MEMORY EFFECTS IN NONLINEAR TRANSPORT: KINETIC EQUATIONS AND RATCHET DEVICES

I. Santamaría-Holek and J. M. Rubí
Departament de Física Fonamental-CER Física de Sistemes Complexos,
Facultat de Física Universitat de Barcelona Diagonal 647, 08028 Barcelona, Spain

We present a new method to derive kinetic equations for systems undergoing nonlinear transport in the presence of memory effects. In the framework of mesoscopic nonequilibrium thermodynamics, we obtain a generalized Fokker-Planck equation incorporating memory effects through time-dependent coefficients. As applications, we first discuss the non-Markovian dynamics of anomalous diffusion in a potential, analyzing the validity of the fluctuation-dissipation theorem. In a second application, we propose a new ratchet mechanism in which the periodic driving acting on the particle is induced by the Onsager coupling of the diffusion current with an oscillating thermodynamic force.

I. INTRODUCTION

The characterization of systems outside equilibrium requires an a priori identification of the relevant time and length scale playing a major role in the dynamics. Once this task has been accomplished one then proceeds to establish the set of kinetic equations governing the behaviour of the probability densities and subsequently to obtain the correlation functions which can be contrasted with experiments. These are the main steps nonequilibrium statistical mechanical theories set up to analyze the dynamics of systems of very different nature evolving under out-of-equilibrium conditions [1].

The present-day-tendency in the study of systems working at micro- and nano-scales, based on the increasing experimental possibilities, demands the implementation of simple theoretical frameworks able to cope with the complexity inherent to the analysis of systems with many competing time and length scales (usually referred to as complex systems). Two are the main characteristics exhibited by those systems. The unavoidable presence of energetic and entropic barriers makes the dynamics intrinsically nonlinear [2]-[5]. The drastic elimination of degrees of freedom usually performed for the sake of simplification is accompanied by the appearance of memory effects [6]-[9]. These two characteristics, together with the fact that frequently the system evolves under the influence of external gradients or fields creating an inhomogeneous environment, must be reflected in the formulation of the kinetic equations. To implement that task, many efforts have been devoted in the framework of kinetic theory [10], projector operator techniques [11]-[13] and in the theory of stochastic processes [14]-[19].

Two types of Fokker-Planck equations incorporating memory effects are frequently presented. The first one introduces the non-Markovianity in terms of retarded kernels, i.e., by incorporating time integrals in the equation [12], [18]. In the second type, non-Markovianity is taken into account through a time dependence of the coefficients [10], [13], [15], [16]. A detailed discussion explaining their differences together with experimental implications can be found in [20].

Our purpose in this paper is to propose a new method to derive kinetic equations of the Fokker-Planck type in which memory effects are incorporated through time-dependent coefficients. In recent works [21]-[25], we have shown that the scheme of nonequilibrium thermodynamics also applies to the mesoscopic domain in which fluctuations strongly influence the dynamics. The kinetic equations can be obtained from the probability density conservation law by specifying the phase space diffusion current which follows from the corresponding entropy production. The theory, called mesoscopic nonequilibrium thermodynamics, has been successfully applied to different situations involving transport [26], [27] and relaxation phenomena [28]-[29]. It is our objective in this paper to show its validity in systems exhibiting memory effects by discussing examples pertaining to the domain of nonlinear transport.

The paper is distributed as follows. In Sec. 2, we present the derivation of the Fokker-Planck equation for non-Markovian systems or generalized Fokker-Planck equation. Section 3 is devoted to obtain the corresponding generalized Langevin equation. In Sec. 4, we apply previous results to the case of anomalous diffusion in an external potential. A second application to the domain of nonlinear transport in ratchet devices is carried out in Sec. 5. Finally, in the discussion Section we summarize our main results and comment on new perspectives.

II. THE GENERALIZED FOKKER-PLANCK EQUATION

Consider a system whose dynamics is determined by the set of variables $\alpha \equiv (\alpha_1, \ldots, \alpha_n)$; their evolution in time $\alpha(t)$ defines a stationary non-Markovian process. Let $\alpha_0$ denote the initial values of the variables, corresponding to $t = 0$. 
The probability of finding the system in the state $\alpha$ at time $t$ is then given by means of the conditional probability density defined as
\[
P(\alpha|\alpha_0, t) = \frac{P(\alpha_0; \alpha, t)}{P(\alpha_0)} ,
\]
where $P(\alpha_0; \alpha, t)$ is the joint probability density and $P(\alpha_0)$ the stationary probability of the state $\alpha_0$. The probability density satisfies the normalization condition
\[
\int P(\alpha_0|\alpha, t)d\alpha = 1 ,
\]
and is governed by the continuity equation
\[
\frac{\partial}{\partial t} P(\alpha_0|\alpha, t) = -\frac{\partial}{\partial \alpha} \cdot J_\mu(\alpha_0; \alpha; t) ,
\]
expressing probability conservation in $\alpha$-space. Here $J_\mu(\alpha_0; \alpha; t)$ represents an unknown probability current.

In order to derive the explicit expression of this current, we will follow the method proposed by mesoscopic nonequilibrium thermodynamics (MNET) [22, 23]. By assuming local equilibrium in $\alpha$-space, we establish the Gibbs equation
\[
\delta S(t) = -\frac{1}{T} \int \mu(\alpha_0; \alpha; t) \delta P(\alpha_0|\alpha; t) d\alpha ,
\]
where $S(t)$ represents the entropy of the system, $\mu(\alpha_0; \alpha; t)$ a nonequilibrium chemical potential and $T$ the temperature, assumed constant. For the Markovian case, in which the joint probability factorizes in the form $P(\alpha_0; \alpha; t) = P(\alpha_0) P(\alpha; t)$, the Gibbs equation reduces to [23]
\[
\delta S(t) = -\frac{1}{T} \int \mu(\alpha; t) \delta P(\alpha; t) d\alpha ,
\]
where the chemical potential $\mu(\alpha; t)$ is related to the one of the non-Markovian case through
\[
\mu(\alpha; t) = \int \mu(\alpha_0; \alpha; t) P(\alpha_0)d\alpha_0 ,
\]
and the probability $P(\alpha_0)$ at the initial state is normalized to the unity.

To determine the value of the current $J_\mu(\alpha_0; \alpha; t)$ we will first calculate the entropy production $\sigma(t)$. Taking the time derivative of Eq. [4], substituting Eq. [3] and integrating by parts with the condition that the flux vanishes at the boundaries of the system, we obtain
\[
\sigma = -\frac{1}{T} \int J_\mu(\alpha_0, \alpha; t) \cdot \frac{\partial}{\partial \alpha} \mu(\alpha_0, \alpha; t) d\alpha .
\]
Now, following the rules of nonequilibrium thermodynamics we may establish a linear relationship between the flux and the thermodynamic force in the general form
\[
J_\mu(\alpha_0, \alpha; t) = -\frac{1}{T} \int L_{ij}(\alpha, \alpha'; t) \cdot \frac{\partial}{\partial \alpha} \mu(\alpha, \alpha'; t) d\alpha' ,
\]
where the Onsager coefficients $L_{ij}(\alpha, \alpha'; t)$ are, in general, function of the state variables $\alpha$ and satisfy the Onsager reciprocal relations $L_{ij}(\alpha_0; \alpha', t) = L_{ji}(\alpha', \alpha; t)$, where $\dagger$ means the transpose of a matrix [31]. These coefficients are related to relaxation functions giving the correlation of the state variables with their initial conditions [30]. In the Markovian case, correlations decay exponentially and the $L$'s become independent of time. In general, the $L$'s may also depend on time through the conditional averages of the state variable defined by
\[
\alpha(t) = \int \alpha P(\alpha_0|\alpha, t)d\alpha .
\]

To determine the expression of the chemical potential, we will use the requirement that the Gibbs equation [4] has to be compatible with the Gibbs entropy postulate [30]
\[
S(t) = -k_B \int P(\alpha_0|\alpha, t) \ln \frac{P(\alpha_0|\alpha, t)}{P_0(\alpha)} d\alpha + S_0 ,
\]
where $k_B$ is Boltzmann’s constant, $P_0(\alpha)$ is the probability density and $S_0$ the entropy of the reference state, considered at local equilibrium. By taking variations of this equation and integrating by parts, we can compare the resulting equation with Eq. (4), obtaining the following expression for $\mu(\alpha_0, \alpha; t)$

$$
\mu(\alpha_0, \alpha; t) = k_B T \ln \frac{P(\alpha_0 | \alpha, t)}{P_0(\alpha)} + \mu_0(\alpha),
$$

(11)

Here $\mu_0(\alpha)$ is the chemical potential at local equilibrium. If we now substitute Eq. (11) into (8), we obtain the constitutive relation for the diffusion current in $(\alpha)$-space

$$
J_\alpha(\alpha_0, \alpha; t) = -\int \tilde{\beta}(\alpha, \alpha'; t) \cdot [k_B T \frac{\partial}{\partial \alpha} P(\alpha_0 | \alpha, t)] \text{d} \alpha' + P(\alpha_0 | \alpha', t) X(\alpha') | d \alpha',
$$

(12)

where we have introduced the thermodynamic force

$$
X(\alpha) = -\frac{\partial}{\partial \alpha} [k_B T \ln P_0(\alpha) - \mu_0(\alpha)],
$$

(13)

and defined the matrix

$$
\tilde{\beta}(\alpha, \alpha'; t) = \frac{1}{T} \frac{L(\alpha, \alpha'; t)}{P(\alpha_0 | \alpha, t)}.
$$

(14)

In the Markovian limit, these coefficients must reduce to the friction coefficients in order to recover the corresponding Fokker-Planck equation from Eqs. (3) and (12). As the $L$’s, the $\tilde{\beta}$’s are invariant under time reversal symmetry [31] and may also be expressed in terms of relaxation functions [30]. Since the entropy production may in general contain contributions from different irreversible processes cross effects among currents and forces of identical tensorial nature might arise. Thus, for the sake of simplicity, the scalar product in Eq. (12) will implicitly indicate a sum over all the corresponding contributions and, consequently, $\tilde{\beta}(\alpha, \alpha'; t)$ is a matrix of matrices containing the coefficients accounting for the possible cross effects. Now, by substituting Eq. (12) into (8) we finally obtain the generalized Fokker-Planck equation

$$
\frac{\partial}{\partial t} P(\alpha_0 | \alpha, t) = \frac{\partial}{\partial \alpha} \left[ k_B T \tilde{\beta}(\alpha, \alpha'; t) \frac{\partial}{\partial \alpha} P(\alpha_0 | \alpha, t) \right] + \tilde{\beta}(\alpha, \alpha'; t) \cdot X(\alpha') P(\alpha_0 | \alpha', t) | d \alpha'.
$$

(15)

This equation accounts for the evolution in time of the conditional probability density for systems exhibiting non-Markovian dynamics when non-local effects are considered. Eq. (15) incorporates the memory effects through the time dependence of the coefficients, [13, 20]. Moreover, it generalizes the non-Markovian Fokker-Planck equation obtained in Refs. [13, 16] by including nonlinear contributions.

A. The slow variable approximation

When the characteristic relaxation time scale of the disturbances produced by thermodynamic forces is short enough when compared with the corresponding one in the evolution of $\alpha$, the process becomes local, i.e., $\tilde{\beta}(\alpha, \alpha'; t) = \tilde{\beta}(\alpha; t) \delta(\alpha' - \alpha)$. Under that condition, Eq. (15) reduces to

$$
\frac{\partial}{\partial t} P(\alpha_0 | \alpha, t) = \frac{\partial}{\partial \alpha} \left[ b(\alpha; t) P(\alpha_0 | \alpha, t) + k_B T \frac{\partial}{\partial \alpha} \tilde{\beta}(\alpha; t) P(\alpha_0 | \alpha, t) \right],
$$

(16)

which constitutes the generalized non-Markovian Fokker-Planck equation in the slow variable approximation [1]. Here we have defined the general thermodynamic force $b(\alpha)$ by

$$
b(\alpha; t) = \tilde{\beta}(\alpha; t) \cdot X(\alpha) - k_B T \frac{\partial}{\partial \alpha} \tilde{\beta}(\alpha; t).
$$

(17)
The Fokker-Planck equation was previously derived from the nonlinear Boltzmann equation [10] and from the master equations in [32], respectively. Its Markovian version follows by considering \( \tilde{\beta}(\alpha; t) \) independent of time. The resulting nonlinear equation agrees with the corresponding one obtained in [1] from projector operators. In the case when the force is linear, \( \tilde{X}(\alpha) = \alpha \), and the coefficients only functions of time, Eq. (16) reduces to

\[
\frac{\partial}{\partial t} P(\alpha; t) = \frac{\partial}{\partial \alpha} \cdot \tilde{\beta}(t) \cdot \left[ \alpha P(\alpha; t) + k_B T \frac{\partial}{\partial \alpha} P(\alpha; t) \right],
\]

where we have used the fact that \( \tilde{\beta}(t) = \tilde{\beta}(t) \). In particular, for the case of Brownian motion \( \alpha \) is simply the velocity of the particle. When \( \tilde{\beta}_{ij}(\alpha; t) = \tilde{\beta}(t) \delta_{ij} \), Eq. (18) agrees with the generalized Fokker-Planck equation found in [15].

B. Determination of the coefficients \( \tilde{\beta}_{ij} \)

The matrix elements \( \tilde{\beta}_{ij} \) can be determined from the coupled set of constitutive equations [12] and the evolution equations for the relaxation functions \( \chi_{ij}(\alpha_i(t)) \) defined by

\[
\chi_{ij}(\alpha_i(t)) = \int \alpha_i \alpha_j \rho(\alpha_i(\alpha_i(t)) d\alpha_i,
\]

where \( \rho(\alpha_i(\alpha_i(t)) \) is the reduced probability

\[
\rho(\alpha_i(\alpha_i(t)) = \int P(\alpha_i(\alpha_i(t)) d\alpha_1 ... d\alpha_{i-1} d\alpha_{i+1} ... d\alpha_n.
\]

The evolution equations for the \( \chi_{ij} \) are then derived by multiplying Eq. (16) by \( \alpha_i \) and integrating over it. One obtains the regression laws

\[
\frac{d}{dt} \chi_{ij} = -\tilde{\beta}_{ij}(t) X_i(\alpha(t)) \alpha_{ij},
\]

For arbitrary forces, Eq. (21) may be approximated by expanding \( \tilde{X}(\alpha) \) in \( \alpha \). The coefficients are then given in terms of a cumulant expansion of \( P(\alpha(t) | \alpha_i(t)) \). In the case of several variables, the remaining conditions for the \( \tilde{\beta}_{ij}(t) \)'s are obtained by comparison of the different terms entering the hierarchy of evolution equations for the moments of \( P(\alpha_i(\alpha_i(t)) \), which have been previously approximated, for times \( t \gg \tilde{\beta}_{ij}^{-1}(t) \), by the corresponding terms obtained from Eqs. (12) (see Refs. 27 and 33).

The simplest example concerns the case of a Brownian particle in which \( \alpha_1 = u \). When \( \tilde{\beta}(t) = \tilde{\beta}(t) u \) with \( u \) the unit matrix, Eq. (21) may be written as

\[
\tilde{\beta}_{uv}(t) = -\chi_{uv}(t) \frac{d}{dt} \chi_{uv}(t),
\]

where we have defined \( \chi_{uv}(t) \) by using Eq. (19). This formula was used in [15] to derive the linear non-Markovian Fokker-Planck equation. Notice that for Markovian processes \( \chi(\alpha(t)) \) decays exponentially. Then, by using Eq. (21), one may verify that \( \tilde{\beta} \) reduces to the friction coefficient \( \beta \).

III. THE GENERALIZED LANGEVIN EQUATION

Our purpose in this section is to present a new derivation of the generalized Langevin equation based on our previous formulation. We first start from the interpretation of the probability density \( P(\alpha_0(\alpha, t)) \) as an ensemble average of the density \( \tilde{\rho}(\alpha_0(\alpha, t)) \) in the \( \alpha \)-space, i.e., \( P(\alpha_0(\alpha, t)) = \langle \tilde{\rho}(\alpha_0(\alpha, t)) \rangle \). The actual value of that density differs then from \( P(\alpha_0(\alpha, t)) \) in the presence of fluctuations

\[
\delta \tilde{\rho}(\alpha_0(\alpha, t)) = \tilde{\rho}(\alpha_0(\alpha, t)) - \langle \tilde{\rho}(\alpha_0(\alpha, t)) \rangle.
\]

Consistently with this interpretation, used in the derivation of the Boltzmann-Langevin equation [31], Eq. (4) results after averaging the equation.
\[ \frac{\partial}{\partial t} \tilde{\rho}(\alpha | \alpha, t) = -\frac{\partial}{\partial \alpha} \cdot \Phi(\alpha | \alpha, \alpha, t), \quad (24) \]

with \( J(\alpha | \alpha, \alpha) = \langle \Phi^R(\alpha | \alpha, \alpha) \rangle \). The current \( \Phi^R(\alpha | \alpha, \alpha) \) splits up into systematic and random contributions in the form

\[ \Phi(\alpha, \alpha, t) = \langle \Phi^R(\alpha, \alpha; t) \rangle + \Phi^R(\alpha, \alpha; t). \quad (25) \]

The random part has zero mean and satisfies the fluctuation-dissipation relation

\[ \langle \Phi^R(\alpha, \alpha; t) \Phi^R(\alpha, \alpha'; t + \tau) \rangle = 2k_B T \tilde{\beta}(\alpha, \alpha'; \tau) P(\alpha | \alpha, t) \delta(\tau). \quad (26) \]

with the bracket denoting a stationary average and where we have taken into account Eq. (14). By substituting (12) into (25) and the result into (24), we obtain the fluctuating Fokker-Planck equation

\[ \frac{\partial}{\partial t} \tilde{\rho}(\alpha, t) = \int[k_B T \tilde{\beta}(\alpha, \alpha'; t) \cdot \frac{\partial}{\partial \alpha} \tilde{\rho}(\alpha, t) + \tilde{\beta}(\alpha(t)) X(\alpha(t)) \tilde{\rho}(\alpha(t), \alpha, t)]d\alpha' - \frac{\partial}{\partial \alpha} \cdot \Phi^R(\alpha | \alpha, \alpha, t), \quad (27) \]

whose average coincides with the generalized Fokker-Planck equation (14). In the Markovian case, Eq. (27) reduces to the Fokker-Planck-Langevin equation derived in (22).

The generalized Langevin equation can now be derived from the evolution equation of \( \alpha(t) \), obtained from Eq. (9), by using in Eq. (27) the slow variable approximation, and choosing the conditional probability \( \tilde{\rho}(\alpha | \alpha, t) = \delta(\alpha(t) - \alpha) \). After integrating by parts one obtains

\[ \frac{d}{dt} \alpha(t) = -B(\alpha(t)) + F^R(t), \quad (28) \]

where we have defined the nonlinear force term by

\[ B(\alpha(t)) = \bar{\beta}(\alpha(t)) X(\alpha(t)) - k_B T \frac{\partial}{\partial \alpha} \tilde{\beta}(\alpha(t)), \quad (29) \]

and the random force by \( F^R(t) = \int \Phi^R(\alpha, t) d\alpha \). Eq. (28) generalizes the Langevin equation used in Refs. (15) and (16) since it incorporates the general force term (29). If the process is Markovian, it reproduces the corresponding Langevin equation since \( \bar{\beta}(\alpha, t) = \beta(\alpha) \) and, by using \( \tilde{\rho}(\alpha | \alpha, t) = \delta(\alpha(t) - \alpha) \), one obtains \( \beta(\alpha(t)) = \int \beta(\alpha) \delta(\alpha(t) - \alpha) d\alpha \).

The fluctuation-dissipation theorem associated to Eq. (28) has been derived in the linear non-Markovian case (13):

\[ \langle F^R(t) F^R(t + \tau) \rangle = -\left( \frac{d}{d\tau} \bar{\beta}(\tau) \right) \langle \alpha(t) \alpha(t + \tau) \rangle, \quad (30) \]

whereas in the nonlinear Markovian case one has (32)

\[ \langle F^R(t) F^R(t + \tau) \rangle = \langle \alpha B(\alpha) + B(\alpha) \alpha \rangle \delta(\tau). \quad (31) \]

The last equation has been obtained for an arbitrary dependency of the stochastic force on \( \alpha \).

The case analyzed in (13), i.e. \( X(\alpha(t)) = \alpha(t) \), follows easily from our formalism. From Eqs. (28) and (29) one obtains

\[ \frac{d}{dt} \alpha(t) = -\bar{\beta}(t) \cdot \alpha(t) + F^R(t), \quad (32) \]

or equivalently to the generalized Langevin equation (1, 11)

\[ \frac{d}{dt} \alpha(t) = -\int_0^t \bar{\beta}(t - s) \alpha(s) ds + F^R(t), \quad (33) \]

where \( \bar{\beta}(t) \) is the memory function. To prove that equivalence, and following (13), we will first take the average of Eqs. (32) and (33). By using Laplace transforms, the solution of Eq. (33) is given by \( \alpha(t) = \chi(t) \alpha_0 \), where the relaxation function is \( \chi(t) = L^{-1} \{ (s + \beta(t))^{-1} \} \). Taking now the time derivative of \( \alpha(t) \), eliminating \( \alpha_0 \) and using the definition (22), we finally arrive at Eq. (32).
IV. BROWNIAN MOTION IN AN ANHARMONIC HEAT BATH

In this section, we will analyze the nonlinear dynamics of a Brownian degree of freedom in an anharmonic bath. The state variable will be in this case $\vec{\alpha} \equiv (\vec{r}, \bar{u})$, where $\vec{r}$ is a coordinate and $\bar{u}$ its conjugate velocity.

Let us consider a reference local equilibrium state characterized by the stationary probability density

$$P_0(\bar{u}, \vec{r}) = e^{\frac{\beta}{2m}[\mu_0 - \frac{1}{2}u^2 - \phi]},$$

where $\mu_0$ is a reference chemical potential per unit mass and $\phi(\vec{r})$ the potential per unit mass imposed on the system by the heat bath. For this system, the corresponding Gibbs equation is

$$\delta s = \frac{1}{T} \delta e + \frac{1}{T} \delta \rho^{-1} - \frac{1}{T} \int \mu \delta c d\bar{u}.$$  

Here $s$ and $e$ are the entropy and the internal energy per unit mass, respectively, $\rho$ the hydrostatic pressure, $c_\bar{u} = \frac{m p}{\rho}$ the Brownian mass fraction and $\rho \equiv \rho(\bar{u}_0, \vec{r}_0|\vec{r}, t)$ is defined through Eq. (20). By taking the total time derivative, $\frac{\partial}{\partial t} = \frac{\partial}{\partial t} + \vec{v} \cdot \nabla$, of Eq. (35) and using Eqs. (34) and (35), we arrive at the entropy production

$$\sigma = -\frac{m}{T} \int \left[ \tilde{J}_\bar{u} \cdot \frac{\partial \mu}{\partial \bar{u}} + \tilde{J} \cdot \nabla (\mu - \phi) + \tilde{J}_\phi \cdot \nabla \phi \right] d\bar{u}.$$  

The average velocity $\vec{v}$ is defined through the first moment of the probability density

$$\rho \vec{v}(\vec{r}, t) = m \int \bar{u} \rho(\bar{u}_0, \vec{r}_0|\bar{u}, \vec{r}, t) d\bar{u}.$$  

The entropy production $\sigma$ adopts the usual form in terms of flux-force pairs. The two first contributions result from the diffusion current in $\bar{u}$-space $\tilde{J}_\bar{u}$ and the current $\tilde{J} \equiv (\bar{u} - \vec{v}) P$ coming up when inertial effects are relevant. The average contributions arising from the pair $\tilde{J}_\phi$ and $\nabla \phi(\vec{r})$ vanish by virtue of Eq. (37), (38). The third contribution is genuine of the effect of the potential and introduces the current $\tilde{J}_\phi \equiv \tilde{J} P$. In the Markovian case, when external forces vanish, the second term on the right-hand-side of (38) contributes to the entropy flux, reproducing in this form the results of Ref. 22. The constitutive laws giving the currents $\tilde{J}_\bar{u}$, $\tilde{J}$ and $\tilde{J}_\phi$ in terms of the forces are, respectively

$$\tilde{J}_\bar{u} = -\tilde{\beta}_\bar{u}(t) \left\{ \bar{u} P + \frac{k_B T}{m} \frac{\partial P}{\partial \bar{u}} \right\} - \tilde{\beta}_{\bar{u}r}(t) \frac{k_B T}{m} \nabla P - \tilde{\beta}_{\bar{u}\phi}(t) \nabla \phi,$$

$$\tilde{J} = -\tilde{\beta}_r(t) \left\{ \bar{u} P + \frac{k_B T}{m} \frac{\partial P}{\partial \bar{u}} \right\} - \tilde{\beta}_{r\bar{u}}(t) \frac{k_B T}{m} \nabla P - \tilde{\beta}_{r\phi}(t) \nabla \phi,$$

and

$$\tilde{J}_\phi = -\tilde{\beta}_{\phi\bar{u}}(t) \left\{ \bar{u} P + \frac{k_B T}{m} \frac{\partial P}{\partial \bar{u}} \right\} - \tilde{\beta}_{\phi r}(t) \frac{k_B T}{m} \nabla P - \tilde{\beta}_{\phi \phi}(t) \nabla \phi,$$

where the Onsager coefficients have been defined consistently with Eq. (14). By substituting Eq. (38) into the corresponding continuity equation, one obtains the generalized Fokker-Planck equation describing the non-Markovian dynamics of the Brownian degree of freedom in the presence of arbitrary bounding forces

$$\frac{\partial P}{\partial t} + \nabla \cdot \bar{u} P = \frac{\partial}{\partial \bar{u}} \left\{ \tilde{\beta}_\bar{u}(t) \left[ \bar{u} P + \frac{k_B T}{m} \frac{\partial P}{\partial \bar{u}} \right] - \tilde{\beta}_{\bar{u}r}(t) \nabla P + \frac{k_B T}{m} \tilde{\beta}_{\bar{u}\phi}(t) \nabla \phi \right\},$$

where $\tilde{X}(\vec{r}) = -\nabla \phi$. In the linear case, it reduces to the corresponding one obtained through the conditional probability associated to the Langevin equation used in 13. As a consequence of the existence of local equilibrium in $\bar{u}$-space, $\tilde{\beta}_\bar{u}(t)$ multiplies both the drift and the diffusion terms entering (41). The presence of forces adds two terms that make the fluctuation-dissipation theorem not longer valid. For Markovian processes in which $\tilde{\beta}_\bar{u}(t) = \beta$
described by non-Markovian Fokker-Planck and Langevin equations, \([7]\) and \([8]\). The dissipation theorem \((44)\) is no longer valid. This fact occurs in systems exhibiting anomalous diffusion, which are Eqs. \((39)\), \((40)\) and \((42)\) must be found independently. Then, even in the absence of external forces, the fluctuation-averaging Eq. \((41)\) over \(\vec{u}\) and combining the resulting equations, we obtain the non-Markovian Smoluchowski equation for the density field \(\rho\)

\[
\frac{\partial \rho}{\partial t} = D(t) \nabla^2 \rho - \eta(t) \nabla \left( \rho \vec{X}(\vec{r}) \right),
\]

where we have defined the diffusion coefficient \(D(t)\) in terms of the generalized Einstein relation

\[
D(t) = \frac{k_B T}{m} \eta(t),
\]

from which it follows that the slow modes of non-Markovian systems satisfy a modified fluctuation-dissipation relation. For the particular case of a harmonic potential, \(\phi(\vec{r}) = \frac{1}{2} \omega \vec{r}^2\), where \(\omega\) is the characteristic frequency, Eqs. \((41)\) and \((43)\) reproduce the generalized Fokker-Planck and Smoluchowski equations derived in \([15]\) and \([14]\), respectively. Now, multiplying Eq. \((43)\) by \(\vec{u}\) and integrating over it, we obtain the evolution equation of the average velocity \(\vec{u}\)

\[
\rho \frac{D \vec{u}}{Dt} = -\vec{\beta}_{\vec{u} \vec{u}}(t) \left[ \rho \vec{u} - \eta(t) \rho \vec{X}(\vec{r}) + D(t) \nabla \rho \right],
\]

where we have assumed that the pressure tensor of the ideal Brownian gas is given by \(\vec{P} = \frac{k_B T}{m} \rho \vec{1}\). For times satisfying \(\tau \gg \vec{\beta}_{ij}\), we have imposed that Eq. \((45)\) must coincide with Eq. \((42)\), obtaining the conditions \(\vec{\beta}_{\vec{u} \vec{u}}(t) = \vec{\beta}_{\vec{u} \vec{u}}(t) \eta(t)\) and \(\vec{\beta}_{\vec{u} \vec{r}}(t) = \vec{\beta}_{\vec{u} \vec{u}}(t) - 1\), consistent with the corresponding ones for the Markovian case. \(\vec{\beta}_{\vec{u} \vec{u}}(t)\) and \(\eta(t)\) may be obtained by using the regression law \([21]\) and Eqs. \((11)\) and \((13)\).

When local equilibrium in \(\vec{r}\)-space is not fulfilled, the coefficients appearing in the diffusion and drift terms of Eqs. \((39)\), \((40)\) and \((42)\) must be found independently. Then, even in the absence of external forces, the fluctuation-dissipation theorem \([14]\) is no longer valid. This fact occurs in systems exhibiting anomalous diffusion, which are described by non-Markovian Fokker-Planck and Langevin equations, \([7]\) and \([8]\).

### V. Ratchet Effect Induced by Onsager Couplings

In this section, we will apply our formalism to show a new manifestation of the ratchet effect which originates from the Onsager coupling of the probability current and a periodic thermodynamic force, when fluctuations are rectified by an external asymmetric potential. We will show that in the scale considered the non-Markovian dynamics makes the ratchet effect more pronounced.

The continuity equation in the presence of external forces takes the form

\[
\frac{\partial P}{\partial t} + \nabla \cdot \vec{u} P + \vec{F} \cdot \frac{\partial P}{\partial \vec{u}} = -\frac{\partial}{\partial \vec{u}} \cdot \vec{J}_\vec{u},
\]

where the external force per unit mass is \(\vec{F}(\vec{r}) = -\nabla V(\vec{r})\), where \(V(\vec{r})\) represents the ratchet potential. In the present case, we will consider that the probability density of the reference state is given by Eq. \((89)\) with \(\phi(\vec{r}) = 0\).

Inhomogeneities in the temperature of the bath induce a heat flux \(\vec{J}_q\) whose appearance modifies the entropy production of the system. In this case, the Gibbs entropy postulate \([10]\) and the Gibbs equation \([35]\) must be complemented with the balance equation for the internal energy \(e\)

\[
\frac{De}{Dt} = -\nabla \cdot \vec{J}_q,
\]

where viscous effects have been neglected. By considering the Gibbs-Duhem relation \([30]\), the entropy production can be written in the form

\[
\sigma = -\vec{J}_q^* \cdot \frac{1}{T} \nabla T - \frac{m}{T} \int \vec{J}_\vec{u} \cdot \frac{\partial \mu}{\partial \vec{u}} d\vec{u},
\]

where \(\vec{J}_\vec{u} = \frac{k_B T}{m} \rho \vec{1}\) and \(\rho \vec{1}\) is the density of the reference state. The result is the energy equation given by Eq. \((39)\) with \(\phi(\vec{r}) = 0\).
where the modified heat flow \( \vec{J}^*_{q} \) is given by
\[
\vec{J}^*_{q} = \vec{J}_{q} - \frac{1}{2} m \int u^2 \vec{J} \, du. \tag{49}
\]

The second term on the right-hand-side of Eq. (49) represents a local flow of kinetic energy.

The diffusion current \( \vec{J}_{d} \) is, according with Onsager theory coupled to the temperature gradient and is given by
\[
\vec{J}_{d} = -\tilde{\beta}_{\vec{u}\vec{a}}(t) \left\{ \vec{u} \vec{P} + \frac{k_B T}{m} \frac{\partial \vec{P}}{\partial \vec{u}} \right\} - \tilde{\beta}_{\vec{T}\vec{a}}(t) \vec{P} \nabla T, \tag{50}
\]

Similarly, the heat current can be formulated as
\[
\vec{J}^*_{q} = -\tilde{\beta}_{TT}(t) \nabla T - \tilde{\beta}_{T\vec{a}}(t) \rho \vec{v}, \tag{51}
\]

where \( \tilde{\beta}_{TT}(t) \equiv \frac{L_{TT}(t)}{\beta} \), and the coupling coefficient \( \tilde{\beta}_{T\vec{a}} \) has been defined accordingly with Eq. (17). By substituting Eq. (50) into the corresponding continuity equation for the probability density, we obtain the generalized Fokker-Planck equation
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{u} \rho + \vec{F} \cdot \frac{\partial \rho}{\partial \vec{u}} = \frac{\partial}{\partial \vec{u}} \left\{ \tilde{\beta}_{\vec{u}\vec{a}}(t) \left[ \vec{u} \vec{P} + \frac{k_B T}{m} \frac{\partial \vec{P}}{\partial \vec{u}} + \tilde{\beta}_{\vec{T}\vec{a}}(t) \frac{\vec{P} \nabla T}{T} \right] \right\}, \tag{52}
\]

which describes the transport of a Brownian particle in an thermally inhomogeneous environment.

By multiplying Eq. (52) by \( \vec{u} \) and integrating over it, we obtain the corresponding evolution equation for the momentum
\[
\rho \frac{D \vec{v}}{D t} = -\tilde{\beta}_{\vec{a}\vec{a}}(t) [\rho \vec{v} + D(t) \nabla \rho + D_T(t) \rho \nabla T] + \rho \vec{F}(\vec{r}), \tag{53}
\]

where \( \tilde{\beta}_{\vec{a}\vec{a}}(t) \) has been given in Eq. (22) and we have defined the diffusion coefficient \( D(t) = \frac{k_B T}{m} \tilde{\beta}_{\vec{a}\vec{a}}^{-1}(t) \) and the thermal diffusion coefficient \( D_T(t) = \frac{D(t)}{\beta} \left( 1 + \frac{m}{k_B T} \tilde{\beta}_{\vec{T}\vec{a}}(t) \right) \). For convenience, we will assume that \( D(t) \) and \( D_T(t) \) will be only functions of time. The diffusion current \( \vec{J}_{d} \) is obtained from Eq. (53) at times \( t \gg \tilde{\beta}_{\vec{a}\vec{a}}^{-1}(t) \). By following the steps indicated in Sec. 4, we arrive at the generalized Smoluchowski equation
\[
\frac{\partial \rho}{\partial t} = D(t) \nabla^2 \rho + D_T(t) \nabla \cdot (\rho \nabla T) - \tilde{\beta}_{\vec{a}\vec{a}}^{-1}(t) \nabla \cdot \left[ \rho \vec{F}(\vec{r}) \right], \tag{54}
\]

where memory effects enter the equation through the time dependence of \( D(t) \), \( D_T(t) \) and \( \tilde{\beta}_{\vec{a}\vec{a}}(t) \). Since in practice the temperature inhomogeneities originated by density gradients are negligible \( \tilde{\beta}_{\vec{a}\vec{a}}(t) \), by substituting the diffusion current, implicit in Eq. (51), and Eqs. (49) and (51) into (47), we arrive at the heat conduction equation
\[
c_v \frac{\partial T}{\partial t} = \lambda_{eff}(t) \nabla^2 T, \tag{55}
\]

where \( c_v \) is the heat capacity. We have used the relation, \( e = c_v T \) and defined the effective heat conduction coefficient \( \lambda_{eff}(t) = \tilde{\beta}_{TT}(t) \left[ 1 + \rho D_T(t) \tilde{\beta}_{\vec{T}\vec{a}}(t) \right] \). To obtain Eq. (55) we have also neglected contributions arising from the kinetic energy flow \( \vec{F} \), and assumed temperature gradients such that \( \left( \frac{\partial \nabla T}{l_0} \right)^2 \ll 1 \), where \( l_0 \) is a characteristic length of the bath. For \( \tilde{\beta}_{TT}(0) \) large enough \( (\sim 10^4 \text{gr cm s}^{-3} \text{K}^{-1}) \) and \( D_T(0) \), \( \tilde{\beta}_{T\vec{a}}(0) \ll 1 \), \( \lambda_{eff} \) is practically constant in first approximation.

To illustrate the ratchet effect, we consider the case of a Brownian particle moving in a bath, filling the space \( x > 0 \), in which a periodic temperature gradient is established when \( T(0, t) = T_0[1 + \cos(\omega t)] \). This situation may be accomplished when the particle to the wall is smaller than the wave length of the thermal waves. In such a case the spatial dependence in the propagating wave
\[
T(x, t) = T_0 \left[ 1 + e^{-kx} \cos(kx - \omega t) \right], \tag{56}
\]

solution of Eq. (55), can be neglected. Here \( \omega \) is a frequency and \( k = (\omega c_v / 2 \lambda_{eff})^{1/2} \) a wave number. The temperature gradient is then given by \( \nabla T = kT_0[\sin(\omega t) - \cos(\omega t)] \). This approximation is valid for values of the parameters
indicated in the figure captions, all of them accessible in experiments. The particle in turn is under the influence of the asymmetric potential (see Fig. 1). We will assume that it undergoes anomalous diffusion with $D(t) \sim t^{\gamma}$ and $\tilde{\beta}(t) \sim t^{-\frac{1}{2}}$. This particular dependence has recently been observed for the Brownian motion of a particle inside an eukaryotic cell [6]. The diffusion coefficient $D(t)$ has been obtained through the time derivative of the mean square displacement measured in [9], and $\tilde{\beta}(t)$ by using Eq. (21). The thermal diffusion coefficient $D_T(t)$ is then determined by assuming that the Soret coefficient $S_T = \frac{D_T(t)}{D(0)}$ is constant in first approximation. According with experimental results [36], we will consider that $D(0) \sim 10^{-7} \text{cm}^2 \text{s}^{-1}$ and that $S_T \sim 10^{-1} \text{K}^{-1}$. Then, by using $\rho(x, t) = \delta(x(t) - x)$ in Eq. (21), after integrating over the system volume we obtain the evolution equation for the position of the particle

$$\frac{d^2 x(t)}{dt^2} + \tilde{\beta}(t) \frac{dx(t)}{dt} = F(x(t)) - \tilde{\beta}(t) D_T(t) \frac{\partial T}{\partial x}(x = x(t)) + F_R(t).$$

(57)

The inertia term is maintained since non-Markovian effects arise at short time scales.

Positions and velocities of the Brownian particle have been determined from this equation by using a fourth order Runge-Kutta method. In Fig. 2, we show the displacement as a function of time for a given initial condition and a time periodic force. After a transient regime determined by $\tilde{\beta}(t)$, in the non-Markovian case the current, proportional to the slope of the curve, becomes practically constant. The average motion has the same frequency as the time periodic force.

In Fig. 3, we represent average displacements for different values of the parameters. In curves a) and b) the strength of the potential and the frequency of temperature gradient have been used to control the magnitude of the current. We have verified that no net current appears when the potential is symmetric. As a consequence of the fact that the damping coefficient decreases with time, we may conclude that, under similar conditions, the non-Markovian system is more efficacious in rectifying the motion than the Markovian one.

VI. DISCUSSION

In this paper, we have proposed a new method to derive the generalized Fokker-Planck equation describing the dynamics of systems when memory effects are relevant. Our formalism is able to derive kinetic equations from the probability density conservation law by providing expressions for the probability current obtained from the entropy production in phase space. It permits to incorporate in a simple way basic ingredients proper of systems outside equilibrium as the presence of external forces and of inhomogeneities in the bath.

We have presented two applications. In the first one, we have discussed the non-Markovian Brownian motion in a bath exerting a force on the Brownian particle [12], [13]. The Fokker-Planck and Smoluchowski equations have been derived for an unspecified force by avoiding the difficulties inherent to the habitual method, obtaining them from the corresponding Langevin equation. Our method relates the validity of the fluctuation-dissipation theorem to the existence of local equilibrium in the space of the mesoscopic variables. An example in which this feature becomes manifest is the case of anomalous diffusion [7], [8]. In the second example, we have analyzed the role played by the presence of inhomogeneities in the bath, due to an imposed temperature gradient, in nonlinear transport. We have found a new ratchet effect which originates from the cooperation of a thermodynamic periodic force with the nonlinear potential. The positiveness of the entropy production imposes restrictions on the values of the parameters entering mathematical models.

These results confirm the usefulness of our method which offers a very promising framework in the study of systems operating at the mesoscale for which the presence of nonlinearities, the participation of many degrees of freedom and the influence of inhomogeneities in the environment become a common feature of the dynamics.

VII. ACKNOWLEDGMENTS

We want to acknowledge Victor Romero-Rochín, D. Reguera, A. Pérez-Madrid, J. M. Vilar, I. Sokolov and M. Boguny a for fruitful discussions. I.S.H. acknowledges UNAM-DGAPA for economic support. This work was partially supported by DGICYT of the Spanish Government under Grant No. PB2002-01267.

[1] R. Zwanzig, Nonequilibrium Statistical Mechanics, (University Press, Oxford, 2001).
[2] K. Ibuki and M. Ueno, J. Chem. Phys. 106, 10113 (1997).
[3] P. Hanggi, Rev. Mod. Phys. 62, 251 (1990).
[4] D. Reguera and J. M. Rubí, Phys. Rev. E 64, 061106 (2001).
[5] P. Reimann, Phys. Rep. 361, 57 (2002).
[6] L. Ibarra-Bracamontes and V. Romero-Rochín, Phys. Rev. E 56, 4048 (1997).
[7] K. G. Wang and M. Tokuyama, Physica A 265, 341 (1999).
[8] R. Morgado, F. A. Oliveira, G. G. Batrouni and A. Hansen, Phys. Rev. Lett. 89 100601 (2002).
[9] A. Caspi, R. Granek and M. Elbaum, Phys. Rev. E 66 011916 (2002).
[10] M. Kac and J. Logan, in Fluctuation Phenomena, edited by E. W. Montroll and J. L. Lebowitz (North-Holland, Amsterdam, 1987).
[11] H. Mori, Prog. Theor. Phys. 33, 423 (1965).
[12] R. Zwanzig, Phys. Rev. 124 983 (1961).
[13] M. Tokuyama and H. Mori, Prog. Theor. Phys. 55, 411 (1976).
[14] S. Okuyama and D. W. Oxtoby, J. Chem. Phys. 84, 5824 (1986); S. Okuyama and D. W. Oxtoby, J. Chem. Phys. 84, 5830 (1986).
[15] S. A. Adelman, J. Chem. Phys. 64, 124 (1976).
[16] R. I. Cukier and K. E. Shuler, J. Chem. Phys. 57, 302 (1972).
[17] P. Hanggi and P. Jung, Adv. Chem. Phys. 89, 239 (1995).
[18] I. M. Sokolov, Phys. Rev. E 66, 041101 (2002).
[19] N. G. van Kampen, Stochastic processes in physics and chemistry, (North-Holland, Amsterdam, 1992).
[20] T. Renger and R. A. Marcus, J. Chem. Phys. 116, 9997 (2002).
[21] J. M. Rubí, P. Mazur, Physica A 250, 253 (1998).
[22] J. M. Rubí, unpublished; P. Mazur, Physica A 274, 491 (1999).
[23] J. M. Rubí and A. Pérez-Madrid, Physica A 264, 492 (1999).
[24] J. M. Rubí and F. Mazur, Physica A 276, 477 (2000).
[25] J. M. G. Vilar and J. M. Rubí, Proc. Natl. Acad. Sci. 98, 11081 (2001).
[26] A. Pérez-Madrid, J. M. Rubí, P. Mazur, Physica A 212, 231 (1994).
[27] I. Santamaría-Holek, D. Reguera and J. M. Rubí, Phys. Rev. E 63 051106 (2001).
[28] I. Pagonabarraga, A. Pérez-Madrid and J. M. Rubí, Physica A 237, 205 (1997).
[29] D. Reguera, J. M. Rubí and L. L. Bonilla, in: Mathematical Modeling for Polymer Processing, V. Capasso (Springer-Verlag, Berlin, 2002).
[30] S. R. de Groot, P. Mazur, Non-equilibrium Thermodynamics (Dover, New York, 1984).
[31] J. W. Dufty, J. M. Rubí, Phys. Rev. A 36, 222 (1987).
[32] N. G. van Kampen, Phys. Lett. A 50, 237 (1974).
[33] G. Wilemski, J. Stat. Phys. 14, 153 (1976).
[34] M. Bixon and R. Zwanzig, Phys. Rev. 187, 267 (1969).
[35] P. Mazur, Phys. Rev. A 45 8957 (1992).
[36] K. J. Zhang, M. E. Briggs, R. W. Gammon and J. V. Sengers, J. Chem. Phys. 111, 2270 (1999).
FIG. 1: Ratchet potential: $V(x) = -\frac{V_0}{\pi} \left[ \sin(9\pi x) + \frac{1}{2} \sin(18\pi x) \right]$; $V_0$ is a constant.

FIG. 2: Position of the Brownian particle versus time. Dotted lines represent different realizations of the noise, whereas the solid line corresponds to the average displacement of the Brownian particle for 20 realizations of the noise in the non-Markovian case. The dashed line represents the average position in the Markovian case. The values of the different parameters are: $F(0) = 1 \times 10^{-3} gr \text{ cm}^2 \text{s}^{-2}$, $\nabla T \simeq 1.3 K \text{cm}^{-1}$, $\omega = 9 \times 10^{-3} \text{s}^{-1}$, $k \simeq 2.1 \times 10^{-2} \text{cm}^{-1}$ and $m \simeq 10^{-4} gr$. 
FIG. 3: Average displacements for different initial positions, frequencies and strengths of the temperature gradient with $F(0) = 6.8 \times 10^{-3} \text{gr cm}^{-2} \text{s}^{-2}$, and $m \simeq 10^{-2} \text{gr}$. In cases a) and c): $\nabla T \simeq 1.3 \text{K cm}^{-1}$ and $\omega = 9 \times 10^{-3} \text{s}^{-1}$ and $k \simeq 2.1 \times 10^{-3} \text{cm}^{-1}$. In cases b) and d): $\nabla T \simeq 0.2 \text{K cm}^{-1}$, $\omega = 6 \times 10^{-4} \text{s}^{-1}$ and $k \simeq 1 \times 10^{-4} \text{cm}^{-1}$. Curves a and b correspond to non-Markovian cases, whereas c and d result from Markovian dynamics.