Einstein's approach to Statistical Mechanics

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Abstract: We summarize the papers published by Einstein in the *Annalen der Physik* in the years 1902-1904 on the derivation of the properties of thermal equilibrium on the basis of the mechanical equations of motion and of the calculus of probabilities. We point out the line of thought that led Einstein to an especially economical foundation of the discipline, and to focus on fluctuations of the energy as a possible tool for establishing the validity of this foundation. We also sketch a comparison of Einstein's approach with that of Gibbs, suggesting that although they obtained similar results, they had different motivations and interpreted them in very different ways.

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1. Introduction

In June 1902, having just been accepted as Technical Assistant level III at the Federal Patent Office in Bern, Albert Einstein submitted to *Annalen der Physik* a manuscript entitled "Kinetic Theory of Thermal Equilibrium and of the Second Law of Thermodynamics" (Einstein 1902). It turned out to be the first of a series of papers on closely related subjects, one each year (Einstein 1903, 1904), acting almost as a prelude to his *annus mirabilis* production which revolutionized physics and soundly established Einstein's fame. In these papers, following the steps of Maxwell and Boltzmann, Einstein attempts "to derive the laws of thermal equilibrium and the second law of thermodynamics using only the equations of mechanics and the probability calculus".[1]

In spite of their importance, the 1902-1904 papers have received comparatively little attention. One of the reasons was the publication in 1902 of Gibbs' treatise (1902). This book is considered, especially since the publication of the influential book by R.C. Tolman (1938), as the founding text of the discipline. Einstein himself contributed to the neglect of the 1902-1904 papers. In his scientific autobiography Einstein remarks in fact:

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[1] Einstein's papers and their translations are available on the Princeton University Press site [PUP].

> Not acquainted with the earlier investigations by Boltzmann and Gibbs, which had appeared earlier and actually exhausted the subject, I developed the statistical mechanics and molecular-kinetic theory of thermodynamics which was based on the former. My major aim in this was to find facts which would guarantee as much as possible the existence of atoms of definite size (Einstein 1949, p. 47).

The last sentence of this quotation highlights the different attitude of Einstein with respect to Gibbs. Einstein aims at using the statistical approach to establish the reality of atoms, while Gibbs aims at a rational foundation of thermodynamics, and consequently focuses on the regularities which emerge in systems with many degrees of freedom. This is exhibited by the different attitude of the two scientists with respect to the equation which relates the size of energy fluctuations with the specific heat: while Gibbs stresses that it intimates the non-observability of such fluctuations, Einstein immediately looks for a case in which they could become observable. He is thus led to consider black-body radiation as such a case. In pursuing this line of research Einstein found an unexpected result, that pointed at an inconsistency between the current understanding of the processes of light emission and absorption and the statistical approach. To resolve this inconsistency, in the first paper of his *annus mirabilis* (Einstein 1905), he renounced the detailed picture of light emission and absorption provided by Maxwell's equations, maintaining his statistical approach, in particular the statistical interpretation of entropy. He introduced therefore the concept of light quanta, presented as a "heuristic point of view".

2. The papers

2.1. The 1902-1903 papers

The first two papers (Einstein 1902, 1903) have a very similar structure. The second paper aims to widen the scope of the first, by attempting to consider "general" dynamical systems and irreversible processes. We shall follow the first paper, and we shall then briefly review the points in which the second paper differs. We adapt Einstein's discussion to modern notation.

Einstein begins by considering a general physical system as represented by a mechanical system with many coordinates $q = (q_1, \ldots, q_n)$ and the corresponding momenta $p = (p_1, \ldots, p_n)$, obeying the canonical equations of motion with a time-independent Hamiltonian that is the sum of a potential energy (function of the q's alone) and of a kinetic energy that is a quadratic function of the p's, whose coefficients are arbitrary functions of the q's (and is implicitly supposed to be positive definite). Following Gibbs, we shall call the p's and q's collectively as the phase variables, and the space they span the phase space. Einstein then considers a very large number N of such systems, with the same Hamiltonian, whose energies E lie between two very close values $\bar{E}$ and $\bar{E}+\delta\mathrm{E}$. He then looks for the stationary distribution of these systems in phase space.

Here Einstein introduces a strong mechanical hypothesis by assuming that, apart from the energy, there is no other function defined on the phase space that is constant in time. He argues that this condition is equivalent to the requirement that the stationary distribution of the systems in phase space depends only on the value of the energy. He then shows that Liouville's theorem implies that the local density of systems in phase space is constant in time and therefore, by the mentioned hypothesis, must be a function of the energy alone. Since the energies of all *N* systems are infinitely close to one another, this density must be uniform on the region of phase space defined by the corresponding value of the Hamiltonian. In this way Einstein has defined what is now called the microcanonical ensemble.

To derive the canonical ensemble, Einstein considers the equilibrium between a system *S* and a system Σ considerably larger. By introducing a clever trick, he is able to show that if the energy of the total system $S \cup \Sigma$ is fixed and equal to E_t, the probability that the system *S* is found in a small region g of its phase space in which its energy is equal to *E* is given by

$$\mathrm{P} = \mathrm{const.}\, e^{-\beta\mathrm{E}}\, dp\, dq,$$

where $dp\, dq = \prod_{i=1}^{n} dp_i\, dq_i$ is the phase-space volume of g and β is a positive quantity given by

$$\beta = \frac{\omega'(E_t)}{\omega(E_t)},$$

where $\omega(E_t)$ is the volume of the phase space available to the larger system Σ when its energy lies between E_t and $E_t+\delta\mathrm{E}$. This derivation is close to one which is most popular nowadays, but should be contrasted with Gibbs' approach, who introduces the canonical distribution axiomatically, as the simplest one which allows physically independent systems to be also statistically independent.

By applying these relations to the case of a system with quadratic Hamiltonian, Einstein then easily derives the equipartition theorem, which allows him to interpret the quantity βin terms of the absolute temperature: $1/\beta = k_{\mathrm{B}}T$, where $k_{\mathrm{B}}$is a universal constant (that we now call Boltzmann's constant). Having found the relation between β and the temperature, Einstein proceeds to the derivation of the second law of thermodynamics, which he here limits to the statement of the integrability of heat divided by the absolute temperature. He considers a system with externally applied forces. These forces are split into ones derived from a potential depending on the system's coordinates, and others that allow for heat transfer. The first ones are assumed to vary slowly with time, while the second ones change very rapidly. The infinitesimal heat $\delta Q$is defined as the work of the second type of forces. Then a reversible transformation is one in which the system is led from an equilibrium state with given values of β and of the volume V to one with the values $\beta + \delta\beta$ and $V + \delta V$. Here Einstein tacitly assumes that the time average of the relevant quantities in a slow transformation can be obtained by averaging the same quantity over the distribution of the N systems in phase space. He thus finds

$$\frac{\delta Q}{T} = d\left(\frac{\langle E\rangle - F}{T}\right),$$

where $\langle E\rangle$ is the average total energy of the system, and F is a constant introduced so that the distribution $P(p,q) = \mathrm{e}^{-\beta E(p,q)-F}$ is normalized. Einstein remarks that this expression contains the total energy, and is independent of its splitting into kinetic and potential terms. One can readily integrate this expression, obtaining an explicit form of the entropy S:

$$S = \frac{\langle E\rangle - F}{T} = \frac{\langle E\rangle}{T} + k_{\mathrm{B}}\log\int e^{-\beta E(p,q)}\, dpdq + \text{const.}$$

In the 1903 paper, Einstein reconsiders the problem within a more general framework of a dynamic system whose state is identified by a collection p of variables satisfying a system of first-order equations of motion, which allow for just one integral of motion. He even thinks that the conditions leading to Liouville's theorem are redundant (but he apparently realized his error soon after its publication). More importantly, he explicitly identifies the probability of finding the system in a region g as the limit for infinite time of the time fraction spent in the region. In the course of this derivation, Einstein more than once states without proof that the energy of a system described by a canonical distribution never differs markedly from its average, before and after the several steps of the process. Within this approach he is able to obtain a more transparent derivation of the expression of entropy (by considering a system undergoing a succession of adiabatic and isopycnic[2] infinitely slow transformations) and attempts to derive the non-decreasing property of the entropy in closed systems by relying on the assumption that "always more probable distributions will follow upon improbable ones" (Einstein 1903). This assumption makes his derivation less than satisfactory.

2.2. The 1904 paper

A change of pace is easily noticed already in the first lines of the 1904 paper, entitled "On the general molecular theory of heat". Here he refers to his previous papers, in which he had spoken of the "kinetic theory of heat" as laying the foundations of thermodynamics, by the less specific expression of "molecular theory of heat". The

[2] Following Boltzmann, Einstein calls "isopycnic" a process in which the system is allowed to exchange energy with a heat reservoir, while the parameters defining its Hamiltonian do not change.

paper contains several results worth mentioning, as announced at the end of the introduction:

> First, I derive an expression for the entropy of a system, which is completely analogous to the expression found by Boltzmann for ideal gases and assumed by Planck in his theory of radiation. Then I give a simple derivation of the second law. After that I examine the meaning of a universal constant, which plays an important role in the general molecular theory of heat. I conclude with an application of the theory to black-body radiation, which yields a most interesting relationship between the above-mentioned universal constant, which is determined by the magnitudes of the elementary quanta of matter and electricity, and the order of magnitude of the radiation wave-lengths, without recourse to special hypotheses (Einstein 1904).

Our interest focuses on the last two points. Once Einstein establishes the equipartition theorem following pretty much his previous steps, he uses his available data to estimate the value of k_{B}. Then, under the title "General meaning of the constant κ" he discusses the fluctuations of the energy in the canonical ensemble, deriving the relation between the specific heat and the amplitude of energy fluctuations as

$$\langle E^2\rangle - \langle E\rangle^2 = k_{\mathrm{B}} T^2 \frac{d\langle E\rangle}{dT}.$$

Gibbs had obtained the same expression in (Gibbs 1902, eq. (205), p. 72), but had almost immediately pointed out that these fluctuations were not observable. Characteristically, Einstein instead goes over immediately to look for a system in which these fluctuations could be observed and he finds that the blackbody radiation could provide such a system. It is worth quoting his reasoning:

> If the linear dimensions of a space filled with temperature radiation are very large in comparison with the wavelength corresponding to the maximum energy of the radiation at the temperature in question, then the mean energy fluctuation will obviously be very small in comparison with the mean radiation energy of that space. In contrast, if the radiation space is of the same order of magnitude as that wavelength, then the energy fluctuation will be of the same order of magnitude as the energy of the radiation of the radiation space (Einstein 1904).

Einstein can thus evaluate the size of the energy fluctuations from the relation above and from the Stefan-Boltzmann law, and obtains an estimate of the size λ of a cavity in which the root-mean-square of the energy fluctuation is comparable with the total energy. This quantity compares well with the wavelength $\lambda_{\max}$ corresponding to the peak of Planck's radiation law. His attention is thus drawn to a more detailed study of the black-body radiation problem. However, in the following months, trying to explicitly apply his theory to that system, he will encounter a paradox, which he will brilliantly overcome by renouncing the classical picture of the emission and absorption of light, based on Maxwell's equations, and by introducing the concept of the light quanta (Einstein 1905).

The importance of this development has been stressed by Kuhn (1978, p. 171), when he states that

> What brought Einstein to the blackbody problem in 1904 and to Planck in 1906 was the coherent development of a research program begun in 1902, a program so nearly independent of Planck's that it would almost certainly have led to the blackbody law even if Planck had never lived.

3. Einstein vs. Gibbs

One usually takes for granted that the research projects pursued by Einstein in these three papers, and by Gibbs in his book (Gibbs 1902) were equivalent, and that the more mathematically refined argumentation contained in the latter made Einstein's approach redundant. A closer scrutiny shows however fundamental differences in their approaches, and makes Einstein's approach more attractive to present-day physicists. Gibbs program focuses in understanding the properties of *ensembles* of mechanical systems, i.e., of systems whose dynamical equations are given, but whose initial conditions are only given in a probability distribution. He gives this discipline the name of "statistical mechanics". He stresses that its relevance goes beyond establishing a foundation of thermodynamics:

> But although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light in departments quite outside of thermodynamics. (Gibbs 1902, Preface, p. viii)

On the other hand, according to Gibbs, our ignorance of the basic constitution of material bodies make unreliable our inferences based on supposed models of matter, even when derived by the methods of statistical mechanics:

> In the present state of science, it seems hardly possible to frame a dynamic theory of molecular action which shall embrace the phenomena of thermodynamics, of radiation, and of the electrical manifestations which accompany the union of atoms. […] Difficulties of this kind have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics. Here, there can be no mistake in regard to the agreement of the hypotheses with the facts of nature, for nothing is assumed in that respect. The only error into which one can fall, is the want of agreement between the premises and the conclusions, and this, with care, one may hope, in the main, to avoid. (Gibbs 1902, Preface, pp. ix-x)

In Gibbs' approach, the probability distribution is a *datum* of the problem, while in Einstein's one it is one of the unknowns. The greatest difference is that Gibbs starts from the equal a priori probability postulate, while for Einstein what is important is to evaluate time averages and these are replaced by phase space averages through an ergodic hypothesis. Thus Gibbs is allowed to introduce the canonical distribution *a priori*, as an especially simple one, endowed with interesting properties, in particular because it factorizes when one considers the collection of two or more mechanically independent systems (Gibbs 1902, p. 33). On the contrary, for Einstein, the canonical distribution is the distribution which describes the mechanical state of a system in contact with a thermal reservoir at a given temperature, while the "simplest" distribution is rather the microcanonical, which represents the state of an isolated system at equilibrium. And the former is derived from the latter.

Even more strikingly, in Einstein's hands, deviations from the expected behavior become a tool for the investigation of the microscopic dynamics. This difference in attitude was already highlighted above, in the discussion of energy fluctuations, but the clearest example is the 1905 paper on light emission and absorption (Einstein 1905), where he brackets the contemporary models of light absorption and propagation, but maintains the statistical interpretation of entropy. He then evaluates the radiation entropy from the empirical distribution law and interprets it in terms of the statistical approach as describing the coexistence of point-like particles in a given volume.

4. Summary

We presented Einstein's approach to statistical mechanics in contrast to the one taken by Gibbs. The results are equivalent since both are based on Boltzmann's contributions. Gibbs' starting point is the equal a priori probability hypothesis in phase space that leads to the microcanonical probability density for an ensemble. Einstein, on the other hand, starts by stating that what is important is the evaluation of time averages of appropriate quantities. These can be replaced by averages of the same quantities over an unknown density function over the phase space, with the help of an ergodic hypothesis. Einstein introduces the assumption that the energy is the only conserved quantity to play the role of the ergodic hypothesis. Using this assumption and Liouville's theorem, Einstein shows that the unknown density function mentioned before must be constant on the energy shell, that is it must be the microcanonical distribution. From there, the interpretation of the canonical distribution is different: for Gibbs, it is the simplest distribution, in which physically independent systems are also statistically independent, while for Einstein it is the distribution which describes the state of a system in contact with a reservoir. Thus the index of the canonical distribution (as defined by Gibbs) is "analogous" to the temperature for Gibbs, but can be "identified" with the temperature for Einstein. It is also interesting to remark that in several points Einstein states (without proof) that the distribution of energy values in the canonical ensemble is sharply peaked, and deduces from this some dubious inequalities for the probability density itself. Only in the 1904 paper he explicitly evaluates the size of fluctuations, obtaining a result already derived by Gibbs. But, while Gibbs had stressed the non-observability of energy fluctuations in macroscopic systems (thus contributing to the "rational foundation of thermodynamics"), Einstein points at the use of fluctuations as a tool for investigating microscopic dynamics.

What interest can a present-day reader find in Einstein's 1902-1904 papers? We think that they sketch a very neat road map for the introduction of the basic concepts of statistical mechanics, focusing on their heuristic value. One first focuses on isolated systems and identifies the microcanonical ensemble as the equilibrium distribution by means of the thermal equilibrium principle. For this step, Einstein's reasoning given above, based on the postulate of the absence of integrals of motion beyond the energy, is excellent. Then, one looks at a small part of such an isolated system, and one shows that the corresponding distribution is the canonical one. Finally, one identifies the mechanical expressions of temperature, infinitesimal heat and, by integration, of entropy. All these steps can be tersely traced by following, more or less closely, Einstein's path. At this point, the focus can be shifted to the evaluation of fluctuations, which allow on the one hand to recover the equivalence of ensembles for large enough systems and, by the same token, to identify situations in which the underlying molecular reality shows up in the behavior of macroscopic systems (like, e.g., in Brownian motion). This road map has been more or less followed by several modern textbooks on statistical mechanics, but we think that it would be fair to stress that it had first been sketched in the papers we described.

A more detailed version of this contribution is being published on *Journal of Statistical Physics* (Peliti, Rechtman 2016).

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