Entropy production in irreversible systems described by a Fokker-Planck equation

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We analyze the irreversibility and the entropy production in nonequilibrium interacting particle systems described by a Fokker-Planck equation by the use of a suitable master equation representation. The irreversible character is provided either by nonconservative forces or by the contact with heat baths at distinct temperatures. The expression for the entropy production is deduced from a general definition, which is related to the probability of a trajectory in phase space and its time reversal, that makes no reference a priori to the dissipated power. Our formalism is applied to calculate the heat conductance in a simple system consisting of two Brownian particles each one in contact to a heat reservoir. We show also the connection between the definition of entropy production rate and the Jarzynski equality.

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I. INTRODUCTION

A thermodynamic system in a stationary state is characterized by having its properties such as energy and entropy invariant in time. In this regime, there can be no flow of a conserved quantity such as energy to or from the outside because it cannot be created. However, there might be a flow of a nonconserved quantity such as the entropy. The flux of entropy to the outside will be equal to the entropy spontaneously generated inside the system. Only in thermodynamic equilibrium there will be no production of entropy. A nonequilibrium thermodynamic system in the stationary state is thus characterized by a continuous production of entropy. In a transient state, the change in the entropy is not only due to the entropy flow but is also due to the spontaneous generation of entropy within the system so that, in general, the time derivative of the entropy S of a system can be split into two parts [1–3]

$$\frac{dS}{dt} = \Pi - \Phi, \qquad (1)$$

where Π is the entropy production rate, which is always nonnegative, and Φ is the entropy flux rate *from* the system to the environment. In the stationary regime, the entropy rate dS/dt vanishes and $\Pi = \Phi$. If in addition the system is out of equilibrium then $\Pi = \Phi > 0$; if it is in equilibrium $\Pi = \Phi = 0$. The quantity Φ, defined as the flux rate from inside to outside of the system, will be positive in the nonequilibrium stationary state.

The construction of a microscopic theory of nonequilibrium thermodynamic systems is faced with two major problems related to entropy. The first concerns the definition of nonequilibrium entropy and the second the definition of entropy production. For systems in equilibrium, the entropy S is related to the probability $P(\eta)$ of finding the system in a certain state η by the well known Boltzmann-Gibbs expression

$$S = -\sum_{\eta} P(\eta) \ln P(\eta). \qquad (2)$$

For nonequilibrium systems, described by a time dependent probability distribution $P(\eta, t)$, it is natural to extend the Boltzmann-Gibbs expression to these systems. The out-of-equilibrium time-dependent entropy $S(t)$ is then defined by

$$S(t) = -\sum_{\eta} P(\eta, t) \ln P(\eta, t), \qquad (3)$$

and therefore varies in time according to the specific dynamics that governs the evolution of the probability distribution $P(\eta, t)$.

The second problem, the definition of entropy production rate Π, is equivalent to the problem of defining the entropy flux rate Φ since these two quantities are related with each other by means of (1). These two quantities should necessarily be related to the time evolution of $P(\eta, t)$ and therefore cannot be defined in terms of $P(\eta, t)$ alone. We need to known the dynamics that governs its time evolution. We assume that the system evolves in time according to a Markovian process on a discretized phase space, defined by a transition rate $W(\eta'|\eta)$ from state η to state η'. Within this framework, Φ and Π will be related to W. The time evolution of the probability distribution is assumed to be governed by the master equation [4, 5]

$$\frac{d}{dt} P(\eta, t) = \sum_{\eta'} \mathcal{J}(\eta'|\eta, t), \qquad (4)$$

where

$$\mathcal{J}(\eta'|\eta, t) = W(\eta|\eta') P(\eta', t) - W(\eta'|\eta) P(\eta, t) \qquad (5)$$

is the probability current. Here we will be concerned mainly with the study of the Fokker-Planck equation [4–6] which we regard as coming from an appropriate continuous limit of the master equation (4), as we shall see.

From the probability current, one determines the flux rate Φ_E of any state function $E(\eta)$, which is

$$\Phi_E(t) = -\sum_{\eta,\eta'} \mathcal{J}(\eta'|\eta,t)E(\eta), \qquad (6)$$

and clearly vanishes in the stationary state as it should. A natural way to define the entropy flux rate is as follows

$$\Phi(t) = -\sum_{\eta,\eta'} \mathcal{J}(\eta'|\eta,t)\ln W(\eta'|\eta). \qquad (7)$$

From this definition we see immediately by means of (1), (3) and (4) that the entropy production rate is given by

$$\Pi(t) = -\sum_{\eta,\eta'} \mathcal{J}(\eta'|\eta,t)\ln[W(\eta'|\eta)P(\eta,t)], \qquad (8)$$

an expression that is always nonnegative and equivalent to that introduced by Schnakenberg [7]. In thermodynamic equilibrium, when microscopic reversibility takes place, $\mathcal{J}$ vanishes and both Φ and Π vanish as well. It worth mentioning that this definition of entropy production makes no a priori reference to any thermodynamic quantity such as dissipated energy as is usually done. It is a universal definition in the same sense as the definition of entropy (3) is universal.

The production of entropy in systems described by a stochastic process or by a master equation has been the subject of several studies [8–25]. This includes the numerical calculation of entropy production in nonequilibrium lattice gas models [16]. Here we are concerned with the production of entropy in nonequilibrium interacting particle systems described by Langevin equations or, in an equivalent way, by the associate Fokker-Planck equation, which is the appropriate framework to describe nonequilibrium system under temperature gradients [10, 25]. Our main purpose here is to use expressions (7) and (8) to determine the entropy flux rate Φ and the entropy production rate Π in irreversible systems described by Langevin equations. The production of entropy in systems described by Langevin equations in the overdamped limit has been previously studied [17, 18]. Here we consider the general case. Systems described by a Fokker-Planck [4–6] equation follows a Markovian process in continuous time and continuous configuration space. The irreversible character comes from the type of forces entering the Langevin equations or from the type of contact of the system with the environment. As we shall see, if the system is in contact with a heat reservoir that keeps the temperature T constant but the forces are nonconservative the resulting entropy production rate is strictly positive. We will show that in this case the dissipated power $\mathcal{P}$ is related to the entropy production rate by $\Pi = \mathcal{P}/T$, which is a fluctuation dissipation type relation.

When the forces become conservative but the system is in contact with more than one heat reservoirs at distinct temperatures the resulting entropy production rate is also nonzero. We apply the results obtained here to a simple system of this type consisting of two Brownian particles connected with each other by a harmonic force and each one to heat baths at distinct temperatures [26, 27]. Whenever the temperatures are distinct there will be a heat flow through the system from one reservoir to the other. By calculating the production of entropy we determine the thermal conductance. Although the forces are conservative, the difference in temperatures keeps the system in a nonequilibrium state. The production of entropy vanishes only when the forces are conservative and the system is in contact with only one heat bath.

We use the expressions (7) and (8) for the entropy flux and entropy production to determine an equality of the Jarzynski type [28–32]. This is carried out by considering the ratio of the probability of a given trajectory in phase space and the probability of the time reversal trajectory.

II. FOKKER-PLANCK EQUATION

A. Langevin equations

We consider a system of n interacting particles that evolves in time according to the following set of coupled Langevin equations

$$m\frac{dv_i}{dt} = F_i - \alpha v_i + \mathcal{F}_i(t), \qquad (9)$$

$$\frac{dx_i}{dt} = v_i, \qquad (10)$$

where x_i and v_i are the position and velocity of the i-th particle. We are assuming that the mass m and the coefficient α are the same for all particles and that the force F_i acting on the i-th particle depends only on the positions. The forces F_i might not be conservative. The quantity $\mathcal{F}_i(t)$ is the random force, a stochastic variable having the properties

$$\langle \mathcal{F}_i(t) \rangle = 0, \qquad (11)$$

and

$$\langle \mathcal{F}_i(t)\mathcal{F}_j(t') \rangle = 2\alpha T_i\,\delta_{ij}\delta(t-t'), \qquad (12)$$

where, $T_i > 0$ is a constant that might be distinct for each particle.

The associate Fokker-Planck equation, that gives the time evolution of the probability distribution $P(x,v,t)$, where x and v denote the vectors whose components are the variables $\{x_i\}$ and $\{v_i\}$, respectively, is given by

$$\frac{\partial}{\partial t}P = -\frac{1}{m}\sum_i \frac{\partial}{\partial v_i}(F_iP - \alpha v_iP) - \sum_i \frac{\partial}{\partial x_i}(v_iP) +$$

$$+\frac{\alpha}{m^2}\sum_i T_i \frac{\partial^2}{\partial v_i^2}P, \qquad (13)$$

which we write in the form

$$\frac{\partial}{\partial t}P = -\sum_i \left(K_i + \frac{\partial}{\partial v_i}J_i\right), \qquad (14)$$

where K_i and J_i are given by

$$K_i = \frac{F_i}{m}\frac{\partial}{\partial v_i}P + v_i\frac{\partial}{\partial x_i}P, \qquad (15)$$

and

$$J_i = -\frac{\alpha v_i}{m}P - \frac{\alpha T_i}{m^2}\frac{\partial}{\partial v_i}P. \qquad (16)$$

The Fokker-Planck equation should be solved inside a certain region of the space spanned by the joint sets of variables $x = \{x_i\}$ and $v = \{v_i\}$. We assume that at the boundary of this region the probability distribution $P(x,v,t)$ vanishes.

The set of Langevin equations (9) and (10) and the associate Fokker-Planck equation (13) are assumed to describe a system that is in contact with several heat baths, each one having a temperature T_i. The contact is accomplished by the random forces $\mathcal{F}_i$. If $T_i = T$ is independent of i then we may say taht the system is in contact with just one heat reservoir at temperature T. If in addition the forces F_i are conservative then in the stationary state the system is in equilibrium.

B. Equilibrium conditions

At the stationary state the probability distribution $P(x,v)$ is independent of time and is the solution of

$$\sum_i (K_i + \frac{\partial}{\partial v_i}J_i) = 0. \qquad (17)$$

When microscopic reversibility holds we shall see in section IV that $J_i = 0$, that is,

$$\frac{\alpha v_i}{m}P + \frac{\alpha T_i}{m^2}\frac{\partial}{\partial v_i}P = 0, \qquad (18)$$

which implies that P must be of the form

$$P(x,v) = \chi(x)\phi(v), \qquad (19)$$

that is x and v are independent random vector variables. Setting (19) into the definition (15) of K_i, it follows that

$$K_i = v_i\phi\left(-\frac{F_i}{T_i}\chi + \frac{\partial}{\partial x_i}\chi\right). \qquad (20)$$

But, since $J_i = 0$, it follows from (17) that the summation of K_i must vanish, that is,

$$\sum_i K_i = 0. \qquad (21)$$

Taking into account that the expression inside the parentheses in equation (20) depends only on x and that (21) must be held for any velocity, it follows that each term of the summation in (21) must vanish, that is, $K_i = 0$, so that

$$\frac{\partial}{\partial x_i}\ln\chi = \frac{F_i}{T_i}. \qquad (22)$$

From this equation it follows immediately that

$$\frac{1}{T_i}\frac{\partial F_i}{\partial x_j} = \frac{1}{T_j}\frac{\partial F_j}{\partial x_i}, \qquad (23)$$

for any pair i,j, which is the desired equilibrium condition. That is, microscopic reversibility implies that the forces F_i and the parameters T_i must be such that they satisfy (23).

If the temperatures are all the same,

$$T_i = T_j, \qquad (24)$$

then

$$\frac{\partial F_i}{\partial x_j} = \frac{\partial F_j}{\partial x_i}, \qquad (25)$$

that is, the forces F_i must be conservative. In this case the system is in thermodynamic equilibrium and is described by the canonical Gibbs probability distribution

$$P(x,v) = \frac{1}{Z}\exp\{-\beta\mathcal{H}(x,v)\}, \qquad (26)$$

which follows directly from (17) and (22), where

$$\mathcal{H}(x,v) = \frac{1}{2}m\sum_i v_i^2 + \mathcal{V}(x) \qquad (27)$$

and $T_i = 1/\beta$. In addition, the forces are related to the potential $\mathcal{V}$ by

$$F_i = -\frac{\partial \mathcal{V}}{\partial x_i}. \qquad (28)$$

When the conditions (25) and (24) are valid, the Langevin equations and the associate Fokker-Planck equation describe a system with conservative forces in contact with a heat reservoir at temperature $T = 1/\beta$. However, our aim here is to study systems that do not satisfy these conditions so that, in the stationary state, they are irreversible. We distinguish two types of nonequilibrium situations. In the first, the forces F_i are conservative but the temperatures T_i are not all the same. In the second, the temperatures are all the same but the forces F_i are nonconservative.

C. Entropy production

To determined an expression for the entropy flux rate and entropy production rate we follow a method similar

to that used by Seifert [17] for the case of overdamped motion. We start from the entropy S, defined by

$$S = -\int P \ln P dx dv. \tag{29}$$

Its time derivative is

$$\frac{dS}{dt} = -\int \ln P \frac{\partial P}{\partial t} dx dv, \tag{30}$$

or, using the Fokker-Planck equation as given by (14),

$$\frac{dS}{dt} = \sum_i \int K_i \ln P dx dv + \sum_i \int \ln P \frac{\partial J_i}{\partial v_i} dx dv. \tag{31}$$

The integral in the first summation vanishes identically as can be seen by replacing K_i by its definition, given by equation (15), and by performing an integration by parts. The result is

$$\int K_i \ln P dx dv = -\int \left(\frac{F_i}{m} \frac{\partial P}{\partial v_i} + v_i \frac{\partial P}{\partial x_i} \right) dx dv = 0, \tag{32}$$

where the second equality is obtained by another integration by parts and by taking into account that F_i depends on x but not on v. Using this last result and integrating the second integral in (31) by parts gives

$$\frac{dS}{dt} = -\sum_i \int J_i \frac{\partial}{\partial v_i} \ln P dx dv. \tag{33}$$

But from the definition of J_i,

$$\frac{\partial}{\partial v_i} \ln P = -\frac{m v_i}{T_i} - \frac{m^2}{\alpha T_i} \frac{J_i}{P}, \tag{34}$$

so that

$$\frac{dS}{dt} = \sum_i \int \left(\frac{m}{T_i} v_i J_i + \frac{m^2}{\alpha T_i} \frac{J_i^2}{P} \right) dx dv. \tag{35}$$

The second term, which is always nonnegative, is identified as the entropy production rate

$$\Pi = \sum_i \frac{m^2}{\alpha T_i} \int \frac{J_i^2}{P} dx dv. \tag{36}$$

A similar expression for Π has been obtained for the case of overdamped motion [17, 18]. In accordance with relation (1), the entropy flux rate should be then

$$\Phi = -\sum_i \frac{m}{T_i} \int v_i J_i dx dv. \tag{37}$$

In the stationary state, $dS/dt = 0$ and $\Pi = \Phi$. In equilibrium $J_i = 0$ and both the entropy flux rate and entropy production rate vanish, $\Pi = \Phi = 0$. In nonequilibrium stationary state, $J_i \neq 0$ and $\Pi = \Phi \neq 0$.

Equations (36) and (37) give the desired expression for the entropy production rate and entropy flux rate for a system described by the Fokker-Planck equation (13). In section IV, we will show that these two expressions can actually be deduced from the general expressions (7) and (8) by an appropriate master equation representation of the Fokker-Planck equation (13).

D. Entropy flux and energy dissipation

Using the definition of J_i, given by equation (16), the entropy flux rate may be written as

$$\Phi = \sum_i \int \left(\frac{\alpha}{T_i} v_i^2 P + \frac{\alpha}{m} v_i \frac{\partial}{\partial v_i} P \right) dx dv. \tag{38}$$

Integrating the second integral by parts,

$$\Phi = \sum_i \int \left(\frac{\alpha}{T_i} v_i^2 P - \frac{\alpha}{m} P \right) dx dv, \tag{39}$$

or

$$\Phi = \sum_i \frac{1}{T_i} \left(\alpha \langle v_i^2 \rangle - \frac{\alpha}{m} T_i \right). \tag{40}$$

Let us determine the average rate of energy dissipation $\mathcal{P}_i$ of each particle. It has two contributions: one is the work dissipated per unit time, $v_i F_i$, and the other is the decrease in kinetic energy per unit time, $(m/2)(d/dt)v_i^2$. That is,

$$\mathcal{P}_i = \langle v_i F_i \rangle - \frac{m}{2} \frac{d}{dt} \langle v_i^2 \rangle. \tag{41}$$

Now, from the Fokker-Planck equation, it is straightfoward to obtain the result

$$\frac{m}{2} \frac{d}{dt} \langle v_j^2 \rangle = \langle v_j F_j \rangle - \alpha \langle v_j^2 \rangle + \frac{\alpha}{m} T_j, \tag{42}$$

which follows after some appropriate integration by parts. Replacing this result in equation (41), we get an equivalent expression for the dissipation power of each particle, namely

$$\mathcal{P}_j = \alpha \langle v_j^2 \rangle - \frac{\alpha}{m} T_j. \tag{43}$$

From this result we may write the entropy flux rate as

$$\Phi = \sum_i \frac{\mathcal{P}_i}{T_i}. \tag{44}$$

If the temperatures are the same $T_i = T$ then

$$\Phi = \frac{\mathcal{P}}{T}. \tag{45}$$

Where $\mathcal{P} = \sum_i \mathcal{P}_i$ is the total energy dissipated per unit time.

In the stationary state, $\langle v_i^2 \rangle$ is a constant so that $d\langle v_i^2 \rangle/dt = 0$ and $\mathcal{P}_i = \langle v_i F_i \rangle$. We are then left with the following expression

$$\Pi = \Phi = \sum_i \frac{\mathcal{P}_i}{T_i} = \sum_i \frac{1}{T_i} \langle v_i F_i \rangle, \tag{46}$$

valid in the stationary regime. Using the interpretation that each particle i is in contact with a heat reservoir

at temperature T_i, this result says that the entropy production rate is a sum of terms each one being the ratio between the dissipation of energy per unit time, that is, the dissipated power, and the temperature of the heat bath.

Let us consider now the case in which the forces are conservative in which case $F_i = -\partial \mathcal{V}/\partial x_i$. From the Fokker-Planck equation and after an appropriate integration by parts it is straightforward to show that

$$\frac{d}{dt}\langle \mathcal{V}\rangle = \sum_i \langle v_i \frac{d\mathcal{V}}{dx_i}\rangle = -\sum_i \langle v_i F_i\rangle. \quad (47)$$

Therefore, the total dissipated power is

$$\mathcal{P} = \sum_i \mathcal{P}_i = -\frac{d}{dt}\left(\langle \mathcal{V}\rangle + \sum_i \frac{m}{2}\langle v_i^2\rangle\right), \quad (48)$$

If, in addition, $T_i = T$ is the same for all sites, then the entropy flux rate is given by

$$\Phi = -\frac{1}{T}\frac{d}{dt}\left(\langle \mathcal{V}\rangle + \sum_i \frac{m}{2}\langle v_i^2\rangle\right). \quad (49)$$

From this equation we see that the entropy flux rate is equal to the ratio between the decrease in the internal energy per unit time and the temperature T of the heat bath.

III. THERMAL CONDUCTION IN A SIMPLE SYSTEM

A. Equations of motion

We apply the previous results to a nonequilibrium simple system consisting of two coupled particles of the same mass m, moving along a straight line. They interact with each other and each one is in contact with thermal reservoirs at different temperatures. Their movements are governed by the Langevin equations

$$m\frac{dv_1}{dt} = -k(x_1 - x_2) - k'x_1 - \alpha v_1 + \mathcal{F}_1(t), \quad (50)$$

and

$$m\frac{dv_2}{dt} = -k(x_2 - x_1) - k'x_2 - \alpha v_2 + \mathcal{F}_2(t), \quad (51)$$

where x_i and $v_i = dx_i/dt$ are the position and velocity of the i-th particle. The quantities k and k' are spring constants and α is the friction constant. The random forces $\mathcal{F}_1$ and $\mathcal{F}_2$ are Gaussian white noises with the properties

$$\langle \mathcal{F}_i(t)\rangle = 0, \quad (52)$$

$$\langle \mathcal{F}_i(t)\mathcal{F}_j(t')\rangle = 2\alpha T_i \delta_{ij}\delta(t - t'), \quad (53)$$

where T_1 and T_2 are the temperature of the thermal reservoirs connected to particles 1 and 2, respectively.

If we define the forces $F_1(x_1, x_2)$ and $F_2(x_1, x_2)$ by

$$F_1 = -k(x_1 - x_2) - k'x_1, \quad (54)$$

and

$$F_2 = -k(x_2 - x_1) - k'x_2, \quad (55)$$

then equations (50) and (51) have the same structure of (9). The associate Fokker-Planck equation for the probability density $P(x_1, x_2, v_1, v_2, t)$ is given by

$$\frac{\partial}{\partial t}P = -\frac{\partial}{\partial x_1}(v_1 P) - \frac{\partial}{\partial x_2}(v_2 P) - \frac{1}{m}\frac{\partial}{\partial v_1}(F_1 P)$$

$$-\frac{1}{m}\frac{\partial}{\partial v_2}(F_2 P) + \lambda\frac{\partial}{\partial v_1}(v_1 P) + \lambda\frac{\partial}{\partial v_2}(v_2 P)$$

$$+\frac{\Gamma_1}{2}\frac{\partial^2}{\partial v_1^2}P + \frac{\Gamma_2}{2}\frac{\partial^2}{\partial v_2^2}P, \quad (56)$$

where $\lambda = \alpha/m$ and $\Gamma_i = 2\alpha T_i/m^2$.

To determine the entropy production rate it is necessary to compute averages of the type $\langle x_i x_j\rangle$, $\langle x_i v_j\rangle$ and $\langle v_i v_j\rangle$. Since the Langevin equations (50) and (51) are linear equations they can be solved exactly and so can the Fokker-Planck equation. From the solution $P(x_1, x_2, v_1, v_2, t)$ of the Fokker-Planck equation we determine the desired averages. Here, however, we follow a distinct procedure. Instead of finding the probability P itself we set up equations for the those averages and solve them. From the Fokker-Planck equations it is straightforward to reach the following equations for the averages

$$\frac{d}{dt}\langle x_1^2\rangle = 2\langle x_1 v_1\rangle, \quad (57)$$

$$\frac{d}{dt}\langle x_2^2\rangle = 2\langle x_2 v_2\rangle, \quad (58)$$

$$\frac{d}{dt}\langle x_1 x_2\rangle = \langle x_1 v_2\rangle + \langle x_2 v_1\rangle, \quad (59)$$

$$\frac{d}{dt}\langle x_1 v_1\rangle = \langle v_1^2\rangle - K\langle x_1^2\rangle + L\langle x_1 x_2\rangle - \lambda\langle x_1 v_1\rangle, \quad (60)$$

$$\frac{d}{dt}\langle x_2 v_2\rangle = \langle v_2^2\rangle - K\langle x_2^2\rangle + L\langle x_1 x_2\rangle - \lambda\langle x_2 v_2\rangle, \quad (61)$$

$$\frac{d}{dt}\langle x_1 v_2\rangle = \langle v_1 v_2\rangle - K\langle x_1 x_2\rangle + L\langle x_1^2\rangle - \lambda\langle x_1 v_2\rangle, \quad (62)$$

$$\frac{d}{dt}\langle x_2 v_1\rangle = \langle v_2 v_1\rangle - K\langle x_1 x_2\rangle + L\langle x_2^2\rangle - \lambda\langle x_2 v_1\rangle, \quad (63)$$

$$\frac{d}{dt}\langle v_1^2\rangle = -2K\langle x_1 v_1\rangle + 2L\langle x_2 v_1\rangle - 2\lambda\langle v_1^2\rangle + \Gamma_1, \quad (64)$$

$$\frac{d}{dt}\langle v_2^2\rangle = -2K\langle x_2 v_2\rangle + 2L\langle x_1 v_2\rangle - 2\lambda\langle v_2^2\rangle + \Gamma_2, \quad (65)$$

$$\frac{d}{dt}\langle v_1 v_2\rangle = -K\langle x_1 v_2\rangle + L\langle x_2 v_2\rangle$$

$$-K\langle x_2 v_1\rangle + L\langle x_1 v_1\rangle - 2\lambda\langle v_1 v_2\rangle, \quad (66)$$

where $K = (k + k')/m$ and $L = k/m$.

B. Entropy production in the steady state

In the stationary regime, the set of equations above are reduced to following set of equations

$$\langle x_1 v_1\rangle = \langle x_2 v_2\rangle = \langle v_1 v_2\rangle = 0, \quad (67)$$

$$\langle x_2 v_1\rangle + \langle x_1 v_2\rangle = 0, \quad (68)$$

$$\langle v_1^2\rangle - K\langle x_1^2\rangle + L\langle x_1 x_2\rangle = 0, \quad (69)$$

$$-K\langle x_1 x_2\rangle + L\langle x_1^2\rangle - \lambda\langle x_1 v_2\rangle = 0, \quad (70)$$

$$-K\langle x_1 x_2\rangle + L\langle x_2^2\rangle - \lambda\langle x_2 v_1\rangle = 0, \quad (71)$$

$$\langle v_2^2\rangle - K\langle x_2^2\rangle + L\langle x_1 x_2\rangle = 0, \quad (72)$$

$$2L\langle x_2 v_1\rangle - 2\lambda\langle v_1^2\rangle + \Gamma_1 = 0, \quad (73)$$

$$2L\langle x_1 v_2\rangle - 2\lambda\langle v_2^2\rangle + \Gamma_2 = 0. \quad (74)$$

These equations are linear in the averages and can readily be solved with the results

$$\langle v_1^2\rangle = \frac{\Gamma_1 + \Gamma_2}{4\lambda} + \frac{K\lambda(\Gamma_1 - \Gamma_2)}{4(L^2 + K\lambda^2)}, \quad (75)$$

$$\langle v_2^2\rangle = \frac{\Gamma_1 + \Gamma_2}{4\lambda} - \frac{K\lambda(\Gamma_1 - \Gamma_2)}{4(L^2 + K\lambda^2)}, \quad (76)$$

$$\langle x_1 v_2\rangle = -\langle x_2 v_1\rangle = \frac{L(\Gamma_1 - \Gamma_2)}{4(L^2 + K\lambda^2)}, \quad (77)$$

$$\langle x_1^2\rangle = \frac{K(\Gamma_1 + \Gamma_2)}{4\lambda(K^2 - L^2)} + \frac{\lambda(\Gamma_1 - \Gamma_2)}{4(L^2 + K\lambda^2)}, \quad (78)$$

$$\langle x_2^2\rangle = \frac{K(\Gamma_1 + \Gamma_2)}{4\lambda(K^2 - L^2)} - \frac{\lambda(\Gamma_1 - \Gamma_2)}{4(L^2 + K\lambda^2)}, \quad (79)$$

$$\langle x_1 x_2\rangle = \frac{L(\Gamma_1 + \Gamma_2)}{4\lambda(K^2 - L^2)}. \quad (80)$$

In the stationary state $\Pi = \Phi$ and we may use expression (40) for the entropy flux rate to get the entropy production rate, given by

$$\Pi = \frac{\alpha}{T_1}\langle v_1^2\rangle + \frac{\alpha}{T_2}\langle v_2^2\rangle - 2\frac{\alpha}{m}, \quad (81)$$

or

$$\Pi = \frac{2\lambda^2}{\Gamma_1}\langle v_1^2\rangle + \frac{2\lambda^2}{\Gamma_2}\langle v_1^2\rangle - 2\lambda. \quad (82)$$

Taking into account the results above for $\langle v_1^2\rangle$ and $\langle v_2^2\rangle$ and after straightforward calculations we arrive at the following expression for the entropy production rate

$$\Pi = \frac{(\Gamma_1 - \Gamma_2)^2}{2\Gamma_1\Gamma_2}\frac{\lambda L^2}{L^2 + K\lambda^2}. \quad (83)$$

Making the substitutions $K = (k + k')/m$, $L = k/m$, $\lambda = \alpha/m$, and $\Gamma_i = 2\alpha T_i/m^2$, we get

$$\Pi = \frac{(T_1 - T_2)^2}{T_1 T_2}\frac{\alpha k^2}{2[mk^2 + (k + k')\alpha^2]}, \quad (84)$$

From the relation $\Phi = \kappa(T_1 - T_2)^2/T_1 T_2$ between entropy production Π and the thermal conduction κ [33], we get

$$\kappa = \frac{\alpha k^2}{2[mk^2 + (k + k')\alpha^2]}. \quad (85)$$

which agrees with the result obtained by a distinct method [27].

IV. PRODUCTION OF ENTROPY IN A MARKOVIAN PROCESS

A. Master equation representation

In this section we demonstrate two important results that we have used previously. The first one is related to the current J_i as defined by equation (16). In the steady state and if microscopic reversibility holds then $J_i = 0$ for each i. The second result refers to the expressions (36) and (37) for the entropy production and entropy flux rates. We show here that these two expressions can be obtained from formulas (7) and (8), valid for systems described by a master equation. The demonstration begins by discretizing the Fokker-Planck equation (13) transforming it on a master equation of the form

$$\frac{\partial}{\partial t}P(\eta) = \sum_{\eta'}\{W(\eta|\eta')P(\eta') - W(\eta'|\eta)P(\eta)\}, \quad (86)$$

where $\eta = (x, v)$ and $\eta' = (x', v')$ denote discretized states in phase space and $W(\eta'|\eta)$ is the rate of transition from the state η to the state η'. To simplify the notation we are omitting the time dependence of $P(\eta)$.

We use two types of discretizations. In the first we assume that the velocity v_i will increase or decrease by an amount a. This procedure is used to write down the following approximations for the derivatives of P with respect to v_i

$$\frac{\partial^2}{\partial v_i^2} P = \frac{1}{a^2} \{P(x, v^{i+}) - 2P(x, v) + P(x, v^{i-})\} \quad (87)$$

and

$$\frac{\partial}{\partial v_i}(v_i P) = \frac{1}{2a}\{(v_i + a)P(x, v^{i+}) - (v_i - a)P(x, v^{i-})\}. \quad (88)$$

The notation $v^{i\pm}$ stands for the vector whose components are the same as those of the vector v except the i-component which equals $v_i \pm a$.

In the second type of discretization the position x_i will increase by an amount bv_i whereas the velocity v_i will increase by $F_i b/m$. This procedure is used to write down the approximation

$$-\frac{1}{m}\frac{\partial}{\partial v_i}(F_i P) - \frac{\partial}{\partial x_i}(v_i P) = \frac{1}{b}\{P(x^{i-*}, v^{i-*}) - P(x, v)\}. \quad (89)$$

The notation $x^{i\pm*}$ stands for the vector whose components are the same as those of the vector x except the i-component which equals $x_i \pm bv_i$ and $v^{i\pm*}$ stands for the vector whose components are the same as those of the vector v except the i-component which equals $v_i \pm bF_i/m$.

Using the approximations given by equations (87), (88) and (89), the Fokker-Planck equation (13) can be represented in the form of a generalized birth and death master equation,

$$\frac{\partial}{\partial t}P(x, v) = \sum_i \{A_i^+(x, v^{i-})P(x, v^{i-}) - A_i^-(x, v)P(x, v)\}$$

$$+ \sum_i \{A_i^-(x, v^{i+})P(x, v^{i+}) - A_i^+(x, v)P(x, v)\}$$

$$+ \sum_i \{B_i(x^{i-*}, v^{i-*})P(x^{i-*}, v^{i-*}) - B_i(x, v)P(x, v)\}, \quad (90)$$

where $A_i^\pm(x, v)$ are the transition rates from (x, v) to $(x, v^{i\pm})$ and are given by

$$A_i^+(x, v) = \frac{\alpha T_i}{m^2 a^2} - \frac{\alpha v_i}{2ma}, \quad (91)$$

and

$$A_i^-(x, v) = \frac{\alpha T_i}{m^2 a^2} + \frac{\alpha v_i}{2ma}, \quad (92)$$

where a is chosen to be sufficiently small so that $A_i^\pm(x, v)$ will be nonnegative. The quantity $B_i(x, v)$, the transition rate from (x, v) to (x^{i+*}, v^{i+*}), is

$$B_i(x, v) = \frac{1}{b}. \quad (93)$$

In the limit $a \to 0$ and $b \to 0$, the master equation (90) turns into the Fokker-Planck equation (13).

B. Microscopic reversibility

The state of thermodynamic equilibrium of a system described by a stochastic process is identified as the state obeying microscopic reversibility, which occurs whenever the probability of any trajectory equals the probability of its time reverse. In a stochastic Markovian process this condition is fullfield if [34]

$$T(\eta|\eta')P(\eta') = T(\eta'|\eta)P(\eta), \quad (94)$$

for any to state η and η', where $T(\eta'|\eta)$ is the conditional probability of the transition $\eta \to \eta'$ and $P(\eta)$ is the stationary probability distribution. In the continuous time limit, we use the relation $T(\eta'|\eta) = \Delta t W(\eta'|\eta)$, valid for small time interval Δt, to get the microscopic reversibility condition for system described by the master equation (86),

$$W(\eta|\eta')P(\eta') = W(\eta'|\eta)P(\eta), \quad (95)$$

From equation (95), we get two independent conditions,

$$A_i^+(x, v^{i-})P(x, v^{i+}) = A_i^-(x, v)P(x, v), \quad (96)$$

and

$$B_i(x^{i-*}, v^{i-*})P(x^{i-*}, v^{i-*}) = B_i(x, v)P(x, v). \quad (97)$$

From this last condition and using (89) and (93) we get

$$\frac{1}{m}\frac{\partial}{\partial v_i}(F_i P) + \frac{\partial}{\partial x_i}(v_i P) = 0. \quad (98)$$

Therefore, the quantity K_i defined by (15) vanishes, which is one of the equilibrium conditions found earlier. The condition given by equation (96) provides

$$[\alpha T_i - \frac{ma}{2}\alpha(v_i - a)]P(x, v^{i-}) = [\alpha T_i + \frac{ma}{2}\alpha v_i]P(x, v). \quad (99)$$

Expanding this expression in powers of a, the linear term in a gives

$$\alpha T_i \frac{\partial}{\partial v_i}P(x, v) + m\alpha v_i P(x, v) = 0 \quad (100)$$

from which follows that J_i, defined by (16), vanishes, which is the other equilibrium condition.

C. Conserved quantity

Let us consider an elementary trajectory $\eta \to \eta'$ in phase space occurring during a small interval of time Δt. Suppose that a quantity $L(\eta'|\eta)$, such as the work done by nonconservative forces, is defined along this elementary trajectory. The flux of this quantity during this time interval is

$$\sum_{\eta',\eta} T(\eta'|\eta)P(\eta)L(\eta'|\eta), \qquad (101)$$

where $T(\eta'|\eta) = \Delta t W(\eta'|\eta)$ is the transition probability from η to η'. The flux per unit time Φ_L is the ratio of this quantity and Δt, that is,

$$\Phi_L = \sum_{\eta',\eta} W(\eta'|\eta)P(\eta)L(\eta'|\eta). \qquad (102)$$

If the forces are conservative, that is, if $L(\eta'|\eta) = E(\eta) - E(\eta')$, which happens for instance in the case where $L(\eta'|\eta)$ is the work of conservative force, we may write

$$\Phi_E = -\sum_{\eta',\eta}\{W(\eta|\eta')P(\eta') - W(\eta'|\eta)P(\eta)\}E(\eta). \quad (103)$$

In this form, which is identical to (6), it is easy to see that Φ_E vanishes in the stationary state. Indeed, the summation in η' is identically zero in the stationary state. From the master equation it follows that the time derivative of $U = \langle E(\eta) \rangle$ is

$$\frac{dU}{dt} = -\Phi_E, \qquad (104)$$

which again shows that Φ_E vanishes in the stationary state. The flux is defined *from* the system to the environment.

D. Entropy production

We assume that the entropy flux rate Φ in a system described by a Markovian process governed by the master equation (86) is given by the expression (102) in which $L(\eta'|\eta)$ is replaced by $\ln[W(\eta'|\eta)/W(\eta|\eta')]$, that is,

$$\Phi = \sum_{\eta',\eta} W(\eta'|\eta)P(\eta) \ln \frac{W(\eta'|\eta)}{W(\eta|\eta')}. \qquad (105)$$

We remark that this expression can be understood as the average of $\sum_{\eta'} W(\eta'|\eta) \ln W(\eta'|\eta)/W(\eta|\eta')$ and in this sense it can actually be used in numerical simulations to calculate the entropy flux rate [16]. Equation (105) can also be written in the form

$$\Phi = \sum_{\eta',\eta}\{W(\eta'|\eta)P(\eta) - W(\eta|\eta')P(\eta')\} \ln W(\eta'|\eta), \qquad (106)$$

which is identical to expression (7). Notice that, $\ln[W(\eta'|\eta)/W(\eta|\eta')]$ cannot, in general, that is, for a irreversible system, be written as a difference of the type $E(\eta) - E(\eta')$, and therefore it does not necessarily vanish, except under thermodynamic equilibrium, in which case this quantity equals $\ln P(\eta') - \ln P(\eta)$, as is evident from equation (95).

Now, from the entropy of a nonequilibrium thermodynamic system, assumed to be given by equation (3), it follows that the rate in which the entropy of the system varies is

$$\frac{dS}{dt} = -\sum_{\eta}\left(\frac{\partial}{\partial t}P(\eta)\right)\ln P(\eta). \qquad (107)$$

Using the master equation (86), equation (107) can be written as

$$\frac{dS}{dt} = -\sum_{\eta,\eta'}\{W(\eta|\eta')P(\eta') - W(\eta'|\eta)P(\eta)\}\ln P(\eta), \qquad (108)$$

or, equivalently,

$$\frac{dS}{dt} = \sum_{\eta,\eta'} W(\eta'|\eta)P(\eta) \ln \frac{P(\eta)}{P(\eta')}. \qquad (109)$$

The entropy production rate is obtained by inserting expressions (105) and (109) into relation (1). We get the following expression for the entropy production rate

$$\Pi = \sum_{\eta,\eta'} W(\eta'|\eta)P(\eta) \ln \frac{W(\eta'|\eta)P(\eta)}{W(\eta|\eta')P(\eta')}, \qquad (110)$$

which can be written in the suggestive form

$$\Pi = \frac{1}{2}\sum_{\eta,\eta'}\{W(\eta'|\eta)P(\eta) - W(\eta|\eta')P(\eta')\}\ln\frac{W(\eta'|\eta)P(\eta)}{W(\eta|\eta')P(\eta')}. \qquad (111)$$

In this form Π is manifestly nonnegative and can be regarded as an extension of the entropy production rate introduced by Schnakenberg [7].

Using the transition rates appropriate for the master equation representation (90) of the Fokker-Planck equation, the entropy flux rate is explicitly given by

$$\Phi = \sum_i \sum_{x,v} A_i^+(x,v)P(x,v) \ln \frac{A_i^+(x,v)}{A_i^-(x,v^{i+})}$$

$$+ \sum_i \sum_{x,v} A_i^-(x,v)P(x,v) \ln \frac{A_i^-(x,v)}{A_i^+(x,v^{i-})}$$

$$+ \sum_i \sum_{x,v} B_i(x,v)P(x,v) \ln \frac{B_i(x,v)}{B_i(x^{i-*},v^{i-*})}. \qquad (112)$$

Using the transitions rates (91), (92) and (93), we get the result

$$\Phi = \sum_i \sum_{x,v}\left(\frac{\alpha}{T_i}v_i^2 - \frac{\alpha}{m}\right)P(x,v), \qquad (113)$$

that is,

$$\Phi = \sum_i \left(\frac{\alpha}{T_i} \langle v_i^2 \rangle - \frac{\alpha}{m} \right), \qquad (114)$$

which is identical to the expression (40) and therefore equivalent to entropy flux rate given by equation (37).

The rate of production of entropy Π can be determined analogously,

$$\Pi = \sum_i \sum_{x,v} A_i^+(x,v) P(x,v) \ln \frac{A_i^+(x,v) P(x,v)}{A_i^-(x,v^{i+}) P(x,v^{i+})} +$$

$$+ \sum_i \sum_{x,v} A_i^-(x,v) P(x,v) \ln \frac{A_i^-(x,v) P(x,v)}{A_i^+(x,v^{i-}) P(x,v^{i-})} +$$

$$+ \sum_i \sum_{x,v} B_i(x,v) P(x,v) \ln \frac{B_i(x,v) P(x,v)}{B_i(x^{i-*},v^{i-*}) P(x^{i-*},v^{i-*})}. \qquad (115)$$

It is straightforward but cumbersome to show that this expression leads us to the result

$$\Pi = \sum_i \frac{m^2}{\alpha T_i} \int \frac{J_i^2}{P} dx dv, \qquad (116)$$

which is identical to the expression (36) found earlier. It suffices to replace $A_i^\pm$ and B_i by their definitions, given by (91), (92) and (93), expand $P(x,v^{i\pm}$ up to second order in a and use relation (89). After taking the limit $a \to 0$ and using the definition of J_i, given by (16), we arrive at the above result.

E. Jarzynski equality

Here we follow a method similar to that used by Crooks [30, 31] and by Gaveau et al. [32]. We discretize the time in intervals Δt so that $\Delta t W(\eta'|\eta) = T(\eta'|\eta)$ will be the transition probability from η to η'. Let us consider a trajectory in phase space

$$\mathcal{C} = (\eta_0 \to \eta_1 \to \eta_2 \to \ldots \to \eta_\ell), \qquad (117)$$

occurring during an interval of time equal to $\ell \Delta t$. The probability of occurrence of such a trajectory will be

$$P(\mathcal{C}) = T(\eta_\ell|\eta_{\ell-1}) \ldots T(\eta_2|\eta_1) T(\eta_1|\eta_0) P(\eta_0), \qquad (118)$$

which can also be written as

$$P(\mathcal{C}) = (\Delta t)^\ell W(\eta_\ell|\eta_{\ell-1}) \ldots W(\eta_2|\eta_1) W(\eta_1|\eta_0) P(\eta_0). \qquad (119)$$

Let us consider now the time reversal path $\mathcal{C}_R$, related to $\mathcal{C}$ and defined by

$$\mathcal{C}_R = (\eta_\ell \to \eta_{\ell-1} \to \ldots \to \eta_1 \to \eta_0), \qquad (120)$$

and its probability of occurrence

$$P(\mathcal{C}_R) = T(\eta_0|\eta_1) T(\eta_1|\eta_2) \ldots T(\eta_{\ell-1}|\eta_\ell) P(\eta_\ell), \qquad (121)$$

which can also be written as

$$P(\mathcal{C}_R) = (\Delta t)^\ell W(\eta_0|\eta_1) W(\eta_1|\eta_2) \ldots W(\eta_{\ell-1}|\eta_\ell) P(\eta_\ell), \qquad (122)$$

with the following understanding: whenever $W(\eta'|\eta)$ in equation (119) is equal to A_i^+ then $W(\eta|\eta')$ in equation (122) will be equal to A_i^- and vice-versa.

The microscopic reversibility happens when a given trajectory and its reverse have the same probability of occurrence, that is, $P(\mathcal{C}) = P(\mathcal{C}_R)$, so that

$$T(\eta_1|\eta_0) P(\eta_0) = T(\eta_0|\eta_1) P(\eta_1), \qquad (123)$$

or

$$W(\eta_1|\eta_0) P(\eta_0) = W(\eta_0|\eta_1) P(\eta_1), \qquad (124)$$

which we use before in equation (95).

Let us consider the ratio

$$\mathcal{R} = \frac{P(\mathcal{C}_R)}{P(\mathcal{C})} = \prod_{j=1}^\ell \frac{W(\eta_{j-1}|\eta_j)}{W(\eta_j|\eta_{j-1})} \frac{P(\eta_\ell)}{P(\eta_0)}. \qquad (125)$$

One finds that

$$\langle \mathcal{R} \rangle = \sum_{\mathcal{C}} \mathcal{R} P(\mathcal{C}) = \sum_{\mathcal{C}} P(\mathcal{C}_R) = 1, \qquad (126)$$

so that

$$\langle e^{\ln \mathcal{R}} \rangle = 1. \qquad (127)$$

Now the ratio $\mathcal{R}$ can be written in the form

$$\mathcal{R} = \prod_{j=1}^\ell \frac{W(\eta_{j-1}|\eta_j) P(\eta_j)}{W(\eta_j|\eta_{j-1}) P(\eta_{j-1})}, \qquad (128)$$

where $P(\eta_j)$ is understood as the probability distribution at time $t = j\Delta t$, solution of the master equation with the initial condition $P(\eta_0)$ at time $t = 0$. From (128), it follows

$$\ln \mathcal{R} = -\sum_{j=1}^\ell \sigma(\eta_j, \eta_{j-1}) \Delta t, \qquad (129)$$

where

$$\sigma(\eta', \eta) = \frac{1}{\Delta t} \ln \frac{W(\eta'|\eta) P(\eta)}{W(\eta|\eta') P(\eta')} \qquad (130)$$

is the intrinsic entropy production rate, with the convention that η is the state occurring at a given time t and η' at a later time $t + \Delta t$. A identity of the Jarzynski type [28–31] follows then

$$\langle \exp\{-\sum_{j=1}^\ell \sigma(\eta_j, \eta_{j-1}) \Delta t\} \rangle = 1, \qquad (131)$$

where the average is to be taken over the probability distribution (119) of the path $\mathcal{C}$. The intrinsic entropy flux rate is given by

$$\phi(\eta', \eta) = \frac{1}{\Delta t} \ln \frac{W(\eta'|\eta)}{W(\eta|\eta')}, \qquad (132)$$

so that

$$\sigma(\eta', \eta) = \phi(\eta', \eta) + \frac{1}{\Delta t}[\mathscr{S}(\eta') - \mathscr{S}(\eta)], \qquad (133)$$

where $\mathscr{S}(\eta) = -\ln P(\eta)$ is the intrinsic entropy. Taking into account that the entropy production rate Π, as given by (110), is the average of σ, that is, $\Pi = \langle\sigma(\eta', \eta)\rangle$, and that the entropy flux rate Φ, as given by (105), is the average of ϕ, that is, $\Phi = \langle\phi(\eta', \eta)\rangle$, we get, in the limit $\Delta t \to 0$

$$\Pi = \Phi + \frac{dS}{dt}, \qquad (134)$$

where S is the average of $\mathscr{S}$, that is, $S = \langle\mathscr{S}\rangle$.

In the continuous time limit we may write the Jarzynski identity as

$$\langle \exp\{-\int_0^t \sigma dt\}\rangle = 1, \qquad (135)$$

where the integral extends over a given trajectory in phase space or, taking into account (133),

$$\langle\exp\{-\int_0^t \phi\, dt - [\mathscr{S}(t) - \mathscr{S}(0)]\}\rangle = 1. \qquad (136)$$

From expression (44) for Φ and bearing in mind that $\Phi = \langle\phi\rangle$ we get

$$\langle \exp\{\sum_i \frac{1}{T_i}\left(\frac{m}{2}[v_i^2(t) - v_i^2(0)] - \int_0^t v_i F_i dt\right)$$

$$-[\mathscr{S}(t) - \mathscr{S}(0)]\}\rangle = 1, \qquad (137)$$

which is the Jarzynski equality for a nonequilibrium systems of particles following a Fokker-Planck equation describing the contact with several heat baths at distinct temperatures.

V. CONCLUSION

We have determined an expression for the entropy production rate and entropy flux rate in irreversible systems described by a Fokker-Planck equation. The irreversible character is represented either by nonconservative forces or by the contact of the system with heat baths at different temperatures. The expression for the entropy production was obtained by using a master equation representation of the Fokker-Planck and through a definition of entropy production rate and entropy flux rate that involve the transition rates and in this sense is related to the ratio between the probabilities of a trajectory in phase space and its time reversal. We have shown that, in the stationary state, the entropy production, or the entropy flux, is related to the dissipated power. More precisely, we have shown that the entropy production in a system in contact with several heat baths is a sum of terms, each one being the ratio between the dissipated power and the temperature of the corresponding heat bath. Usually this relation is actually used to define entropy flux. The definitions of entropy production and entropy flux as we used here make no a priori reference to the dissipated power. In this sense they are universal definitions being valid for general open systems not necessarily in contact with heat reservoirs. As an example of our formalism, we have used the expression for the entropy production rate to determine the heat conductance of a simple system consisting of two Brownian particles, each one in contact to heat reservoirs at distinct temperatures. Our results agree with those obtained by other methods. Finally, we have made a connection between the definition of entropy production rate and the Jarzynski equality.

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