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Stochastic approach to equilibrium and nonequilibrium thermodynamics

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We develop the stochastic approach to thermodynamics based on stochastic dynamics, which can be discrete (master equation) and continuous (Fokker-Planck equation), and on two assumptions concerning entropy. The first is the definition of entropy itself and the second the definition of entropy production rate, which is non-negative and vanishes in thermodynamic equilibrium. Based on these assumptions, we study interacting systems with many degrees of freedom in equilibrium or out of thermodynamic equilibrium and how the macroscopic laws are derived from the stochastic dynamics. These studies include the quasiequilibrium processes; the convexity of the equilibrium surface; the monotonic time behavior of thermodynamic potentials, including entropy; the bilinear form of the entropy production rate; the Onsager coefficients and reciprocal relations; and the nonequilibrium steady states of chemical reactions.

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I. INTRODUCTION

The kinetic theory, introduced and developed in the second half of the 19th century by Clausius [1], Maxwell [2], and Boltzmann [3,4], aimed to derive the macroscopic properties of matter, which include the laws of thermodynamics, from the underlying microscopic movement, governed by the laws of mechanics. In principle, this task can be achieved if we assume that the macroscopic laws are connected to the microscopic laws. We cannot know *a priori* whether the connection exists or not. But, considering that it is an experimental fact that the laws of mechanics, classical or quantum, are obeyed at the microscopic level by the same particles that constitute a macroscopic body, which obeys macroscopic laws, it is reasonable to assume that the connection exists. Once we assume this connection, the next task is to perform the actual derivation of macroscopic laws from the microscopic laws of mechanics. This task was in fact undertaken by the founders of the kinetic theory and many macroscopic laws were in fact derived. This includes the theorem of equipartition of energy, the Maxwell distribution of velocities [2], the Boltzmann H-theorem [3], and the Gibbs probability distribution [5]. However, many results cannot be said to have been derived from pure mechanics alone [6,7]. A new ingredient was introduced in the course of derivation, namely the stochastic behavior, in most cases in an implicit form.

The derivation from pure mechanics of the results just mentioned would be accomplished if we could show that the new ingredient, the stochastic behavior, is a consequence of the microscopic mechanical motion, which is deterministic. At first sight the random behavior seems to be in contradiction with a deterministic motion. However, the results coming from the theory of deterministic chaos [8] has proven that a deterministic motion can behave stochastically. In fact, the possibility of mapping chaotic dynamics into a stochastic process has already been addressed [9]. The Gibbs probability distribution, for instance, is believed to come from the underlying mechanics through a stochastic behavior, although there is no known general derivation from pure mechanics. In some cases, the derivation is known [10]. In other cases, such as a system of hard spheres, numerical simulations of the equations of motion may, for instance, show the validity of the equipartition of energy or may provide the macroscopic properties directly [11].

The reasoning and examples given above lead us to presume that the macroscopic properties are obtained from microscopic mechanics in two major steps: (1) from the underlying mechanics to a probabilistic or stochastic approach and (2) from this approach to the macroscopic properties. This is particularly clear in the case of equilibrium thermodynamic properties, which are derived from the Gibbs probability distribution, which in turn comes from the underlying mechanics, a step not yet fully demonstrated and known as ergodic hypothesis. The first step will not concern us here. The second step, which is the purpose of the present paper, aims to derive the macroscopic properties, which include equilibrium and nonequilibrium thermodynamic properties, from a stochastic approach.

The stochastic approach to equilibrium and nonequilibrium thermodynamics or, in short, stochastic thermodynamics, which is the second step of our scheme and the subject of the present paper, has been adopted by several authors and become a consistent theory of nonequilibrium thermodynamics [12–49]. An important step in this direction occurred when Schnakenberg [17] introduced the stochastic definition of entropy production rate which has a fundamental role in our approach in addition to the probabilistic definition of entropy itself, introduced by Boltzmann [4] and generalized by Gibbs [5].

Our approach here is based on the adoption of a Markovian stochastic evolution on a discrete or on a continuous space and on two assumptions concerning entropy. The first is the definition of entropy itself and the second the definition of entropy production rate. Based on these assumptions we will consider systems in equilibrium and out of thermodynamic equilibrium and how the macroscopic nonequilibrium laws can be derived from the stochastic dynamics, which is the second step mentioned above. We will treat some fundamental issues that have barely been considered or that have not been addressed in the context of stochastic thermodynamics. This includes several thermodynamic results of systems in equilibrium [50,51] and out of equilibrium [52–58] such as the quasiequilibrium processes; the convexity of the equilibrium

surface in thermodynamic space; the monotonic time behavior of thermodynamic potentials, including entropy; the bilinear form of the entropy production rate; the Onsager coefficients and reciprocal relations; and the nonequilibrium steady states of chemical reactions.

The stochastic approach in continuous state space was used by Einstein [59], Smoluchowski [60], and Langevin [61] to explain Brownian motion. It was generalized to the case of Brownian particles subject to an external force by Fokker [62], Smoluchowski [63], Planck [64], and Ornstein [65], and the equation governing the time evolution of the probability distribution became known as the Fokker-Planck equation. Kramers [66] extended the Fokker-Planck equation to the case of a massive particle and studied the escape of a Brownian particle over a potential barrier arriving at the Arrhenius factor.

Markovian stochastic dynamics [67–70] has been used in various problems in physics, chemistry, and biology, either in continuous or discrete state space. In the former case, the evolution of the probability distribution is governed by a Fokker-Planck equation and in the later by a master equation. We mention the study of chemical reactions [16,19,20,30,46], population dynamics and epidemiology [71–73], and biological systems in general [15,28,43,45,74–78]. We wish to mention particularly the stochastic models with many degrees of freedom such as the so-called stochastic lattice models usually used to describe phase transitions and criticality in physics, chemistry, and biology [26,79–86].

II. MASTER EQUATION

A. Entropy and entropy production

We assume that the system follows a microscopic stochastic dynamics. More precisely, we assume that the system is described by a continuous-time Markovian stochastic process. Considering a discrete space of states, this assumption posits that the time evolution equation is set up once the transition rates are given. The transition rates play thus a fundamental role in the present approach and we may say that a system is considered to be theoretically defined when this quantity is given *a priori*. Given the transition rates, the probability $P_i(t)$ of state i at time t is obtained by solving the evolution equation, in this case a master equation,

$$\frac{d}{dt}P_i(t) = \sum_j \{W_{ij}P_j(t) - W_{ji}P_i(t)\}, \tag{1}$$

where W_{ij} denotes the transition rate from state j to state i. In this section and the next we will consider transitions with the following property: If the rate W_{ij} of the transition $j \to i$ is nonzero, then the rate W_{ji} of the reverse transition $i \to j$ is also nonzero. Later, in the study of the Fokker-Planck equation, we will have the opportunity to treat the case in which the reverse transition rate may vanish.

As mentioned above, the derivation of the macroscopic properties, including the laws of thermodynamics, is carried out by the introduction of two assumptions concerning entropy. The first is the definition of entropy itself. The entropy S of a system in equilibrium or out of equilibrium is taken to be the following expression:

$$S(t) = -k_B \sum_i P_i(t) \ln P_i(t), \tag{2}$$

which is the extension of the equilibrium Boltzmann-Gibbs entropy to nonequilibrium situations, where k_B is the Boltzmann constant.

The second assumption concerns the definition of the production of entropy. This quantity should meet two fundamental properties. It must be non-negative and vanish identically in thermodynamic equilibrium. Following Schnakenberg [17], we assume the following expression for the entropy production rate:

$$\Pi(t) = \frac{k_B}{2}\sum_{ij}\{W_{ij}P_j(t) - W_{ji}P_i(t)\}\ln\frac{W_{ij}P_j(t)}{W_{ji}P_i(t)}, \tag{3}$$

which is clearly non-negative because each term is of the form $(x-y)\ln(x/y)$. This form of entropy production rate has been used by several authors [18,19,26–30,32,37,38,40,42,70] within stochastic dynamics and applications.

B. Entropy flux

Let us consider the time variation of the average of a state function, such as energy, given by

$$U(t) = \sum_i E_i P_i(t). \tag{4}$$

Using the master equation (1) it follows that

$$\frac{dU}{dt} = \Phi_u, \tag{5}$$

where

$$\Phi_u(t) = \sum_{ij}(E_i - E_j)W_{ij}P_j(t) \tag{6}$$

is the total flux of energy from outside to the system. Equation (5) represents the conservation of energy.

Equation of the type (5) is valid for any conserved quantity and this is not the case of entropy. For instance, in a nonequilibrium stationary state the total flux of energy vanishes but not the total flux of entropy, which is nonzero because entropy is continuously being produced. The equation for the time variation of entropy S should be written as [55]

$$\frac{dS}{dt} = \Pi - \Phi, \tag{7}$$

where Φ is the flux of entropy from the system to the outside and Π is the entropy production per unit time, given by Eq. (3). It is common to write d_iS/dt and d_eS/dt for the entropy production rate and entropy flux, respectively, but we avoid this terminology because these quantities are not in fact time derivatives of any quantity.

Taking the time derivative of Eq. (2) and using the master equation (1), we may write the time derivative of entropy as

$$\frac{dS}{dt} = k_B\sum_{ij}\{W_{ij}P_j(t) - W_{ji}P_i(t)\}\ln P_i(t), \tag{8}$$

or, in an equivalent form,

$$\frac{dS}{dt} = k_B \sum_{ij} W_{ij} P_j(t) \ln \frac{P_i(t)}{P_j(t)}. \tag{9}$$

Comparing with (7) we see that the right-hand side of this equation should equal $\Pi - \Phi$. Using the definition of Π, given by (3), which we write in the form

$$\Pi(t) = k_B \sum_{ij} W_{ij} P_j(t) \ln \frac{W_{ij} P_j(t)}{W_{ji} P_i(t)}, \tag{10}$$

and, comparing with Eq. (9), we get the flux of entropy from the system to outside,

$$\Phi(t) = k_B \sum_{ij} W_{ij} P_j(t) \ln \frac{W_{ij}}{W_{ji}}, \tag{11}$$

which is equivalent to

$$\Phi(t) = \frac{k_B}{2} \sum_{ij} \{W_{ij} P_j(t) - W_{ji} P_i(t)\} \ln \frac{W_{ij}}{W_{ji}}. \tag{12}$$

The integration of (7) in a time interval will lead us to the Clausius inequality. Indeed, from Eq. (7) we may write

$$\Delta S = \int \Pi dt - \int \Phi dt. \tag{13}$$

If we identify the entropy flux Φ as the ratio between the heat flux dQ/dt and the temperature T of the environment, then $\int \Phi dt = -\int (dQ/T)$. But the first integral is non-negative because $\Pi \geqslant 0$ so

$$\Delta S \geqslant \int \frac{dQ}{T}, \tag{14}$$

which is the Clausius inequality [87]. In equilibrium, $\Delta S = \int dQ/T$, equality that was used by Clausius to define entropy. The difference between ΔS and the integral $\int dQ/T$, which is the production of entropy, represents, according to Clausius, the "uncompensated transformation" [87].

In the recent literature it is common to use another nomenclature for the entropy production Π, the entropy flux Φ, and the time derivative of entropy dS/dt. The quantities that correspond to the time integral of these three quantities are called, respectively, the total entropy change, the environment entropy change, and internal entropy change [44,48].

C. Thermodynamic equilibrium

The microscopic definition of thermodynamic equilibrium, from the static point of view, is usually characterized in terms of the Gibbs probability distribution. From the dynamic point of view, the description of equilibrium by the Gibbs distribution is necessary but not sufficient. There are examples [88–90] of spin models that are described by the Gibbs distribution but are not in thermodynamic equilibrium in the sense that entropy is continuously being generated. From a dynamic point of view, the thermodynamic equilibrium is characterized by the vanishing of the entropy production rate and, of course, by a time-independent probability distribution. The vanishing of (3) gives

$$W_{ij} P_j = W_{ji} P_i, \tag{15}$$

which is the detailed balance condition that characterizes the thermodynamic equilibrium [14] and is equivalent to microscopic reversibility.

In the stationary state, that is, when the probability P_i is independent of time, the right-hand side of (1) vanishes, that is,

$$\sum_j \{W_{ij} P_j - W_{ji} P_i\} = 0, \tag{16}$$

which we may call the global balance. The reversibility condition (15) thus can be understood as detailed balance condition because each term of the global balance equation vanishes. Although the global balance is a necessary condition for reversibility, it is not a sufficient condition.

Considering that the equilibrium distribution P_i^e is known, the solution of (15) for the transition rate is

$$W_{ij} = K_{ij} \left(\frac{P_i^e}{P_j^e} \right)^{1/2}, \tag{17}$$

where K_{ij} is symmetric, that is, $K_{ij} = K_{ji}$. The transition rates for the various situation in which the system is found in equilibrium in the stationary state can now be constructed. For an isolated system (microcanonical ensemble) the equilibrium probability distribution P_i is a constant whenever the energy function E_i equals a given energy, say, U, and vanishes otherwise. Therefore, in this case $W_{ij} = K_{ij}$ when $E_i = E_j$ and vanishes otherwise. In short, $W_{ij} = W_{ji}$.

For a system in contact with a heat reservoir (canonical ensemble) at temperature T, the equilibrium probability distribution is given by

$$P_i^e = \frac{1}{Z} e^{-\beta E_i}, \tag{18}$$

where $\beta = 1/k_B T$, so in this case the transition rate fulfills the relation

$$\frac{W_{ij}}{W_{ji}} = e^{-\beta(E_i - E_j)} \tag{19}$$

and is given by

$$W_{ij} = K_{ij} e^{-\beta(E_i - E_j)/2}. \tag{20}$$

If, in addition, to be in contact with a heat reservoir, the system is in contact with a reservoir of particles, then

$$P_i^e = \frac{1}{\Xi} e^{-\beta E_i + \beta \mu n_i}, \tag{21}$$

where μ is the chemical potential and n_i is the number of particles. In this case the transition rate fulfills the relation

$$\frac{W_{ij}}{W_{ji}} = e^{-\beta(E_i - E_j) + \beta\mu(n_i - n_j)} \tag{22}$$

and is given by

$$W_{ij} = K_{ij} e^{-\beta(E_i - E_j)/2 + \beta\mu(n_i - n_j)/2}, \tag{23}$$

where, again, $K_{ij} = K_{ji}$.

D. The approach to equilibrium

Let us consider the transient regime of a system that approaches equilibrium. The time-dependent probability

distribution is the solution of the master equation (1) with transition rates that satisfy the detailed balance and is appropriate for each type of contact of the system with the environment.

We treat first the case of microcanonical distribution, which describes an isolated system. In this case, as we have seen, $W_{ij} = W_{ji}$ so the entropy flux (11) vanishes identically, $\Phi = 0$. Therefore,

$$\frac{dS}{dt} = \Pi, \tag{24}$$

so

$$\frac{dS}{dt} \geqslant 0. \tag{25}$$

That is, the entropy of an isolated system is a monotonically increasing function of time.

Next we consider the canonical distribution which describes the contact of a system with a heat reservoir. The transition rate is given by (20), which, replaced in the entropy flux (11), gives

$$\Phi = -k_B\beta \sum_{ij} \{W_{ij} P_j(t) - W_{ji} P_i(t)\} E_i. \tag{26}$$

Using the master equation (1), the flux of entropy can be written in the form

$$\Phi = -\frac{1}{T}\frac{dU}{dt}, \tag{27}$$

where U is the average of energy, given by (4). Equation (27) shows that the quantity Φ is proportional to dU/dt. Notice that (27) implies that Φ vanishes in the equilibrium regime ($t \to \infty$) as it should.

Equation (7) gives

$$\frac{dU}{dt} - T\frac{dS}{dt} = -T\Pi. \tag{28}$$

If we define the free energy by $F = U - TS$ and take into account that T is constant, that is, it does not depend on time, we get

$$\frac{dF}{dt} = -T\Pi, \tag{29}$$

so

$$\frac{dF}{dt} \leqslant 0. \tag{30}$$

That is, the free energy of a system in contact with a heat reservoir is a monotonically decreasing function of time. In other terms, the free energy decreases monotonically to its equilibrium value.

Equation (30) is also the expression of the Boltzmann H-theorem [3]. Indeed, the Boltzmann H function is defined by

$$H(t) = \sum_i P_i(t) \ln \frac{P_i(t)}{P_i^e}, \tag{31}$$

where P_i^e is the equilibrium canonical distribution given by Eq. (18). It is straightforward to show that $F = F_0 + H/\beta$, where F_0 does not depend on time. Therefore, the inequality (30) is equivalent to $dH/dt \leqslant 0$, which is the Boltzmann H-theorem.

The grand-canonical distribution describes the contact of the system with a particle reservoir and with a heat reservoir. The transition rate for this case is given by (23), which, replaced in the expression (11) and using the master equation (1), allows us to reach the following expression for the entropy flux:

$$\Phi = -\frac{1}{T}\frac{dU}{dt} + \frac{\mu}{T}\frac{dN}{dt}, \tag{32}$$

where U is the average energy, given by (4), and N is the average number of particles,

$$N(t) = \sum_i n_i P_i(t). \tag{33}$$

Taking into account that $dS/dt = \Pi - \Phi$, we get

$$\frac{dU}{dt} - T\frac{dS}{dt} - \mu\frac{dN}{dt} = -T\Pi, \tag{34}$$

which can be written as

$$\frac{d\phi}{dt} = -T\Pi, \tag{35}$$

where $\phi = U - TS - \mu N$ is the grand thermodynamic potential and we have taken into account that T and μ are constant. Since $\Pi \geqslant 0$ it follows that $d\phi/dt \leqslant 0$.

Let us integrate equation (34) from an initial time $t = t_0$ to infinity,

$$(U - U_0) - T(S - S_0) - \mu(N - N_0) = -T\int_{t_0}^{\infty} \Pi dt, \tag{36}$$

from which follows the inequality

$$(U - U_0) - T(S - S_0) - \mu(N - N_0) \leqslant 0, \tag{37}$$

because $\Pi \geqslant 0$. Taking into account that, for large-enough times, the system reaches equilibrium at a temperature T and imposing that at $t = t_0$ the system was in equilibrium, at a different temperature, say, T_0, we may conclude from the inequality (37) that U, S, and N make up a convex surface, in accordance with equilibrium thermodynamics.

E. Quasiequilibrium

It is common to state the laws of equilibrium thermodynamics in terms of thermodynamic processes. This seems at first sight contradictory because a process implies a change in the thermodynamic state and thus a displacement from equilibrium. To overcome this problem, one introduces the quasistatic process, a process which is so slow that the system may be considered to be in equilibrium. We will show below that the production of entropy in this process is negligible so in fact the system may be considered to be in equilibrium. In which sense the production is negligible will be shown below.

Let us consider a system in contact with a heat bath and a particle reservoir whose temperature and chemical potential, understood as control parameters, are slowly varying in time. To describe this situation we assume a time-dependent transition rate $W_{ij}(t)$ of the form (23), where $K_{ij}(t)$ may depend on time, that is,

$$W_{ij}(t) = K_{ij}(t) e^{-\beta(E_i - E_j)/2 + \beta\mu(n_i - n_j)/2}, \tag{38}$$

where $K_{ij}(t) = K_{ji}(t)$, so

$$\frac{W_{ij}(t)}{W_{ji}(t)} = \frac{e^{-\beta(E_i-\mu n_i)}}{e^{-\beta(E_j-\mu n_j)}}, \tag{39}$$

where $\beta = 1/k_B T$ and $T(t)$ depends on time and the chemical potential $\mu(t)$ also depends on time. We assume, moreover, that $d\beta/dt = \alpha$ and $d\mu/dt = \gamma$ are small and are both of the same order of magnitude.

Replacing Eq. (39) in expression (11) for the entropy flux and after some straightforward algebraic manipulation we reach again the result

$$\Phi = -\frac{1}{T}\frac{dU}{dt} + \frac{\mu}{T}\frac{dN}{dt}. \tag{40}$$

Now $dS/dt = \Pi - \Phi$ so

$$\frac{dU}{dt} = T\frac{dS}{dt} + \mu\frac{dN}{dt} - T\Pi. \tag{41}$$

Let us now find the solution of the master equation. To this end, we write the solution as

$$P_i(t) = P_i^*(t) + A_i(t), \tag{42}$$

where

$$P_i^*(t) = \frac{1}{\Xi(\beta,\mu)}\exp\{-\beta(E_i - \mu n_i)\}, \tag{43}$$

and $\Xi(\beta,\mu)$ is a time-dependent quantity such that $P_i^*(t)$ is normalized at any time and A_i is small when compared to P_i^*. It is important to bear in mind that although $P_i^*(t)$ obeys the relation

$$W_{ij}(t)P_j^*(t) = W_{ji}(t)P_i^*(t), \tag{44}$$

and can be interpreted as a probability distribution, it is not the solution of the master equation, given by (1). The substitution of P_i^* on the master equation (1) makes the right-hand side equal to zero but not the left-hand side. Replacing Eq. (42) into the master equation, we get, up to first order in the perturbation A_i,

$$\frac{d}{dt}P_i^*(t) = \sum_j \{W_{ij}(t)A_j(t) - W_{ji}(t)A_i(t)\}. \tag{45}$$

Now

$$\frac{dP_i^*}{dt} = \frac{\partial P_i^*}{\partial\beta}\alpha + \frac{\partial P_i^*}{\partial\mu}\gamma, \tag{46}$$

which, in view of Eq. (45), implies that the perturbation $A_j(t)$ is of the order of α and γ. From the expression (40) for the entropy flux Φ, it follows that Φ is also of the order α and γ. On the other hand, if we consider the expression (3) for the entropy production Π, it follows that Π is of of second order in α and γ. Therefore, in the quasiequilibrium regime, in which we consider only terms up to first order in α and γ, the relation $dS/dt = \Pi - \Phi$ becomes $dS/dt = -\Phi$, that is, the production of entropy vanishes when compared with the flux of entropy. Using this result it follows from (41) that the following thermodynamic relation holds:

$$\frac{dU}{dt} = T\frac{dS}{dt} + \mu\frac{dN}{dt}. \tag{47}$$

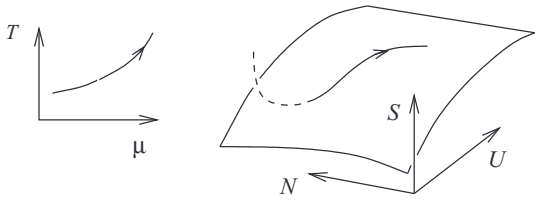

FIG. 1. A path in the T,μ space and the corresponding trajectory in the thermodynamic space S,U,N. If the variations in T and μ are very slow, then the trajectory in the thermodynamic space approaches and remains on a certain surface which has the property of convexity and is identified as the thermodynamic equilibrium surface. The portions of the trajectory outside and on the surface are represented by dashed and solid lines, respectively.

Let us take a look at the thermodynamic space spanned by the variables S, U, and N. From the solution of the master equation, we may determine these quantities as a function of time by using the definitions (2), (4), and (33). The evolution of the system may be represented by a trajectory of a point in this space, as shown in Fig. 1. The representative point will describe a generic trajectory in this space. But if T and μ start to vary very slowly, the trajectory, according to the result (47), will approach and remain on a certain surface of this space, as seen in Fig. 1. According to (47), the surface is represented by the equation

$$dU = TdS + \mu dN, \tag{48}$$

so the temperature T of the thermal reservoir becomes identified as the tangent to the surface $U(S,N)$ along the S direction, $T = \partial U/\partial S$, and thus can be interpreted as the temperature of the system. Similarly, the chemical potential of the particle reservoir becomes identified as the tangent to the surface $U(S,N)$ along the N direction, $\mu = \partial U/\partial N$, and thus can be interpreted as the chemical potential of the system. Notice that, according to the inequality (37), this surface has the property of convexity.

We should remark that, far from equilibrium, the temperature of the system cannot be defined because S, U, and N are not connected by relation (48). The same can be said about the free energy of systems far from equilibrium. Notice, however, that the quantity $F = U - TS$, defined previously and called free energy, is not properly a property of the system because T is the temperature of the reservoir and not the temperature of the system, since it cannot be defined. In equilibrium or quasiequilibrium, however, it becomes a well-defined quantity as much as the temperature. It is worth mentioning in addition that according to the approach just presented, the control parameters should be the thermodynamic variables known as thermodynamic field variables [51].

F. Fluxes and forces

We consider here the contact of a system with two distinct reservoirs. To treat this situation properly, we assume that each pair of states (i,j) is either associated to the first reservoir or to the second reservoir or to neither of them. In other words, the set of pairs (i,j) is partitioned into three subsets, associated to the first reservoir, to the second reservoir and neither of them,

which we denote by A, B, and C, respectively. The transition rates associated to the reservoirs 1 and 2 are denoted by W_{ij}^1 and W_{ij}^2, respectively, and are assumed to be of the same form of (23), that is,

$$W_{ij}^r = K_{ij}^r e^{-\beta_r(E_i-E_j)/2+\beta_r\mu_r(n_i-n_j)/2}, \tag{49}$$

for $r = 1,2$, where K_{ij}^r is symmetric as before. In addition, K_{ij}^1 depends on T_1 and μ_1 and is nonzero only if $(i,j) \in A$, and K_{ij}^2 depends on T_2 and μ_2 and is nonzero only if $(i,j) \in B$. We are denoting by T_1 and μ_1 and T_2 and μ_2 the temperatures and chemical potentials of the two reservoirs and $\beta_r = 1/k_B T_r$. The full transition rate is given by

$$W_{ij} = W_{ij}^0 + W_{ij}^1 + W_{ij}^2, \tag{50}$$

where W_{ij}^0 may be nonzero only if $(i,j) \in C$. In this case it is nonzero if $E_i = E_j$ and $N_i = N_j$, in which case $W_{ij}^0 = W_{ji}^0$.

In the following, we consider the stationary regime for which the stationary probability distribution P_i fulfills the global balance (16) but not the detailed balance. In the present case $\Pi = \Phi$ and using the expression (11) we may write

$$\Pi = k_B \sum_{r=1,2} \sum_{ij} W_{ij}^r P_j \ln \frac{W_{ij}^r}{W_{ji}^r}, \tag{51}$$

where the first summation runs only over $r = 1,2$. The terms corresponding to $r = 0$ vanish because $W_{ij}^0 = 0$ or because $W_{ij}^0 = W_{ji}^0$. Replacing expression (49) in this equation, the entropy production can be written as

$$\Pi = k_B \sum_{r=1,2} \sum_{ij} W_{ij}^r P_j \beta_r [(E_j - E_i) - \mu_r(n_j - n_i)]. \tag{52}$$

Now the flux of energy $\mathcal{J}_u$ and the flux of particles $\mathcal{J}_n$ from reservoir 1 into the system are given by

$$\mathcal{J}_u = \sum_{ij} W_{ij}^1 P_j (E_i - E_j), \tag{53}$$

$$\mathcal{J}_n = \sum_{ij} W_{ij}^1 P_j (n_i - n_j). \tag{54}$$

The substitution of (53) and (54) into (52) and the use of the global balance condition (16) allow us to write the entropy production rate in the bilinear form [52,53,55]

$$\Pi = X_u \mathcal{J}_u + X_n \mathcal{J}_n, \tag{55}$$

where X_u and X_n are the thermodynamic forces

$$X_u = \frac{1}{T_2} - \frac{1}{T_1}, \quad X_n = \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}, \tag{56}$$

conjugated to the flux of energy and particles, respectively.

G. Onsager coefficients

When $T_2 = T_1$ and $\mu_2 = \mu_1$, that is, when $X_u = 0$ and $X_n = 0$, the fluxes $\mathcal{J}_u$ and $\mathcal{J}_n$ vanish. Therefore, up to linear terms in X_u and X_n we expect the following linear behavior of the fluxes:

$$\mathcal{J}_u = L_{uu} X_u + L_{un} X_n, \tag{57}$$

$$\mathcal{J}_n = L_{nu} X_u + L_{nn} X_n. \tag{58}$$

The coefficients L_{uu}, L_{un}, L_{nu}, and L_{nn} are the Onsager coefficients. According to Onsager, the cross coefficients are equal, $L_{un} = L_{nu}$, which is the Onsager reciprocal relation. In the following we will derive expressions for these coefficients and prove the reciprocal relation.

We will suppose that T_1 and μ_1 are fixed and let $T_2 \to T_1$ and $\mu_2 \to \mu_1$. Let P_i^e be the probability distribution corresponding to the equilibrium case, given by

$$P_i^e = \frac{1}{\Xi} e^{-\beta_1(E_i-\mu_1 n_i)}. \tag{59}$$

The transition rate W_{ij}^e obeys the detailed balance

$$W_{ij}^e P_j^e = W_{ji}^e P_i^e \tag{60}$$

and is given by

$$W_{ij}^e = K_{ij}^e e^{-\beta_1(E_i-E_j)/2+\beta_1\mu_1(n_i-n_j)/2}, \tag{61}$$

where $K_{ij}^e = K_{ij}^1 + K_{ij}^* + K_{ij}^0$ and K_{ij}^* equals K_{ij}^2 when $T_2 \to T_1$ and $\mu_2 \to \mu_1$ and $K_{ij}^0 = W_{ij}^0$.

The stationary solution P_i of the master equation (16) is written as

$$P_i = P_i^e (1 + a_i X_u + b_i X_n), \tag{62}$$

up to linear term in X_u and X_n. Replacing into the expressions (53) and (54) we get the Onsager coefficients in the form

$$L_{uu} = \frac{1}{2} \sum_{ij} W_{ij}^1 P_j^e (a_j - a_i)(E_i - E_j), \tag{63}$$

$$L_{un} = \frac{1}{2} \sum_{ij} W_{ij}^1 P_j^e (b_j - b_i)(E_i - E_j), \tag{64}$$

$$L_{nu} = \frac{1}{2} \sum_{ij} W_{ij}^1 P_j^e (a_j - a_i)(n_i - n_j), \tag{65}$$

$$L_{nn} = \frac{1}{2} \sum_{ij} W_{ij}^1 P_j^e (b_j - b_i)(n_i - n_j), \tag{66}$$

where we have used the detailed balance condition (60). In the form given by Eqs. (64) and (65) we cannot tell whether the coefficients L_{nu} and L_{un} are equal. Next we perform a transformation to find expressions that will show that these coefficients are indeed equal to each other.

Replacing (62) into (16), and expanding the result up to linear terms in X_u and X_n, we end up with the following equations for a_i and b_i:

$$\sum_j W_{ij}^e P_j^e (a_j - a_i) + \frac{1}{k_B} \sum_j W_{ij}^* P_j^e (E_j - E_i) = 0, \tag{67}$$

$$\sum_j W_{ij}^e P_j^e (b_j - b_i) + \frac{1}{k_B} \sum_j W_{ij}^* P_j^e (n_j - n_i) = 0, \tag{68}$$

where W^*_{ij} equals W^2_{ij} when $T_2 \to T_1$ and $\mu_2 \to \mu_1$ and is given by

$$W^*_{ij} = K^*_{ij} e^{-\beta_1(E_i - E_j)/2 + \beta_1\mu_1(n_i - n_j)/2}. \tag{69}$$

Multiplying (67) by E_i and by a_i and summing in i we are led to two equations from which we may obtain the following expression for L_{uu}:

$$L_{uu} = \frac{1}{2k_B}\sum_{ij} W^*_{ij} P^e_j (E_j - E_i)^2 - \frac{k_B}{2}\sum_{ij} W^e_{ij} P^e_j (a_j - a_i)^2. \tag{70}$$

Multiplying (68) by n_i and by b_i and summing in i we are lead to two equations from which we may obtain the following expression for L_{nn}:

$$L_{nn} = \frac{1}{2k_B}\sum_{ij} W^*_{ij} P^e_j (n_j - n_i)^2 - \frac{k_B}{2}\sum_{ij} W^e_{ij} P^e_j (b_j - b_i)^2. \tag{71}$$

Multiplying (67) by n_i and (68) by a_i and summing in i, we get two equations from which we reach an expression for L_{nu}. Similarly, multiplying (67) by b_i and (68) by E_i and summing in i, we get an expression for L_{un} which is equal to L_{nu}, proving the reciprocal relation. The expression for these two quantities is given by

$$L_{un} = L_{nu} = \frac{1}{2k_B}\sum_{ij} W^*_{ij} P^e_j (E_j - E_i)(n_j - n_i) - \frac{k_B}{2}\sum_{ij} W^e_{ij} P^e_j (b_j - b_i)(a_j - a_i). \tag{72}$$

It is worth mentioning that in the course of derivation of these expressions, we have made use of the detailed balance condition, which is thus a necessary condition to prove the reciprocal relation. However, the expressions for the Onsager coefficients do not depend on the equilibrium distribution alone but depend also on the deviations a_i and b_i.

H. Several species of particles

We will now treat the case of a system composed by several types of particles in contact with two particle reservoirs, denoted by 1 and 2. In the steady state, fluxes of particles of the various types will be established between the two reservoirs. Each reservoir is in fact a set of reservoirs, one for each type of particles. As before, denoting by E_i the energy of state i and by n^k_i the number of particles of species k in state i, the rate of the transition $j \to i$ associated to the reservoir r and species k is given by

$$W^{rk}_{ij} = K^{rk}_{ij} e^{-\beta[(E_i - E_j) - \mu^r_k (n^k_i - n^k_j)]/2}, \tag{73}$$

where μ^r_k is the chemical potential of species k associated to reservoir r and K^{rk}_{ij} is symmetric. The reservoirs are also thermal reservoirs with a common temperature T and $\beta = 1/k_B T$. A transition rate that is not associated to any reservoir is denoted by W^0_{ij} and is assumed to be of the form

$$W^0_{ij} = K^0_{ij} e^{-\beta(E_i - E_j)/2}, \tag{74}$$

which describes the contact with a heat reservoir at temperature T, where K^0_{ij} is symmetric.

At the stationary state, the entropy production rate equals the flux of entropy and is given by

$$\Pi = k_B \sum_{r=0,1,2}\sum_k \sum_{ij} W^{rk}_{ij} P_j \ln \frac{W^{rk}_{ij}}{W^{rk}_{ji}}, \tag{75}$$

which follows from the general expression (11). The substitution of (73) and (74) into this expression gives

$$\Pi = \frac{1}{T}\sum_{r=1,2}\sum_k \sum_{ij} W^{rk}_{ij} P_j \mu^r_k \left(n^k_i - n^k_j\right), \tag{76}$$

where the terms involving the energy vanish. Taking into account that the flux $\mathcal{J}_k$ of particles of type k, from the reservoir 1 to the system, is given by

$$\mathcal{J}_k = \sum_{ij} W^{1k}_{ij} P_j \left(n^k_i - n^k_j\right), \tag{77}$$

and using the total balance equation (16), we may write again the entropy production rate in the bilinear form

$$\Pi = \sum_k X_k \mathcal{J}_k, \tag{78}$$

where

$$X_k = \frac{1}{T}\left(\mu^1_k - \mu^2_k\right) \tag{79}$$

is the thermodynamic force associated to species k.

For the case of two types of particles, it follows from expression (78) that $X_1\mathcal{J}_1 + X_2\mathcal{J}_2 \geqslant 0$ because $\Pi \geqslant 0$. If $X_1 < 0$, it is possible to have $\mathcal{J}_1 > 0$, as long as $X_2\mathcal{J}_2 > |X_1|\mathcal{J}_1$, so the flux of particles of type 1 will occur against the chemical potential gradient. This is, for instance, a mechanism for the active transport across a cell membrane. A simple model [74] of this type of transport is examined next.

A cell membrane is assumed to have a certain number of channels through which two types of molecules may cross the membrane from the exterior to the interior of the cell. The channels function independent of each other so it suffices to consider just one of them. A channel may be open to the exterior, understood as reservoir 1, or to the interior, understood as reservoir 2, and can be either empty or hold a molecule A or two molecules, one A and another B. The possible states and transitions are shown in Fig. 2.

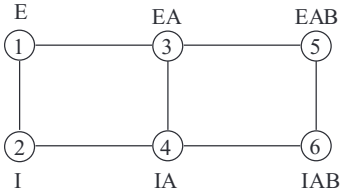

FIG. 2. Transition diagram for a model for active transport across a cell membrane. The circles represent the possible states of a channel and the bonds represent the possible transitions. The possible states of the channel are (a) open to exterior and empty (E), holding a molecule (EA), or holding two molecules (EAB); (b) open to interior and empty (I), holding a molecule (IA), or holding two molecules (IAB).

Denoting by w_{ij} the rate of the transition $j \to i$, then w_{31}, w_{13}, w_{53}, and w_{35} are associated to the reservoir 1, whereas w_{42}, w_{24}, w_{64}, and w_{46}, associated to reservoir 2. In this simple model, the energies of the state are assumed to be the same so, according to (73), they hold the following relations:

$$\frac{w_{31}}{w_{13}} = e^{\beta\mu_A^1}, \quad \frac{w_{53}}{w_{35}} = e^{\beta\mu_B^1}, \tag{80}$$

$$\frac{w_{42}}{w_{24}} = e^{\beta\mu_A^2}, \quad \frac{w_{64}}{w_{46}} = e^{\beta\mu_B^2}, \tag{81}$$

where μ_A^k and μ_B^k are the chemical potentials of molecules A and B associated to reservoir k. The other rates are not related to the reservoirs and are symmetric, $w_{21} = w_{12}$, $w_{43} = w_{34}$, and $w_{65} = w_{56}$. Assuming that chemical potentials are given, the model has seven independent transition rates.

At the stationary state, the probability distribution P_i obeys the global balance equation

$$\sum_j (w_{ij}P_j - w_{ji}P_i) = 0, \tag{82}$$

but do not obey the detailed balance condition, which means that $w_{ij}P_j - w_{ji}P_i \neq 0$ in general. The fluxes $\mathcal{J}_A$ and $\mathcal{J}_B$ of molecules A and B, respectively, from the exterior to the interior, are given by

$$\mathcal{J}_A = w_{13}P_3 - w_{31}P_1, \tag{83}$$

$$\mathcal{J}_B = w_{35}P_5 - w_{53}P_3, \tag{84}$$

and are nonzero because detailed balance does not hold. The entropy production rate is $\Pi = X_A\mathcal{J}_A + X_B\mathcal{J}_B$, where $X_A = (\mu_A^1 - \mu_A^2)/T$ and $X_B = (\mu_B^1 - \mu_B^2)/T$. By an appropriate choice of the transition rates, it is thus possible to have a flux of particles B against its chemical potential gradient [74], that is, it is possible to have $\mathcal{J}_B > 0$ and $X_B < 0$, as long as the flux of particles A agrees with the gradient of its chemical potential, that is, $X_A\mathcal{J}_A > 0$.

III. CHEMICAL REACTIONS

A. Equilibrium

We will be concerned in this section with a system composed by q species of particles that react among themselves according to r reactions. The system is in contact with a heat reservoir and may be closed to particles or may be open and exchange particles with the environment. This last situation is carried out by placing the system with particle reservoirs. We will treat in the following the more general open case. The results for the closed case will readily be obtained from the results of the open case by formally imposing the vanishing of the particle flux.

The system is placed in contact with q particle reservoirs, one for each type of particle. Each particle reservoir is also a thermal reservoir. The k-th reservoir exchanges heat, at temperature T, and only particles of type k at a chemical potential μ_k. Notice that all reservoirs are at the same temperature T. The number of particle of species k in state i is denoted by n_i^k. If the k-th reservoir causes a change from state j to state i, then

$$n_i^k \neq n_j^k \quad \text{and} \quad n_i^{k'} = n_j^{k'}, \quad k' \neq k, \tag{85}$$

because we are assuming that the k-th reservoir causes a change in the number of particles of type k but causes no changes in the number of particles of the other types.

When the system is in thermodynamic equilibrium with the reservoirs, the probability distribution describing the system is the Gibbs distribution

$$P_i^e = \frac{1}{\Xi} e^{-\beta E_i + \beta\sum_k \mu_k n_i^k}, \tag{86}$$

where $\beta = 1/k_BT$.

To set up the transition rate $\widehat{W}_{ij}^k$ describing the contact of the system with the k reservoir we use the detailed balance condition with respect to the probability distribution (86),

$$\frac{\widehat{W}_{ij}^k}{\widehat{W}_{ji}^k} = \frac{P_i^e}{P_j^e}, \tag{87}$$

where i and j are states such that condition (85) is fulfilled, so

$$\frac{\widehat{W}_{ij}^k}{\widehat{W}_{ji}^k} = e^{-\beta(E_i - E_j) + \beta\mu_k(n_i^k - n_j^k)}, \tag{88}$$

which leads us to the following form:

$$\widehat{W}_{ij}^k = \widehat{K}_{ij}^k e^{-\beta(E_i - E_j)/2 + \beta\mu_k(n_i^k - n_j^k)/2}, \tag{89}$$

where $\widehat{K}_{ij}^k$ is symmetric, that is, $\widehat{K}_{ij}^k = \widehat{K}_{ji}^k$, and is positive or vanishes according to whether the condition (85) is fulfilled. The total transition rate $\widehat{W}_{ij}$, due to the contact with all reservoirs, is written as the sum

$$\widehat{W}_{ij} = \sum_{k=1}^{q} \widehat{W}_{ij}^k. \tag{90}$$

Notice that at most one of the q terms on the right-hand side can be nonzero.

Let us consider now the occurrence of chemical reactions. The number of particles of each species will vary not only because of the contact with the reservoirs but also because of the reactions. We consider the occurrence of r reactions described by the chemical equations

$$\sum_{k=1}^{q} \nu_{k\ell} B_k = 0, \quad \ell = 1,2,\ldots,r, \tag{91}$$

where B_k denotes the chemical formula of species k and $\nu_{k\ell}$ are the stoichiometric coefficients, which are negative for the reactants and positive for the products of the reaction. If the ℓ-th reaction causes a change from state j to state i, then

$$n_i^k - n_j^k = \nu_{k\ell} \quad \text{or} \quad n_i^k - n_j^k = -\nu_{k\ell}. \tag{92}$$

To set up the transition rate $\widetilde{W}_{ij}^\ell$ describing the change caused by the ℓ-th reaction we assumed that it obeys the Arrhenius equation [91,92]

$$\frac{\widetilde{W}_{ij}^\ell}{\widetilde{W}_{ji}^\ell} = e^{-\beta(E_i - E_j)}. \tag{93}$$

The most general form of the transition rate is

$$\widetilde{W}_{ij}^\ell = \widetilde{K}_{ij}^\ell e^{-\beta(E_i - E_j)/2}, \tag{94}$$

where the prefactor is symmetric, that is, $\widetilde{K}_{ij}^{\ell} = \widetilde{K}_{ji}^{\ell}$, and is positive if condition (92) is fulfilled and vanishes otherwise. The transition rate $\widetilde{W}_{ij}$ due to all reactions is written as the sum

$$\widetilde{W}_{ij} = \sum_{\ell=1}^{r} \widetilde{W}_{ij}^{\ell}. \tag{95}$$

Notice that at most one of the r terms on the right-hand side can be nonzero.

The full transition rate W_{ij} describing the r reactions as well as the contact with the q reservoirs is given by

$$W_{ij} = \widetilde{W}_{ij} + \widehat{W}_{ij}. \tag{96}$$

Again, just one of the two terms on the right-hand side can be nonzero.

In equilibrium, detailed balance should be obeyed for each one of the transition rates on the right-hand side of (96). We have seen that this is the case of the transition rates $\widehat{W}_{ij}^{k}$, related to the contact with each reservoir, when the probability distribution is that given by (86). It suffices, therefore, to impose detailed balance to the transition rate associated to each chemical reaction. To this end we compare the ratio (93) with the ratio

$$\frac{P_i^e}{P_j^e} = e^{-\beta(E_i - E_j) + \beta \sum_k \nu_{k\ell}\mu_k}, \tag{97}$$

obtained from (86) and valid when the first of the two conditions in (92) is fulfilled. The condition of detailed balance is obeyed when the two ratios are equal to each other, that is, when

$$\sum_k \nu_{k\ell}\mu_k = 0, \tag{98}$$

for each reaction ℓ. The same conclusion is obtained if we use the second of the two conditions in (92). Equation (98) is the well-known equilibrium condition that should be fulfilled when chemical reactions take place in a system [50,51]. In the presence of chemical reactions and in equilibrium, the chemical potentials of the chemical species cannot be independent but are related by (98). In other words, the equilibrium occurs only when the chemical potentials μ_k of the particle reservoirs are tuned so (98) is fulfilled. Otherwise, the system will be out of equilibrium, as we shall see next.

B. Nonequilibrium regime

Let us now suppose that the condition (98) is not obeyed. In this case the detailed balance condition is not fulfilled and the system cannot be in equilibrium. Each reaction is shifted either to the products or to the reactants. That is, for a given reaction, either the products are being created and the reactants being annihilated (forward reaction) or the reactants are being created and the products being annihilated (backward reaction). In this nonequilibrium regime the time variation in the number of particles has two parts: one due to the flux of particles from the reservoirs and the other due the creation and annihilation caused by the reactions.

Using the master equation (1), we see that the average number of particles N_k of type k,

$$N_k(t) = \sum_i n_i^k P_i(t), \tag{99}$$

evolves as

$$\frac{dN_k}{dt} = \sum_{ij} W_{ij} P_j \left(n_i^k - n_j^k\right). \tag{100}$$

According to (96), the transition rate W_{ij} has two parts, one related to the reservoirs, which is $\widehat{W}_{ij}$, and the other related to the chemical reactions, which is $\widetilde{W}_{ij}$, so (100) can be written in the form

$$\frac{dN_k}{dt} = \sum_{ij} \widetilde{W}_{ij} P_j \left(n_i^k - n_j^k\right) + \Phi_k, \tag{101}$$

where Φ_k is given by

$$\Phi_k = \sum_{ij} \widehat{W}_{ij} P_j \left(n_i^k - n_j^k\right) \tag{102}$$

and describes the flux of particle from the k-th reservoir to the system. The contact of the system with the k-th reservoir, described by the transformation (85), causes no changes in $n_i^{k'}$, $k' \neq k$. As a consequence,

$$\widehat{W}_{ij}^{k}(n_i^{k'} - n_j^{k'}) = 0, \quad k \neq k'. \tag{103}$$

Using (90) and the result (103), the flux of particle (102) is written as

$$\Phi_k = \sum_{ij} \widehat{W}_{ij}^{k} P_j \left(n_i^k - n_j^k\right). \tag{104}$$

The summation in the right-hand side of (101) describes the change in the number of particle due to the chemical reactions. To describe properly this part, which corresponds to the creation and annihilation of particles caused by the reactions, it is convenient to use a new set of variables in the place of the set of variables n_i^k, $k = 1,2,\ldots,q$. The new variables are denoted by σ_i^{ℓ}, $\ell = 1,2,\ldots,r$ and x_i^{ℓ}, $\ell = r+1, r+2,\ldots,q$ and defined by the linear transformation

$$n_i^k = x_i^k + \sum_{\ell=1}^{r} \nu_{k\ell}\sigma_i^{\ell}, \quad k = 1,2,\ldots,q, \tag{105}$$

where the quantities x_i^k, $k = 1,2\ldots,r$ are not variables but arbitrary constants chosen to be the same for all i. If a transformation $n_i^k \to n_j^k$ is performed according to the ℓ-th chemical reaction (91), described by the transformation (92), the variables x_i^k remains unchanged, that is, $x_j^k = x_i^k$. As a consequence of this invariance,

$$\widetilde{W}_{ij}^{\ell}\left(x_i^k - x_j^k\right) = 0. \tag{106}$$

In addition, according to the transformation (92), the variables σ_i^m, $m \neq \ell$, associated to the other reactions remain unchanged, $\sigma_j^m = \sigma_i^m$, and, as a consequence,

$$\widetilde{W}_{ij}^{m}\left(\sigma_i^{\ell} - \sigma_j^{\ell}\right) = 0, \quad m \neq \ell. \tag{107}$$

Using (105) and the results (106) and (107), we obtain

$$\sum_{ij} \widetilde{W}_{ij} P_j \left(n_i^k - n_j^k\right) = \sum_{\ell} \nu_{k\ell}\chi_{\ell}, \tag{108}$$

where the quantity χ_ℓ is

$$\chi_\ell = \sum_{ij} \widetilde{W}_{ij}^{\ell} P_j \left(\sigma_i^{\ell} - \sigma_j^{\ell}\right). \tag{109}$$

The variation in the number of particles then can be written as

$$\frac{dN_k}{dt} = \sum_{\ell} \nu_{k\ell} \chi_\ell + \Phi_k. \tag{110}$$

When $\chi_\ell > 0$, the ℓ-th chemical reaction is shifted to the right, in the direction of the products. When $\chi_\ell < 0$, it is shifted to the left, in the direction of the reactants. The extent of reaction ξ_ℓ is defined as the average of σ_i^{ℓ},

$$\xi_\ell = \sum_i \sigma_i^{\ell} P_i. \tag{111}$$

From the master equation and using the properties (103) and (107), we get

$$\frac{d\xi_\ell}{dt} = \chi_\ell, \tag{112}$$

and we may conclude that the quantity χ_ℓ is the rate of the extent of the ℓ-th reaction.

The time variation of the internal energy is written as

$$\frac{dU}{dt} = \sum_{ij} W_{ij} P_j (E_i - E_j). \tag{113}$$

Let us now consider the time variation of entropy

$$\frac{dS}{dt} = \Pi - \Phi, \tag{114}$$

where the flux Φ is given by (3), which, by the use of (96), (95), and (90), is given by

$$\Phi = k_B \sum_{ij} \sum_k \widehat{W}_{ij}^k P_j \ln \frac{\widehat{W}_{ij}^k}{\widehat{W}_{ji}^k} + k_B \sum_{ij} \sum_\ell \widetilde{W}_{ij}^{\ell} P_j \ln \frac{\widetilde{W}_{ij}^{\ell}}{\widetilde{W}_{ji}^{\ell}}. \tag{115}$$

Substituting the rates (88) and (93) into this equation we get

$$\Phi = k_B \sum_{ij} W_{ij} P_j (-\beta)(E_i - E_j) + k_B \sum_{ij} \sum_k \widehat{W}_{ij}^k P_j \beta \mu_k \left(n_i^k - n_j^k\right). \tag{116}$$

Using Eqs. (113) and (104) we may write the flux of entropy as

$$\Phi = -\frac{1}{T}\frac{dU}{dt} + \frac{1}{T}\sum_k \mu_k \Phi_k. \tag{117}$$

Substituting into (114) and taking into account Eqs. (113), we get

$$\frac{dS}{dt} = \Pi + \frac{1}{T}\frac{dU}{dt} - \frac{1}{T}\sum_k \mu_k \Phi_k. \tag{118}$$

Using (110), we reach the result

$$\frac{dS}{dt} = \Pi + \frac{1}{T}\frac{dU}{dt} - \sum_\ell \frac{A_\ell}{T}\chi_\ell - \frac{1}{T}\sum_k \mu_k \frac{dN_k}{dt}, \tag{119}$$

where A_ℓ is the De Donder affinity [52],

$$A_\ell = -\sum_k \nu_{k\ell}\mu_k, \tag{120}$$

associated to the ℓ-th chemical reaction.

In the stationary state $dS/dt = 0$, $dU/dt = 0$, and $dN_k/dt = 0$, and we reach the following expression for the production of entropy in the stationary state [52,55,57,58]:

$$\Pi = \sum_\ell \frac{A_\ell}{T}\chi_\ell, \tag{121}$$

or, in the equivalent form,

$$\Pi = \sum_\ell \frac{A_\ell}{T}\frac{d\xi_\ell}{dt}, \tag{122}$$

equation originally introduced by De Donder [52]. In equilibrium there is no production of entropy and the affinities vanish, $A_\ell = 0$, in accordance with (98), and the rate in which the ℓ-th reaction proceeds vanish as well, $\chi_\ell = d\xi_\ell/dt = 0$.

In a nonequilibrium stationary state, a flux of particles is continuously taking place, which sustains the chemical reactions. The quantities Φ_k and χ_ℓ are nonzero, in general. At the same time there is a flux of heat toward the system, characterizing an endothermic reaction, or from the system, characterizing an exothermic reaction. To understand this situation we write down the variation in the energy, given by Eq. (113) in the form

$$\frac{dU}{dt} = \sum_\ell R_\ell + \Phi_u, \tag{123}$$

where R_ℓ is the energy delivered by the ℓ-th reaction per unit time, given by

$$R_\ell = \sum_{ij} \widetilde{W}_{ij}^{\ell} P_j (E_i - E_j), \tag{124}$$

and Φ_u is the heat flux to the system, given by

$$\Phi_u = \sum_{ij}\sum_k \widehat{W}_{ij}^k P_j (E_i - E_j). \tag{125}$$

In the stationary state $dU/dt = 0$ and $\Phi_u = -\sum_\ell R_\ell$. If $\Phi_u < 0$, the reactions are exothermic. If $\Phi_u > 0$, they are endothermic. Notice that there is no contribution to the entropy production rate coming from the flux of heat because the temperatures of the reservoirs are the same.

Although we have considered a system in contact with one reservoir for each type of particle, the formulas can easily be adapted to the case in which the system is closed to some types of particles. If the system is closed to particles of type k, then it suffices to formally set $\mu_k = 0$ and $\widehat{W}_{ij}^k = 0$ so $\Phi_k = 0$ for this species. It is worth mentioning that in the case of a closed system, when there is no flux of particles from the environment, $\Phi_k = 0$ for all species, and using equation (118), we see that $dF/dt = -T\Pi$, where $F = U - TS$ is the free energy, so $dF/dt \leqslant 0$. Therefore, the chemical reactions occur

in a direction such that the variations in the number of particles will decrease the free energy [93].

As an example of the approach just developed we analyze a system with four species of particles and two reactions, which are

$$B_1 + B_2 = B_3, \quad B_3 = B_2 + B_4, \tag{126}$$

and represent the Michaelis-Menten mechanism in which a the substrate B_1 is converted, in two steps, into the product B_4 by the action of an enzyme. The substrate B_1 reacts with the enzyme B_2 giving rise to a complex B_3 which in turn breaks up into the product B_4 and the enzyme B_2. It is assumed that both reactions have reverses. The system is assumed to be closed to the particles B_2 and B_3 and is in contact with reservoirs of particles of type B_1 and B_4.

Using formula (120), and bearing in mind that we should set $\mu_2 = 0$ and $\mu_3 = 0$ in this formula, the affinities A_1 and A_2 associated to the two reactions are given by

$$A_1 = \mu_1, \quad A_2 = -\mu_4. \tag{127}$$

The variations in the number of particles of each species are

$$\frac{dN_1}{dt} = -\chi_1 + \Phi_1, \quad \frac{dN_2}{dt} = -\chi_1 + \chi_2, \tag{128}$$

$$\frac{dN_3}{dt} = \chi_1 - \chi_2, \quad \frac{dN_4}{dt} = \chi_2 + \Phi_4. \tag{129}$$

In the stationary state, $\chi_1 = \chi_2 = \Phi_1 = -\Phi_4$, so, using (121), the entropy production rate is found to be

$$\Pi = \frac{\chi_1}{T}(\mu_1 - \mu_4). \tag{130}$$

We may now draw the following conclusion for the case of a nonequilibrium steady-state situation, for which $\Pi > 0$. If $\mu_1 > \mu_4$, then $\chi_1 > 0$ and $\chi_4 > 0$ so the two reaction equations are shifted to the right, establishing a continuous annihilation of particles of type B_1, which come from reservoir B_1 because $\Phi_1 > 0$, and production of particles of type B_4, which go to reservoir B_4 because $\Phi_4 < 0$.

C. Onsager coefficients

In the nonequilibrium stationary state but close to equilibrium we may expand the rates of the extents of reaction χ_ℓ in terms of the affinities A_ℓ to get

$$\chi_\ell = \sum_m L_{\ell m} A_m, \tag{131}$$

where $L_{\ell m}$ are the Onsager coefficients. They obey the reciprocal relations, which we demonstrate next.

We start by expanding the stationary probability distribution P_i, that satisfies the global balance equation (16), around the equilibrium distribution P_i^e given by

$$P_i^e = \frac{1}{Z} e^{-\beta E_i + \beta \sum_k \mu_k^* n_i^k}, \tag{132}$$

where the chemical potentials μ_k^* obey the equilibrium condition

$$\sum_k \nu_{k\ell} \mu_k^* = 0. \tag{133}$$

We assume an expansion of the form

$$P_i = P_i^e \left(1 + \sum_{\ell=1}^{r} R_{i\ell} A_\ell + \sum_{k=r+1}^{q} a_{ik} \Delta\mu_k \right), \tag{134}$$

where $\Delta\mu_k = \mu_k - \mu_k^*$.

We also expand $\widehat{W}_{ij}^k$, given by (89), around its value at equilibrium,

$$\widehat{W}_{ij}^{*k} = \widehat{K}_{ij}^k e^{-\beta(E_i - E_j)/2 + \beta\mu_k^*(n_i^k - n_j^k)/2}, \tag{135}$$

to get

$$\widehat{W}_{ij}^k = \widehat{W}_{ij}^{*k} \{ 1 + \beta \Delta\mu_k (n_i^k - n_j^k)/2 \}. \tag{136}$$

The transition rate $\widetilde{W}_{ij}^\ell$ needs no expansion because this quantity is also its value at equilibrium since it does not depend on the chemical potentials.

Replacing the expansions (134) and (136) into the global balance equation (16), we get

$$\begin{aligned} &\sum_j W_{ij}^* P_j^e \sum_{\ell=1}^{r} A_\ell (R_{j\ell} - R_{i\ell}) \\ &\quad + \sum_j W_{ij}^* P_j^e \sum_{k=r+1}^{q} (a_{jk} - a_{ik}) \Delta\mu_k \\ &\quad + \sum_j \sum_k \widehat{W}_{ij}^* P_j^e \beta \Delta\mu_k (n_i^k - n_j^k) = 0, \end{aligned} \tag{137}$$

where

$$\widehat{W}_{ij}^* = \sum_k \widehat{W}_{ij}^{*k}, \quad \text{and} \quad W_{ij}^* = \widehat{W}_{ij}^* + \widetilde{W}_{ij}. \tag{138}$$

Using (105) and taking into account relation (133), we see that

$$\begin{aligned} \sum_k \Delta\mu_k (n_i^k - n_j^k) &= \sum_{k=r+1}^{q} \Delta\mu_k (x_i^k - x_j^k) \\ &\quad - \sum_{\ell=1}^{r} A_\ell (\sigma_i^\ell - \sigma_j^\ell), \end{aligned} \tag{139}$$

which is replaced in (137) to get an expression linear in A_ℓ and $\Delta\mu_k$. Since the coefficients of A_ℓ and $\Delta\mu_k$ in this expression should vanish, we obtain

$$\sum_j W_{ij}^* P_j^e (a_{jk} - a_{ik}) + \sum_j \widehat{W}_{ij}^* P_j^e (x_i^k - x_j^k) = 0, \tag{140}$$

valid for $r + 1 \leqslant k \leqslant q$, and

$$\sum_j W_{ij}^* P_j^e (R_{j\ell} - R_{i\ell}) - \beta \sum_j \widehat{W}_{ij}^* P_j^e (\sigma_i^\ell - \sigma_j^\ell) = 0, \tag{141}$$

valid for $1 \leqslant \ell \leqslant r$. These last two equations determine a_{ik} and $R_{i\ell}$.

Let us consider now the expansion of the rate of the extent of reaction χ_ℓ, given by (109). Replacing the expansion (134) into (109), we get an expression linear in A_m and $\Delta\mu_k$. The coefficient of A_m is the Onsager coefficient $L_{\ell m}$ which is

given by

$$L_{\ell m} = \sum_{ij} \widetilde{W}_{ij} P_j^e (R_{jm} - R_{im})\left(\sigma_i^\ell - \sigma_j^\ell\right). \tag{142}$$

Next we use equation (141) to write the Onsager coefficient in a more appropriate form. To this end we proceed as follows. We multiply (141) by σ_i^m and sum in i to get a first equation. Next we multiply (141) by R_i^m and sum in i to get a second equation. From these two equations we get an equation for the right-hand side of (142) from which we reach the following expression:

$$L_{\ell m} = \frac{\beta}{2} \sum_{ij} \widehat{W}_{ij}^* P_j^e \left(\sigma_i^m - \sigma_j^m\right)\left(\sigma_i^\ell - \sigma_j^\ell\right) - \frac{1}{2\beta} \sum_{ij} W_{ij}^* P_j^e (R_{i\ell} - R_{j\ell})(R_{im} - R_{jm}). \tag{143}$$

From this expression it follows that

$$L_{m\ell} = L_{\ell m}, \tag{144}$$

which is the Onsager reciprocal relation [53].

IV. FOKKER-PLANCK EQUATION

A. Langevin equations

In this section we are concerned with systems that follow a continuous time Markovian process in the continuous state space, the phase space. We consider a system of particles that follows a dynamics described by the following set of Langevin equations, interpreted according to Itô,

$$m \frac{dv_i}{dt} = F_i(x) - \alpha_i v_i + \mathfrak{F}_i(t), \tag{145}$$

where m is the mass of each particle, $v_i = dx_i/dt$ and x_i is the position of the i-th particle, and x denotes the vector $x = (x_1, \ldots, x_n)$. We will also use the notation $v = (v_1, \ldots, v_n)$. The quantity $F_i(x)$ is the force acting on the i-th particle, and $\mathfrak{F}_i(t)$ is a stochastic variable with the properties

$$\langle \mathfrak{F}_i(t) \rangle = 0, \tag{146}$$

$$\langle \mathfrak{F}_i(t) \mathfrak{F}_j(t') \rangle = 2B_{ij} \delta(t - t'), \tag{147}$$

where B_{ij} may depend on x and v.

Notice that we are considering the so-called underdamped systems, for which the state of a particle is defined by its position and velocity [38], in opposition to the overdamped case, for which the state of a particle is defined only by its position [29].

The quantities $\mathfrak{F}_i(t)$ are random forces acting on the particles including the ones that describe the contact of the system with the environment. We will treat two cases: one in which the system is isolated (microcanonical ensemble) and the other in which the system is in contact with a heat reservoir (canonical ensemble). In the first case the forces F_i are conservative and the stochastic forces are set up in such a way that the energy is conserved in any stochastic trajectory. In thermodynamic equilibrium they will lead to the Gibbs microcanonical probability distribution. In the second case the forces F_i are also conservative and the random forces are set up in such a way that in thermodynamic equilibrium they will lead to the Gibbs canonical distribution.

Using the Itô interpretation, we can show that the Langevin equations (145) are associated to the following Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(v_i P) - \frac{1}{m} \sum_i \frac{\partial}{\partial v_i}(F_i P) + \sum_i \frac{\alpha_i}{m} \frac{\partial}{\partial v_i}(v_i P) + \frac{1}{m^2} \sum_{ij} \frac{\partial^2}{\partial v_i \partial v_j}(B_{ij} P), \tag{148}$$

equation that gives the time evolution of the probability distribution $P(x,v,t)$ of x and v at time t. It is convenient to write down the Fokker-Planck equation in the following form:

$$\frac{\partial P}{\partial t} = -\sum_i \left(K_i + \frac{\partial J_i}{\partial v_i} \right), \tag{149}$$

where K_i and J_i are given by

$$K_i = v_i \frac{\partial P}{\partial x_i} + \frac{F_i}{m} \frac{\partial P}{\partial v_i} \tag{150}$$

and

$$J_i = -\frac{\alpha_i}{m} v_i P - \frac{1}{m^2} \sum_j \frac{\partial}{\partial v_j}(B_{ij} P). \tag{151}$$

Let us consider now the time variation of entropy S, given by

$$S(t) = -k_B \int P(x,v,t) \ln P(x,v,t) dx dv. \tag{152}$$

The derivative of S gives

$$\frac{dS}{dt} = -k_B \int \left(\frac{\partial P}{\partial t} \right) \ln P dx dv. \tag{153}$$

After replacing (149) into this equation and performing appropriate integrations by parts we reach the following expression:

$$\frac{dS}{dt} = -k_B \sum_i \int \frac{J_i}{P} \left(\frac{\partial P}{\partial v_i} \right) dx dv. \tag{154}$$

The terms corresponding to K_i vanish, that is,

$$-k_B \sum_i \int K_i \ln P dx dv = 0. \tag{155}$$

We are assuming that P and its derivatives vanish at the boundary of integration.

B. Microcanonical ensemble

Here we treat the case of an isolated system, with no contact with the environment so the energy is strictly conserved. We thus assume that the force F_i are conservative so $F_i = -\partial V/\partial x_i$, which allows us to define the energy function $E(v,x)$ as

$$E(x,v) = \sum_i \frac{m}{2} v_i^2 + V(x). \tag{156}$$

The strict conservation of energy means to say that $E(x,v)$ should be a constant along any stochastic trajectory in phase space. This condition is fulfilled by the following set of Langevin equations, understood according the Stratonovich interpretation:

$$m\frac{dv_i}{dt} = F_i(x) + \sum_{j(\neq i)} \xi_{ij} v_j, \tag{157}$$

where ξ_{ij} are stochastic variables with the antisymmetric property $\xi_{ji} = -\xi_{ij}$. The multiplicative noise at the right-hand side changes the velocities of the particles while keeping the kinetic energy invariant and can be interpreted as random elastic collisions of the particles with themselves or with immobile scatters. A similar noise has been used do describe a particle that moves at constant speed but changes direction at random times [94,95].

Multiplying (157) by v_i and summing in i we may conclude, after using the antisymmetric relation $\xi_{ji} = -\xi_{ij}$, that $E(v,x)$ is strictly conserved along any stochastic path $x(t)$, $v(t)$. Therefore, the equation of motion (157) describes a system of particles evolving in time in such a way that the energy is strictly constant. In analogy with equilibrium statistical mechanics, this defines a microcanonical ensemble.

The stochastic variables $\xi_{ij}(t)$ are defined by the relations

$$\langle \xi_{ij}(t) \rangle = 0 \tag{158}$$

and

$$\langle \xi_{ij}(t)\xi_{ij}(t') \rangle = 2\lambda_{ij}\delta(t-t'), \tag{159}$$

where $\lambda_{ij} \geqslant 0$ is a parameter that gives the strength of the stochastic noise. Using the Stratonovich interpretation, and taking into account the antisymmetric property $\xi_{ji} = -\xi_{ij}$ of the noise, we may write down the associate Fokker-Planck equation, given by

$$\frac{\partial P}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(v_i P) - \frac{1}{m}\sum_i \frac{\partial}{\partial v_i}(F_i P) + \frac{1}{m^2}\sum_{ij}\lambda_{ij}\left(v_j\frac{\partial}{\partial v_i}v_j\frac{\partial P}{\partial v_i} - v_j\frac{\partial}{\partial v_i}v_i\frac{\partial P}{\partial v_j}\right), \tag{160}$$

an equation that gives the time evolution of the probability distribution $P(x,v,t)$ of x and v at time t. The last summation extends over $i \neq j$ and we recall that $\lambda_{ji} = \lambda_{ij} \geqslant 0$.

It is worth mentioning that Eq. (157), understood in the Stratonovich sense, is equivalent to the following equation, interpreted according to Itô:

$$m\frac{dv_i}{dt} = F_i(x) - \alpha_i v_i + \sum_{j(\neq i)} \xi_{ij} v_j, \tag{161}$$

where

$$\alpha_i = \sum_{j(\neq i)} \lambda_{ij}. \tag{162}$$

Of course, this equation leads to the same Fokker-Planck equation (160).

It is convenient to write down the Fokker-Planck equation in the form given by (149) where K_i is given by (150) and J_i is given by

$$J_i = \sum_{j(\neq i)} J_{ij} v_j, \tag{163}$$

$$J_{ij} = \frac{1}{m^2}\lambda_{ij}\left(v_i\frac{\partial P}{\partial v_j} - v_j\frac{\partial P}{\partial v_i}\right), \tag{164}$$

Let us determine now the time derivative of entropy, which is given by Eq. (154). After replacing (163) into Eq. (154) and performing appropriate integration by parts we reach the following expression:

$$\frac{dS}{dt} = \frac{k_B}{m^2}\sum_{i<j}\lambda_{ij}\int \frac{1}{P}\left(v_j\frac{\partial P}{\partial v_i} - v_i\frac{\partial P}{\partial v_j}\right)^2 dxdv. \tag{165}$$

We are assuming that P and its derivatives vanish at the boundary of integration. The right-hand side of this equation is clearly non-negative and is therefore identified as the entropy production rate,

$$\Pi = \frac{k_B}{m^2}\sum_{i<j}\lambda_{ij}\int \frac{1}{P}\left(v_j\frac{\partial P}{\partial v_i} - v_i\frac{\partial P}{\partial v_j}\right)^2 dxdv, \tag{166}$$

which can also be written in the form

$$\Pi = k_B\sum_{i<j}\frac{m^2}{\lambda_{ij}}\int \frac{J_{ij}^2}{P}dxdv, \tag{167}$$

where the summation is over ij such that $\lambda_{ij} \neq 0$, so

$$\frac{dS}{dt} = \Pi. \tag{168}$$

In the present case there is no entropy flux,

$$\Phi = 0, \tag{169}$$

which is consistent with our interpretation that Eqs. (157) describe an isolated system. Taking into account that $\Pi \geqslant 0$ it follows at once that $dS/dt \geqslant 0$ for an isolated system.

In the stationary state, which is a thermodynamic equilibrium, the probability distribution $P^e(x,v)$ depends on x and v only through $E(x,v)$, that is, $P^e(x,v)$ is a function of $E(x,v)$. This statement can be checked by substitution on the right-hand side of the Fokker-Planck equation (160). Since $E(x,y)$ is invariant along any path in phase space and supposing that initially its value is U, it follows that

$$P^e(x,v) = \frac{1}{\Omega}\delta[U - E(x,v)], \tag{170}$$

where Ω is a normalization constant that depends on U. We remark that in this case Π, given by (166), vanishes, as expected.

C. Canonical ensemble

Now we consider the case of a system in contact with a heat reservoir. In fact, we will consider the more general case in which each particle i is in contact with a reservoir at temperature T_i. The appropriate set of Langevin equations that describes this situation is given by

$$m\frac{dv_i}{dt} = F_i(x) - \alpha_i v_i + \zeta_i(t), \tag{171}$$

where $\zeta_i(t)$ is a stochastic variable with the properties

$$\langle \zeta_i(t) \rangle = 0, \tag{172}$$

$$\langle \zeta_i(t)\zeta_j(t') \rangle = 2\alpha_i k_B T_i \, \delta_{ij}\delta(t-t'), \tag{173}$$

where T_i and α_i are parameters. The two last terms in Eq. (171) are interpreted as describing the contact of the i-th particle with the heat bath at a temperature T_i and α_i is the strength of the interaction with the heat reservoir.

To the set of Langevin equations (171) is associated the Fokker-Planck equation

$$\frac{\partial P}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(v_i P) - \frac{1}{m}\sum_i \frac{\partial}{\partial v_i}(F_i P) + \frac{1}{m}\sum_i \alpha_i \frac{\partial}{\partial v_i}(v_i P) + \frac{k_B}{m^2}\sum_i \alpha_i T_i \frac{\partial^2 P}{\partial v_i^2}, \tag{174}$$

an equation that gives the time evolution of the probability distribution $P(x,v,t)$ of x and v at time t.

The Fokker-Planck equation again can be written in the form given by (149) where K_i is given by (150) and J_i is given by

$$J_i = -\frac{\alpha_i v_i}{m} P - \frac{\alpha_i k_B T_i}{m^2}\frac{\partial P}{\partial v_i}. \tag{175}$$

Again the derivative of entropy is given by (154). Replacing (175) into (154) we get the following expression [38]:

$$\frac{dS}{dt} = \sum_i \int \left(\frac{m^2}{\alpha_i T_i}\frac{J_i^2}{P} + \frac{m}{T_i} v_i J_i \right) dxdv. \tag{176}$$

The summation in (176) extends only to the terms for which $\alpha_i \neq 0$ and $T_i \neq 0$.

The first term on the right-hand side of equation (176) is non-negative and is identified as the entropy production rate [38],

$$\Pi = \sum_i \frac{m^2}{\alpha_i T_i} \int \frac{J_i^2}{P} dxdv. \tag{177}$$

Although this identification may seem to be arbitrary, as has been argued [41], we will see in the next section that in fact it is in accordance with the expression (3). It vanishes only when $J_i = 0$, which is the equilibrium condition. The second summation is thus the entropy flux

$$\Phi = -\sum_i \frac{m}{T_i} \int v_i J_i dxdv, \tag{178}$$

which can also be written as

$$\Phi = \sum_i \frac{1}{T_i}\left(\alpha_i \langle v_i^2 \rangle - \frac{\alpha_i T_i}{m} \right). \tag{179}$$

After replacing J_i, given by (175), into (178) and performing an integration by parts, the variation of the entropy of the system becomes

$$\frac{dS}{dt} = \Pi - \Phi. \tag{180}$$

Let us assume that the forces are conservative, $F_i = -\partial V/\partial x_i$. In this case, we define the energy of the system as

$$E(x,v) = \frac{m}{2}\sum_i v_i^2 + V(x). \tag{181}$$

Using the Fokker-Planck equation in the form (149) we get the following expression for the time derivative of the average energy $U = \langle E(x,v) \rangle$:

$$\frac{dU}{dt} = -\Phi_u, \tag{182}$$

where

$$\Phi_u = -\sum_i m \int v_i J_i dxdv \tag{183}$$

is the flux of energy from the system to outside. To reach this expression we have performed appropriate integration by parts and assumed that P and its derivatives vanish at the boundaries of integration. Using the definition of J_i, given by (175), we may write the energy flux as

$$\Phi_u = \sum_i \alpha_i \left(\langle v_i^2 \rangle - \frac{k_B T_i}{m} \right). \tag{184}$$

When all temperatures are the same $T_i = T$ we have $\Phi = \Phi_u/T$ so

$$\frac{dS}{dt} - \frac{1}{T}\frac{dU}{dt} = \Pi, \tag{185}$$

from which it follows that the time variation of $F = U - TS$ is given by $dF/dt = -T\Pi$ so $dF/dt \leqslant 0$.

Thermodynamic equilibrium occurs when all temperatures are the same, $T_i = T$, and the forces are conservative, $F_i = -\partial V/\partial x_i$. In this case, $K_i = 0$ and $J_i = 0$, which leads to the following result for the equilibrium probability distribution:

$$P^e(x,v) = \frac{1}{Z} e^{-E(x,v)/k_B T}, \tag{186}$$

where Z is a normalization constant.

If we integrate Eq. (185) in time, from an initial time t_0 until infinity, when the system is in equilibrium, we get

$$S - S_0 - \frac{1}{T}(U - U_0) \geqslant 0. \tag{187}$$

Let us suppose that the system is in contact with just one heat reservoir at temperature T and that is temperature is varying slowly so $dT/dt = \alpha$ is small. This is again the quasistatic process that we have already discussed. In this case, the quantity J_i will be of the order α so Π will be of the order α^2. On the other hand, Φ remains at the linear order in α and we may write from (185) $dS/dt = (1/T)dU/dt$. It follows that the entropy and energy cannot be arbitrary but are connected by the relation $TdS = dU$ so a system performing a quasistatic process may be considered to be in equilibrium. From the result (187) we see that the curve that connect U and S has the property of convexity. To perceive this it suffices to imagine that at the initial time t_0 the energy U_0 and entropy S_0 correspond to values of equilibrium at a certain temperature T_0.

D. Nonequilibrium stationary state

Let us take a look at the the energy variation per unit time, or power, $\mathcal{P}_i$, associated to the i-th particle, given by

$$\mathcal{P}_i = \langle v_i F_i \rangle + \frac{m}{2}\frac{d}{dt}\langle v_i^2 \rangle, \tag{188}$$

where the first term is associated to the dissipation due to the force F_i acting on the particle and the second the time variation of its kinetic energy. Using the Fokker-Planck equation it is straightforward to show that

$$\mathcal{P}_i = \alpha_i \langle v_i^2 \rangle - \frac{\alpha_i T_i}{m}. \tag{189}$$

Therefore,

$$\Phi_u = \sum_i \mathcal{P}_i \tag{190}$$

and

$$\Phi = \sum_i \frac{\mathcal{P}_i}{T_i}, \tag{191}$$

and we recall that the summation is over i such that $\alpha_i \neq 0$ and $T_i \neq 0$.

Let us consider the contact of the system with two reservoirs A and B at temperatures T_1 and T_2, respectively. The heat flux from reservoir A to the system is given by

$$\mathcal{J} = \sum_{i\in A} \mathcal{P}_i, \tag{192}$$

where the summation is over the particles that are in contact with reservoir A. A similar expression holds,

$$\mathcal{J}' = \sum_{i\in B} \mathcal{P}_i, \tag{193}$$

for the heat flux $\mathcal{J}'$ from reservoir B to the system. In the stationary state, $\Pi = \Phi$, and taking into account the expression (191) for Φ, we get

$$\Pi = \frac{\mathcal{J}}{T_1} + \frac{\mathcal{J}'}{T_2}. \tag{194}$$

But in the stationary state $\Phi_u = \mathcal{J} + \mathcal{J}' = 0$ so

$$\Pi = X\mathcal{J}, \tag{195}$$

where

$$X = \frac{1}{T_1} - \frac{1}{T_2}. \tag{196}$$

Let us assume that X is small so $\Delta T = T_2 - T_1$ is small. In this case $\mathcal{J} = L\Delta T$, where L is the thermal coefficient. Writing the probability distribution as $P(x,v) = P^e(x,v)[1 - \Delta T a(x,v)]$, where $P^e(x,v)$ is the equilibrium distribution when the temperatures of the reservoir is T_1, we may calculate $\mathcal{J}$ to get

$$L = \sum_{i\in A} \alpha_i \int v_i^2 a(x,v) P^e(x,v) dx dv, \tag{197}$$

which may be understood as an average over the equilibrium distribution.

V. MASTER EQUATION REPRESENTATION OF THE FOKKER-PLANCK EQUATION

A. Microcanonical ensemble

It is possible to represent the Fokker-Planck in terms of a master equation. This can be done by a discretization of the phase space in a such a way that the continuum limit will reduce the master equation to the Fokker-Planck equation. From the representation we can easily identify the transition probabilities from which we can obtain, for instance, the entropy production rate.

To set up the discrete stochastic dynamics we imagine a representative point in the phase space following a stochastic trajectory. We consider two types of transitions from a given point in the phase space. The first type is defined by the transitions determined by the Hamiltonian flow. This type of transition is defined by

$$(x,v) \to (H_i^+ x, H_i^+ v), \tag{198}$$

where $H_i^+ x$ and $H_i^+ v$ are vectors with the same components of the vectors x and v except the i-th components x_i and v_i which are transformed to x_i' and v_i', where x_i' is given by

$$x_i' = x_i + b v_i, \tag{199}$$

and v_i' is determined in such a way that the energy is conserved, that is,

$$E(H_i^+ x, H_i^+ v) = E(x,v), \tag{200}$$

where $b > 0$ is a parameter. Each transition occurs with rate $1/b$. If b is sufficient small, v_i' is given by

$$v_i' = v_i + b\frac{F_i}{m}. \tag{201}$$

Notice that the Hamiltonian transition defined above has no reverse in the sense that from a point $(H_i^+ x, H_i^+ v)$ we cannot reach the point (x,v) with this type of transition.

The transitions of the second type changes only the velocities and preserves the kinetic energy. This type is defined by

$$(x,v) \to (x, M_{ij} v), \tag{202}$$

where $M_{ij} v$ is a vector with the same components of the vector v except the components i and j which are v_i' and v_j' given by

$$v_i' = v_i \cos\theta - v_j \sin\theta, \quad v_j' = v_i \sin\theta + v_j \cos\theta, \tag{203}$$

where $\theta > 0$, so $(v_i')^2 + (v_j')^2 = v_i^2 + v_j^2$ and the kinetic energy is preserved. Another possible transition is defined by

$$(x,v) \to (x, M_{ji} v). \tag{204}$$

Each of these transition occurs with rate equal to $\lambda_{ij}/m^2\theta^2$. Notice that this second type of transition has a reverse since from the point $(x, M_{ij} v)$ it is possible to reach the point (x,v). It is sufficient to observe that $M_{ji}(M_{ij} v) = v$.

The transitions above lead us to the following master equation:

$$\frac{\partial}{\partial t}P(x,v) = \sum_i \frac{1}{b}\{P(H_i^- x, H_i^- v) - P(x,v)\} + \sum_{ij}\frac{\lambda_{ij}}{2\varepsilon^2}\{P(x,M_{ij}v)+P(x,M_{ji}v)-2P(x,v)\}, \tag{205}$$

where H_i^- is defined in a way similar to H_i^+ except that the sign in front of b in Eq. (199) is negative. It is straightforward to show that expression (205) reduces to the Fokker-Planck (160) in the limit $\varepsilon \to 0$ and $b \to 0$.

Taking into account that all transitions preserve the energy $E(x,v)$, we see that in equilibrium the probability distribution $P^e(x,v)$ depends on (x,v) through $E(x,v)$. If at initial time the energy is equal to U, then $P^e(x,v)$ vanishes if $E(x,v) \neq U$ and is a constant if $E(x,v) = U$, which is the Gibbs microcanonical distribution.

B. Canonical ensemble

Next we set up a discrete stochastic dynamics, described by a master equation, whose continuous limit gives the Fokker-Planck equation (174). The representative point in phase space (x,v) performs a stochastic trajectory. We consider again two types of transitions from a given point in the phase space. The first type is the transition defined by the Hamiltonian flow given by Eq. (198). The transition of the second type changes only the velocities but in general it does not preserve the kinetic energy. This type of transition is defined by

$$(x,v) \to (x, C_i^{\pm} v), \tag{206}$$

where $C_i^{\pm} v$ is a vector with the same components of the vector v except the i-th component v_i' which is given by

$$v_i' = v_i \pm a, \tag{207}$$

where $a > 0$ is a parameter and each transition occurs with rate

$$A_i^{\pm}(v) = \frac{\alpha_i k_B T_i}{m^2 a^2} e^{\mp a m v_i / 2 k_B T_i}. \tag{208}$$

The master equation is written as

$$\frac{\partial}{\partial t}P(x,v) = \sum_i \frac{1}{b}\{P(H_i^- x, H_i^- v) - P(x,v)\} = \sum_i \{A_i^+(C_i^- v)P(x,C_i^- v) - A_i^-(v)P(x,v)\} + m\sum_i \{A_i^-(C_i^+ v)P(x,C_i^+ v) - A_i^+(v)P(x,v)\}. \tag{209}$$

It is straighfoward to show that in the limit $a \to 0$ and $b \to 0$, the master equation reduces to Eq. (174), and the master equation indeed can be understood as a representation of the Fokker-Planck equation (174).

The stationary solution of the master equation when all temperatures are the same, which corresponds to the thermodynamic equilibrium, is the Gibbs distribution. Indeed, the detailed balance of the master equation gives us the relation

$$P^e(H_i^- x, H_i^- v) = P^e(x,v), \tag{210}$$

which means that $P^e(x,v)$ depends on (x,v) through $E(x,v)$. Writing

$$P(x,v) = \frac{1}{Z} e^{-E(x,v)/k_B T}, \tag{211}$$

we see that the other relation,

$$A_i^+(C_i^- v)P^e(x,C_i^- v) = A_i^-(v)P^e(x,v), \tag{212}$$

is fulfilled if we take into account that all temperatures are the same, $T_i = T$.

C. Entropy production

We have seen that the entropy production rate of a system described by a master equation is obtained by expression (3). This expression is appropriate when the rates of the reversed transitions are nonzero. This is the case of transitions defined by (202). The entropy production rate Π_M associated to these transitions, according to (3), is given by

$$\Pi_M = \frac{k_B}{2}\sum_{x,v}\sum_{ij}\frac{\lambda_{ij}}{2m^2\theta^2}\{P(x,M_{ij}v) - P(x,v)\} \times \ln\frac{P(x,M_{ij}v)}{P(x,v)}. \tag{213}$$

In the limit $\theta \to 0$, the right-hand side reduces to expression on the right-hand side of (165). The entropy flux Φ_M associated to the transitions (202) is obtained by using (12), but it vanishes identically,

$$\Phi_M = 0. \tag{214}$$

Let us consider now the entropy production rate Π_C associated to the transitions defined by (206). According to expression (3), it is given by

$$\Pi_C = \frac{k_B}{2}\sum_{x,v}\sum_i \{A_i^+(C_i^- v)P(x,C_i^- v) - A_i^-(v)P(x,v)\} \times \ln\frac{A_i^+(C_i^- v)P(x,C_i^- v)}{A_i^-(v)P(x,v)}. \tag{215}$$

After taking the limit $a \to 0$ this expression is reduced to the result (177). The corresponding entropy flux Φ_C is obtained from (12) and is given by

$$\Phi_C = \frac{k_B}{2}\sum_{x,v}\sum_i \{A_i^+(C_i^- v)P(x,C_i^- v) - A_i^-(v)P(x,v)\} \times \ln\frac{A_i^+(C_i^- v)}{A_i^-(v)}. \tag{216}$$

The limit $a \to 0$ leads us to the result (178).

We now wish to consider the entropy production rate and the flux of entropy coming from the parts of the stochastic trajectory associated to the Hamiltonian flow, given by the transitions defined by (200). We postulate that the entropy flux associated to the Hamiltonion flow vanishes identically, $\Phi_H = 0$. Therefore, the entropy production rate associated

to the Hamiltonian flow should be equal to part of dS/dt coming from the Hamiltonian flow. This part can be obtained by inserting the first summation of the right-hand side of the master equation (205) into Eq. (8). After doing this, we get the following expression for the entropy production rate associated to the Hamiltonian flow:

$$\Pi_H = k_B \sum_{x,v} \sum_i \frac{1}{b} P(x,v) \ln \frac{P(x,v)}{P(H^+x, H^+v)}, \qquad (217)$$

which is similar to expression (10).

Next we have to show that $\Pi_H \geqslant 0$. To this end, we expand each term in the summation in powers of b. Up to linear terms in b the i element of the summation equals

$$\left(v_i \frac{\partial P}{\partial x_i} + \frac{F_i}{m} \frac{\partial P}{\partial v_i}\right) + \frac{b}{2P} \left(v_i \frac{\partial P}{\partial x_i} + \frac{F_i}{m} \frac{\partial P}{\partial v_i}\right)^2. \qquad (218)$$

But the integral in x and v of the first term vanishes so $\Pi_H \geqslant 0$. In fact, it vanishes in the continuum limit $b \to 0$. Therefore, in the continuum limit $\Pi_H = 0$. From this result it follows that Π_M is the total production of entropy for the microcanonical case. Since in the continuous limit, it goes into (167), it follows that the expression given by (167) is indeed the entropy production rate, as we have assumed. Similarly, it follows that Π_C is the total production rate for the canonical case. In the continuous limit it is identified with (177) so the expression given by (177) is indeed the entropy production rate, as assumed.

VI. CONCLUSION

We developed the stochastic approach to thermodynamics based on the stochastic dynamics. More specifically, we used the master equation, in the case of discrete state space, and the Fokker-Planck, in the case of continuous state space. Our approach is founded on the use of a form for the production of entropy which is non-negative by definition and vanishes in equilibrium. Based on these assumptions we studied interacting systems with many degrees of freedom in equilibrium or out of thermodynamic equilibrium and how the macroscopic laws can be derived from the stochastic dynamics. This required the introduction of the transition rates which thus play a fundamental role in the present approach, similar to the Gibbs distribution in the case of equilibrium.

Using the property that the production of entropy is non-negative, which is understood as the dynamic formulation of the second law of thermodynamics, we were able to show that in the quasi-static process, the representative point in the thermodynamic space approaches a surface and that this surface has the property of convexity. These statements are usually introduced as postulates in equilibrium thermodynamics. We have also shown the bilinear form of entropy production, which is a sum of terms, each one being a product of a force and a flux. We remark that this is the macroscopic form used in nonequilibrium thermodynamics and should not be confused with the microscopic definition of entropy production itself, which looks like a bilinear form. From the bilinear form of entropy production, we have determined the Onsager coefficients and shown that they obey the reciprocal relations. The nonequilibrium steady states of a system with several chemical species and chemical reactions were studied by the use of appropriate transition rates. From the definition of the entropy production rate it was possible to derive the bilinear form, which in this case is written in terms of affinities and the rates of the extents of reaction. In equilibrium the affinities vanish, which is the condition for chemical equilibrium.

Using appropriate transition rates or appropriate stochastic noise, in the case of the Fokker-Planck, it was possible to study several situations that were analogous to those related to the microcanonical, canonical, and grand-canonical Gibbs ensembles. For the microcanonical case in continuous state space we have introduced an energy-conserving stochastic noise. For the canonical case we used the usual white Gaussian noise. To make contact with the master equation, we have used a master equation representation of the Fokker-Planck. Using this representation we confirmed the expression for the production of entropy that was introduced by the splitting of the time derivative of entropy. In this case we postulated that a Hamiltonian transition induces no flux of entropy. Since the entropy is constant along a Hamiltonian flow in continuous space, this implies no production of entropy.

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