

MODERN ANALYSIS OF THE BOLTZMANN DISTRIBUTION

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Abstract. Modern analysis of the Boltzmann distribution on the basis of probability theory and Gibbs quantum canonical distribution is proposed. It is shown that the Boltzmann distribution function is neither a reliable result of probability theory nor a consequence of Gibbs quantum canonical distribution. The conclusion is that the Boltzmann distribution function has no physical-statistical meaning, and the concept “Boltzmann distribution” should be abolished.

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Introduction

As is known, the Boltzmann distribution function – one of achievements of 19th century’s statistical physics – is widely used in modern physics, for example, in the theory of ideal gas, laser physics, chemical physics, plasma physics. However, this circumstance is neither a criterion of validity nor convincing proof of correctness of the Boltzmann distribution function because a derivation of this function is not based on the concept of random quantity in heat phenomena – probability theory’s fundamental concept. Also, in my opinion, the generally accepted statement that the Boltzmann distribution represents the particular case of Gibbs quantum canonical distribution is groundless. To date, no one has cast doubt on the concept “Boltzmann distribution”. The purpose of the present work is to analyse this concept on the basis of probability theory and Gibbs quantum canonical distribution.

1. Gibbs quantum canonical distribution

As is known [1], the concept of random quantity is a starting-point for any physical-statistical theory, and the distribution of probabilities gives the correct and complete statistical description of the physical system. If the physical system is a “macroscopic set of free quantum particles”, it is called an ideal gas. Ideal gas is called normal (non-quantum) gas if the particles “interact only by way of mutual collisions” (Einstein). And if the particles of gas do not interact with each other, the ideal gas is called abnormal (quantum) gas. In the case of heat phenomena in an isolated macroscopic system, “ideal (normal) gas of molecules”, molecules collide with each other in a random way. Since the change of energy of a molecule occurs as a result of the great number of random collisions, the energy of the molecule represents a discrete random quantity. If ideal (normal) gas is reduced to the system “molecule + molecular gas” (where “molecule” is a subsystem and “molecular gas” surrounds it,) then the following quantum-statistical assertions are valid [1].

1) The random quantity takes on the values E_n , $n = 0, 1, 2, \dots$ where $E_0 = 0$ is origin of counting of the random quantity.

- 2) Every element E_n of the set of possible values of energy is in unambiguous (one-to-one) correspondence with the probability $f_n(t)$ of the energy state of the molecule. The distribution of probability $f_n(t)$ gives the complete quantum-statistical description of a molecule of gas.
- 3) Statistical ensemble of identical systems, “molecule in n th quantum state + molecular gas” defines the probability $f_n(t)$ that the molecule is in the quantum state n with energy E_n :

$$f_n(t) \equiv \lim_{N \rightarrow \infty} \frac{N_n(t)}{N}, \quad N = \sum_{n=0}^{\infty} N_n(t), \quad 0 \leq t < \infty,$$

where $N_n(t)$ is number of systems of a “molecule in n th quantum state + molecular gas” in a moment of time t ; N is the full number of systems of “molecule + molecular gas” in the ensemble (this number does not depend on time).

- 4) Probability $f_n(t)$ characterizes ensemble of systems and satisfies conditions of normalization (and conservation of normalization),

$$\sum_{n=0}^{\infty} f_n(t) = 1, \quad 0 < f_n(t) < 1,$$

of unambiguity and of uniqueness.

- 5) The statistical-average energy $E(t)$ of the molecule is defined by the relationship

$$E(t) \equiv \sum_{n=0}^{\infty} E_n f_n(t).$$

- 6) A unique limit of quantity $f_n(t)$ at $t \rightarrow \infty$ exists. The limit characterizes the statistical equilibrium state in the system “molecule + molecular gas”:

$$f_n(\infty) \equiv f_n^\circ, \quad f_n^\circ = f_0^\circ \exp(-E_n/T)$$

where f_n° is Gibbs quantum canonical distribution, T is statistical temperature of molecule (i.e. the universal statistical parameter of molecules, statistical potential of the system).

- 7) Gibbs quantum canonical distribution defines the correct relationship between the statistical-average (microscopic) energy E of the molecule, the statistical-average (microscopic) entropy s of the molecule, and its statistical temperature. This relationship has the form:

$$s = E/T, \quad E \equiv \sum_{n=0}^{\infty} E_n f_n^\circ, \quad s \equiv \sum_{n=0}^{\infty} s_n f_n^\circ, \quad s_n \equiv E_n/T = -\ln(f_n^\circ/f_0^\circ).$$

The following main statements results from the above:

- (a) The number $N_n(t)$ of the system, “molecule in n th quantum state + molecular gas” in the ensemble and the full number N of the systems “molecule + molecular gas” in the ensemble does not represent the numbers of molecules in the system;

(b) If the energy of the molecule is a random quantity, then distribution function f_n° (Gibbs quantum canonical distribution) does not depend on the number of molecules in the system. These statements are a basis for discussion of the Boltzmann distribution function.

2. Analysis of the Boltzmann distribution function

As is known, the Boltzmann distribution function has the following form:

$$b_i = b g_i Z^{-1} \exp(-E_i/T)$$

where b is the total density of the molecules; b_i is the density of molecules in state i ; T is the temperature; g_i is the degeneracy of state i ; and Z is the partition function. From the viewpoint of probability theory and Gibbs quantum canonical distribution, the Boltzmann distribution function is open to objections. The objections are as follows:

(a) The Boltzmann distribution function is not a consequence of Gibbs quantum canonical distribution. In order to prove this statement, one should assume that the contrary is valid: Boltzmann distribution function and Gibbs quantum canonical distribution are identical at some conditions, i.e.

$$\exp(-E_i/T) = b_i Z / b g_i \equiv f_i^\circ / f_0^\circ .$$

The identity is reduced to the following form:

$$f_i^\circ \equiv f_0^\circ \frac{b_i Z}{b g_i}, \quad \text{i.e.} \quad f_i^\circ \propto \frac{b_i}{b} .$$

This expression means that the probability is defined by the densities of molecules, i.e. the probability f_i° depends on the number of molecules in the system at any conditions. But this result contradicts the correct definition of probability. Consequently, the assumption is not valid. Thus, The Boltzmann distribution function is not a consequence of Gibbs quantum canonical distribution;

(b) The Boltzmann distribution function is not based on probability theory: in the Boltzmann theory of gas, a set of molecules is a statistical ensemble. But such representation contradicts probability theory: from the viewpoint of probability theory, the number of systems, “molecule in i th quantum state + molecular gas” in the ensemble represents the number of occurrences of the random event “molecule in i th quantum state + molecular gas”. Therefore, probability is a limit of the ratio of two numbers of occurrences. This means that the Boltzmann distribution function is not a reliable result of probability theory.

Conclusion

Thus, modern analysis of the Boltzmann distribution on the basis of probability theory and Gibbs quantum canonical distribution leads to the conclusion that it is open to objections. The main objection is that it is neither a reliable result of probability theory nor the consequence of Gibbs quantum canonical distribution. From this viewpoint, the Boltzmann distribution function has no physical-statistical meaning, and the concept should be abolished.

Reference

[1] T.Z. Kalanov, "The correct theoretical analysis of the foundations of classical thermodynamics", Bull. of Pure and Applied Sciences, Vol. 26D, No 2 (2007), pp. 109-118 (www.bulletinpureappliedscience.com).