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EINSTEIN'S STATISTICAL MECHANICS

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ABSTRACT

The foundations of equilibrium classical statistical mechanics were laid down in 1902 independently by Gibbs and Einstein. The latter's contribution, developed in three papers published between 1902 and 1904, is usually forgotten and when not, rapidly dismissed as equivalent to Gibb's. We review in detail Einstein's ideas on the foundations of statistical mechanics and show that they constitute the beginning of a research program that led Einstein to quantum theory. We also show how these ideas may be used as a starting point for an introductory course on the subject.

RESUMEN

Los fundamentos de la mecánica estadística de equilibrio fueron presentados en 1902 de manera independiente por Gibbs y Einstein. La contribución de este último, desarrollada en tres trabajos publicados entre 1902 y 1904, es generalmente olvidada y cuando no, se le menciona de paso como una formulación equivalente a la de Gibbs. En este trabajo revisamos en detalle las ideas de Einstein respecto a los fundamentos de la mecánica estadística y mostramos que constituyen la base de un programa de investigación que más tarde llevó a Einstein a la teoría cuántica. Mostramos también como las ideas de Einstein pueden ser usadas en un curso introductorio sobre el tema.

1. INTRODUCTION

In 1902, a few days after being appointed to the Patent Office in Bern, Einstein submitted for publication his third scientific paper under the tittle of "Kinetic Theory of Equilibrium and the Two Principles of Thermodynamics"(1). In this paper he laid down the foundations of statistical mechanics independently of Gibb's work published the same year(2). As regards the subsequent development of the subject, Einstein's contribution has passed unnoticed and has only recently received some attention(3,4,5,6). It is the object of this study to try to explain Einstein's ideas on the foundations of statistical mechanics, since they form the basis of a research program that led to the study of Brownian motion and of black-body radiation(7,8), and also because they could be used as an alternative introduction to the subject.

In his next paper published the following year, "A Theory of the Foundations of Thermodynamics"(9), Einstein elaborated on the same theory in a more general manner discussing explicitly how the concept of probability is used. In the following section we will present Einstein's theory following mainly this paper. This is done in a way that might be useful when discussing the foundations of classical statistical mechanics in a course on the subject.

Section 3 is dedicated to Einstein's 1904 paper "Towards a Universal Molecular Theory of Heat"(10), where energy fluctuations are discussed in particular for black-body radiation. Finally, we shall briefly comment in section 4 on the importance of Einstein's contribution to the foundations of statistical mechanics.

2. EINSTEIN'S STATISTICAL MECHANICS

2.1) In the introduction to his 1902 paper Einstein stated that:

> the mechanics has not achieved the goal of establishing a sufficient basis for a general theory of heat. This is due to the fact that the theorem of heat equilibrium and the second fundamental theorem are not deduced using exclusively the mechanical equations and the probability theory although Maxwell's as well as Boltzmann's theories have come close to this goal. Hence, it is the purpose of this paper to fill this gap. (11)

In the discussion that followed Einstein developed a theory, now called statistical mechanics, which extracted the thermodynamical behavior of general systems governed by mechanical equations of motion. Before discussing the concept of temperature, he remarked that the theory might be redeveloped in a more general way[(12)]. This reformulation was presented the following year. Although both papers are similar in content, we shall restrict our attention to the second one, since it is a more nature presentation and deals in detail on the need of a non-mechanical hypothesis in order to be able to speak of probabilities and establish the theory.

In a letter to his friend Michele Besso dated January 1903 Einstein wrote enthusiastically about this second paper on the foundations of statistical mechanics:

> At last on Monday I sent away my paper after many modifications and corrections. Now it is completely clear and simple and I am fully satisfied. The concepts of temperature and entropy follow from the principle of energy conservation and the atomistic theory. By employing the hypothesis that the state distributions of isolated systems never pass into those which are less probable, there follows the second law of thermodynamics in its more general form, namely the impossibility of a *perpetuum mobile* of the second kind. (13)

The paper is divided into nine sections beginning with a general mechanical description of isolated systems, and then passes on to the discussion of an ergodic hypothesis and how observable quantities may be calculated as averages over a large ensemble of similar isolated systems once their distribution is known. The discussion of the distribution of a large ensemble of systems in thermal contact with a heat bath and of the concepts of temperature and entropy form the next part of the paper, while the last sections are devoted to a proof of the second law of thermodynamics.

2.2) Consider an isolated physical system described by a great number, say n, of scalar quantities $p_1, \dots, p_n$ called state variables. Einstein did not say what these state variables represent, but since the system is isolated "it become evident that the state of the system at a given instant will uniquely determine the transformation of the system"(14). That is, the state variables must satisfy equations of the form

$$\frac{dp_i}{dt} = \varphi_i(p_1 , \dots , p_n) , \qquad (i = 1, \dots , n) . \tag{1}$$

Einstein also assumed that the total energy E is the only constant of the motion,

$$E = E(p_1 , \dots , p_n) = \text{const.} \tag{2}$$

In the 1902 paper the state variables represented the positions and momenta of a great number of particles. However, as we mentioned before, he then remarked that the discussion could possible be extended to systems defined in a still more general way. This more general formulation is the one that appears in the above paragraph; the state variables are not divided into positions and momenta (or velocities) and one does not need to speak of atoms as the constituents of the physical system.

2.3) From a modern perspective, the greatest merit of Einstein's paper belongs to the second section where probabilistic concepts and an ergodic hypothesis are introduced. This section begins with a statement that the theory applies only to equilibrium states:

> Experience shows us that an isolated system after a lapse of time reaches a state in which no observable quantity will suffer variations in time; we will then say that this state is stationary. (15)

To understand what condition must be satisfied by the state variables $p_1, \ldots, p_n$ in a stationary state it is neccesary to provide a relationship between these and the observable quantities of the system. Einstein assumed "that an observable quantity can always be determined by the time average of a certain function of the state variables $p_1, \ldots, p_n$"(16). That is, if $\hat{f}$ denotes an observable quantity, there must exist a function of the state variables f such that

$$\hat{f} = \lim_{T=\infty} \frac{1}{T} \int_0^T f(p_1(t), \ldots, p_n(t))\, dt \qquad , \qquad (3)$$

where $(p_1(t)m \ldots, p_n(t))$ is a solution of the equations of motion (1).

Einstein also assumed, that in order that all observable quantities remain constant in time, the state variables "always take the same values with the same frequency"(17). This phrase constitutes Einstein's ergodic hypothesis. Its origins are to be found in Boltzmann in 1871 and Maxwell in 1879. Boltzmann state that:

> the great irregularity of the thermal motion and the variety of extrinsic forces acting upon bodies make it probable that in virtue of the motion we call heat the atoms of bodies take on all positions and velocities compatible with the equation of energy. (18)

Maxwell, in order to prove Boltzmann's theorem on the average distribution of energy assumed that:

> The system, if left to itself in its actual state of motion, will, sooner of later, pass through every phase which is consistent with the equation of energy. (19)

Boltzmann's and Maxwell's hypotheses are equivalent, but not to Einstein's. Indeed, the former imply the existence of only one trajectory on the set of state variables consistent with the equation of energy(2), while Einstein's hypothesis allows the existence of any number of independent trajectories. However, when Einstein used the ergodic hypothesis, he did so more in the sense of Boltzmann and Maxwell as we shall see below.

Let us consider an isolated physical system described by equations (1) with a total energy E which is in a stationary state. Assume that the values of the state variables p_1, ... p_n are known at any instant of a time interval of length T and let Γ be an arbitrary region of the space of state variables while τ is the total time the state variables take values inside Γ. Einstein's ergodic hypothesis now states that "the quantity τ/T for $T = \infty$ has, for any region Γ a well defined limit"[20].

In order to be able to speak of probabilities Einstein considered:

> a great number (N) of independent physical systems all of them described by the system of equations (1). We choose an arbitrary instant t and ask for the distribution of the possible states of these N systems provided that the total energy E takes a value between E^* and $E^* + \delta E^*$. (21)

Due to the ergodic hypothesis Einstein then concluded that

> the probability that the state variables of a system chosen at random from the N at time t take values in the region Γ, assumes the values
>
> $$\lim_{T=\infty} \frac{\tau}{T} = \text{const.} \tag{4}$$
>
> The number of systems [dN] such that their state variables belong to the region Γ is therefore
>
> $$N \lim_{T=\infty} \frac{\tau}{T} \quad . \qquad (22) \tag{5}$$

Einstein did not go into the details of the relation between Eqs. (4) and (5). However, we will presently give an argument to show that probabilities may be calculated through averages over a large collection of systems.

We have quoted at length from Einstein's paper, since as mentioned earlier, one of its greatest merits lies in establishing the ergodic hypothesis as a central postulate of statistical mechanics. In 1912 Paul and Tatiana Ehrenfest suggested that the ergodic hypothesis be replaced by their quasi-ergodic hypothesis which states that any trajectory approaches arbitrarily closely any point consistent with the eqution of energy[23].

Einstein knew of Boltzmann's work through his lectures on Gas Theory[24]. There the ergodic hypothesis as quoted above is not mentioned, but when dealing with the proof of Liouville's theorem, Boltzmann referred to both his work and Maxwell which we quoted. On the other hand, Boltzmann considered "an enormously large number of mechanical systems, all of which have the same properties"[25], and how they may be distributed over the space of state variables. He concluded that the "simplest case of a stationary state distribution"[26] is one that is constant over the set of states consistent with the equation (2) of conservation of energy and called such a distribution an ergodic one*. He then discussed the equality of time averages as those defined by equation (3) and averages taken over the ensemble of systems distributed ergodically which is the content of equations (4) and (5).

To see this, let $P(\Gamma;t)$ denote the probability that the values of the state variables of a system chose at random from the N be found in the region Γ at time t. Then

$$P(\Gamma;t) = \frac{dN(t)}{N} \quad , \tag{6}$$

where $dN(t)$ is the number of systems of the ensemble that satisfy the condition just stated. Now let f_Γ be the characteristic function of the region Γ** and $\hat{f}_\Gamma$ its time average as defined by Eq. (3). Since this time average does not depend on the initial conditions

$$\hat{f}_\Gamma = \lim_{T=\infty} \frac{\tau}{T} \quad . \tag{7}$$

Define the average of the function f_Γ over the collection of systems at time t, $\overline{f}_\Gamma$ by

$$\overline{f}_\Gamma(t) = \sum_{i=1}^{N} \frac{1}{N} f_\Gamma(P_1^{(i)}(t), \ldots , P_n^{(i)}(t))$$

$$= \frac{dN(t)}{N} \quad , \tag{8}$$

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* Such a distribution was termed "microcanonical" by Gibbs[27], which is the name now commonly used, while Einstein did not assign to it any name in particular. According to Brush[28], the name "ergodic" became associated with the hypothesis we have been discussing by Paul and Tatiana Ehrenfest[23].

** The function f_Γ takes the value 1 for points inside Γ and zero otherwise.

where $(p_1^{(i)}(t), \ldots, p_n^{(i)}(t))$ denotes the values of the state variables of the i-th system at time t.

From Einstein's ergodic hypothesis, it follows that the state variables of all the members of the ensemble spend the same fraction of time in the region Γ, so that

$$\bar{\hat{f}} = \hat{f} \quad .$$

Also, since all the members of the ensemble are in a steady state'

$$\hat{\bar{f}} = \bar{f} \quad .$$

It is plausible to assume that it is immaterial whether time averaging or state space averaging is performed first, so it is now clear that

$$\bar{f} = \hat{f} \quad .$$

which, on behalf of Eqs. (6), (7) and (8) may be written as

$$p(\Gamma) = \frac{dN}{N} = \lim_{T=\infty} \frac{\tau}{T} \quad . \tag{9}$$

To be able to calculate probabilities Einstein proposed that for any small region g in the space of state variables such that the first state variable lies between p_1 and $p_1 + dp_1$, ..., the n-th between p_n and $p_n + dp_n$, the number of systems of the ensemble that at time t lie within g dN_t is given by

$$dN_t = \varepsilon(p_1, \ldots, p_n)\, dp_1, \ldots, dp_n \quad ,$$

where ε is an unknown function. Using Eqs. (1) and an argument similar to that used in the proof of Liouville's Theorem[29], the number of systems of the ensemble which at time t + dt lie within the same region g is

$$dN_{t+dt} = dN_t - \sum_{\nu=1}^{n} \frac{\partial(\varepsilon\phi_\nu)}{\partial p_\nu} dp_1 \ldots dp_n dt \quad . \tag{10}$$

Since the distribution of systems in the state space is stationary, $dN_t = dN_{t+dt}$. Hence, Eq. (10) may be solved and Einstein found that

$$\varepsilon = \exp\left\{-\int \sum_{\nu=1}^{n} \frac{\partial\varphi_\nu}{\partial p_\nu}\, dt + \psi(E)\right\} \quad , \tag{11}$$

where the function ψ is a constant of integration. It now follows that for any region g

$$dN = \text{const.}\ e^{-m}\int_g dp_1 \ldots dp_n \quad ,$$

where m stands for the integral that appears in the argument of the exponential of Eq. (11). Introducing new state variables $\pi_1 , \ldots , \pi_n$ that absorb the factor e^{-m}, Einstein arrived at the important formula

$$dN = \text{const.} \int d\pi_1 \ldots d\pi_n \tag{12}$$

If the state variables are the positions and momenta of the constituents of the system and the equations of motion (1) are Hamilton's equations of motion, the sum

$$\sum_{\nu=1}^{n} \frac{\partial\varphi_\nu}{\partial p_\nu}\, dt$$

that appears in Eq. (11) is zero, provided that the potential energy depends only on the positions. The same is true if the state variables are positions and velocities and Eqs. (1) are obtained from Lagrange's or Newton's equations of motion. Hence, it is not clear why Einstein chose such an abstract formulation and what kind of equations of motion he had in mind.

2.4) Einstein now turned to the problem of finding the distribution that describes a small system in thermal contact with a much larger one. He considered an ensemble of systems such that each system has an energy E between E^* and $E^* + \delta E^*$ and is formed two subsystems Σ and σ with energies H and η, respectively, so that $E = H + \eta$, and with state variables

$\Pi_1, \ldots, \Pi_\lambda$ and $\pi_1, \ldots, \pi_\ell$, respectively.

Let dN_1 denote the number of systems of the ensemble whose state variable $\Pi_1, \ldots, \Pi_\lambda\, \pi_1, \ldots \pi_\ell$ lie between Π_1 and $\Pi_1 + d\pi_1, \ldots, \pi_\ell$ and $\pi_\ell + d\,\pi_\ell$, respectively. According to Eq. (12)

$$dN_1 = C d\Pi_1 \ldots d\Pi_\lambda\, d\pi_1 \ldots d\pi_\ell \quad ,$$

where C = const.

Einstein assumed that Ψ could be written as

$$\Psi = -\,2h\,E \quad ,$$

with h some yet unknown function. Then

$$dN_1 = \text{const.}\; e^{-2h(H+\eta)}\, d\Pi_1 \ldots d\Pi_\lambda\, d\pi_1 \ldots d\pi_\ell \quad .$$

Now let dN denote the number of systems of the ensemble that satisfy the condition that the variables $\pi_1, \ldots, \pi_\ell$ lie within the values mentioned before while no restriction is placed upon the variables $\Pi_1, \ldots, \Pi_\lambda$. If we define the quantity by

$$\chi(e) = \int e^{-2hH}\, d\Pi_1 \ldots d\Pi_\lambda \quad , \tag{13}$$

where the integral extends to all the values of the state variables for which H lies within E* and E* + δE*:

$$dN_2 = \text{const.}\; \chi(E^* - \eta)\; e^{-2hH}\, d\pi_1 \ldots d_\ell \quad . \tag{14}$$

We way now write

$$\chi(E) = {}^{-2hE}\, \omega(E) \quad , \tag{15}$$

where by definition

$$\omega(E) = \int d\Pi_1 \ldots d\Pi_\lambda \quad ,$$

with the region of integration as in Eq. (13). Since η is small compared with E*:

$$\chi(E^* - \eta) = \chi(E^*) - \eta\chi'(E^*) \quad , \tag{16}$$

where $\chi'(E^*)$ is the partial derivative of χ with respect to E valued at E*. From Eq. (15)

$$\chi' (E^*) = e^{-2hE}[\omega'(E) - 2h\omega(E)] \quad . \tag{17}$$

At this point, Einstein argued that if $\chi'(E^*) = 0$ then $\chi(E^* - \eta)$ will not depend on the state of the small system. As can be seen easily from Eq. (17) this condition is fulfilled if

$$h = \frac{\omega'(E)}{z\omega(E)} \quad , \tag{18}$$

which defines the function h. "The quantity h depends only on the state of the system Σ which possesses an energy which is relatively infinite"[30].

The probability that the state variables of a small system in contact with a much larger one lie between the values π_1 and $\pi_1 + d\pi_1$, ... , π_ℓ and $\pi_\ell + d\pi_\ell$ is given, according to Eqs. (14), (16) and (18) by

$$dN_2 = \text{const. } e^{-2h\eta} d\pi_1 \ldots d\pi_\ell \quad . \tag{19}$$

The distribution given by Eq. (19), now known as canonical, was obtained an the assumption that $\chi'(E^*) = 0$. This assumption is not necessary as can be seen readily. Starting from Eq. (12) and integrating over all the values of the state variables such that the energy of the system lies between E* and E* + δE* we find that

$$\omega(E^*) = \text{const. } e^{-\psi(E)} \quad . \tag{20}$$

On the other hand

$$dN_2 = \text{const.} \left[\int e^{\psi(H+\eta)} \, d\Pi_1 \dots d\Pi_\lambda \right] d\pi_1 \dots d\pi_\lambda \quad ,$$

where the integration is carried over all the values of the state variables of the system Σ for which its energy lies close to the value H. We may now write

$$dN_2 = \text{const.}\ e^{\psi(E^*)}\ \omega(H) d\pi_1 \dots d\pi_\ell \quad ,$$

or, with the help of Eq. (20)

$$dN_2 = \text{const.}\ e^{\psi(E^*)}\ e^{\psi(H)}\ d\pi_1 \dots d\pi_\ell \quad .$$

Now,

$$\psi(H) = \psi(E) - \eta\psi'(E^*) \quad ,$$

where $\psi'(E^*)$ is the partial derivative of ψ with respect to the energy evaluated at E^*. Hence,

$$dN_2 = \text{const.}\ e^{-2h\eta}\ d\pi_1 \dots d\pi_\ell \quad ,$$

where we have defined h by

$$h = -\frac{1}{2}\psi'(E^*) \quad .$$

From Eq. (26) we find that

$$\psi'(E^*) = -\frac{\omega'(E^*)}{\omega(E^*)} \quad ,$$

and that

$$h = \frac{\omega'(E^*)}{2\omega(E^*)} \quad .$$

2.5) In the 1902 paper, Einstein discussed in detail the quantity h, first showing that it is a positive quantity and arguing that "the equality of the quantities h is then the necessary and sufficient condition for the stationary coupling (thermal equilibrium) of the two systems"(31). Following Boltzmann(32) he went on to discuss the mechanical meaning of the quantity h by considering the subsystem σ as a single molecule and the sybsystem Σ as the remaining molecules and found that the mean kinetic energy of a single molecule $\bar{\varepsilon}$ is given by

$$\bar{\varepsilon} = \frac{3}{4h} \quad . \tag{21}$$

On the other hand, since "the kinetic theory of gases shows us that this quantity is proportional to the pressure at constant volume"(33) and the pressure proportional to the temperature, Einstein concluded that

$$\frac{1}{4h} = kT \quad , \tag{22}$$

where k is a universal constant*.

The discussion presented in the 1903 paper is somewhat briefer. It starts by postulating relation (22) where T is the absolute temperature, then shows that the equality of the quantity h for two systems establishes thermal equilibrium between them and that Eq. (21) holds**. Again using the results of kinetic theory Einstein argued that the mean kinetic energy is proportional to the absolute temperature and concluded that "the quantity we have denoted by absolute temperature ... is nothing but the temperatures of a system measured with the gas thermometer"(34).

Before continuing with our presentation we would like to remark that there is a great methodological rigor in Einstein's discussion in that he tries to deduce the thermodynamic behavior of a system from the movement of its constituent parts. Through relations (18) and (22) the central concept of temperature assumes a microscopic character.

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* This constant is one half of Boltzmann's constant.

**The factor 3 is missing, however, the mistake was corrected in the 1904 paper.

2.6) Now that the temperature is defined, it is necessary in order to complete a theory of the principles of thermodynamics to find out what the entropy or any other thermodynamic potential is from a microscopic point of view, and then prove the second law. Einstein began by defining interminably slow processes as "those transformations of stationary states which are so slow that the state distribution at an arbitrary instant is infinitely close to the stationary state distribution"(35).

During an interminably slow process the system under study may interact with other subsystems Σ^*; this interaction is characterized by the value of certain external parameters $\lambda_1, \lambda_2, \ldots$. The equations of motion (1) are still valid but the functions $\varphi_\nu (\nu = 1, \ldots, n)$ and the energy E now depend also on the external parameters. The change in energy dE is therefore given by

$$dE = \frac{\partial E}{\partial \lambda} d\lambda + \sum \frac{\partial E}{\partial p_\nu} dp_\nu \quad . \tag{23}$$

An adiabatic transformation is defined by Einstein by the condition that

$$\sum \frac{\partial E}{\partial p_\nu} \varphi_\nu = 0 \quad ,$$

and an isopicnic transformation by the condition that the external parameters remain constant. In the latter case the change in energy dE is defined as the heat loss and denote by dQ. That is

$$dQ = \sum \frac{\partial E}{\partial p_\nu} dp_\nu \quad . \tag{24}$$

For any interminably slow process we may write

$$dE = dQ + \sum \frac{\partial E}{\partial \lambda} d\lambda \quad . \tag{25}$$

The probability dW that the state variables of the system lie between p_1 and $p_1 + dp_1, \ldots p_n$ and $p_n + dp_n$ respectively before the process begins is given by

$$dW = e^{c-2hE} dp_1 \ldots dp_n \quad ,$$

where C is a constant defined through the normalization condition

$$\int e^{c-2hE}\, dp_1 \ldots dp_n = 1 \qquad . \tag{26}$$

After an interminably slow process where h changes to h + dh, E to E + dE, c changes to c + dc according to the normalization condition

$$\int e^{(c+dc)-\,2(h+dh)\left(E+\sum \frac{\partial E}{\partial \lambda} d\lambda\right)} dp_1 \ldots dp_n = 1 \qquad .$$

From these two last equations it follows that

$$\int \left(dc - 2Edh - 2h \sum \frac{\partial E}{\partial \lambda} d\lambda\right) e^{c-2hE}\, dp_1 \ldots dp_n = 0 \qquad .$$

Einstein argued that the quantity in parenthesis in the integrand of the last equation must be constant and therefore zero. With the help of Eqs. (22) and (25) he found that

$$\frac{dQ}{T} = d\left(\frac{E}{T} - 2kc\right) \qquad ,$$

thus showing that "dQ/T is an exact differential of a quantity which we would like to call the entropy S of the system"(36). Taking into account Eq. (26) we may write

$$S = \frac{E}{T} - 2kc \qquad , \tag{27}$$

where

$$c = -\log \int e^{-2hE}\, dp_1 \ldots dp_n \qquad , \tag{28}$$

and the integration extends to all possible values of the state variables.

From a modern perspective one would write, instead of Eqs. (23)-(25),

$$\overline{dE} = \sum \overline{\left(\frac{\partial E}{\partial p_\nu}\right)} dp_\nu + \sum \overline{\left(\frac{\partial E}{\partial \lambda}\right)} d\lambda \quad ,$$

$$dQ = \sum \overline{\left(\frac{\partial E}{\partial p_\nu}\right) dp_\nu}$$

and

$$\overline{dE} = dQ = \sum \overline{\left(\frac{\partial E}{\partial \lambda}\right)} d\lambda \quad ,$$

where the barred quantities are averages using the state distribution given by Eq. (19). In an interminably slow process where h changes to $h + dh$, λ_1 to $\lambda_1 + d\lambda_1$, λ_2 to $\lambda_2 + d\lambda_2$, ... , c changes by an amount dc, which, with the help of Eq. (26) is found to be given by

$$dc = \frac{-1}{2kT^2} \overline{E}\, dT + \frac{1}{2kT} \sum \overline{\left(\frac{\partial E}{\partial \lambda}\right)} d\lambda \quad .$$

From the last two equations

$$dQ = -2kdc - \frac{1}{T^2} \overline{E}\, dT - \frac{1}{T} \overline{dE}$$

or

$$\frac{dQ}{T} = d\left(\frac{\overline{E}}{T} - 2kc\right) \quad .$$

2.7) What now follows is a proof that the quantity defined as the entropy indeed possesses the properties it should; that is, a proof of the second law of thermodynamics. As we shall see, Einstein was not wholly succesful, since he had to introduce an extra hypothesis taken from kinetic theory, and hence defeated his purpose expressed in the introduction of the 1902 and 1903 papers of deriving the fundamental principles of thermodynamics without recourse to kinetic theory.

Let us consider a great number (N) of identical isolated systems all satisfying the equations of motion (1) and with energy between E^* and $E^* = \delta E^*$. If the region of state space determined by the allowed values of the energy is subdivided into ℓ regions g_1 , ... , g_ℓ all of them with the same extension and if W_1 , ... , W_ℓ are the probabilities that the state variables of a system chosen at random lie in g_1 , ... , g_ℓ respecvely, then

$$W_1 = W_2 = \ldots = W_\ell = \frac{1}{\ell} \quad .$$

The probability W that of the N systems ε_1 be found in the region g_1 , ... , ε_ℓ be found in the region g_ℓ is given by

$$W = \left(\frac{1}{\ell}\right)^N \frac{N!}{\varepsilon_1!\ \varepsilon_2!\ \ldots\ \varepsilon_\ell!} \quad ,$$

and if ℓ is sufficiently large, by

$$\log W = \text{const.} - \int \varepsilon \log \varepsilon \, dp_1 \ldots dp_n \quad ,$$

the sum being replaced by an integral.

For a stationary distribution ε is constant and the probability W a maximum. However, if the distribution ε depends on the state variables it can be shown that the expression log W does not possess an extremum. Hence, Einstein assumed that

> if we examine the N systems considered during an arbitrary time interval we can be sure that the state distribution (and therefore also W) vary continuously in time and we must therefore assume that state distributions which are less probable are always followed by more probable ones. That is, W always increases until the state distribution becomes constant and W a maximum (37).

From this proposition Einstein argued that if ε and ε' denote the state distribution at a time t and a later time t' the inequality

$$-\log \varepsilon' \geq \log \varepsilon \qquad (29)$$

holds.

The quantity log W is very similar to Boltzmann's H function and the assumption that follows is the content of Boltzmann's theorem[38]. Hence, as we mentioned before, Einstein's purpose of eliminating kinetic theory in the derivation of the principles of thermodynamics was not wholly successful. As Klein comments Einstein's assumption "was far from adequate as a basis for understanding the puzzle of irreversibility"[39].

2.8) Before proving the second law of thermodynamics by proving the impossibility of a perpetual motion machine of the second kind, Einstein applied the results found above to a particular case. Let us consider an infinite number of subsystems σ_1, σ_2, ... that form an isolated system. In principle these systems may only interact adiabatically. The state distribution for the subsystem σ_1 is given by

$$dW_1 = \exp\{c_1 - 2hE_1\} \int_g dp_1^{(1)} \dots dp_n^{(1)} \quad ,$$

where the index 1 refers to the subsystem σ_1. The state distribution for the other subsystems are given by similar relations. The state distribution for the complete system dW is therefore given by

$$dW = dW_1 dW_2 \dots = \exp\{\Sigma(c_\nu - 2h_\nu E_\nu)\} \int_g dp_1 \dots dp_n \quad ,$$

where the sum extends to all the subsystems and the integral to an arbitrarily small region g.

Let us now assume that the subsystems interact arbitrarily being the whole system isolated, until thermal equilibrium is attained. The state distribution will now be given by

$$dW' = dW_1' \, dW_2' \dots = \exp\{\Sigma(c_\nu' - 2h_\nu' E_\nu')\} \int_g dp_1 \dots dp_n \quad .$$

Hence,

$$\varepsilon = N \exp\{\Sigma(c_\nu - 2h_\nu E_\nu)\} \quad ,$$

$$\varepsilon' = N \exp\{\Sigma(c_\nu' - 2h_\nu' E_\nu')\} \quad ,$$

and using equality (29)

$$\sum(2h_\nu{}'E_\nu{}' - c_\nu{}') \geqq \sum(2h_\nu E_\nu - c_\nu) \quad .$$

Since the quantities inside the parentheses are, except for a constant, the entropies, Einstein concluded that

$$S_1' + S_2' + \ldots \geqq S_1 + S_2 + \ldots \quad . \tag{30}$$

2.9) Finally, Einstein considered an isolated system composed by several subsystems: the heat reservoir W, the machine M and some other subsystems Σ_1, Σ_2, ... which may interact with M adiabatically and have, relatively infinite energy compared to that of the machine. All the subsystems are in a stationary state.

The machine M follows an arbitrary cycle in a way that the state distributions of the subsystems Σ_1, Σ_2, ... may vary by adiabatic interactions and produces a certain amount of work while receiving a certain quantity of heat Q from W. The change in entropy experienced by W is $-Q/T$, while the entropy of M does not change since the process is cyclic. Since the subsystems Σ_1, Σ_2, ... interacted adiabatically, they did not change their entropy either. Hence.

$$S' - S = -\frac{Q}{T} \quad ,$$

and using inequality (30)

$$Q \leqq 0 \quad .$$

"This relation expresses the impossibility of the existence of a perpetuum mobile of the second kind"[40].

In section 4 we shall comment on how, from a modern point of view, one may prove the second law of thermodynamics.

3. THE SCALE OF ATOMIC MAGNITUDES

3.1) In March of 1904 Einstein sent for publication his third paper on the foundations of statistical mechanics under the title "On the General Molecular Theory of Heat", where he presented some complementary results(10). The paper starts with a simple derivation of an expression for the entropy which we shall discuss presently and a derivation of the second law of thermodynamics which we will not go into since it essentially repeats the argument given in the 1903 paper. The last three sections of the paper, dealing with the general meaning of the constant k and an application of a fluctuation formula to black-body radiation form the most interesting part of the paper and will occupy our attention in this section. As remarked by Kelin(41), this is the first paper that shows the unique qualities that characterize Einstein's mature science.

3.2) The derivation presented by Einstein of an expression for the entropy holds for a system that can absorb energy only in the form of heat. From the definition of entropy and equations (18) and (22) he found that

$$S = \int \frac{dE}{T} = 2k \int \frac{\omega'(E)dE}{\omega(E)} = 2k \log [\omega(E)] \qquad , \qquad (31)$$

omitting the constant of integration. For a general derivation he remitted the author to the section of the 1903 paper we have discussed in section 2.6.

3.3) The meaning of the constant k was made evident by Einstein through the following argument. Consider a system described by the state variables $x_1, y_1, z_1, \ldots x_n, y_n, z_n, \xi_1, \eta_1, \zeta_1, \ldots, \xi_n, \eta_n, \zeta_n$ which denote the rectangular coordinates and corresponding velocities of the atoms that form the system. If the system is in thermal contact with a system that acts as a heat bath at temperature T_0, its state distribution is given, recalling Eqs. (19) and (22), by

$$dW = C \exp\left\{-\frac{E}{2kT_0}\right\} dx_1 dy_1 dz_1 \ldots d\xi_n \, d\eta_n \, d\zeta_n \qquad , \qquad (32)$$

where C is a constant.

The mean kinetic energy of the ν-th particle is then found to be given by

$$\overline{L}_\nu = 3kT_0 \quad .$$

On the other hand, using the ideal gas law

$$pv = RT \quad ,$$

where $R = 8.31 \times 10^{-7}$ erg/deg and from kinetic theory the relation

$$pv = \frac{2}{3} N\overline{L} \quad ,$$

where $N = 6.4 \times 10^{23}$ (Einstein quotes the value given by O.E. Meyer) is Avogadro's number and $\overline{L}$ is the mean free energy of any molecule, it follows that

$$N \cdot 2k = R \quad .$$

Using the values mentioned for the constants N and R,

$$k = 6.5 \times 10^{-17} \text{ erg/deg.}$$

3.4) By integrating expression (32) over all values of the state variables such that the energy of the system is found to be between E and E + dE, the probability dW that the energy of the system is found between the mentioned limits is

$$dW = C\, e^{-\frac{E}{2kT}} \omega(E)\, dE \quad .$$

The average energy $\overline{E}$ of the system is then found to be given by

$$\overline{E} = \int_0^\infty C\, e^{-\frac{E}{2kT}} \omega(E)\, dE \quad .$$

From this equation and the normalization condition for the probability distribution one obtains

$$\int_0^\infty (\overline{E} - E)e^{-\frac{E}{2kT}}\omega(E)\ dE = 0$$

and taking the derivative of this expression with respect to T

$$\int_0^\infty \left(2kT^2 \frac{d\overline{E}}{dT} + \overline{E}E - \overline{E}^2\right) e^{-\frac{E}{2kT}}\omega(E)\ dE = 0 \qquad .$$

Evaluating the integral

$$2kT^2 \frac{d\overline{E}}{dT} = \overline{E^2} - \overline{E}\,\overline{E} \qquad .$$

The instantaneous value of the energy E differs from the average value $\overline{E}$ by an amount which Einstein called the "energy vacillation" ε (now know as the energy fluctuation) in such a way that

$$E = \overline{E} + \varepsilon \qquad .$$

With the help of the last two equations, Einstein found that the mean energy fluctuation $\overline{\varepsilon^2}$ is given by

$$\overline{\varepsilon^2} = 2kT^2 \frac{d\overline{E}}{dT} \qquad . \tag{33}$$

As Einstein remarked this result is especially interesting because "the absolute constant k thus determines the thermal stability of the system ... and because it no longer contains any more quantities reminiscent of the underlying hypotheses of the theory"[(42)].

3.5) In the final section of this paper Einstein looked for an independent determination of the universal constant k from the determination of the energy fluctuations of a system using equation (33). However, "in the present state of our knowledge ... this does not apply". Indeed, for only one sort of physical system can we presume from experience that an energy fluctuation occurs. That system is empty space filled with thermal radiation".[(43)]

Thermal radiation in equilibrium with the cavity which contains it is a system where fluctuations are negligible unless the linear dimensions of the cavity are of the order of magnitude of the wavelength at which the radiation spectrum has its maximum λ_m. In this case, Einstein argued, energy fluctuations are comparable to the energy itself; that is

$$\overline{\varepsilon^2} = \overline{E}^2 \quad .$$

Taking into account Stefan-Boltzmann's law which states that

$$\overline{E} = cvT^4 \quad ,$$

where v is the volume of the cavity and $c = 7.06 \times 10^{-5}$ erg/cm^{3}deg^4 is a constant, it follows, with the help of equation (68) that

$$(v)^{1/3} = 2 \left(\frac{k}{c}\right) \frac{1}{T}$$

$$= \frac{0.42}{T} \quad , \qquad (34)$$

where the value of k found before was used.

This last quantity, $(v)^{1/3}$, must be the wavelength where the energy spectrum has its maximum. On the other hand, this quantity λ_m was known from experiments to be given by

$$\lambda_m = \frac{0.293}{T} \quad .$$

Einstein concluded that

> not only the type of dependence of the temperature but also the order of magnitude of λ_m obtained by means of the universal molecular theory can be correctly determined and I feel this agreement should not be ascribed to chance, given the great generality of our assumptions. (44)

By the time Einstein wrote this paper he had already read Planck's papers on black-body radiation(45). Kuhn(46) suggests that after discovering Eq. (34), Einstein had begun to seek a black-body law of his own, but had quickly encountered a paradox, that was discussed in a paper published the following year[47]. This paper discusses Planck's radiation law, but not Planck's theory; this was left to another paper published in 1906[8] where he proved that Planck's theory rested on a quantum hypothesis.

Fluctuations had already been encountered by Boltzmann and Gibbs, however, they argued that one could never expect to observe such behavior[48]. Einstein, on the contrary, instead of applying the theory he had developed to the realm of thermodynamics, went on to look for new extensions in fluctuation phenomena. The following year he found another system where fluctuations could be observed: small particles suspended in a liquid[6].

4. FINAL COMMENTS

As we mentioned in the introduction, in 1902 J.W. Gibbs published his Principles in Statistical Mechanics where he laid down the foundations of the subject. Gibbs had been thinking about the problem at least since 1889 when he announced a "A short course on the a priori Deduction of Thermodynamic Principles from the Theory of Probabilities" for the academic year 1889-1890 at Yale University[49].

What Gibbs attempted in his book was to construct a theory of an ensemble of similar mechanical systems. As he stated in the preface, for such an ensemble of systems he pursued "statistical enquiries as a branch of rational mechanics"[50]. However, the relation of this collection to a single system (the one in the laboratory) was not stated explicitly. This was left to Tolman who developed Gibbs' ideas introducing the concept of a representative ensemble of systems and arguing that the hypothesis of equal a priori probabilities was essential in order to construct the theory[29]. This hypothesis, Tolman added, can only be justified by the agreement of the theoretical and experimental results. Gibbs' methodological point of view is the analogy between the properties he finds for the canonical ensemble and the properties of a thermodynamic system.

Einstein, as we saw in section 2 took a different point of view. From the beginning he stated the purpose of deriving the laws of thermodynamics from mechanical and probabilistic considerations. He assumed that any thermodynamic quantity could be calculated as the time average of a suitable function (Eq. (3)), and hence, that the object of the theory was to calculate these averages. Through an ergodic hypothesis these averages could be calculated by averages over and ensemble of systems similar to the one under study.

Einstein's approach can be profitably used as a starting point for a discussion on the foundations of classical statistical mechanics in an introductory course on the subject*. In order to do so, we have supplemented Einstein's exposition wherever we thought it useful. An example is the discussion of the ergodic hypothesis and the use of averages over the ensemble of systems instead of time averages.

As we noted above, Einstein's proof of the second law was not successful. Noting, from Eqs. (20) and (31) that the quantity ψ is equal to the entropy with a minus sign, one could try to prove the following theorem:

(a) If the system can be considered as formed by two subsystems, each one with well defined values of energy then

$$\psi = \psi_1 + \psi_2 \quad ,$$

where the subindices 1,2, refer to each one of the subsystems.

(b) The quantity ψ is continuous and differentiable and monotonically decreasing as a function of the energy.

(c) In equilibrium, the values taken by the parameters that define the quantity ψ (energy, volume, number of particles) are those that minimize ψ over the set of constrained states.

The content of this theorem is the second law of thermodynamics as postulated by Callen[51]. A rigorous proof may be constructed from the one found in Ruelle's book on statistical mechanics[52], while a proof more adequate for an introductory course may be constructed by assuming that the energy E and the quantity ψ are both proportional to the number of state variables.

*One of us (R.R.S.) has used the contents of this discussion in an undergraduate course on statistical mechanics during the past two years.

Finally we would like to stress the importance of the papers we have discussed as the beginning of Einstein's research program on quantum theory. We agree completely with Kuhn when he states that

> What brought Einstein to the black-body 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 black-body law even if Planck had never lived. (53)

Einstein's mastery of statistical mechanics and fluctuation phenomena were to be the basic tools in this contribution to quantum theory.

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