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Extensivity of entropy and modern form of Gibbs paradox

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Abstract. The extensivity property of entropy is clarified in the light of a critical examination of the entropy formula based on quantum statistics and the relevant thermodynamic requirement. The modern form of the Gibbs paradox, related to the discontinuous jump in entropy due to identity or non-identity of particles, is critically investigated. Qualitative framework of a new resolution of this paradox, which analyses the general effect of distinction mark on the Hamiltonian of a system of identical particles, is outlined.

Keywords. Extensivity of entropy; Gibbs paradox; distinguishability; identical particles; Hamiltonian.

1. Introduction

In this paper we first examine the expression for entropy of a system of N non-interacting particles in the high temperature-low density limit, as given by Bose-Einstein (B-E) and Fermi-Dirac (F-D) statistics. We point out that for a finite N-particle system, the formula for entropy has a valid term non-proportional to N, which is given by $(k/2) \ln N$. The usual arguments put forward for the neglect of this term have been critically scrutinized. Then the question arises whether such a term, non-proportional to N in the entropy formula, leads to any genuine contradiction with thermodynamics. This necessitates a careful analysis of the thermodynamic requirement regarding the extensivity property of entropy, which is dealt with in § 3. We conclude that thermodynamics demands only that part of entropy to be proportional to N which depends on the thermodynamic variables; hence the term $(k/2) \ln N$ in the entropy formula based on quantum statistics does not contradict any thermodynamic principle. The widely prevalent notion that the formula for entropy based on the concept of distinguishability presents conceptual contradiction with thermodynamics essentially due to the presence of a term non-proportional to N (Gibbs paradox in its old form) is shown to be incorrect. In § 4, the modern form of the Gibbs paradox, regarding the apparent discontinuous jump in the entropy value as distinction marks are ascribed in a system of identical particles, is discussed. Explanations proposed so far have been critically reviewed and the basic ideas of a new resolution are suggested with a view to providing deeper qualitative insight into this paradox.

2. Entropy in quantum statistics

We consider a system of N non-interacting particles. In the limit of high temperature and low density, entropy in both B-E and F-D statistics is given by

$$S = Nk\ [(5/2)\ln T - \ln P + \ln A + (5/2)] - (k/2)\ln N + g(N), \quad (1)$$

where $A=(2\ \pi\ m/h^2)^{3/2}\ K^{5/2}$ and $g(N)$ is an arbitrary function of N implied in the statistical definition of entropy. For origin of the term $(k/2)\ln N$ in (1), see the expression for the partition function as given by 7.12 in Schrödinger's treatment (Schrödinger 1967), which is obtained by the Darwin-Fowler method of steepest descent and from which (1) including the $(k/2)\ln N$ term can be derived using the high temperature-low density approximation. It needs to be emphasized that the consistent use of the approximation involved in the steepest descent method does not as such warrant dropping of the term $(k/2)\ln N$ in (1). Usually the term $(k/2)\ln N$ in (1) is ignored since it is empirically insignificant. However, the very existence of such a term non-proportional to N in the entropy formula is intriguing because it apparently leads to contradiction with thermodynamics if one follows the formulation of the so-called Gibbs paradox in its old form (Gibbs 1931; Huang 1963; Reif 1965; Sudarshan and Mehra 1970). It is widely believed that in the region where U and V are proportional to N, thermodynamics demands that S must also be proportional to N; (1) does not satisfy this requirement, unless one goes to the limit $N\to\infty$ in evaluating S/N. Schrödinger (1967) has justified the limit $N\to\infty$ on the ground that for finite N, the so-called surface effects become important (see remarks following 7.15 in the treatment by Schrödinger 1967). But it is to be remembered that only the low-lying energy states are sensitive to the surface. At high temperatures where (1) applies, the occupation for the low-lying surface-dependent energy states is negligible. Hence to avoid surface effects, it is not necessary in this case to go to the limit $N\to\infty$. It is also usually asserted that the statistical definition of entropy is consistent with that of thermodynamics only in the so-called thermodynamic limit, *i.e.* for $N\to\infty$ (see, for example, Münster 1969). Here we note that in statistical mechanics the definition of any thermodynamic function requires some form of a limiting process to make the definition consistent with the laws of thermodynamics. One can use the limiting process $N\to\infty$. But this is not the only possible procedure. For a system with finite N, one can ensure consistency with thermodynamics by considering the thermodynamic functions as averages over the members of an ensemble of replicas of the given system (the Gibbs-Einstein ensemble formalism) and going to the limit of infinitely large number of members (the effects of fluctuations are then eliminated). In deriving (1), the latter limiting process is used. Hence in this case the question of going to the limit $N\to\infty$ in (1) to ensure consistency with thermodynamics does not arise. We emphasize the term $(k/2)\ln N$ in the entropy formula (1) because, though empirically insignificant, it is conceptually important—revealing that even in statistics based on the concept of indistinguishability, entropy is not strictly proportional to N, thereby necessitating a close look at the thermodynamic requirement regarding the extensivity of entropy (significance of this particular property of entropy will be evident from discussions by Landsberg 1961; Wright 1970; Landsberg and Tranah 1980).

3. Extensivity of entropy in thermodynamics

If U and V are extensive for some region of the variables T, P we may write

$$U = N\,u\,(T, P);\;\; V = N\,v\,(T, P).$$

Integrating the thermodynamic expression $dS = (dU + PdV)/T$, we then obtain for entropy in this region

$$S = N\,s\,(T, P) + f(N), \tag{2}$$

where the constant of integration $f(N)$ must be regarded as a function of N, because for various states of a given system, N is a constant; to be noted that $f(N)$ cannot be determined thermodynamically (for relevant remarks pointing out the difficulties associated with the determination of N-dependence of entropy, see Ehrenfest and Trkal 1921; Fowler 1966). The well-known partition removal method for a gas of identical particles (usually discussed in connection with the old form of Gibbs paradox) cannot lead to the requirement $S \propto N$ because partition removal with the given number of gas molecules in the two sub-volumes of the system is not a reversible process (see discussion by Casper and Freier 1973 with reference to what they call ' microscopic preparation ' of the system).

Comparing (1) and (2) we obtain

$$f(N) = N\,k\,[\ln A + (5/2)] - (k/2) \ln N + g(N). \tag{3}$$

We conclude that the presence of the term $(k/2) \ln N$ in (1) does not lead to any contradiction with thermodynamics because that part of entropy given in (1) which depends on the thermodynamic variables T, P is extensive, and this is the precise form of the thermodynamic requirement regarding the extensivity of entropy.

If the identical particles are considered distinguishable, the expression for entropy becomes according to classical statistics

$$S = Nk\;[(5/2) \ln T - \ln P + \ln A + (3/2)] + Nk \ln N + g(N). \tag{4}$$

Since that part of entropy which depends on T and P is proportional to N, (4) as such presents no conceptual contradiction with thermodynamics (for relevant discussion on this point see Jackson 1968).

4. Modern Gibbs paradox and its resolution

According to the modern viewpoint, identical particles are necessarily indistinguishable and distinguishability is taken to imply non-identity of particles. Thus (4) gives the correct value of entropy for a system of N non-identical particles. Then it is evident that for distinction marks, however small, the entropy value for a system of identical particles can change abruptly from (1) to (4). Such a discontinuous change in macroscopic property is thought to be puzzling and this forms the crux of the modern version of the Gibbs paradox (see, *e.g.*, Yourgrau *et al* 1966).

It has been argued by Bridgman (1961), Penrose (1970), Sommerfeld (1956) and Fong (1963) that the discontinuous jump in the measurable properties during transition from identity to non-identity is a reflection of the inherent discontinuity in the operational procedure of distinguishing identical particles from non-identical particles. However, Landsberg and Tranah (1978) have pointed out that this type of argument 'is not sound'. A deeper investigation, aimed at bridging the apparent discontinuous change of entropy on the basis of microscopic analysis, has been developed by Von Neumann (1955), Klein (1958) and Lande (1960), the essence of which may be outlined as follows: It is assumed that the effect of distinction mark on a system of identical particles is to throw the particles into different quantum states. The state function ψ of a system of particles with distinction marks is considered in the form

$$\psi = (1 - b^2)^{1/2}\, \psi_1 + b\, \psi_2, \tag{5}$$

where ψ_1 and ψ_2 are orthogonal states. In the case of complete identity, $b = 0$; for complete non-identity, $b = 1$. It is then shown that the change in entropy due to transition from identity to non-identity is a continuous function of the parameter b. But this analysis essentially assumes that the Hamiltonian of the system is unaffected by distinction mark, which is not true in general. We shall now propose a new resolution of this paradox, which attempts to probe the general effect of distinction mark on the Hamiltonian of a system of identical particles.

For a system of identical particles, the Hamiltonian is symmetric with respect to the interchange of any two particles. The degenerate states of the N-particle system are classified according to the symmetry character of the wave functions, of which the completely symmetric and completely antisymmetric wave functions are the two special cases. With symmetric Hamiltonian, transitions between states of different symmetry characters are impossible. The general effect of any distinction mark on a system of identical particles (with respect to some permanent property of the system) will be to generate a non-symmetric term in the Hamiltonian of the system. This will induce transitions between states of different symmetry characters.

Let T_j be a measure of the relaxation time for transitions between states of different symmetry characters, and T is the relaxation time for transitions between states of the same symmetry type. The quantity $d = T/T_j$ may be regarded as a quantitative measure of the distinguishability of the particles. In the absence of any distinction mark, $T_j \to \infty$ which implies $d = 0$; *i.e.*, the particles are to be regarded as identical. In the case of strong distinction mark, $T_j < T$ which implies $d > 1$; then the particles are to be considered non-identical. The case of $0 < d < 1$ corresponds to weak distinction mark. Consideration of the thermodynamic behaviour of a system with weak distinction mark provides a clue for an interesting resolution of the Gibbs paradox in its modern form.

When $0 < d < 1$, transitions between states of the same symmetry type will be faster compared to transitions between states of different symmetry types. Hence the metastable thermodynamic equilibrium induced by the relaxation time T will be established quite early. It becomes meaningful then to discuss the thermodynamic properties of a system in such a metastable state and these properties will depend on the symmetry type of the initial state of the system. As an example, if the initial state is completely symmetric, the properties of the system in the metastable equilibrium will resemble that of a system of bosons whose entropy in the appropriate limit is given by (1). As an effect of the weak distinction marks, the metastable state will slowly change with time as transitions are induced to states of other symmetry characters. After some time, the state of the system will be a superposition of states of different symmetry types and and resulting situation may be interpreted as that of a mixture of gases obeying different types of statistics, B-E, F-D, and others which are theoretically permissible but unknown in systems of fundamental particles. In such a condition, entropy of the system will have some value intermediate between those given by (1) and (4). Entropy expressions in these intermediate metastable states are functions of the particle distribution among states of different symmetry types and this distribution changes with time. Consequently, the entropy expression changes continuously, ultimately reaching its final value given by (4); complete non-identity of particles is then said to have been established. Thus the entropy grows from its initial value (1) to its final value (4) through a continuous series of metastable states and there is no discontinuity in the whole phenomenon. Usually this time evolution is overlooked and the attention is focussed only on the final equilibrium state; then one finds the apparent discontinuity in entropy and hence the so-called modern form of Gibbs paradox arises. Our analysis suggests that the time required for transition from identity to non-identity is a continuous function of the distinguishability parameter d (*i.e.* effectively the strength of the distinction mark); it decreases with the increase in the value of d. Quantitative model calculation based on this approach is presently under investigation. In particular, the case $0 < d < 1$ may be operationally significant for a system of identical macro-molecules where sufficiently weak distinction marks can be ascribed.

5. Concluding remarks

The focal point of the new resolution of the modern form of the Gibbs paradox discussed in § 4 is the way we have interpreted the effect of distinction mark, *viz.* to generate transitions between states of different symmetry types and the possibility of time-evolution of entropy flowing from it. As a consequence, the problematic discontinuity in the paradox can be resolved by considering time-evolution of entropy from its value for a system of identical particles to that of a system of non-identical particles. In this connection it needs to be emphasized that so far as the final equilibrium state properties are concerned, there is no difference between non-identity and distinguishability. But the crucial point is that the time required for transition from identity to non-identity depends on the strength of the distinction mark.

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