Constants of motion, accessible states, and information theory

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Dynamical aspects of the entropy are discussed within the information-theory context. General invariants of the motion are formulated and related both to the entropy and to the number of accessible states. Examples on finite systems (Schottky anomaly, echo spins) are presented. The entropy evolution through nonequilibrium states is also discussed.

I. INTRODUCTION

The concept of entropy is, undoubtedly, one of the most important concepts in the whole of physics. It plays a central role both in thermodynamics and in statistical mechanics and has been the subject of an enormous amount of fascinating work. We will here cite just three recent review articles.[1–3] Entropy may also play a significant *dynamical* role, although work in this respect is scarce (at least in comparison with its thermodynamical aspects). In this "new" sense, an illuminating alternative is to be found in the pioneer work of Jaynes[4] in connection with information theory (IT) and the maximum-entropy principle (MEP). Extensions of Ref. 4 to quantum-mechanical systems have been made recently[5–8] that explicitly exploit the dynamical relevance of the entropy S. These developments are based on the fact that if $\hat{\rho}$ stands for the statistical operator, then (Boltzmann's constant equal to unity)

$$S=-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho}) \tag{1.1}$$

is a constant of motion if $\hat{\rho}$ verifies

$$i\hbar\frac{\partial\hat{\rho}}{\partial t}=[\hat{H}(t),\hat{\rho}] \tag{1.2}$$

even if the Hamiltonian $\hat{H}$ is explicitly time dependent.

The aim of the present effort is that of exploiting the IT form of $\hat{\rho}$ (Refs. 5–9) in order to shed some additional light onto the dynamical aspects of S. In particular, we wish to dwell upon the relationship between the number M of accessible states[1–3] of the system (a well-defined quantum-mechanical quantity[10)]) and several dynamical quantities. To this end a brief resume of basic IT concepts is given in Sec. II. A set of novel invariants of the motion is derived in Sec. III and their relationship with the number of states established in Sec. IV. Section V is devoted to second law, accessibles states and completeness of the Hilbert space; examples of finite systems are presented in Sec. VI. Finally, in Sec. VII some conclusions are drawn.

II. BRIEF REVIEW OF BASIC IT CONCEPTS

Within the IT context (following the work of Jaynes[4)]), the statistical operator $\hat{\rho}$ is constructed according to a well-defined prescription.[4–8] Starting from the knowledge of the expectation values of, say, $N+1$ operators $\hat{O}_j$ (including $\hat{O}_0=\mathbb{1}=$identity operator)

$$\langle \hat{O}_j/\hat{\rho}\rangle_t=\mathrm{Tr}[\hat{\rho}(t)\hat{O}_j]=O_j,\quad j=0,1,\ldots,N\ , \tag{2.1}$$

where the subindex 0 refers to the normalization condition $\mathrm{Tr}\hat{\rho}=1$, the IT version of $\hat{\rho}$ reads

$$\hat{\rho}(t)=\exp\left[-\lambda_0-\sum_{j=1}^{N}\lambda_j(t)\hat{O}_j\right],$$
$$\ln\hat{\rho}(t)=-\lambda_0-\sum_{j=1}^{N}\lambda_j(t)\hat{O}_j\ , \tag{2.2}$$

and is thus seen to be given in terms of $N+1$ Lagrange multipliers λ_j, determined so as to fulfill the requirements (2.1). This statistical operator is guaranteed to maximize the entropy S (we take the Boltzmann constant equal to unity)

$$S=-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})=\lambda_0+\sum_{j=1}^{N}\lambda_j\langle\hat{O}_j/\hat{\rho}\rangle\ , \tag{2.3}$$

subject, of course, to the constraints (2.1). The temporal evolution of $\hat{\rho}$, and that of any analytical function f of $\hat{\rho}$, is governed by[5]

$$i\hbar\frac{\partial f(\hat{\rho})}{\partial t}=[\hat{H},f(\hat{\rho})]\ , \tag{2.4}$$

so that it becomes mandatory to ask under what conditions is the entropy (2.3) a constant of the motion. This is tantamount to finding the set of those (relevant) operators $\hat{O}_j$ entering (2.2) so as to ensure that $\hat{\rho}$ complies with (2.4). It is easy to verify[5–7] that the relevant operators are those that close a partial Lie algebra under commutation with the Hamiltonian $\hat{H}$

$$[\hat{H},\hat{O}_j]=\sum_{i=0}^{q}g_{ij}\hat{O}_i\ , \tag{2.5}$$

where the g_{ij} are the elements (c numbers) of $q\times q$ matrix G (which may depend upon the time if $\hat{H}$ is time dependent). Consequently, in order to build $\hat{\rho}(t)$ we need q observables $\hat{O}_i$. When (as usual) $N<q$, matters are to be dealt as discussed in Ref. 5. For our present purposes, it suffices to restrict our attention to the case $N=q$.

The importance of the closure condition (2.5) lies in the fact that the time-dependent Schrödinger equation [or, equivalently, Eq. (2.4)] can be replaced by a set of coupled equations for the λ_i's (Refs. 5–7)

$$\frac{d\lambda_i}{dt}=\sum_{l=0}^{q} g_{il}\lambda_l \ . \tag{2.6}$$

III. GENERAL INVARIANTS

We shall now employ the results previously reviewed in order to find invariants of the motion, the idea underlying such an approach being, of course, that of having a compact way of encompassing the whole Hamiltonian dynamics (examples of the usefulness of such a treatment, within an IT context, are to be found in Refs. 7 and 9). To this end we notice that a special case of (2.4) reads

$$i\hbar\frac{\partial}{\partial t}(\ln\hat{\rho})^n=[\hat{H}(t),(\ln\hat{\rho})^n] \ , \tag{3.1}$$

that holds for any integer n. From (3.1) the following invariant of the motion can be deduced without any difficulty

$$I^{(n)}=\langle(\ln\hat{\rho})^n/\hat{\rho}\rangle-(\langle\ln\hat{\rho}/\hat{\rho}\rangle)^n=I_1^n-I_2^n \ . \tag{3.2}$$

A more detailed expression can be obtained by inserting (2.2) into (3.2)

$$I^{(n)}=\left\langle\left[-\sum_{j=0}^{q}\lambda_j\hat{O}_j\right]^n\right\rangle-\left[\left\langle-\sum_{j=0}^{q}\lambda_j\hat{O}_j\right\rangle\right]^n \ . \tag{3.3}$$

For the particular (and very important) case $n=2$, (3.3) adopts the interesting form

$$I^{(2)}=\sum_{r,j=1}^{q}\lambda_r\lambda_j K_{rj} \tag{3.4}$$

in terms of the so-called "centered" correlation coefficients[11]

$$K_{rj}=\tfrac{1}{2}\langle[\hat{O}_r,\hat{O}_j]_+\rangle-\langle\hat{O}_r\rangle\langle\hat{O}_j\rangle \ . \tag{3.5}$$

In some cases, it is also possible to employ noncentered correlation coefficients

$$K_{rj}^0=\tfrac{1}{2}\langle[O_r,O_j]_+\rangle \ . \tag{3.6}$$

Equation (3.4) can be generalized for $n>2$, leading to a more involved type of correlation coefficient, namely,

$$I^{(n)}=\sum_{i_1}\sum_{i_2}\cdots\sum_{i_m}\lambda_{i_1}(t)\cdots\lambda_{i_m}(t)\Xi(\hat{O}_1\cdots\hat{O}_m) \ , \tag{3.7}$$

where Ξ is a sum of terms $T_{i_1\cdots i_m}$, over all possible permutations of the operators $\hat{O}_i$ entering expressions of the form

$$T_{i_1\cdots i_m}=\langle\hat{O}_{i_1}\hat{O}_{i_2}\cdots\hat{O}_{i_m}\rangle-\langle O_{i_1}\rangle\langle O_{i_2}\rangle\cdots\langle O_{i_m}\rangle \ . \tag{3.8}$$

Equation (3.8) provides us with a very general type of correlation coefficient that arises as a result of the quantal nature of the system under consideration.

IV. ENTROPY, INVARIANTS, AND NUMBER OF STATES

We are now in a position to establish an interesting relationship between the invariants of Sec. III, the entropy S, and the number of possible states, M, in which our system can be found. We start by rewriting the identity operator $O_0=\hat{1}$ in the form

$$\hat{1}=\hat{\rho}\exp(-\ln\hat{\rho}) \ , \tag{4.1}$$

and assume that the number of possible eigenstates of the statistical operator is M. Thus

$$\begin{aligned}M&=\mathrm{Tr}\hat{1}=\mathrm{Tr}[\hat{\rho}\exp(-\ln\hat{\rho})]\\&=\langle\exp(-ln\hat{\rho})/\hat{\rho}\rangle \ .\end{aligned} \tag{4.2}$$

Equation (4.2) allows one to regard M as a "constant of the motion" which expresses our "zero-order" knowledge about the system. This is a trivial statement. A nontrivial consequence, however, is to be found in the fact that $\hat{\rho}$ is constructed out of the measured expectation values (2.1), which allows one to assert that the measurement process places a bound on the possible values of M (see, for example, Refs. 12 and 13 for a related, enlightening discussion).

If we now expand the exponential in (4.2) we obtain

$$\begin{aligned}M&=\mathrm{Tr}\hat{\rho}\left[1+\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}(\ln\hat{\rho})^n\right]\\&=1+S+\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}\langle(\ln\hat{\rho})^n\rangle\\&=1+\sum_{n=1}^{\infty}\frac{(-1)^n}{n!}I_1^{(n)} \ ,\end{aligned} \tag{4.3}$$

which establishes a relationship between the number of states, M, and the noncentered invariants $I_1^{(n)}$. If we insert centered operators $I^{(n)}$ into (4.3) we find

$$M=\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}I^{(n)}+\exp(S) \ , \tag{4.4}$$

or

$$M-e^S=\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}I^{(n)} \ , \tag{4.5}$$

which is the relationship we had anticipated, that relates S, invariants of the motion $I^{(n)}$, and the number of states, M. The last result can also be put into the form

$$S=\ln\left[M-\sum_{n=2}^{\infty}\frac{(-1)^n}{n!}I^{(n)}\right] \ . \tag{4.6}$$

It is of interest to study the properties of the infinite sum that appears in (4.5). For this purpose we introduce a normalized operator $\hat{\xi}$ by means of

$$\hat{\xi}=\frac{\hat{\rho}\ln\hat{\rho}}{\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})} \ , \tag{4.7}$$

and employ the well-known inequality[5]

$$-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})\le-\mathrm{Tr}(\hat{\xi}\ln\hat{\rho}) \ , \tag{4.8}$$

in order to obtain

$$S^n \leq -\frac{I_1^{(n+1)}}{I_1^{(n)}} , \tag{4.9}$$

which for $n=1$ yields

$$S^2 \leq I_1^{(2)} . \tag{4.10}$$

As $S^2 \geq 0$ we can write

$$0 \leq S^2 \leq I_1^{(2)} , \tag{4.11}$$

or, equivalently,

$$0 \leq I_1^{(2)} - S^2 = I_1^{(2)} - I_2^{(2)} = I^{(2)} , \tag{4.12}$$

so that[14]

$$I^{(2)} = \sum_{r,j}^{q} \lambda_r \lambda_j K_{rj} \geq 0 . \tag{4.13}$$

Returning to (4.9) and taking now $n=2$ we have

$$S \leq -\frac{I_1^{(3)}}{I_1^{(2)}} , \tag{4.14}$$

which leads to

$$I^{(3)} \leq 0 . \tag{4.15}$$

Following a similar procedure for higher values of n we easily obtain

$$I^{(2n)} \geq 0 , \quad I^{(2n+1)} \leq 0 , \tag{4.16}$$

which guarantees that the sum on the right-hand side (rhs) of (4.5) is positive definite, thus entitling us to write

$$M - e^S \geq 0 , \tag{4.17}$$

or

$$S \leq \ln M , \tag{4.18}$$

which modifies the well-known Boltzmann's equation ($S=\ln M$), in the presence of quantal correlations [cf. Eq. (4.6)].

V. ACCESSIBLE STATES AND TIME EVOLUTION

A. The second law

Let us now consider an isolated system, whose Hamiltonian is ($t<0$) $H_<(t)$. Relevant properties of the system are described by a set of operators $\{\hat{O}_r\}$ that close a partial Lie algebra with $\hat{H}_<(t)$ according to Eq. (2.5). The usual canonical distribution belongs to the special case $r=1$, with

$$\hat{O}_1 = \hat{H}_<(t) . \tag{5.1}$$

Let us call $\{\hat{B}_i\}$ the set of operators that do not close algebra with $H_<(t)$. The set $\{\hat{B}_i\}$ belongs to an irrelevant subspace decoupled from the set of relevant operators $\{\hat{O}_r\}$.[15] We shall ignore $\{\hat{B}_i\}$ as long as $t<0$.

A subindex G (Gibbs formalism) will be used to denote the density matrix built according Eqs. (2.1) and (2.2) and maximizing (2.3). Consequently, if Eq. (2.4) is fulfilled, the entropy S will be a constant of motion.[5–7] From now on we assume that the time evolution of $\hat{H}_<(t)$ satisfies the hypothesis of an adiabatic theorem.[16,17] Basically, $\hat{H}_<(t)$ is an analytic function of t and the eigenstates are not degenerated for $t<0$. The eigenvectors can be written as

$$|\alpha, \chi(t)\rangle , \tag{5.2}$$

where $\chi(t)$ is a parameter which controls the evolution of $\hat{H}_<$.

A complete set of constants of motion will be associated with these eigenvectors and their variation will follow that of $\chi(t)$.[16]

These constants of motion can be easily obtained starting from bilinear products among the operators $\{\hat{O}_r\}$.[17] These operators are the components of a normed vectorial space.[17] The changes in $\hat{H}_<(t)$ are correlated with enlargements of compressions in the norm. However, the dimension of the vectorial space remains constant throughout these changes. As the consequence, the (Hilbert) space dimension does not change. This continuity is associated to the constant S_G.[18] Thus, the relative probability for each eigenstate is completely determined at any time $t<0$.

Now we suppose that at $t=0$ two additional but unknown interactions, $\hat{V}(t)$ and $\hat{W}(t)$, are turned on,

$$\hat{H}(t) = \hat{H}_>(t) + \hat{V}(t) h(t+\Delta t) + \hat{W}(t)[h(t) - h(t+\Delta t)] , \tag{5.3}$$

where $\hat{H}_>(t)$ changes adiabatically,[16] $h(t)$ is a Heaviside function, $\hat{H}$ is the analytical continuation of $\hat{H}_<$ for $t>0$, and $\hat{V}(t), \hat{W}(t)$ belong to an enlarged Hilbert space. The set of eigenvalues of $\hat{H}$ is not in (unambiguous) one-to-one correspondence with that of $\hat{H}_<(t)$. The upper bound $S=\ln M$ will be greater than the previous one [see Eq. (4.18)]. However, something can be said about the time evolution of the entropy, even if the detailed structure of $\hat{V}(t)$ and $\hat{W}(t)$ is not known. From a practical point of view, we have only an approximate control over the system. As we do not know $\hat{V}(t)$ and $\hat{W}(t)$ we are forced to attempt to estimate the state of the system using the old information gathered at $t<0$. It is clear, however, that the set of relevant operators will become larger, and that some of the $\hat{B}_i$ will be included in it. The missing information will be represented formally by[16]

$$\ln \hat{\rho}_e = \sum_r \lambda_r \hat{O}_r + \sum_i \lambda_i B_i , \quad t>0 . \tag{5.4}$$

In particular, the case (5.1) would now read

$$\ln \hat{\rho}_e = -\beta\{\hat{H}_>(t) + \lambda_1 \hat{V}(t) h(t+\Delta t)/\beta + \lambda_2 W(t)[h(t) - h(t+\Delta t)]/\beta\} - \lambda_0 I , \quad t>0 . \tag{5.5}$$

A diagonalization of $\hat{H}(t)$ will be general present unsurmountable difficulties (for example) $\hat{W}(t)$ could be not analytic. Then the best approximation to $S(t>0)$ will be given by the "estimated" entropy,

$$S_e^T = -\mathrm{Tr}(\hat{\rho}_G \ln\hat{\rho}_e) , \tag{5.6}$$

where the trace is taken over the Hilbert space of $\hat{H}_<(t)$. Recourse to a well-known relation[6,18] leads to

$$S_e^T = -\mathrm{Tr}(\hat{\rho}_G \ln\hat{\rho}_e \geq -\mathrm{Tr}(\hat{\rho}_G \ln\hat{\rho}_G) = S_G, \quad t>0 . \tag{5.7}$$

An extended discussion of (5.7) is relegated to the Appendix. As S_G is a constant of motion, we have

$$S_e^T(t>0) \geq S_G(t<0) \tag{5.8}$$

and, as we can impose over $\ln\hat{\rho}_e$ the boundary condition[6]

$$\ln\hat{\rho}_e = \ln\hat{\rho}_G, \quad t=0 \tag{5.9}$$

which implies setting all $\lambda_i = 0$, we see that

$$S_G(0) = S_e^T(0) = S_e(0) \tag{5.10}$$

and, therefore,

$$S_e^T(t>0) \geq S_e(0) . \tag{5.11}$$

These results are similar to some obtained previously in Ref. 18. However, we have extended here the corresponding formalism, using a generalization of the Gibbs entropy and an estimation of the experimental entropy. The canonical distribution (to which Ref. 19 is restricted) is a particular case, where the only relevant operator is $\hat{H}$. Relation (5.11) is in accordance with the second thermodynamic principle.

B. Completeness and accessible states

Now we can extent the concepts of Ref. 19 related to the intuitive meaning of the second law. Let us consider that $\hat{W}(t)$ is not well defined, but $\hat{V}(t)$ can be diagonalized and changes adiabatically, together with $\hat{H}_<(t)$ and $\hat{H}_>(t)$. A simple and illuminating example is the one-dimensional ideal gas.

Our system consists of N noninteracting particles in one dimension, confined within a segment of length L. The single-particle eigenstates of energy are characterized by values of the linear momentum, given by

$$p = nh/2L, \quad n=1,2,3,\ldots . \tag{5.12}$$

The wave functions (WF) possess a sinusoidal character and vanish at the end points. We now consider an adiabatic change in L, the one-dimensional volume to which our ideal gas is confined. While L is changed adiabatically, the adiabatic theorem[16,17] assures that the probabilities $P(n_1,n_2,\ldots,n_N)$

$$P(n_1,n_2,\ldots,n_N) = \exp[-\lambda_0 - \beta E(n_i,n_2,\ldots,n_N)] \tag{5.13}$$

(where n_j is the eigenstates of the jth distinguishable particle) remain unchanged. The new energy value is[16]

$$E'(n_1,n_2,\ldots,n_N) = (L/L')^2 E(n_1,n_2,\ldots,n_N) , \tag{5.14}$$

and the temperature is given by[16]

$$\beta'/\beta = T/T' = (L'/L)^2 . \tag{5.15}$$

This example and the concomitant three-dimensional problem are extensively treated in Ref. 16. We are interested in studying how the "accessibility" of the different states evolves. In Fig. 1(a) we show the behavior of the eigenfunctions with $n=0$ and $n=1$, when the length increases from L to $2L$. Obviously, the parity does not change with an adiabatic[16] change in length.

Alternatively we can consider a 'free expansion," where energy is conserved. In the absence of perturbations, the evolution of the corresponding WF is depicted in Fig. 1(b), with

$$\begin{aligned} E_1 &= [(n_1^2+n_2^2)/L^2]h^2/8m \\ &= [(n_2+n_4^2)/(2L)^2]h^2/8m = E_2 \end{aligned} \tag{5.16}$$

because $n_2 = 2n_1$ and $n_4 = 2n_2$.

However, this is only a particular instance in which the parity has not been conserved. If we would have considered all the possible eigenfunctions, the end result would be the same. *Note that the new accessible space is not complete.* The evolution is isoentropic but not adiabatic. Any small interaction populates adjacent states with different parity and "completes" the accessible Hilbert space. [See Fig. 1(c).]

As long as small residual interactions cannot be included in a Hamiltonian, the entropy will not be a constant of the motion and as we need more states in order to reproduce the same value of the internal energy, the entropy grows up.

Note that the same small perturbations that "enforces" the second law, allows for an adiabatic change in a three-dimensional ideal gas.[16]

Completeness is a *mathematical* assumption,[20] but transitions from higher potential energies to lower ones follow from a very general physical principle. In some sense and with some abuse of language, one may perhaps assert that the second law fulfills the physical principle in order to insure accessibility to the complete set of states.

An essential point remains obscure, however, the length of the time interval needed insure accessibility to the complete new Hilbert space. If that time is long enough we may perhaps detect a "deterministic reversibility." In fact, there is a process of this type called spin echo:[21,22] A set of N identical noninteracting spins at low temperature, where the interaction between the magnetic moment and a slight inhomogeneous magnetic field is given by

$$H = -\mu B \tag{5.17}$$

the magnetic moment being proportional to the spin,

$$\mu = \gamma\hbar J . \tag{5.18}$$

The energy-level splitting ΔE in a sample of spins is

$$\Delta E(i) = \Delta E(B(x)) = \Delta E(x) . \tag{5.19}$$

(We use i to name each spin subsystem and x stands for the coordinate.)

Working with good enough experimental conditions,

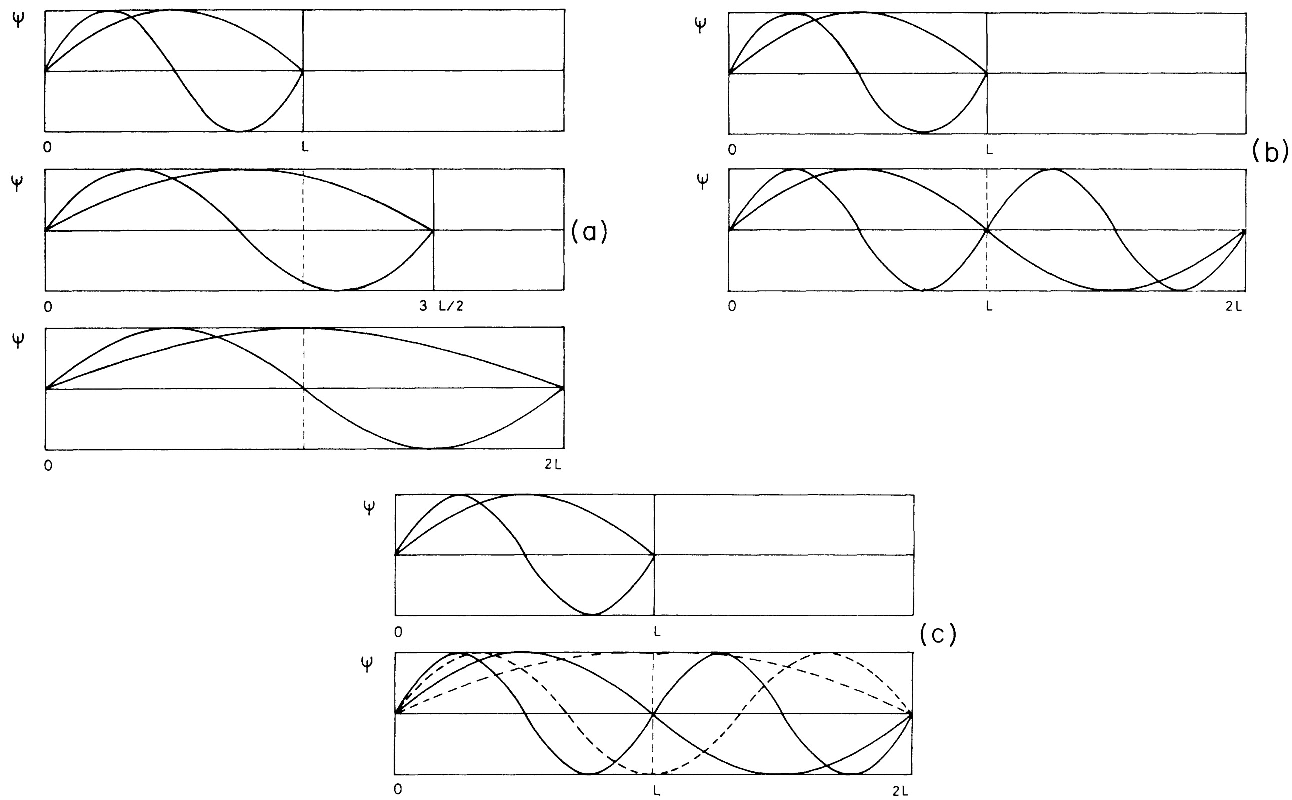

FIG. 1. One-dimensional ideal gas in a box whose length L is changed to $2L$. (a) Dynamical adiabatic movement of the wall. Only eigenfunctions for $n=0,1$ are shown as examples. (b) Free expansions without residual interactions. The system does not access all the Hilbert space. The evolution is isoentropic but not dynamically adiabatic. Only eigenfunctions for $n\le 3$ are shown as examples. (c) Free expansion with residual interactions. The system acceeds to the complete Hilbert space. The evolution is not isoentropic. Only eigenfunctions for $n\le 3$ are shown as examples.

the magnet field inhomogeneity is so small that each subsystem can be considered with approximately the same frequency. When the temperature is sufficiently low ($kT \ll \Delta E$) most of the spins will be found in the ground state. A radio-frequency electromagnetic field of frequency $w/2\pi$,

$$w=\gamma\hbar B_z \tag{5.20}$$

can induce transitions to an excited state when a given "pulse"[21,22] is applied. Then, after a $\pi/2$ pulse, these spins will be pointing along a fixed line of longitude and towards the equator. When the radio-frequency field is turned off, the spins spread out along the equator because their Larmor (precession) frequencies differ. A detector that measures the total magnetization of the sample (the components of each spin along a particular direction) will record a progressively degraded, or randomized, signal.

Can the energy stored in the dephased moments be recovered in any coherent fashion? At first glance it appears obvious that there can be no way to arrange coherent emission from the dephased dipoles. The individual dipole moments get out of phase with each other because they have slightly different oscillation frequencies.

As long as the frequencies differ in a continuous way, we could expect to return to the original phased condition only after an interval $\delta t \to \infty$. However, there is another way in which the original phase condition could be recovered. Instead of waiting for an spontaneously recurrence of the initial conditions, it might be possible to interfere with the oscillations after a time t to force the reversal of their dephasing.[23] It is easy to see that a rotation of all vectors using a pulse produces a collection of rephasing moments. This shows that not all decaying processes need to be irreversible. The free induction decay is easily reversed long after the free induction signal has disappeared completely.

We can assert that the dephasing of the dipole moments of resonant atoms is a deterministic process. The recovery would have to be carried out in the interval between the lifetime due to homogeneous effects T_1 and the transverse inhomogeneous lifetime T_2 (which contain incoherent interactions such as collisions, radiative decay, etc.). The expression[20]

$$1/T_3=1/T_2+1/T_1 \tag{5.21}$$

defines the total transverse decay time T_3.

Relation (5.21) defines the number of accessibles states in each space

$$\Delta w_3 = \Delta w_2 + \Delta w_1 \ . \tag{5.22}$$

After a long time the incoherent interaction populates the residual states over $\Delta w_3 > \Delta w_1$. Then, the "equatorial" Hilbert space is completed and we can not invert the process.

From these examples it is clear that a gas can not be compressed in a free way because, in such a case, the residual interactions would have to select a particular set of states in order to limit the accessibility. Systems where these small interactions can be delayed could be treated as reversible ones.[24]

VI. EXAMPLES

A. Schottky anomaly

It is a well known fact that for system with a finite number of accessible states the specific heat has a maximum. This effect is called the "Schottky anomaly."[25]

We consider here that the system has N accessible states with energies; $e_0, e_1, \ldots, e_{n-1}$. In this case, the equilibrium density matrix will be

$$\hat{\rho} = \exp(-\lambda_0 - \beta\hat{H}) \tag{6.1}$$

with

$$\lambda_0 = \ln\left[\sum_{i=0}^{N-1} \exp(-\beta\epsilon_i)\right] . \tag{6.2}$$

The mean energy, $\langle H \rangle$, is

$$\langle H \rangle = \exp(-\lambda_0) \sum_{i=0}^{N-1} e_i \exp(-\beta e_i) \ . \tag{6.3}$$

Finally, the entropy is evaluated via Eq. (2.3),

$$S = \ln\left[\sum_{i=0}^{N-1} \exp(-\beta e_i)\right] + \beta\left[\sum_{i=0}^{N-1} e_i \exp(-\beta e_i)\right] \Big/ \sum_{i=0}^{N-1} \exp(-\beta e_i) \ . \tag{6.4}$$

It is easy to verify that the entropy takes its maximum value for $\beta = 0$:

$$S = \ln N \tag{6.5}$$

in agreement with Eq. (4.18). The invariants generated in Sec. III can be calculated in this example. For instance, from (3.4) we evaluate $I^{(2)}$

$$I^{(2)} = \beta^2(\langle H^2 \rangle - \langle H \rangle^2) = C/k \tag{6.6}$$

with C, the specific heat, and k, the Boltzmann constant.

We now consider that the separation of the energy states is K, upwards from the fundamental level e_0

$$e_n = nK + e_0, \quad n = 0, 1, \ldots, N-1 \ . \tag{6.7}$$

In this case we have

$$\exp(\lambda_0) = \exp(-\beta e_0)[1 - \exp(-\beta KN)]/[1 - \exp(-\beta K)] \ , \tag{6.8}$$

$$\langle H \rangle = e_0 + K/[\exp(\beta K) - 1] + NK/[\exp(\beta KN) - 1] \ , \tag{6.9}$$

and

$$C = kK^2\beta^2\{\exp(\beta K)/[\exp(\beta K) - 1]^2 - N^2 \exp(\beta KN)/[\exp(\beta KN) - 1]^2\} \ . \tag{6.10}$$

As shown in Fig. 2, the specific heat has a maximum value. The temperature associated with it increases with N. For high N, C converges to Einstein's equation and the maximum disappears.

If we know the number of accessible states and the specific heat of the system we can use Eq. (4.6) to evaluate the entropy. Applying Eq. (4.16) we can demonstrate that

$$\Delta = \ln(N - I^{(2)}/2) - S > 0 \ . \tag{6.11}$$

Figure 3 depicts both $\ln(N - C/2k)$ and S versus T for different N. In the limit of high temperature ($K\beta$ much smaller than $1/N$) we can give an analytic expression for Δ:

$$\Delta \cong (K\beta)^2 N/24 \ . \tag{6.12}$$

As Fig. 2 shows, $\ln(N - C/2k)$ is an upper bound to the entropy. For high temperature Δ is negligible and the knowledge of N and C suffices to ascertain the entropy value. For a given temperature, the approximation becomes worse as N increases: the higher correlations become more and more important and all the terms of the expansion (4.6) have to be considered.

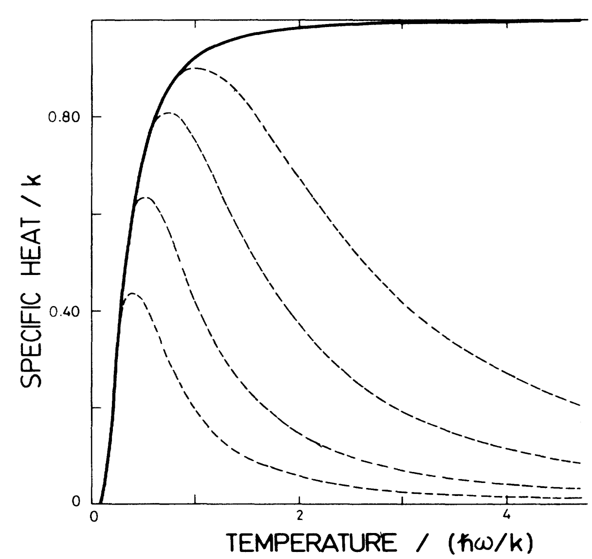

FIG. 2. Dashed line: Schottky anomaly. Specific heat in temperature parametrized with $N = 2, 3, 5, 8$. Solid line: Einstein's specific heat, $N \to \infty$.

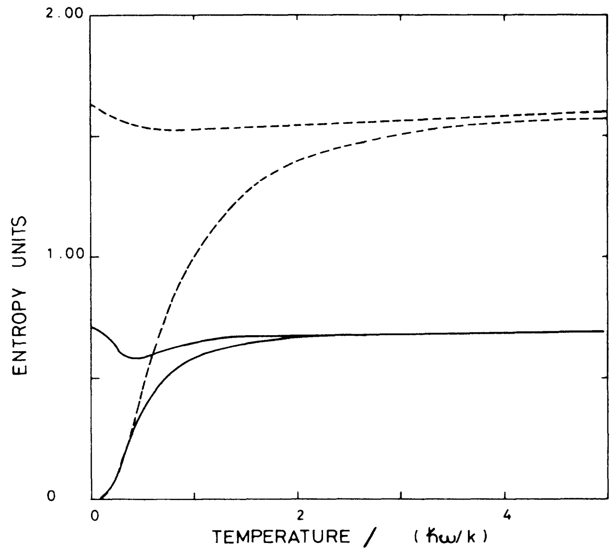

FIG. 3. Entropy and $\ln(N - I^{(2)}/2)$ versus temperature [see Eqs. (4.6), (6.6), and (6.31)]. Dashed line for $N=5$, solid line for $N=2$.

B. Zeeman effect

We now return to the problem of a particle with angular momentum $\hat{J}$ in a magnetic field $\mathbf{B}=B\mathbf{z}$ [see (5.17) and (5.18)].

Here we are interested in the particular case in which only $\langle J_x \rangle$ and $\langle J_y \rangle$ are known. Therefore $\{1, J_x, J_y\}$ are the relevant operators that close a partial Lie algebra with $\hat{H}$, and the density operator is

$$\hat{\rho}=\exp(-\lambda_0-\lambda_1\hat{J}_x-\lambda_2\hat{J}_y) . \tag{6.13}$$

If the total angular momentum is j, then the number of accessible states is

$$N=2j+1 . \tag{6.14}$$

In order to evaluate the mean value of the operators associated with any particular set of Lagrange multipliers (λ_1,λ_2) we define

$$\boldsymbol{\beta}=-i(\lambda_1\mathbf{x}+\lambda_2\mathbf{y})=\beta\mathbf{n} \tag{6.15}$$

with

$$\beta=(\lambda_1^2+\lambda_2^2)^{1/2} .$$

Applying the normalization condition we obtain

$$\lambda_0=\ln\{\mathrm{tr}[\exp(-i\boldsymbol{\beta}\cdot\mathbf{J})]\}=\ln[\mathrm{tr}(R_{\boldsymbol{\beta}})] , \tag{6.16}$$

where $R_{\boldsymbol{\beta}}$ is a rotation (angle $\boldsymbol{\beta}$). Rotation theory allows to evaluate the elements of the matrix $R_{\boldsymbol{\beta}}$ for any value of j provided that we know the elements of $R_{\boldsymbol{\beta}}$ for $j=\frac{1}{2}$. In this case $R_{\boldsymbol{\beta}}$ is

$$R_{\boldsymbol{\beta}}=\mathbb{1}\cosh(\hbar\beta/2)-i\sigma_{\boldsymbol{\beta}}\sinh(\hbar\beta/2) \tag{6.17}$$

with

$$\boldsymbol{\sigma}_{\boldsymbol{\beta}}=\boldsymbol{\sigma}\cdot\mathbf{n} \tag{6.18}$$

and $\boldsymbol{\sigma}$, the Pauli matrices. Thus

$$R_{\boldsymbol{\beta}}=\begin{bmatrix}\alpha & \gamma^* \\ \gamma & \alpha\end{bmatrix} \tag{6.19}$$

with

$$\begin{aligned}\alpha&=\cosh(\hbar\beta/2)\\ &=-\sinh(\hbar\beta/2)(\lambda_1+i\lambda_2)/\beta .\end{aligned} \tag{6.20}$$

If j is different from $\frac{1}{2}$, the elements of $R_{\boldsymbol{\beta}}$ are

$$\langle jm' | R_{\boldsymbol{\beta}} | jm \rangle = \frac{N_{jm}}{N_{jm'}} \sum_{\substack{p,q \\ p+q=j+m'}} \begin{bmatrix} j+m \\ p \end{bmatrix} \begin{bmatrix} j-m \\ q \end{bmatrix} \alpha^{p+j-m-q}(\gamma^*)^{j-m-p}\gamma^q , \tag{6.21}$$

with $N_{jm}=[(j+m)!(j-m)!]^{-1/2}$.

The mean values of the operators can be calculated via Eq. (2.1)

$$\langle \hat{O}_i \rangle = \exp(-\lambda_0)\mathrm{tr}(R_{\boldsymbol{\beta}}\hat{O}_i) . \tag{6.22}$$

Elementary angular momentum theory allows us to evaluate λ_0,

$$\lambda_0=\ln\left[\sum_m \exp(m\beta\hbar)\right] \tag{6.23}$$

with m the projections of $\tilde{J}$ $(m=-j,-j+1,\ldots,j-1,j)$. Thus the mean value of the relevant operators can be evaluated, leading to

$$\begin{aligned}\langle \hat{J}_x \rangle &= -\frac{\partial\lambda_0}{\partial\lambda_1}\\ &= -h\lambda_1\left[\sum_m m\exp(m\beta\hbar)\right] \Big/ \left[\beta\sum_m \exp(m\beta\hbar)\right] ,\end{aligned} \tag{6.24a}$$

$$\begin{aligned}\langle \hat{J}_y \rangle &= -\frac{\partial\lambda_0}{\partial\lambda_2}\\ &= -h\lambda_2\left[\sum_m m\exp(m\beta\hbar)\right] \Big/ \left[\beta\sum_m \exp(m\beta\hbar)\right] .\end{aligned} \tag{6.24b}$$

Applying Eqs. (6.22), (6.23), and (6.24), we can evaluate the invariants generated in Sec. III. From (3.4), we obtain the second-order invariant

$$I^{(2)}=\lambda_1^2(\langle \hat{J}_x^2\rangle-\langle \hat{J}_x\rangle^2)+\lambda_2^2(\langle \hat{J}_y^2\rangle-\langle \hat{J}_y\rangle^2) +2\lambda_1\lambda_2(\langle[\hat{J}_x,\hat{J}_y]_+\rangle/2-\langle \hat{J}_x\rangle\langle \hat{J}_y\rangle)\ , \qquad (6.25)$$

and from Eq. (4.13) we can assure that

$$I^{(2)}\geq 0\ . \qquad (6.26)$$

In this example, the relevant operators do not commute with $\hat{H}$, so that their mean values depend upon the time. Ehrenfest's theorem[7] allows us to evaluate the temporal evolution of the mean values

$$\langle \hat{J}_x\rangle(t)=\langle \hat{J}_x\rangle_0\cos(wt)-\langle \hat{J}_y\rangle_0\sin(wt)\ ,$$
$$\langle \hat{J}_y\rangle(t)=\langle \hat{J}_x\rangle_0\sin(wt)+\langle \hat{J}_y\rangle_0\cos(wt)\ , \qquad (6.27)$$

with $w=\mu_B B/\hbar$.

Using the structure constants associated with the closure condition it is possible to evaluate the invariants of the system.[17] They are

$$\{\mathbb{1},\hat{J}_x^2+\hat{J}_y^2,[\hat{J}_x,\hat{J}_y]_+\}\ . \qquad (6.28)$$

It is important to notice the difference between these invariants and those obtained in Eq. (3.3) [i.e., Eq. (6.25)]. The mean values of the observables given in (6.28) are time independent because the observables commute with $\hat{H}$. On the other hand, the invariant given in Eq. (6.25) is a particular combinations of mean values and Lagrange multipliers, which are time dependent.

The entropy of the system

$$S=\lambda_0+\lambda_1\langle \hat{J}_x\rangle+\lambda_2\langle \hat{J}_y\rangle \qquad (6.29)$$

is an invariant of the second case (I_2^1) and takes its maximum value when $\lambda_1=\lambda_2=0$ [Eq. (4.18)], namely,

$$S=\ln(2j+1)\ . \qquad (6.30)$$

As in Sec. VI A, we can evaluate S via Eq. (4.6)

$$S=\ln(2j+1-I^{(2)}/2) \qquad (6.31)$$

and this approximation would be a good one if $\hbar\beta \ll (2j+1)^{-1}$.

Finally, if the system has no correlated spin particles, the time evolution of the mean values also will be given by Eq. (6.27), although w might be different for each particle if the magnetic field is inhomogeneous. Now, coming back to the echo-spin example, it is possible to consider (6.13) as a one-particle density matrix $\hat{\rho}_i$. If the particles are uncorrelated we can obtain a total density matrix of the form

$$\hat{\rho}=\prod_{i=1}^{n}\hat{\rho}_i\ , \qquad (6.32)$$

where n is the particle number and the product is performed over the different state spaces of each particle. The eigenvectors of (6.32) will be

$$|j\rangle=\prod_{i=1}^{n}|j\rangle_i \qquad (6.33)$$

with eigenstates

$$P_j=\prod_{i=1}^{n}P_{ij}\ , \qquad (6.34)$$

where the P_{ij} $(j=1,2,\ldots,n)$ are the eigenstates of each $\hat{\rho}_i$. We suppose that all the subspaces has the same dimension (n) and, with

$$\mathrm{Tr}\hat{\rho}=1 \qquad (6.35)$$

we find

$$S_B=-\mathrm{Tr}(\hat{\rho}\ln\hat{\rho})=-\mathrm{Tr}\left\{\left[\prod_l\hat{\rho}_i\right]\left[\ln\prod_k\hat{\rho}_k\right]\right\}$$
$$=-\mathrm{Tr}\left\{\left[\prod_i\hat{\rho}_i\right]\sum_k(\ln\hat{\rho}_k)\right\}=-\mathrm{Tr}\left\{\sum_k\left[\prod_i\hat{\rho}_i\right](\ln\hat{\rho}_k)\right\}$$
$$=\sum_i\mathrm{Tr}(\hat{\rho}_i\ln\hat{\rho}_i)=\sum_i S_i\ , \qquad (6.36)$$

where S_B (Boltzmann entropy) has not been maximized. However, Eq. (6.36) is a good approximation to the experimental entropy because there are no correlations. When the correlations become important, the only thing that we can assert is that relation (5.8) [or better, (A10)] holds.

From the very beginning, the absence of correlations insures the reversibility of the process, although the dipoles can smear out through dephasing. If the information stored in the dephase moments can be recovered in a coherent fashion before the incoherent interactions (collisions, radioactive decays, spin exchanges) become important, we observe the echo-spin phenomena. Otherwise, for long times, the spread in frequencies covers all the new space, the correlations become important and Eq. (5.8) holds.

VII. CONCLUSIONS

Our main result is to be found in Eq. (4.6), where an original expression for the entropy is given in terms of the number of states, on one hand, and the (dynamical) invariants of the motion, on the other. Moreover, Eqs. (4.18) and (4.6) clearly exhibit the fact that (quantal) correlations [cf. Eq. (3.8)] *destroy* the equiprobability of (accessible) states,[10] so that the celebrated Boltzmann's relation ($S=\ln M$) ceases to hold in their presence.

A similar result was obtained some years ago by Jaynes,[19] although our relations appear as a generalization of Jaynes's previous equation. The connection of entropy with the invariants of motion, stresses its dynamical character and fully justifies the success of the MEP in prescribing the temporal evolution of expectation values, via the entropy conservation principle.[7]

Also, it is interesting to point out, in a quite different vein, that our invariants [cf. Eq. (4.13)] resemble entropy production sources,[14] although the former are written in terms of the Lagrange multipliers λ_i and *not* (the usual case) in terms of their fluctuations.[14] Moreover, I^2 possesses a dynamical character that the entropy production, obviously, does not have.

As can be observed, in Sec. V a quite clear distinction is made between the dynamical adiabatic evolution of the system and the behavior of the related entropy. All along our work, the term "adiabatic" is used only in connection with the adiabatic theorem prescription for Hamiltonian temporal evolution.

This kind of evolution guarantees the conservation of entropy and the number of states comprised, at $t=t_0$, in the Hilbert space of the system.

It is due to the residual interactions that the system can access a broadened Hilbert space and then the growing of entropy takes place. In fact, the second law of thermodynamics could be also expressed taking into account not only the thermal behavior of matter, but also the quantal laws which govern the dynamics of every physical system saying "The macroscopic spontaneous evolutions liberate the system to reach new states of its Hilbert space, and the entropy increases."

The free expansion of a one-dimensional gas and the echo-spin phenomena exemplified the above considerations.

In particular, the echo-spin process is a beautiful example of a reversible isoentropic but non adiabatic system.

In Sec. VI A Eq. (4.6) is applied to the anomalous Schottky effect leading to the interesting equation [(6.11) and (6.12)] graphically shown in Fig. 3. It would be emphasized that Eq. (6.11) has a universal validity for all systems with equally space levels.

In Sec. VI B and using the well-known Zeeman effect the relation between uncontrolled correlations and irreversibility is exemplified using the results of Secs. III and IV. Besides, and as was mentioned Eq. (6.11) is also valid for the Zeeman effect.

As a final remark we want to say that our approach fulfills not only the requirements of quantum mechanics, but also allow us to work with a statistical operator $\hat{\rho}$, that describes, in general, an off-equilibrium situation. Indeed, $\hat{\rho}$ is expressed in terms of operators $\hat{O}_i$ that do not necessarily commute with the Hamiltonian. Consequently, our results apply both to equilibrium and nonequilibrium situations.

APPENDIX

When $\hat{\rho}^e$ and $\hat{\rho}^G$ do not commute we must be careful with the inequality (5.7).[26] Let us now consider the diagonal matrix elements ρ_i^G and ρ_i^e taken over eigenstates of $\hat{\rho}^G$. Defining

$$x_i=\rho_i^e/\rho_i^G \tag{A1}$$

with

$$\sum_i \rho_i^e=1\ , \qquad \sum_i \rho_i^G=1\ , \tag{A2}$$

and applying that $x_i-1\geq \ln(x_i)$, the inequality (5.7) can be obtained. It must be noted that $\hat{\rho}_e$ may have off-diagonal elements.

If we want to study the relation between the two corresponding spaces, we can use the diagonal matrix elements ρ_i^G,ρ_j^e taken over each Hilbert space. It is even possible to define

$$x_{ij}=\rho_j^e/\rho_i^G\ , \tag{A3}$$

with

$$\sum_i \rho_j^e=1,\quad \sum_i \rho_i^G=1 \tag{A4}$$

so that

$$\rho_j^e/\rho_i^G-1\geq \ln\rho_j^e-\ln\rho_i^G\ . \tag{A5}$$

Multiplying by ρ_i^G and summing up over i,

$$M\rho_j^e-1\geq \ln\rho_j^e+S_G\ . \tag{A6}$$

Multiplying by ρ_j^e and summing up over j we are led to

$$M\,\mathrm{Tr}[(\hat{\rho}^e)^2]-1\geq -S_e+S_G \tag{A7}$$

or

$$S_e+M\,\mathrm{Tr}[(\hat{\rho}^e)^2]-1\geq S_G\ . \tag{A8}$$

As is well known, $\mathrm{Tr}[(\hat{\rho}^e)^2]$ has an upper bound

$$\mathrm{Tr}[(\hat{\rho}^e)^2]\geq 1\ , \tag{A9}$$

so that

$$S_e+M-1\geq S_G \tag{A10}$$

is trivially satisfied because $M>\ln M$.

However, a lower bound of $\mathrm{Tr}[(\hat{\rho}^e)^2]$ can be obtained applying (A3) over the same Hilbert space with different diagonal matrix elements

$$x_{jk}=\rho_j/\rho_k\ , \tag{A11}$$

$$N\,\mathrm{Tr}(\hat{\rho}^2)-1\geq 0\ , \tag{A12}$$

and then

$$\mathrm{Tr}(\hat{\rho}^2)\geq 1/N\ . \tag{A13}$$

Applying this lower bound in Eq. (A8) we obtain

$$S_e+M/N-1\geq S_G \tag{A14}$$

and if $M\leq N$,

$$S_e\geq S_G\ . \tag{A15}$$

Relation (A15) must be confronted with (5.8). Then the result (5.11) can be extended to the exact entropy if $\hat{\rho}^e$ is distributed over all the new accessible states.

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