Paradoxes of gas mixing

I. P. Bazarov

Moscow State University
Usp. Fiz. Nauk. **118**, 539–543 (March 1976)

A unified explanation of the Gibbs and Einstein paradoxes and of a new paradox in the mixing of quantum ideal gases is given. It is shown that all three paradoxes are due to the same physical cause—the corresponding discontinuity in the partial density on going from mixing of different gases to mixing of identical gases.

PACS numbers: 05.70.–a

Analyzing the change in entropy in the diffusion of gases, Gibbs[1] established that the entropy increase produced by mixing gases of different kinds at constant temperature and pressure does not depend on the nature of these gases, while mixing of two masses of the same ideal gas does not give rise to any entropy increase. Thus, mixing of two identical gases cannot be regarded as the limiting case of mixing two different gases, and, in going over from mixing of arbitrarily close gases to mixing of identical gases the entropy change experiences a discontinuity (the Gibbs paradox)

$$\Delta S = 2kN \ln 2, \tag{1}$$

where k is the Boltzmann constant and N is the number of atoms of each of the gases being mixed.

In a paper on the quantum theory of the ideal gas, Einstein[2] drew attention to a paradox to which this theory leads; this consists in the fact that a mixture of degenerate gases with N_1 atoms with mass m_1 and N_2 atoms with mass m_2 (differing by an arbitrarily small amount from m_1) at a given temperature has a different pressure from that of a simple gas, with $N_1 + N_2$ atoms, possessing practically the same mass of atoms and situated in the same volume.

It can also be established that on adiabatic mixing of quantum ideal gases a new paradox occurs—a discontinuity in the temperature change when we go from mixing of arbitrarily close gases to mixing of identical gases.

Here we wish to show that all three paradoxes are due to the same physical cause—the discontinuity in the change in the partial density of the gas when we go from mixing with arbitrarily close gases to mixing with identical gases; allowance for this discontinuity makes it possible to explain the paradoxes named.

We shall find the change in density of a gas when it is mixed. Suppose that in two equal volumes V, separated by a partition, there are N particles of each of the gases A and B, respectively. The particle-number density of gas A before mixing is equal to $n_1 = N/V$, and after isothermal mixing its density will be $n_2 = N/2V$. As a result of the mixing, the density of gas A is decreased by an amount

$$\Delta n = n_1 - n_2 = \frac{n_1}{2}; \tag{2}$$

this decrease does not depend on the nature of the other gas B or on its arbitrarily small difference from gas A, whereas mixing of two masses of the same gas A produces no change in its density.

Thus, the mixing of two masses of identical gases cannot be regarded, using (2), as the limiting case of the mixing of two different gases, and when we go over from mixing of arbitrarily close gases to mixing of identical gases the change in the density of gas A experiences the discontinuity (2).

In its formulation, this result coincides completely with the formulation of the Gibbs paradox, and could be called the density paradox; it is, however, so obvious that it does not seem unusual or paradoxical. But it leads to consequences which do seem paradoxical. We emphasize that the discontinuity in the change in density of the gas as we go from mixing of two different gases to mixing of identical gases does not depend on whether the difference between the gases changes discretely or continuously: the discontinuity (2) in the density change will be the same in both cases. Therefore, hardly anybody will assert that this discontinuity is due to the impossibility in the real world of an arbitrarily small difference between gases inasmuch as the atoms of gases differ from each other by some discrete quantum number.

We shall consider the paradoxical consequences of the discontinuity in the change in the partial density of the gas.

1. *The Gibbs paradox (entropy paradox)*. We shall calculate the entropy change when quantum ideal gases are mixed. The configurational part of the entropy[1)] of a weakly degenerate gas of N particles in a volume V at temperature T is equal to[3]

$$S = kN\left[\ln\frac{V}{N} + \frac{\delta}{32}\frac{Nh^3}{V(\pi mkT)^{3/2}}\right],$$

where m is the particle mass, h is Planck's constant, $\delta = -1$ for a Bose gas and $\delta = 1$ for a Fermi gas.

Before mixing, the entropy of gases A and B with masses m_1 and m_2 will be

$$S_{\mathrm{I}} = 2kN\left[\ln\frac{V}{N} + \frac{\delta}{64}\frac{Nh^3}{V(\pi kT)^{3/2}}\left(m_1^{-3/2} + m_2^{-3/2}\right)\right], \tag{3}$$

1)Only this part of the entropy is necessary in the analysis of isothermal processes.

and, after isothermal mixing of them, when each gas occupies a volume $2V$, the entropy of the mixture becomes

$$S_{II}=2kN\left[\ln\frac{2V}{N}+\frac{\delta}{128}\frac{Nh^3}{V(\pi kT)^{3/2}}(m_1^{-3/2}+m_2^{-3/2})\right]. \qquad (4)$$

Consequently, the change in the entropy of the system on mixing is equal to

$$\Delta S=S_{II}-S_I=2kN\left[\ln 2-\frac{\delta}{128}\frac{Nh^3}{V(\pi kT)^{3/2}}(m_1^{-3/2}+m_2^{-3/2})\right].$$

On mixing of arbitrarily close gases, when $m_2 \approx m_1 = m$, the entropy change is equal to

$$\Delta S=2kN\left[\ln 2-\frac{\delta}{64}\frac{Nh^3}{V(\pi mkT)^{3/2}}\right]. \qquad (5)$$

It is impossible to obtain the entropy of the mixture in the limiting case of mixing of two identical gases ($m_2 = m_1 = m$) from formula (4), because it does not take into account the discontinuity in the density of the gases which occurs when this limit is taken. In order to find the entropy S_{II}^0 of the system in the limiting case of mixing of identical gases using (4), when putting $m_2 = m_1 = m$ in this formula we must simultaneously replace the density N/V by the quantity $2N/V$. We then obtain, in agreement with thermodynamics,

$$S_{II}^0=2kN\left[\ln\frac{V}{N}+\frac{\delta}{32}\frac{Nh^3}{V(\pi mkT)^{3/2}}\right]=2S,$$

whence it follows automatically that the entropy change on mixing of identical gases is equal to zero.

Thus, when we go from mixing of arbitrarily close gases to mixing of identical gases the entropy change experiences the discontinuity (5). This is the quantum Gibbs paradox. In the classical case ($h \to 0$) the discontinuity in the quantity ΔS does not depend on the nature of the gases being mixed and is equal to (1).

It can be seen from this account that the origin of the Gibbs paradox is the discontinuity in the change of the partial density of the gas when we go over from mixing it with a close gas to mixing it with an identical gas; allowance for this discontinuity makes it possible to understand the origin of the discontinuity in the above limiting process, i.e., it explains the Gibbs paradox.

2. *The Einstein paradox (pressure or internal-energy paradox).* Using the well-known relation for an ideal gas:

$$pV=\frac{2}{3}U,$$

where p is the pressure of a gas in volume V and U is its internal energy, we formulate the Einstein paradox in the following form: although the internal-energy change ΔU on isothermal mixing of degenerate ideal gases depends on the nature of the gases being mixed, when we go over from mixing of arbitrarily close gases to mixing of identical gases ΔU experiences a discontinuity. The internal energy of a weakly degenerate ideal gas of N particles in volume V at temperature T is equal to[2)][3]

$$U=\frac{3}{2}NkT\left[1+\frac{\delta}{16}\frac{Nh^3}{V(\pi mkT)^{3/2}}\right].$$

Let the masses of the atoms of gases A and B be equal to m_1 and m_2 respectively. Then the internal energies of the system before and after isothermal mixing of the gases are, respectively, equal to

$$U_I=3NkT\left[1+\frac{\delta}{32}\frac{Nh^3}{V(\pi kT)^{3/2}}(m_1^{-3/2}+m_2^{-3/2})\right], \qquad (6)$$

$$U_{II}=3NkT\left[1+\frac{\delta}{64}\frac{Nh^3}{V(\pi kT)^{3/2}}(m_1^{-3/2}+m_2^{-3/2})\right], \qquad (7)$$

and the change in internal energy of the system on mixing the gases will be

$$\Delta U=U_{II}-U_I=-\frac{3\delta}{64}\frac{N^2h^3}{V(kT)^{1/2}\pi^{3/2}}(m_1^{-3/2}+m_2^{-3/2}). \qquad (8)$$

Hence, on mixing of arbitrarily close gases, when $m_2 \approx m_1 = m$, we find

$$\Delta U'=-\frac{3\delta}{32}\frac{N^2h^3}{V(\pi m)^{3/2}(kT)^{1/2}}. \qquad (9)$$

From formula (7) it is impossible to obtain the expression for the internal energy in the limiting case of mixing of identical gases ($m_1 = m_2 = m$) since (7) does not take into account the discontinuity in the density of the quantum gases that occurs in this mixing. In order to find the internal energy of the system in the limiting case of mixing of identical gases by means of formula (7), it is necessary to replace the density N/V by the quantity $2N/V$ in this formula. Then we obtain directly that the change of internal energy on isothermal mixing of identical gases is equal to zero and consequently, in going over from mixing of arbitrarily close gases to mixing of identical gases the change in internal energy of degenerate ideal gases experiences the discontinuity given by formula (9); this constitutes the Einstein paradox.

For a Bose gas the discontinuity ΔU is equal to

$$\Delta U=\frac{3}{32}\frac{N^2h^3}{V(\pi m)^{3/2}(kT)^{1/2}}, \qquad (10)$$

and, correspondingly, the pressure discontinuity will be

$$\Delta p=\frac{3}{2}\frac{\Delta U}{V}=\frac{9}{64}\frac{N^2h^3}{V^2(\pi m)^{3/2}(kT)^{1/2}}. \qquad (11)$$

From this account it can be seen that, as in the case of the Gibbs paradox, the source of the Einstein paradox is the discontinuity in the change in density of the gas when we go from mixing it with an arbitrarily close gas to mixing it with an identical gas; allowance for this discontinuity explains away (makes compreshensible and natural) the Gibbs and Einstein paradoxes.

In the classical case ($h \to 0$) the discontinuity (10) is

2)This expression for the internal energy takes into account the quantum-mechanical indistinguishability of the particles.

equal to zero, i. e., the Einstein paradox has no classical analog. This is due to the fact that the internal energy of a classical ideal gas is independent of its density.

3. *The temperature paradox.* The Einstein paradox arises in the isothermal mixing of quantum ideal gases. In adiabatic mixing of such gases it is absent. However, in this case, a new paradox is displayed—a discontinuity in the temperature change on going from adiabatic mixing of arbitrarily close quantum ideal gases to mixing of identical gases.

We shall consider adiabatic mixing of N particles of each of the weakly degenerate gases A and B, with masses m_1 and m_2 respectively, in equal volumes V separated by a thermally conducting partition and having temperature T_0.

Before mixing, the internal energy of the gases is equal to

$$U_{\mathrm{I}} = 3NkT_0\left[1 + \frac{\delta}{32}\frac{Nh^3}{V(\pi kT_0)^{3/2}}(m_1^{-3/2} + m_2^{-3/2})\right].$$

After removal of the partition and adiabatic mixing of the gases, when each gas occupies a volume $2V$, for unchanged internal energy of the system the temperature of the gases will be different (T) and the expression for the internal energy of the mixture takes the form

$$U_{\mathrm{II}} = 3NkT\left[1 + \frac{\delta}{64}\frac{Nh^3}{V(\pi kT)^{3/2}}(m_1^{-3/2} + m_2^{-3/2})\right]. \tag{12}$$

For adiabatic mixing of arbitrarily close gases ($m_2 \approx m_1 = m$) we have

$$U'_{\mathrm{I}} = 3NkT_0\left[1 + \frac{\delta}{16}\frac{Nh^3}{V(\pi mkT_0)^{3/2}}\right],$$
$$U'_{\mathrm{II}} = 3NkT\left[1 + \frac{\delta}{32}\frac{Nh^3}{V(\pi mkT)^{3/2}}\right]$$

and we find the resulting temperature change $T - T_0$ from the condition $U'_{\mathrm{I}} = U'_{\mathrm{II}}$, i. e, from the equation

$$T - T_0 = \frac{\delta}{32}\frac{Nh^3}{V(\pi mk)^{3/2}}\left(\frac{2}{\sqrt{T_0}} - \frac{1}{\sqrt{T}}\right). \tag{13}$$

In the limiting case of adiabatic mixing of two portions of an identical gas ($m_2 = m_1 = m$) we find the expression for the internal energy of the system from (12) by taking into account the density discontinuity which occurs in this mixing; this leads to $T - T_0 = 0$.

Thus, on going from adiabatic mixing of arbitrarily close quantum ideal gases to mixing of identical gases the temperature change in the mixing experiences the discontinuity given by Eq. (13). This new paradox for the temperature in the adiabatic mixing of quantum ideal gases is also due to the discontinuity in the density of the gas when we go from mixing of arbitrarily close gases to mixing of identical gases.

[1]J. W. Gibbs, The Collected Works, Vol. I., Thermodynamics, Longmans, N. Y., 1931 (p. 226 in Russ. transl., Gostekhizdat, M.–L., 1950).

[2]A. Einstein, Sobranie nauchnykh trudov (Collected Scientific Works), Vol. 3, p. 488, Nauka, M. 1966.

[3]L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, M., 1964 [English translation published by Pergamon Press, Oxford, 1969].

Translated by P. J. Shepherd

On the problem of the "retardation" of the relativistic contraction of moving bodies

S. I. Syrovatskiĭ

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR

Usp. Fiz. Nauk. **118**, 545–547 (March 1976)

PACS numbers: 03.30.+p

The relativistic contraction of moving bodies of systems of bodies sometimes leads to misunderstandings associated with the confusion of two essentially different phenomena. On the one hand we have the difference in the dimensions of a body as measured in two reference frames moving relative to each other, and on the other we have the change in dimensions of a body that is set in motion (or stopped) in a given coordinate frame. Whereas in the first case the answer is unique and is given by the Lorentz-transformation formulas, in the second case the answer depends essentially on precisely how the body under consideration has moved between two measurements. Despite the obviousness of these statements, it is useful to illustrate them by a simple example, especially as it shows in what conditions the difference disappears and the result can be expressed by the Lorentz transformation in both cases.

The one-dimensional problem of the motion of a plane layer of charges under the action of a plane electromagnetic wave serves as such an example. This problem arises in the problem of acceleration of particles in neutral current layers in a plasma. [1,2] We shall consider it in its simplest variant.

Suppose that a plane electromagnetic wave with a square front is incident on a thin layer of charged particles (in the (x, y)-plane; see the figure) along the normal to the layer. The problem is especially simple in