A Generalization of Gibbs’ Ensemble
to Nonequilibrium Statistical Mechanics

Masakazu ICHIYANAGI

Department of Applied Physics, Osaka University, Suita 565

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It is shown that a nonequilibrium density matrix, which is a solution of the Liouville-von Neumann equation, may be employed to prove a nonequilibrium fluctuation-dissipation theorem.

The description of a macroscopic system in thermodynamic equilibrium is, in principle, quite simple. For fixed values of the volume, energy, particle number and of any other controllable constants of the motion, there is only one state of thermodynamic equilibrium. The ensemble theory of Gibbs has been universally accepted as a theoretical foundation for dealing with such a thermodynamic state. No comparable theory has gained wide acceptance in nonequilibrium statistical mechanics. We would like to propose a formalism which is a generalization of the Gibbs theory to nonequilibrium statistical mechanics.

The number of nonequilibrium states of a macroscopic system is huge. In fact, the term “nonequilibrium” is so indefinite as to be hardly less restrictive than “microscopic state”. In almost any physical situation, the following questions thus inevitably arise: (1) What are the right ensembles for nonequilibrium situations? (2) How can one reconcile the reversibility of microscopic dynamics with the irreversibility of macroscopic processes? To answer these, it is important to realize, for a given treatment of nonequilibrium states, at what point irreversibility has been incorporated. If it has not been incorporated, the treatment is not sufficient for nonequilibrium systems. If we do not see clearly where the irreversibility is introduced, we do not clearly understand what we are doing. In this short note, therefore, we will show that a nonequilibrium density matrix, which is a formal solution of the Liouville-von Neumann equation, may be employed to derive fluctuation-dissipation relations, in the sense that transport coefficients are expressed in terms of the time-correlation functions.

Our problem may be summarized as follows: We have a closed system. If the system were in nonequilibrium, it would be described by a density matrix \( \rho(t) \) that obeys the Liouville-von Neumann equation

\[
\frac{\partial \rho(t)}{\partial t} + i[H, \rho(t)] = 0 ,
\]

\( H \) being the time-independent Hamiltonian of the system. Our problem consists in finding the general solutions of Eq. (1). In principle, there must be an extremely large class of density matrices that satisfy Eq. (1). The fact to be noted here is that it is possible to express any density matrix of the system in terms of operators which, as a whole, close a partial Lie algebra under commutation with the Hamiltonian \( H \).
Accordingly, writing operators in a complete set (in the sense that operators close the partial Lie algebra) $\mathcal{A} = \{ A_0 (= I, \text{the identity}), A_1, \ldots, A_f, \ldots \}$, we can express the density matrix $\rho(t)$ or its logarithm $\ln \rho(t)$ at any time $t$ in terms of these operators as \(^2\)

$$\ln \rho(t) = -\beta H + \sum_{j=0}^{\infty} A_j \cdot x_j(t).$$

By making use of Eq. (2) into Eq. (1), we get at once

$$dx_j(t)/dt = \sum_{k=0}^{\infty} G_{jk} \cdot x_k(t), \quad (j=0, 1, \ldots, f, \ldots)$$

where the $G_{jk}$ are the so-called structure constants of the partial Lie algebra,

$$[H, A_j] = i \sum_{k=0}^{\infty} G_{jk} \cdot A_k.$$ \hspace{1cm} (4)

We have taken $A_0$ to be the identity operator so that $\rho(t)$ is normalized: $\text{Tr} \rho(t) = 1$. The set of operators is determined either from some theoretical considerations or from experimental results.

In the Schrödinger picture, the time evolution is described by a unitary evolution operator $U(t, t_0)$:

$$\partial U(t, t_0)/\partial t = -i H U(t, t_0). \quad (U(t_0, t_0) = 1)$$ \hspace{1cm} (5)

Then, in particular, we have

$$\ln \rho(t) = U(t, t_0) \rho(t_0) U^*(t, t_0).$$ \hspace{1cm} (6)

Therefore, this precise density matrix $\rho(t)$ does not describe any entropy production.

It is important to realize that the ansatz (2) is valid iff there exists a time-dependent matrix $M$ whose matrix elements are given by

$$U(t, t_0) A_j U^*(t, t_0) = \sum_{k=0}^{\infty} A_k \cdot M_k(t, t_0).$$ \hspace{1cm} (7)

Then, using Eq. (2)

$$x_j(t) = \sum_{j=0}^{\infty} M_{0j}(t, t_0) \cdot x_j(t_0),$$ \hspace{1cm} (8)

and from Eq. (3) we get at once

$$G_{ij} = i \partial M_{ij}(t, t_0)/\partial t|_{t=t_0}. \hspace{1cm} (9)$$

The advantage of using the structure constants $G_{ij}$ is that the same structure constants apply irrespective of the magnitude of the initial values, $x_j(t_0), (j=0, 1, \ldots)$. Within the information-theory framework,\(^2\) the density matrix is constructed according to a well-defined prescription starting from the knowledge of the expectation values of operators $A_j$. The quantities $x_j(t)$, which are often called Lagrangian multipliers, are determined so as to fulfill the set of relations

$$a_j(t) = \text{Tr} \rho(t) A_j, \quad (j=1, \ldots, f, \ldots)$$ \hspace{1cm} (10)
where the $a(t)$ are determined from the experimental results. The density matrix $\rho(t)$ maximizes the informational "entropy" $S(t) = -k_b \text{Tr} \rho(t) \ln \rho(t)$ subject to Eq. (10). The word "entropy" is in quotation marks because the definition is only formal. It should be stressed that the number of the operators that close the algebra under commutation with the Hamiltonian is huge and is nearly infinite. Accordingly, the conditions (10) may not be manageable in the usual thermodynamical sense. Our present aim here, therefore, is reinterpreting certain concepts of the algebraic treatment of operator space.

We must first take into account that the problem under investigation is not simple quantum mechanical processes but the thermodynamic processes. It is sufficient to make use of the subset of relevant operators in the linear space $\mathcal{A}$ of operators of the system. We shall regard the subset $\{A_j; j=0, \ldots, f\}$ as the relevant set. It must be determined from a physical point of view how many and which of operators are to be taken. Mori\(^3\) has used the projection operator technique to eliminate the irrelevant operators from the complete set. To this purpose he has decomposed the space of operators into a relevant subspace $\mathcal{A}_{\text{rel}}$ containing all linear combinations of $\{A_j; j=0, 1, \ldots, f\}$ and an irrelevant subspace $\mathcal{A}_{\text{irr}}$. Then, every operator $A \in \mathcal{A}$ may be decomposed in various ways according to $A = A_{\text{rel}} + A_{\text{irr}}$, where $A_{\text{rel}} \in \mathcal{A}_{\text{rel}}$, $A_{\text{irr}} \in \mathcal{A}_{\text{irr}}$. By means of a projection operator $P$ he has derived an exact equation of motion for the relevant operators.

There are many choices for the relevant set.\(^4\) In this short note, we assume that there is a time interval $\tau$, a microscopic relaxation time for the system under study, and that

$$\int_0^\tau x_j(t_0+s)ds/\tau = 0, \quad (j=f+1, \ldots)$$

(11)

while

$$X_j(t_0) \equiv \int_0^\tau x_j(t_0+s)ds/\tau \neq 0. \quad (j=0, 1, \ldots, f)$$

(12)

Accordingly, we have the expression

$$\ln D(t_0) = \int_0^\tau \ln \rho(t_0+s)ds/\tau$$

$$= -\beta H + \sum_{j=0}^f A_j \cdot X_j(t_0).$$

(13)

Here we have made use of Eq. (2). If in building up our initial density matrix $D(t_0)$ we use relevant operators that do not commute with the Hamiltonian, then this initial situation is not an equilibrium one. It is just in this sense that we claim we can generalize Gibbs' ensemble to nonequilibrium systems.

This setting calls for some comment. It should be pointed out that it is not legitimate to write for $j \geq f+1$

$$\int_0^\tau x_j(t+s)ds/\tau = 0 \quad \text{(false)}$$

(11')
at any time \( t \) instead of Eq. (11). The reason for this is as follows. Let us define the time-smoothed density matrix \( D(t) \) by the equation

\[
\ln D(t) = \int_0^t \ln \rho(t + s) ds / \tau
\]

for \( t \geq t_0 \). Then, it is readily verified that the time-smoothed density matrix \( D(t) \) also obeys the Liouville-von Neumann equation

\[
\frac{\partial \ln D(t)}{\partial t} + i[H, \ln D(t)] = 0
\]

as the precise density matrix \( \rho(t) \) does. However, it is not legitimate to write \( \ln D(t) = -\beta H + \sum_{j=0}^f A_j \cdot X_j(t) \) for the subset \( \mathcal{A}_{rel} \) is not a complete set closed under commutation with the Hamiltonian. It should be noted that

\[
\sum_{j=0}^f U(t, t_0) A_j U^*(t, t_0) X_j(t_0) = \sum_{j=0}^\infty A_j \cdot X_j(t) .
\]

Then, it follows that the thermodynamic forces are given by

\[
X_k(t) = \sum_{j=0}^f M_k(t, t_0) X_j(t_0)
\]

for \( k = 0, 1, \ldots, f, \ldots \). The occurrence of irrelevant operators in Eq. (16) is intimately related to the occurrence of irreversibility. The procedure, in which the relevant operators are those belonging to a set that is closed under commutation with the Hamiltonian, is discussed in Ref. 2. The result is a closed set of coupled integrodifferential equations for the macroscopic operators.

An alternative way to state the condition (16) is obtained by writing \( \ln D(t) \) in the following form

\[
\ln D(t) = -\beta H + \sum_{j=0}^f A_j \cdot X_j(t) + \Phi(t) ,
\]

in which the operator \( \Phi(t) \) satisfies the equation of motion

\[
\frac{\partial \Phi(t)}{\partial t} + i[H, \Phi(t)] - \sum_{j=0}^f [A_j \cdot X_j + i[H, A_j] \cdot X_j(t)] = 0
\]

with the initial condition \( \Phi(t_0) = 0 \). By introducing a projection operator \( P \) to eliminate the irrelevant operators from the complete set of operators, Eq. (19) can be rewritten in the form

\[
\frac{\partial \Phi(t)}{\partial t} + Qi[H, \Phi(t)] = \sum_{j=0}^f Qi[H, A_j] \cdot X_j(t) ,
\]

where \( Q = I - P \). The definition of the projection operator \( P \) is not unique. One may define it either in the form given by Mori or in a generalized form. The formal solution of Eq. (20) is

\[
\Phi(t) = \sum_{j=0}^f \int_{t_0}^t ds e^{-i(t-s)QH} Q[iH, A_j] e^{i(t-s)QH} \cdot X_j(s) .
\]

Hence, we have obtained the exact solution of the Liouville-von Neumann equation.
which describes nonequilibrium states of the system. So far, we have been concerned with an initial value problem. We have solved the Liouville-von Neumann equation in the form which satisfies the principle of causality that is an axiom of the present treatment. It is noted that the operator $\Phi(t)$ describes microscopic excitations which did not exist in the initial state. Such excitations are incorporated to the occurrence of an irreversible behavior of the system.

As an interesting application of the above formalism, we will show that the time-smoothed density matrix $D(t)$ can be employed to prove a fluctuation-dissipation theorem. It is readily seen that

$$\beta \text{Tr} D(t)[iH, A_k]=\sum_{j=0}^{\infty} \text{Tr} D(t)[iA_j, A_h]\cdot X\%(t)
$$

\[+\sum_{j=0}^{\infty}\int_{t_0}^{t} ds \text{Tr} D(t)[iA_k,e^{-i(t-s)QH}Q[iH, A_j]e^{i(t-s)QH}]\cdot X\%(s) . \tag{22} \]

The proof is simple. Note that

$$\text{Tr} e^{A+B}[B, C]=\text{Tr} e^{A+B}[C, A] . \tag{23}$$

Now we assume that the relevant operators are commutable with each other on the average. That is,

$$\text{Tr} D(t)[A_k, A_j]=0 . \quad (k, j=1, \cdots, f) \tag{24}$$

These conditions may be fulfilled by macroscopic operators of a system. This is an essential condition when one makes a choice of a relevant set of operators.

It should be noted that while the left-hand side of (22) does indeed describe macroscopic currents that characterize the nonequilibrium situation, the right-hand side of it describes a purely dynamical correlation. It essentially reflects the fact that the nonequilibrium density matrix is determined by the unitary evolution operator $U(t, t_0)$ with $D(t_0)$ given by (13). Accordingly, if the conditions (24) are fulfilled, the right-hand side of Eq. (22) is nothing but the time-correlation function expression for the transport coefficients in our case. It is a fluctuation-dissipation theorem for nonequilibrium systems. The formula (18) is thus useful for developing a nonequilibrium ensemble theory. In a separate paper, we will apply this formula to derive a quantum kinetic equation from the Liouville-von Neumann equation.

4) See also, B. Robertson, Phys. Rev. 144 (1966), 153.