

Gibbs, Einstein and the Foundations of Statistical Mechanics

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Abstract

It is generally accepted that, around the turn of the century, GIBBS and EINSTEIN independently developed two equivalent formulations of statistical mechanics. GIBBS' version is taken as genuine and rigorous, while EINSTEIN's, despite some features which are characteristic of him, is usually considered a not totally satisfactory attempt.

It will be shown in the present work that such a picture is oversimplified and requires further nuancing. In fact, there are significant differences, with important implications which have not been sufficiently examined, between the two formulations. Several issues relating to the impact of the two versions will also be addressed.

1. Introduction

Between 1902 and 1904, ALBERT EINSTEIN published three articles in *Annalen der Physik* which were little read but contained a proper formulation of statistical mechanics¹. It was an independent presentation of what JOSIAH WILLARD GIBBS had introduced in his *Elementary Principles in Statistical Mechanics*, first published in 1902².

GIBBS' original method is clearly explained, in full rigour and cogency, in his short book. However, there is no equivalent version of EINSTEIN's formulation. Although his three 1902-1904 papers enable the theory to be reconstructed formally, this task is not easy, as will be shown later. There is in fact no manual containing EINSTEIN's version in a form directly comparable to GIBBS'.

Moreover, in EINSTEIN's case, a methodologically rigorous analysis of his contribution practically obliges the reader to conclude that the period of elaboration of the theory can only be considered properly closed in 1905, when he completed his work with the publication of his theory on Brownian motion³. With this theory EINSTEIN tried to prove theoretically the reality of molecules; this was key to his formulation of statistical mechanics, for it was a theory based on the description of thermodynamic systems from their constituent molecules, as was supposed at the time⁴:

My major aim in this was to find facts which would guarantee as much as possible the existence of atoms of definite size. In the midst of this I discovered that, according to atomistic theory, there would have to be a movement of suspended microscopic particles open to observation, without knowing that observations concerning the Brownian motion were already long familiar.

Despite the unevenness of the two versions, they are usually understood as two equivalent formulations of the same theory: classical statistical mechanics of equilibrium. GIBBS' is normally considered the definitive form, thanks to its detail; EINSTEIN's is instead taken, when not completely ignored, as a not fully successful attempt to reach similar conclusions by means of more intuitive, and less rigorous, arguments. The absolute independence of both approaches was never questioned.

EINSTEIN himself undoubtedly contributed to his work being valued below GIBBS', as he made slighting comments about his own contributions to statistical mechanics. PAUL HERTZ criticised in 1910 certain assumptions about the behaviour of the absolute

¹ EINSTEIN (1902), (1903) and (1904).

² GIBBS (1902). This is an extremely difficult book, due to its level of abstraction and subtlety. This was acknowledged by POINCARÉ in the 1904 St. Louis Congress, and by EINSTEIN in a letter to BESSO in 1918; see SOPKA (1986), 286 and SPEZIALI (1979), 75, respectively.

³ EINSTEIN (1905).

⁴ EINSTEIN (1949), 47.

temperature in EINSTEIN's formulation⁵. EINSTEIN then wrote a short reply in which he explicitly acknowledged the superiority of GIBBS' formulation over his own⁶.

Despite this opinion of EINSTEIN's, whose precise meaning I will refine later, there can be no doubt that there are significant differences between his formulation and GIBBS', some of which have already been noted by other authors⁷. But the subject is not exhausted; on the contrary, I think it demands further attention. I shall thus try to prove in the present paper that a comparative analysis of the objectives, methods, results and consequences of both formulations clearly shows that there are relevant points not previously considered, and also gives a more accurate view of the generally assumed equivalence between the theories of GIBBS and EINSTEIN.

2. Objectives and premises

GIBBS published his *Elementary Principles* in 1902, the year before his death. In his sixties at the time, he enjoyed an international reputation based on his contributions to thermodynamics 25 years earlier. He had been elected a member of scientific institutions and honoured in various countries. The culmination of his life's work was the 1901 award of the Copley Medal by the Royal Society of London, perhaps the highest distinction a scientist could be given at the time⁸.

So GIBBS presented his elaborated formulation of statistical mechanics after 30 years of work of the highest quality on thermodynamics, vector analysis, quaternion algebra and the electromagnetic theory of light, amongst other topics. He is considered one of the three North American scientists who, towards the end of the 19th century, developed research work which was the equal of that of their most outstanding European colleagues⁹.

EINSTEIN began to formulate his ideas on statistical mechanics in 1902, in his early twenties and with almost no experience in presenting research work; he was then a mere beginner, of no particular excellence either as student or researcher, who was trying to settle down both personally and professionally. He had had no time as yet to acquire the necessary skills and maturity to draw up articles which could open new horizons in a subject which had consistently resisted the efforts of JAMES C. MAXWELL and

⁵ HERTZ (1910).

⁶ EINSTEIN (1911), 176; English translation in BECK (1993), 250.

⁷ See, for example, MEHRA (1975); PAIS (1982), chap. 4; KLEIN (1982); BARACCA & RECHTMAN (1985); DARRIGOL (1988), 32-41; NAVARRO (1991), 40-42. See also "Editorial note: Einstein on the foundations of statistical physics", in STACHEL (1989), 41-55.

⁸ GIBBS' official biography is by WHEELER (1970). An abridged account of his life and scientific work can be found in NAVARRO (1997).

⁹ The other two were H. A. ROWLAND and A. A. MICHELSON; see KEVLES (1979), 25-44.

LUDWIG BOLTZMANN, amongst others. Nor had EINSTEIN had the opportunity to benefit from discussions with prestigious members of the scientific community.

These considerations already show an important initial difference between GIBBS and EINSTEIN, at least regarding personal circumstances. But it was not just their academic status which characterised their essential difference: in their search for a mechanistic explanation of thermodynamics, they did not follow exactly parallel paths.

2.1 GIBBS

Thermodynamics is essentially concerned with the explanation of the behaviour of certain macroscopical systems by means of fundamental laws directly induced from experience. This aim is however compatible with different basic conceptions. In particular GIBBS habitually understood thermodynamics as a theory of the properties of matter in equilibrium. This was not a widespread point of view in 1873, when he wrote his first papers on thermodynamics, and was quite distinct from the conceptions of RUDOLF CLAUSIUS and WILLIAM THOMSON, for whom thermodynamics was the mechanical theory of heat¹⁰. Obviously their view enabled a more natural relationship between thermodynamics and the kinetic theory of gases to be established. This attempt to explain the behaviour of gases from the mechanical description of their molecules reached its high point in the last quarter of the 19th century. The theory of probability appeared as a suitable mathematical tool for relating the thermodynamic properties of gas to that mechanical description¹¹.

In spite of numerous successful results, especially after MAXWELL and BOLTZMANN's contributions, the kinetic theory never enjoyed general acceptance, due to important conceptual difficulties hardly ever surmounted. Some of these were fundamental such as the supposedly molecular constitution of matter, which was hardly anything more than a working hypothesis at that time; or its inability to reconcile the irreversibility of thermodynamical processes to the time reversibility of the molecular evolution equations given by Newtonian mechanics. Other difficulties were experimental, such as the marked discrepancy between the measured heat capacity of polyatomic gases and the corresponding theoretical predictions.

Although it is possible to find in GIBBS' formulation a number of formal analogies with the kinetic theory of gases, a detailed analysis unambiguously reveals that the differences are marked and deep, as they are to a large extent due to matters of principle. For example, in GIBBS' book molecules are not a working hypothesis, and the explanation of thermodynamics in terms of molecules is not the ultimate goal. Statistical mechanics, the name GIBBS gave his new approach, was born with quite different

¹⁰ See KLEIN (1983), especially 149–150.

¹¹ BRUSH (1976).

explicit objectives: the generalisation of Newtonian mechanics to conservative systems with an arbitrary, though finite, number of degrees of freedom.

Given that GIBBS' method pursues essentially a generalisation of Newtonian mechanics, one may candidly wonder how probability occurs in such a context: is it an additional hypothesis or is it a consequence of the new approach? The answer to this question shows a fundamental trait of GIBBS' formulation, clearly different from EINSTEIN'S: the probabilistic ideas in GIBBS are neither hypotheses nor results, but are rather part of the data of the mechanical problem, posed in non-usual terms. This point needs further clarification.

Large-scope generalisation of Newtonian mechanics must also be applicable to the analysis of complex systems such as macroscopical ones. In these, due to elementary cogency, one can not assume that an exact determination of all the mechanical variable values at a given instant is possible. A reasonable way to proceed would be to pose the problem on the basis of initial statistical information, depending on which macroscopical situation was involved. GIBBS initially proposed the study of the properties of an ensemble formed by a large number of independent mechanical systems, all of them of identical nature but each of them with its own initial conditions which followed a probability distribution law. This law characterises the ensemble and is part of the mechanical problem's data; this is why a significant part of the mechanical properties inferred for the behaviour of the ensemble must necessarily be of statistical nature¹².

The connection with thermodynamics appears later in the form of certain analogies which spring from the application of the general theory, with some approximations, to systems with many degrees of freedom (with many particles, in mechanistic jargon)¹³:

The laws of thermodynamics, as empirically determined, express the approximate and probable behaviour of systems of a great number of particles, or, more precisely, they express the laws of mechanics for such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results. The laws of statistical mechanics apply to conservative systems of any number of degrees of freedom, and are exact. This does not make them more difficult to establish than the approximate laws for systems of a great many degrees of freedom (...). The laws of thermodynamics may be easily obtained from the principles of statistical mechanics, of which they are the incomplete expression.

GIBBS' subtlety in achieving the maximum generality in his formulation must be stressed. He does not assume that thermodynamic systems are made up of molecules.

¹² If one wishes to operate with a continuous distribution of initial conditions, what obviously simplifies the analytical treatment of the problem, then the ensemble may not be constituted by a finite number of systems; see GIBBS (1902), footnote p. 5.

¹³ *Ibid.*, vi–vii.

He rather operates with abstract mechanical systems, and detects that thermodynamic systems obey the same laws as many particle mechanical systems, after a few reasonable approximations are made. But it is not possible to go coherently beyond the demonstration of the existence of analogies between the two types of system. This is the way GIBBS frees the validity of his results from molecular vicissitudes, as his formulation must only suffer from any incorrect use of logic, mechanical laws or mathematics. Nothing better than his own words to clarify definitively the objectives of his statistical approach¹⁴:

Moreover, we avoid the gravest difficulties when giving up the attempt to frame hypotheses concerning the constitution of material bodies, we pursue statistical inquires as a branch of rational mechanics (...) Even if we confine our attention to the phenomena distinctively thermodynamic, we do not escape difficulties in as simple a matter as the number of degrees of freedom of a diatomic gas. It is well known that while theory would assign to the gas six degrees of freedom per molecule, in our experiments on specific heat we cannot account for more than five. Certainly, one is building on an insecure foundation, who rests his work on hypotheses concerning the constitution of matter.

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.

2.2 *EINSTEIN. Comparison with GIBBS*

EINSTEIN's formulation, in sharp contrast with GIBBS', can be considered to follow faithfully the pathway opened up by the kinetic theory of gases. His declared objective is to infer the laws of thermodynamics from those of Newtonian mechanics. To this end, EINSTEIN needs certain additional hypotheses on the nature and behaviour of thermodynamic systems. For example, the system needs to be formed by a very large number of molecules, the introduction of a thermodynamic probability must be adequately justified, the result of a measurement must be able to be identified with a time average, equality needs to be proved between this time average and an average calculated over the constant energy hypersurface, etc.¹⁵

¹⁴ *Ibid.*, vii–viii.

¹⁵ Of course, the kinetic theory of gases also requires certain hypotheses of a similar nature. By way of example, see BOLTZMANN's ergodic hypothesis, close to EINSTEIN's, in VON PLATO (1991), especially 76–83.

One of the main characteristics of EINSTEIN's formulation is precisely this unavoidable necessity of additional hypotheses. It is the high cost of his daring to try to reduce completely thermodynamics to mechanics, as he makes crystal clear at the beginning of his 1902 article¹⁶:

Great as the achievements of the kinetic theory of heat have been in the domain of gas theory, the science of mechanics has not yet been able to produce an adequate foundation for the general theory of heat, for one has not yet succeeded in deriving the laws of thermal equilibrium and the second law of thermodynamics using only the equations of mechanics and the probability calculus, though Maxwell's and Boltzmann's theories came close to this goal. The purpose of the following considerations is to close this gap. At the same time, they will yield an extension of the second law that is of importance for the application of thermodynamics. They will also yield the mathematical expression for entropy from the standpoint of mechanics.

How does probability arise in EINSTEIN's formulation if it is only intended to apply Newtonian mechanics to an aggregate of particles? The role of probability is essential here, and yet is completely different from its role in GIBBS' formulation. Now, it is not just a datum accounting for the distribution of possible initial conditions of the problem, but rather is introduced as an appropriate tool to describe thermodynamic systems in microscopic terms. The precise description of each situation (i.e. of each thermodynamic state) is now characterised by a probability distribution: the probability that each microscopic state has of being a realisation of the given macroscopic state.

For all these reasons, the precise definition of what is to be understood by thermodynamic probability, and its actual evaluation in different situations (isolated systems, systems in thermal equilibrium, etc.), are essential points in EINSTEIN's formulation, where the introduction *ab initio* of hypotheses which justify the adequacy of the statistical approach is absolutely necessary¹⁷. It was also necessary to add an ingredient common to all attempts at microscopic descriptions: the thermodynamic system had to be formed by a large number of molecules, for otherwise it would not be possible to arrive properly at the concept of absolute temperature¹⁸.

So the differences between the two formulations, as regards their objectives, are enormous. GIBBS' generalisation of Newtonian mechanics, with the corresponding approximations, creates a framework which is formally analogous to that of thermodynamics. His formulation follows an axiomatic approach against which one can only argue

¹⁶ EINSTEIN (1902), 417; English translation in BECK (1989), 30.

¹⁷ Thermodynamic probability, the relationship between the measured values of the physical quantities and time averages, and the ergodic hypothesis appear in §2 of EINSTEIN (1903). Certain clarifications on these ideas can be found in BARACCA & RECHTMAN (1985), 698-703; DARRIGOL (1988), 35-36; STACHEL (1989), 47-55.

¹⁸ EINSTEIN (1902), 417-422; English translation in BECK (1989), 30-36. See also EINSTEIN (1903), 170-176; English translation in BECK (1989), 48-55.

on the basis of inference error from the premises, thereby giving it very high standards of methodological rigour. This formulation is however confined to the establishment of analogies between two different frameworks (mechanical and thermodynamic), and therefore its reductionist value is dubious.

EINSTEIN, by means of the above-mentioned additional hypotheses, does indeed seek a true reduction of each thermodynamic state to the corresponding mechanical one¹⁹. The deduction of thermodynamic laws and properties, directly from a mechanistic description of the behaviour of molecules, results in a clearer visualisation of the physical situation. The difficulties are rooted in finding an adequate justification for those hypotheses; it cannot be said that EINSTEIN accomplished this satisfactorily.

3. Methods and results

Given the great disparity of premises and objectives, in addition to the different scientific background of their authors, it is not surprising that GIBBS' and EINSTEIN's formulations followed such different lines of development, though a narrower view of the methods used and the results obtained might suggest a full equivalence between the two approaches, at least from an operational viewpoint. Without going into a comprehensive analysis, I will try to show certain characteristics of the two approaches which will clearly display deep differences, some of which have not yet, in my opinion, received the attention they deserve.

3.1 GIBBS

GIBBS essentially bases his formulation on the canonical ensemble, which describes situations analogous to thermal equilibrium. He makes a very restrictive use of the microcanonical ensemble, which is the most appropriate for dealing with the treatment of isolated systems in equilibrium²⁰. Near the beginning of chapter IV of his book, GIBBS introduces the canonical distribution in the form

$$P = e^{\frac{\psi - \epsilon}{\theta}} \quad (1)$$

P is the so called *coefficient of probability*, whose logarithm is termed *index of probability*; ψ is a constant which is determined by the condition that the integral of P over

¹⁹ In fact, to a set of mechanical states: the set of all the states which are possible microscopic realisations of the given macroscopic state. As will be shown below, this can not be fully identified with GIBBS' ensemble.

²⁰ For modern classical and quantum definitions of the various types of ensembles describing systems in thermal equilibrium, and also for the equivalence of these ensembles, see BALESCU (1975), chap. 4.

the entire phase space considered be equal to 1; ε is the system energy; and θ is a characteristic constant called the *modulus* of the distribution. θ must be positive to ensure the normalisation of P , since ε is positive due to the conventional value zero adopted for the minimum energy.

But from (1) is not inferred from any considerations about thermal equilibrium, which plays no role whatsoever *a priori*. GIBBS argues with remarkable originality: he assigns protagonism to the canonical distribution by virtue, he says, of its privileged mathematical properties, and because, being exponential, each one of the parts of a set of independent systems will then satisfy the same distribution law as the whole²¹:

The distribution [P] (...) seems to represent the most simple case conceivable, since it has the property that when the system consists of parts with separate energies, the laws of the distribution in phase of the separate parts are of the same nature, a property which enormously simplifies the discussion, and is the foundation of extremely important relations to thermodynamics.

Perhaps oversynthesising, it can be said that GIBBS' formulation as contained in his book essentially consists in proving a number of general properties of phase space and of the distributions associated with statistical equilibrium (chapters I, II, III, IV, VI and XI), and in obtaining from the canonical distribution some average values and relations amongst them (chapters V, VII, VIII and IX). Some of these results are extended to the microcanonical ensemble in chapter X and to the grand-canonical ensemble in chapter XV. This is all done by abstract reasoning, so far as the physics is concerned, with sound mathematical rigour following a purely deductive line of development.

GIBBS also addresses, albeit in passing, the question of the evolution of systems and ensembles over long periods of time, as well as some properties of statistical equilibrium. Finally, he points to a number of formal analogies between certain elements and results of the theory thus constructed and those of thermodynamics. I will come back to this later.

It is indispensable for a comparison with EINSTEIN to comment on GIBBS' treatment of fluctuations, which he calls *anomalies*. He refers to them for the first time in relation to the fluctuations of energy in thermal equilibrium²²:

Of special importance are the anomalies of the energies, or their deviations from their average values. The average value of these anomalies are of course zero. The natural measure of such anomalies is the square root of their average square.

After a detailed analysis of the expressions obtained for the fluctuations of the energies (total, kinetic and potential) GIBBS reaches the conclusion that, in general, they are not really relevant as regards their possible detection in real systems²³:

²¹ GIBBS (1902), 33.

²² *Ibid.*, 71-72.

²³ *Ibid.*, 74.

It follows that to human experience and observation (...), when the number of degrees of freedom is of such order of magnitude as the number of molecules in the bodies subject to our observation and experiment, $\varepsilon - \bar{\varepsilon}$, $\varepsilon_p - \bar{\varepsilon}_p$, $\varepsilon_q - \bar{\varepsilon}_q$ would be in general vanishing quantities, since such experience would not be wide enough to embrace the more considerable divergencies from the mean values, and such observation not nice enough to distinguish the ordinary divergencies. In other words, such ensembles would appear to human observation as ensembles of systems of uniform energy (...).

So, even though GIBBS' book contains explicit expressions for the fluctuations of the energies around their mean values in the canonical ensemble, we are immediately cautioned that such fluctuations would be irrelevant in systems with a large number of degrees of freedom (of the order of AVOGADRO's number), as they would be unobservable²⁴. Therefore, fluctuations merit no particular attention in GIBBS' book.

An additional observation. In the most recent quotation above from GIBBS, as on other occasions, explicit reference is made to the molecules of a material body. It should not be inferred from this that the theory presupposes the molecular constitution hypothesis. I have already stressed that, as is made clear in the prologue of *Elementary Principles*, such a hypothesis is explicitly relinquished from the very beginning. What GIBBS actually says is that fluctuations are irrelevant in a general mechanical system with a number of degrees of freedom of the order which the molecular theory, not his theory!, assigns to thermodynamic systems; and nothing else.

In order to compare his contributions with EINSTEIN's, it is worth pointing out that the generalisation proposed by GIBBS requires a finite number, no matter how large, of degrees of freedom. He considers this a sufficient reason to anticipate that the application of his statistical approach to electromagnetism will not be viable²⁵:

The phenomena of radiant heat, which certainly should not be neglected in any complete system of thermodynamics, and the electrical phenomena associated with the combination of atoms, seem to show that the hypothesis of systems of a finite number of degrees of freedom is inadequate for the explanation of the properties of bodies.

²⁴ GIBBS of course stresses that, under certain conditions and for well-determined values of the characteristic parameters of the distribution, energy fluctuations behave in a peculiar manner, since the mean values of the total and the potential energies as functions of the absolute temperature are not well determined in those cases. See the example quoted in the footnote of GIBBS (1902), 75.

²⁵ *Ibid.*, 167.

3.2 EINSTEIN. Comparison with GIBBS

EINSTEIN takes as his starting-point the microcanonical distribution, i.e. that associated with an isolated system, a familiar abstraction in Newtonian mechanics, whose only constant of motion is energy. Thermal equilibrium is the state eventually reached by an isolated system made up of two weakly interacting subsystems; one of them (the *thermometer*) having much less energy than the other. The analysis of the distribution of states of the *thermometer* leads to canonical distribution, after introducing absolute temperature as a quantity characteristic of thermal equilibrium. At the same time the so-called “zero principle of thermodynamics” is also obtained in the form²⁶:

Equality of the quantities h [“the temperature function”; $1/h$ is proportional to the absolute temperature] is thus the necessary and sufficient condition for the stationary combination (thermal equilibrium) of two systems. From this follows immediately: If the systems Σ_1 and Σ_2 , as well as Σ_1 and Σ_3 , can be combined in a stationary fashion mechanically (in thermal equilibrium), then so can Σ_2 and Σ_3 .

The particularisation of the canonical distribution to the case in which the *thermometer* is a single molecule of gas, and the rest constitutes the large system in interaction with the first, enables EINSTEIN to infer MAXWELL’s distribution law for ideal gases²⁷.

I am not going to consider here the differences between EINSTEIN’s contributions of 1902, 1903 and 1904; this has already been covered by various authors²⁸. However I do wish to mention one question regarding the introduction of absolute temperature in an isolated system. It is a curious difficulty which, though in a clearly different form, also arises in GIBBS’ formulation: the impossibility of guaranteeing, in the microcanonical ensemble, an adequate definition of the absolute temperature of a small part of an isolated system in thermal equilibrium with the rest, when the subsystem has fewer than three degrees of freedom.

Indeed, in the first of his foundation papers in 1902, EINSTEIN already stresses that it is only possible to properly introduce absolute temperature in systems with more than two degrees of freedom²⁹. He must have been dissatisfied with his approach, for he evades the difficulty in 1903 with a more intuitive argument: he replaces the abstract system with an ideal gas. Since this is formed by molecules it guarantees three degrees of freedom for the minimum subsystem (one molecule). So the problem arises for abstract

²⁶ EINSTEIN (1902), 427; English translation in BECK (1989), 40.

²⁷ *Ibid.*, 428; 42 in the English translation.

²⁸ More or less detailed analysis of these three foundation papers by EINSTEIN can be found, e.g., in MEHRA (1975); KLEIN (1982); PAIS (1982), chap. 4; BARACCA & RECHTMAN (1985). See also “Editorial note: Einstein on the foundations of statistical physics”, in STACHEL (1989), 41–55.

²⁹ EINSTEIN (1902), 423–424; English translation in BECK (1989), 36–38.

general systems, but disappears in thermodynamic systems made up of molecules. Very much EINSTEIN's style, I believe.

GIBBS came across the same difficulty, though in a different context. His axiomatic method led him to the conclusion that in a system with less than three degrees of freedom, it is not guaranteed that the volume inside the hypersurface $\varepsilon = \text{constant}$ be a continuously increasing function of ε ³⁰. This implies that the continuous increase of entropy with energy is not guaranteed, either; nor is, therefore, the positivity of absolute temperature³¹.

This difficulty is certainly insurmountable if one is dealing with abstract systems³². It however disappears when a thermodynamic system like an ideal gas is specified. In GIBBS' case, given that he is considering a general formulation, it is not possible to ignore completely the pathology in the microcanonical ensemble. Nevertheless, since the American physicist's star formalism is the canonical one, the problem does not arise, since in this case, it is recalled, absolute temperature is not obtained but is introduced as a characteristic numerical datum which must be positive in order to assure the normalisation of the probability distribution.

The above difference is remarkable and representative. While EINSTEIN gets rid of the possibility of negative temperatures by disregarding the general case to specifically concentrate on ideal gases, exactly the opposite happens with GIBBS: he does not meet the difficulty in abstract when he operates with canonical formalism, but only when he considers, in the penultimate chapter of his book, an isolated system to show the "thermodynamic analogies" offered by his approach.

The differences in fluctuations were very clear from the moment when they were relegated by GIBBS due to their unobservability in actual practice. However, as is well documented, fluctuations were a powerful tool in EINSTEIN's hands not only to unveil the enigmas associated with the nature of thermal radiation, but also to understand a variety of problems such as Brownian motion, stochastic phenomena, critical opalescence, or the blue colour of the sky³³.

³⁰ GIBBS (1902), 87 and 96.

³¹ *Ibid.*, 172–175.

³² Today it is known that negative temperatures are characteristic of a system of 1/2 spin magnetic ions in the presence of an external magnetic field. This is a real system with that property which both EINSTEIN and GIBBS regarded as a hindrance to defining absolute temperature: the number of states compatible with a given energy does not continuously increase with this energy.

³³ On the role played by fluctuations in EINSTEIN's investigations see KLEIN (1982); and also "Editorial note: Einstein on critical opalescence" in KLEIN & KOX & RENN & SCHULMANN (1993), 283–285. Specially the fluctuations of linear momentum were a recurring issue for EINSTEIN hands between 1909 and 1916, and gave remarkable fruits in his investigations on the light quantum; see BERGIA & NAVARRO (1988) and references therein.

It is in chapter XIV of his *Elementary Principles*, “Discussion of thermodynamic analogies”, that the new approach is systematically applied by GIBBS to obtain important results on the foundation of thermodynamics³⁴:

If we wish to find in rational mechanics an *a priori* foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy.

These look the same as EINSTEIN’s objectives. But in GIBBS’ book neither the expression for absolute temperature or entropy, nor the laws of thermodynamics are obtained as consequences of a deductive line of argument based on a mechanistic approach. What is found in fact, after consideration of the above-mentioned approximations, is that a framework of relationships valid for the general systems studied, which is formally analogous to that of thermodynamics, can be deduced.

GIBBS, for example, does not define the absolute temperature of a general mechanical system *a priori*, then apply it to one with a large number of degrees of freedom. He rather applies his general approach to this particular category of systems, and only afterwards verifies that the *modulus* of the canonical distribution has in this case properties formally identical to the absolute temperature of thermodynamic systems. The same happens between the sign-reversed *index of probability* and entropy. The establishment of this analogy between two frameworks (general mechanical systems with the corresponding approximations and thermodynamic systems) constitutes the final result in GIBBS’ formulation so far as the explanation of thermodynamics in mechanistic terms is concerned.

This is not EINSTEIN’s way. In his formulation there is only one framework: that of the mechanical systems of aggregates of large numbers of molecules which *are* (not which are formally analogous to) the thermodynamic systems.

It is worth stressing a peculiarity concerning GIBBS’ formulation. Since temperature and entropy correspond in his approach to limits of certain quantities as the number of degrees of freedom becomes infinite, these quantities do not have to be defined uniquely in the general framework. Different starting criteria for the definitions of temperature and entropy may lead, and GIBBS actually proves that they do, to limiting expressions which correspond just as well with the results of thermodynamics³⁵:

We have thus precisely defined quantities, and rigorously demonstrated propositions, which hold for any number of degrees of freedom, and which, when the number of degrees of freedom (n) is enormously great would appear to human faculties as the quantities and propositions of empirical thermodynamics.

It is evident, however, that there may be more than one quantity defined for finite values of n , which approach the same limit, when n is increased indefinitely, and

³⁴ GIBBS (1902), 165.

³⁵ *Ibid.*, 169.

more than one proposition relating to finite values of n , which approach the same limiting form for $n = \infty$. There may be therefore, and there are, other quantities which may be thought to have some claims to be regarded as temperature and entropy with respect to systems of a finite number of degrees of freedom.

Amongst the possible choices, GIBBS gives preference to the formalism based on the canonical ensemble, due to the greater simplicity of this approach and given the equivalence of the results obtained with other ensembles in the limiting case of infinite degrees of freedom. For the comparison with EINSTEIN, a point which GIBBS stresses immediately after the preceding quotation should be mentioned³⁶:

The definitions and propositions which we have been considering relate essentially to what we have called a canonical ensemble of systems. This may appear a less natural and simple conception than what we have called a microcanonical ensemble of systems, in which all have the same energy, and which in many cases represents simply the *time-ensemble*, or ensemble of phases through which a single system passes in the course of time.

It is important to emphasise the extraordinary opportunity GIBBS had at this point to make some kind of reference to the ergodic hypothesis, as MAXWELL and BOLTZMANN had done before him. But it is also true that this was a controversial matter which could be skipped, at least so far as the analogies mentioned were concerned. Another point, relevant to the comparison I am making, can be seen in the preceding quotation where GIBBS admits (from a strictly mechanistic viewpoint, one can assume) the more natural character of the microcanonical ensemble, the permanent starting-point of the Einsteinian formulation.

EINSTEIN obtained direct expressions, not analogies!, for the temperature and entropy of a gas in terms of mechanical quantities associated to an aggregate of molecules, always building his construct on the concept, familiar in mechanics, of an isolated system³⁷. The additional hypotheses are described in a letter to his friend and confidant MICHELE BESSO, in which EINSTEIN explains that he has just submitted for publication a corrected and improved version of his 1902 paper³⁸:

Monday, after many revisions and corrections, I finally sent off my paper [EINSTEIN (1903)]. But now the paper is perfectly clear and simple, so that I am quite satisfied with it. The concepts of temperature and entropy follow from the assumption of the energy principle and the atomistic theory, and so does also the

³⁶ *Ibidem*.

³⁷ Expressions for temperature and entropy, as well as relationships containing a formulation of the second law of thermodynamics, are found in all three foundation articles by EINSTEIN. For temperature: (1902), §7 and (1903), §4. For entropy: (1902), §9; (1903), §6 and (1904), §1. Second law: (1902), §8; (1903), §9 and (1904), §2.

³⁸ Letter to BESSO, January (22?), 1903; English translation in BECK (1995), 7–8.

second law in its most general form, namely the impossibility of a *perpetuum mobile* of the second kind, if one uses the hypothesis that state distributions of isolated systems never evolve into more improbable ones.

In this letter, though, EINSTEIN does not explicitly specify all the hypotheses underlying his formulation. The last hypothesis he mentions serves rather to characterise thermal equilibrium in mechanical terms. But in his 1903 article, to which the letter alludes, he includes the idea of addressing the tendency to equilibrium, and introduces a property of averages which turns out to be crucial for reaching the constancy of the numerical values of the physical quantities in the equilibrium state³⁹:

If we now assume that a perceptible quantity is always represented by a time average of a certain function of the state variables $p_1 \dots p_n$, and that these state variables $p_1 \dots p_n$ keep on assuming the same systems of values with always the same unchanging frequency, then it necessarily follows from this condition, which we shall elevate to a postulate, that the averages of all functions of the quantities $p_1 \dots p_n$ must be constant; hence, in accordance with the above, all perceptible quantities must also be constant.

What does EINSTEIN mean when he mentions in the introduction of his 1902 paper a generalisation of the second law of thermodynamics?⁴⁰ “Extension of the second law” is the promising title of the extremely short final paragraph of the article: ten lines which do not live up to the expectations raised. EINSTEIN does not actually present there a more general formulation of the second law. What he underlines is that his inference, based on mechanics, is in fact more general than may appear at first sight: although a mechanistic system in terms of forces has been assumed, the results are independent of the specific types of forces associated with the potential representing external conditions (gravity, effect of the containers walls, etc.). I come to these matters below, where I will compare the degree of generality which can be attached to the two formulations. The subject presents certain subtleties.

4. Other questions on the two formulations

4.1 On the degree of generality

Although EINSTEIN’s 1903 paper can be considered a refinement of his 1902 one, it also includes some novelties particularly pertinent to a comparison with GIBBS. Certainly, EINSTEIN’s formulation of 1903 does not require any particular set of time evolution equations to remain valid. It is sufficient that such a set of equations respects a more general property, namely that a suitably defined “incompressibility”, in the phase

³⁹ EINSTEIN (1903), 171; English translation in BECK (1989), 49.

⁴⁰ EINSTEIN (1902), 433; English translation in BECK (1989), 47.

space of an aggregate of molecules, be preserved in the time evolution. The usual decomposition of energy into kinetic and potential is not required, either⁴¹.

This feature of EINSTEIN's formulation has been taken sometimes as a step toward ridding mechanics of the concept of force, under the direct influence of HEINRICH HERTZ⁴². Quite independently of this, though, one can say that EINSTEIN's formulation leads to greater generalisation than GIBBS' in the sense that GIBBS' is necessarily based on the Hamiltonian version of classical mechanics⁴³.

All the above is compatible with the simultaneous recognition of a higher degree of generality in GIBBS' formulation in another aspect: that no additional hypotheses on the nature and behaviour of complex systems are required. For this reason it could be more easily generalised and applied to other fields of physics, as did indeed happen, especially after the advent of quantum mechanics: magnetism is a good example. However, the additional hypotheses required by EINSTEIN's formulation, such as the ergodicity of thermodynamic systems, have still not been adequately justified.

4.2 *The equipartition of energy*

It is useful to compare the attitudes of GIBBS and EINSTEIN towards two of the most important problems in kinetic theory, tackled without much success towards the end of the 19th century: the inability of the energy equipartition theorem to predict correctly the specific heats of polyatomic gases, and the difficulty of explaining thermodynamic irreversibility in purely mechanistic terms.

GIBBS already indicates, in the prologue of *Elementary Principles*, his intention to separate his formulation from any hypothesis about the constitution of matter, a question very closely linked at the time with the energy equipartition theorem, given that its applicability required a precise knowledge of the number of degrees of freedom of a gas molecule. Even though the theorem is expressed several times in the book as a result of the application of canonical formalism, the fact is that GIBBS does not explicitly mention equipartition, nor does he make any reference to the problems which had arisen because of the experimental results⁴⁴. In fact, it seems that GIBBS never defined his view of the theorem⁴⁵.

The energy equipartition theorem already appears in the first of EINSTEIN's foundation papers, that of 1902, in which he calculates the mean kinetic energy of a gas

⁴¹ EINSTEIN (1903), 171–174; English translation in BECK (1989), 49–52.

⁴² KLEIN (1982), 41.

⁴³ GIBBS (1902), 3–5.

⁴⁴ *Ibid.*, 47, 73, 76, 120, 181 and 184.

⁴⁵ KLEIN (1987), 285.

molecule and invokes the kinetic theory of gases in order to relate it to the absolute temperature of the gas⁴⁶. In the 1903 paper he uses the same approach⁴⁷.

The theorem seems to be most elaborately formulated in his 1904 paper, in which absolute temperature is first defined (or identified) and only then is the mean value of the kinetic energy of an atom calculated as a function of that temperature⁴⁸. At first sight it looks as if the kinetic theory of gases is no longer used to prove the theorem but rather, *a posteriori*, to relate what was later called BOLTZMANN's constant to what was later known as AVOGADRO's number and to the universal constant of ideal gases. A deeper analysis of the article, however, shows that the liberation from the kinetic theory of gases is only apparent, for EINSTEIN refers to his 1903 paper for his prior definition of temperature, which in that paper had been identified after a calculation of mean kinetic energy and a comparison with results using kinetic theory⁴⁹.

In spite of the appearance of the energy equipartition theorem in his three foundation papers, in none of them did EINSTEIN allude to the related problems. This is amazing, especially since he was fully acquainted with BOLTZMANN's ideas. This refusal of EINSTEIN to commit himself to the problems associated with the equipartition of energy amongst the different degrees of freedom of the system only changed after 1905, and became particularly clear at the First Solvay Conference⁵⁰.

4.3 Thermodynamic irreversibility

Chapter XII of *Elementary Principles*, entitled "On the motion of systems and ensembles of systems through long periods of time", is devoted to the study of two subjects which are not characteristic of equilibrium, and which therefore constitute an exception within the context of the book. The first question addressed there is under which conditions and with which limitations a general mechanical system eventually returns to its origin in phase space, within a prefixed degree of approximation. Secondly, the tendency of an ensemble of isolated systems towards equilibrium is analysed.

In both cases GIBBS seems to strive for a characterisation of statistical equilibrium rather than for a rigorous explanation of irreversibility. He does not present a complete theory, but a number of qualitative arguments which do not contribute new ideas relevant

⁴⁶ EINSTEIN (1902), 428; English translation in BECK (1989), 42. This translation has an error which is not found in the original: $\frac{3h}{4}$ is written instead of $\frac{3}{4h}$ for the mean value of kinetic energy.

⁴⁷ EINSTEIN (1903), 178; English translation in BECK (1989), 56. Both the original and the translation contain an error: $\frac{1}{4h}$ is written instead of $\frac{3}{4h}$ for the mean value of kinetic energy. It is clearly a typing error, since it does not appear either in the 1902 article (see the previous footnote) or in the 1904 one.

⁴⁸ EINSTEIN (1904), 358; English translation in BECK (1989), 72–73.

⁴⁹ *Ibid.*, 354–356; 68–70 in the English translation.

⁵⁰ For the evolution of EINSTEIN's thought on the energy equipartition theorem, see BERGIA & NAVARRO (1997).

to the understanding of irreversibility in the behaviour of thermodynamic systems. It is worth stressing here that time evolution is assimilated to a “mixing” type process in phase space⁵¹. Anyway, the above considerations on time evolution must have been judged by GIBBS himself as not very relevant, since in the book’s prologue (six pages), in which he presents his objectives, announces his method, and outlines the results, he does not mention at all either of the two problems, not even this chapter of *Elementary Principles*⁵².

Although in his 1902 paper EINSTEIN concentrates exclusively on equilibrium problems, in his more mature paper of 1903 he presents his conception of how the time reversibility of mechanics can be reconciled with thermodynamic irreversibility. To this end he includes a basic additional hypothesis⁵³:

If we follow the N systems considered for an arbitrary time interval, the distribution of states (...) will continually change with time, and we will have to assume that always more probable distributions of states will follow upon improbable ones (...).

From such a premise he succeeded in proving that the entropy of an isolated system never decreases with time⁵⁴. This answer of EINSTEIN to the riddle of irreversibility reappears, slightly refined, in his 1904 paper⁵⁵. But as it was based on such a poorly justified hypothesis and did not even mention its compatibility with other hypotheses, it rightly became a target of strong criticism by P. HERTZ⁵⁶. Actually, EINSTEIN’s was never accepted as the definitive solution to the problem.

4.4 GIBBS’ grand-canonical ensemble

Before closing this comparison of results, mention ought to be made of a contribution by GIBBS which has no counterpart in EINSTEIN’s formulation. The last chapter of *Elementary Principles* is entitled “Systems composed of molecules”. This does not mean a new hypothesis is being introduced, but that the method is applied to “systems composed of a great number of entirely similar particles, or, it may be, of a great number of particles of several kinds, all of each kind being entirely similar to each other”⁵⁷.

⁵¹ A “mixing” type evolution implies ergodicity, within a hierarchy of properties for the time evolution of general systems. See LEBOWITZ & PENROSE (1973).

⁵² It has been suggested by KLEIN that the pressure suffered by GIBBS to have his book finished for Yale College’s bicentennial celebrations probably made him publish his ideas on this subject too soon. It was an indispensable subject for a book “developed with especial reference to the rational foundation of thermodynamics”, as is stated in the subtitle; see KLEIN (1990), 15.

⁵³ EINSTEIN (1903), 184; English translation in BECK (1989), 63.

⁵⁴ *Ibid.*, 187; 66–67 in the English translation.

⁵⁵ EINSTEIN (1904), 355–357; English translation in BECK (1989), 66–67.

⁵⁶ See “Editorial note: Einstein on the foundations of statistical physics” in STACHEL (1989), 41–55, especially 53.

⁵⁷ GIBBS (1902), 187.

GIBBS here endeavours to generalise the method by considering how the number of particles of each species can vary and tackles the problem of how to define statistical equilibrium in such a situation, with the aim of characterising chemical equilibrium.

On consideration of an aggregate of identical particles, a problem which at once arises is the following⁵⁸:

The essence of statistical equilibrium is the permanence of the number of systems which fall within any given limits with respect to phase. We have therefore to define how the term “phase” is to be understood in such cases. If two phases differ only in that certain entirely similar particles have changed places with one another, are they to be regarded as identical or different phases? If the particles are regarded as indistinguishable, it seems in accordance with the spirit of the statistical method to regard the phases as identical.

Considerations of this sort led GIBBS to define more precisely what is understood by “phase” in such circumstances. In particular, he made a distinction between “generic phases” (those which are not altered by the interchange of identical particles) and “specific phases” (those which are modified by the interchange of the coordinates of particles), and concluded that, in the case of systems formed by one or more classes of identical particles, the generic phases assume protagonism in the new treatment.

In the *petit ensembles* (canonical and microcanonical) elements differ between each other according to their phase. Thus, in the case of molecular aggregates, all the elements of the ensemble have the same nature and number of molecules, but differ in the initial conditions. GIBBS introduced the *grand ensembles*, whose elements do not necessarily have the same number of particles of each class; their elements can thus differ according to phase, as in the *petit ensembles*, or by the number of molecules of each class that they contain.

Amongst the *grand ensembles*, GIBBS focuses on “canonically distributed” ones, as they best describe a situation of statistical equilibrium against the interchange of energy and particles between the parts of an isolated system. This generalisation of the canonical ensemble (equilibrium against exclusive energy exchange) is referred to as the grand-canonical ensemble, an original creation of the American physicist. This new ensemble showed its potential mainly in applications which emerged after the replacement of classical by quantum mechanics in GIBBS’ statistical approach. Just as the canonical ensemble can be understood as a superposition of microcanonical ensembles, in which the weight of each individual is determined by absolute temperature, the grand-canonical ensemble can also be conceived as a superposition of canonical ensembles, in which the weight of each individual is now determined by chemical potential.

In the last paragraph of *Elementary Principles*, we find a clear example of the relevant role GIBBS assigns to generic phases in a system of identical particles. He considers two gaseous masses, each formed by identical molecules, enclosed in contiguous chambers

⁵⁸ *Ibidem*.

which can be interconnected through a valve. It was widely known that total entropy increased when the valve was opened, provided the two gases were different; whereas total entropy remained the sum of each individual gas's entropy, if the two chambers contained the same gas (GIBBS' paradox). The introduction of generic phases for entropy calculation makes this an additive quantity and eliminates the difficulty⁵⁹.

Certain considerations by GIBBS about the adaptations which his new method required in order to become applicable to systems of identical particles, such as the introduction of generic phases, have sometimes led commentators to see in this last chapter of *Elementary Principles* seeds of future quantum indistinguishability of identical particles. Personally, I share the view of those who believe that such an axiomatic approach as GIBBS', not very committed to physics, cannot be seen as a forerunner of ideas about the innermost structure of matter⁶⁰.

5. The EHRENFESTs, GIBBS and EINSTEIN

In 1912 PAUL and TATIANA EHRENFEST published "The conceptual development of the statistical approach in mechanics", an article which had been commissioned by the prestigious *Encyklopädie der mathematischen Wissenschaften*, which wanted a rigorous critical updating of kinetic theory and statistical mechanics⁶¹. Given PAUL's knowledge of the ideas of his teacher BOLTZMANN, as well as of the new statistical mechanics, he was in an outstanding position to assess properly the value of recent developments, both the rigour and elegance of GIBBS' method and the more physical insight of EINSTEIN's formulation, very much in the style of BOLTZMANN. However, the EHRENFESTs' article did not live up to these expectations⁶².

The article claims to follow "an essentially historic approach", and so an analysis of the older formulation of the foundation of the theory is said to be required⁶³. The first chapter opens with the early development of kinetic theory; the second focuses on BOLTZMANN's ideas; and the third and final chapter analyses critically GIBBS' book. An appendix devoted to the innovations between the completion of the article (January, 1910) and its going to press (September, 1911) is also included.

The EHRENFESTs thought that BOLTZMANN's method and results continued to be fully applicable, even though he had occasionally not expressed his ideas with sufficient clarity. This is why part of the article was devoted to clarifying, refining and updating

⁵⁹ *Ibid.*, 206–207.

⁶⁰ See DARRIGOL (1991), 261–290; especially 268–270.

⁶¹ EHRENFEST (1959).

⁶² The EHRENFESTs' paper is not, nor pretends to be, comprehensive. They had not been commissioned for a general analysis of statistical mechanics because BOLTZMANN had already published one for the same *Encyklopädie* in 1905, in collaboration with J. NABL. See KLEIN (1985), 119–120.

⁶³ EHRENFEST (1959), 3.

the basic points of BOLTZMANN's formulation, for they did not find in GIBBS' book the final solution to the fundamental problems of statistical mechanics⁶⁴.

The third chapter is of course the most closely connected to the problems addressed here⁶⁵. It does not contain a systematic analysis of GIBBS' formulation, but confines itself to the following two questions⁶⁶:

1. To what extent has Gibbs achieved his announced goal of founding a statistical mechanics free of internal contradictions?
2. What is the relationship between the analogies to thermodynamics given by Gibbs and those given by Boltzmann?

This being the case, it is surprising there are so few references to EINSTEIN in the article. The EHRENFESTs only mention him in section twenty-five ("Articles following or related to GIBBS' treatment"), to quote his papers of 1902 and 1903 for the use of the ergodic hypothesis and of the microcanonical and canonical ensembles. Then, within the same section, EINSTEIN's papers on the Brownian motion are also quoted, but he is never explicitly associated with the founding of statistical mechanics, and his 1904 article is not quoted at all⁶⁷.

In the conclusions, in which, strange as it may seem, neither GIBBS' nor EINSTEIN's names are mentioned, it is stressed that, in spite of the fragility of the foundations of statistical mechanics, which the EHRENFESTs have shown in their article, physicists have achieved good practical results. Their final verdict is nevertheless crushing⁶⁸:

At least in this respect [the difficulties in the applications of the theory], therefore, a further development of the foundations of statistical mechanics has unquestionably become necessary.

Due to the depth of the EHRENFESTs' treatment, their article soon became famous. Because of its important influence later on, it is worth commenting on certain aspects of the article connected with the subject of the present paper⁶⁹.

For the EHRENFESTs, the basic problem in the foundations of statistical mechanics was rooted in finding an adequate justification for macroscopic irreversibility. Like

⁶⁴ In KLEIN's words (1985), 120–121: "GIBBS had attempted to create a deductive system of statistical mechanics, but the Ehrenfests considered this attempt to be premature and inadequate in many ways".

⁶⁵ A summarised analysis of the contents of the first two chapters of the EHRENFESTs' paper can be found in KLEIN (1985), 121–128.

⁶⁶ EHRENFEST (1959), 45.

⁶⁷ *Ibid.*, 64–67.

⁶⁸ *Ibid.*, 70.

⁶⁹ The omission of EINSTEIN's name, as well as his formulation of statistical mechanics, in the EHRENFESTs' paper was not accidental. The English translation of 1959 was published with a prologue by TATIANA (PAUL had committed suicide in 1933) with a few additions to the original version. Mention of EINSTEIN is omitted here, too.

BOLTZMANN, they traced this to the clarification of the validity and meaning of the *H*-theorem. This is, however, a marginal issue in GIBBS' book, where non-stationary ensembles play only a secondary role⁷⁰. Such a difference of criterion led the EHRENFESTs to view GIBBS' contribution, despite its acknowledged merits, as not the final solution to the problem of the foundations of the statistical method.

I have made reference above to GIBBS' cautious approach, in contrast with EINSTEIN's, to delicate situations. Thus the EHRENFESTs do not find in GIBBS' book what they most appreciate, and consequently do not show much enthusiasm for what the book offers. For example, they do not mention the naturalness, and remarkable advantages, of canonical formalism in the study of thermal equilibrium, nor how well grand-canonical formalism handles chemical equilibrium. They even state⁷¹:

Thus, from the point of view of Boltzmann's presentation, the introduction of the canonical distribution seems to be an analytical trick reminiscent of Dirichlet's "discontinuous factor".

In the last appendix of their article the EHRENFESTs insist on an issue previously discussed by them, namely the probability hypotheses implied in physical theories in general, and in statistical mechanics in particular. Again, there is no mention of EINSTEIN's contributions to the subject, despite his sustained interest from the very beginning in the physical meaning of the probabilities in the theory; they do however discuss certain aspects of MAX PLANCK's counter-position to BOLTZMANN's.

Therefore, against all expectations, the EHRENFESTs' famous article does not contribute to a GIBBS-EINSTEIN comparison, but only to a BOLTZMANN-GIBBS one. The authors of the article consider that even though GIBBS' book represented, due to its rigour and precision, a significant step forward in the treatment of thermal equilibrium, it did not contain the solution to the major foundation problems of statistical mechanics; in fact several of these problems are not even mentioned in *Elementary Principles*, and those which are, the EHRENFESTs claim, constitute no advance on BOLTZMANN.

The almost absolute total absence of references to EINSTEIN in the EHRENFESTs' article is even more surprising if one takes into account the authoritative testimony of MARTIN J. KLEIN about the knowledge PAUL had, around 1912, of EINSTEIN's work⁷²:

Ehrenfest [Paul] had been reading Einstein's papers for almost a decade; he shared so many of Einstein's scientific interests that he could well appreciate the unprecedented boldness and depth of Einstein's ideas.

I do not know what reasons, probably good ones, KLEIN had to assert this. Actually, the EHRENFESTs' scientific production before 1912 contains almost no references to

⁷⁰ See GIBBS (1902), chaps. XII and XIII.

⁷¹ EHRENFEST (1959), 50.

⁷² KLEIN (1985), 175.

EINSTEIN's work. It is certain that they quickly knew of GIBBS' book through the German translation by ERNST ZERMELO, published in 1905: in February 1906 P. and T. EHRENFEST presented a memoir in the *Akademie der Wissenschaften in Wien* in which they criticised GIBBS' approach to equilibrium in *Elementary Principles*⁷³. A scrutiny of the EHRENFESTs' articles however does not supply clear evidence that they were aware of, or at least that they appreciated, EINSTEIN's ideas on statistical mechanics, even though they often addressed similar issues.

In the EHRENFESTs' publications prior to their article in the *Encyklopädie* I have only found EINSTEIN cited twice: once in 1907, on his contributions to relativity, and again in 1911 for his ideas on the light quantum⁷⁴. The last paper of EINSTEIN's trilogy, that of 1904, is not quoted until 1914 in a paper by PAUL on BOLTZMANN's principle, where the 1902 and 1903 papers are also quoted, to state that EINSTEIN and GIBBS, amongst others, make use of the constant energy hypersurface in their respective approaches⁷⁵.

The fact that the EHRENFESTs "forgot" about EINSTEIN's ideas in their article must have had a decisive influence on the scarce impact and diffusion of his formulation later on, given the rapidity with which that critical article became a classic on the foundation of statistical mechanics.

6. HERTZ's criticism and EINSTEIN's later attitude

6.1 On the EINSTEIN-HERTZ controversy

One of the most commonly used arguments to diminish the importance of EINSTEIN's contributions to statistical mechanics is his written reply to a criticism by P. HERTZ. This is how that reply ends⁷⁶:

I only wish to add that the road taken by Gibbs in his book, which consists in one's starting directly from the canonical ensemble, is in my opinion preferable to the road I took. Had I been familiar with GIBBS' book at that time, I would not have published those papers at all, but would have limited myself to the discussion of just a few points.

Given that this self-deprecating statement is often seen as conclusive, I think a few comments on the issue are necessary. It must be stressed first of all that in his two *Annalen* papers of 1910 about EINSTEIN's articles of 1902–1903, P. HERTZ by no means presented a general criticism of EINSTEIN's formulation, but only of two specific

⁷³ The memoir is entitled "Bemerkung zur Theorie der Entropiezunahme in der *Statistischen Mechanik* von W. Gibbs"; it is reproduced in KLEIN (1959), 107–116.

⁷⁴ See KLEIN (1959), 144 and 203–208, respectively.

⁷⁵ *Ibid.*, 350.

⁷⁶ EINSTEIN (1911), 176; English translation in BECK (1993), 250.

aspects of it⁷⁷. One was related to the behaviour of absolute temperature in the contact and separation of systems in thermal equilibrium, and the other to the basic hypothesis used for the proof of the second law which I have already mentioned in section 4.3 above.

EINSTEIN did not go into specific detail on the points criticised. In his extremely short reply (less than one page) he limited himself to affirming the correctness of the criticism, and at the same time stressed that he had already cleared up the question with P. HERTZ personally, since the whole affair was due to “(...) a misunderstanding caused by an all-too terse and insufficiently careful formulation of that argument”⁷⁸.

These criticisms, as well as similar ones on the nature of the hypotheses adopted by EINSTEIN, are generally logical and correct for, as I have been emphasising, the additional assumptions cannot be fully justified, but are ultimately based on plausibility arguments; this is undoubtedly the weakest point of EINSTEIN’s formulation. I nevertheless believe there are arguments which help to clarify the precise meaning of EINSTEIN’s above reply, and which lead one to think that it in no way represents an absolute renunciation of his own formulation. As a matter of fact, he never ratified his 1911 “*mea culpa*”, even though he had excellent opportunities to do so. Let us begin with the consideration of some of these opportunities.

In the proceedings of the First Solvay Conference, for example, there is a discussion of the form in which EINSTEIN introduces the phenomenological probability of a state⁷⁹. HENRI POINCARÉ made a comment trying to relate this probability with that of GIBBS, not mentioning explicitly the latter but making reference to his characteristic notion of “extension in phase”. HENDRIK A. LORENTZ replied: “Mr. EINSTEIN does not follow the path of GIBBS”. In this discussion, EINSTEIN not only refrained from indicating the virtues of GIBBS’ formulation, but also insisted on certain favourable aspects of his own way of introducing probability⁸⁰.

Long afterwards there was an occasion in which EINSTEIN made no comment on the presumed superiority of GIBBS’ formulation, even though he had more than enough time to make written clarifications and replies; this happened at the commemoration of his seventieth birthday, almost forty years on, when MAX BORN said⁸¹:

Einstein’s approach to the subject [statistical mechanics] seems to me slightly less abstract than that of Gibbs. This is also confirmed by the fact that Gibbs made no striking application of his new method, while Einstein at once proceeded to

⁷⁷ HERTZ (1910).

⁷⁸ EINSTEIN (1911), 176; English translation in BECK (1993), 250.

⁷⁹ EINSTEIN’s intervention in the First Solvay Conference (October 30–November 3, 1911) took place more than a year after he met P. HERTZ to discuss certain matters in the latter’s criticism. See the letters of EINSTEIN to HERTZ dated August 14 and 26, 1910 in KLEIN & KOX & SCHULMANN (1993), 250 and 251, respectively.

⁸⁰ The discussion I refer to is in LANGEVIN & DE BROGLIE (1912), 436–450; see especially 440–442.

⁸¹ See SCHILPP (1970), 165.

apply his theorems to a case of utmost importance, namely to systems of a size suited for demonstrating the reality of molecules and the correctness of the kinetic theory of matter.

Finally, I would like to dig deeper into something which I consider the clearest evidence of the fact that EINSTEIN did not really think that GIBBS' formulation made his own irrelevant: the viewpoint and contents of EINSTEIN's lectures on statistical mechanics, both before and after his controversy with P. HERTZ.

6.2 *EINSTEIN on kinetic theory in 1910*

I refer here to EINSTEIN's lecture notes for the course he gave on the kinetic theory of heat at the University of Zurich, in the summer semester of 1910⁸². These notes already show what, after GIBBS' book, was to become EINSTEIN's standard approach to statistical mechanics. On the one hand, he tries to push as far as possible the arguments of his foundation trilogy, including those aspects of the contributions of the American physicist which improve the rigour of his own approach. On the other hand, he insists upon the increasing variety of applications of statistical mechanics, which is completely alien to the very abstract presentation of GIBBS.

Here is a list of a number of specific points in those lecture notes which show, in my opinion, the continuity of EINSTEIN's thinking with the direction spelled out in his initial articles, in clear contrast with the essential traits of GIBBS' formulation:

(i) The introduction of the probability of a state on the basis of physical arguments⁸³. No comparison can be made with GIBBS' approach, in which probability is just a datum which represents the distribution of initial conditions in an abstract mechanical system.

(ii) The introduction of microcanonical distribution, which assigns equal probability to all points in the constant energy hypersurface as a fundamental premise⁸⁴. From this distribution EINSTEIN obtains canonical distribution, the starting-point for GIBBS.

(iii) The resort to specific physical systems, ideal gases in this case, to identify absolute temperature⁸⁵. This is very much along the line of his 1903 approach, but very far from GIBBS' considerations based on formal analogies.

(iv) The systematic application of statistical mechanics, once canonical distribution is attained, to a large variety of fields. This is a sample list of the applications presented in the lecture notes: paramagnetism, Brownian motion, magnetic properties of solids, electron theory of metals, thermoelectricity, particle suspensions and viscosity⁸⁶. GIBBS invented, instead, a method whereby he could find no direct physical application other

⁸² See KLEIN & KOX & RENN & SCHULMANN (1993), 179–247

⁸³ *Ibid.*, 195–202 and 240–241.

⁸⁴ *Ibid.*, 202–204 and 231–232.

⁸⁵ *Ibid.*, 208–213.

⁸⁶ *Ibid.*, 221–239.

than the detection of the already mentioned thermodynamic analogies. Had GIBBS lived longer (he died the year after the publication of *Elementary Principles*) this might have changed. But, given his rigorous and extremely cautious attitude, any assumption on the issue is enormously risky.

I want to stress something which, although not very closely related to the subject, may look surprising: even though EINSTEIN had put together statistical mechanics and quantum ideas in previous work with remarkable success⁸⁷, there is no mention whatsoever of quantum concepts in these notes. I think this has no major significance, given the time when they were written; it can be interpreted just as an indication of how little the first quantum concepts were implanted.

6.3 EINSTEIN on statistical mechanics in 1917–18

Those lecture notes must have been ready by April 1910, when the course began. Given that EINSTEIN's controversy with P. HERTZ and supposed "mea culpa" came later, the present analysis would be incomplete without an assessment of the extent to which this episode affected EINSTEIN's ideas on statistical mechanics.

For this I have made use of the notes taken by WERNER BLOCH, a student who attended a course on statistical mechanics delivered by EINSTEIN in Berlin during the winter semester of 1917–18⁸⁸. Since the latter was at the time aware of the EHRENFESTS' critical article to which I have referred in section 5 above, BLOCH's notes can be expected to reflect the evolution of EINSTEIN's thinking on the formulation of statistical mechanics.

But it is soon clear that the contents of these 1917–18 notes are very similar to the 1910 ones. Although GIBBS' influence can be appreciated in the more problematical points of EINSTEIN's original formulation, he essentially remains loyal to the fundamental characteristics of his initial version. One must also keep in mind that the molecular nature of matter, a central hypothesis in EINSTEIN's approach, had already been fully confirmed at the time.

For example, EINSTEIN insists upon the introduction of the probability of a state on the basis of physical considerations; he continues basing his formulation on micro-canonical distribution, from which he obtains canonical distribution; he again resorts to the ideal gas for a full identification of absolute temperature; and he shows the usefulness of canonical distribution in different applications. Let me insist: everything very similar to 1910. It is thus apparent that neither the EHRENFESTS' article nor the controversy with P. HERTZ had a decisive influence on EINSTEIN's thought; at least not on his lectures on statistical mechanics.

⁸⁷ See EINSTEIN (1907) on the theory of specific heat of solids.

⁸⁸ Unpublished notes, to which I have had access through KARL VON MEYENN.

In the 1917–18 notes there are certainly some novelties relative to the 1910 ones, but of little relevance for the present study. For example, the importance of the fluctuations is now analytically related to the number of degrees of freedom of the system; this was already contained in GIBBS' book, but EINSTEIN had not worried about it earlier.

There are no references to the incipient quantum theory in these 1917–18 notes, either, and this may seem even more surprising; let us not forget that the First Solvay Conference spread the quantum seeds in 1911, that NIELS BOHR introduced his atomic model in 1913, that the quantisation rules of WILLIAM WILSON, JUN ISHIWARA and ARNOLD SOMMERFELD in 1915–16 enabled the possible values of the energy of a mechanical system (a crucial point for the application of the canonical formalism) to be found, etc.⁸⁹ But this can again be interpreted as a sign of how provisionally quantum ideas were viewed at the time, even by EINSTEIN, as is reflected in a letter to BESSO in the summer of 1918⁹⁰:

I have spent innumerable hours thinking about the problem of quanta, of course without making any substantial progress. But I do not doubt anymore about the *reality* of the quanta of radiation, although I am still the only one who has this conviction.

And a final curiosity: although in BLOCH's notes the names of BOLTZMANN, DRUDE, POINCARÉ, LANGEVIN, WEISS and PERRIN, amongst others, appear explicitly, I have not found GIBBS' name. This is not particularly relevant since no firm conclusion can be drawn that EINSTEIN did not mention the American physicist in his lectures. However, GIBBS' name does appear in EINSTEIN's 1910 lecture notes, albeit, surprisingly, in connection with a marginal issue in the former's formulation: microcanonical distribution⁹¹.

In summary, it appears that neither the controversy with P. HERTZ nor EINSTEIN's declarations afterwards about his own formulation of statistical mechanics had significant effects on EINSTEIN's lectures. I think a decisive role should not be attributed to his 1911 "mea culpa" when his contributions to statistical mechanics are assessed. GIBBS' influence, though undoubtedly real, did not lead to EINSTEIN renouncing the essential characteristics of his own formulation, but rather to a logical refinement of the original version. The arguments deployed here endorse and extend, I believe, the statement with which the "Editorial note: Einstein on the foundations of statistical mechanics", in the *Collected Papers*, closes⁹²:

But in spite of the fact that GIBBS' approach had gained a wide following amongst physicists by the end of the first decade of this century, EINSTEIN treated the essential issues in much the same way as in his earlier papers.

⁸⁹ See e.g. JAMMER (1966), 69–109.

⁹⁰ Letter to BESSO, July 29, 1918; in SPEZIALI (1979), 77.

⁹¹ See KLEIN & KOX & RENN & SCHULMANN (1993), 204.

⁹² STACHEL (1989), 54–55.

7. Epilogue

GIBBS' and EINSTEIN's formulations can be considered equivalent in the sense that both explain thermodynamics coherently in mechanistic terms. Indeed, they produce a justification, on the basis of mechanics, not only of thermodynamic laws but also of other characteristic results of thermal equilibrium, such as the energy equipartition principle.

Thus, from a purely operational point of view, one formulation seems redundant; and GIBBS', as already argued, appears a more elaborate final product than that of the newcomer EINSTEIN. This is a fairly general view amongst physicists, and also very common amongst historians of science⁹³.

As a matter of fact, GIBBS' formulation had a great and favourable impact from the very beginning. The importance of the method put forward in *Elementary Principles* was immediately grasped and grew with the passage of time. A look at the contributions to the 1904 St. Louis Congress shows the high esteem GIBBS' book was held in by illustrious physicists like CARL BARUS, BOLTZMANN and POINCARÉ, just two years after its publication⁹⁴. A reading of the proceedings of the First Solvay Conference in 1911 confirms that GIBBS' method was already widely known by the first researchers into quantum theory⁹⁵.

It should be stressed that not everybody showed the same degree of enthusiasm for the new statistical approach of GIBBS. For example, LORENTZ expressed in a lecture delivered to the Société Française de Physique in April 1905 the opinion that neither GIBBS' book nor BOLTZMANN's works contained a statistical deduction of the second law of thermodynamics⁹⁶.

A specific and deep criticism emerged, which even today is difficult to silence, relating to the very idea of founding a mechanistic explanation of thermodynamics on the canonical ensemble: the adoption of absolute temperature as a basic initial datum involves an important incoherence, since this quantity has no proper physical meaning in a mechanical system. Objections of this nature were magnificently explained, for instance, by PIERRE DUHEM in 1907⁹⁷:

Les systèmes canoniques sont définis par une propriété algébrique: leur coefficient de probabilité est de la forme donnée par l'équation (1) [also (1) in the present paper]. Mais ils n'ont reçu jusqu'ici aucune définition mécanique. Comment doivent être agencés les corps qui composent un élément du système, à

⁹³ It is necessary to insist on the scarce exceptions, to whom I alluded in footnote 7.

⁹⁴ SOPKA (1986), 121, 277 and 286, respectively.

⁹⁵ LANGEVIN & DE BROGLIE (1912). See especially LORENTZ's report in 12–39 and PLANCK's in 93–144.

⁹⁶ LORENTZ (1905), 539.

⁹⁷ DUHEM (1908), 37–38. This essay is a transcription of another one appearing in the *Bulletin des Sciences Mathématiques* in 1907, on occasion of the publication the previous year of GIBBS' *Scientific Papers*; see BUMSTEAD & VAN NAME (1906).

quelles sortes de forces ces corps doivent-ils être soumis pour que le système soit un système canonique? Cette question n'a reçu aucune réponse.

Or, une telle réponse paraît indispensable si l'on ne veut pas que la théorie des systèmes canoniques paraisse un pur exercice d'Algèbre, sans intérêt pour le physicien.

The EHRENFESTs' article significantly helped the diffusion of GIBBS' approach, despite the article's general tone which, as I stressed above, was quite critical of the American's contributions to the foundations of statistical mechanics. That paper by the EHRENFESTs soon became a classical reference in the German language. P. HERTZ, for example, placed it, only four years after its publication, in the same category as GIBBS' book, since he quoted that article as one of the three general references in the extensive article on statistical mechanics he wrote for the famous *Repertorium*⁹⁸.

The absolute preponderance of GIBBS' formulation was consolidated amongst physicists after the appearance of the influential book by RICHARD C. TOLMAN in 1938, destined to become the reference treatise on statistical mechanics par excellence⁹⁹. The author states his unequivocal intentions in the book's prologue¹⁰⁰:

Throughout the book, although the work of earlier investigators will not be neglected, the deeper point of view and the more powerful methods of Gibbs will be taken as ultimately providing the most satisfactory foundation for the development of a modern statistical mechanics.

Thus TOLMAN recognises from the very beginning his preference for GIBBS' approach, even if it requires a slight modification to include quantum theory into the formulation¹⁰¹. However, since some of the difficulties which had made GIBBS extremely cautious were already solved, TOLMAN claims to be in a position to develop GIBBS' method with "a more positive attitude" to the relationship between the abstract systems in *Elementary Principles* and real physical systems¹⁰².

Reference to GIBBS is constant throughout TOLMAN's book. Even in the chapter on macroscopic irreversibility, one of the weaker points of GIBBS' approach as against BOLTZMANN's in the EHRENFESTs' view, the author presents a generalisation of BOLTZMANN's *H*-theorem on the basis of GIBBS' ideas and concludes as follows¹⁰³:

In concluding this chapter on the *H*-theorem it is evident that we must now regard the original discovery of this theorem by Boltzmann as supplemented in a fundamental and important manner by the deeper and more powerful methods of Gibbs.

⁹⁸ The third reference is LORENTZ's *Gesammelte Abhandlungen*; see HERTZ (1916), 436.

⁹⁹ TOLMAN (1938).

¹⁰⁰ *Ibid.*, ix.

¹⁰¹ *Ibid.*, 14.

¹⁰² *Ibid.*, 14–15.

¹⁰³ *Ibid.*, 179.

TOLMAN quotes several times, as is to be expected, the EHRENFESTS' article. But reference to EINSTEIN is very seldom made, and is essentially confined to his contributions to quantum theory. As a matter of fact, EINSTEIN is never quoted in relation to the foundation of statistical mechanics¹⁰⁴.

In view of this, there can be little doubt that the enormous impact of both the EHRENFESTS' article and TOLMAN's book greatly affected physicists' knowledge of EINSTEIN's contributions to statistical mechanics.

I would like to conclude with what is, in my view, paradigmatic of the extent to which EINSTEIN's contribution to this field has been overlooked. I specifically refer to the attitude of a physicist of such widely acknowledged intellectual stature and fine sensitivity to the course of history as LÉON ROSENFELD¹⁰⁵.

In 1955 he wrote a long article devoted to the analysis of the foundations of statistical thermodynamics¹⁰⁶. He often quotes the contributions of MAXWELL, BOLTZMANN and GIBBS, and also the EHRENFESTS' article. But neither in the text, nor in the notes, nor in the bibliography is a single reference made to EINSTEIN's papers. Not even his name is mentioned. This is amazing if one looks into the contents of the article.

Like the EHRENFESTS, ROSENFELD contrasts GIBBS' approach with BOLTZMANN's and finally opts for the latter. In spite of its length, I think it is worth quoting in full¹⁰⁷:

To appreciate the superiority of Boltzmann's philosophical standpoint, it is instructive to contrast it with the timid and ambiguous attitude of Gibbs. While Boltzmann remained undaunted, Gibbs retreated before the difficulties. He endeavoured to make use only of those parts of the formal structure of statistical mechanics which were susceptible to a fully rigorous treatment with the methods then available. This means that he shunned the whole problem of the ergodic hypothesis, in spite of its fundamental importance, and that with regard to the physical interpretation he took refuge to the crudest Platonistic conception of mechanical 'analogies' of the thermodynamical laws. If one takes this view, the real physical basis of the theory, and especially the essential character of uniqueness of the atomistic interpretation, is utterly lost. In fact, the paradoxical outcome of such an idealistic treatment is an atomic theory of heat from which the concept of atom is wellnigh banished. The exquisite formal elegance of Gibbs' treatise should not blind us to the fundamental inadequacy of the underlying philosophy.

¹⁰⁴ In TOLMAN (1938), references to EINSTEIN are found on pages 181–183 for different contributions to the quantum theory; on page 380 for his theory of specific heats; on page 454 for quantum statistics; on page 631 for his calculations of fluctuations in quantum statistics; and on page 636 for his work on critical opalescence.

¹⁰⁵ Amongst ROSENFELD's *Selected Papers* included in COHEN & STACHEL (1979) there are twenty-five papers on the history of science, some of them published in very prestigious journals, such as *Isis* or *Archive for History of Exact Science*.

¹⁰⁶ ROSENFELD (1955).

¹⁰⁷ *Ibid.*, 763.

ROSENFELD considers that a statistical-mechanical explanation of thermodynamics must rest on the idea that the macroscopic phenomena are a manifestation of elementary processes which involve an enormous number of atoms. The logical construction of statistical mechanics has to rest on this base and must proceed in three major steps. First, one must look at isolated systems for which ergodic theorems, which enable equilibrium distribution (microcanonical distribution) to be determined, will have to be established. Then, the equilibrium distribution of a small part of such an isolated system (canonical distribution) has to be obtained. Finally, in order to fully explain thermodynamics in statistical-mechanical terms, rules have to be found which relate the canonical distribution to the thermodynamic quantities; “this is achieved by setting up, in each case, a function of the statistical distribution which has all the properties of the corresponding characteristic function in thermodynamics”¹⁰⁸.

These requirements which ROSENFELD considers ought to be met by any attempt at a logical construction of statistical mechanics are completely absent in GIBBS’ formulation, which should therefore be considered unsatisfactory as a complete theory. On the contrary, the enunciation of the above precepts constitutes a remarkably accurate description of the formal structure of EINSTEIN’s approach; nevertheless he is not mentioned.

I can think of only one possible explanation of this generalised oversight of EINSTEIN’s contributions to the foundations of statistical mechanics: the belief that his view fully coincides with BOLTZMANN’s, and his results are not significantly new. There are however historiographic studies which have shown the existence of important differences between EINSTEIN’s and BOLTZMANN’s formulations in a number of specific aspects. Marked differences have been pointed out, for example, in their respective objectives, their ways of conceiving and introducing probability in the theory, the methodology used, and also the results obtained¹⁰⁹.

Through the comparative analysis of GIBBS’ and EINSTEIN’s formulations of statistical mechanics I have tried to stress the need to define more accurately the supposed equivalence between them and the feasibility of doing so. Perhaps a similar comparative analysis of BOLTZMANN’s and EINSTEIN’s formulations would be a useful complement of this work; no doubt it would contribute to the clarification of questions regarding the foundations of statistical mechanics which are still open.

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¹⁰⁸ *Ibid.*, 770–771.

¹⁰⁹ See, for example, “Editorial note: Einstein on the foundations of statistical physics” in STACHEL (1989), 47–48.

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- appear the five principal works of EINSTEIN on the Brownian motion; the first one is the famous paper mentioned above. The third is a slight modified version of his doctoral thesis, finished on 30 April 1905 and submitted to the University of Zurich on 20 July of the same year. FÜRTH's book was originally published in 1926.
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