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A New Perspective of the Fluctuation-Dissipation Theorem

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A new formulation is presented of the fluctuation-dissipation (FD) theorem. It is stressed that the (time-independent) Hamiltonian plays a dual role in the derivation of the FD theorem. It determines the ensemble to be used and governs the dynamic out from equilibrium. By generalizing this point of view, a fluctuation-dissipation theorem is derived for nonequilibrium stationary states far from equilibrium.

§ 1. Introduction

Nonequilibrium statistical mechanics aims to derive macroscopic laws of systems not in thermal equilibrium, starting out from the microscopic laws of motion. In general, macroscopic laws are found for dissipative systems. Hence, we encounter here fundamental difficulties, because we must make a joint analysis of dissipation and Hamiltonian dynamics.

It is fundamental that a mechanism of energy dissipation is closely related to thermal fluctuations. An exact relation between the noise spectrum and the linear response of the system to applied forces is the fluctuation-dissipation (FD) theorem. This theorem is proved for a Hamiltonian system, without dissipation. In practice, however, it is applied to non-Hamiltonian systems, which are described by macroscopic laws of motion that explicitly contain dissipation parameters.

The present article casts some light on the meaning of the FD theorem. This theorem is one of the most fundamental cornerstones supporting nonequilibrium statistical mechanics. Nyquist[1)] first gave an example of fluctuation-dissipation relation and provided a proof of it based upon the second law of thermodynamics. In electrical circuits, thermal motion of electrons in conductors gives rise to current fluctuations which can be heard by ear if suitably amplified. More generally, every macroscopic observable is accompanied by similar fluctuations due to thermal motion of macroscopic degrees of freedom in the system under study. There is, however, an ambiguity to the fluctuation-dissipation theorem in that it does not make no difference as to whether the fluctuations occur spontaneously from equilibrium or whether they are the result of an imposed constraint. In other words, it is assumed that near-equilibrium systems are insensitive to the way in which fluctuations occur. In this article, we examine the existence of a fluctuation-dissipation theorem in nonequilibrium systems driven by external forces.

We preface our remark by clearly stating the limitation of our treatment. The limitation is that the present theory strongly hinges on our possibility to distinguish thermodynamical forces from macroscopic currents in the nonequilibrium stationary states which are arbitrarily far from equilibrium. This is to say that we are developing nonequilibrium statistical mechanics in the spirit of Onsager.[2)] Our main result is that a fluctuation-dissipation theorem is established, as long as the response to external perturbations is considered in terms of the generalized response functions.

§ 2. Fluctuation-Dissipation Theorem for Systems not far from Equilibrium

As is well-known, the fluctuation-dissipation (FD) theorem provides us with a profound basis of experimental verification that macroscopic motions are in fact related to the thermal motion of particles consisting macroscopic systems. In this sense, this theorem is one of the most fundamental cornerstones for nonequilibrium statistical mechanics.

According to Nyquist's theorem[1)], the thermal fluctuations in voltage (a generalized force) are related, not to the standard thermodynamic parameters of linear electrical system, but to the electric resistance. Therefore, Nyquist's theorem is of a unique form correlating a property of a system in equilibrium with a parameter which characterizes an irreversible process (i.e., the electrical resistance). Generalizations have been made by many authors.[2-5] The generalized theorem establishes a relation between the impedance in a general linear dissipative system and the fluctuations of appropriate generalized forces. Nyquist's theorem thus obtained the name fluctuation-dissipation (FD) theorem.

It should be pointed out that the fluctuation-dissipation theorem is proved for Hamiltonian systems, which have no dissipation at all. This is due to the fact that a systematic treatment is possible only for Hamiltonian systems. On the other hand, the Kubo theory[5], a large part of which can be carried over into non-Hamiltonian dynamics, tacitly assumes that response currents can be replaced by phenomenological currents. It is in this stage of the replacement that phenomenological coefficients are accordingly expressed in terms of equilibrium correlation functions. Whether this is true or not depends upon the structure of the system under study.

As is well-known the fluctuation-dissipation theorem is the statement of the equivalence between the correlation function and the response function, since we represent thermal fluctuation by the correlation function. It is essentially reflects the fact that the quantum mechanical dynamics of a system is determined by the Hamiltonian, while the equilibrium density matrix is specified by the Hamiltonian. The fact is used to generate a series of fluctuation-dissipation relations.[6]

In order to see whether such a fact provide for a new perspective of the fluctuation-dissipation theorem, one must have a formalism in which the realization of the above mentioned equivalence is clearly brought to the foreground. To do this, let us introduce the quantity

$$F^{(eq)}{}_{BA}(x;t) = \mathrm{Tr}\ \rho_c{}^{1-x}A\rho_c{}^{x}B(t), \qquad (|x| < 1), \qquad (1)$$

where

$$\rho_c = K \exp(-\beta H), \tag{2}$$

and

$$B(t) = \exp(iHt)B\exp(-iHt). \tag{3}$$

Here, in (2), K is a normalization constant so that $Tr\rho_c=1$ and $\beta=(kT)^{-1}$, k being Boltzmann's constant.

Since the trace operation is invariant under the permutation of operators, we get from the definition (2)

$$F^{(eq)}{}_{BA}(1-x;t) = Tr\rho_c{}^{1-x}B(t)\rho_c{}^xA = F^{(eq)}(x;t). \tag{4}$$

Equation (4) is a formula which is equivalent to the so-called KMS condition.[7] It is customary to use the KMS condition as the definition of an equilibrium state. It is also known that with suitably short-range forces the KMS and thermodynamic stability conditions are equivalent.

It is fundamental to observe that in terms of the function $F^{(eq)}{}_{BA}(x;t)$ the three fundamental quantities of nonequilibrium statistical mechanics are written in the following forms:

(1) The canonical correlation

$$(A,B(t)) \equiv Tr\int_0^\beta d\lambda\ \rho_c e^{\lambda H} A\ e^{-\lambda H} B(t)/\beta$$
$$= \int_0^1 dx\ F^{(eq)}(x;t). \tag{5}$$

(2) The symmetrized correlation function

$$C^{(eq)}(t) \equiv (1/2)Tr\rho_c\{ AB(t) + B(t)A \}$$
$$= (1/2)\{ F^{(eq)}{}_{BA}(0;t) + F^{(eq)}{}_{AB}(0;t) \}$$
$$= (1/2)\{ F^{(eq)}{}_{BA}(0;t) + F^{(eq)}{}_{BA}(1;t) \}. \tag{6}$$

(3) The response function

$$\Phi_{BA}(t) \equiv (1/i)\mathrm{Tr}\rho_c[\, A,B(t)\,]$$

$$= (1/i)\{\, F^{(eq)}{}_{BA}(0;t) - F^{(eq)}{}_{BA}(1;t)\,\}. \qquad (7)$$

We represent thermal fluctuation by the canonical correlation or by the symmetrized correlation function.

It will be useful to introduce the translation operator **p**, which is defined by

$$p \equiv -i\partial/\partial x. \qquad (8)$$

Then, it is easy to verify that

$$F^{(eq)}{}_{BA}(x+y;t) = \exp(iyp)F^{(eq)}{}_{BA}(x;t) \qquad (9)$$

for $|x+y| \leqq 1$, and $|x| \leqq 1$.

By making use of eq.(9), the symmetrized correlation function can be written in the form

$$C^{(eq)}{}_{BA}(t) = (1/2)(\, 1 + \exp(ip)\,)F^{(eq)}(x;t)|_{x=0}. \qquad (10)$$

Similarly, for the response function we have

$$\Phi_{BA}(t) = (1/i)(\, 1 - \exp(ip)\,)F^{(eq)}{}_{BA}(x;t)|_{x=0}. \qquad (11)$$

In consequence, we see that it is the function $F^{(eq)}{}_{BA}(x;t)$ in terms of which each of the tree fundamental quantities of non-equilibrium statistical mechanics can be expressed. The function $F^{(eq)}{}_{BA}(x;t)$ bears all the informations needed to know these functions.

This is the implication of the fluctuation-dissipation theorem potential to generalize it beyond the near equilibrium cases. A little thought shows that, in the fluctuation-dissipation theorem, the Hamiltonian H of the system does play a double role:

It generates dynamics out from equilibrium and at the same time it determines which ensemble has to be used.

§ 3. Fluctuation-Dissipation Theorem for Nonequilibrium Stationary States

Many years ago, Bernard and Callen[9] provided formulas for second-, third-, and higher-order correlation moments in terms of the response of extensive quantities to static external forces. They showed that a knowledge of the response to a static force provides a knowledge of all moments written in terms of an equilibrium ensemble. In their theory, the usual fluctuation-dissipation theorem is expressed as the relationship between the linear response and the equilibrium second-moment. They found the triplet of relationships which exists among the second-order response, the first-order term in the driven second-moment, and the third-moment of the equilibrium fluctuations. Such a triplet can be thought of as a generalized fluctuation-dissipation theorem.

The work of Bernard and Callen is not particularly helpful in studying nonequilibrium fluctuations, since quantum mechanics furnishes no unique a priori prescription for symmetrizing a product of three (or more) operators. It is important to note that the fluctuation-dissipation theorem establishes a power balance between the rate at which energy is observed by the system and the rate at which energy is dissipated in the system. Therefore, the fluctuation-dissipation theorem is no longer expected to hold beyond the linear approximation, if the irreversible process happens to be nonlinear, since the process might not be Markovian. The system should be assumed to be unable to store energy.

Intuitively, we may say that once established the power balance there exists a fluctuation-dissipation theorem regardless of whether fluctuations are occurring from an equilibrium or a nonequilibrium stationary sta0te. Indeed, for linear processes it was found that the regression of fluctuations to a nonequilibrium stationary state is identified to the regression of fluctuations to an equilibrium state.[10)]

In order to establish a fluctuation-dissipation theorem for nonequilibrium states, we must first make it clear what kind of irreversible processes we are formulating. The description of a system in thermal equilibrium is, in principle, quite simple. For fixed values of controllable constants of motion there is only one state of equilibrium. Just as the equilibrium situation represents the time-invariant state of a closed system, which can exchange energy with its surroundings, a stationary state characterizes the time-invariant state of an open system which exchanges energy and matter with other systems. The latter situation is, in a sense, the simplest type of irreversible process since, while there are currents, they are constant in time.

Then, the statistical mechanical treatment of nonequilibrium stationary states can be implemented by assuming that the currents in the system can be expressed as

$$J_i = \mathrm{Tr}\, D[\, iH, A_i\,], \qquad (i=1,2,...,f). \tag{12}$$

where A_i denote the corresponding operators and D a nonequilibrium density matrix. Here, by either measurement or design we must determine the density matrix D. Such determination constitutes data which must be incorporated into the density matrix D. In appendix, we will give an example for such density matrix devised in the spirit of the linear response theory.

Let us now study fluctuations around a nonequilibrium stationary state described by the density matrix D. This study is limited to normal situations. Fluctuations in the neighborhood of an unstable state are not considered here. Nakano[11)] has shown that for such normal fluctuations about nonequilibrium state far from equilibrium both Onsager's and Prigogine's types of variation principle can be applied. The variation principles can be approached from a unified point of view of thermodynamical theory of stochastic processes which uses the joint-probability concept. Therefore, these variation principles are a very general and transparent formulation of the second law of thermodynamics.

It is plausible to assert that the statistical properties of nonequilibrium fluctuations can be described by a symmetrized correlation function of the form

$$C_{BA}(t) = (1/2)\mathrm{Tr}\, D\{\ AB(t) + B(t)A\ \}. \tag{13}$$

Here, B(t) is a Heisenberg operator:

$$B(t) = U(t,-\infty)BU^{*}(t,-\infty), \tag{14}$$

where $U(t,-\infty)$ is a solution of the equation of motion

$$(\partial/\partial t)U(t,-\infty) = -i[\ H + V(t)\ ]U(t,-\infty) \tag{15}$$

with a time-dependent perturbation V(t). We assume that

$$\lim_{t\to-\infty} V(t) = 0, \qquad \lim_{t\to-\infty} U(t,-\infty) = 1. \tag{16}$$

The recipe given in the previous section can be adopted to establish a fluctuation-dissipation theorem for nonequilibrium stationary states. Let us introduce the quantity

$$F_{BA}(x;t) \equiv \mathrm{Tr}\ D^{1-x}AD^{x}B(t). \tag{17}$$

This function bears the same properties as the function $F^{(eq)}{}_{BA}(x,t)$ does. For instance,

$$F_{BA}(1-x;t) = F_{AB}(x;t)\ , \tag{18}$$

$$F_{BA}(x+y;t) = \exp(iyp)F_{BA}(x;t). \tag{19}$$

Now let us introduce the (generalized) response function

$$\Phi_{BA}(t) \equiv (1/i)\mathrm{Tr}\, D[\, A, B(t)\,]. \qquad (20)$$

In terms of the new function $F_{BA}(x;t)$, we can write the two fundamental quantities as

$$C_{BA}(t) = (1/2)\{\, 1 + \exp(ip)\, \}F_{BA}(x;t)|_{x=0}, \qquad (21)$$

$$\Phi_{BA}(t) = (1/i)\{\, 1 - \exp(ip)\, \}F_{BA}(x;t)|_{x=0}. \qquad (22)$$

Equations (21) and (22) constitutes the generalized fluctuation-dissipation theorem for nonequilibrium stationary states who have well-defined phenomenological currents and their conjugate forces.

Remark: In the previous paper,[12] the present author has established that a generalized response function defines the so-called generalized response which is defined as a derivative of the response current with respect to the applied field.

§ 4. Summary

We may summarize by describing the procedure for establishing a generalization of the fluctuation-dissipation theorem to nonequilibrium stationary situations. First, we must take it for granted that it is possible to distinguish phenomenological currents from thermodynamic forces in the (open) system under study. This might be difficult to do for some systems far from equilibrium. Let D be a nonequilibrium density matrix. Then, our assumption tells us that stationary currents must be defined by $J_i = \mathrm{Tr}\, D[\, iH, A_i\,]$ ($\neq 0$). The thermodynamic forces are combined with the boundary conditions imposed upon the system at its boundaries. The currents are the given functions of the forces.

The fluctuations in the nonequilibrium stationary state, which is described by the well-defined density matrix D, are related to the extra dissipation beyond the spontaneous, constant dissipation brought about by the external perturbation. We have postulated that the fluctuations are defined in terms of the symmetrized correlation function like (13). The key quantity in our procedure is the function $F_{BA}(x;t)$. Then, we have proven the generalized fluctuation-dissipation theorem which relates the extra dissipation to the generalized response.[13] The generalized response is defined as a derivative of response current with respect to the strength of the external field. This is an interesting difference between equilibrium states and nonequilibrium stationary states who have well-defined currents and forces.

Appendix

Let $\rho(t)$ be the density matrix giving the time evolution in an external field $f(t)$. Then, the Liouville-von Neumann equation reads

$$(\partial/\partial t)\rho(t) + i[H - Bf(t), \rho(t)] = 0. \tag{A.1}$$

After Nakano,[14] we shall consider two situations:

(1)The time dependence of the external field is

$$f(t) = f\exp(\varepsilon t), \qquad \text{for } t < 0, \tag{A.2}$$

and the density matrix is required to satisfy the condition

$$\lim_{t\to-\infty} \rho(t) = \rho_c. \tag{A.3}$$

(2)

$$f(t) = f\exp(-\varepsilon t), \qquad \text{for } t > 0, \tag{A.4}$$

and

$$\lim_{t\to+\infty} \rho(t) = \rho_c. \tag{A.5}$$

Here, f is a constant field and ε an infinitesimal positive number.

It is easy to get the solution

$$\rho_+(t) = U(t,-\infty)\rho_c U^*(t,-\infty), \quad \text{for } t < 0, \tag{A.6}$$

and

$$\rho_-(t) = U(t,\infty)\rho_c U^*(t,\infty), \quad \text{for } t > 0. \tag{A.7}$$

Here, $U(t,s)$ is given by (15). Accordingly, we obtain the density matrix for the nonequilibrium density matrix in the constant field f:

$$D = \rho_-(t=0) = \rho_+(t=0). \tag{A.8}$$

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