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Microdynamics and Nonlinear Stochastic Processes of Gross Variables

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Starting from classical Hamiltonian mechanics, we derive for the dynamics of gross variables in nonequilibrium systems exact nonlinear generalized Fokker–Planck and Langevin equations in which the effect of the initial preparation is taken into account explicitly. This latter concept allows for the construction of a uniquely determined projection operator. The memory functions occurring in the Langevin equations are related to the random forces by a fluctuation-dissipation theorem of the second kind. We discuss the connection with the generalized Fokker–Planck equation. The known results for equilibrium fluctuations are recovered as a special case.

KEY WORDS: Nonlinear relaxation; nonequilibrium fluctuations; nonlinear generalized Langevin equation ; generalized Fokker–Planck equation ; fluctuation-dissipation theorem.

1. INTRODUCTION

Nonlinear couplings among gross variables play an important role in many problems of irreversible statistical thermodynamics currently receiving attention. In systems where the steady state is a thermal equilibrium state these couplings are particularly important near critical points,(1,2) but they also play a major role for certain effects which occur outside the critical regime.(3,4) The nonlinear couplings are of fundamental relevance in systems far from equilibrium,(5) where the steady state is itself a true nonequilibrium state.

In an irreversible system the gross variables undergo fluctuations and their motion can only be characterized by means of a stochastic process. Two well-known descriptions for such processes exist: The Langevin equation and the Fokker–Planck equation. The enormous success of these originally

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phenomenological methods has raised the question of their statistical mechanical foundation.

The investigation of this problem was pioneered by Green,(6) who derived a generally nonlinear Fokker–Planck equation from statistical mechanics under the assumption that the stochastic process of the gross variables is Markovian. A generalized Fokker–Planck equation which allows for memory effects was put forward by Zwanzig,(7) who made use of the projection operator technique. Mori(8) used a modified projection operator technique in order to derive linear Langevin equations, and Kawasaki(9) extended this approach to nonlinear Langevin equations where couplings among the gross variables are apparent. In all of these approaches it is explicitly or tacitly assumed that the steady state of the system is a thermal equilibrium state.

In the present paper we extend the statistical mechanical foundation of the Fokker–Planck and the Langevin approaches to systems which may be far from equilibrium. A generalization of the equilibrium methods has already been attempted in some previous papers,(10,11) However, the resulting equations generally display some undesirable features, such as an inhomogeneity in the Fokker–Planck equation and nonvanishing mean values of the Langevin random forces.

It has been pointed out previously(12) that the macroscopic dynamics depends on the preparation of the initial state. We incorporate the effect of preparation by an adequate choice of the projection operator and obtain uniquely defined equations of motion of the same basic structure as in the equilibrium case. For instance, a nonequilibrium situation is not described by additional terms in the equations of motion, but by modified transport coefficients which may lack some of the properties of the corresponding equilibrium quantities.

The paper is organized as follows: In the next section we decompose the phase space into a set of hypersurfaces which correspond to the macroscopic states of the system. The probability distribution of the molecular realizations of a given macroscopic state in the initial ensemble, as it results from the preparation procedure, defines an adequate measure for the averaging over the microscopic degrees of freedom at fixed values of the gross variables. In Section 3 we use this quantity to define a projection operator which projects the phase functions into the subspace of the state functions in such a way that their mean value in the initial ensemble remains unchanged.

By means of this projection operator we derive in Section 4 an exact equation of motion for the occupation probabilities of the state space cells. From this equation we obtain in Section 5 both a generalized Fokker–Planck equation and a generalized Langevin equation. We show that the Fokker–Planck equation describes the relaxation of the macroscopic single event probability as well as the time evolution of initial correlation functions. In order to extract information from the associated generalized Langevin equations the properties of the random forces determined by the fluctuation-dissipation theorem are generally not sufficient, because of the nonlinearities in the equations of motion.[3] On the other hand, additional properties of the random forces can in principle be obtained by use of the given molecular expressions of the random forces.

In the last section we discuss the simplifications that occur if the stochastic process of gross variables is stationary.

2. INITIAL DISTRIBUTION AND PREPARATION CLASS

We confine ourselves to classical statistical mechanics. The macroscopic state of the system will be defined by a set $a = (a^1,..., a^i,...)$ of gross variables, quantities like energy, magnetization, electric charge. These gross variables represent coordinates in the state space Σ, and every point in Σ corresponds to a macroscopic state of the system.

On the molecular level the gross variables are represented as phase functions $A(\Gamma)$, where Γ is a point in the phase space. Clearly, there is a huge number of microscopic states Γ which are molecular realizations of the same macroscopic state α. In the phase space these realizations constitute the hypersurface $S(a)$ on which the phase functions $A(\Gamma)$ assume the values a.

The microscopic dynamics is governed by the Hamilton function $H(\Gamma)$ of the system. Hamilton's equations of motion determine the time evolution of a microscopic state Γ in a deterministic way. One of the characteristic features of macroscopic systems is the fact that their initial microscopic state is not known; at best, we will know the probability distribution $\rho_0(\Gamma)$ of the microscopic states Γ at the initial time $t_0 = 0$.

The initial microscopic probability distribution $\rho_0(\Gamma)$ can be viewed as a probability density of initial states of an ensemble of systems to which the same preparation procedure has been applied. In fact, a preparation procedure may just be defined as an experimental device which, when applied to an ensemble of systems, yields in a reproducible way a well-defined distribution function $\rho_0(\Gamma)$ at a given instant of time t_0.

Usually a point Γ in the phase space is specified by a set of conjugate position and momentum coordinates: $\Gamma = (q^1, p^1,..., q^\alpha, p^\alpha,...)$. However, we might as well write $\Gamma = (a, \Omega_a)$, where Ω_a specifies a point on the hypersurface $S(a)$. In the latter case we first give the macroscopic state a which is

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[3] An approach which avoids this difficulty, splitting the dynamics into a nonlinear mean value dynamics and a linear but nonstationary fluctuation dynamics, has been given in a recent work.(13)

associated with a microscopic state Γ and then we specify the specific molecular realization of this state by Ω_a.

Correspondingly, the phase space volume element $d\Gamma$ splits into the state space volume element da and a volume element $d\Omega_a$ of the hypersurface $S(a)$:

$$d\Gamma = da\, d\Omega_a \tag{1}$$

The volume element $d\Omega_a$ may be written

$$d\Omega_a = \delta(A(\Gamma) - a)\, d\Gamma \tag{2}$$

where $\delta(a)$ is a multidimensional δ-function.

To the decomposition (1) of the volume element $d\Gamma$ there corresponds a decomposition of the probability distribution $\rho_0(\Gamma)$ into the probability distribution $p_0(a)$ of the associated macroscopic states a and the probability distribution $w_0(a, \Omega_a)$ of the molecular realizations Ω_a of a given state a, i.e.,

$$\rho_0(a) = p_0(a) w_0(a, \Omega_a) \tag{3}$$

where $\Gamma \equiv (a, \Omega_a)$.

The macroscopic probability distribution $p_0(a)$ determines the probability of finding the system on the hypersurface $S(a)$ and it is obtained from the microscopic probability distribution $\rho_0(\Gamma) = \rho_0(a, \Omega_a)$ by adding up the probabilities of the molecular realizations Ω_a. With (2) we have

$$p_0(a) = \int d\Omega_a \rho_0(a, \Omega_a) = \int d\Gamma\, \delta(A(\Gamma) - a) \rho_0(\Gamma) \tag{4}$$

The function $w_0(a, \Omega_a) = w_0(\Gamma)$ gives the probability of finding a specific molecular realization Ω_a of a known macroscopic state a. This probability is normalized on every hypersurface $S(a)$

$$\int d\Omega_a w_0(a, \Omega_a) = \int d\Gamma\, \delta(A(\Gamma) - a) w_0(\Gamma) = 1 \tag{5}$$

While the statistics of the gross variables a at the initial time $t_0 = 0$ is completely specified by $p_0(a)$, their future statistics will be influenced by $w_0(\Gamma)$ as well, since the gross variables couple to the remaining degrees of freedom. In a macroscopic description $p_0(a)$ is explicitly taken into account as the initial distribution of the gross variables, whereas the influence of $w_0(\Gamma)$ appears only implicitly in the form of the macroscopic evolution laws. Since the form of those laws only depends on $w_0(\Gamma)$ and not on $p_0(a)$, it is natural to introduce preparation classes of initial microscopic distributions $\rho_0(\Gamma)$ which lead to the same probability distribution $w_0(a, \Omega_a) = w_0(\Gamma)$ for the molecular realizations Ω_a of a given state a. This probability distribution for the Ω_a which is common to the distributions $\rho_0(\Gamma)$ forming a preparation class will be denoted by $w(\Gamma)$ henceforth. A special member of a preparation class differs from other members by the form of $p_0(a)$. In other words, the elements of a preparation class may assign different probabilities to the hypersurfaces $S(a)$; however, the probabilities on the hypersurfaces are common to the whole class.(12)

3. MICROSCOPIC DYNAMICS AND STOCHASTIC PROCESSES OF GROSS VARIABLES

In a macroscopic description of the system we want to determine the macroscopic state a_t at time t. Even if we know the initial macroscopic state a_0, we cannot determine the future state a_t with certainty since we have only probabilistic information about the molecular realization of the initial state. This means that the gross variables describing the state have to be considered as stochastic variables.

In a stochastic theory we may ask for the probability $p_t(a)\,da$ that the gross variables assume values in the state space volume element da around a at time t. The probability $p_t(a)\,da$ can be viewed as the average occupation probability of the state space cell da in the considered ensemble of systems. On the molecular level the occupation number of the cell da is represented by a phase function $\Psi^a(\Gamma)\,da$, where

$$\Psi^a(\Gamma) = \delta(A(\Gamma) - a) \tag{6}$$

The quantities $\Psi^a(\Gamma)$ have the properties

$$\Psi^a(\Gamma)\Psi^{a'}(\Gamma) = \delta(a - a')\Psi^a(\Gamma) \tag{7}$$

$$\int d\Gamma\, w(\Gamma)\Psi^a(\Gamma) = 1 \tag{8}$$

and their ensemble average yields the macroscopic probability distribution

$$p_t(a) = \int d\Gamma\, \Psi^a(\Gamma)\rho_t(\Gamma) \tag{9}$$

where $\rho_t(\Gamma)$ is the microscopic probability distribution at time t.

In statistical mechanics every state function $f(a)$ is represented by a phase function $F(\Gamma)$ which is a linear combination of the $\Psi^a(\Gamma)$,

$$F(\Gamma) = \int da\, f(a)\Psi^a(\Gamma) = f(A(\Gamma)) \tag{10}$$

We now introduce a scalar product in the space of phase functions by

$$(X, Y) = \int d\Gamma\, w(\Gamma)X(\Gamma)Y(\Gamma) \tag{11}$$

Then, because of (7) and (8), the $\Psi^a(\Gamma)$ are orthonormal with respect to this scalar product

$$(\Psi^a, \Psi^{a'}) = \delta(a - a') \tag{12}$$

and according to (10) the $\Psi^a(\Gamma)$ provide a basis in the subspace of those phase functions that are state functions. For an arbitrary phase function $X(\Gamma)$ the orthogonal projection into this subspace reads

$$\mathbb{D}X(\Gamma) = \int da\, \Psi^a(\Gamma)(\Psi^a, X) \tag{13}$$

The operator $\mathbb{D}$ has the usual properties of an orthogonal projection operator

$$\mathbb{D}^2 = \mathbb{D} \tag{14}$$

$$(X, \mathbb{D}Y) = (\mathbb{D}X, Y) \tag{15}$$

and it projects out the $\Psi^a(\Gamma)$

$$\mathbb{D}\Psi^a(\Gamma) = \Psi^a(\Gamma) \tag{16}$$

Hence, $\mathbb{D}$ reduces the set of all variables of the system to the subset of those variables that are still taken into consideration in a macroscopic description.

In Eq. (9) the time dependence of $p_t(a)$ originates from the time dependence of the microscopic probability distribution $\rho_t(\Gamma)$. On the other hand, we might look upon the phase functions $\Psi^a(\Gamma)$ as time-dependent quantities and take the average over the initial distribution $\rho_0(\Gamma)$

$$p_t(a) = \int d\Gamma\, \Psi_t^a(\Gamma)\rho_0(\Gamma) \tag{17}$$

where

$$\Psi_t^a(\Gamma) = \Psi^a(\Gamma_t) \tag{18}$$

The phase point Γ_t is the microscopic state into which a system initially at the point Γ evolves in the time t according to Hamilton's equations of motion. Hence, we have

$$\Gamma_t = e^{-\mathbb{L}t}\Gamma \tag{19}$$

where the Liouville operator $\mathbb{L}$ acts upon a phase function $X(\Gamma)$ as the Poisson bracket with the Hamilton function

$$\mathbb{L}X(\Gamma) = \{H(\Gamma), X(\Gamma)\} \tag{20}$$

This Poisson bracket structure of the Liouville operator leads to the relations

$$\int d\Gamma\; X(\Gamma)\mathbb{L}Y(\mathbb{L}) = -\int d\Gamma\; Y(\Gamma)\mathbb{L}X(\Gamma) \tag{21}$$

$$\mathbb{L}XY(\Gamma) = Y(\Gamma)\mathbb{L}X(\Gamma) + X(\Gamma)\mathbb{L}Y(\Gamma) \tag{22}$$

and in particular

$$\mathbb{L}\Psi^a(\Gamma) = -\sum_i \frac{\partial}{\partial a^i}\Psi^a(\Gamma)\mathbb{L}A^i(\Gamma) \tag{23}$$

Because of (19) and (22), Eq. (18) reads

$$\Psi_t^a(\Gamma) = e^{-\mathbb{L}t}\Psi^a(\Gamma) \tag{24}$$

The time evolution of the phase function $F(\Gamma)$ associated with a state function $f(a)$ reads

$$F_t(\Gamma) = \int da\, f(a)\Psi_t^a(\Gamma) \tag{25}$$

just because of Eqs. (10) and (24).

Multitime moments (correlation functions) of arbitrary state functions $f^1(a),\ldots,f^n(a)$ are, on the molecular level, defined by

$$\langle f^1_{t_1} f^2_{t_2} \cdots f^n_{t_n} \rangle = \int d\Gamma\, F^1_{t_1}(\Gamma) F^2_{t_2}(\Gamma) \cdots F^n_{t_n}(\Gamma) \rho_0(\Gamma) \tag{26}$$

If we insert (25), we obtain

$$\begin{aligned}\langle f^1_{t_1} f^2_{t_2} \cdots f^n_{t_n} \rangle \\ &= \int da_1\, da_2 \cdots da_n\, f^1(a_1) f^2(a_2) \cdots f^n(a_n) \\ &\quad \times P_{t_1,t_2,\ldots,t_n}(a_1, a_2,\ldots,a_n)\end{aligned} \tag{27}$$

where

$$P_{t_1,t_2,\ldots,t_n}(a_1, a_2,\ldots, a_n) = \int d\Gamma\, \Psi^{a_1}_{t_1}(\Gamma) \Psi^{a_2}_{t_2}(\Gamma) \cdots \Psi^{a_n}_{t_n} \rho_0(\Gamma) \tag{28}$$

is the joined n-time probability distribution function. These quantities characterize the stochastic process of the gross variables a completely. Hence, we should look at the evolution law of the $\Psi_t^a(\Gamma)$ in order to see the connection between the macroscopic irreversible process of the gross variables and the underlying microscopic dynamics.

4. TIME EVOLUTION OF $\Psi_t^a(\Gamma)$

In this section we want to split the time rates of change of the $\Psi_t^a(\Gamma) = \Psi_t^a(a', \Omega_{a'})$ into two parts: a first part describing the systematic evolution which is common to all realizations $\Omega_{a'}$ of a process starting out from a state a', and a second part describing a "random" contribution. This latter contribution to $(\partial/\partial t)\Psi_t^a(\Gamma)$ will be denoted by $R_t^a(\Gamma)$. The random part depends on $\Omega_{a'}$. On the other hand, in order that it does not contribute to the systematic evolution of the gross variables, we have to demand that its average over the realizations $\Omega_{a'}$ of a given intial state a' should vanish:

$$\begin{aligned}&\int d\Omega_{a'}\, w(a', \Omega_{a'}) R_t^a(a', \Omega_{a'}) \\ &\qquad = \int d\Gamma\, \delta(A(\Gamma) - a') w(\Gamma) R_t^a(\Gamma) = 0\end{aligned} \tag{29}$$

where $w(a', \Omega_{a'})$ is the probability distribution of the molecular realizations $\Omega_{a'}$ of an initial macroscopic state a' in the considered preparation class.

In view of (6) and (11), Eq. (29) reads

$$(\Psi^{a'}, R_t^a) = 0 \tag{30}$$

which equally well may be written

$$\mathbb{D}R_t^a = 0 \tag{31}$$

where $\mathbb{D}$ is the projection operator defined by (13). Hence, the random contribution R_t^a to the time rate of change of Ψ_t^a has to be orthogonal to the subspace of those phase functions that are state functions.

A decomposition of $(\partial/\partial t)\Psi_t^a$ of the desired form can be obtained by means of the well-known projection operator technique. In the following we outline the basic steps of the procedure only and obtain the main result in Eq. (48). We start by noting that the microscopic time evolution operator $e^{-\mathbb{L}t}$ splits into

$$\begin{aligned} e^{-\mathbb{L}t} &= e^{-\mathbb{L}t}\mathbb{D} + (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}t}(\mathbb{1} - \mathbb{D}) \\ &\quad - \int_0^t dS\, e^{-\mathbb{L}(t-s)}\mathbb{D}\mathbb{L}(\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D}) \end{aligned} \tag{32}$$

This identity can be verified by differentiation. Next, we have from (24)

$$(\partial/\partial t)\Psi_t^a = -e^{-\mathbb{L}t}\mathbb{L}\Psi^a \tag{33}$$

If we insert (32) into (33), we obtain

$$\begin{aligned} \frac{\partial}{\partial t}\Psi_t^a &= -\int da'\, \Psi_t^{a'}(\Psi^{a'}, \mathbb{L}\Psi^a) + \int_0^t ds \int da'\, \Psi_{t-s}^{a'}(\Psi^{a'}, \mathbb{L}(\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s} \\ &\quad \times (\mathbb{1} - \mathbb{D})\mathbb{L}\Psi^a) + R_t^a \end{aligned} \tag{34}$$

where we have made use of (13) and (24) and where

$$R_t^a = -(\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}t}(\mathbb{1} - \mathbb{D})\mathbb{L}\Psi^a \tag{35}$$

is the random part of the time rate of change, which satisfies (31) quite obviously.

The structure of the basic equation of motion (24) becomes more explicit if we further evaluate the scalar products appearing therein. To this purpose we first mention that the Liouville operator $\mathbb{L}$ may not be antisymmetric with respect to the scalar product (11); it rather satisfies

$$(X, \mathbb{L}Y) = -(\mathbb{L}X, Y) + (X\dot{A}^0, Y) \tag{36}$$

where the phase function $A^0(\Gamma)$ is the logarithm of the probability distribution $w(\Gamma)$ of the molecular realizations, i.e.,

$$A^0 = \ln w \tag{37}$$

and where

$$\dot{A}^0 = -\mathbb{L}A^0 \tag{38}$$

By use of (7) and (23) we obtain

$$(\Psi^{a'}, \mathbb{L}\Psi^{a}) = \sum_{i} \frac{\partial}{\partial a^{i}} v^{i}(a)\, \delta(a - a') \tag{39}$$

where $v^{i}(a)$ is the drift vector

$$v^{i}(a) = (\Psi^{a}, \dot{A}^{i}) = \int d\Gamma\, \delta(A(\Gamma) - a) w(\Gamma) \dot{A}^{i}(\Gamma) \tag{40}$$

and

$$\dot{A}^{i} = -\mathbb{L}A^{i} \tag{41}$$

Further, using (7), (23), and (36) we find

$$\begin{aligned}(\Psi^{a'}, \mathbb{L}(\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D})\mathbb{L}\Psi^{a}) \\ = -\sum_{i,j} \frac{\partial^{2}}{\partial a^{i}\, \partial a'^{j}} D_{s}^{ij}(a, a') + \sum_{i} \frac{\partial}{\partial a^{i}} D_{s}^{i0}(a, a')\end{aligned} \tag{42}$$

where we have introduced the generalized diffusion kernels

$$\begin{aligned}D_{s}^{ij}(a, a') &= (\Psi^{a'}\dot{A}^{j}, (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D})\Psi^{a}\dot{A}^{i}) \\ &= \int d\Gamma\, w(\Gamma)\, \delta(A(\Gamma) - a')[\dot{A}^{j}(\Gamma) - v^{j}(a')]e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s} \\ &\quad \times [\dot{A}^{i}(\Gamma) - v^{i}(a)]\, \delta(A(\Gamma) - a)\end{aligned} \tag{43}$$

and

$$\begin{aligned}D_{s}^{i0}(a, a') &= (\Psi^{a'}\dot{A}^{0}, (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D})\Psi^{a}\dot{A}^{i}) \\ &= \int d\Gamma w(\Gamma)\, \delta(A(\Gamma) - a')[\dot{A}^{0}(\Gamma) - v^{0}(a')]e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s} \\ &\quad \times [\dot{A}^{i}(\Gamma) - v^{i}(a)]\, \delta(A(\Gamma) - a)\end{aligned} \tag{44}$$

The drift $v^{0}(a)$ reads

$$v^{0}(a) = (\Psi^{a}, \dot{A}^{0}) = \sum_{i} \frac{\partial}{\partial a^{i}} v^{i}(a) \tag{45}$$

Finally, using (23), we may write the random part (35) of the time rate of change of Ψ_{t}^{a} as

$$R_{t}^{a} = -\sum_{i} \frac{\partial}{\partial a^{i}} \varphi_{t}^{ia} \tag{46}$$

where

$$\varphi_{t}^{ia} = (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}t}(\mathbb{1} - \mathbb{D})\dot{A}^{i}\Psi^{a} \tag{47}$$

Now, because of (39), (42), and (46), the equation of motion (34) for the $\Psi_t{}^a$ takes the form

$$\begin{aligned}\frac{\partial}{\partial t}\Psi_t{}^a = {} & -\sum_i \frac{\partial}{\partial a^i} v^i(a)\Psi_t{}^a \\ & + \int_0^t ds \sum_i \frac{\partial}{\partial a^i} \int da' \left[\sum_j D_s^{ij}(a, a') \frac{\partial}{\partial a'^j} + D_s^{i0}(a, a')\right]\Psi_{t-s}^{a'} \\ & - \sum_i \frac{\partial}{\partial a^i}\varphi_t^{ia} \qquad (48)\end{aligned}$$

This is the first main result of the present work. It should be emphasized that the consideration of the preparation has played a major role in the derivation of (48); by taking the effect of preparation explicitly into account we obtained a unique decomposition of the time rate of change into a systematic and a random part, where the random part has the property that its statistical average over the realizations of the stochastic process starting from a given macroscopic state vanishes. This property of the random part establishes the connection with the preparation since the preparation determines the probability distribution of the realizations.

Furthermore, the preparation also affects the systematic part of the time evolution because that part is related to the random part by the fluctuation-dissipation theorem of the second kind. In the present case, this theorem has the form

$$D_s^{ij}(a, a') = (\varphi_s^{ia}, \varphi_0^{ja'}) \qquad (49)$$

which can easily be seen by inspection of the molecular expressions (43) and (47). While the random part φ_t^{ia} depends on the specific realization $\Omega_{a'}$, the generalized diffusion kernels $D_s^{ij}(a, a')$ are only affected by the probability distribution $w(\Gamma)$ of the $\Omega_{a'}$, which is common to all processes within the considered preparation class!

5. GENERALIZED FOKKER–PLANCK AND LANGEVIN EQUATIONS

Our further investigations are based on Eq. (48). First we average the equation over the initial microscopic probability distribution $\rho_0(\Gamma)$. According to (17), the average of $\Psi_t{}^a$ yields the macroscopic probability distribution $p_t(a)$. The average of the φ_t^{ia} defined in (47) vanishes, since

$$\mathbb{D}\varphi_t^{ia} = 0 \qquad (50)$$

by construction. Consequently, the average over Eq. (48) reads

$$\frac{\partial}{\partial t} p_t(a) = -\sum_i \frac{\partial}{\partial a^i} v^i(a) p_t(a) + \int_0^t ds \sum_i \frac{\partial}{\partial a^i} \int da' \left[\sum_j D_s^{ij}(a, a') \frac{\partial}{\partial a'^j} + D_s^{i0}(a, a') \right] P_{t-s}(a') \tag{51}$$

This equation of motion for the probability distribution of the gross variables has the form of a generalized Fokker–Planck equation. The derivation of this master equation for a non-Markov process has been accomplished in a previous study.(12) It has been pointed out there that the lack of an inhomogeneity in this exact equation of motion and its uniquely defined form result from the fact that the initial preparation has been taken into account explicitly.

Besides the relaxation of an initial macroscopic probability distribution $p_0(a)$, the master equation (51) also governs the time evolution of initial correlation functions $\langle f_t g_0 \rangle$ where the first time of observation coincides with the initial time of preparation $t_0 = 0$. This is so because the associated probability density $p_{t,0}(a, a')$ is the solution of the master equation (51) with the initial condition

$$p_{0,0}(a, a') = \delta(a - a') p_0(a) \tag{52}$$

as can be seen from (48) and (28), if we observe that the average of φ_t^{ia} vanishes on every hypersurface $S(a')$.

In what follows we consider the nonlinear generalized Langevin equations for the gross variables. The phase functions $A_t(\Gamma)$ associated with the gross variables are related to the Ψ_t^a by

$$A_t^a(\Gamma) = \int da\, a^i \Psi_t^a(\Gamma) \tag{53}$$

Consequently, an equation of motion for the A_t is obtained from (48) if we multiply by a and afterwards integrate over the entire state space Σ. The result reads

$$\frac{\partial}{\partial t} A_t^i = v^i(A_t) + \int_0^t ds \left[\sum_j \frac{\partial}{\partial A_{t-s}^j} \gamma_s^{ij}(A(t-s)) - \gamma_s^{i0}(A(t-s)) \right] + \xi_t^i \tag{54}$$

where

$$\gamma_s^{ij}(a') = \int da\, D_s^{ij}(a, a') \tag{55}$$

$$\gamma_s^{i0}(a') = \int da\, D_s^{i0}(a, a') \tag{56}$$

$$\zeta_t^i = \int da\, \varphi_t^{ia} \tag{57}$$

Note that the knowledge of the diffusion kernels D_s^{ij} in the generalized Fokker–Planck equation (51) allows one to determine the memory functions γ_s^{ij} in the generalized Langevin equation (54) but not vice versa.

Using Eqs. (43), (44), and (47), we obtain for the memory functions γ_s^{ij} and the random forces ζ_t^i molecular expressions of the form

$$\gamma_s^{ij}(a) = (\Psi^a \dot{A}^j, (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D})\dot{A}^i) \tag{58}$$

$$\gamma_s^{i0}(a) = (\Psi^a \dot{A}^0, (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}s}(\mathbb{1} - \mathbb{D})\dot{A}^i) \tag{59}$$

$$\zeta_t^i = (\mathbb{1} - \mathbb{D})e^{-(\mathbb{1}-\mathbb{D})\mathbb{L}t}(\mathbb{1} - \mathbb{D})\dot{A}^i \tag{60}$$

The average of the random forces vanishes on every hypersurface $S(a)$

$$(\Psi^a, \zeta_t^i) = \int d\Gamma\, w(\Gamma)\, \delta(A(\Gamma) - a)\zeta_t^i(\Gamma) = 0 \tag{61}$$

and the correlation functions of the random forces ζ_t^i on a hypersurface $S(a)$ are related to the memory functions $\gamma^{ij}(a)$ by a fluctuation-dissipation theorem of the form

$$\gamma_t^{ij}(a) = (\Psi^a, \zeta_t^i \zeta_0^j) = \int d\Gamma\, w(\Gamma)\, \delta(A(\Gamma) - a)\zeta_t^i(\Gamma)\zeta_0^j(\Gamma) \tag{62}$$

This follows from the molecular expressions (58), (60) by use of (14), (15) and

$$\mathbb{D}\Psi^a X = \Psi^a \mathbb{D} X \tag{63}$$

The Langevin equations (54) determine the stochastic process of the gross variables A in terms of another process, the stochastic process of the random forces ζ. This means that we have to know the stochastic process of the random forces completely in order to determine the stochastic process of the gross variables. The properties (61) and (62) of the random forces are not sufficient to obtain any exact nontrivial result from the Langevin equations (54), so that one might question the usefulness of an approach by nonlinear generalized Langevin equations.

In order to overcome this difficulty one either has to calculate further properties of the random forces by use of their molecular expressions (60), or one has to make approximations. The usefulness of Eq. (54) lies in the fact that it is particularly suitable for such approximations.

The Langevin equations (54) as they stand are equations for phase functions and we might ask for their connection with stochastic differential equations as they appear in the theory of stochastic processes. Whenever we specify the initial microscopic state Γ the gross variables $A_t(\Gamma)$ are uniquely defined functions of t and so is each single term of Eq. (54).

The $A_t(\Gamma)$ specify a trajectory a_t in the state space Σ, and (54) decomposes the velocity vector $\dot{a}_t = (\partial/\partial t)A_t(\Gamma)$ into three parts. The first two parts depend only on the end point a_t and on that part of the trajectory which the system has already run through, respectively. This means that these terms are implicit functions of Γ via $a_s = A_s(\Gamma)$, $s \leqslant t$. Only the third part, the random force ζ_t, depends on Γ explicitly. Consequently, Eq. (54) can be solved for $A_t(\Gamma)$ as a function of $a = A_0(\Gamma)$ and as a functional of the random forces $\zeta_t(a, \Omega_a)$. The dependence on both a and $\zeta_t(a, \Omega_a)$ may be nonlinear. The quantities which we want to determine are certain functions of the $A_t(\Gamma)$ averaged over $\rho_0(\Gamma)$. Such an average splits into an average over the molecular realizations Ω_a of a state a and an average over the macroscopic states a, according to Eqs. (1) and (3).

The average over the molecular realizations affects only the random forces. It can be done if one knows the correlations of the random forces on a given hypersurface $S(a)$, microscopically defined by

$$(\Psi^a, \zeta_{t_1} \cdots \zeta_{t_n}) = \int d\Gamma\, w(\Gamma)\, \delta(A(\Gamma) - a)\zeta_{t_1}(\Gamma) \cdots \zeta_{t_n}(\Gamma) \tag{64}$$

These quantities specify the stochastics of the random forces. The usual interpretation of a Langevin equation is that of an equation which specifies trajectories in the state space Σ, and two kinds of averages are explained: the average over the random forces, which is done with fixed values of the gross variables a and which is specified by the correlations $\langle \zeta_{t_1} \cdots \zeta_{t_n}; a\rangle$, $n = 1, 2,\ldots$, and an average over the gross variables. Naturally, the expression of A_t as a function of $a = A_0$ and a functional of ζ_t resulting from (54) is quite independent of an interpretation of those quantities as phase functions. Consequently, if we identify $\langle \zeta_{t_1} \cdots \zeta_{t_n}; a\rangle$ with $(\Psi^a, \zeta_{t_1} \cdots \zeta_{t_n})$, our Langevin equations (54) show precisely the features of the familiar stochastic differential equations in Σ space. This clarifies a recent discussion of the meaning of statistical mechanical Langevin equations.(14)

6. STATIONARY NONLINEAR FLUCTUATION DYNAMICS

We now restrict ourselves to the dynamics of spontaneous fluctuations in a stationary state. Let $\hat{\rho}(\Gamma)$ be a stationary distribution function satisfying

$$\mathbb{L}\hat{\rho} = 0 \tag{65}$$

The steady macroscopic probability distribution reads

$$\hat{p}(a) = \int d\Gamma\, \delta(A(\Gamma) - a)\hat{\rho}(a) \tag{66}$$

and the probability distribution $\hat{w}(\Gamma)$ of the molecular realization of a given macroscopic state is defined by

$$\hat{\rho}(\Gamma) = \hat{w}(\Gamma)\hat{p}(A(\Gamma)) \tag{67}$$

In the stationary preparation class the time rate of change of the variable A^0 defined in Eq. (37) is related to the time rates of change of the gross variables A by

$$\dot{A}^0 = -\sum_i \frac{\partial \ln \hat{p}(A)}{\partial A^i} \dot{A}^i \tag{68}$$

This follows by use of Eqs. (22), (23), and (65)–(67). Because of (68) the diffusion kernels defined by (43) and (44) are related by

$$D_s^{i0}(a, a') = -\sum_j D_s^{ij}(a, a') \frac{\partial \ln \hat{p}(a')}{\partial a'^j} \tag{69}$$

It is now easy to show that the generalized Fokker–Planck equation (51) can be recast into the form

$$\begin{aligned} \frac{\partial}{\partial t} p_t(a) = {} & -\sum_i \frac{\partial}{\partial a^i} v^i(a) p_t(a) \\ & + \int_0^t ds \sum_i \frac{\partial}{\partial a^i} \int da' \sum_j D_s^{ij}(a, a') \hat{p}(a') \frac{\partial}{\partial a'^j} \frac{p_{t-s}(a')}{\hat{p}(a')} \end{aligned} \tag{70}$$

Now, (68) implies

$$v^0 = -\sum_i \frac{\partial \ln \hat{p}(a)}{\partial a^i} v^i \tag{71}$$

which yields with Eq. (45)

$$\sum_i \frac{\partial}{\partial a^i} v^i(a) \hat{p}(a) = 0 \tag{72}$$

so that $\hat{p}(a)$ is in fact the stationary solution of Eq. (70).

The relaxation of an arbitrary initial probability distribution $p_0(a)$ as well as the time evolution of the stationary two-point correlation functions

$$\langle f_{t+s} g_s \rangle = \langle f_t g_0 \rangle \tag{73}$$

are governed by the generalized Fokker–Planck equation (70), which is the master equation for a stationary non-Markov process.

The associated generalized Langevin equation reads

$$\frac{\partial}{\partial t} A_t^i = v^i(A_t) + \int_0^t ds\, \hat{p}(A_{t-s})^{-1} \sum_j \frac{\partial}{\partial A_{t-s}^j} \gamma_s^{ij}(A_{t-s}) \hat{p}(A_{t-s}) + \zeta_t^i \tag{74}$$

where we have used the relationship

$$\gamma_s^{i0}(a') = -\sum_j \gamma_s^{ij}(a') \frac{\partial \ln \hat{p}(a')}{\partial a'^j} \tag{75}$$

which follows from (69) by means of (55) and (56).

Let us restate the known properties of the random forces. The hypersurface averages and the initial hypersurface correlation functions are given by

$$(\Psi^a, \zeta_t^i) = 0 \tag{76}$$

$$(\Psi^a, \zeta_t^i \zeta_0^j) = \gamma_t^{ij}(a) \tag{77}$$

The correlation functions in the stationary ensemble $\hat{\rho}(\Gamma)$ read

$$\langle \zeta_t^i \zeta_s^j \rangle = \langle \zeta_{t-s}^i \zeta_0^j \rangle = \int da\, \gamma_{t-s}^{ij}(a)\hat{\rho}(a) \tag{78}$$

The stationarity of these correlations is due to the fact that in Eq. (78) we average over the complete phase space with the stationary probability distribution $\hat{\rho}(\Gamma)$. A similar property does not hold for the conditional average (77).

As we have already mentioned, we have to determine further properties of the random forces if we want to extract information about the stochastic properties of the gross variables from Eq. (74). Generally this has to be done by use of the molecular expressions (60), and the resulting formulas get increasingly more involved the higher is the order of the considered correlation function. This is so because, up to this point, we have not made any assumption about the considered set of gross variables and the outlined theory is formally exact even for the most inadequate choice of the set of gross variables.

Considerable simplification occurs if the gross variables form a so-called complete set of macroscopic variables. This means that the state functions exhaust the set of slowly varying quantities of the system. In this case we might treat the time rates of change $\dot{A}$ of the gross variables as small quantities and derive approximate equations of motion which generally are well suited to describe the dynamics of macroscopic systems. A discussion of this problem would be beyond the scope of this paper, where we have restricted ourselves to exact results only. We hope to return to this problem in a future communication.

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