Fluctuation theorems for systems under Fokker-Planck dynamics

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(Received 18 August 2008; published 5 January 2009)

We study Brownian motion driven with both conservative and nonconservative external forces. By using the thermodynamic approach of the theory of Brownian motion we obtain the Fokker-Planck equation and derive expressions for the fluctuation theorem in local equilibrium and in quasiequilibrium. In local equilibrium the expressions we obtain coincide with previous results.

DOI: 10.1103/PhysRevE.79.011101 PACS number(s): 05.70.Ln, 05.40.Jc

I. INTRODUCTION

Since the first formulation of a fluctuation theorem (FT) [1] there has been an increasing interest in this subject. Further contributions [2] have broadened the scope of the physical situations where a FT arises. An extensive account of the literature can be found in Refs. [3,4]. The search for certain symmetries or rules in the different systems or situations we can find far from equilibrium is the major element of interest in the different expressions of the FT. It seems that the FT plays a role similar to the partition function in equilibrium statistical mechanics.

These theorems are concerned with the relation between nonequilibrium measurements and certain thermodynamic magnitudes such as entropy, heat, and free energies [4]. They involve pairs of nonequilibrium trajectories in the phase space, one and its reverse, and their corresponding probabilities.

Our contention here is to clarify the thermodynamical roots of the FT, determining their scope for systems with Fokker-Planck dynamics. We will obtain the expression of the FT in local equilibrium and in states of quasiequilibrium.

The paper is organized as follows. In Sec. II, we perform the thermodynamic analysis of an ensemble of noninteracting Brownian particles under the action of both conservative and nonconservative forces, deriving the Fokker-Planck equation. In Sec. III, we derive the configurational relaxation equations when the system is in local equilibrium and in quasiequilibrium and obtain the parameters that characterize these states. Section IV is devoted to the derivation of the FTs. Finally, in Sec. V we formulate our main conclusions.

II. THERMODYNAMIC ANALYSIS

Consider an ensemble of noninteracting Brownian particles subjected to a potential field $V(x)$, which is initially in equilibrium with a heat bath at temperature T_0. In the canonical ensemble, the system is distributed according to

$$\rho_{eq} \sim \exp\left[-\frac{H(\Gamma)}{k_B T_0}\right], \tag{1}$$

where $H(\Gamma)=(1/2)mu^2+mV(x)$ is the Hamiltonian and $\Gamma=(x,u)$ represents a point of the one-particle phase space spanned by the position x and the velocity u of the particle.

Let us assume that at a certain moment ($t=0$), a nonconservative force $f(t)$ is applied on the system. Then, the system evolves in time and can be described by using the nonequilibrium probability density $\rho(\Gamma,t)$ and the nonequilibrium entropy of the system, which is given through the Gibbs entropy postulate [5,6]

$$S(t) = -k_B \int \rho(\Gamma,t) \ln \frac{\rho(\Gamma,t)}{\rho_{eq}} d\Gamma + S_{eq}, \tag{2}$$

where S_{eq} is the equilibrium entropy of the Brownian particles plus the bath. The variations in the probability density $\rho(\Gamma,t)$, imply changes in the nonequilibrium entropy, which can be obtained from Eq. (2),

$$\delta S = -\frac{1}{T_0} \int \mu(\Gamma,t)\, \delta\rho(\Gamma,t) d\Gamma. \tag{3}$$

The thermodynamically conjugated nonequilibrium chemical potential $\mu(\Gamma,t)$ of the density $\rho(\Gamma,t)$ has been defined by

$$\mu(\Gamma,t) = k_B T_0 \ln \frac{\rho(\Gamma,t)}{\rho_{eq}} + \mu_{eq}, \tag{4}$$

where μ_{eq} is the equilibrium chemical potential. Equation (3) is similar to the Gibbs' equation of thermodynamics [7–9].

After the force $f(t)$ has been applied, the variation in time of $\rho(\Gamma,t)$ is given by the generalized Liouville equation

$$\frac{\partial}{\partial t}\rho(\Gamma,t) + V_\Gamma(\Gamma,t)\nabla_\Gamma \rho(\Gamma,t) = -\frac{\partial}{\partial u}\rho(\Gamma,t) f(t) - \frac{\partial}{\partial u} J(\Gamma,t), \tag{5}$$

where $V_\Gamma(\Gamma,t)=(u,-\nabla V(x))$ is the phase-space velocity corresponding to the Hamiltonian flow, $\nabla_\Gamma=(\nabla,\partial/\partial u)$ with ∇ the spatial derivative and $J(\Gamma,t)$ constitutes a diffusion current in phase space. By using Eqs. (3) and (5) and performing partial integrations assuming that the currents vanish at boundaries, one obtains that the total rate of change of the nonequilibrium entropy (2) is

$$\frac{dS}{dt} = -\frac{1}{T_0}\langle f(t)u\rangle - \frac{1}{T_0}\int J(\Gamma,t)\frac{\partial}{\partial u}\mu(\Gamma,t)d\Gamma, \tag{6}$$

where the quantity $\langle f(t)u\rangle = \int f(t)u\rho(\Gamma,t)d\Gamma$ constitutes the power dw/dt supplied by the external force $f(t)$, which is dissipated as heat into the bath. Thus, assuming that [20]

$$\rho(\Gamma,t) = \delta[x(t)-x]\delta[\dot{x}(t)-u], \tag{7}$$

we can write

$$\frac{dw}{dt} = f(t)\dot{x}(t), \tag{8}$$

where dw is the amount of work done on the system in a time dt by the external force f.

The second term on the right-hand side of Eq. (6), represents the change of the entropy due to a gradient of the chemical potential and therefore constitutes the entropy production σ due to diffusion in the phase space

$$\sigma = -\frac{1}{T_0}\int J(\Gamma,t)\frac{\partial}{\partial u}\mu(\Gamma,t)d\Gamma. \tag{9}$$

This quantity accounts for the internal dissipative processes and it is assumed, according to the second law of thermodynamics, that it does not take negative values: $\sigma \geqslant 0$ [6].

Hence, by introducing the exchange of entropy due to the interactions with the environment as

$$\frac{d_{ext}S}{dt} = \frac{1}{T_0}\frac{dw}{dt}, \tag{10}$$

which has an undefined sign, we finally obtain

$$\frac{dS}{dt} = \frac{d_{ext}S}{dt} + \sigma, \tag{11}$$

which expresses the entropy balance between the exchange of entropy with the bath and the entropy generated in the irreversible processes established in the system when removed from its equilibrium state.

To completely characterize the stochastic dynamics of the system, we must find the expression of the current $J(\Gamma,t)$. According to Eq. (9) and following the rules of nonequilibrium thermodynamics [6], this can be achieved by establishing a linear relation between the current $J(\Gamma,t)$ and their conjugated thermodynamic force $\partial\mu/\partial u$. This relation can be expressed by

$$J(\Gamma,t) = -\frac{L}{T_0}\frac{\partial}{\partial u}\mu(\Gamma,t), \tag{12}$$

where L is a phenomenological coefficient. By using the expression of the chemical potential given through Eq. (4) in Eq. (12), one obtains

$$J(\Gamma,t) = -\gamma\left(\frac{k_BT_0}{m}\frac{\partial}{\partial u} + u\right)\rho(\Gamma,t), \tag{13}$$

where we have identified $mL/\rho T_0 = \gamma$, with γ being the friction coefficient per unit mass of the Brownian particles. By substituting now Eq. (13) into Eq. (5) we obtain

$$\frac{\partial}{\partial t}\rho = -\nabla u\rho + \frac{\partial}{\partial u}[\nabla V(x) - f(t)]\rho + \gamma\frac{\partial}{\partial u}\left(\frac{k_BT_0}{m}\frac{\partial}{\partial u} + u\right)\rho, \tag{14}$$

which is the Fokker-Planck (or Klein-Kramers) equation governing the time evolution of the nonequilibrium probability density $\rho(\Gamma,t)$ in the presence of a conservative potential $V(x)$ and a nonconservative force $f(t)$.

III. LOCAL EQUILIBRIUM AND QUASIEQUILIBRIUM

When the dynamics of the system can be characterized by two or more time scales, its long-time behavior can manifest different dynamical regimes depending on the existence (or not) of a local equilibrium state. Here, we will show the conditions that must be satisfied by the system in order to reach a local equilibrium state and how, when these conditions are not satisfied, the system enters in a quasiequilibrium state leading to a different long-time dynamical behavior.

Assuming the presence of two time scales in which u is the fast variable, the dynamical processes associated to configurational changes in the system are related to the slow variable x. Thus, the long-time behavior of the system can be more conveniently described by writing [10]

$$\rho(\Gamma,t) = \phi_x(u,t)n(x,t), \tag{15}$$

where $\phi_x(u,t)$, is a conditional probability density and $n(x,t) = \int \rho(\Gamma,t)du$ is a reduced probability density in x space, which evolves according to

$$m\frac{\partial}{\partial t}n(x,t) = -\nabla\int mu\rho(\Gamma,t)du. \tag{16}$$

This equation can be obtained by integration over u of Eq. (14) and thus implicitly defines the current $J(x,t) = \int mu\rho(\Gamma,t)du$.

(i) *Local equilibrium*. In order to achieve a local equilibrium state, the system must satisfy that $\phi_x(u,t) \sim \exp(-mu^2/2k_BT_0)$, i.e., that the distribution of velocities is given by the equilibrium Maxwellian. In this case, by multiplying Eq. (14) by mu and performing a partial integration over u space, we obtain the evolution equation for $J(x,t)$

$$\frac{\partial}{\partial t}J(x,t) + \gamma J(x,t) = -mn(x,t)[\nabla V(x) - f(t)] - k_BT_0\nabla n(x,t). \tag{17}$$

For times $t \gg \gamma^{-1}$ Eq. (17) gives

$$J(x,t) \simeq -\gamma^{-1}\{mn(x,t)[\nabla V(x) - f(t)] + k_BT_0\nabla n(x,t)\}. \tag{18}$$

In order that our results be valid, here and henceforth we will assume that the time scale over which $f(t)$ varies should be larger than γ^{-1}. Otherwise, the time derivative of Eq. (17) must be taken into account. Once we substitute Eq. (18) into Eq. (16) we obtain the Smoluchowski equation in the presence of external forces

$$\frac{\partial}{\partial t}n(x,t)=D\,\nabla\left\{\frac{m}{k_BT_0}n(x,t)[\nabla V(x)-f(t)]+\nabla n(x,t)\right\}, \tag{19}$$

with $D=k_BT_0/m\gamma$ being the diffusion coefficient. The Smoluchowski equation (19) admits a local equilibrium solution given by

$$n_{l\ eq}(x;f)\sim\exp\left[-\frac{m}{k_BT_0}\int^x[\nabla V(x')-f(t)]dx'\right]. \tag{20}$$

Hence, the nonequilibrium entropy given through Eq. (2) reduces to

$$S(t)=-k_B\int n(x,t)\ln\frac{n(x,t)}{n_{l\ eq}}dx+S_{l\ eq}(t), \tag{21}$$

where $S_{l\ eq}(t)=-k_B\int n(x,t)\ln[n_{l\ eq}(x;f)/n_{eq}]dx+S_{eq}$ is the local equilibrium entropy. It is important to emphasize that through Eq. (20), the local equilibrium state is characterized by a probability density containing the temperature of the bath T_0.

(ii) *Quasiequilibrium*. Released from the restrictive condition of local equilibrium, instead of obtaining the expression (18) for the diffusion current $J(x,t)$, at long time we find

$$J(x,t)=-\gamma^{-1}\{mn(x,t)[\nabla V(x)-f(t)]+k_B\nabla n(x,t)T(x,t)\}, \tag{22}$$

where the local temperature of the system $T(x,t)$ has been defined through a generalization of the equipartition theorem as the second moment of $\phi_x(u,t)$ [11,12]

$$k_BT(x,t)=m\int u^2\phi_x(u,t)du. \tag{23}$$

The current given in Eq. (22) can be rewritten as

$$J(x,t)=-D(x,t)\left[\nabla n(x,t)+\frac{mn(x,t)}{k_BT(x,t)}[\nabla\Phi(x,t)-f(t)]\right], \tag{24}$$

where $\Phi(x,t)=V(x)+k_BT(x,t)$ is an effective potential and $D(x,t)=k_BT(x,t)m^{-1}\gamma^{-1}$ is the bare effective diffusion coefficient. Hence, by substituting Eq. (24) into Eq. (16) we obtain

$$\frac{\partial}{\partial t}n(x,t)=\nabla\left\{D(x,t)\left[\nabla n(x,t)+\frac{mn(x,t)}{k_BT(x,t)}[\nabla\Phi(x,t)-f(t)]\right]\right\}. \tag{25}$$

The diffusion equation (25) given above admits a quasiequilibrium solution

$$n_{eq}(x,f)\sim\exp\left[-\int^x\frac{m}{k_BT(x',f)}[\nabla\Phi(x',f)-f(t)]dx'\right], \tag{26}$$

obtained when the probability current instantaneously vanishes.

An estimation of the temperature T independent of the position can be obtained by first deriving the evolution equation of the temperature field $T(x,t)$. Thus, by multiplying Eq. (14) by mu^2 and integrating in u one has

$$\frac{1}{2}k_B\frac{\partial}{\partial t}n(x,t)T(x,t)=-\nabla n(x,t)h(x,t)-[\nabla V(x)-f(t)]J(x,t)-\gamma k_Bn(x,t)[T(x,t)-T_0], \tag{27}$$

where we have defined the heat flow as

$$h(x,t)=\frac{1}{2}m\int u^3\phi_x(u,t)du. \tag{28}$$

For times $t\gg\gamma^{-1}$, Eq. (27) reduces to

$$k_Bn(x,t)[T(x,t)-T_0]=-\gamma^{-1}\nabla n(x,t)h(x,t)-\gamma^{-1}[\nabla V(x)-f(t)]J(x,t). \tag{29}$$

In the particular case of local equilibrium $J(x,t)=h(x,t)=0$, which would lead to $T(x,t)=T_0$. If, on the other hand, we substitute the expression of $J(x,t)$ given through Eq. (22) into Eq. (29), up to order γ^{-2} we obtain

$$\begin{aligned}k_Bn(x,t)[T(x,t)-T_0]={}&-\gamma^{-1}\nabla n(x,t)h(x,t)\\&+\gamma^{-2}\{mn(x,t)[\nabla V(x)-f(t)]^2\\&-k_BT_0[\nabla V(x)-f(t)]\nabla n(x,t)\},\end{aligned} \tag{30}$$

which after performing an average over x space leads to

$$k_BT(t)\simeq k_BT_0+m\gamma^{-2}\langle\nabla V(x)-f(t)\rangle^2. \tag{31}$$

Here $T(t)=\langle T(x,t)\rangle$ and we have neglected a term $k_BT_0\langle\nabla[\nabla V(x)-f(t)]\rangle$. Relation (31) means that for sufficiently large gradients and forces applied on the system, its temperature will, in general, differ from that of the heat bath. On the contrary, it must be emphasized that for small gradients and forces the quasiequilibrium temperature $T(t)$ given by Eq. (31) reduces to the bath temperature T_0 implying that the system reaches local equilibrium. This is precisely the hypothesis of small forces and gradients, which is usually behind the local equilibrium hypothesis [13]. A correction to the temperature similar to Eq. (31) has been previously obtained in a different context in Ref. [11].

IV. FLUCTUATION THEOREMS FOR LOCAL EQUILIBRIUM AND QUASIEQUILIBRIUM

The transition from the initial state x_0 to the final state x_t, can be modeled by a set of N-coupled unimolecular chemical reactions having x as their reaction coordinate. This approach is based on the fact that the kinetic or rate equation corresponding to a unimolecular chemical reaction represents a gain and loss process, which can be interpreted probabilistically as the result of the balance of two opposite probability currents.

To compute the ratio between the forward and reverse probabilities of a path between x_0 and x_t, we define a partition $t_1,t_2,\ldots\ldots,t_{N+1}$ of the entire time interval $[0,t]$, with $t_1=0$ and $t_{N+1}=t$, which divides the process in N steps. The initial state for these reactions coincides with x_0 and the final state with x_t, while the intermediate states correspond with $x_{t_2}, x_{t_3}, \ldots$. Thus, given the probability n_i of being in the state x_{t_i} at time t_i, the elementary kinetics is given by the set of equations

$$\frac{d}{d\tau} n_i = J^i - J^{i-1}, \quad i = 1, \ldots, N+1, \tag{32}$$

where

$$J^i = v^R_{i+1,i} n_{i+1} - v^F_{i,i+1} n_i, \quad J^0 = J^{N+1} = 0. \tag{33}$$

Here, the symbols F and R stand for the forward and reverse transitions. On the other hand, it must be stressed that the values of the rate constants $v^{F,R}_{ij}(\tau)$ depend on whether the system is in a local equilibrium or a quasiequilibrium state. Therefore, since the reaction constant $r_{i,j}$ characterizing the asymmetry of the reversible reaction is defined by the ratio between the rate constants, this will depend also on the state of the system. According to its definition, $r_{i,j}$ gives us the ratio of the probabilities of the forward and backward reactions.

In the quasistationary state $J^1 = J^2 = \cdots = J^N = 0$ and from Eqs. (32) and (33) we find

$$\lim_{\tau \to \infty} \frac{n_{i+1}(\tau)}{n_i(\tau)} = \frac{n^0_{i+1}(f)}{n^0_i(f)} = \frac{v^F_{i,i+1}(f)}{v^R_{i+1,i}(f)} = r_{i,i+1}(f), \tag{34}$$

where the upper index o stands for the long time value of n_k, and $r_{i,i+1}(f)$ is the partial equilibrium constant corresponding to the ith reaction (step), which depends on time through f. Thus, for the forward and reverse driven processes between t_1 and t_{N+1}, we obtain the general relations

$$\begin{aligned} r_{1,N+1}(f) &= r_{1,2}(f) r_{2,3}(f) \cdots r_{N,N+1}(f) \\ &= \frac{n^0_2(f)}{n^0_1(f)} \frac{n^0_3(f)}{n^0_2(f)} \cdots \frac{n^0_{N+1}(f)}{n^0_N(f)} \\ &= \Pi^N_{i=1} \frac{n^0_{i+1}(f)}{n^0_i(f)}, \end{aligned} \tag{35}$$

where now n^0_i will have different dependencies on the temperature depending on whether the system is in a local equilibrium or a quasiequilibrium state.

(i) *Local equilibrium*. By making use repeatedly of Eq. (20) in Eq. (35) one obtains that the ratio between the forward $\mathrm{prob}^F(\mathrm{path})$ and reverse $\mathrm{prob}^R(\mathrm{path})$ path probabilities is given by

$$\begin{aligned} \frac{\mathrm{prob}^F(\mathrm{path})}{\mathrm{prob}^R(\mathrm{path})} = r_{1,N+1}(f) &= \exp\left[\frac{m}{k_B T_0} \int_0^t [-\nabla V(y) + f(\tau)] \dot{y} \, d\tau\right] \\ &= \exp\left[-\frac{\Delta F}{k_B T_0}\right] \exp\left[\frac{W_f}{k_B T_0}\right], \end{aligned} \tag{36}$$

where $W_f = m \int_0^t f(\tau) \dot{y} \, d\tau$ is the work due to the nonconservative force in the forward path. Equation (36) constitutes the ratio between the forward and backward path probabilities providing us the Fluctuation Theorem at local equilibrium [14]. Additionally, by using Eqs. (8) and (10), we can rewrite Eq. (36) in the form

$$\frac{\mathrm{prob}^F(\mathrm{path})}{\mathrm{prob}^R(\mathrm{path})} = e^{-\Delta F / k_B T_0} e^{\tilde{\sigma} / k_B}, \tag{37}$$

where $\tilde{\sigma} = \int_0^\tau \frac{d_{\mathrm{ext}} S}{dt} dt$ is the total entropy produced by the nonconservative force along the process. Equation (37) expresses that the ratio of forward and backward probabilities is related to the entropy production [15]. Nonetheless, it should be pointed out that $\tilde{\sigma}$ is the entropy change of the system with its surroundings and therefore is of undefined sign. Another consequence of Eq. (36) is the following:

$$\begin{aligned} \left\langle \exp\left[-\frac{W_f}{k_B T_0}\right] \right\rangle &= \sum_{\mathrm{path}} \mathrm{prob}^F(\mathrm{path}) \exp\left[-\frac{W_f}{k_B T_0}\right] \\ &= \sum_{\mathrm{path}} \mathrm{prob}^R(\mathrm{path}) \exp\left[\frac{-\Delta F}{k_B T_0}\right] \\ &= \exp\left[\frac{-\Delta F}{k_B T_0}\right], \end{aligned} \tag{38}$$

which constitutes the so-called nonequilibrium work relation [16]. Despite the common belief, Eq. (38) is only valid at local equilibrium as was stated previously [17,18].

It is convenient to emphasize that the fluctuation theorem adopts so simple and elegant expressions like Eqs. (36) and (37) because we have derived them in the conditions of local equilibrium, i.e., when the fluctuation-dissipation regime is satisfied. Otherwise, more fuzzy expression is obtained, as we will show next.

(ii) *Quasiequilibrium*. Following a similar analysis as in the previous case, from the quasiequilibrium solution given in Eq. (26) we find

$$\begin{aligned} \frac{\mathrm{prob}^F(\mathrm{path})}{\mathrm{prob}^R(\mathrm{path})} &= r_{1,N+1}(f) \\ &= \exp\left[\int_0^t \frac{m}{k_B T(\tau)} [-\nabla V(y) + f(\tau)] \dot{y} \, d\tau\right], \end{aligned} \tag{39}$$

giving us the ratio between the forward and backward paths probabilities at quasiequilibrium. Equation (39) constitutes a generalization of the fluctuation theorem to the case in which the system is not yet relaxed to local equilibrium, but it is still at a quasiequilibrium. As we have mentioned previously, in far from equilibrium conditions, it is not generally correct to assume that the temperature of the system is that of the heat bath, and therefore in far from equilibrium conditions Eq. (39) must be used in place of Eq. (36). From Eq. (39) it is not possible to obtain a relation similar to Eq. (38) because of the dependence of the quasiequilibrium temperature in f and time along the path.

V. CONCLUSIONS

In this paper based on the thermodynamic theory of Brownian motion [6,19], we have derived the Fokker-Planck equation for a system of Brownian particles subjected to both conservative and nonconservative forces. In this scenario we have obtained expressions for the FT in local equilibrium and in quasiequilibrium. Local equilibrium coincides with the fluctuation-dissipation regime where the fluctuation-dissipation theorem is satisfied and the intensive parameters characterizing the state of the system coincide with those of the bath. In this case our expressions for the FT agree with previous results in the literature.

Nonetheless, when arbitrary forces remove the system from equilibrium with the bath and keep it out of equilibrium modifying the intensive parameters characterizing the state of the system, the fluctuation-dissipation theorem is no longer valid. However, if these external forces vary quite slowly in time, one can define a state of quasiequilibrium. Fluctuations around this quasiequilibrium state are characterized by a generalization of the FT in which the existence of a quasiequilibrium state is taken into account. The theory we have presented here enables us to derive steady-state fluctuation theorems for arbitrary forcing, something which we will do in a later work.

ACKNOWLEDGMENT

I.S.H. acknowledges financial support by UNAM-DGAPA under the Grant No. IN-102609.

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