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Concept of entropy for nonequilibrium states of closed many-body systems

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In this paper we study three fundamental questions: the characterization of the nonequilibrium states of a macroscopic system using exclusively the information that is controllable by the experimenter through the constraints imposed on the system, the construction of a variational method generating a probability distribution function in which the information available to the experimenter is contained, and finally the study of the time behavior of a functional, here referred to as the Shannon-Jaynes entropy, in order to examine the existence of a criterion for irreversibility. It is shown that the answer to the first two questions is provided by a theorem establishing the equivalence between the coarse-graining operation in phase space as suggested by Ehrenfest and the action of a projection operator, in fact, Zwanzig's projector, acting on the full probability distribution function containing all the information available when the system is initially prepared. The third question is partially answered by deriving an inequality characterizing the fact that every time the system is observed, information is lost. Yet the full proof establishing the equivalent of Boltzmann's H theorem is only qualitatively analyzed. The connection between this work and a similar one carried out from a macroscopic point of view is also established.

I. INTRODUCTION

The question of how to define the entropy function for nonequilibrium states of arbitrary systems has been a long debated question. Furthermore, this task has often been confused with the definition of coarse-grained H functions appropriate to time-irreversible mesoscopic evolution equations, which, as in Boltzmann's case of the dilute gas, do provide criteria for irreversibility and asymptotically converge to $-S_{\text{eq}}k^{-1}$, where S_{eq} is the equilibrium entropy and k is Boltzmann's constant, but are not by any means justified to define the entropy of nonequilibrium states. To do so, one should be able to incorporate in those functions the macroscopic variables describing the states of the system in much the same way that the temperature and the density are introduced into Boltzmann's H function through the well-known functional assumption.[1-3] Recently, there have been many efforts devoted to the clarification of the concept of entropy in these regimes,[4-10] but no satisfactory answer has yet been provided in the sense described above.

It is also pertinent to mention at this point that, from the macroscopic point of view, the problem is quite controversial. The definition of the state itself beyond the local equilibrium regime and consequently the concept of entropy has been a subject of a profound and inconclusive debate,[11-13] a feature of this whole treatment to which we will return later.

The purpose of this paper is to discuss some ideas that will hopefully lead to a convincing solution of this problem, at least in the context set forth by Jaynes many years ago.[14] This point of view is intimately related to the extension of Gibbs's conception of representative ensembles to cope with the motion in phase space in such a fashion that they are capable of describing the underlying irreversible process. In Sec. II we briefly summarize the physical ideas behind Boltzmann's H theorem; in Sec. III we prove that the act of coarse graining in the Ehrenfest way is identical to the construction of a maximal solution to the Jaynes-Shannon conception of a nonequilibrium entropy, constrained by the information accessible to the observer only through the act of measuring the relevant dynamical variables chosen to describe the states of the system; and in Sec. IV we show how the result allows us to establish rather interesting properties about the time dependence of the Jaynes-Shannon entropy compared with the Gibbs entropy. Among these properties, the most important is the one that has some resemblance to Boltzmann's H theorem, although the fine details have yet to be refined. The paper ends with a small section containing the important physical ideas implied in our results.

II. BOLTZMANN'S H THEOREM

Let $f(r,v,t)$ be the single-particle distribution function describing the nonequilibrium states of a dilute monatomic gas. This function is assumed to obey Boltzmann's integro-differential equation, which we need not specify here.[1-3] The H function is then defined as

$$H=\underset{(\mu)}{\int\int} d\mathbf{r}\,d\mathbf{v}\,f(\mathbf{r},\mathbf{v},t)\ln f(\mathbf{r},\mathbf{v},t)\ , \tag{1}$$

where the (μ) index to $\int\int$ indicates integration over the entire μ space.

If one now assumes that all integrals in μ space converge and that the microscopic equations of motion are invariant under time reversal, thus guaranteeing that both direct and inverse or restitutive binary collisions exist, he is led to the result that

$$\frac{dH}{dt}\le 0\ , \tag{2}$$

which is the well-known H theorem. The equality holds true only if detailed balance is achieved, namely, the rate at which direct and inverse collisions occur is the same; and this condition alone, in a homogeneous gas, leads to the Maxwellian distribution value for the function f. This result, however, is not free from assumptions. Indeed, to get the Maxwellian form for f, one must assume that it becomes a time-independent functional of the conserved densities, defined as the first five moments of f, and that this information is fully concentrated in the equilibrium form for f. This is how in equilibrium the thermodynamic values of the temperature and density appear in f, and therefore $-kH_{\text{eq}}$ can be identified with the equilibrium entropy S_{eq}. It must be emphasized that this identification is so far justified only for the equilibrium state. The inequality expressed by Eq. (2) with a minus sign and multiplied by k is not the second law of thermodynamics. $H(t)$ is a function of time alone, and not of the state variables describing the nonequilibrium states of the gas. Since entropy is a property of a state and not of a system, one is not permitted to identify it with H unless by some additional assumption, as in equilibrium, one could express $f(\mathbf{r},\mathbf{v},t)$ as a time-independent functional of a set of observables. But this is not the case, and it still remains an open question. Therefore, $-kH(t)$ is not the nonequilibrium entropy of a dynamical state of the dilute gas,[15] and Eq. (1) is not related to the second law of thermodynamics. We emphasize here that the second law refers only to the difference in the values of the entropy between two equilibrium states of any arbitrary closed system when it undergoes a reversible or irreversible process between two such states, but says nothing about the values of the entropy in the intermediate states of the latter one.

III. THE ACT OF COARSE-GRAINING

In this section we want to show how one can proceed to describe the nonequilibrium states of an arbitrary system using only the information that an observer has about the system through the external constraints that are selected to conform to it. Let $A_i(\Gamma)$ $(i=1,2,\dots)$ be a set of dynamical variables whose values depend on the coordinates of a phase-space point Γ that are chosen to describe the states of the system. For our specific purposes, we take $A_1(\Gamma)=H(\Gamma)$ to be the Hamiltonian of the system. Clearly, these functions evolve in time according to the deterministic laws of classical mechanics, which are invariant under time reversal. Next, assume that the observer decides to carry out an "experiment" to measure the values of these observables. For each one, the observer obtains a number a_i such that $a_i\le A_i(\Gamma)\le a_i+da_i$, where da_i is the experimental error. Clearly, the numerical values of the A's are expressed in terms of a nonequilibrium distribution function $g_{\text{ne}}(\mathbf{a},t)d\mathbf{a}$, namely,

$$g_{\text{ne}}(\mathbf{a},t)d\mathbf{a}=\text{Prob}[\mathbf{a}\le\mathbf{A}(\Gamma)\le\mathbf{a}+d\mathbf{a}]\ , \tag{3}$$

where $\mathbf{a}=(a_1,\dots,a_l,\dots)$ and the same for $\mathbf{A}$. Notice that $g_{\text{ne}}(\mathbf{a},t)$ is defined in $\mathbf{a}$ space and not in Γ space, so that its motion is no longer governed by the deterministic laws of classical mechanics.[16,17] Nevertheless, for our purposes we need not worry about its specific dynamics.

We now define the Jaynes-Shannon entropy $S_I(t)$ for our system at time t according to the expression

$$S_I(t)=-k\int\hat{\rho}(\Gamma,t)\ln\hat{\rho}(\Gamma,t)d\Gamma\ , \tag{4}$$

where the subscript I denotes information and $\hat{\rho}(\Gamma,t)$ is a function to be determined as that which maximizes the value of the integral in Eq. (4), consistent with the constraints

$$\int\hat{\rho}(\Gamma,t)d\Gamma=1\ , \tag{5a}$$

$$\int\hat{\rho}(\Gamma,t)\delta(H(\Gamma)-E)\delta(\mathbf{A}'(\Gamma)-\mathbf{a}')d\Gamma=g_{\text{ne}}(\mathbf{a},t)\ . \tag{5b}$$

Equation (5b) is the statement asserting that the set of microstates that are accessible to the representative phase point of the system lies in the hypersurface in phase space determined by the numerical values of the dynamical quantities selected to specify the macrostate of the system. Thus the phase-space region determined by the vector $\mathbf{a}$ is of course nothing else than the microcanonical phase-space cell defined through Ehrenfest's concept of coarse-graining. The similarity between Eqs. (4) and (5a) and (5b) with Eq. (1) and the definition of $f(\mathbf{r},\mathbf{v},t)$ is straightforward.

As is shown in the Appendix, the solution to the variational problem leads to the result

$$\hat{\rho}(\Gamma,t)=Z^{-1}\exp[-\lambda(H(\Gamma),\mathbf{A}'(\Gamma),t)]\ , \tag{6}$$

where Z is an undetermined Lagrange parameter and λ is an undetermined Lagrange function, both to be determined by Eqs. (5).

Now, for reasons of convenience, we denote the characteristic microcanonical function in phase space $G(\mathbf{a},0)$, which is expressed as

$$\begin{aligned}G(\mathbf{a},0)&=\prod_i\delta(A_i(\Gamma)-a_i)\\&=\delta(H(\Gamma)-E)\prod_{i\,(>1)}\delta(A_i'(\Gamma)-a_i')\\&=\delta(H(\Gamma)-E)G(\mathbf{a}',0)\ ,\end{aligned} \tag{7}$$

where $A_i(\Gamma)=A_i(\Gamma,t=0)$.

If we now use $G(\mathbf{a},0)$ to express Eq. (6) as an integral over E and $\mathbf{a}'$ and use the properties of the δ function, one easily arrives at the result

$$Z^{-1}e^{-\lambda(E,\mathbf{a}',t)}=\frac{g_{\mathrm{ne}}(\mathbf{a},t)}{\Omega(E,\mathbf{a}')}\,, \tag{8}$$

where $\Omega(E,\mathbf{a}')$ is the extension of the microcanonical phase-space cell given by

$$\Omega(E,\mathbf{a}')=\int d\Gamma\, G(\mathbf{a},0)=\int d\Gamma\, \delta(H-E)G(\mathbf{a}',0)\,. \tag{9}$$

Equation (8), which is just the value of $\hat{\rho}(\Gamma,t)$ evaluated at $\mathbf{A}(\Gamma)=\mathbf{a}$, clearly indicates that its time evolution is no longer governed by Liouville's equation, but rather by the nondeterministic evolution of $g_{\mathrm{ne}}(\mathbf{a},t)$. Moreover, use of Eqs. (6) and (9) in Eq. (4), together with the properties of the δ function, allows us to write

$$S_I(t)=-k\int dE\int d\mathbf{a}'g_{\mathrm{ne}}(E,\mathbf{a}',t)\ln\frac{g_{\mathrm{ne}}(E,\mathbf{a}',t)}{\Omega(E,\mathbf{a}')}\,, \tag{10}$$

which is the maximum value of the entropy at time t. Notice once more that the time behavior of $S_I(t)$ is no longer governed by a deterministic equation, but rather by the time evolution of $g_{\mathrm{ne}}(\mathbf{a},t)$.[16,17]

In thermodynamic equilibrium, where $\rho_{\mathrm{eq}}=\Phi(H(\Gamma))$ is some function of the constants of the motion, the energy in our case, we easily see from Eq. (5b) that $g_{\mathrm{eq}}(E,\mathbf{a}')=\Phi(E)\Omega(E,\mathbf{a}')$, a result that when combined with Eq. (6) appropriately written as an integration in $\mathbf{a}$ space leads to the result

$$\hat{\rho}(\Gamma,t)=\rho_{\mathrm{eq}}(\Gamma)\int d\mathbf{a}\frac{g_{\mathrm{ne}}(\mathbf{a},t)}{g_{\mathrm{eq}}(\mathbf{a})}G(\mathbf{a},0)\,. \tag{11}$$

So far in this approach we have only used a definition of the concept of entropy in terms of the variables that characterize the state of the system. We will now introduce the only assumption required in this whole treatment, namely,

$$\lim_{t\to\infty} g_{\mathrm{ne}}(\mathbf{a},t)=g_{\mathrm{eq}}(\mathbf{a})\,. \tag{12}$$

Equation (12) resembles again the condition that one imposes on $f(\mathbf{r},\mathbf{v},t)$ in the dilute-gas case, namely, that its long-time limit becomes the Maxwellian equilibrium distribution function. Of course, we could still argue that Eq. (12) would hold true if the system were ergodic (mixing) or obey similar conditions, but we will not resort to such profound concepts. When this result is substituted back into Eq. (11) we get

$$\lim_{t\to\infty}\hat{\rho}(\Gamma,t)=\rho_{\mathrm{eq}}(\Gamma)\,, \tag{12$'$}$$

or, in other words, the Jaynes-Shannon distribution function is compatible with equilibrium and this in turn implies, from Eq. (4), that

$$\lim_{t\to\infty} S_I(t)=-k\int \rho_{\mathrm{eq}}(\Gamma)\ln\rho_{\mathrm{eq}}(\Gamma)d\Gamma \tag{13}$$

in the equilibrium state, the information-based entropy is identical to Gibbs's expression for this thermodynamic function. If one compares this result with that derived from the Boltzmann H function, a similarity between both is observed, except for the substantial difference that the "entropy density in $\mathbf{a}$ space" according to Eq. (10) is now a function of the state variables E and $\mathbf{a}'$. In this sense, $S_I(E,\mathbf{a}',t)$, the integrand of this equation may be regarded as the nonequilibrium entropy density for the states accessible to the system under observation.

Notice here that, once more, we are able to speak of an entropy function, the entropy density in this case, only after the macroscopic information available to the observer is introduced in the H function. In the Boltzmann equation, this is precisely the idea behind the functional assumption. Once we substitute $f(\mathbf{r},\mathbf{v},t)$ by $f(\mathbf{r},\mathbf{v}|n(\mathbf{r},t),\mathbf{u}(\mathbf{r},t),\varepsilon(\mathbf{r},t))$, where $n(\mathbf{r},t)$ is the local density, $\mathbf{u}(\mathbf{r},t)$ is the local velocity, and $\varepsilon(\mathbf{r},t)$ is the local internal energy density, the integrand of H, $f\ln f$, depends explicitly on the macroscopic variables determining, in this case, the hydrodynamic states of the system thus allowing the identification of such a term with an entropy density.[1,18,19]

Finally, let us now seek a more physical interpretation of the distribution function $\hat{\rho}(\Gamma,t)$. For this purpose we fix our attention on the initial distribution function $\rho(\Gamma,\mathbf{a},0)$, defined as

$$\rho(\Gamma,\mathbf{a},0)=\frac{G(\mathbf{a},0)}{\Omega(E,\mathbf{a}')}=\frac{G(E,\mathbf{a}',0)}{\Omega(E,\mathbf{a}')}\,, \tag{14}$$

which is clearly normalized to 1. Substituting (14) into Eq. (11), one gets

$$\hat{\rho}(\Gamma,t)=\int dE\int d\mathbf{a}'g_{\mathrm{ne}}(E,\mathbf{a}',t)\rho(\Gamma,\mathbf{a},0)\,. \tag{15}$$

Defining the scalar product of two arbitrary phase-space functions $A(\Gamma)$ and $B(\Gamma)$ as[17]

$$(A,B)=\int d\Gamma\, A(\Gamma)B^{*}(\Gamma)\,, \tag{16}$$

and noticing that, in general,

$$g_{\mathrm{ne}}(\mathbf{a},t)=(\rho(\Gamma,t),G(\mathbf{a},0))\,, \tag{17}$$

we may rewrite, using Eqs. (14), (15), and (16), that

$$\hat{\rho}(\Gamma,t)=P_Z\rho(\Gamma,t)\,, \tag{18}$$

where P_Z is Zwanzig's projection operator, defined by[20]

$$P_Zf(\Gamma,t)=\int d\mathbf{a}\frac{(f(\Gamma,t),G(\mathbf{a},0))}{(1,G(\mathbf{a},0))}G(\mathbf{a},0)\,, \tag{19}$$

and $f(\Gamma,t)$ is an arbitrary function of the phase-space point Γ and time t.

This is a rather satisfactory result, namely, that the Jaynes-Shannon probability distribution function maximizing the value of $S_I(t)$ given in Eq. (4) is nothing else than the "coarse-grained" distribution function obtained by projecting the Gibbs $\rho(\Gamma,t)$ probability distribution function onto the microcanonical cell determined only by constraints imposed on the system. This result is rather pertinent, in view of the rather distressing opinion that Jaynes himself wrote about this question in his seminal paper in this subject almost 25 years ago.[15] We quote from Jaynes:

"Past attempts to demonstrate the second law for systems other than dilute gases have generally tried to retain the basic idea to the Boltzmann H theorem. Since the Gibbs H is dynamically constant, one has resorted to some kind of coarse-graining operation, resulting in a new quantity $\hat{H}$, which tends to decrease. Such attempts cannot achieve their purpose, because (a) mathematically, the decrease in $\hat{H}$ is due only to the artificial coarse-graining operation and it cannot, therefore have any physical significance; (b) as in the Boltzmann H theorem, the quantity whose increase is demonstrated is not the same thing as the entropy. For the fine-grained and coarse-grained probability distribution lead to just the same predictions for the observed macroscopic quantities, which alone determine the experimental entropy; the difference between H and $\hat{H}$ is characteristic, not of the macroscopic state, but of the particular way in which we choose to coarse-grain. Any really satisfactory demonstration of the second law must therefore be based on a different approach than coarse-graining."

As we see from the result expressed by Eq. (18), there is no ambiguity in the procedure undertaken to coarse-grain, provided $\hat{\rho}(\Gamma,t)$ is determined only through the external constraints imposed on the system.

IV. THE PROPERTIES OF $S_I(t)$

In this section we want to study how the function $S_I(t)$ defined in Eq. (4) behaves in time, compared at different times, and against the conventional definition of Gibbs's entropy. Substituting Eq. (18) back into Eq. (4) we find that

$$S_I(t)=-k\int\rho(\Gamma,t)\ln P_Z\rho(\Gamma,t)d\Gamma\ , \tag{20}$$

where use has been made of the Hermitian property of P_Z and that $P_Z\ln P_Z\rho(\Gamma,t)=\ln P_Z\rho(\Gamma,t)$. Since the Gibbs definition of entropy is

$$S_G(t)=-k\int\rho(\Gamma,t)\ln\rho(\Gamma,t)d\Gamma\ , \tag{21}$$

where $\rho(\Gamma,t)$ is a solution to Liouville's equation, thus implying that $dS_G/dt=0$, and using the fact that for $x>0$, $\ln x\ge 1-x^{-1}$, we get, comparing Eqs. (20) and (21),

$$S_I(t)\ge S_G(t)\ , \tag{22}$$

the equality holding only if $\hat{\rho}(\Gamma,t)=\rho(\Gamma,t)$. Thus at every time t the Jaynes-Shannon entropy cannot be less than the Gibbs entropy. In a finite time interval this latter function remains constant, which means that at time $t'>t$ we know that Eq. (22) holds true, but we are not yet in a position to assert whether $S_I(t)$ is larger, equal to, or less than $S_I(t')$, only that both values cannot be less than the lower bound provided by $S_G(t)$.

To establish a relationship between the values of S_I at different times, we start with our system prepared at the initial time t_0 according to the prescription indicated in Eq. (14) and call $\rho(\Gamma,\mathbf{a},0)=\rho_0(\Gamma,t_0)$. Clearly, at this point $S_G^{(0)}(t_0)=S_I^{(0)}(t_0)$, where the superscript zero will indicate the stage at which the observation was made. Take now any time $t>t_0$ and compute $\rho_0(\Gamma,t)$ according to the laws of classical statistical mechanics.

Therefore,

$$\rho_0(\Gamma,t)=U(t,t_0)\rho_0(\Gamma,t_0)\ , \tag{23}$$

where $U(t',t)=\exp[-i(t-t')L]$ and L is Liouville's operator. It is then clear from Eq. (22) that

$$S_I^{(0)}(t)\ge S_G^{(0)}(t),\quad t>t_0\ .$$

We arrive at the crucial stage of the proof, which is related to what Jaynes refers to as the act of conveying information from one observer to another. For simplicity, take an arbitrary time $t_1>t_0$ at which another observer performs an independent measurement on the state of the system. According to Eq. (18), what he obtains is that

$$\hat{\rho}_1(\Gamma,t_1)=P_Z\rho_0(\Gamma,t_1)\ , \tag{24}$$

where $\rho_0(\Gamma,t_1)$ is given by Eq. (23) evaluated at $t=t_1$. If he decides to study the dynamical evolution of the system with $\hat{\rho}_1(\Gamma,t_1)$ as the initial value for the probability density, he would find that at any time t'

$$\rho_1(\Gamma,t')=U(t',t_1)P_Z\rho_0(\Gamma,t_1)\ , \tag{25}$$

and also that

$$S_I^{(1)}(t')\ge S_G^{(1)}(t')=S_G^{(1)}(t_1) \tag{26}$$

for $t'>t_1$, the last equality following because in the time interval (t_1,t'), $S_G^{(1)}$ remains constant. However, the two constant values of $S_G(t)$ in the time intervals (t_0,t_1) and (t_1,t') are not the same. Indeed,

$$\begin{aligned}S_G^{(1)}(t_1)&=-k\int\rho_1(\Gamma,t_1)\ln\rho_1(\Gamma,t_1)d\Gamma\\&=-k\int\rho_0(\Gamma,t_1)\ln P_Z\rho_0(\Gamma,t_1)d\Gamma\\&\ge-k\int\rho_0(\Gamma,t_1)\ln\rho_0(\Gamma,t_1)d\Gamma\ ,\end{aligned}$$

the second and third equalities following from Eq. (24) and the same arguments that led to Eq. (22), respectively. Hence,

$$S_G^{(1)}(t_1)=S_I^{(1)}(t_1)\ge S_G^{(0)}(t_1)\ , \tag{27}$$

the first equality arising from the definition of the initial state for the second observer.

Therefore, from the fact that $S_G^{(0)}(t_1)=S_G^{(0)}(t_0)=S_I(t_0)$ and (27) we are led to the conclusion that

$$S_I^{(1)}(t_1)\ge S_I^{(0)}(t_0)\ , \tag{28}$$

so that the Jaynes entropy cannot decrease in time. Thus the following physical picture evolves: For a given finite time interval in which a system initially prepared in an arbitrary initial state is allowed to age, the Gibbs entropy remains constant, while the Jaynes-Shannon entropy increases. If at any time t greater than the initial time t_0 an *independent measurement* is performed on the system's state, the information conveyed to the observer is no longer provided by the dynamics alone but by the mere act of measurement expressed by Eq. (18). After that time, the system ages following the same pattern until it reaches equilibrium, where only the unique value for the equilibrium entropy subsists. Once more, one must clearly realize that the mere act of measurement upon the system introduces a discontinuity in the value of $S_G(t)$.

This discontinuity arises precisely from the knowledge about the states of the system available to the observer,

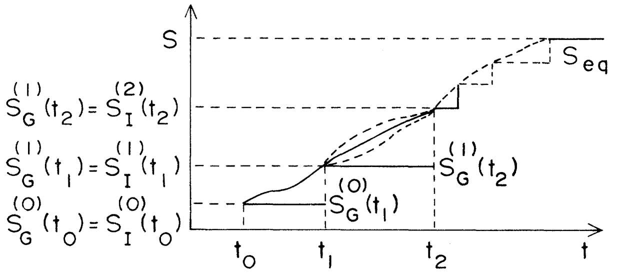

FIG. 1. Gibbs vs Shannon-Jaynes entropy as a function of time after different independent observations at $t_0, t_1, \ldots$.

clearly expressed by Eq. (18). So each time we observe the aged system, the initial value of $\rho(\Gamma,t)$ is determined by Eq. (18), after which the corresponding value of the Gibbs entropy never changes, but the Shannon-Jaynes entropy increases. This pattern is shown in Fig. 1, where each step is drawn according to these results.

It should be clearly stressed that Eq. (28) is not yet in the form of an H theorem. Indeed, if we want to compare the relative values of $S_I(t)$ during the different aging periods, as observed in different measurements, we would have to solve the problem, which is schematically represented by the dotted lines in Fig. 1, providing a criteria to know how observer 2 in (t_1,t_2) would compare his values of $S_I(t)$ with those of the first observer, had the latter one continued to follow the system until equilibrium was reached. $S_I^{(0)}(t)$ and $S_I^{(1)}(t)$ for $t>t_1$ have to be compared between themselves. The problem will be examined in a forthcoming paper.

We also note that the inequality (28) is not a new result. Indeed, in various forms it has been mentioned in the past by several authors.[21-24]

Finally, comparing $S_I(t)$ and $S_G(t)$, both of which are identical to S_{eq} when $t\to\infty$, the question arises as to how one can visualize this process if only one observer is present. The only picture compatible with the underlying theoretical discussion for times $t<\infty$ when the inequality given by Eq. (22) is satisfied and $S_G(t)=\text{const}$ is given in Fig. 2. At $t=\infty$, $S_G(t)$ has to change discontinuously, since $\rho(t)\to\rho_{\text{eq}}$, and, as shown before, the two entropies are identical in equilibrium. Notice, however, that the path describing the time dependence of $S_I(t)$ is uncertain as long as the inequality expressed by Eq. (22) is fulfilled.

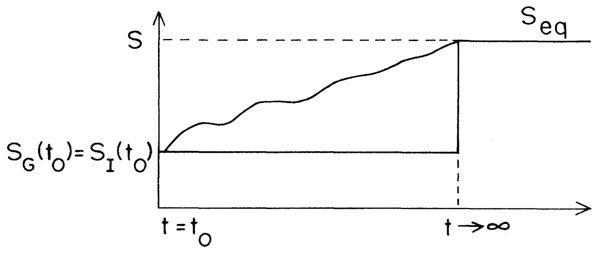

FIG. 2. Under the observation of a single experimenter, the Shannon-Gibbs entropy follows an unknown curve (continuous curve), consistent with the condition that $S_I(t)\geq S_G(t)$ for all times, but at $t\to\infty$, in equilibrium, both entropies are identical.

V. CONCLUDING REMARKS

Equations (18) and (28) are the main results of this study. The former is a generalization of a well-established result in equilibrium statistical mechanics to nonequilibrium states. Indeed, recall that the microcanonical ensemble for equilibrium characterizes the state of the system, given a set of external constraints. Equation (18) represents the only accessible microstates to the phase-space point representative of the condition of the system described by the set of dynamical variables $\{A_i(\Gamma)\}$. These accessible states are defined by the intersection of all these hypersurfaces defined by the equations $A_i(\Gamma)=\text{const}$, $i=1,\ldots,n$. Mathematically, this region is precisely the one associated with the projection operator as defined by Zwanzig 30 years ago. In the words of Jaynes, transcribed here *ad verbatim*,[25] "If any macrophenomenon is found to be reproducible then it follows that all microscopic details that were not under the experimenter's control must be irrelevant for understanding and predicting it." Equation (18) is precisely the mathematical expression for one part of this statement, namely the only information controllable by the experimenter is extracted through the operation indicated by P_Z.

The second question underlying this statement is how to construct a variational principle such that it allows the prediction of the desired macrophenomena. This principle was first devised by Gibbs[26] and is here expressed by the results of Sec. II. Although we have not yet fully exploited all the consequences, concentrating on the problem of extracting an irreversibility criterion similar to the H theorem, we have proved what may be considered a preliminary result, expressed by Eq. (28). This inequality simply expresses the fact that a sequence of observations performed on a macroscopic system undergoing an irreversible process always results in a loss of information in Shannon's sense. This is, however, not in the form of an H theorem. A final step has to be undertaken, namely, to study the time derivative of $S_I(t)$ starting from its fundamental expression, that given by Eq. (10). Yet this is not a trivial one, since it involves the appearance of $dg_{\text{ne}}(\mathbf{a},t)/dt$, which is a rather complicated expression, such that, although not invariant under time reflections, it is nonlocal in time and in the $\mathbf{a}'$ variables.

Here one will be confronted with the eternal question; namely, is one justified in speaking about the definition of the states when the variables describing it depend on the previous history, or only when their values are to be regarded as instantaneous? In the first case, Meixner has shown[27] that from a macroscopic point of view, the entropy is either undefined or there are infinitely many ways of defining it. In the second case, one always falls into a somewhat generalized conception of the local equilibrium assumption,[1,3,19,28] and the definition of entropy poses no problem at all. As it turns out, both postures are consistent with the nature of the time solution equation for

$g_{\text{ne}}(\mathbf{a},t)$, but we shall leave all the details and results that may be extracted from this analysis to a forthcoming paper.

APPENDIX

The problem we wish to solve is a little bit different from the standard one in statistical mechanics[26] because of the functional nature of the conditions imposed on the distribution function in its dependence on the macroscopic variables.[29] We wish to maximize the value of $S_I(t)$ given by

$$S_I(t)=-k\int\hat{\rho}(\Gamma,t)\ln\hat{\rho}(\Gamma,t)d\Gamma\;, \tag{A1}$$

subject to the following conditions: first, that it is normalized in Γ space [see Eq. (5a)]; and secondly, that the following n conditions are obeyed, namely,

$$\int_{\mathbf{a}_i\le\mathbf{A}(\Gamma,0)\le\mathbf{a}_i+\Delta\mathbf{a}}\hat{\rho}(\Gamma,t)d\Gamma=P(\mathbf{a}_i,t)\Delta\mathbf{a} \tag{A2}$$

for $i=1,\dots,n$, n being an arbitrary positive number, and $P(\mathbf{a}_i,t)\Delta\mathbf{a}$ the known probability that, upon measurement, the *initial* value of the phase function $\mathbf{A}(\Gamma,0)$ takes a value lying in the range $(\mathbf{a}_i,ai+\Delta\mathbf{a})$. Clearly $\mathbf{A}(\Gamma,0)$ is assumed to be known, since it corresponds to a constraint imposed in preparing the system at $t=0$.

We now construct the auxiliary function $I(t)$:

$$\begin{aligned}I(t)=&S_I(t)-\mu\int\hat{\rho}(\Gamma,t)d\Gamma\\&-\sum_{i=1}^{n}\lambda(\mathbf{a}_i,t)\int_{\mathbf{a}_i\le\mathbf{A}(\Gamma,0)\le\mathbf{a}_i+\Delta\mathbf{a}}\hat{\rho}(\Gamma,t)d\Gamma\;,\end{aligned} \tag{A3}$$

where μ is an undetermined parameter, as well as $\lambda(\mathbf{a}_i,t)$, which depends parametrically on $\mathbf{a}_i$ and time t. Equation (A3) may also be written as

$$\begin{aligned}I(t)=&S_I(t)-\mu\int\hat{\rho}(\Gamma,t)d\Gamma\\&-\sum_{i=1}^{n}\lambda(\mathbf{a}_i,t)\Delta\mathbf{a}\frac{1}{\Delta\mathbf{a}}\int\hat{\rho}(\Gamma,t)D\left[\frac{\mathbf{A}(\Gamma,0)-\mathbf{a}}{\Delta\mathbf{a}}\right]d\Gamma\;,\end{aligned} \tag{A4}$$

where D is Heaviside's function defined as

$$D\left[\frac{x-x_0}{\Delta x}\right]=\begin{cases}1 & \text{if } x\in(x_0,x_0+\Delta x)\\ 0, & \text{otherwise}\;.\end{cases} \tag{A5}$$

We will now take the limit of expression (A4) and assume that $P(\mathbf{a}_i,t)\Delta\mathbf{a}$ may be substituted by a probability function $P(\mathbf{a}_i,t)d\mathbf{a}$ for all possible values of the vector phase function $\mathbf{A}(\Gamma,0)$ so that

$$\int_{\mathbf{a}\le\mathbf{A}(\Gamma,0)\le\mathbf{a}+\Delta\mathbf{a}}\hat{\rho}(\Gamma,t)d\Gamma=P(\mathbf{a},t)\Delta\mathbf{a} \tag{A6}$$

for all possible values of $\mathbf{a}$. This is equivalent to the form

$$\lim_{\Delta\mathbf{a}\to0}\frac{1}{\Delta\mathbf{a}}\int\hat{\rho}(\Gamma,t)D\left[\frac{\mathbf{A}(\Gamma,0)-\mathbf{a}}{\Delta\mathbf{a}}\right]d\Gamma=P(\mathbf{a},t) \tag{A7}$$

or

$$\int\hat{\rho}(\Gamma,t)\delta(\mathbf{A}(\Gamma,0)-\mathbf{a})d\Gamma=P(\mathbf{a},t)\;. \tag{A8}$$

From this we see that the form of the auxiliary function $I(t)$ defined in Eq. (A3) that corresponds to the limiting process specified in Eq. (A7) is given by

$$\begin{aligned}I(t)=&S_I(t)-\mu\int\hat{\rho}(\Gamma,t)d\Gamma\\&-\lim_{\substack{n\to\infty\\ \Delta\mathbf{a}\to0}}\sum_{i=1}^{n}\lambda(\mathbf{a}_i,t)\Delta\mathbf{a}\frac{1}{\Delta\mathbf{a}}\\&\times\int\hat{\rho}(\Gamma,t)D\left[\frac{\mathbf{A}(\Gamma,0)-\mathbf{a}_i}{\Delta\mathbf{a}}\right]d\Gamma\;,\end{aligned}$$

or using Eq. (A8),

$$\begin{aligned}I(t)=&S_I(t)-\mu\int\hat{\rho}(\Gamma,t)d\Gamma\\&-\int d\mathbf{a}\,\lambda(\mathbf{a},t)\left[\int\hat{\rho}(\Gamma,t)\delta(\mathbf{A}(\Gamma,0)-\mathbf{a})d\Gamma\right]\;.\end{aligned}$$

The function $\hat{\rho}(\Gamma,t)$, which is a solution to the extremum problem defined by $\delta I=0$ for all possible values of $\delta\hat{\rho}$, is now readily obtained by standard methods and leads precisely to Eq. (6) in the text. Clearly, the probability function here denoted $P(\mathbf{a},t)$ corresponds to the one we have called $g_{\text{ne}}(\mathbf{a},t)$ in the text.

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