Gibbs Paradox and Equivalence Relation Between Quantum Information and Work.

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Abstract

The physical meaning of the entropy defect and information in quantum systems is analyzed in connection with Gibbs paradox and the maximum work obtainable by use of a non-equilibrium system. The question is studied of the maximum amount of heat that can be converted into mechanical work in the process of isothermic mixing of two gases, whose molecules differ only in their quantum states, having non-commuting density matrices. It is shown that schemes for producing work that involve direct discrimination of nonorthogonal states (such as the method of semipermeable partitions) yield an amount of work that is determined not by the entropy defect, but by the information in the system about its state, which reflects the fundamental irreversibility of the measurement process. An "equivalence relation" is suggested between quantum information and work.

In their original sense, entropy defect and amount of information characterize the properties of physical systems as carriers of information. [1,2]. The question arises whether these two quantities have direct physical sense, whether they can be associated, say, with the work that can be produced by a non-equilibrium system in the process of relaxation. In this paper we shall obtain a positive answer to this question, based on consideration of phenomena related to the Gibbs paradox. It will be shown that the maximum amount of heat convertible into mechanical work by isothermic mixing of gases which are in different but nonorthogonal quantum states, is determined not by the entropy defect buy by the amount of information. This process is accompanied by an increase in total entropy of the gas and the thermostat, i.e., it is in principle irreversible. There exists, however, a more complex, reversible process, in which the amount of work is determined by the entropy defect.

Consider a vessel divided by a partition into two parts of equal volume V_0, filled with different gases 1 and 2 at the same pressure and temperature (it is assumed that these are ideal Boltzmann gases, i.e., sufficiently rarefied). Let the number of molecules of each gas be N. After the partition has been removed and the gases mixed, the entropy (in natural units) increases by an amount

$$\Delta S = 2N \ln 2 \tag{1}$$

However, if the gases on either side of the partition are the same, there is no increase of entropy when diffusion occurs. This is the classical Gibbs paradox. The entropy increase occurring when different gases are mixed indicates that, when separated, the gases constitute a non-equilibrium system which can be used to obtain work. Indeed, if the partition is replaced by two movable semipermeable partitions (contiguous to each gas is a partition permeable to that gas but impermeable to the other), the gases are forced to push on the partitions, owing to the difference between the total pressure of the gases in the space between the partitions and the pressure of one of the gases on the other side of the partition. A simple calculation shows that under isothermic conditions the work obtained in this way is equal to

$$R = 2NkT \ln 2 \tag{2}$$

where k is the Boltzmann constant and T the absolute temperature. This work is derived from the heat removed from the thermostat, since the internal energy of the gases remains unchanged when they are mixed. This process is reversible, and the entropy increase of the gases is exactly equal to the entropy decrease in the thermostat:

$$\Delta S + \frac{\Delta Q}{kT} = \Delta S - \frac{R}{kT} = 0$$

Of course, when identical gases are mixed one cannot obtain any work. Thus, the possibility of converting heat into mechanical work is intimately bound up with the possibility of distinguishing between the molecules of the gases, i.e., of using the information contained in each molecule about the fact, in which half of the vessel the

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molecule was located. From the contemporary standpoint, the essence of the Gibbs paradox is that, whereas the entropy increase (or maximum obtainable mechanical work) when two identical gasses are mixed is zero, this quantity is abruptly increased when the identical gases are replaced by different gases, however similar their properties may be. Lyuboshits and Podgretskii [3] considered the case in which the molecules of gases 1 and 2 are the same particles, but in different quantum states $\psi^{(1)}$ and $\psi^{(2)}$ (e.g., with different spin orientation). If these states are not orthogonal, the molecules of the two gases can be distinguished only with a certain probability, and the entropy increase of the system when the gases are mixed is determined not by (1), but by the formula

$$\Delta S = 2NI_0 \tag{3}$$

where I_0 is the entropy defect of one molecule (see[2], formula (22)). Thus, these authors' measure of non-equilibrium for a system of two gases is precisely the entropy defect of the system for the particular case of two pure states. (Note that in this context, the states of all molecules of the gas are assumed to be statistically independent.) In the general case of mixed states, the measure of non-equilibrium is the entropy defect, defined by formula(7) in [2]. According to the physical meaning of entropy, the quantity I_0 should define the maximum work (per molecule of the gas) that can be obtained from heat removed from the thermostat in isothermic reversible mixing of gases; in other words, we should have

$$R_0 = 2\,N\,k\,T\,I_0 \tag{4}$$

But the situation is not so simple. It turns out that, if the density matrices describing the states of the molecules of gases 1 and 2 do not commute, in particular, if they correspond to two pure but nonorthogonal states $\psi^{(1)}$ and $\psi^{(2)}$, the work R_0 cannot be derived directly by mixing the gases. The point is that any procedure of discrimination between the molecules of the two gases involves a certain quantum-mechanical measurement applied to the molecules, thus introducing a fundamental irreversibility into the evolution of the entire system.

Let us consider our previous device for obtaining work with the help of two semipermeable partitions (Fig. 1).

Suppose that the partition facing gas 1 passes only molecules which are in a certain pure state ϕ_1 while that facing gas 2 passes only molecules in a state ϕ_2 orthogonal to ϕ_1. Thus, we are actually trying to distinguish between the molecules of the gases by measuring a certain physical quantity (denote it by L), the eigenfunctions of whose operator are our basis wave functions ϕ_1 and ϕ_2. Let $\rho_{11}^{(1)}$, $\rho_{22}^{(1)}$, and $\rho_{11}^{(2)}$, $\rho_{22}^{(2)}$ denote the diagonal elements of the matrices $\hat{\rho}^{(1)}$ and $\hat{\rho}^{(2)}$ in the basis $L = \{\phi_1, \phi_2\}$. Upon collision with the partition, there is a probability $\rho_{11}^{(1)}$ that a molecule of gas 1 will pass into state ϕ_1 and go through the partition, and a probability $\rho_{22}^{(1)}$ that it will pass into state ϕ_2. and remain on the same side, say to the left, of the partition as before. The molecules of gas 2 behave similarly with respect to the right-hand partition, which passes molecules in state ϕ_2.. Thus, the density matrices are reduced - their off-diagonal elements vanish - and instead of $\hat{\rho}^{(1)}$ and $\hat{\rho}^{(2)}$ the states of the gases are described now by the matrices

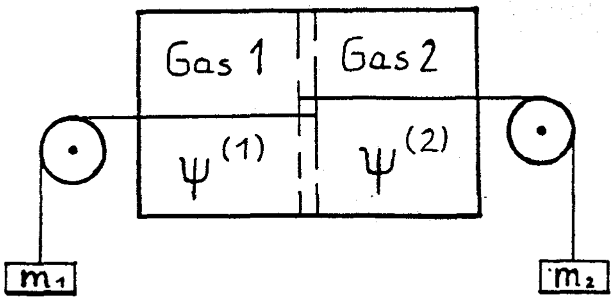

Fig.1. **Scheme for obtaining work by mixing gases. The excess pressure of the gases between the semipermeable partitions pushes them apart and lifts loads m_1 and m_2. Due to interaction with the partitions, the initial states $\psi^{(1)}$ and $\psi^{(2)}$ of the gas molecules change to a mixture of states ϕ_1 and ϕ_2.**

$$\rho_{u'}^{(1')} = \rho_{u'}^{(1)}\delta_{u'} \quad ; \quad \rho_{u'}^{(2')} = \rho_{u'}^{(2)}\delta_{u'} \tag{5}$$

As a result of this reduction, the states of the gas to the left, to the right and in between the partitions are different mixtures of state ϕ_1 (call it gas A) and of state ϕ_2 (gas B). Consider the instant when the left partition moves to the left by a volume V and the right partition to the right by a volume V′. Gas A, "produced" from gas 1, will then fill the volume $V_0 + V'$ and gas B (produced from gas 1) the volume V_0 - V'. Similarly, gas A (from gas 2) will fill the volume V_0 - V' and gas B (from gas 2) the volume $V_0 + V'$). The pressures of the gases to the left, to the right and in between the partitions are, respectively,

$$P_\iota = NkT\left(\frac{\rho_{11}{}^{(1)}}{V_0 + V'} + \frac{\rho_{22}{}^{(1)}}{V_0 - V}\right)$$

$$P_d = NkT\left(\frac{\rho_{22}{}^{(2)}}{V_0 + V} + \frac{\rho_{11}{}^{(2)}}{V_0 - V'}\right) \tag{6}$$

$$P_m = NkT\left(\frac{\rho_{11}{}^{(1)}}{V_0 + V'} + \frac{\rho_{22}{}^{(2)}}{V_0 + V}\right)$$

The work produced by the gas in the quasi-static isothermic process associated with the measurement of the quantity L is

$$R = \int_0^{V_1} (P_m - P_\iota)\, dV \; + \; \int_0^{V_2} (P_m - P_d)\, dV' \tag{7}$$

where V_1 and V_2 are defined by the conditions

$$P_m(V_1) = P_\iota(V_1) \;\; ; \;\; P_m(V_2) = P_d(V_2) \tag{8}$$

From (6), (7) and (8), we obtain

$$\begin{aligned} R_L = NkT[&\rho_{11}{}^{(1)} \ln \rho_{11}{}^{(1)} + \rho_{22}{}^{(1)} \ln \rho_{22}{}^{(1)} + \\ &+ \rho_{11}{}^{(2)} \ln \rho_{11}{}^{(2)} + \rho_{22}{}^{(2)} \ln \rho_{22}{}^{(2)} - \\ &- (\rho_{11}{}^{(1)} + \rho_{11}{}^{(2)}) \ln \frac{\rho_{11}{}^{(1)} + \rho_{11}{}^{(2)}}{2} - \\ &- (\rho_{22}{}^{(1)} + \rho_{22}{}^{(2)}) \ln \frac{\rho_{22}{}^{(1)} + \rho_{22}{}^{(2)}}{2} = \\ &= 2\, N\, k\, T\, I_L \end{aligned} \tag{9}$$

where I_L is defined as in ([2], formula (9)).

Thus the maximum amount of work obtainable in this process is

$$R = 2\, N\, k\, T\, I \tag{10}$$

where I is determined, in the case of pure initial states, by formula (23) in [2].

Why does this work fall short of R_0? The reason is that the process is irreversible. It is accompanied by an increase in the total entropy of the gas and the thermostat. Indeed, as the initial states of the gas were pure, the entropy increase of the gas is

$$\Delta S = -2N \sum_\iota \rho_{\iota\iota} \ln \rho_{\iota\iota} = 2N \ln 2$$

and

$$\Delta S + \frac{\Delta Q}{kT} = \Delta S - \frac{R}{kT} = 2N(\ln 2 - I) \geq 0 \tag{11}$$

(equality holding only when the initial states are orthogonal). The reason for this irreversibility is the increase of entropy in the measurement process, due to reduction of the density matrices [4] (when we pass on from the matrices $\hat{\rho}^{(1)}$, $\hat{\rho}^{(2)}$ to $\hat{\rho}'^{(1)}$, $\hat{\rho}'^{(2)}$). Note that the final state of the mixture of the gases is described not by the density matrix $\hat{\rho} = \frac{1}{2}(\hat{\rho}^{(1)} + \hat{\rho}^{(2)})$ but by the matrix $\rho'_{\iota\iota'} = \rho_{\iota\iota'}\delta_{\iota\iota'}$. Thus the maximum work obtained by direct isothermic mixing of gases is determined not by the entropy defect but by the amount of information I.

The question now arises, whether an isothermic process of mixing of the gases exists in which the amount of heat equal to R_0 can be converted to work. If such a process were in principle impossible, this would imply the need for a drastic revision of the physical meaning of entropy. However, this is not the case. Work corresponding to the entropy defect I_0 may indeed be obtained, but indirectly. Let us again consider the case of pure initial states whose vectors $\psi^{(1)}$ and $\psi^{(2)}$ form an angle α. The final density matrix $\rho_{\iota\iota'} = \frac{1}{2}(\psi_\iota{}^{(1)}\, \overline{\psi}_{\iota'}{}^{(1)} + \psi_\iota{}^{(2)}\, \overline{\psi}_{\iota'}{}^{(2)})$ when these states are mixed is a mixture of the two orthogonal pure states $\psi^{(1)}$ and $\psi^{(2)}$ defined by

$$\psi_1 = \frac{\psi^{(1)} + \psi^{(2)}}{2\cos\frac{\alpha}{2}} \;\; ; \;\; \psi_2 = \frac{\psi^{(1)} - \psi^{(2)}}{2\sin\frac{\alpha}{2}} \tag{12}$$

The states ψ_1, ψ_2 occur with probabilities equal to the eigenvalues of the matrix $\hat{\rho}$: $\lambda_1 = \cos^2\frac{\alpha}{2}$, $\lambda_2 = \sin^2\frac{\alpha}{2}$. We now proceed as follows: without removing the initial partition, we divide the whole volume of the vessel by an additional partition into two parts, $2V_0\cos^2\frac{\alpha}{2}$ and $2V_0\sin^2\frac{\alpha}{2}$. All molecules located in the first part of the vessel we shall bring into the state ψ_1, and all those in the second part into the state ψ_2 (see Fig. 2).

Since both the initial and the final states of the molecules are pure, the entropy is not changed thereby, and the process may, in principle be reversible. Note that this process is described by a unitary transformation - a rotation of the state vectors. This may be accomplished physically by some appropriate interactions - different interactions for molecules initially in the state $\psi^{(1)}$ and in $\psi^{(2)}$. After this transformation the usual scheme with semipermeable partitions must be used. As a result one obtains a reversible process in which the amount of heat converted to mechanical work is given by formula (4).

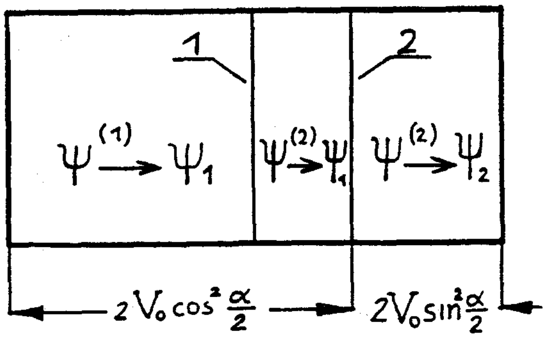

Fig. 2 Preliminary transformation of states of gas molecules to obtain work proportional to the entropy defect. After the transformation, partition 1 is removed and partition 2 is replaced by two membranes which are semipermeable for states ψ_1 and ψ_2, respectively, as in the scheme of Figure 1.

The obtained results show that the concepts of entropy defect and quantum information have an important thermodynamical meaning. There exists a close relationship between the use of non-equilibrium physical system to obtain work, on the one hand, and their use to transmit information, on the other. To obtain work one must carry out a quantum-mechanical measurement on the system, and this implies, as well as in the case of information transmission, essential irreversibility and unavoidable losses. These losses may be avoided only through a preliminary state transformation, i.e., through replacing the original physical system by another system with the same entropy defect. (In the information-transmission case, this means that one uses as signals an ensemble of orthogonal states, described by the same density matrix as the original ensemble or nonorthogonal states.) It is to be expected that the equivalence relation (10) between amount of information and work is valid for any non-equilibrium system (rather than for mixing gases only). This relation determines the maximum amount of heat convertible into work in irreversible processes, in contrast with reversible ones, in which the maximum work is determined by the entropy increase.

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