ENTROPY OF A POLARIZED GAS AND THE GIBBS PARADOX

PHYSICS

1970

SovietRxiv

Abstract

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UDC 536.751:539.121.42

PHYSICS

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ENTROPY OF A POLARIZED GAS AND THE GIBBS PARADOX

(Presented by Academician B. M. Pontecorvo, March 5, 1970)

1. As is well known, the entropy of a mixture of several distinct ideal gases is determined by the formula

$$S = k \sum_i N_i \ln \frac{V}{N_i}. \tag{1}$$

Here k is Boltzmann' s constant; V is the volume; N_i is the number of atoms of the i-th kind of gas (here and below we omit the term, immaterial for us, of the form $\sum_i N_i f_i(T)$, which depends on the temperature). On the basis of relation (1), the widely known Gibbs paradox arises ([1]).

Let us imagine two identical volumes V, separated by an impermeable partition and filled with different gases A and B at equal pressures and temperatures. After the partition is removed, as a result of diffusion the entropy of the system increases by the amount

$$\Delta S = k \left(2N \ln \frac{2V}{N} - 2N \ln \frac{V}{N} \right) = 2kN \ln 2, \tag{2}$$

where N is the number of atoms of each of the gases. It is essential that expression (2) does not depend on the nature of the difference between the mixing gases A and B. On the other hand, if both volumes are filled with one and the same gas, removal of the partition does not change the state of the system, and in accordance with (1)

$$\Delta S = k \left(2N \ln \frac{2V}{2N} - 2N \ln \frac{V}{N} \right) = 0. \tag{3}$$

The jump-like change in the magnitude of ΔS in the transition from gases close in their properties (but differing in some respect) to absolutely identical gases constitutes the aforementioned paradox.

The reasons for such a jump have been discussed many times in the literature and, in particular, the fundamental role of the discreteness of the states of the atoms of the gases under consideration has been noted. We agree that under conditions in which the properties of gases can change only discretely, there is nothing paradoxical in the difference between the values (2) and (3). The paradox would indeed exist if it were possible to find a continuous parameter of closeness (difference) of gases and, nevertheless, the jump were to persist. In the present work we shall show that such a continuous parameter exists. In this case no paradox arises, since, depending on the degree of closeness (difference) of the gases, the change in the entropy of the system under the conditions described above assumes a continuous series of values in the interval

$$0 \leq \Delta S \leq 2kN \ln 2. \tag{4}$$

Relation (4), in our opinion, gives the final resolution of the Gibbs paradox.

2. Suppose that gases A and B are homogeneous mixtures of two different gases C and D. In this case gas A contains Nx_1 atoms of C and Nx_2 atoms of D, while gas B contains Ny_1 atoms of C and Ny_2 atoms of D ($x_1 + x_2 = y_1 + y_2 = 1$).

Naturally there arises the question of the degree of closeness of such mixtures. As the corresponding continuous parameter one may take the quantity $\eta = |x_1 - x_2| = |y_1 - y_2|$. For $\eta = 0$ ($x_1 = y_1,\ x_2 = y_2$) the two gases A and B are absolutely identical, while for $\eta = 1$ ($x_1 y_1 = x_2 y_2 = 0$) we are dealing with two maximally different gases C and D.

Applying relation (1), we obtain for the change in entropy after mixing gases A and B the expression

$$\Delta S = kN \left[\sum_{i=1}^{2} x_i \ln x_i + \sum_{i=1}^{2} y_i \ln y_i - \sum_{i=1}^{2} (x_i + y_i) \ln \frac{x_i + y_i}{2} \right] =$$

$$= kN \left[\sum_{i=1}^{2} x_i \ln \frac{x_i}{x_i + y_i} + \sum_{i=1}^{2} y_i \ln \frac{y_i}{x_i + y_i} \right] + 2kN \ln 2. \tag{5}$$

If $\eta = 0$, $\Delta S = 0$; if $\eta = 1$, then $\Delta S = 2kN \ln 2$. Since for $x_i \geq 0,\ y_i \geq 0$ the quantity $x_i \ln \dfrac{x_i}{x_i + y_i} \leq 0$, it follows from the second equality (5) that

$$\Delta S \leq 2kN \ln 2.$$

On the basis of the known inequality (2)

$$\sum_{i=1}^{m} x_i \ln x_i \geq \sum_{i=1}^{m} x_i \ln z_i \quad \left(\sum_{i=1}^{m} x_i = 1,\ \sum_{i=1}^{m} z_i = 1,\ x_i \geq 0,\ z_i \geq 0 \right)$$

we come to the conclusion that $\Delta S \geq 0$. Thus relation (4) holds. It is easy to see that if A and B are mixtures of m different components ($m > 2$), the formula for the change in entropy upon mixing will have the form (5) with the replacement $\sum_{i=1}^{2} \to \sum_{i=1}^{m}$. Thus, in the general case, ΔS depends continuously on the variables x_i and y_i ($x_i \geq 0,\ y_i \geq 0,\ \sum_{i=1}^{m} x_i = 1,\ \sum_{i=1}^{m} y_i = 1$) and satisfies inequality (4). For $x_1 = y_1,\ x_2 = y_2, \dots, x_m = y_m$ the quantity $\Delta S = 0$. The maximum change in entropy, equal to $2kN \ln 2$, occurs only under the condition $x_1 y_1 = x_2 y_2 = \dots = x_{my} m = 0$, i.e., in the case when mixtures A and B contain no atoms of coinciding species.

3. In the preceding section the continuous parameter referred to the gases as a whole, but did not concern the individual atoms. From the point of view of quantum mechanics the concept of the degree of closeness and difference has a deeper meaning. This is connected with the fact that, according to the superposition principle, the internal states of atoms may be nonorthogonal to one another and thereby not fully distinguishable (see ([3])). For clarity, we shall carry out all further consideration using the example of spin polarization, although the results obtained below have a more general significance.

Suppose that gas A, filling one of two equal volumes, consists of N atoms with spin 1/2 (for example, He^3), completely polarized along the vector $\mathbf{n}$, while gas B, filling the other volume, contains N identical atoms, completely polarized along the vector $\mathbf{m}$ ($\mathbf{m}^2 = \mathbf{n}^2$)*. It is easy to see that in this case the continuous parameter of closeness of atoms A and B is the angle θ between the vectors $\mathbf{m}$ and $\mathbf{n}$. For $\theta = 0$ the atoms A and B are absolutely identical; for $\theta = \pi$ they are completely different. Let us show that the change–

* In view of the fact that recently gas targets with a high degree of polarization have been created (see, for example, ([4])), the example of a polarized gas is not purely academic.

the entropy change upon mixing such gases depends continuously on the angle θ.

To this end, first of all let us find the dependence of the entropy on the degree of polarization P. From the macroscopic point of view, a gas containing N atoms with polarization $\mathbf{P}$ is an incoherent mixture of $N(1+P)/2$ atoms C with the projection of the spin on the vector $\mathbf{P}$ equal to $+1/2$, and $N(1-P)/2$ atoms D with the projection of the spin on the vector $\mathbf{P}$ equal to $-1/2$ (everywhere $P = |\mathbf{P}|$). Since the states C and D are completely different, we may use formula (1) for the entropy of a mixture of unlike gases*. Hence

$$S(P, V, N) = -kN \frac{1+P}{2} \ln \frac{1+P}{1} - kN \frac{1-P}{2} \ln \frac{1-P}{2} + kN \ln \frac{V}{N}, \quad (6)$$

It is easy to see that the entropy is a decreasing function of P. Its maximum value ($S = kN \ln 2 + kN \ln V/N$) corresponds to an unpolarized gas, and its minimum ($S = kN \ln V/N$) to a completely polarized gas.

We shall assume that, when the gases of interest to us are mixed, the spin-relaxation time is many times greater than the characteristic diffusion time. Then, after the impermeable partition is removed, there will be a gas occupying the volume $2V$ and containing $2N$ atoms with polarization $\mathbf{P} = \frac{1}{2}(\mathbf{n} + \mathbf{m})$. In this case the degree of polarization is $P = \cos\theta/2$.

Taking (9) into account, the change in entropy after mixing gases A and B is equal to

$$\Delta S(\theta) = S\left(\cos\frac{\theta}{2},\, 2V,\, 2N\right) - 2kN \ln\frac{V}{N} =$$

$$= -kN\left(1 + \cos\frac{\theta}{2}\right)\ln\frac{1+\cos\theta/2}{2} - kN\left(1 - \cos\frac{\theta}{2}\right)\ln\frac{1-\cos\theta/2}{2}. \quad (7)$$

For $\theta = 0$ the quantity $\Delta S = 0$, while for $\theta = \pi$ the quantity $\Delta S = 2kN \ln 2$. In the intermediate case $d(\Delta S)/d\theta > 0$, and, consequently, inequality (4) is satisfied. Thus, the Gibbs paradox does not occur.

Let us note that in the case of spin 1/2 the quantity $\cos\theta/2 = |\langle\psi_A|\psi_B\rangle|$, where ψ_A and ψ_B are the spin functions of the atoms in the first and second volumes. Thus, ΔS is a continuous function of the degree of nonorthogonality $|\langle\psi_A|\psi_B\rangle|$. The corresponding formula has the form

$$\Delta S = -kN(1 + |\langle\psi_A|\psi_B\rangle|)\ln\frac{1+|\langle\psi_A|\psi_B\rangle|}{2} - -$$

$$-kN(1 - |\langle\psi_A|\psi_B\rangle|)\ln\frac{1-|\langle\psi_A|\psi_B\rangle|}{2}. \quad (8)$$

It can be shown that expression (8), in contrast to (7), is valid already for arbitrary values of the spin (and, in general, for superpositions of any nature).

For atoms A and B with spin 1/2 and arbitrary polarization vectors $\mathbf{P}_1$ and $\mathbf{P}_2$, the entropy change, according to (6), is equal to

$$\Delta S(\theta, P_1, P_2) = S(P, 2V, 2N) - S(P_1, V, N) - S(P_2, V, N), \quad (9)$$

where

$$P = \frac{1}{2}|\mathbf{P}_1 + \mathbf{P}_2| = \frac{1}{2}(P_1^2 + P_2^2 + 2P_1P_2\cos\theta)^{1/2}.$$

For $P_1 = P_2 = 1$ expression (9) goes over into (7). It is easy to see that if $\mathbf{P}_1 = \mathbf{P}_2$ (identical gases), then $\Delta S = 0$. Since $\partial S(P, V, N)/\partial P|_{V,N} \leq 0$, for fixed P_1 and P_2 the obvious inequality holds

$$\Delta S(0, P_1, P_2) \leq \Delta S(\theta, P_1, P_2) \leq \Delta S(\pi, P_1, P_2). \quad (10)$$

* For a rigorous justification see (3).

In other words, the maximum change of entropy upon mixing polarized gases corresponds to the antiparallel orientation of P_1 and P_2, and the minimum to the parallel orientation. Moreover, if $P_1 \neq P_2$, the inequalities hold

$$\Delta S(0, P_1, P_2) > 0; \qquad \Delta S(\pi, P_1, P_2) < \Delta S(\pi, 1, 1) = 2kN \ln 2. \quad (11)$$

In conclusion we note that a point of view on the Gibbs paradox analogous to ours was previously developed in the works of Landé [(5–7)]. However, owing to a fundamental error made by the author in defining the entropy of a mixture of two not completely distinguishable gases, the specific formulas obtained in [(5–7)] are incorrect.

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Received
12 II 1970

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Note: Figure translations are in progress. See original paper for figures.