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Abstract

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PHYSICS

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EXTREMAL PROPERTIES OF ENTROPY IN THE MIXING OF POLARIZED GASES

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1. Earlier, using the example of polarized gases consisting of identical atoms with spin $1/2$, a new approach to the Gibbs paradox was developed ⁽⁸⁾. It turned out that the change in entropy upon mixing the two gases decreases monotonically to zero as the polarization vectors characterizing them approach one another. Under conditions in which, before mixing, both gases occupy equal volumes at equal pressures, the quantity ΔS can assume a continuous series of values in the interval

$$0 \leq \Delta S \leq 2kN \ln 2, \quad (1)$$

where N is the number of atoms of each of the gases, and k is Boltzmann's constant.

The aim of the present work is to investigate the extremal properties of the entropy for mixtures of two polarized gases at arbitrary values of the spin s . It will be shown that inequality (1) is valid in the general case*.

2. Let there be, in a volume V_1 , a gas containing N atoms in a spin state with density matrix $\hat{A}$, and in a volume $V_2 (= V_1)$, separated from V_1 by an impermeable partition, a gas containing N of the same atoms in a spin state with density matrix $\hat{B}$. In the general case $\hat{A}$ and $\hat{B}$ are Hermitian positive definite $(2s + 1)$ -row matrices with trace equal to 1^{**} . Up to additive terms of the type $Nf(T)$, which do not interest us and depend on the temperature, the entropies of gases A and B before mixing have the form:

$$\begin{aligned} S_A(N, V) &= -kN \operatorname{Sp} \hat{A} \ln \hat{A} + kN \ln \frac{V}{N}; \\ S_B(N, V) &= -kN \operatorname{Sp} \hat{B} \ln \hat{B} + kN \ln \frac{V}{N}, \end{aligned} \quad (2)$$

where

$$\text{Sp } \hat{A} \ln \hat{A} = \sum_{i=1}^{2s+1} a_i \ln a_i, \quad \text{Sp } \hat{B} \ln \hat{B} = \sum_{i=1}^{2s+1} b_i \ln b_i,$$

a_i and b_i are the eigenvalues of the matrices $\hat{A}$ and $\hat{B}$, respectively ($a_i \geq 0$, $b_i \geq 0$). A formula of the type (2) for mixed quantum ensembles was first indicated by von Neumann ⁽²⁾. If the spin-relaxation time is much longer than the characteristic diffusion time (see ⁽¹⁾), then after complete mixing of the gases in the volume $2V$ the density matrix will have the form

$$\hat{C} = \frac{1}{2}(\hat{A} + \hat{B}). \quad (3)$$

Hence the change in entropy is

$$\begin{aligned} \Delta S_{AB}(N) &= S_C(N, 2V) - S_A(N, V) - S_B(N, V) = kN \text{Sp } \hat{A} \ln \hat{A} + \\ &+ kN \text{Sp } \hat{B} \ln \hat{B} - kN \text{Sp}(\hat{A} + \hat{B}) \ln \frac{\hat{A} + \hat{B}}{2}. \end{aligned} \quad (4)$$

* As in work ⁽¹⁾, for definiteness we speak of spin, although all further conclusions apply to any discrete quantum number characterizing the internal state of the atom.

** For spin $1/2$, $A = \frac{1}{2}(1 + \sigma \mathbf{P}^{(A)})$, $B = \frac{1}{2}(1 + \sigma \mathbf{P}^{(B)})$, where σ is the Pauli vector operator, and $\mathbf{P}^{(A)}$ and $\mathbf{P}^{(B)}$ are the polarization vectors of the gases.

3. Let us consider an important special case, when $\hat{A}$ and $\hat{B}$ correspond to pure ensembles with wave functions $\psi^{(A)}$ and $\psi^{(B)}$. For pure states one of the eigenvalues of the density matrix is equal to 1, the others are zero. Consequently, in formula (2) we must put $\text{Sp } \hat{A} \ln \hat{A} = \text{Sp } \hat{B} \ln \hat{B} = 0$. Solving further the standard problem of determining the eigenvalues of the Hermitian matrix $\hat{C}$, we obtain

$$\begin{aligned} c_1 &= \frac{1}{2} (1 + |\langle \psi^{(A)} | \psi^{(B)} \rangle|), & c_2 &= \frac{1}{2} (1 - |\langle \psi^{(A)} | \psi^{(B)} \rangle|), \\ c_3 &= c_4 = \dots c_{2s+1} = 0. \end{aligned} \quad (5)$$

The eigenvalues c_1 and c_2 correspond to the spin functions

$$\psi_1^{(C)} = \frac{\psi^{(A)} + \psi^{(B)} e^{i\eta}}{\sqrt{2(1 + |\langle \psi^{(A)} | \psi^{(B)} \rangle|)}}, \quad \psi_2^{(C)} = \frac{\psi^{(A)} - \psi^{(B)} e^{i\eta}}{\sqrt{2(1 - |\langle \psi^{(A)} | \psi^{(B)} \rangle|)}}, \quad (6)$$

where $\eta = \arg \langle \psi^{(B)} | \psi^{(A)} \rangle$. Taking (3), (4), and (5) into account, we arrive at the relation

$$\Delta S = -kN \left[(1 + |\langle \psi^{(A)} | \psi^{(B)} \rangle|) \ln \frac{1 + |\langle \psi^{(A)} | \psi^{(B)} \rangle|}{2} + (1 - |\langle \psi^{(A)} | \psi^{(B)} \rangle|) \ln \frac{1 - |\langle \psi^{(A)} | \psi^{(B)} \rangle|}{2} \right], \quad (7)$$

obtained in ⁽¹⁾ for $s = 1/2$.

4. Let us return to the general expression (4). Suppose first that the matrices $\hat{A}$ and $\hat{B}$ commute. Then we can write

$$\Delta S_{AB}(N) = kN \left(\sum_{i=1}^{2s+1} a_i \ln a_i + \sum_{i=1}^{2s+1} b_i \ln b_i - \sum_{i=1}^{2s+1} (a_i + b_i) \ln \frac{a_i + b_i}{2} \right). \quad (8)$$

Since

$$\sum_{i=1}^{2s+1} a_i \ln a_i \geq \sum_{i=1}^{2s+1} a_i \ln \frac{a_i + b_i}{2} \quad (\text{see } ^{(1,3)}),$$

it is clear that $\Delta S_{AB} \geq 0$.

On the other hand, from the inequality $a_i \ln \frac{a_i}{a_i + b_i} \leq 0$ it follows that $\Delta S_{AB}(N) \leq 2kN \ln 2$. Thus, for commuting matrices $\hat{A}$ and $\hat{B}$ inequality (1) is proved. Moreover, according to (8), for $\hat{A} = \hat{B}$ (the criterion of identity of gases) the quantity $\Delta S = 0$. If, however, $\hat{A}\hat{B} = \hat{B}\hat{A} = 0$ (the criterion of complete distinguishability of gases), then the entropy change is $\Delta S = 2kN \ln 2$.

5. We now pass to the general case. Let the matrices $\hat{A}$ and $\hat{B}$, generally speaking, not commute with each other. We associate with the matrix $\hat{B}$ two matrices $\hat{B}^{(1)}$ and $\hat{B}^{(2)}$, which we define as follows:
 - a) the eigenvalues of $\hat{B}^{(1)}$ and $\hat{B}^{(2)}$, up to a permutation of the indices numbering them, coincide with the eigenvalues of the matrix $\hat{B}$;
 - b) $\hat{B}^{(1)}$ and $\hat{B}^{(2)}$ commute with each other and with the matrix $\hat{A}$;

c) if the eigenvalues of $\hat{A}$ are numbered in the order

$$a_1 \geq a_2 \geq a_3 \dots \geq a_{2s+1}, \quad (9)$$

then the eigenvalues of $\hat{B}^{(1)}$ and $\hat{B}^{(2)}$ corresponding to the same basis functions are arranged in the order

$$b_1^{(1)} \geq b_2^{(1)} \geq \dots \geq b_{2s+1}^{(1)}, \quad (10a)$$

$$b_1^{(2)} = b_{2s+1}^{(2)} \leq b_2^{(2)} = b_{2s}^{(1)} \leq \dots \leq b_{2s+1}^{(2)} = b_1^{(1)}. \quad (10)$$

The following is valid.

Theorem. Let $\hat{A}$ and $\hat{B}$ be Hermitian positive definite matrices of the same rank with trace equal to 1, and let $F(x)$ be a twice differen-

function in the interval $0 \leq x \leq 2$. Then, if in this interval $\frac{d^2 F(x)}{dx^2} \geq 0$, then

$$\text{Sp } F(\hat{A} + \hat{B}^{(2)}) \leq \text{Sp } F(\hat{A} + \hat{B}) \leq \text{Sp } F(\hat{A} + \hat{B}^{(1)}) \quad (11)$$

(recall that $\text{Sp } F(\hat{A} + \hat{B}) = \sum_{i=1}^{2s+1} F(\lambda_i)$, where λ_i are the eigenvalues of the matrix $\hat{A} + \hat{B}$).

Proof. Consider the set of Hermitian positive-definite matrices $\hat{B}$ related to one another by unitary transformations. All matrices of this set have the same eigenvalues. Therefore, if the matrix $\hat{A}$ is fixed, we can put them in correspondence with the same matrices $\hat{B}^{(1)}$ and $\hat{B}^{(2)}$. Let the quantity $\text{Sp } F(\hat{A} + \hat{B})$, defined on the set of matrices $\hat{B}$, take an extremal value (maximum or minimum) at $\hat{B} = \tilde{B}$. Denote

$$Z = \text{Sp } F(\hat{A} + \hat{U}^+ \tilde{B} \hat{U}) - \text{Sp } F(\hat{A} + \tilde{B}),$$

where $\hat{U}$ is a unitary matrix. For $\hat{U}$ the representation $\hat{U} = e^{i\varepsilon \hat{H}}$ is valid, where ε is a real quantity and $\hat{H}$ is a Hermitian matrix. Accordingly, for small $|\varepsilon|$,

$$\hat{A} + \hat{U}^+ \tilde{B} \hat{U} = \hat{A} + \tilde{B} - i\varepsilon(\hat{H} \tilde{B} - \tilde{B} \hat{H}) + \varepsilon^2 \hat{H} \tilde{B} \hat{H} - \frac{1}{2} \varepsilon^2 (\hat{H}^2 \tilde{B} + \tilde{B} \hat{H}^2) + o(\varepsilon^3). \quad (12)$$

Represent Z in the form

$$Z = \sum_{i=1}^{2s+1} F'(\lambda_i)(\lambda'_i - \lambda_i) + o((\lambda'_i - \lambda_i)^2), \quad (13)$$

where λ_i and λ'_i are the eigenvalues of the matrices $\hat{A} + \tilde{B}$ and $A + \hat{U}^+ \tilde{B} \hat{U}$, respectively, and $F'(x) = dF(x)/dx$.

If $\tilde{B}$ corresponds to a maximum of the quantity $\text{Sp } F(\hat{A} + B)$, then, independently of the sign of ε and of the specific form of $\hat{H}$, $Z \leq 0$; in the case of a minimum, always $Z \geq 0$. This means that the quantity Z , and consequently also the differences $\lambda'_i - \lambda_i$, cannot be of order ε . According to perturbation theory,

$$\lambda'_i - \lambda_i = 2\varepsilon \text{Im} \sum_{k=1}^{2s+1} H_{ik} \tilde{B}_{ki} + o(\varepsilon^2), \quad (14)$$

where H_{ik} and $\tilde{B}_{ki}$ are the matrix elements of $\hat{H}$ and $\hat{B}$ in the representation of the eigenstates of the matrix $\hat{A} + \tilde{B}$. The requirement

$$\text{Im} \sum_{k=1}^{2s+1} H_{ik} \tilde{B}_{ki} = 0$$

(taking into account the Hermiticity of $\hat{H}$ and $\hat{B}$) gives

$$\tilde{B}_{ki} = \tilde{b}_i \delta_{ik}. \quad (15)$$

It follows from this that the matrices $\tilde{B}$ and $\hat{A}$ must commute. In this case $\lambda_i = a_i + \tilde{b}_i$.

Using perturbation theory, we now find $(\lambda'_i - \lambda_i)$ to second order in the parameter ε . According to (12) and (15),

$$\begin{aligned} \lambda'_i - \lambda_i &= \varepsilon^2 \sum_{l=1}^{2s+1} |H_{il}|^2 \tilde{b}_l - \varepsilon^2 \sum_{l=1}^{2s+1} |H_{il}|^2 \tilde{b}_i + \varepsilon^2 \sum_{l \neq i}^{2s+1} \frac{|H_{il}|^2 (\tilde{b}_l - \tilde{b}_i)^2}{a_i - a_l + \tilde{b}_i - \tilde{b}_l} = \\ &= -\varepsilon^2 \sum_{l \neq i}^{2s+1} |H_{il}|^2 \frac{2(a_i - a_l)(\tilde{b}_i - \tilde{b}_l)}{a_i - a_l + \tilde{b}_i - \tilde{b}_l}. \end{aligned} \quad (16)$$

Hence

$$Z = -\varepsilon^2 \sum_{i=1}^{2s+1} \sum_{l>i}^{2s+1} \frac{F'(a_i + \tilde{b}_i) - F'(a_l + \tilde{b}_l)}{a_i + \tilde{b}_i - a_l - \tilde{b}_l} |H_{il}|^2 (a_i - a_l)(\tilde{b}_i - \tilde{b}_l). \quad (17)$$

Since, by definition,

$$\frac{d^2 F(x)}{dx^2} \geq 0,$$

it is clear that all quantities

$$K_{il} \equiv \frac{F'(\lambda_i) - F'(\lambda_l)}{\lambda_i - \lambda_l} \geq 0.$$

As a result, from the maximum condition $Z \leq 0$ it follows that, for all i and l ,

$$(a_i - a_l)(\tilde{b}_i^{(\max)} - \tilde{b}_l^{(\max)}) \geq 0. \quad (18)$$

Similarly, from the minimum condition $Z \geq 0$ it follows that, for all i and l ,

$$(a_i - a_l)(\tilde{b}_i^{(\min)} - \tilde{b}_l^{(\min)}) \leq 0. \quad (19)$$

It is easy to see that conditions (18) and (19) are completely equivalent to the definitions of the matrices $\widehat{B}^{(1)}$ and $\widehat{B}^{(2)}$, respectively, with respect to A (see (9), (10a), (10b)). Thus, $\widehat{B}^{(\max)} = \widehat{B}^{(1)}$, $\widehat{B}^{(\min)} = \widehat{B}^{(2)}$.

Thereby relation (11) has been proved.

6. If in the interval $0 \leq x \leq 2$

$$\frac{d^2 F(x)}{dx^2} \leq 0,$$

then in formula (11), obviously, the replacement $\widehat{B}^{(1)} \leftrightarrow \widehat{B}^{(2)}$ should be made. In particular,

$$\begin{aligned} -\text{Sp}(\widehat{A} + \widehat{B}^{(1)}) \ln \frac{\widehat{A} + \widehat{B}^{(1)}}{2} &\leq -\text{Sp}(\widehat{A} + \widehat{B}) \ln \frac{\widehat{A} + \widehat{B}}{2} \leq \\ &\leq -\text{Sp}(\widehat{A} + \widehat{B}^{(2)}) \ln \frac{\widehat{A} + \widehat{B}^{(2)}}{2}. \end{aligned} \quad (20)$$

Hence, on the basis of (4), for the change of entropy we can write (for $\widehat{B} \neq \widehat{B}^{(1)}, \widehat{B}^{(2)}$)

$$\Delta S_{AB^{(1)}}(N) < \Delta S_{AB}(N) < \Delta S_{AB^{(2)}}(N). \quad (22)$$

Since, in accordance with the conclusions of section (4), for the quantities $\Delta S_{AB^{(1)}}(N)$ and $\Delta S_{AB^{(2)}}(N)$ relation (1) is valid ($\widehat{A}$, $\widehat{B}^{(1)}$, and $\widehat{B}^{(2)}$ commute), it is clear that from (21) there follows the validity of (1) for arbitrary density matrices A and B (of course, under the mixing conditions indicated above). At the same time, the equalities written earlier, $\widehat{A} = \widehat{B}$ and $\widehat{A}\widehat{B} = 0$ (for

pure ensembles, respectively, $\psi^{(A)} = \psi^{(B)}$ and $\langle \psi^{(A)} | \psi^{(B)} \rangle = 0$), in the general case constitute necessary and sufficient conditions for the minimal and maximal change of entropy upon mixing polarized gases.

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

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