

# One of Gibbs's ideas that has gone unnoticed (comment on chapter IX of his classic book)

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**Abstract.** We show that contrary to the commonly accepted view, Chapter IX of Gibbs's book [1] contains the prolegomena to a macroscopic statistical theory that is qualitatively different from his own microscopic statistical mechanics. The formulas obtained by Gibbs were the first results in the history of physics related to the theory of fluctuations in any macroparameters, including temperature.

J W Gibbs's famous book *Elementary Principles in Statistical Mechanics* [1]<sup>1</sup> was published in the USA in the summer of 1902. However, it was not until the legendary year of 1905 that the book came to be widely known in Europe, after the publication of its German translation [3] made by E Zermelo. It is therefore quite appropriate to place this event among other outstanding scientific events whose centenary is celebrated in the context of the World Year of Physics.

Beginning with the mid-1930s, Gibbs's fundamental ideas in the area of statistical mechanics gained widespread acceptance in scientific and educational literature while enjoying numerous successful applications in theoretical scientific investigations owing to the effort mounted by Fowler [4], Landau and Lifshitz [5], Tolman [6], and their followers. As a result, the scientific community formed a strong opinion that Gibbs's book was a consistent development and, in a sense, the completion of equilibrium statistical mechanics, which dated back to Maxwell's and Boltzmann's works in the second half of the XIXth century. It would be well to identify it as the microscopic statistical theory.

However, close examination of the text of Gibbs's book (especially of Chapter IX) can also reveal the prolegomena to the *macroscopic statistical theory*, which is qualitatively different from *microscopic statistical mechanics*. It turned out that the ideas expressed in Chapter IX went far beyond those objectives which had initially been proclaimed by Gibbs himself in the title of his book. As the title implies, Gibbs intended to *derive* the thermodynamic description of a macroscopic system as a whole from the dynamic description

of a large number of microscopic objects that make up this system.

According to Gibbs, the mathematical instrument of such a description (for a fixed volume  $V$  and number of particles  $N$  in the system) is the *microscopic* canonical distribution function defined in the *phase space* of the system [2, formulas (90) and (91)]:

$$\begin{aligned} d\rho(p_i, q_i) &= \exp \left\{ \frac{\psi - \varepsilon(p_i, q_i)}{\Theta} \right\} \prod dq_i dp_i \\ &= \exp \{-\eta\} \prod dq_i dp_i, \end{aligned} \quad (1)$$

where the  $q_i$ - and  $p_i$ -dependent quantity  $\eta$  was labeled by Gibbs as the *phase probability index*; the product  $\prod$  is taken over all the microobjects (for brevity, particles) that constitute the system.

Distribution (1) contains two constants,  $\Theta$  and  $\psi$ , which have the dimensionality of energy and are independent of phase variables. Gibbs referred to the  $\Theta$  quantity as the *modulus of distribution* (1); at present, it is universally accepted that  $\Theta = k_B T_0$ , where  $k_B$  is the Boltzmann constant and  $T_0$  is the thermostat temperature. By definition, a thermostat has an infinite number of degrees of freedom, and hence the value of  $T_0$  is strictly fixed.

The value of  $\psi$  is defined by the normalization condition for distribution (1) and has the thermodynamic interpretation of the free energy of the system. The generalized coordinates  $q_i$  and momenta  $p_i$  that enter distribution (1) and characterize the phase space of the system are random variables owing to the thermal contact between the system and the thermostat. Accordingly, the  $p_i$ - and  $q_i$ -dependent total system energy  $\varepsilon$  is also a random function.

The total energy  $\varepsilon$  is additive with respect to the total kinetic energy  $\varepsilon_p$  and the total potential energy  $\varepsilon_q$ . That is why Gibbs distribution (1) in statistical mechanics factors into the product of the distributions  $d\rho(p_i)$  and  $d\rho(q_i)$ , which depend, respectively, on only the momenta and only the coordinates of individual particles. This circumstance permits calculating both the average values and arbitrary higher-order moments of these distributions.

This had the effect that the Gibbs method based on microscopic distribution (1) yielded for the first time a direct and regular method of calculating the fluctuations of any quantities admitting a mechanical interpretation, i.e., dependent on the momenta  $p_i$  and coordinates  $q_i$  of individual particles of the system. Knowing the  $\varepsilon(p_i, q_i)$  dependence and using distribution (1), one can then determine the mean values and fluctuations of any system macroparameters whose microlevel prototypes depend on  $p_i$  and  $q_i$ .

On the contrary, those macroparameters of the system that are devoid of such prototypes (first and foremost, the

<sup>1</sup> Hereinafter, citations from this book (including page and formula numbers) are made with reference to its second Russian edition published in the series "The Classics of Science" [2].

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temperature) are believed to be strictly fixed and coincident with the similar macroparameters of the thermostat. In particular, the *zeroth law* of thermodynamics is given by the identity  $T \equiv \Theta$ , and therefore the modulus  $\Theta$  of the canonical distribution in statistical mechanics corresponds to the thermodynamic temperature  $T$  (in energy units) of the system that is in thermal equilibrium with the thermostat.

Distribution (1) may also be given, following Gibbs, another, equivalent form — that of a distribution over the energy  $\varepsilon$  of the *system as a whole* [2, formulas (266)–(268)]:

$$d\rho(\varepsilon) = \exp \left\{ \frac{\psi - \varepsilon}{\Theta} \right\} \frac{dV}{d\varepsilon} d\varepsilon. \quad (2)$$

Here,  $V(\varepsilon) = \int \prod dq_i dp_i$  is the phase volume containing the system microstates whose energy lies below some limiting value  $\varepsilon$ . In the framework of statistical mechanics, the quantity  $V(\varepsilon)$  plays an auxiliary role, which practically reduces to a change of the normalization condition. It can be found, in principle, from the microscopic characteristics of the dynamic model of the system.

Mathematically, the transition from distribution (1) to distribution (2) in the framework of statistical mechanics is merely a ‘change of variables,’ specifically, the transition from the *set* of  $6N$  random variables  $(p_i, q_i)$  to *one* random variable  $\varepsilon$ . In this case,  $V(\varepsilon)$  is the transformation Jacobian, which can be calculated if the dependence  $\varepsilon(p_i, q_i)$  is known. Therefore, although the quantity  $\varepsilon$  in distribution (2) has the meaning of the energy of the system as a whole, i.e., might be formally treated as a random *macroparameter*, it actually remains a microparameter in the phase space owing to the ‘genetic’ relation of the phase volume  $V(\varepsilon)$  to the initial microparameters  $p_i$  and  $q_i$ .

The remarkable success achieved during the past century in the application of the *microscopic* canonical distribution in the form of either distribution (1) or distribution (2) has led to the establishment of a tradition whereby it is commonly supposed that Gibbs’s book is dedicated to the presentation of equilibrium statistical mechanics in the phase space and to the substantiation with its aid of the foundation of thermodynamics. However, it should be remembered that this goal is possible to achieve only in the *thermodynamic limit*, when the number of particles (or, in a more general sense, the number of the degrees of freedom) in the system  $N \rightarrow \infty$  and the system volume  $V \rightarrow \infty$ , with  $N/V = \text{const}$ . Of course, any macroparameter fluctuations are out of the question in this limit.

Furthermore, the most important intensive macroparameters, and above all the temperature, are introduced *ad hoc* and are therefore not substantiated at all. For finite but macroscopic values of the number  $N$  of particles in the system, there exist fluctuations of only its extensive macroparameters, but their relative magnitude is of the order of  $1/\sqrt{N}$ . The fluctuations of intensive macroparameters of suchlike systems are absent as before.

In this context, the development of the fluctuation theory for arbitrary macroparameters, including temperature (see, e.g., Ref. [5], 5th ed., Ch. 12), was widely believed to be alien to Gibbs’s basic ideas. Meanwhile, in the preface to his book [2, p. 353], Gibbs himself warned about the possible ambiguity of the statistical description of nature at thermal equilibrium:

“We meet with *other quantities*, in the development of the subject, which, when the number of degrees of freedom is very

great, *coincide sensibly* with the modulus, and with the average index of probability, taken negatively, in a canonical ensemble, and which, therefore, may also be regarded as corresponding to *temperature* and *entropy*. The correspondence is however imperfect, when the number of degrees of freedom is *not very great...*” (italics added).

The aim of our brief article is to show that Gibbs’s book also contains another, *macroscopic*, version of the statistical description of nature directly in the macroparameter space, which is different from the prevalent *microscopic* version of the statistical description in the phase space.

To do this, it suffices to address ourselves to the contents of Chapter IX of Gibbs’s book, in which the author proposes to return “...to the consideration of the canonical distribution, in order to investigate those properties which are especially related to the function of the energy which we have denoted by  $\varphi$ .” Formally, this function was already introduced by him in Chapter VIII [2, formula (266)] as a quantity in terms of which it was convenient to write the Jacobian  $V(\varepsilon)$  for the transformation from the individual microscopic characteristics  $p_i, q_i$  of the constituent particles to the variable  $\varepsilon$  characterizing the system as a whole:

$$\varphi = \ln \frac{dV}{d\varepsilon}. \quad (3)$$

However, it is significant that in Chapter IX, Gibbs no longer recalled that the quantity  $\varphi$  might be calculated from the phase volume  $V$  defined by the dynamic model of the system in the phase space. Proceeding from the *microscopic* distribution in the form of distribution (2), he postulated the *macroscopic* canonical distribution [2, formula (317)]<sup>2</sup>

$$d\rho(\mathcal{E}) = \exp \left\{ \frac{\Psi - \mathcal{E}}{\Theta} \right\} \exp \Phi(\mathcal{E}) d\mathcal{E}, \quad (4)$$

which is seemingly similar to distribution (2) but is nevertheless qualitatively different from it.

What is new here is that the quantity  $\Phi(\mathcal{E})$  is initially introduced as a *random macroparameter* that is independent of any phase-space description. This signifies that the system energy  $\mathcal{E}$ , which appears in it, is also regarded initially as a random macroparameter, which may depend only on other macroparameters, for instance, the volume  $V$  and temperature  $T$  of the system, but not on the microparameters  $p_i, q_i$ .

Precisely this step by Gibbs opens up the way to the development of a *macroscopic* statistical theory, in which the fluctuations of any macroparameters, including temperature, turn out to be possible. (Presently, it is commonly called the *statistical thermodynamics*.) This was successfully demonstrated by Gibbs himself in Chapter IX.

However, it is regrettable that this chapter, the most important as regards its idea content, was not timely noticed by the broad scientific community and, in particular, was not given adequate interpretation in the comments made by the leading experts concerning Gibbs’s book [7, 8].

Meanwhile, it is precisely in this chapter that Gibbs proves the two most important formulas, (336) and (337), specifically,

$$\frac{1}{\Theta} = \left( \frac{d\Phi}{d\mathcal{E}} \right)_0, \quad -d\bar{\eta} = d\Phi_0, \quad (5)$$

<sup>2</sup> To distinguish between these two distributions, we use capital letters instead of lowercase letters to denote random extensive macroparameters of the system.

where the subscript 0 labels the quantities corresponding to the peak of distribution (4), i.e., to the most probable energy value  $\mathcal{E}_0$  of the system.

Further, Gibbs writes as follows: “Now we have already noticed a certain *correspondence* between the quantities  $\Theta$  and  $-\bar{\eta}$  and those which in thermodynamics are called temperature and entropy. The property just demonstrated, with those expressed by equation (336), therefore suggests that the quantities  $d\mathcal{E}/d\Phi$  and  $\Phi$  may also correspond to the thermodynamic notions of temperature and entropy.”

Therefore, according to Gibbs, there exist *two* pairs of quantities, and *not one* pair, that can equally be considered thermodynamic quantities — *temperature* and *entropy*. How should they be treated?

It would appear quite natural that the pair of quantities

$$-\bar{\eta} = \frac{\Psi - \bar{\mathcal{E}}}{\Theta} \quad \text{and} \quad \Theta$$

would correspond to the entropy and temperature of a system only under perfect equilibrium, which can be achieved only in the limit as  $N \rightarrow \infty$ . At the same time, the pair of quantities  $\Phi$  and  $d\mathcal{E}/d\Phi$  characterizes the system with a macroscopic but finite number of the degrees of freedom  $N$ . One can see from relations (5) that the above pairs of quantities coincide with each other only to the lowest approximation.

All this allows us to assume that Gibbs's  $\Phi(\mathcal{E})$  is the entropy of a system with a large but finite number of the degrees of freedom, which is a random function of the macroparameter — the energy  $\mathcal{E}$  — and therefore pertains not only to perfect equilibrium. This is confirmed by the expansion [2, formula (338)]

$$\Phi(\mathcal{E}) = \Phi_0 + \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 (\mathcal{E} - \mathcal{E}_0) + \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 \frac{(\mathcal{E} - \mathcal{E}_0)^2}{2} + \dots, \quad (6)$$

which is, on the one hand, the expansion of  $\Phi(\mathcal{E})$  around the most probable energy value  $\mathcal{E}_0$  and, on the other hand, as justly noted by Gibbs, an expansion in powers of  $1/\sqrt{N}$ .

If we restrict our consideration, as was done by Gibbs, to the lowest terms in expansion (6), then after its substitution in distribution (4) we can see, in view of relations (5), that the terms linear in  $\mathcal{E}$  cancel. The result is given by an approximate distribution [2, formula (341)] with a new normalization [2, formula (342)]:

$$d\rho(\mathcal{E}) = \exp \left\{ -\eta_0 + \Phi_0 + \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 \frac{(\mathcal{E} - \mathcal{E}_0)^2}{2} \right\} d\mathcal{E}, \quad (7)$$

where  $-\eta_0 = (\Psi - \mathcal{E}_0)/\Theta$  and the quantity  $(d^2\Phi/d\mathcal{E}^2)_0$  is negative.

As regards formula (341), Gibbs noted that “this shows that for a very great number of degrees of freedom the probability of deviations of energy from the most probable value  $\mathcal{E}_0$  approaches the form expressed by the ‘law of errors,’” i.e., the normal Gaussian distribution. As is well known, this result corresponds to the universally recognized theory of macroparameter fluctuations (see, e.g., Ref. [5], 5th ed., Ch. 12).

Next, Gibbs differentiates expansion (6), which yields, in view of relation (5),

$$\frac{d\Phi}{d\mathcal{E}} - \left(\frac{d\Phi}{d\mathcal{E}}\right)_0 \equiv \frac{1}{T(\mathcal{E})} - \frac{1}{\Theta} = \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 (\mathcal{E} - \mathcal{E}_0), \quad (8)$$

where  $T(\mathcal{E}) = d\mathcal{E}/d\Phi$  has the meaning of the temperature of the system (in energy units). Gibbs thereby obtains (supposedly for the first time in the history of physics) the quantity that characterizes, in thermal equilibrium, the difference between the temperature  $T$  of a macrosystem with a finite number of degrees of freedom and the thermostat temperature  $\Theta$ , which corresponds to a less strict form of the *zeroth* law of thermodynamics,  $T \pm \Delta T = \Theta$ .

By next differentiating expression (8) at the peak of distribution (4), it is easy to find that

$$\frac{d^2\Phi}{d\mathcal{E}^2} = \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 = \left[\frac{d}{d\mathcal{E}} \left(\frac{1}{T(\mathcal{E})}\right)\right]_0 = -\frac{1}{\Theta^2} \frac{1}{C_V}, \quad (9)$$

where  $C_V \equiv (d\mathcal{E}/dT)_0$  is the specific heat of the system at constant volume. For the normal distribution (7), the average energy value  $\bar{\mathcal{E}}$  coincides with the most probable value  $\mathcal{E}_0$ , and hence the system energy fluctuation (at constant volume:  $V = \text{const}$ ) assumes, in view of expression (9), the well-known form [2, formula (343)]

$$\overline{(\Delta\mathcal{E})^2} \equiv \overline{(\mathcal{E} - \bar{\mathcal{E}})^2} = \overline{(\mathcal{E} - \mathcal{E}_0)^2} = -\left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0^{-1} = C_V \Theta^2. \quad (10)$$

Gibbs next obtains, again for the first time, the expressions for the inverse temperature–energy correlator [2, formula (349)]

$$\overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right) \Delta\mathcal{E}} = \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 \overline{(\Delta\mathcal{E})^2} = -1 \quad (11)$$

and for the fluctuation of the inverse temperature [2, formula (350)]:

$$\overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right)^2} = \left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0^2 \overline{(\Delta\mathcal{E})^2} = -\left(\frac{d^2\Phi}{d\mathcal{E}^2}\right)_0 = \frac{1}{\Theta^2} \frac{1}{C_V}. \quad (12)$$

Unfortunately, at this point, Gibbs did not use the Cauchy–Bunyakowsky–Schwartz inequality for the mean values of the momenta of random quantities  $X$  and  $Y$ , which was already known then and which states that these quantities satisfy the universal relation

$$\overline{X^2} \overline{Y^2} \geq (\overline{XY})^2. \quad (13)$$

If it is applied in the macroparameter space with  $X = \Delta(1/T(\mathcal{E}))$  and  $Y = \Delta\mathcal{E}$ , then in the general case (for  $V \neq \text{const}$ ), we obtain the *inequality*

$$\overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right)^2} \overline{(\Delta\mathcal{E})^2} \geq \left\{ \overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right) \Delta\mathcal{E}} \right\}^2, \quad (14)$$

which has the meaning of the *thermodynamic uncertainty relation* for the energy and the inverse temperature [9]. However, in the context of macroscopic statistical theory outlined by Gibbs in Chapter IX [see formulas (10)–(12) above], uncertainty relation (14) is ‘saturated’ (i.e., becomes an equality) because the system volume  $V = \text{const}$ .

We note that in passing from the distribution modulus  $\Theta$  to the temperature  $T_0$ , there appears a factor  $k_B$  on the right-hand sides of formulas (10)–(12) and a factor  $(k_B)^2$  on the right-hand side of formula (14). As a result, uncertainty

relation (14) becomes

$$\overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right)^2} \overline{(\Delta\mathcal{E})^2} \geq \left\{ \overline{\Delta\left(\frac{1}{T(\mathcal{E})}\right) \Delta\mathcal{E}} \right\}^2 \equiv k_B^2, \quad (15)$$

where the right-hand side is defined by the Boltzmann constant.

We emphasize once again that formula (15) for  $V = \text{const}$  follows directly from the foregoing Gibbs formulas. The prolegomena to the macroscopic statistical theory contained in Chapter IX of Gibbs's book are presumably the first (the year 1902!) example of a *nonclassical* theory involving uncertainty relations. It is quite surprising that discussions about the validity of suchlike relations in thermodynamics still persist.

Thus, one is forced to accept the fact that Gibbs's book does not reduce, as is commonly supposed, exclusively to the construction of the microscopic theory, i.e., statistical mechanics. As follows from the foregoing, in his last writings, Gibbs intuitively came close to the formulation of the macroscopic theory, i.e., statistical thermodynamics, which equally allows the fluctuations of extensive and intensive thermodynamic characteristics.

One is thereby forced to admit that the rather common belief about the absence, in Gibbs's book, of the notions of temperature fluctuations in a system and of a correlation between its energy and temperature, which was also shared by the authors of this article earlier [10], is a fallacy. In reality, for more than a century, there have existed two qualitatively different statistical theories based on canonical distributions of similar form — the *microscopic* distribution in the form of distribution (1) or (2) in the phase space and the *macroscopic* distribution (4) in the macroparameter space. Of fundamental significance is the fact that these two theories are based on *different* versions of the *zeroth law* of thermodynamics and therefore lead to different results for the thermodynamic fluctuations of some macroparameters and the correlations between them.

Unfortunately, Gibbs's fate left him no time to elaborate the views embodied in Chapter IX of his book. In particular, only once (in Chapter XIV) did he apply formula (12) for temperature fluctuations to show that increasing the number of the degrees of freedom of a thermostat entails an unrestricted decrease in its temperature fluctuation — the magnitude of  $\Delta\Theta$ . By and large, Gibbs nevertheless regarded, as suggested by his numerous statements, the problem of macroparameter fluctuations as physically insufficiently interesting due to the impossibility of their experimental observation. We let Gibbs have the floor [2, p. 484]:

“When we wish to give a body a certain temperature, we place it in a bath of the proper temperature, and when we regard what we call thermal equilibrium as established, we say that the body has the same temperature as the bath. Perhaps we place a second body of standard character, which we call a thermometer, in the bath, and say that the first body, the bath, and the thermometer, have all the same temperature. But the body under such circumstances, as well as the bath, and the thermometer, even if they were entirely isolated from external influences (which it is convenient to suppose in a theoretical discussion), *would be continually changing in phase* (i.e., in entropy<sup>3</sup>), *and in energy as well as in other respects, although*

*our means of observation are not fine enough to perceive these variations*” (italics added).

From this standpoint, to the accomplishments of physics of the past century must undoubtedly be added the fact that the development of statistical thermodynamics as a *macroscopic* statistical theory, the credit for which indisputably goes to Einstein [11–13] and his followers, has led to the construction of the modern theory of thermodynamic fluctuations and its numerous applications (for details, see review Ref. [14]).

In this connection, we recall that precisely the fluctuation analysis of thermal radiation permitted Einstein to arrive at the notion of a photon, which gave impetus to the construction of quantum radiation theory. Today, the fluctuation study of the cosmic background radiation in its turn has become one of the main methods of investigating the past and future of the Universe, which opens up a new chapter in the progress of physics as a whole [15].

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