}{n_1! \cdots n_\ell!}, \quad (29)$$

where $\sum_{i=1}^{\ell} n_i = N$. For large values of n_1, \dots, n_ℓ this reduces to

$$\log \mathcal{W} = \text{const.} - \sum_{i=1}^{\ell} n_i \log n_i, \quad (30)$$

and if the regions g_i are small enough, one may approximate:

$$\log \mathcal{W} = \text{const.}' - \int \rho_t(p_1, \dots, p_n) \log \rho_t(p_1, \dots, p_n) dp_1 \cdots dp_n. \quad (31)$$

This gives the “probability” \mathcal{W} that the ensemble at time t is described by the state distribution ρ_t .

Now, Einstein assumes (“*wir werden anzunehmen haben*”), that \mathcal{W} never decreases, i.e.:

$$- \int \rho_{t'} \log \rho_{t'} dp_1 \cdots dp_n \geq - \int \rho_t \log \rho_t dp_1 \cdots dp_n \quad \text{for } t' \geq t. \quad (32)$$

He notes that a maximum is attained if and only if the state distribution ρ_t is independent of the variables p_1, \dots, p_n , in which case it is also stationary.

Reading this through modern eyes, one might almost expect him to identify the expression $-\int \rho \log \rho$ as a non-equilibrium version of entropy, to interpret (31) as a form of “Boltz-

¹⁸I put the term in scare quotes to distinguish between the probability of a system being in a certain state (a region g of state space) and the “probability” of an ensemble of systems being governed by a state distribution ρ .

mann's principle", relating this entropy to $\log \mathcal{W}$, and to see (32) as the extension of the second law to irreversible processes, and perhaps to verify that if we take ρ to have the canonical form $\rho \propto e^{-2hE}$, the expression $-\int \rho \log \rho$ coincides with (23). But Einstein does not do any of this. His road to the relation between probability and entropy, and to entropy increase, is quite different.

He continues by inferring from (32) and the normalization condition

$$\int \rho_{t'} dp_1 \cdots dp_n = \int \rho_t dp_1 \cdots dp_n = N \quad (33)$$

the puzzling inequality

$$-\log \rho_{t'} \geq -\log \rho_t. \quad (34)$$

This inference is more than a little bizarre. If $\rho_{t'}$ is less than ρ_t in some region of state space, (33) implies it must be higher in another region, so (34) simply cannot be correct everywhere. Perhaps, the idea is to assume that both initially and finally the ensemble is in a stationary equilibrium state, i.e., that both $\rho_{t'}$ and ρ_t are constants. To escape the implication from (33), that they ought then be equal, one might suppose that initially the systems are constrained to a particular subregion of state space, and that some constraints are lifted (e.g., by removing a partitioning wall in a container), so that at time t' the accessible region in state space is larger than at time t . In that case, (34) holds everywhere where $\rho_t \neq 0$. Of course, the removal of walls or other constraints conflicts with Einstein's own statement that the systems in question are isolated, but I see no other way to understand his inequality (34).

In the next section, Einstein considers a finite number of systems, $\sigma_1, \sigma_2, \dots$, which collectively form an isolated system. The subsystems are only allowed to exchange heat among each other, i.e., to interact adiabatically.¹⁹ Initially, each subsystem σ_ν is in an equilibrium state at an arbitrary temperature. Einstein argues that its state distribution is formally indistinguishable from the state distribution it would have if it were in thermal contact with a heat bath at the same temperature. Thus, σ_ν may be described by a canonical distribution, now written as

$$dw_\nu = e^{c_\nu - 2h_\nu E_\nu} dp_1^\nu \cdots dp_n^\nu. \quad (35)$$

¹⁹During adiabatic interactions, Einstein assumes, the validity of the dynamical equations (18) is suspended.

Assuming the subsystems to be independent, he obtains the expression

$$dw = dw_1 \cdot dw_2 \cdots = e^{\sum_{\nu} c_{\nu} - 2h_{\nu} E_{\nu}} \prod_{\nu} dp_1^{\nu} \cdots dp_n^{\nu}$$

for the total system. Now suppose that the subsystems enter into an adiabatic interaction, remaining isolated from the environment, and that, after a while, they occupy a final equilibrium state. For the probability of that final state one can similarly put²⁰

$$dw' = dw'_1 \cdot dw'_2 \cdots = e^{\sum_{\nu} c'_{\nu} - 2h'_{\nu} E'_{\nu}} \prod_{\nu} dp_1^{\nu} \cdots dp_n^{\nu}.$$

In an ensemble of N such total systems, one can now apply (34), with

$$\rho = N e^{\sum_{\nu} c_{\nu} - 2h_{\nu} E_{\nu}} \quad \rho' = N e^{\sum_{\nu} c'_{\nu} - 2h'_{\nu} E'_{\nu}}$$

or

$$\sum_{\nu} 2h'_{\nu} E'_{\nu} - c'_{\nu} \leq \sum_{\nu} 2h_{\nu} E_{\nu} - c_{\nu}. \quad (36)$$

According to (24), each term in these sums represents, up to a universal constant, the entropy of the corresponding partial system. Hence, after an adiabatic process, the final total entropy will not be less than the initial total entropy:

$$\sum_{\nu} S'_{\nu} \geq \sum_{\nu} S_{\nu}. \quad (37)$$

He ends the paper with an argument that the result (37) implies the impossibility of a perpetuum mobile of the second kind. As Gearhart (1990) has noted, the details of his argument show Einstein's familiarity with Planck's (1897) *Lectures on Thermodynamics*.

Comments: Einstein's focus in the (1903) paper is on the generalization of the statistical formalism to arbitrary physical systems. Of course, he was not the first to discuss the formalism in a setting that abstracts from kinetic concepts. Boltzmann (1871b) likewise avoided the distinction between coordinates and momenta (as he does in *Gastheorie* sec. 29). Gibbs

²⁰Einstein ignores the possibility that systems might become correlated during the interaction.

(1902) did not use the distinction between kinetic and potential parts of the Hamiltonian either, whenever he had no need to. But these authors had no other motivation than the simple fact that in a mathematical argument one may ignore distinctions that are irrelevant to the conclusion. In contrast, we have seen that Einstein (1902) considered this issue as a physically important problem. But the 1903 paper still offers no clue why it should be important.

The calculation leading to (32) is reminiscent of Boltzmann's (1877) combinatorial argument to determine the probability of a state distribution ('*Zustandsverteilung*') or what we now call a macrostate. (This argument was also discussed in the *Gastheorie*, Vol. I, sec. 5.) But there is a conceptual difference. In that argument, Boltzmann did not consider an ensemble but an ideal gas, and divided its molecular state space into equally sized cells. Then he calculated the number of ways in which the molecules could be distributed over these cells in order to obtain the same *Zustandsverteilung* or macrostate. This calculation led him to an expression formally similar to (31). Einstein, however, does not consider molecules in a gas, but N systems from an ensemble. As a result, the analysis is transplanted one level upwards in abstraction: Einstein's expression $\int \rho \log \rho$ is not the Boltzmann H -function $\int f(\vec{x}, \vec{v}) \log f(\vec{x}, \vec{v}) d\vec{x} d\vec{v}$, but what we today call (minus) the Gibbs entropy. Moreover, it becomes highly problematic to apply a time-average interpretation to the "probability" of such a state distribution.

The fact that Einstein does *not* draw a link between $-\int \rho \log \rho$ and entropy might be due to his relying on the *Gastheorie*, sec. 5, where Boltzmann presents his derivation as a link between the 'probability Z ' of a state distribution, and 'the quantity H '. He does not identify this abstract quantity H as a measure of entropy in that section. This physical meaning of H is only established—and even then only for monatomic ideal gases—in sec. 8 of the book. The *Gastheorie* certainly does not contain an explicit and general statement that Einstein could have recognized as a "Boltzmann principle". Instead, Einstein obtained the relation between entropy and probability from (24), which depends on the strong assumption that energy fluctuations in the canonical distribution are negligible.

At first, Einstein thought he really had obtained results of high generality. He wrote to Besso that

[t]he concepts of temperature and entropy follow from the assumption of the energy

principle and the atomistic theory, and so does also the second law in its most general form, namely the impossibility of a *perpetuum mobile* of the second kind (Einstein to Besso, 22 January 1903, CPAE , Vol. 5, Doc. 5).

Two months later, he boasted of even greater generality: “[the paper] assumes only the generality of the foundations of atomic physics, no further physical hypothesis” (Einstein to Ehrat, last week of March 1903, CPAE , Vol. 5, Doc. 11).

However, he soon realized that he had not achieved quite as much as he initially thought. Discussions with Sauter and Besso convinced him that he had silently presupposed the ‘incompressibility condition’ (22). On 17 March 1903, he wrote to Besso:

If you look at my paper more closely, you will find that the assumption of the energy principle & of the fundamental atomistic idea alone does not suffice for an explanation of the second law; instead, coordinates p must exist for the representation of things, such that for every conceivable total system $\sum \partial\phi_\nu/\partial p_\nu = 0$ [...] If that is true, then the entire generalization attained in my last paper consists in the elimination of the concept of force as well as in the fact that E can possess an arbitrary form (yet not completely)? (CPAE , Vol. 5, Doc. 7).

In fact, the oversight has disastrous consequences for his attempt to derive the second law, as we shall see below. But first note that there is one more assumption involved that Einstein does not mention in these last two letters: a state distribution is never followed by a less “probable” one. This claim is, again, probably taken from the *Gastheorie*, Vol. I, sec. 8, where Boltzmann presents this as an almost obvious, general claim about all systems in nature.²¹ But even from a contemporary perspective the assumption could hardly be regarded as a satisfactory one. Even if Einstein had known (Boltzmann 1877), he would not have found anything there beyond the mere assertion that systems tend to evolve from less to more probable states, not a proof. Boltzmann’s discussions with Culverwell, Burbury and Zermelo in 1896 and 1897, and his derivation of the H -theorem from a condition of molar and molecular disorder in the earlier pages of the *Gastheorie* went considerably deeper. Yet they only applied to dilute gases, a case that was clearly too special for Einstein’s interests. Still, the assumption that “probability” never decreases surely does not follow from

²¹But note that, in that context, the “state distribution” referred to the macrostate of a single system, not to the probability density ρ of an ensemble.

mechanics (whether Hamiltonian or of the more general form (18)) and probability calculus alone. The argument invites the obvious objection that it assumes what it has to prove. This objection was indeed raised by Paul Hertz (1910). In his reply Einstein (1911) writes that even at the time of publication he was no longer convinced by his 1903 argument, and that he had therefore replaced it by another argument in (Einstein 1904). Einstein’s reply is curious because the 1904 argument similarly derives the increase of entropy from a postulate that probability increases, and is thus equally open to the objection that it begs the question. Einstein must have confused Hertz’s critique with another problem, most likely his oversight of the incompressibility condition (22).

Actually, the flaw in Einstein’s attempt to derive the second law is much deeper than the mere objection that his assumption begs the question. The condition (22) implies that the expression $-\int \rho \log \rho$ will be conserved over time, and there is thus never inequality in the relation (32). So, the assumption that \mathcal{W} will increase as we follow the ensemble of isolated systems over time is simply inconsistent within his 1903 approach.

Then there is still the ergodic hypothesis. As we have seen, Einstein’s descriptions of what was assumed in the paper indicate that he did not think of this as a restriction of any importance. However, it probably came up in his discussions. In the letter to Besso cited above he wrote “The condition that E be the *only* integral of the equations of the given form is no limitation, since I free myself of it when I consider “adiabatically influenced systems” (CPAE , Vol. 5, Doc. 7). Even on a charitable reading, this statement amounts to a serious underestimation of how deeply his approach relied on the ergodic hypothesis. Most of the results prior to a discussion of adiabatic processes—starting from the assumed equality of microcanonical averages and time averages—depend on it.

The role of the ergodic hypothesis in Einstein’s work was criticized by Ornstein (1910), on the grounds that no system can literally pass through all states on the energy hypersurface in a finite time.²² Its dubious status was brought out prominently by the Ehrenfests (1912).²³

²²Ornstein also discussed counterexamples to the ergodic hypothesis: if the Hamiltonian has a symmetry (e.g. invariance under spatial reflections) there generally exist trajectories that are not invariant under the same operation. Such a trajectory must then be disjoint from its mirror image, and points on one of them will never be visited by a system following the other.

²³Klein (1970, p. 175) records that when Paul Ehrenfest met Einstein in Prague early in 1912, they immediately fell into a discussion on the ergodic hypothesis. Whether Einstein learned from his visitor or from other

The following year, Plancherel (1913) and Rozenthal (1913) proved that the hypothesis can be true only if the energy hypersurface is at most one-dimensional.

2.3 1904: *On the general molecular theory of heat*

Einstein's next paper is, by comparison to the preceding one, much more rewarding, even though it is not as clear and coherent as the 1902 paper. Again, Einstein emphasizes generality, abstracting from the "kinetic" element of the theory. In fact he proposes a new, non-kinetic name for the theory: he aims to develop a general "molecular theory of heat", which, however, relies essentially on the assumptions of his 1903 paper. Actually, the reference to molecules here is formal too. The only sense in which they play a part in the theory is that the number of degrees of freedom of a system is assumed to be finite, not that the system should be composed of corpuscles.

The fact that Einstein presupposed the assumptions and results of his 1903 paper has an unfortunate consequence. As we have seen, in that paper he assumed that energy fluctuations in the canonical ensemble vanish, in which case there is no difference between E and $\langle E \rangle$. Since the most salient point of the present paper, however, is an investigation into the size of energy fluctuations $\langle (E - \langle E \rangle)^2 \rangle$, the earlier assumption is obviously inappropriate. Consequently, it is not always easy to follow when E stands for energy taken as a stochastic variable and when it stands for its expectation value.

Einstein's introductory remarks offer a glimpse into what kind of generality he is after, and why he takes a non-kinetic theory of heat to be desirable. He emphasizes that the expression for entropy he is about to present is completely analogous to an expression found by Boltzmann for ideal gases and assumed by Planck in his theory of radiation. He is implicitly referring to (Planck 1901), where an hypothesis of the form $S = k \log W + \text{const.}$ is employed to obtain his famous expression for the entropy of black-body radiation.

sources to distrust the ergodic hypothesis, it is noteworthy that, while Einstein's lecture notes on kinetic theory from 1910 still relied on the ergodic hypothesis (CPAE, Vol. 3, p.196, 204), his lecture notes on statistical mechanics (Einstein 1913) avoid it. Instead, he now assumed what the Ehrenfests called the quasi-ergodic hypothesis, and falls back on an even more dubious assumption of considering open curves in phase space to be approximately closed after a sufficiently long time, an assumption reminiscent of Boltzmann's early paper of 1866.

Einstein makes no explicit reference to dynamical equations, but starts immediately from the 1903 relation

$$h = \frac{\omega'(E)}{2\omega(E)} = \frac{1}{4\kappa T}, \quad (38)$$

with a “slight change in definition” of the structure function ω . It is now defined as:²⁴

$$\omega(E)\delta E = \int_E^{E+\delta E} dp \cdots dp_n. \quad (39)$$

The slight change here is that, on the left-hand side, an extra factor δE is inserted. As Kuhn (1978, p. 177) has argued, it shows that $\omega(E)$ becomes independent of δE . A much more drastic change is that ω is now interpreted as the structure function of the system σ , whereas before it was the structure function of the *environment* (i.e., the integral is taken over the variables of the system Σ). Moreover, while the function ω was previously evaluated at the total energy E_{tot} , which, in first approximation, is equal to the energy of Σ , it is now taken as the energy of σ . It is unclear to me how Einstein could present such a drastic reinterpretation without any comment. Neither have I seen any discussion in secondary literature.

He claims that (38) leads immediately to an expression for entropy:

$$S = 2\kappa \log \omega(E), \quad (40)$$

where the additive constant is suppressed. Perhaps, this “immediate” derivation went as follows: $d\omega(E) = \omega'(E)dE \stackrel{(38)}{=} \omega(E)dE/(2\kappa T)$. Putting $dE/T = dS$, one obtains the desired result by integration. This calculation is easy to do once we interpret E as the energy of system σ , and think of h or T as functions of E —contrary to how they were thought of before—and assume that this system can only exchange energy in the form of heat. However, Einstein claims that the result is *not* restricted to energy exchange in the form of heat, but holds for arbitrary changes. He says this can be proved from the equation (23) of his earlier paper, but that he does not want to go into details.

Again, this claim is puzzling, since expression (40), known today as the microcanonical entropy, is generally different from the canonical entropy (23). Presumably, Einstein’s

²⁴The integral should obviously be understood as extending over the shell in state space where the energy $E(p_1, \dots, p_n)$ lies between the indicated limits.

“proof” consists of the observation that (23) and (40) coincide under the assumption that $e^{2hE}\omega(E)$ is an extremely sharply peaked function of E .²⁵

He then considers a system brought in thermal contact with an environment at constant temperature T_0 . Experience tells us that the system will then also attain the temperature T_0 , and remain at this temperature for all times. But according to the molecular theory of heat, he says, this statement is only approximately true. As mentioned above, this interest in fluctuations is in marked contrast to his earlier paper. Moreover, this passage refers to temperature fluctuations, whereas he later discusses only energy fluctuations. Perhaps he thought of temperature as a function of energy, or perhaps he blurred the distinction between expected and actual values.²⁶

The canonical distribution is now presented in the form of a probability distribution over the various values of energy

$$d\mathcal{W} = Ce^{-E/2\kappa T_0}\omega(E)dE. \quad (41)$$

in which the microscopic state variables no longer appear. Given a relative time interpretation of probability, this result means that a system in contact with a heat bath must experience fluctuations in its energy. Using (40), one can rewrite (41) in the form²⁷

$$d\mathcal{W} = Ce^{\frac{1}{2\kappa}(S-\frac{E}{T})}dE. \quad (42)$$

He uses this expression for a new derivation of the second law. Consider a number (ℓ) of systems (heat reservoirs) at a common temperature T_0 . The probability that the first has

²⁵This assumption is explicitly made in Einstein’s second light-quantum paper (Einstein 1906c, p. 201), motivated by the further assumption that σ consists of a very large number of molecules. In fact, Einstein claims on that occasion that the relation (23) would otherwise not be meaningful. However, in (Einstein 1902, p. 428) and (Einstein 1903, p. 177) the system σ was taken to consist of just a single molecule.

²⁶The question whether it is meaningful at all to speak of temperature fluctuations in statistical thermodynamics is a topic still open to a wide range of viewpoints. See (Uffink & van Lith 1999) and references therein.

²⁷Actually, he presents a discrete version, in which $\mathcal{W} = Ce^{(S-E/T)/2\kappa}$ is the probability of the energy lying between “ E and $E + 1$ ”. Perhaps, Einstein felt that a postulate of increasing probability is less awkward when formulated for non-infinitesimal probabilities than the differential formulation (41) and (45) used in the text. This notation is adapted from (Einstein 1906a, 1907a)

energy E_1 , the second an energy E_2 , etc, is

$$d\mathcal{W}_{\text{tot}} = \prod_{i=1}^l d\mathcal{W}_i = C_1 \cdots C_\ell e^{\frac{1}{2\kappa} \left(\sum_i S_i - \frac{\sum_i E_i}{T} \right)} \prod dE_i. \quad (43)$$

Suppose the heat reservoirs take part in a process with some machine, where the machine executes a cycle, under the assumption that neither the heat reservoirs nor the machine exchange heat with the environment. At the end of this process the heat reservoirs settle into new stationary states. The total probability of that later state is now

$$d\mathcal{W}'_{\text{tot}} = \prod_{i=1}^l d\mathcal{W}_i = C_1 \cdots C_\ell e^{\frac{1}{2\kappa} \left(\sum_i S'_i - \frac{\sum_i E'_i}{T} \right)} \prod dE_i. \quad (44)$$

Assuming that probability never decreases,

$$d\mathcal{W}'_{\text{tot}} \geq d\mathcal{W}_{\text{tot}} \quad \text{for } t' \geq t, \quad (45)$$

and that energy is conserved,

$$\sum_i E_i = \sum_i E'_i, \quad (46)$$

one obtains

$$\sum_i S'_i \geq \sum_i S_i, \quad (47)$$

i.e., the non-decrease of total entropy in adiabatic processes.

This derivation is conceptually simpler than the one presented in (1903). In the latter, \mathcal{W} represented the probability of a state distribution, i.e., a “probability” of the probability density ρ . But now, $d\mathcal{W}_i$ is just the probability that the subsystem i has an energy between E_i and $E_i + dE_i$. This new version of the second law is also much weaker since Einstein assumes all systems to have a fixed common temperature. However, the assumption (45) is no less dubious than the previous version (34). It is obvious from the normalization requirement $\int d\mathcal{W}' = \int d\mathcal{W} = 1$ that (45) cannot be valid for all values of the subsystem energies.

Einstein then proceeds to discuss the physical meaning of the constant κ . He does so by considering the following issues: (i) Consider a mechanical system consisting of point

particles, with Hamiltonian

$$\Phi(x_1, \dots, z_n) + \sum_i^n \frac{m_i}{2} \vec{v}_i^2. \quad (48)$$

The equipartition theorem (15) gives $\langle \frac{m_i \vec{v}^2}{2} \rangle = 3\kappa T_0$ (recall that $\kappa = k/2$). Hence, for such a system, the constant κ provides the ratio of the mean kinetic energy per particle to the absolute temperature.

(ii) Comparing the ideal gas law

$$pV = RT, \quad (49)$$

to the relation $pV = \frac{2}{3}\langle L \rangle$ of the kinetic theory of the ideal gas, we get

$$N_A 2\kappa = R. \quad (50)$$

Thus κ is closely related to Avogadro's number N_A , the number of real molecules in a gram-molecule. Putting $R = 8.31 \cdot 10^7$ (in gram/centimeter units) and $N_A = 6.4 \cdot 10^{23}$, Einstein obtains $\kappa = 6.5 \cdot 10^{-17}$.

(iii) For a general molecular system, Einstein draws a connection between κ and energy fluctuations. Taking $\langle \epsilon^2 \rangle = \langle (E - \langle E \rangle)^2 \rangle$ as a measure for energy fluctuations, Einstein obtains from (41) the famous result

$$\langle \epsilon^2 \rangle = 2\kappa T_0^2 \frac{d\langle E \rangle}{dT}, \quad (51)$$

also obtained by Gibbs (1902). Thus, Einstein notes, κ influences the thermal stability of the system. He notes that equation (51) is particularly interesting because it contains nothing that reminds us of the assumptions of the underlying theory. I take it that he means that the relation does not depend on the assumption of a specific system like the ideal gas, or the more general Hamiltonian for point particles. It should therefore be valid for arbitrary physical systems, including systems for which no distinction can be made between kinetic and potential energy.

He points out that the value of κ could thus be determined exactly if it were possible to

observe the energy fluctuations. Unfortunately, he says, that does not seem to be the case in the present state of knowledge. There is, however, one kind of system for which one may expect to observe fluctuations: black body radiation.

He argues that in a cavity of the same size as the predominant wave-length λ_{\max} of black-body radiation, energy fluctuations should be of the same order of magnitude as the mean energy:

$$\langle \epsilon^2 \rangle = \langle E \rangle^2. \quad (52)$$

Using the Stefan-Boltzmann law $\langle E \rangle = cVT^4$, with $c = 7.06 \cdot 10^{-16}$, and the value for κ above, Einstein obtains

$$\lambda_{\max} = V^{1/3} = \frac{0.42}{T}, \quad (53)$$

which is in qualitative agreement with the experimental result $\lambda_{\max} = 0.293/T$.

Comments: We have seen that Einstein claimed that the microcanonical expression for entropy (40) was “completely analogous” to a relation obtained by Boltzmann and assumed by Planck. That relation, surely, is the “Boltzmann principle” $S = k \log \mathcal{W} + \text{const}$, that Planck had assumed in his radiation theory. His own relation was (40). Was Einstein correct? Although there is a typographical resemblance, Boltzmann’s view of the relation between entropy and probability was quite different. For Boltzmann, entropy was proportional to the H function associated with a macrostate, and, for an ideal gas, the latter was shown to be proportional to the surface area of a subset on the energy surface corresponding to that macrostate. For an equilibrium (or “most probable”) macrostate of a system with an immense number of degrees of freedom, that subset happens to occupy an overwhelmingly large part of the energy surface. So, in that case, the microcanonical entropy $2\kappa \log \omega(E)$ and the Boltzmann entropy $k \log W$ are approximately the same. But Boltzmann’s relation between entropy and probability is intended to apply also to non-equilibrium macrostates (cf. *Gastheorie* Vol. I, sec. 8), in which case H has no relation to the microcanonical entropy.

The 1904 presentation of the second law still assumes (45) that probability never decreases—and hence as I have argued in section 2.2, invites the objection that it begs the question. There are however also differences between the 1904 and the 1903 approach. In 1903, Einstein conceived of the “probability” of a state distribution, i.e., of a distribution function ρ that itself assigns probabilities to various regions in state space. In 1904, $d\mathcal{W}$ refers to the probability

density of a value of energy. In other words, just as the 1903 argument was “one level up” in abstraction, as compared to Boltzmann’s *Gastheorie*, the 1904 version takes it one level down again: from an ensemble to an ℓ -body system. Also, the argument proceeds by comparing the initial and final equilibrium states in an adiabatic process, but avoids considering the entropy or probability of the non-equilibrium stages in between.

Why would he have done that? My suggestion is that he might have realized that Liouville’s theorem blocks his 1903 approach to the second law. This obstacle is insurmountable for the evolution of an ensemble of isolated systems, because the members of an ensemble do not interact. But the subsystems of his ℓ -body system are allowed to interact. In fact, they interact adiabatically, which for Einstein means that the equations of motion are not applicable (cf. footnote 19). Thus Liouville’s theorem, even when it applies, no longer obstructs the 1904 approach.

We also see how Einstein develops an interest in determining the actual value of κ or N_A . He realized that if there were a method of observing these fluctuations in some system, it would provide ways of determining κ , and thus of seeing whether his general approach—which depends on a minimum of constitutive assumptions—is applicable to that kind of system. But clearly, the thought that Brownian motion provides such an example had not occurred to him yet.

Einstein had no qualms about treating light as a molecular system. There is a remark that shows he realized this was odd:

Of course, one can object that we are not permitted to assert that a *space* filled with radiation should be viewed as a *system* of the kind we have assumed, not even if the applicability of the general molecular theory is conceded. Perhaps one would have to assume, for example, that the boundaries of the space vary with its electromagnetic states. However, these circumstances need not be considered, as we are dealing with orders of magnitude only. (Einstein 1904, p. 361).

Note how Einstein does not even raise the point that one might not accept the applicability of the general molecular theory of heat to radiation at all. That point, i.e., the fundamental contrast between Maxwell’s theory, a field theory with an infinite number of degrees of freedom, and the molecular theory, which demands that the number of degrees of freedom is finite, is first mentioned in his paper on the light-quantum (Einstein 1905a).

But Einstein had already taken the revolutionary step of regarding radiation as just another type of molecular system, to be treated on a par with gases, liquids, etc. The success of his comparison with experimental data may have contributed to the confidence needed to publish the heretical light-quantum hypothesis the following year.

2.4 The statistical program

We have seen that throughout his statistical trilogy Einstein's aim was to achieve generality in his approach to statistical physics, beyond the case of mere mechanical systems, and in particular to abstract from the distinction between potential and kinetic energy, or coordinates and canonical momenta. One can only conjecture why he thought that was an important endeavor. It has been suggested that he might have been influenced by H. Hertz's mechanics (1894). This book, which Einstein is known to have read, proposes an approach to mechanics in which the notion of force, and the associated concept of potential energy is avoided and replaced by constraints exerted by (possibly hidden) bodies.

However, there also seem to be more mundane reasons for Einstein's striving for generality. In his correspondence, Einstein repeatedly reported his interest in and studies of concrete problems discussed in the physics literature. Apart from gas theory (Boltzmann and O.E. Meyer) he studied the theory of metals²⁸ (Drude, Reinganum). In that theory one assumes the existence of freely moving electrons in the metal (i.e., the metal is represented as an 'electron gas') and aims to derive relations between electric and thermal conductivity, and other thermal, optical and magnetic effects. He also studied various issues in physical chemistry, in particular the dilute solutions of salts and undissociated substances, and the specific heats of solids (the Dulong-Petit law and deviations from it). Then, of course, he studied Planck's papers on black-body radiation since 1901.

It thus seems plausible that he aimed for a general framework applicable to the variety of thermal phenomena in which he was interested, regardless of whether they concerned gases, metals, dilute solutions, solids or radiation.²⁹ And although a treatment of a dilute solution

²⁸Einstein even worked out a theory of his own on the topic, although he soon became dissatisfied with it (cf. Renn 1998).

²⁹Another Hamiltonian system in which a distinction between kinetic and potential energy makes no sense is a magnet, where one uses $H = \sum \vec{\mu}_i \cdot \vec{B}$ for a system of non-interacting dipole moments $\vec{\mu}_i$. I don't know

might reasonably be contemplated with a Hamiltonian of the form (48), other aspects have to be taken into account for charged particles (electrons or ions). In a magnetic field, forces become velocity-dependent and are not derivable from a scalar potential. And if Einstein intended to apply his theory to black-body radiation, he clearly had further reasons to avoid kinetic concepts, even when one thinks of radiation in the form of light quanta. As Stachel (2000) has emphasized, it was not until 1916 that he attributed momentum to light quanta.

What is more, in his *Autobiographical Notes*, Einstein records that soon after the appearance of Planck's work, it became clear to him that neither classical mechanics nor Maxwell's theory of electromagnetism could "claim exact validity" (Einstein 1949, p. 52-53). Obviously one must be careful in assessing reminiscences decades after the fact. Nevertheless, the passage in (Einstein 1902), where he stressed the importance of going beyond the mechanical equations, and the equally striking remark in (Einstein 1906b, p. 375) that there is an "elementary imperfection in our physical concepts," add contemporary support to the idea that Einstein did indeed question the empirical adequacy of classical mechanics early on. If so, he would have had an even stronger motivation to avoid relying on its concepts.

In any case, by the end of 1904, he had a theoretical program cut out for him, and the tools to carry it out: a general molecular theory of heat that, at least in his own mind, used only a bare minimum of assumptions about the microscopic constitution and dynamics of thermal systems, but relied on the canonical ensemble for describing states of thermal equilibrium, established the general validity of the equipartition theorem, the canonical or micro-canonical formula for entropy and the relation between entropy and probability ("Boltzmann principle"). He had recognized the importance of the phenomenon of energy fluctuations at a characteristic scale, the interpretation of the universal constant κ as a measure of thermal stability, and the insight that if fluctuations were observable, they would yield a method for determining κ or, equivalently, Avogadro's number N_A .

His next paper (Einstein 1905a) extended the application of this program to radiation, and introduced the light-quantum hypothesis. I will not discuss that paper (see Norton 2006), except to note that it considers ideal gases, dilute solutions, and black-body radiation as

whether Einstein could have been thinking of applying his molecular theory of heat to magnetism in this period. It is discussed in his lectures of 1913.

analogous systems. In particular, Einstein proposes the “Boltzmann principle” in the form

$$S - S_0 = \frac{R}{N_A} \log \mathcal{W}, \quad (54)$$

and applies it to a system consisting of n mobile points in a volume V_0 . He argues that we do not need to know anything about the laws of motion of these points. Indeed other particles may also be present in the same space, with which they interact. The only assumptions are: (i) in a stationary state, the points have no preference for any part of the volume V_0 , or for moving in any particular direction. That is, their distribution is homogeneous and isotropic. (ii) We can ignore interaction between them. The probability of finding all n points in any subvolume V of V_0 is then equated with

$$\mathcal{W} = \left(\frac{V}{V_0} \right)^n. \quad (55)$$

He shows that by application of the thermodynamic relations $F \equiv E - TS$ and $p = \partial F / \partial V$, (54) implies

$$pV = \frac{R}{N_A} nT, \quad (56)$$

which is the ideal gas law in the case of gases, or the van ’t Hoff law for osmotic pressure in the case of dilute solutions. He emphasizes that the osmotic pressure is thus obtained “without making any hypothesis about the laws according to which the molecules move” (Einstein 1905a, p. 142).

The execution of this program did not stop in 1905. (Einstein 1907a) on specific heat, (Einstein 1907b, 1908) on potential fluctuations in metals, (Einstein 1909a) on radiation fluctuations, and (Einstein 1910) on critical opalescence all follow the general program described above. Other aspects of the program were soon abandoned. Einstein never returned to the attempt to obtain the second law from a postulate of increasing probability, apart from the casual dismissal of his 1903 approach in (Einstein 1911). Similarly, the ergodic hypothesis is not mentioned again after his discussions with Ehrenfest.

In hindsight, it is remarkable how strongly Einstein trusted this statistical framework. In the discussions at the 1911 Solvay meeting, Einstein insisted that, in his view, one should absolutely hold on to the Boltzmann principle. (CPAE , Vol. 3, Doc. 27, p. 353). For someone

willing to sacrifice the ether, the wave theory of light, the Newtonian doctrine of space and time, etc, his confidence in this principle is quite remarkable, in particular when one realizes how little empirical support Boltzmann's principle had and how its precise formulation and validity have always remained controversial in statistical physics (cf. Khinchin 1949 p. 142; or Adib (2004) for a recent discussion).

3 Einstein 1905 on molecules

Einstein's two 1905 papers concerned with molecules have often been seen as aiming to establish the real existence of molecules, against a widespread skepticism about the molecular/atomic hypothesis. The source for this viewpoint is undoubtedly Einstein's own recollection in his *Autobiographical Notes*:

My major aim in this was to find facts which would guarantee as much as possible the existence of atoms of a definite size . . . the agreement between these considerations with experience . . . convinced the skeptics who were quite numerous at that time (Ostwald, Mach) (Einstein 1949, p. 47).

Yet I think it is questionable whether he had this intention at the time. For one thing, the popular books and highschool textbooks Einstein read as an adolescent were already written from a molecular standpoint (Gregory 1998). And the very fact that molecules showed up in the high school curriculum indicates that doubt about their existence was hardly ubiquitous in the 1890s. Similarly, the lectures by Weber he followed as a student in Zürich show no sign of skepticism in their treatment of molecules.³⁰

Furthermore, the leading figures in physical and chemical research in which Einstein became interested in the early 1900s (Planck,³¹ Boltzmann, Nernst, van 't Hoff, Lorentz, Drude, etc.) had few if any reservations about the existence of atoms or molecules. It seems more likely, therefore, that when he started to publish his own research, Einstein did not see the existence of molecules as controversial but as established fact.

³⁰Judged from Einstein's own lecture notes (CPAE , Vol. 1, Doc. 37, p. 92–100).

³¹Planck did have reservations about molecular-kinetic theory. But that was principally due to his belief in the absolute validity of the second law for irreversible processes, and his doubt that one could derive this law from mechanics, rather than doubt about the reality of molecules.

It is true that the energeticists Ostwald and Helm were skeptical about atoms, but their followers were few (Deltete 1999), and they had already suffered a famous defeat at the Lübeck *Naturforscherversammlung* in 1895.³² Mach's skepticism was mainly epistemological in nature. Although his philosophical views were influential, especially on Einstein's own thought, they played no direct role in the front-line research on the physical-chemical topics Einstein was pursuing.

However this may be, the two 1905 papers do not state as their aim to demonstrate the real existence of molecules, or to convince skeptics—unlike, for example, the books by Svedberg (1912) or Perrin (1913) who performed or repeated the experiments Einstein considered in these papers. In fact, his dissertation mentions straightaway that a determination of the true size of atoms had already been provided by kinetic theory of gases.

Instead, an explicitly stated common aim of the two papers is to provide experimentally feasible methods of determining Avogadro's number N_A . Indeed, both papers conclude with an expression for N_A : a numerical value in the dissertation; and a theoretical one—accompanied by a dramatic call for an experimental test—in the Brownian motion paper. Note also that Einstein often referred to Avogadro's number by the phrase “the true size of the atom” (see, e.g., Einstein 1905c, p. 549) or “the size of molecules” (see below). This habit may have contributed to the view that his aim was to determine the existence of atoms. At least, it seems to me that, in view of this habit, Einstein's (1949) phrase “the real existence of atoms of a definite size” might also be read as “the real existence of a definite value of Avogadro's number”.

In any case, in a letter to Perrin of November 11, 1909, Einstein explained his aims as follows:

A precise determination of molecular sizes seems to me of enormous importance for the reason that Planck's radiation formula can be more rigorously tested by means of such a determination than by radiation measurements. For Planck's theory of radiation also leads to a determination of the absolute size of the atom, one that claims *exact* validity

³²It is not certain whether Einstein was aware of this dispute in 1905. Gearhart (1990) points out that some phrases used in Einstein's letters in 1901 suggest his familiarity with Ostwald's *Chemische Energie* from 1893, which is written from an energeticist standpoint. Gearhart speculates that Einstein might have supported energeticism at least in part and for a while. Still, Gearhart also concludes that Einstein never seems to have seriously questioned the molecular hypothesis.

(CPAE , Vol. 5, Doc. 186).

Clearly, as expressed here, Einstein's overriding objective was not to establish the existence of atoms or molecules, but to obtain checks on Planck's radiation theory by independent determinations of Avogadro's number.

3.1 The dissertation

In his dissertation, entitled "A new determination of molecular dimensions," Einstein considers a dilute undissociated solution of some soluble substance (sugar) in a solvent (water). The molecules are pictured as hard spheres of diameter P , with number density n . The solvent is represented as a continuous, incompressible viscous medium subject to the laws of hydrodynamics, in particular the Navier-Stokes equation.

Einstein then presents two lines of thought. The first is to calculate how the viscosity of the solvent is affected by the presence of the molecules. A tedious calculation shows how the motion of the fluid is obstructed by having to flow around the spheres. Here Einstein relies on methods presented by Kirchhoff (1897, lecture 26).

His result is

$$nP^3 = \frac{3}{4\pi} \left(\frac{\eta^*}{\eta} - 1 \right), \quad (57)$$

where η^* and η denote the viscosity of the solution and the pure solvent respectively. Substituting

$$\frac{n}{N_A} = \frac{\rho}{m}, \quad (58)$$

where m is the molecular weight of the dissolved substance, and ρ the mass of the dissolved substance per unit volume, (57) provides an expression for $N_A P^3$ in terms of experimentally observable quantities.

The second theme is a discussion of diffusion. If a constant force K is exerted on a sphere in a viscous medium, it will reach a stationary velocity v , given by Stokes's law:

$$v = \frac{K}{6\pi\eta P}. \quad (59)$$

Again, Einstein obtained the formula from (Kirchhoff 1897).

Assume now that the concentration of molecules ρ is non-uniform. For simplicity, say that ρ is a function that varies only in the x -direction. Einstein argues that the molecules will be subject to an osmotic force K in the opposite direction, due to the concentration gradient $\partial\rho/\partial x$. Through Van 't Hoff's law for ideal solutions, this force can be expressed as

$$K = -\frac{RT}{N_A\rho} \frac{\partial\rho}{\partial x}. \quad (60)$$

Comparing (59,60) to the diffusion equation (Fick's first law),

$$v\rho = -D \frac{\partial\rho}{\partial x}. \quad (61)$$

one can write the diffusion coefficient D as:

$$D = \frac{RT}{6\pi\eta} \frac{1}{N_A P}, \quad (62)$$

yielding a second equation for the unknowns P and N_A in terms of measurable quantities. Solving the equations (57) and (62) and using experimental values for D and η for sugar solutions, he obtained ³³

$$P = 9.9 \cdot 10^{-8} \text{cm}, \quad N_A = 2.1 \cdot 10^{23}. \quad (63)$$

Comments. To me, the most striking point about the dissertation is that it involves no statistical physics at all. The methods used are those of pure hydrodynamics. There is no mention of probability, ensembles, entropy or fluctuations, in sharp contrast to his earlier papers and his next one, dated eleven days later.

Why should Einstein avoid the program he had cut out for himself? The dissertation announces his choice of method and assumptions as follows:

The earliest determinations of real sizes of molecules were made possible by the kinetic

³³Einstein made a calculational error, which was later corrected. A second improvement came from more accurate experimental data, which Einstein reported in an appendix to the published version of the dissertation (Einstein 1906a), i.e., $N_A = 4.15 \cdot 10^{23}$. After the calculational error is corrected one obtains $N_A = 6.56 \cdot 10^{23}$, a result extraordinarily close to the actual value.

theory of gases, whereas the physical phenomena observed in liquids have thus far not served for the determination of molecular sizes. This is no doubt due to the insuperable difficulties confronting the development of a detailed molecular-kinetic theory of liquids. It will be shown in this paper that the size of molecules of substances dissolved in an undissociated dilute solution can be obtained from the internal friction of the solution and the pure solvent and from the diffusion of the dissolved substance within the solvent if the volume of the molecule of the dissolved substance is large compared with the volume of the molecule of the solvent. This is because, with respect to its mobility in the solvent and its effect on the internal friction of the latter, such a molecule will behave approximately as a solid body suspended in a solvent, and it will be permissible to apply to the motion of the solvent in the immediate vicinity of a molecule the hydrodynamic equations in which the liquid is considered to be homogeneous and hence its molecular structure is not taken into consideration. For the shape of the solid body that shall represent the dissolved molecule, we will choose the spherical shape (Einstein 1905b, p. 5)

Insuperable difficulties in the development of the molecular-kinetic theory of liquids? ³⁴ This seems quite a different Einstein from the one who was aiming to develop just such a theory, which would apply to all physical systems, *including* dilute solutions. Of course, in reading this quote, much depends on emphasis. If we stress “until now” and “detailed”, the statement that a detailed molecular-kinetic theory of liquids did not exist was obviously true. (In fact, depending on how detailed one requires such a theory to be, it is true today, and probably will be in perpetuity.) But the validity of the statement is not the point. What is remarkable is its strategic role: Einstein presents a defeatist observation about the molecular-kinetic theory as applied to fluids in order to *avoid* this theory, where he previously aimed at extending and generalizing it. Would not one expect him to continue by saying that a *detailed* kinetic-molecular theory of fluids is actually not necessary, but that a general consideration, relying on the methods of his previous work would suffice, at least for a treatment of the

³⁴I cannot help but be reminded of a quite similar phrase in the famous preface of Planck’s (1897) *Lectures on Thermodynamics*, where he motivates his preference for thermodynamics against the molecular-kinetic approach by pointing to the “at present insuperable obstacles” in the development and application of the latter theory to solids and fluids. An earlier remark in (Planck, 1891) addressed the subject of Einstein’s dissertation (dilute solutions) even more explicitly.

osmotic pressure? That is exactly what he did one-and-a-half month earlier in (Einstein 1905a), and eleven days later in (Einstein 1905c) (cf. section 3.2).

One wonders why Einstein ignored his own statistical program in his dissertation. Perhaps he simply did not need it. Indeed, one might argue, his results were more impressive precisely because he avoided this program. Surely, it should count as a remarkable feat to obtain an empirical estimate of the molecular size relying only on the familiar equations of hydrodynamics. From a strategic perspective, an argument that avoided the molecular-kinetic theory would thus appear even more persuasive.

But from a logical perspective, there must have been a sleight of hand in such an argument. Did Einstein really arrive at an estimate of the size of molecules by consistent application of his hydrodynamical model? No. To see why, recall that Einstein had argued that an osmotic force is exerted on the spheres, due to the concentration gradient. But in a consistent application of his own model, the spheres are surrounded by pure solvent—there is no concentration gradient, and hence no osmotic force on the spheres.

Einstein was well aware of this weak point in the argument. He included a remark on p. 20 of the dissertation acknowledging that his identification of the force K in (59) as an osmotic force is troublesome, and pointed out that a treatment from the point of view of the molecular-kinetic theory would reveal osmotic pressure as a virtual force, explained by the collisions of the solute spheres with the solvent molecules. He referred to his subsequent paper, (Einstein 1905c), for a more extensive discussion. It is clear, therefore, that this first explanation will not hold: Einstein knew that his argument did need recourse to a molecular constitution of the solvent.

But this insight only redoubles the puzzle. Why should his introduction to the dissertation declare that the molecular constitution of the solvent is ignored in favour of a hydrodynamical model—only to admit at a later stage that the molecular constitution of the solvent is essential for the treatment of osmotic pressure? Moreover, the reference in the dissertation to the Brownian motion paper implies that he had already written or drafted the latter. And, as we shall see below, (Einstein 1905c) makes no mention of insuperable difficulties in the molecular-kinetic view of liquids. Instead, those difficulties are noted, but simply brushed aside³⁵ Similarly, the light-quantum paper had emphasized that the osmotic pressure for

³⁵“Even if the molecular picture [of the liquid] were provided in all details, the calculation ... would offer

dilute solutions can be obtained from molecular-kinetic theory in spite of further details.

What is more, the Brownian motion paper points out prominently that the hydrodynamical point of view is incapable of determining the osmotic pressure for spheres in a medium, and presents this incapacity as a fundamental conflict between “classical thermodynamics” and the molecular-kinetic theory. (I will argue below that that “classical thermodynamics” includes hydrodynamics for Einstein.) Why then should he choose hydrodynamics above kinetic-molecular theory in the dissertation? In fact, there is also a more general thematic contrast. The Brownian motion paper, and much of Einstein’s other work, focuses on theoretical conceptions. In the dissertation, however, Einstein addresses a more pragmatic issue: a method of determining the size of sugar molecules in solution from experimental data.

A likely explanation may be found in the difficulties that Einstein had experienced in obtaining his doctorate. Perhaps, his advisor did not favor kinetic-molecular theory, either for philosophical reasons (like Mach), or because of its lack of success (like Planck). Then, the Ph.D. dissertation might be seen as a kind of compromise, in which Einstein avoided a molecular-kinetic treatment in order to gain approval of the advisor. I shall discuss this conjecture in more detail in section 4.

3.2 Brownian motion

Einstein (1905c) opens with an exposition of two contrasting broad theoretical pictures: the kinetic-molecular theory, and “classical thermodynamics”. He aims to display a decisive confrontation between these two theories by focusing on the motion of small, yet microscopically observable, particles suspended in a liquid. If the motion Einstein predicts is observed, he says, classical thermodynamics can no longer be seen as strictly valid and an exact determination of “the true size of atoms”³⁶ becomes possible. If on the other hand, the prediction fails, one would have a weighty argument against molecular-kinetic theory.

He presents a simple thought experiment: consider a volume V of liquid. Small particles

such difficulties that an exact calculation of [the free energy] F can hardly be contemplated. However, we need to know only how F depends on the value of the volume $V^* \dots$ ” (Einstein 1905c, p.552). Cf. (Einstein 1907b, p. 569) for similar passages.

³⁶Note that this phrase must refer to the value of Avogadro’s number, otherwise the claim is nonsensical (cf. p. 33).

or molecules are suspended in a subvolume V^* , which is enclosed by semipermeable walls (cf. figure 1.) The walls are permeable for the liquid, but not for the particles or molecules. He first analyzes the set-up from the point of view of thermodynamics. In this case a sharp distinction must be made. In the case of a solution there will be an osmotic pressure on the semi-permeable walls, due to the difference in concentration of the dissolved substance on both sides (Fig. 1.a). But in the case of suspended particles, there is no osmotic pressure. The particles are simply external objects in the liquid; in a thermodynamic analysis they would be treated as parts of the walls, not of the system (cf. Fig. 1.b).

However, from the point of view of molecular-kinetic theory one reaches different conclusions. There is now no place for a phenomenologically imposed notion of osmotic pressure associated with concentration gradients. Instead, the molecules of the solvent exert forces on the solute molecules by incessant and chaotic collisions, which in turn make these molecules partake in a common thermal motion. As a consequence, solute molecules will collide with the walls, leading to the phenomenon that thermodynamics describes as osmotic pressure (cf. Fig. 1.c).

But, from this point of view, there is no essential distinction between solute molecules and suspended particles; they are only different in size. From the molecular-kinetic point of view, one should therefore conclude that suspended particles will also partake in thermal motion and give rise to the same phenomenon, in marked contradistinction to the classical thermodynamical picture.

The next section presents a more detailed argument that the molecular-kinetic theory indeed implies this generalized conception of osmotic pressure. Einstein's starting point is the theory he expounded in 1902 and 1903. (Curiously, Einstein does not refer to his 1904 paper in which he first drew attention to fluctuations!) He assumes a physical system, with state variables p_1, \dots, p_ℓ and equations of motions (18) obeying the incompressibility condition (22). The entropy is given by (23), and the free energy is then:

$$F \equiv \langle E \rangle - TS = -2\kappa T \log \int e^{-E/(2\kappa T)} dp_1 \dots dp_\ell. \quad (64)$$

Assuming the suspended particles are constrained by the semi-permeable walls to a volume

V^* , all we need to know is how the integral depends on V^* . Einstein shows that

$$F = -2\kappa T(\log J + n \log V^*), \quad (65)$$

where J is a term independent of V^* . It follows that

$$p \equiv -\frac{\partial F}{\partial V^*} = 2\kappa \frac{nT}{V^*}.$$

This is the familiar van 't Hoff law for osmotic pressure, but now valid for suspensions as well as solutions.

In the next section Einstein replaces the semipermeable walls by an external constant force K acting on the particles. A dynamic equilibrium follows from the superposition of two processes: (i) the motion of the particles as they move under the influence of the force K and (ii) a diffusion process. As in the dissertation, this equilibrium leads to a consideration of Stokes's law in a viscous medium and a diffusion equation, yielding the same expression for the diffusion coefficient derived earlier (62).

The next section presents a non-equilibrium analysis of the motion of the particles in one dimension, in the form of what is now known as a stochastic process. Assuming that each particle performs its movement independent of the others, Einstein asks for the number of particles dn that are displaced by a distance Δ within a time interval τ , which is assumed to be small compared to the observation time, but large enough that the motion of each single particle within consecutive intervals can be regarded as independent.

Letting $f(x, t)dx$ represent the number of particles per unit volume between x and $x + dx$ at time t , he argues that the change of this function will (under some approximations) obey the familiar diffusion equation (Fick's second law):

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2}. \quad (66)$$

The solution of this equation, given an initial condition $f(x, 0) = \delta(x)$, is

$$f(x, t) = (4\pi Dt)^{-1/2} e^{-x^2/(4Dt)}. \quad (67)$$

This solution allows him to calculate the mean displacement $\lambda \equiv \sqrt{\langle x_t^2 \rangle}$ as:

$$\lambda = \sqrt{2Dt}, \quad (68)$$

which, upon substitution of (62) yields an empirically testable expression:

$$\lambda = \sqrt{\frac{RTt}{3\pi\eta N_A P}}. \quad (69)$$

The predicted mean displacement is about 6 microns per minute for particles of 0.001 mm in water of 17° C. Conversely, experimental determination of λ , D and η would allow a new way of determining the value of N_A .

Comments: The Brownian motion paper has already been scrutinized by many excellent commentators (e.g., De Haas-Lorentz 1912, Klein 1982, Sarkar 1998, Nelson 1967, von Plato 1994, Renn 2005). I will therefore attempt to focus merely on some aspects not covered elsewhere.

First, it might be interesting to see exactly where Einstein places the conflict between classical thermodynamics and molecular-kinetic theory. His central point is that according to thermodynamics, suspended particles should not be subject to osmotic pressure, whereas the molecular-kinetic theory implies they are. But how did he arrive at the claim that thermodynamics does not allow an osmotic pressure associated with suspensions? He refers to a calculation of the free energy, but that calculation, of course, depends on the assumptions. It seems to me that the crucial assumption to make here is that, in a solution, both the solute and the solvent are treated as continuous media, with a continuously varying concentration, and the osmotic force is due to the concentration gradient. These assumptions do indeed lead to the conflict Einstein observed, because in a suspension of particles in a pure solvent, there is no gradient of concentration, and hence no osmotic force. Apparently, Einstein understands “classical thermodynamics” to imply a continuum view on the constitution of matter. This viewpoint was not unusual at the time. It is explicit in Kirchhoff’s *Theory of Heat* (1894), and often implicit in other texts. In that case, thermodynamics and molecular-kinetic theory contradict each other by definition. (Einstein’s achievement, of course, was to design an experimental test between them.) However, another orthodox presentation of thermodynamics,

(Planck 1897), views thermodynamics as a theory that remains neutral with respect to the constitution of matter. In that case, there would be no ground for Einstein's claim that the strict validity of thermodynamics rules out osmotic pressure in suspensions.

It is interesting to note that in later articles on Brownian motion, Einstein shifted the location of a conflict between molecular-kinetic theory and classical thermodynamics from osmotic pressure to the notion of equilibrium. In (Einstein 1906a p. 372; 1907b p. 569) he points out that according to thermodynamics, any isolated system reaches a state of equilibrium in which all observable quantities remain constant (the “minus first law” of Brown and Uffink (2001)), whereas kinetic-molecular theory implies the persistence of fluctuations. As we have seen, he had already made this remark in (Einstein 1904).

Apart from the impact of this paper on experimental physics, it may also have had an influence on the development of mathematics. Einstein's discussion views the evolution of the particle density f as a stochastic process, or more particularly as a Markov process in continuous time. However, one should note that Einstein nowhere calls f a probability density. Indeed, that would be inconsistent with his time-average interpretation of probability.

The theory of Markov processes has applications in many areas, not only in physics, and took a huge flight after the work of A.A. Markov in 1906. It is often said in the physics literature that Markov was inspired by Einstein's Brownian motion paper. However, I am unable to verify that. A biography of Markov (Basharin *et al.* 2004) does not mention Einstein as a source of inspiration.

4 Einstein and Kleiner

Einstein's first attempt to obtain a Ph.D. under Weber at the ETH was abandoned soon after its inception, in the summer of 1901. Next, Einstein went for a doctorate under the supervision of Alfred Kleiner, professor of physics at the University in Zürich. He prepared a dissertation in November 1901. At that time, Einstein thought that Kleiner would accept this dissertation, but he also expressed his frank opinion on his advisor in his letters to Mileva Maric:

So far I have not heard from Kleiner. I don't think he would dare to reject my dissertation, but otherwise, in my opinion, there is nothing that can be done with that

short-sighted man. If I had to carry his head on my shoulders to become a university professor—I wouldn't want to change places, but would rather remain a poor private tutor (Einstein to Mileva Maric, 28 November 1901, CPAE , Vol. 1, Doc. 126).

and:

Since that bore Kleiner still hasn't answered, I am going to drop in on him on Thursday [...] To think of all the obstacles that these old philistines put in the way of a person who is not of their ilk, it's really ghastly! This sort instinctively considers every intelligent young person as a danger to his frail dignity (Einstein to Mileva Maric, 17 December 1901, CPAE , Vol. 1, Doc. 128).

It is evident that Einstein did not see Kleiner as a kindred spirit.³⁷ However, Einstein's subsequent meeting with Kleiner made him more mellow.

Today I spent the whole afternoon with Kleiner in Zurich and explained my ideas on the electrodynamics of moving bodies to him & otherwise talked with him about all kinds of physical problems. He is not quite as stupid as I thought, and, moreover, he is a good guy. He said I may refer to him whenever I need a recommendation. Isn't that nice of him? He must go away during the vacation and he hasn't read the thesis yet (Einstein to Mileva Maric, 19 December 1901, CPAE , Vol. 1, Doc. 130).

But in the end, Kleiner did not approve the dissertation, and Einstein had to withdraw his request for a Doctoral exam.

The content of this dissertation, which has not survived, remains obscure. Einstein had said in the spring of 1901 that he intended to work on molecular forces, mainly for fluids. A letter from Mileva mentions that Einstein had written a dissertation on molecular forces for

³⁷Einstein's impression that Kleiner saw him as a threat is corroborated by an independent source. Friedrich Adler, who had long been Kleiner's assistant, recorded his impression of a conversation with Kleiner in 1909 about delays in Einstein's appointment as extraordinary professor (a position, for which Adler had also been candidate): "The essential point is rather that what he did not say, but what became very clear to me from the conversation. He told me in the greatest honesty. That the matter was terribly difficult, and it was clear to me that it was particularly difficult for him personally; that he fears for his own existence, that is, he fears to become cornered or pushed aside by a stranger [i.e., Einstein], whom he has not treated as decently as he treated me. That is the true motive for the eternal delay and hesitation" (Ardelt 1984, p. 165). However, see (Schulmann 2004) for a different view of the Einstein-Kleiner relationship.

gases. Einstein later wrote that it was on a topic in the kinetic theory of gases. The reasons for rejection remain clouded too. The only reference in the literature is a remark in the biography of Einstein's son-in-law Kayser saying that it was rejected because it contained sharp criticism of Boltzmann. Evidence presented by (Renn 1998) suggests it contained criticism of Drude.

More information about Kleiner's views may be gathered from an address to the *Schweizerische Naturforschende Gesellschaft* in 1901. Here, Kleiner reviews the revolutionary changes in the theoretical conceptions of physics throughout history, and the last ten years in particular. He gives as illustrations a history of the concept of force, and in a later part, of the nature of electricity and magnetism. Clearly, given the interest Kleiner displays in fundamental theoretical concepts, and his awareness that they could be open to revolutionary change, Einstein could hardly have found a more sympathetic and suitable advisor.

However, Kleiner comes to a viewpoint very different from Einstein's. His historical survey on the concept of force culminates in the enthusiastic approval of Kirchhoff's (1897) statement that the goal of mechanics is to describe the motions found in Nature in a complete and simple fashion. Kleiner argues that we can never "know" or "understand" the nature or cause of attraction and all such theoretical attempts are idle speculation. Therefore, theoreticians should descend from their "haughty heights" (*stolze Höhe*) of aiming to reveal a hidden necessary connection behind the phenomena, and accept that the only role for scientific theory is to describe the actual phenomena. And they should accept this role gladly, because nothing is more certain than the facts.

Of course, Kleiner concedes that theories are not superfluous. A theoretical principle can do more to advance knowledge than a single observation. But no matter how well-confirmed the consequences drawn from a theory may be, one may not infer its correctness. Theories are no more than mental pictures.

He goes on to discuss changes in the theoretical views on the nature of electrical charge and magnetism. At this stage, his tone becomes more sardonic towards theories, and he eagerly displays a multitude of theoretical pictures employed in the last centuries. While 17th-century physicists saw charge as a material substance, it was later seen as a mere divergence in the electric force field. But the recent experiments on cathode rays had led to the hypothesis of the so-called "electrons". As Kleiner points out, this discovery leads us

back, after a period of “ethereal volatilization” (*ätherische Verflüchtigung*) to the picture of an electrical substance of the early, naive doctrines.

In short, Kleiner’s address lays down a manifesto for how physics should be done. In his view theoretical concepts are only provisional tools. What is regarded today as received and well-established theory may be overthrown tomorrow. We can never pretend that theories reflect the true nature of things. It is unfortunate, for my purpose, that he does not address molecular-kinetic theories in particular. Hence my suggestion that he objected to such a theory in particular must remain a conjecture.

Many other authors (e.g. Helmholtz, Hertz, Boltzmann) at the end of the 19th century had emphasized that theories are mental constructs. In this respect Kleiner was not unique. Nevertheless, the reader will have perceived points in Kleiner’s outlook that are quite opposite to the priorities and aims of Einstein’s work. Einstein was deeply concerned with the conceptual unity and generality of physical theory. He surely did not disregard the facts or even pragmatic issues. But it seems safe to say that Einstein believed that observations are a means to test theoretical pictures—and not that theory was the means for describing the observations. In this respect he must have been at loggerheads with Kleiner. So, it seems that the real compromise toward Kleiner in Einstein’s dissertation does not lie in his avoidance of molecular-kinetic theory but in his avoidance of a discussion of the clash between this theory and classical thermodynamics, and to remain close to what could be obtained from observed data.

Acknowledgement I am grateful for many invaluable comments and helpful references from Clayton Gearhart, Jan Hilgevoord, Michel Janssen, John Norton, Rob Rynasiewicz and Robert Schulmann.

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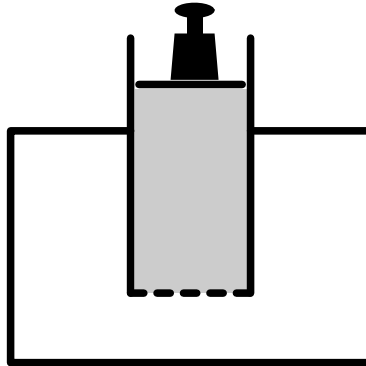


Figure 1.a: *In a pure hydrodynamical model of both solvent and solute matter, the osmotic pressure is due to the jump in concentration across the semipermeable membrane.*

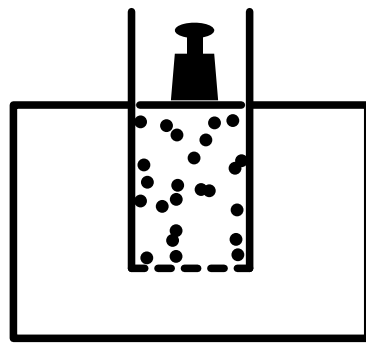


Figure 1.b: *There is no osmotic pressure in a model in which the solvent is represented as a continuous medium, but the solute/suspended substance as particles.*

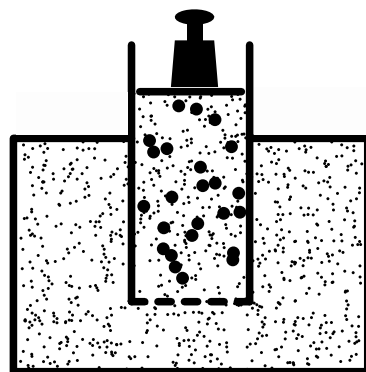


Figure 1.c: *A molecular model of both solvent and the solute/suspended substance. All particles partake in a common thermal motion, and the osmotic pressure is due to collisions of the solute/suspended particles on the walls.*

Figure 1: *Illustrating the distinctions in Einstein's thought experiment between the case where (a) both solvent and solute are modeled as continuous media; (b) the solvent is a continuous medium but the solute/suspended substance consists of particles; and (c) both solvent and solute matter consist of particles. The dashed line represents a semipermeable membrane; the variable column and weight are not present in Einstein's discussion. They have been added in order to visualize the osmotic pressure.*