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Nonlinear Transport and Dynamics of Fluctuations

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The time evolution of the macroscopic variables of a system initially in a state far from thermal equilibrium is studied from a statistical mechanical point of view. Exact nonlinear transport equations for the mean values and linear nonstationary Langevin equations for the fluctuations around the mean path are derived. Connections between the dynamics of fluctuations and the transport equations are discussed. The Langevin random forces depend on the macroscopic state and they are related to the transport kernels by a fluctuation-dissipation formula.

KEY WORDS: Macrovariables; relaxation and fluctuation; nonlinear transport equation; generalized Langevin equation; projection operator technique; fluctuation-dissipation theorem.

1. INTRODUCTION

Macroscopic systems composed of a great number of identical constituents exhibit on a macroscopic level a rather simple behavior described by equations of motion for a few macrovariables. The statistical mechanical theory relates this macroscopic dynamics with the underlying microscopic process. In spite of its complexity in detail the microscopic process has simple formal properties: it is a special Markovian process which is completely determined by the Hamiltonian H and the initial density matrix $\rho(t_0)$. These formal properties of the microscopic process lead to a definite structure of the macroscopic dynamics. In the present paper we examine this connection for closed systems which are initially in a state of *constrained* equilibrium arbitrarily far from thermal equilibrium.

The consideration of a special class of initial states is a necessary restriction inherent in every statistical mechanical theory of macroscopic

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dynamics. The macroscopic laws describe in general an irreversible process and therefore they cannot have the same form for *every* initial state $\rho(t_0)$. We are mainly interested in initial states that are experimentally attained in a reproducible preparation. The most important class of such states are the states of constrained equilibrium.

The time evolution of the macroscopic variables of a system consists generally of two parts: the organized motion and the disorganized motion. The organized motion describes a reversible "ideal" subdynamics of the macrovariables in which the time rates of change of the variables are completely determined by the macroscopic state at the considered instant of time. The disorganized motion reflects the influence of the large number of microscopic variables and can again be decomposed into two parts: the systematic irreversible part and the random part. The first part is determined by the macroscopic states at former times. The past history affects the time rates of change of the macrovariables at the considered instant of time by a retarded interaction of the macrovariables established by intermediate microscopic excitations. The systematic part leads to the damping terms in the macroscopic equations. The random part drives the fluctuations of the macrovariables and thus maintains their irregular motion.

For systems in the linear regime near thermal equilibrium this decomposition of the macroscopic motion has been carried out by Mori [(1)] using projection operator techniques. Mori's projection operator extracts a linear term from the time rates of change of the macrovariables. This linear term coincides with the organized motion part in the vicinity of thermal equilibrium. The evolution law of systems far from equilibrium is generally nonlinear. In a previous work[(2)] we have proposed a method to derive exact nonlinear equations of motion for the macrovariables. This approach will be used to extend Mori's theory to the region far from equilibrium.

The systematic and random parts of the disorganized motion are not independent, but they are related by the second fluctuation-dissipation theorem.[(1,3)] This internal relationship is of a very general nature, as both the systematic irreversible part and the random part come from the same origin.

As long as a system is in the linear regime near thermal equilibrium the random part of the time rate of change of a macrovariable is independent of the macroscopic state. For such systems the second fluctuation-dissipation theorem has been derived from a unified statistical mechanical point of view by Mori.[(1)] Systems far from equilibrium are driven by random forces that depend on the macroscopic state. We shall establish in this context a generalized form of the second fluctuation-dissipation theorem.

The present work has features in common with several other works. An early attempt to develop a general foundation of a statistical mechanics of irreversible processes was made by Green.[(4)] By assuming a stationary

Markov process of the macrovariables, Green derived a Fokker–Planck equation for the macroscopic joint probability and established general expressions for the transport coefficients. Zwanzig[5] introduced the projection operator technique that leads to formally exact equations of motion and enables systematic perturbative approaches. For classical systems that are initially described by a microcanonical distribution, Zwanzig[6,7] derived an exact generalized master equation for the macroscopic single-event probability. Equations of motion for the joint and conditional probabilities that describe the time evolution of correlation functions have been obtained recently.[8]

From Zwanzig's master equation closed transport equations for the mean values of the macrovariables can be derived by making several assumptions.[6,7] On the other hand, it seems to be more straightforward to derive the transport equations directly from the microscopic dynamics. By extending the projection operator technique, Robertson[9] put forward closed equations of motion for the mean values of the macrovariables. More recently, this approach has been used by Kawasaki and Gunton[10] to determine nonlinear transport coefficients in fluids. However, this theory does not treat the time evolution of fluctuations.

Both relaxation and fluctuations of the macrovariables have been studied by Mori[1] using projection operator techniques in the space of observables. But he uses a high-temperature approximation to his initial density matrix, which restricts the theory to the linear regime near thermal equilibrium. The aim of the present work is to get rid of this restriction and to develop a theory that leads to closed transport equations in the nonlinear regime and determines the time evolution of fluctuations around the mean path.

The paper is organized as follows. We work in the framework of quantum mechanics, as the corresponding classical argumentation is obvious. The macrovariables are assumed to be represented by Hermitean Hilbert space operators. The system is closed and the dynamics is governed by a time-independent Hamiltonian. Both the generalizations to non-Hermitean macrovariables and to time-dependent Hamiltonians are straightforward, but they would complicate the notation unnecessarily.

In the next section we consider the organized motion of the macrovariables. The disorganized motion is decomposed into a systematic and a random part in Section 3. There, we also derive exact transport equations for the mean values and establish exact Langevin equations for the fluctuations around the mean values. The correlations of the random forces are related to the disorganized motion terms of the transport equations. Some features of the results obtained are summarized in Section 4. A short summary of the main results has been given in Ref. 11.

2. ORGANIZED MOTION

2.1. Generalized Canonical Density Matrix

Let $\{A_j\}$ be the set of macrovariables of a system. The mean values of these variables at time t are denoted by $\{a_j(t)\}$. These mean values specify the macroscopic state of the system. The full microscopic state is specified by the density matrix $\rho(t)$. Suppose we only know the macroscopic state. Can we say anything about the microscopic state? It is well known that we may use information theory to determine the "best" microscopic state corresponding to the given information about the system. This state is the one having maximum Gibbs entropy consistent with the given information and it has the form of a generalized canonical density matrix

$$\bar{\rho}(t) = Z^{-1}(t)e^{-\lambda_j(t)A_j} \tag{1}$$

(summation over repeated indices is implied) where the parameters $\{\lambda_j(t)\}$ and the normalization factor $Z(t)$ are determined by

$$\mathrm{tr}\ \bar{\rho}(t) = \mathrm{tr}\ \rho(t) = 1, \qquad \mathrm{tr}\ A_j\bar{\rho}(t) = \mathrm{tr}\ A_j\rho(t) = a_j(t) \tag{2}$$

These equations explain the parameters $\{\lambda_j(t)\}$ as functions of the mean values $\{a_j(t)\}$, and vice versa. It is clear that the generalized canonical density matrix $\bar{\rho}(t)$ is just a part of the precise density matrix $\rho(t)$. It is the part that is already determined by the macroscopic state. By definition, the generalized canonical density matrix yields correct mean values of the macrovariables. On the other hand, it is completely determined by these mean values, so that the time dependence of the generalized canonical density matrix arises only through $\{a_j(t)\}$ or $\{\lambda_j(t)\}$, respectively. We write

$$\bar{\rho}(t) \equiv \bar{\rho}[a_j(t)] \equiv \bar{\rho}[\lambda_j(t)] \tag{3}$$

2.2. Organized Motion of Mean Values

The dynamics of the system is governed by the Liouville operator defined by

$$\mathbb{L}X = [H, X] \tag{4}$$

where H denotes the Hamiltonian. If the microscopic state at time t is described by the density matrix $\rho(t)$, the time rate of change of a mean value $a_j(t)$ reads

$$\dot{a}_j(t) = \mathrm{tr}\ \rho(t)\dot{A}_j \tag{5}$$

where

$$\dot{A}_j = i\mathbb{L}A_j \tag{6}$$

The organized motion part of the time rate of change of a macrovariable is already determined by the macroscopic state at the considered instant of time and is given by

$$\bar{\dot{a}}_j(t) = \operatorname{tr} \bar{\rho}(t)\dot{A}_j \equiv v_j(t) \tag{7}$$

The *organized drift* $v_j(t)$ is not an explicit function of time but depends on t only through $\{a_j(t)\}$ or $\{\lambda_j(t)\}$, respectively:

$$v_j(t) \equiv v_j[a_k(t)] \equiv v_j[\lambda_k(t)] \tag{8}$$

The organized drift is reversible. To make this clear, we define the entropy of the system by

$$S(t) = -\operatorname{tr} \bar{\rho}(t) \ln \bar{\rho}(t) = \ln Z(t) + \lambda_j(t) a_j(t) \tag{9}$$

It is well known that there is not a unique way to extend the equilibrium definition of the entropy to nonequilibrium states. Clearly, Eq. (9) defines the entropy as a *macroscopic* quantity and it ensures that familiar thermodynamic relations like

$$\lambda_j(t) = \partial S(t)/\partial a_j(t) \tag{10}$$

are still valid in nonequilibrium. These relations are easily shown if we use

$$Z(t) = \operatorname{tr} e^{-\lambda_j(t)A_j}; \qquad \partial[\ln Z(t)]/\partial\lambda_j(t) = -a_j(t) \tag{11}$$

and observe that the parameters $\{\lambda_j(t)\}$ are functions of the mean values $\{a_j(t)\}$. The formal similarity of $S(t)$ to the equilibrium entropy has led others[9,12–14] to this definition of the nonequilibrium entropy.

Using (10), we find for the time rate of change of the entropy

$$\dot{S}(t) = \lambda_j(t)\dot{a}_j(t) \tag{12}$$

This bilinear form shows that the parameters $\{\lambda_j(t)\}$ are the forces conjugate to the flows $\{\dot{a}_j(t)\}$.

With the aid of Kubo's identity[15]

$$[Y, e^X] = \int_0^1 d\alpha\, e^{\alpha X}[Y, X]e^{(1-\alpha)X} \tag{13}$$

and the definition (1) of $\bar{\rho}(t)$ one readily establishes that

$$-i\mathbb{L}\bar{\rho}(t) = \lambda_j(t) \int_0^1 d\alpha\, e^{-\alpha\lambda_k(t)A_k}\dot{A}_j e^{\alpha\lambda_k(t)A_k}\bar{\rho}(t) \tag{14}$$

The trace of this expression vanishes, and we obtain

$$\lambda_j(t)v_j(t) = 0 \tag{15}$$

where we used (7). As a consequence of (12) and (15) we find that the organized motion does not contribute to the time rate of change of the entropy. Consequently, the organized drift is reversible.

2.3. Organized Motion of Fluctuations

We shall now consider the organized motion of the fluctuations of the macrovariables. The fluctuations are defined by

$$\delta A_j(t) = A_j(t) - a_j(t) \tag{16}$$

where

$$A_j(t) = e^{i\mathbb{L}t} A_j \tag{17}$$

is the macrovariable in the Heisenberg representation. The time rate of change of a fluctuation reads

$$\delta \dot{A}_j(t) = i\mathbb{L} A_j(t) - \dot{a}_j(t) \tag{18}$$

To determine the organized motion part $\delta\overline{\dot{A}}_j(t)$ of this time rate of change, we require that the organized motion describes a closed subdynamics of the macrovariables in which the system propagates along a succession of generalized canonical density matrices. Let us assume that the system is in a state described by a generalized canonical density matrix at time t. Then the precise time rate of change of the density matrix is given by Eq. (14). In terms of the time rates of change of the mean values and the fluctuations at the considered instant of time, this may be written as

$$\begin{aligned} -i\mathbb{L}\bar{\rho}(t) &= \lambda_j(t)\dot{a}_j(t)\bar{\rho}(t) \\ &\quad + \lambda_j(t)\int_0^1 d\alpha\, e^{-\alpha\lambda_k(t)A_k}[e^{-i\mathbb{L}t}\delta\dot{A}_j(t)]e^{\alpha\lambda_k(t)A_k}\bar{\rho}(t) \end{aligned} \tag{19}$$

This precise time evolution will lead to a deviation from the generalized canonical form as the evolution law of the generalized canonical density matrix is given by

$$\frac{\partial}{\partial t}\bar{\rho}(t) = \frac{\partial\bar{\rho}[a_k(t)]}{\partial a_j(t)}\dot{a}_j(t) \tag{20}$$

so that in general

$$\frac{\partial}{\partial t}\bar{\rho}(t) \neq -i\mathbb{L}\bar{\rho}(t) \tag{21}$$

Using (1) and (11), we find

$$\frac{\partial \bar{\rho}[\lambda_k(t)]}{\partial \lambda_j(t)} = -\int_0^1 d\alpha\, e^{-\alpha\lambda_k(t)A_k}[A_j - a_j(t)]e^{\alpha\lambda_k(t)A_k}\bar{\rho}(t) \tag{22}$$

and Eq. (20) may be written as

$$\frac{\partial}{\partial t}\bar{\rho}(t) = -\int_0^1 d\alpha\, e^{-\alpha\lambda_k(t)A_k}[A_l - a_l(t)]\frac{\partial \lambda_l(t)}{\partial a_j(t)}\dot{a}_j(t)e^{\alpha\lambda_k(t)A_k}\bar{\rho}(t) \tag{23}$$

Since the organized motion will not lead to deviations from the generalized canonical form of the density matrix, the right-hand sides of (19) and (23) must be identical if the precise time rates of change $\dot{a}_j(t)$ and $\delta\dot{A}_j(t)$ are replaced by their organized motion parts $\bar{\dot{a}}_j(t) = v_j(t)$, $\delta\bar{\dot{A}}_j(t)$. This requirement leads to

$$\lambda_j(t)\delta\bar{\dot{A}}_j(t) = -\delta A_k(t)\frac{\partial \lambda_k(t)}{\partial a_j(t)}v_j(t) \tag{24}$$

We have used (15) and (16). With (10) is easy to show that

$$\partial\lambda_j(t)/\partial a_k(t) = \partial\lambda_k(t)/\partial a_j(t) \tag{25}$$

and from (15) we find

$$\frac{\partial \lambda_j(t)}{\partial a_k(t)}v_j(t) = -\lambda_j(t)\frac{\partial v_j(t)}{\partial a_k(t)} \tag{26}$$

so that (24) may be written as

$$\lambda_j(t)\delta\bar{\dot{A}}_j(t) = \lambda_j(t)\frac{\partial v_j(t)}{\partial a_k(t)}\delta A_k(t) \tag{27}$$

This equation determines only a certain linear combination of the organized motion parts of the time rates of change of the fluctuations. However, from (7) we get

$$\frac{\partial v_j(t)}{\partial a_k(t)} = \mathrm{tr}\left[\frac{\partial \bar{\rho}(t)}{\partial a_k(t)}e^{-i\mathbb{L}t}\delta\dot{A}_j(t)\right] \tag{28}$$

and we should certainly require that $\delta\bar{\dot{A}}_j(t)$ is a part of the precise time rate of change $\delta\dot{A}_j(t)$ of the *same* variable. Hence, we obtain

$$\delta\bar{\dot{A}}_j(t) = \Omega_{jk}(t)\delta A_k(t) \tag{29}$$

where

$$\Omega_{jk}(t) \equiv \Omega_{jk}[a_l(t)] = \frac{\partial v_j(t)}{\partial a_k(t)} \tag{30}$$

is an effective frequency that depends on the macroscopic state.

In this way the organized motion has a self-reproducing property. In fact, if we insert $\delta\bar{\dot{A}}_j(t)$ instead of $\delta\dot{A}_j(t)$ in the right-hand side of Eq. (28), we again obtain the same frequencies $\Omega_{jk}(t)$. This is easily seen by using the relations

$$\mathrm{tr}\,\frac{\partial\bar{\rho}(t)}{\partial a_k(t)} = 0, \qquad \mathrm{tr}\,\frac{\partial\bar{\rho}(t)}{\partial a_k(t)}\,A_j = \delta_{kj} \tag{31}$$

which follows from (2).

2.4. Generalized Canonical Correlations

For the following it is convenient to introduce a "generalized canonical correlation function" of time-dependent variables $X(t)$ and $Y(s)$ by $(t \geqslant s)$

$$\begin{aligned}(X(t),\ Y(s)) &= (Y(s),\ X(t))^* \\ &= \int_0^1 d\alpha\ \mathrm{tr}\{\bar{\rho}(s)[e^{-i\mathbb{L}s}X(t)]e^{-\alpha\lambda_j(s)A_j}[e^{-i\mathbb{L}s}\,Y^+(s)]e^{\alpha\lambda_j(s)A_j}\}\end{aligned} \tag{32}$$

This correlation function is particularly simple for dynamical variables in the Heisenberg representation

$$X(t) = e^{i\mathbb{L}t}X \tag{33}$$

In this case (32) may be written as

$$(X(t),\ Y(s)) = \int_0^1 d\alpha\ \mathrm{tr}\{\bar{\rho}(s)X(t-s)e^{-\alpha\lambda_j(s)A_j}\,Y^+e^{\alpha\lambda_j(s)A_j}\} \tag{34}$$

Equation (34) makes it obvious that the generalized canonical correlation function reduces to Kubo's correlation function [15] in thermal equilibrium. For classical systems that are at time s in a state described by a generalized canonical distribution function, (34) coincides with the ordinary definition of the correlation function. Further, it can easily be shown that the generalized canonical correlation function at equal times $(X(t),\ Y(t))$ has the usual properties of a scalar product in the space of dynamical variables. The time dependence of $(X(t),\ Y(t))$ arises only through $\{a_j(t)\}$, and it can in principle be completely evaluated if the mean motion is known. This clearly shows that (34) generally has little in common with the ordinary correlation function of dynamical variables. The generalized canonical correlation function should be looked upon as an appropriate arithmetic quantity. Its usefulness appears if we notice that (14), (22), and (32) lead to $(t \geqslant s)$

$$\mathrm{tr}[\bar{\rho}(s)i\mathbb{L}e^{-i\mathbb{L}s}X(t)] = (i\mathbb{L}X(t),\ I(s)) = (X(t),\ \dot{A}_k(s))\lambda_k(s) \tag{35}$$

and

$$\operatorname{tr}\left(\frac{\partial\bar{\rho}(s)}{\partial\lambda_k(s)}\, e^{-i\mathbb{L}s}X(t)\right) = -(X(t), \delta A_k(s)) \tag{36}$$

where I denotes the identity operator. Equations (35) and (36) can be used to derive

$$v_j(t) = (A_j(t), \dot{A}_k(t))\lambda_k(t) \tag{37}$$

$$\partial v_j(t)/\partial\lambda_k(t) = -(\dot{A}_j(t), \delta A_k(t)) \tag{38}$$

$$\partial a_j(t)/\partial\lambda_k(t) = -(\delta A_j(t), \delta A_k(t)) \tag{39}$$

Equation (37) makes some of the dependence of the organized drift on the conjugate forces more explicit. In particular, we immediately get the linear approximation if the generalized canonical correlation functions are evaluated with the equilibrium density matrix. From (38) and (39) we find

$$\Omega_{jk}(t) = \frac{\partial v_j(t)}{\partial a_k(t)} = (\delta A_k(t), \delta A_l(t))^{-1}(\dot{A}_j(t), \delta A_l(t)) \tag{40}$$

This equation gives us the connection of $\Omega_{jk}(t)$ with Mori's collective frequencies[1] which are the equilibrium values of $\Omega_{jk}(t)$.

2.5. Projection Operator

The organized motion can be extracted from the microscopic dynamics by means of a time-dependent projection operator. From (7) and (29) we get

$$\begin{aligned}\overline{\dot{A}_j}(t) &= \bar{\dot{a}}_j(t) + \delta\overline{\dot{A}_j}(t)\\ &= \operatorname{tr}\bar{\rho}(t)\dot{A}_j + \delta A_k(t)\operatorname{tr}\frac{\partial\bar{\rho}(t)}{\partial a_k(t)}\dot{A}_j\\ &= e^{i\mathbb{L}t}\,\mathbb{P}(t)\dot{A}_j\end{aligned} \tag{41}$$

where $\mathbb{P}(t)$ is defined by

$$\mathbb{P}(t)X = \operatorname{tr}\bar{\rho}(t)X + [A_j - a_j(t)]\operatorname{tr}\frac{\partial\bar{\rho}(t)}{\partial a_j(t)}X \tag{42}$$

The projection operator $\mathbb{P}(t)$ is not an explicit function of time, but its time dependence arises only implicitly through the mean values $\{a_j(t)\}$. Projection operators of this type have been introduced in a previous work[2] in a more general context. With the aid of (32), (36), and (39) the projection operator $\mathbb{P}(t)$ can be written as

$$\mathbb{P}(t)X = \operatorname{tr}\bar{\rho}(t)X + [A_j - a_j(t)](\delta A_j(t), \delta A_k(t))^{-1}(e^{i\mathbb{L}t}X, \delta A_k(t)) \tag{43}$$

This form clearly shows that $\mathbb{P}(t)$ is a natural generalization of Mori's time-independent projection operator.[1]

The following properties of $\mathbb{P}(t)$ are easily established with the use of (31), (42), and (43):

$$\mathbb{P}(t)\mathbb{P}(t') = \mathbb{P}(t') \tag{44}$$

$$\mathbb{P}(t)(c_0 + c_jA_j) = c_0 + c_jA_j \tag{45}$$

$$\mathrm{tr}[\rho(t)\mathbb{P}(t)X] = \mathrm{tr}\, \bar{\rho}(t)X \tag{46}$$

$$(e^{i\mathbb{L}t}\mathbb{P}(t)X, \delta A_j(t)) = (e^{i\mathbb{L}t}X, \delta A_j(t)) \tag{47}$$

The first relation implies the projection operator property for $t = t'$. Equation (45) shows that $\mathbb{P}(t)$ projects out the macrovariables. $e^{i\mathbb{L}t}\mathbb{P}(t)X$ is the Heisenberg representation of the projected part of a dynamical variable X. According to (46), the expectation value of $e^{i\mathbb{L}t}\mathbb{P}(t)X$ is given by the generalized canonical expectation value of X. Finally, (47) shows that $e^{i\mathbb{L}t}\mathbb{P}(t)X$ and $X(t) = e^{i\mathbb{L}t}X$ have the same generalized canonical correlations with the fluctuations of the macrovariables at the same time.

For later use we also consider the time derivative of $\mathbb{P}(t)$. By differentiating (44) with respect to t and t', respectively, one easily establishes that

$$\dot{\mathbb{P}}(t) = \mathbb{P}(t)\dot{\mathbb{P}}(t)[\mathbb{1} - \mathbb{P}(t)] \tag{48}$$

An explicit expression for $\dot{\mathbb{P}}(t)$ follows from (42). We find

$$\dot{\mathbb{P}}(t)X = [A_j - a_j(t)]\dot{a}_k(t)\, \mathrm{tr}\, \frac{\partial^2 \bar{\rho}(t)}{\partial a_j(t)\, \partial a_k(t)}\, X \tag{49}$$

3. ORGANIZED AND DISORGANIZED MOTION

3.1. Memory Functions and Random Forces

The precise time rate of change of a macrovariable $A_j(t)$ splits up into

$$\dot{A}_j(t) = \overline{\dot{A}_j}(t) + \Gamma_j(t) \tag{50}$$

This decomposition defines the disorganized-motion part $\Gamma_j(t)$. By using (41) we see that

$$\Gamma_j(t) = e^{i\mathbb{L}t}[\mathbb{1} - \mathbb{P}(t)]\dot{A}_j \tag{51}$$

$\Gamma_j(t)$ may be looked upon as the total microscopic force acting on a macrovariable. It has the property

$$(\Gamma_j(t), M(t)) = 0 \tag{52}$$

for every macrovariable $M(t) = c_0I(t) + c_jA_j(t)$. This follows from (46), (47), and (51), and it expresses the fact that $\Gamma_j(t)$ gives no contribution to the organized motion of the macrovariables. We may say that the microscopic force $\Gamma_j(t)$ is not correlated with the macrovariables at the same instant of time (in the sense of generalized canonical correlations). However, $\Gamma_j(t)$ is correlated with the macrovariables at earlier times s. These correlations can be used to split off a systematic part of $\Gamma_j(t)$.

The appropriate quantities characterizing the influence of the macrovariables at time s on the time rate of change at time t are the *memory functions* $K_j(t, s)$ and $\phi_{jk}(t, s)$ defined implicitly by the decomposition

$$\Gamma_j(t) = \int_s^t du\, [K_j(t, u) + \phi_{jk}(t, u)\, \delta A_k(u)] + F_j(t, s) \tag{53}$$

where $F_j(t, s)$ is not correlated with the macrovariables at the earlier time s[3]

$$(F_j(t, s), I(s)) = \mathrm{tr}[\bar{\rho}(s) e^{-i\mathbb{L}s} F_j(t, s)] = 0 \tag{54}$$

$$(F_j(t, s), \delta A_k(s)) = 0 \tag{55}$$

It follows that the generalized canonical correlation of $\Gamma_j(t)$ with a macrovariable $M(s) = c_0 I(s) + c_j A_j(s)$ takes the form

$$(\Gamma_j(t), M(s)) = \int_s^t du\, [K_j(t, u)(I(u), M(s)) + \phi_{jl}(t, u)(\delta A_l(u), M(s))] \tag{56}$$

which makes explicit the effect of correlations between macrovariables. These long-lived correlations are not included in the memory functions.

Equation (53) can be viewed as a decomposition of the microscopic force $\Gamma_j(t)$ into a systematic and a random part. The first term on the right-hand side of (53) describes a systematic contribution of the history of the macrovariables in the time interval $s < u < t$ to the microscopic force $\Gamma_j(t)$. The remaining part is described by the *random force* $F_j(t, s)$.

The decomposition depends on time s. Up to that time the history is taken into account. The effect of the macrovariables at times prior to s on the time rate of change at time t is included in the random force $F_j(t, s)$. That is why we might consider (53) with s equal to the initial time of preparation $t_0 = 0$ as the genuine decomposition of $\Gamma_j(t)$ into a systematic and a random part. However, the more general decomposition with variable s will turn out to be very useful.

The decomposition (53) is uniquely determined by the requirements (54) and (55), which can be expressed as

$$\mathbb{P}(s) e^{-i\mathbb{L}s} F_j(t, s) = 0 \tag{57}$$

[3] Note that the $\{F_j(t, s)\}$ are not dynamical variables, so that the basic definition (32) of the generalized canonical correlation function has to be used. If the correlated variables depend on several times, we agree to average over the generalized canonical density matrix at the earliest time.

Here we have made use of (46) and (47). From (53) we get

$$\frac{\partial}{\partial s} F_j(t, s) = K_j(t, s) + \phi_{jk}(t, s)\, \delta A_k(s) \tag{58}$$

This can only be true if

$$\frac{\partial}{\partial s} F_j(t, s) = e^{i\mathbb{L}s}\mathbb{P}(s)e^{-i\mathbb{L}s} \frac{\partial}{\partial s} F_j(t, s) \tag{59}$$

By differentiating (57), we find with (48)

$$\mathbb{P}(s)e^{-i\mathbb{L}s} \frac{\partial}{\partial s} F_j(t, s) = \mathbb{P}(s)[i\mathbb{L} - \dot{\mathbb{P}}(s)]e^{-i\mathbb{L}s}F_j(t, s) \tag{60}$$

which combines with (59) to give

$$\frac{\partial}{\partial s} F_j(t, s) = e^{i\mathbb{L}s}\mathbb{P}(s)[i\mathbb{L} - \dot{\mathbb{P}}(s)]e^{-i\mathbb{L}s}F_j(t, s) \tag{61}$$

This differential equation for $F_j(t, s)$ has to be solved with the final condition

$$F_j(t, t) = \Gamma_j(t) = e^{i\mathbb{L}t}[\mathbb{1} - \mathbb{P}(t)]\dot{A}_j \tag{62}$$

The solution can easily be derived if we put

$$F_j(t, s) = e^{i\mathbb{L}s}[\mathbb{1} - \mathbb{P}(s)]Z_j(t, s) \tag{63}$$

This ansatz suggests itself, since $F_j(t, s)$ obeys (57). It turns out that $F_j(t, s)$ satisfies (61) and (62) if $Z_j(t, s)$ satisfies

$$\frac{\partial}{\partial s} Z_j(t, s) = -i\mathbb{L}[\mathbb{1} - \mathbb{P}(s)]Z_j(t, s) \tag{64}$$

with the final condition

$$Z_j(t, t) = \dot{A}_j \tag{65}$$

The result is

$$F_j(t, s) = e^{i\mathbb{L}s}[\mathbb{1} - \mathbb{P}(s)]\mathbb{G}(s, t)\dot{A}_j \tag{66}$$

where $\mathbb{G}(s, t)$ is the time-ordered exponential ($s \leqslant t$)

$$\mathbb{G}(s, t) = T_- \exp\left\{i\int_s^t du\, \mathbb{L}[\mathbb{1} - \mathbb{P}(u)]\right\} \tag{67}$$

in which operators are ordered from left to right as time increases. The propagator $\mathbb{G}(s, t)$ is an operator-valued functional of the mean path $\{a_j(u)\}$ in the time interval $s < u < t$, since $\mathbb{P}(u) = \mathbb{P}[a_j(u)]$. Consequently, the random force $F_j(t, s)$ depends on the macroscopic states at times prior to t.

If we insert (66) into (61) we find

$$\frac{\partial}{\partial s} F_j(t, s) = e^{i\mathbb{L}s}\mathbb{P}(s)[i\mathbb{L} - \dot{\mathbb{P}}(s)][\mathbb{1} - \mathbb{P}(s)]\mathbb{G}(s, t)\dot{A}_j \tag{68}$$

On the other hand, Eq. (58) expresses $(\partial/\partial s)F_j(t, s)$ in terms of the memory functions. With (42) and (49) we obtain from (58) and (68)

$$K_j(t, s) = \mathrm{tr}\{\bar{\rho}(s)i\mathbb{L}[\mathbb{1} - \mathbb{P}(s)]\mathbb{G}(s, t)\dot{A}_j\} \tag{69}$$

and

$$\begin{aligned}\phi_{jk}(t, s) = \mathrm{tr}&\left\{\frac{\partial\bar{\rho}(s)}{\partial a_k(s)}\, i\mathbb{L}[\mathbb{1} - \mathbb{P}(s)]\mathbb{G}(s, t)\dot{A}_j\right\} \\ &- \dot{a}_l(s)\,\mathrm{tr}\left[\frac{\partial^2\bar{\rho}(s)}{\partial a_k(s)\,\partial a_l(s)}\,\mathbb{G}(s, t)\dot{A}_j\right]\end{aligned} \tag{70}$$

Clearly, the memory functions are functionals of the mean path between the former time s and the present time t, and $\phi_{jk}(t, s)$ is in addition a function of $\{\dot{a}_j(s)\}$.

3.2. Transport Equations for the Mean Values

The time rate of change of a mean value $a_j(t)$ splits up into

$$\dot{a}_j(t) = v_j(t) + \gamma_j(t) \tag{71}$$

where $\gamma_j(t)$ is the disorganized motion part of the mean flow $\dot{a}_j(t)$. Since $v_j(t)$ is reversible, dissipation is included in the disorganized drift $\gamma_j(t)$. From Eq. (50) we find

$$\gamma_j(t) = \langle\Gamma_j(t)\rangle \tag{72}$$

where $\langle\cdots\rangle$ denotes the average over the initial ensemble $\rho(0)$. Hence, $\gamma_j(t)$ is equal to the mean microscopic force. With the use of (53), $\gamma_j(t)$ can be decomposed into

$$\gamma_j(t) = \int_s^t du\, K_j(t, u) + f_j(t, s) \tag{73}$$

where

$$f_j(t, s) = \langle F_j(t, s)\rangle \tag{74}$$

is the mean random force. From Eq. (66) we get more explicitly

$$f_j(t, s) = \mathrm{tr}[\delta\rho(s)\mathbb{G}(s, t)\dot{A}_j] \tag{75}$$

where

$$\delta\rho(s) = \rho(s) - \bar{\rho}(s)$$

denotes the deviation of the microscopic state at time s from the generalized canonical form.

We now assume the initial density matrix $\rho(0)$ is of the generalized canonical form

$$\rho(0) = \bar{\rho}(0) \tag{76}$$

In this case we have

$$f_j(t, 0) = \mathrm{tr}[\delta\rho(0)\mathbb{G}(0, t)\dot{A}_j] = 0 \tag{77}$$

For systems that are initially in a state of constrained equilibrium the assumption (76) is fulfilled. States of constrained equilibrium can be prepared by an application of external fields which couple to the macrovariables and maintain a definite nonequilibrium state. If these fields are switched off at time $t = 0$, a reproducible relaxation process takes place. Therefore, (76) will be satisfied for quite a few interesting processes.

We now specialize (73) to $s = 0$ and take (77) into account. By using (69), we obtain the disorganized drift $\gamma_j(t)$ as a functional of the part history of the mean values

$$\begin{aligned} \gamma_j(t) &= \gamma_j\{a_k(u), 0 \leqslant u \leqslant t\} \\ &= \int_0^t du\, \mathrm{tr}\{\bar{\rho}(u)i\mathbb{L}[\mathbb{1} - \mathbb{P}(u)]\mathbb{G}(u, t)\dot{A}_j\} \end{aligned} \tag{78}$$

As the conjugate forces $\{\lambda_j(t)\}$ are functions of the mean values $\{a_j(t)\}$, we just as well may interpret (78) as a functional of the past history of $\{\lambda_j(t)\}$.

The functional (78) has already been derived by Robertson[9] and more recently by Kawasaki and Gunton[10] with the aid of a generalized master equation for $\bar{\rho}(t)$. The present derivation within the generalized Langevin equation approach will enable us to examine the connection of the disorganized drift with the dynamics of fluctuations.

If we insert the explicit expressions (7) and (78) for the organized and disorganized drift into (71), we obtain a set of nonlinear integrodifferential equations that determine the mean path $\{a_j(t)\}$:

$$\begin{aligned} \dot{a}_j(t) &= v_j[a_k(t)] + \gamma_j\{a_k(u), 0 \leqslant u \leqslant t\} \\ &= \mathrm{tr}[\bar{\rho}(t)\dot{A}_j] + \int_0^t du\, \mathrm{tr}\{\bar{\rho}(u)i\mathbb{L}[\mathbb{1} - \mathbb{P}(u)]\mathbb{G}(u, t)\dot{A}_j\} \end{aligned} \tag{79}$$

The only assumption needed to derive these equations was the generalized canonical form of the initial ensemble.

3.3. Langevin Equations for the Fluctuations

Let us insert the decomposition (53) of the microscopic force into Eq. (50) and then subtract on both sides the average over the initial ensemble. This way we obtain a decomposition of the time rate of change of a fluctuation $\delta A_j(t)$ of the form

$$\delta \dot{A}_j(t) = \Omega_{jk}(t)\, \delta A_k(t) + \int_s^t du\, \phi_{jk}(t, u)\, \delta A_k(u) + \delta F_j(t, s) \tag{80}$$

where

$$\delta F_j(t, s) = F_j(t, s) - f_j(t, s) \tag{81}$$

is the fluctuation of the random force with the properties

$$\langle \delta F_j(t, s) \rangle = 0 \tag{82}$$

$$(\delta F_j(t, s), \delta A_k(s)) = 0 \tag{83}$$

Equation (80) is an exact Langevin equation for the fluctuations. The first term on the right-hand side is the organized motion part of $\delta \dot{A}_j(t)$. It is connected with the organized drift $v_j(t)$ by (30). The second term is a systematic disorganized motion part. The memory kernels $\phi_{jk}(t, u)$ are determined by the mean path. An explicit expression is given in (70). This part can be related to the disorganized drift $\gamma_j(t)$ in the following way:

We consider the time evolution of the mean values of the macrovariables starting with an initial ensemble of the form

$$\rho^1(0) = \bar{\rho}(0) + \frac{\partial \bar{\rho}(0)}{\partial a_k(0)} \Delta a_k(0) = \bar{\rho}(0) + \Delta \rho(0) \tag{84}$$

By specializing (83) to $s = 0$, we find with (36)

$$\operatorname{tr} \frac{\partial \bar{\rho}(0)}{\partial \lambda_k(0)}\, \delta F_j(t, 0) = 0 \tag{85}$$

and, consequently,

$$\operatorname{tr} \Delta \rho(0)\, \delta F_j(t, 0) = 0 \tag{86}$$

For sufficiently small $\{\Delta a_k(0)\}$ the ensemble $\rho^1(0)$ is of the generalized canonical form, and hence, both the mean values

$$a_j(t) = \operatorname{tr} \bar{\rho}(0) A_j(t) \tag{87}$$

and

$$a_j^1(t) = \operatorname{tr} \rho^1(0) A_j(t) = a_j(t) + \Delta a_j(t) \tag{88}$$

are solutions of Eq. (79). In the limit of infinitesimal $\{\Delta a_k(0)\}$ we find

$$\Delta \dot{a}_j(t) = \frac{\partial v_j(t)}{\partial a_k(t)} \Delta a_k(t) + \int_0^t du\, \frac{\delta \gamma_j(t)}{\delta a_k(u)} \Delta a_k(u) \tag{89}$$

where $\delta\gamma_j(t)/\delta a_k(u)$ is a functional derivative of the functional $\gamma_j\{a_k(u), 0 \leqslant u \leqslant t\}$.

On the other hand, we have

$$\Delta\dot{a}_j(t) = \operatorname{tr} \Delta\rho(0)\dot{A}_j(t) = \operatorname{tr} \Delta\rho(0)\, \delta\dot{A}_j(t) \tag{90}$$

where $\delta A_j(t)$ is the fluctuation around $a_j(t)$. With the use of (30) and (80), specialized to $s = 0$, we find

$$\Delta\dot{a}_j(t) = \frac{\partial v_j(t)}{\partial a_k(t)} \Delta a_k(t) + \int_0^t du\, \phi_{jk}(t, u)\, \Delta a_k(u) \tag{91}$$

where we have taken (86) into account. By comparing (89) and (91), we obtain

$$\phi_{jk}(t, u) = \delta\gamma_j(t)/\delta a_k(u) \tag{92}$$

This equation expresses the memory functions $\phi_{jk}(t, s)$ in terms of the disorganized drift.

Equation (92) can also be derived directly from (70) and (78).[2] In this case one has to express $\dot{a}_l(s)$ in Eq. (70) as a functional of the past history of $\{a_k(s)\}$ by (79). The present derivation does not use the molecular expressions and shows that (92) ensures the compatibility of the nonlinear macroscopic evolution law (79) with the linear evolution law for the microscopic state $\rho(t)$.

There is a further connection of the dynamics of fluctuations with the mean value equations (79). The disorganized drift $\gamma_j(t)$ defined by (71) may be written as

$$\begin{aligned}\gamma_j(t) &= \operatorname{tr} \rho(0)\dot{A}_j(t) - \operatorname{tr} \bar{\rho}(t)\dot{A}_j(0) \\ &= -\int_0^t ds \frac{\partial}{\partial s} \operatorname{tr}[\bar{\rho}(s) e^{-i\mathbb{L}s}\delta\dot{A}_j(t)]\end{aligned} \tag{93}$$

where we have used (7) and (76). We now insert (80) to yield

$$\begin{aligned}\gamma_j(t) = &-\Omega_{jk}(t)\int_0^t ds \frac{\partial}{\partial s} \operatorname{tr}[\bar{\rho}(s) e^{-i\mathbb{L}s}\delta A_k(t)] \\ &-\int_0^t du\phi_{jk}(t, u)\int_0^u ds \frac{\partial}{\partial s} \operatorname{tr}[\bar{\rho}(s) e^{-i\mathbb{L}s}\delta A_k(u)] \\ &-\int_0^t ds \operatorname{tr}\left[\frac{\partial\bar{\rho}(s)}{\partial s} e^{-i\mathbb{L}s}\delta F_j(t, s)\right] \\ &+\int_0^t ds \operatorname{tr}[\bar{\rho}(s) i\mathbb{L} e^{-i\mathbb{L}s}\delta F_j(t, s)]\end{aligned} \tag{94}$$

Since $\bar{\rho}(t)$ gives correct mean values of the macrovariables, we have

$$\int_0^t ds \frac{\partial}{\partial s} \operatorname{tr}[\bar{\rho}(s) e^{-i\mathbb{L}s} \delta A_k(t)] = \operatorname{tr} \bar{\rho}(t) A_k - \operatorname{tr} \bar{\rho}(0) A_k(t) = 0 \tag{95}$$

and from (36) and (83) we obtain

$$\operatorname{tr}\left[\frac{\partial \bar{\rho}(s)}{\partial s} e^{-i\mathbb{L}s} \delta F_j(t, s)\right] = -(\delta F_j(t, s), \delta A_k(s)) \dot{\lambda}_k(s) = 0 \tag{96}$$

Consequently, (94) reduces to

$$\gamma_j(t) = \int_0^t ds \operatorname{tr}[\bar{\rho}(s) i\mathbb{L} e^{-i\mathbb{L}s} \delta F_j(t, s)] \tag{97}$$

This relation can also be derived directly from the molecular expressions (66) and (78). We may replace $\delta F_j(t, s)$ on the right-hand side of (97) by $F_j(t, s)$. Then, by use of (35) we obtain

$$\gamma_j(t) = \int_0^t ds\, (F_j(t, s), \delta \dot{A}_k(s)) \lambda_k(s) \tag{98}$$

where we have taken (54) into account. Finally, we insert (80), specialized to $t = s$, and find

$$\gamma_j(t) = \int_0^t ds\, (F_j(t, s), F_k(s, s)) \lambda_k(s) \tag{99}$$

This relation gives us a connection between the generalized canonical correlations of the random forces and the disorganized drift characterizing the dissipation of the macrovariables. The correlation function $(F_j(t, s), F_k(s, s))$ determines the influence of the conjugate force $\lambda_k(s)$ at time s on the time rate of change of the mean value $a_j(t)$ at time t. Equation (99) may be looked upon as a generalized *second fluctuation-dissipation theorem*. It is an extension of the familiar fluctuation-dissipation theorem associated with Mori's Langevin equation.[1,3]

The Langevin equation (80) determines the stochastic process of the fluctuations $\{\delta A_j(t)\}$ in terms of another process, the stochastic process of the random forces. The usefulness of this description lies in the fact that it provides a better basis for approximations than the Heisenberg equations of motion. The random forces describe the influence of the eliminated microscopic degrees of freedom on the macroscopic dynamics, and they vary on a short time scale. The slow macrovariables are not much influenced by the details of the random force process within such short time intervals. That is why the stochastic process of random forces needs to be determined only approximately. A particularly simple situation occurs if there is a clear-cut separation of the time scales of the slowly varying macroscopic and the rapidly varying microscopic processes. In this case, which will be considered elsewhere, the stochastic process of the macrovariables is approximatively Markovian.

4. CONCLUSIONS

In this article we have investigated the time evolution of closed systems initially in a nonequilibrium state. Separating an organized motion part of the time rates of change, we derived exact equations of motion (79) and (80) for the mean values and the fluctuations from the mean path, respectively. These equations are valid arbitrarily far from thermal equilibrium. In contrast to others,[17–20] we have not treated the nonlinear system by a nonlinear Langevin equation for the macrovariables $\{A_j(t)\}$ themselves; rather, we decomposed $A_j(t)$ into a mean value and a fluctuation and treated them separately.

This way, we directly obtained closed, generally nonlinear, equations of motion for the mean values (transport equations) and avoided the introduction of "bare" transport kernels.[18] We displayed linear Langevin equations describing the nonstationary process of fluctuations around the mean path. The collective frequencies and the memory functions of the Langevin equations depend on the mean path. The random forces are related to the correct transport kernels by a fluctuation-dissipation theorem (99).

Van Kampen's objection to the nonlinear Langevin equation[21] does not apply to our treatment of nonlinear systems. Moreover, our exact equations of motion yield under the Markovian assumption approximate equations of motion that are in accordance with the results of the phenomenological theory using the system-size expansion.[22–24] This will be discussed in more detail separately.

Recently Furukawa[25] put forward another generalization of Mori's Langevin equation using semiphenomenological arguments. Furukawa relates the correlations of the random forces directly to the memory functions of the Langevin equations and not to the transport kernels as we do. The two forms of the fluctuation-dissipation theorem are only equivalent in the linear approximation. Further investigation shows that Furukawa's memory functions depend themselves on the unknown correlations of the macrovariables and are not determined by the mean path.

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