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Entropy of continuous Markov processes in local thermal equilibrium

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The Boltzmann's entropy of a continuous Markov process, in local thermal equilibrium, in contact with a reservoir at temperature T, is analyzed. Assuming that the corresponding Fokker-Planck equation has constant coefficients and satisfies detailed balance, an equation for the entropy density is derived, from which it is possible to obtain expressions for the transport coefficients as functions of the diffusion matrix. Expressions for the entropy production terms of the system and of the combination of system plus reservoir are obtained. Known relations among transport coefficients are derived. The multicomponent case is also analyzed and the Prigogine theorem of minimum entropy production is derived in the context of reaction diffusion systems. The derivations presented in this paper are proposed as a framework for a deeper understanding of concepts used in nonequilibrium diffusion systems.

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I. INTRODUCTION

There is still controversy about the nature of irreversibility, and there is not a general accepted definition of entropy for systems out of equilibrium. These problems are part of an interesting debate that has lasted more than a century and is not completely solved [1,2]. Following the ideas of Goldstein and Lebowitz [3–5], I will consider that the Boltzmann's definition provides an appropriate entropy for the systems under consideration, in particular when local thermal equilibrium is assumed, and that a large number of degrees of freedom is an essential ingredient for irreversibility. In this paper I will consider a stochastic system, in local thermal equilibrium, whose evolution is described by a Fokker-Planck equation, with coefficients independent of time that satisfies detailed balance. The coefficients of a Fokker-Planck equation must fulfill some relations in order to have detailed balance ([6], Sec. 5.3.5). These conditions guarantee detailed balance *in equilibrium*. Out of equilibrium, detailed balance is generally broken. The case of multicomponent systems, where reactions can take place, will also be analyzed. The main purpose of the paper is to obtain an entropy balance equation for these systems and analyze the entropy production term.

There are not many statistical physical systems with a known equation for the one-particle reduced distribution function (RDF), from which irreversibility can be demonstrated. Some of them are the Boltzmann equation for dilute gases [7,8], Landau equation for weakly coupled systems [9], and Balescu-Lenard equation for plasmas [10,11]. The system treated in this paper is simpler since the particles are noninteracting, and therefore, no collision term appears in the equation for the RDF. Although collisions among system particles are not taken into account, the particles do interact, through collisions, with the host medium, and the effect of these collisions is represented by the stochastic behavior. The system, besides being in thermal contact with the reservoir, is embedded in the reservoir, as, for example, ink (system) diffusing in water (reservoir).

In Sec. III, expressions for the entropy density of system, reservoir, and combination of both are derived in a general framework, in the sense that the results are independent of the kind of evolution of the RDF or number density. A balance equation for the entropy density of a system described by a Fokker-Planck equation is presented in Sec. IV. In the entropy production term it is possible to identify transport coefficients that satisfy the Onsager relations. Multicomponent systems are analyzed in Sec. VII. It is assumed that, since the solutions are dilute, they diffuse without interacting, but they can react with probabilities that depend on the densities. The result is an additional term in the entropy production, through which it is possible to derive the Prigogine theorem of minimum entropy production for general reaction diffusion systems. The research in possible applications, and limitations, of the minimum entropy production principle did not decay during the last decades; I can mention a few examples of the recent papers on this subject, such as [12–18], and references cited therein. The procedure described in Sec. VII allows the evaluation of the entropy of far from equilibrium steady states (since the state is stationary, its entropy is constant, but the entropy of the universe must continually increase to sustain it). The Brusselator model is used as an illustrative example.

II. EVOLUTION EQUATION OF THE NUMBER DENSITY

The system is formed by N particles, with $N \gg 1$. Each particle obeys a d dimensional Markov process described by the stochastic variable $\mathbf{x}_i$. In general, $\mathbf{x}_i$ could represent position and momentum, i.e., a combination of even and odd variables under time inversion. The available information about a particle i is given by $p_i(\mathbf{x}_i, t)$: the conditional probability density of having the particle in $\mathbf{x}_i$ at time t given that it was in $\mathbf{x}_i^0$ at $t=0$. The evolution of $p_i(\mathbf{x}_i, t)$ is given by

$$\frac{\partial p_i(\mathbf{x}_i,t)}{\partial t} = M[p_i(\mathbf{x}_i,t)], \tag{1}$$

where M is a linear operator that gives a Fokker-Planck equation if the Markov process is continuous or a master

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equation if it is discontinuous (jump process).

The probability density in phase space of dimension Nd is

$$\rho(\mathbf{X},t) = [p_1(\mathbf{x}_1,t)p_2(\mathbf{x}_2,t)\cdots p_N(\mathbf{x}_N,t) + p_1(\mathbf{x}_2,t)p_2(\mathbf{x}_1,t)\cdots p_N(\mathbf{x}_N,t) + \cdots + p_1(\mathbf{x}_N,t)p_2(\mathbf{x}_{N-1},t)\cdots p_N(\mathbf{x}_1,t)]/N!\,, \tag{2}$$

where $\mathbf{X}=\{\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N\}$. Two assumptions were used: noninteracting and indistinguishable particles. The sum is over the $N!$ permutations of the particle labels; this makes the probability density in phase space symmetric under interchange of particle labels.

The one-particle reduced distribution function is

$$f(\mathbf{x},t) = N\int d\mathbf{x}_2\cdots d\mathbf{x}_N\rho(\mathbf{X},t) = \sum_{i=1}^{N} p_i(\mathbf{x},t), \tag{3}$$

where $\mathbf{x}_1$ was replaced by $\mathbf{x}$. The evolution equation of the RDF, or number density, is

$$\frac{\partial f(\mathbf{x},t)}{\partial t} = \sum_{i=1}^{N} M[p_i(\mathbf{x},t)] = M[f(\mathbf{x},t)], \tag{4}$$

where the linearity property of M was used. Therefore, the same equation that describes the evolution of the probability density of one particle also describes the evolution of the number density f. The result is not surprising, nevertheless its derivation is presented here in order to make clear the different physical meaning of $f(\mathbf{x},t)$ and $p_i(\mathbf{x},t)$. The quantity that is related to entropy is $f(\mathbf{x},t)$.

III. ENTROPY

The Boltzmann entropy is $S=k\ln W$, where W is the number of microscopic states consistent with a given macroscopic state. I will apply the definition to a small region in phase space, of volume $\Delta_\mathbf{x}$, centered on $\mathbf{x}$, and will use the same kind of approximations used by Boltzmann for a dilute gas that in our case corresponds to a dilute solution. The number of particles in $\Delta_\mathbf{x}$ is $N_\mathbf{x}$, and the number of states of one particle in $\Delta_\mathbf{x}$ is $M_\mathbf{x}$. We assume that $M_\mathbf{x} \gg N_\mathbf{x} \gg 1$. The number of microscopic states $W_\mathbf{x}$ is given by the number of different ways in which it is possible to accommodate $N_\mathbf{x}$ identical particles in $M_\mathbf{x}$ sites:

$$W_\mathbf{x} = \frac{(N_\mathbf{x}+M_\mathbf{x}-1)!}{(M_\mathbf{x}-1)!\,N_\mathbf{x}!} \simeq \frac{M_\mathbf{x}^{N_\mathbf{x}}}{N_\mathbf{x}!}. \tag{5}$$

Using Stirling's formula, the entropy in volume $\Delta_\mathbf{x}$ is $S_\mathbf{x} = N_\mathbf{x} - N_\mathbf{x}\ln(N_\mathbf{x}/M_\mathbf{x})$ and, dividing by Δ_x, we obtain the following known relation:

$$s(\mathbf{x},t) = kf - kf\ln(f/c), \tag{6}$$

where $s(\mathbf{x},t)=S_\mathbf{x}/\Delta_\mathbf{x}$ is the entropy density in the one-particle phase space, c is a factor to be determined, and $f=N_\mathbf{x}/\Delta_\mathbf{x}$. Factor c comes from a proportionality relation between number of states for one particle and volume in phase space: $M_\mathbf{x}=c\Delta_\mathbf{x}$.

The interaction with a reservoir at temperature T is the cause of the stochastic behavior of the system. The reservoir is big enough so that the interaction with the system does not modify its state. Assuming that the total energy of reservoir plus system is much greater than the energy of the system, we can write the entropy of the reservoir as $S_R=S_0-E/T$, where S_0 is a constant and $E=\int d\mathbf{x}ef$ is the energy of the system, with e being the energy per particle that can be a function of $\mathbf{x}$. We can write $S_R=S_0-\int d\mathbf{x}ef/T$. The total entropy of system plus reservoir is

$$S_T = S_{T,0} - k\int d\mathbf{x}f(\ln f + e/kT), \tag{7}$$

where $S_{T,0}$ is another constant. Using Lagrange multipliers, with the constraint $\int d\mathbf{x}f=N$, we obtain that the number density that maximizes S_T is

$$f_e(\mathbf{x}) = N\exp(-e/kT)/z, \tag{8}$$

where $z=\int d\mathbf{x}\exp(-e/kT)$.

Assuming that the state variable $\mathbf{x}$ represents position in real space, the first law of thermodynamics can be written as (see, e.g., [19], p. 537)

$$ds = \frac{1}{T}du - \frac{\mu}{T}df = \frac{f}{T}de + \frac{e-\mu}{T}df, \tag{9}$$

where we have replaced the energy density u by ef, μ is the chemical potential, and local thermal equilibrium was assumed. The local thermal equilibrium assumption allows us to have well-defined local thermodynamic variables and also allows us the replacement of an infinitesimal amount of heat by $T\,ds$ in the first law. The temperature of the system is equal to the temperature of the reservoir since, as mentioned in the introduction, the system is assumed to be embedded in the reservoir. From Eqs. (6) and (9) we have $\frac{\partial s}{\partial f}\big|_e = (e-\mu)/T = -k\ln(f/c)$. The previous expression can be evaluated at equilibrium, where $\mu=0$ and $f=f_e$, to obtain $c=N/z$. Therefore,

$$\mu = kT\ln(f/f_e). \tag{10}$$

In Eq. (9) it was assumed that the state variables $\mathbf{x}$ represent position in real space. If they include momenta, the calculation is slightly more involved, but the relation $c=N/z$ is also obtained.

Now, we can write the entropy densities of the system, reservoir, and the sum of system plus reservoir as follows:

$$s(\mathbf{x},t) = kf - kf\ln(zf/N), \tag{11}$$

$$s_R(\mathbf{x},t) = kf\ln(zf_e/N), \tag{12}$$

$$s_T(\mathbf{x},t) = kf - kf\ln(f/f_e), \tag{13}$$

where additive constants were ignored. Equations (11)–(13) are general in the sense that no specific assumption about the evolution of f was used for their derivation. An H-theorem (a demonstration that the system evolves irreversibly to the stationary state) follows from the total entropy $S_T=\int d\mathbf{x}s_T(\mathbf{x},t)$ for Fokker-Planck or master equations since it has the same mathematical form than the Lyapunov functional used in, for example, Ref. [6], Sec. 3.7.3. The demonstration requires the following conditions: the drift and diffusion matrix (for a

Fokker-Planck equation) and the transition probabilities (for a master equation) must be independent of time, the transition probabilities must be different from zero, the diffusion matrix must be positive definite (it is positive semidefinite by definition), and there must exist a stationary solution, $f_e(\mathbf{x})$, different from zero for all $\mathbf{x}$.

In several textbooks (e.g., [20]) the functional form $-f\ln(f/f_e)$ is proposed for the entropy of Markov processes, and afterwards it is shown to have the correct properties. Here, the form of the entropy is deduced from the Boltzmann's definition (as Boltzmann did for dilute gases) and, for the combination of system and reservoir, is equal to $f-f\ln(f/f_e)$. At first glance, the difference does not seem relevant, because the additional term, equal to f, has no effect in the evaluation of total entropy changes. But it is important for the derivation of the entropy balance equation, as will be shown in the next section.

IV. ENTROPY BALANCE EQUATION

Let us consider that the density number is governed by a Fokker-Planck equation

$$\frac{\partial f}{\partial t}=-\nabla\cdot\mathbf{J}, \tag{14}$$

with

$$\mathbf{J}=\mathbf{A}f-\frac{1}{2}\nabla\cdot(\mathsf{B}f), \tag{15}$$

where $\mathbf{J}$ is the particle current, $\mathbf{A}$ is the drift, and B is the diffusion matrix. $\mathbf{A}$ and B can depend on $\mathbf{x}$ but do not depend on time. By definition, matrix B is positive semidefinite (all eigenvalues non-negative). It is convenient to use the reversible drift [21,22] defined as

$$\mathbf{v}(\mathbf{x})=[\mathbf{A}(\mathbf{x})-\varepsilon\mathbf{A}(\varepsilon\mathbf{x})]/2, \tag{16}$$

where ε is a diagonal matrix with values 1 for even variables and -1 for odd variables under time reversal. I assume that, in equilibrium, detailed balance conditions are fulfilled: $\varepsilon\mathbf{A}(\varepsilon\mathbf{x})f_e=-\mathbf{A}(\mathbf{x})f_e+\nabla\cdot[\mathsf{B}(\mathbf{x})f_e]$ and $\varepsilon\mathsf{B}(\varepsilon\mathbf{x})\varepsilon=\mathsf{B}(\mathbf{x})$. Using these conditions in Eq. (16), the reversible drift is $\mathbf{v}=\mathbf{A}-\frac{1}{2f_e}\nabla\cdot(\mathsf{B}f_e)$. The particle current in terms of $\mathbf{v}$ is

$$\mathbf{J}=\mathbf{v}f+\frac{f}{2f_e}\nabla\cdot(\mathsf{B}f_e)-\frac{1}{2}\nabla\cdot(\mathsf{B}f)=\mathbf{v}f-\frac{f}{2}\mathsf{B}\cdot\nabla\ln(f/f_e). \tag{17}$$

Then, the particle current can be written as $\mathbf{J}=\mathbf{J}^r+\mathbf{J}^i$, with

$$\mathbf{J}^r=\mathbf{v}f, \tag{18}$$

$$\mathbf{J}^i=-\frac{f}{2}\mathsf{B}\cdot\nabla\ln(f/f_e), \tag{19}$$

representing the reversible and irreversible parts, respectively. The time derivative of the system entropy density is

$$\begin{aligned}\frac{\partial s}{\partial t}&=k(\nabla\cdot\mathbf{J})\ln(zf/N)=k\nabla\cdot[\mathbf{J}\ln(zf/N)]-k\mathbf{J}\cdot\nabla\ln(zf/N)\\&=k\nabla\cdot[\mathbf{v}f(1-s/kf)+\mathbf{J}^i\ln(zf/N)]-k\mathbf{J}^i\cdot\nabla\ln(zf/N)\\&\quad-kf\mathbf{v}\cdot\nabla\ln(zf/N)=-\nabla\cdot[s\mathbf{v}-k\mathbf{J}^i\ln(zf/N)]\\&\quad-k\mathbf{J}^i\cdot\nabla\ln(zf/N)+k\nabla\cdot(f\mathbf{v})-k\mathbf{v}\cdot\nabla f\\&=-\nabla\cdot[s\mathbf{v}-k\mathbf{J}^i\ln(zf/N)]-k\mathbf{J}^i\cdot\nabla\ln(zf/N)+kf\nabla\cdot\mathbf{v}.\end{aligned} \tag{20}$$

In many cases we can eliminate the last term, $kf\nabla\cdot\mathbf{v}$, since the reversible part of the dynamics is usually given by a Hamiltonian H so that $\mathbf{v}=(\partial_{\mathbf{p}}H,-\partial_{\mathbf{r}}H)$ and $\nabla\cdot\mathbf{v}=0$ [the state variables are $\mathbf{x}=(\mathbf{r},\mathbf{p})$, where $\mathbf{r}$ is even and $\mathbf{p}$ is odd under time reversal, and $\nabla=(\partial_{\mathbf{r}},\partial_{\mathbf{p}})$]. Here I will consider the more general situation, in which $\nabla\cdot\mathbf{v}$ can be different from zero. Finally, the time derivative of the system entropy takes the form of a balance equation,

$$\frac{\partial s}{\partial t}=-\nabla(\mathbf{J}_s^r+\mathbf{J}_s^i)+\sigma, \tag{21}$$

with

$$\mathbf{J}_s^r=\mathbf{v}s, \tag{22}$$

$$\mathbf{J}_s^i=-k\ln(zf/N)\mathbf{J}^i, \tag{23}$$

$$\sigma=-k\mathbf{J}^i\cdot\nabla\ln(zf/N)+kf\nabla\cdot\mathbf{v}, \tag{24}$$

where $\mathbf{J}_s^r$ is the reversible (or reactive) entropy current, $\mathbf{J}_s^i$ is the irreversible (or dissipative) entropy current, and σ is the entropy production term.

For the combination of system and reservoir, following the same steps as in Eq. (20), we have

$$\begin{aligned}\frac{\partial s_T}{\partial t}&=k(\nabla\cdot\mathbf{J})\ln(f/f_e)=-\nabla\cdot[s_T\mathbf{v}-k\mathbf{J}^i\ln(f/f_e)]\\&\quad-k\mathbf{J}^i\cdot\nabla\ln(f/f_e)+k\nabla\cdot(f\mathbf{v})-k\mathbf{v}\cdot\nabla f+k(f/f_e)\mathbf{v}\cdot\nabla f_e\\&=-\nabla\cdot[s_T\mathbf{v}-k\mathbf{J}^i\ln(f/f_e)]-k\mathbf{J}^i\cdot\nabla\ln(f/f_e)\\&\quad+k(f/f_e)\nabla\cdot(\mathbf{v}f_e)=-\nabla\cdot[s_T\mathbf{v}-k\mathbf{J}^i\ln(f/f_e)]\\&\quad-k\mathbf{J}^i\cdot\nabla\ln(f/f_e).\end{aligned} \tag{25}$$

In the last step, we have used that, in equilibrium, $\mathbf{J}=\mathbf{J}_e=\mathbf{v}f_e$ [see Eq. (17)] and $\nabla\cdot\mathbf{J}_e=0$. Therefore, the time derivative of the total entropy also takes the form of a balance equation, $\frac{\partial s_T}{\partial t}=-\nabla(\mathbf{J}_{s,T}^r+\mathbf{J}_{s,T}^i)+\sigma_T$, with

$$\mathbf{J}_{s,T}^r=\mathbf{v}s_T, \tag{26}$$

$$\mathbf{J}_{s,T}^i=-k\ln(f/f_e)\mathbf{J}^i, \tag{27}$$

$$\sigma_T=-k\mathbf{J}^i\cdot\nabla\ln(f/f_e). \tag{28}$$

The total entropy production can also be written as

$$\sigma_T=\frac{kf}{2}[\nabla\ln(f/f_e)]^T\cdot\mathsf{B}\cdot\nabla\ln(f/f_e). \tag{29}$$

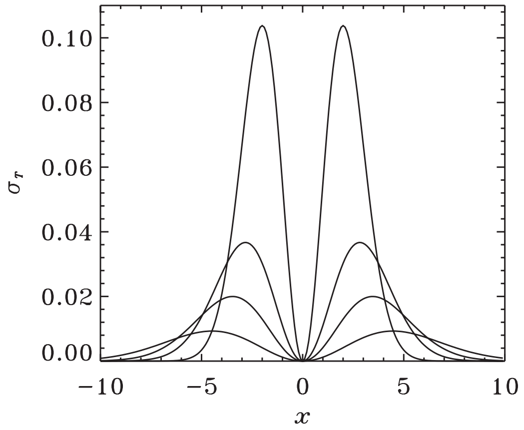

FIG. 1. Entropy production versus position for a diffusion process. The initial condition is a Gaussian function of width L. From top to bottom, time is equal to 0, L^2/D, $2L^2/D$, and $4L^2/D$. The units of the vertical and horizontal axis are kDN/L^3 and L, respectively

This equation shows, in agreement with the second law, that $\sigma_T \geq 0$ since $\mathbf{B}$ is positive semidefinite.

V. EXAMPLES

A simple example is a one-dimensional diffusion process described by $\partial_t f = D\partial_x^2 f$ with an initial condition given by a Gaussian function of width L, $f(x,0)=\frac{N}{2\sqrt{\pi}L}\exp(-x^2/4L^2)$. The total entropy production term is $\sigma_T=\frac{kDN}{L^3}x^2\exp[-x^2/4(t+1)]/[8\sqrt{\pi}(t+1)^{5/2}]$, where the scaling $x\to x/L$ and $t\to tD/L^2$ was used. Figure 1 shows σ_T as a function of x for different values of time.

Another example is the Kramers equation [23] for Brownian motion of a particle, with mass m and momentum p, moving in a one-dimensional potential $U(x)$. The density number evolution equation for N particles is

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial x}\frac{p}{m}f + \frac{\partial}{\partial p}[U'(x)+\zeta p/m]f + \zeta kT\frac{\partial^2}{\partial p^2}f, \tag{30}$$

where ζ is the friction coefficient. The stationary solution is $f_e = N\exp[-(p^2/2m+U)/kT]/z$. It can be shown that the total entropy production is

$$\sigma_T = \zeta k^2 T f\left(\frac{1}{f}\frac{\partial f}{\partial p} + \frac{p}{mkT}\right)^2. \tag{31}$$

We can see that σ_T is always positive and that it is equal to 0 when $f=f_e$.

VI. TRANSPORT COEFFICIENTS

To evaluate transport coefficients we will suppose that the state variables $\mathbf{x}$ correspond to position in real space. In this case, ε is equal to the identity matrix and $\mathbf{v}=0$ [see Eq. (16)]. Now, the entropy and particle currents are $\mathbf{J}_s=\mathbf{J}_s^i$ and $\mathbf{J}=\mathbf{J}^i$.

From Eqs. (10) and (19) we have the following relation between force and current:

$$\mathbf{J} = -\frac{f}{2k}\mathbf{B}\cdot\nabla(\mu/T), \tag{32}$$

where $\nabla(\mu/T)$ is interpreted as the force that drives the particle current. Therefore, the total entropy production [Eq. (28)] is the product: $\sigma_T = -\mathbf{J}\cdot\nabla(\mu/T)$. The matrix of transport coefficients that relates current and force is

$$\mathbf{L} = \frac{f}{2k}\mathbf{B}. \tag{33}$$

Onsager relations $L_{ij}=L_{ji}$ are satisfied since $\mathbf{B}$ is symmetric by definition, see Eq. (3.4.3) in [6]. The relation between matrix $\mathbf{L}$ and diffusion matrix $\mathbf{B}$ was first derived in [24] in a different context; see also [21].

Let us consider a specific case in which the energy per particle is given by an external electric potential, $e=q\phi$, where q is the charge per particle, and the matrix diffusion is $\mathbf{B}/2=D\mathbf{I}$, where D is the diffusion coefficient and $\mathbf{I}$ is the identity matrix. It is useful to write the particle current $\mathbf{J}$ in terms of the chemical potential $\mu=\mu_f+e$, where $\mu_f = kT\ln(zf/N)$ [see Eqs. (10) and (19)],

$$\mathbf{J} = -\frac{fD}{kT}\left(\nabla\mu_f - \frac{\mu}{T}\nabla T + q\nabla\phi\right). \tag{34}$$

We have split the force in three parts corresponding to gradients of μ_f, T, and ϕ. The corresponding currents are proportional to $\mathbf{J}$; the total entropy current is $\mathbf{J}_{s,T}=-(\mu/T)\mathbf{J}$ [Eqs. (10) and (27)], and that the electric current is $\mathbf{J}_e=q\mathbf{J}$, so we get

$$\begin{pmatrix}\mathbf{J}\\ \mathbf{J}_{s,T}\\ \mathbf{J}_e\end{pmatrix} = -\frac{fD}{kT}\begin{pmatrix}1 & -\frac{\mu}{T} & q\\ -\frac{\mu}{T} & \frac{\mu^2}{T^2} & -q\frac{\mu}{T}\\ q & -q\frac{\mu}{T} & q^2\end{pmatrix}\begin{pmatrix}\nabla\mu_f\\ \nabla T\\ \nabla\phi\end{pmatrix}. \tag{35}$$

It turns out that the matrix of transport coefficients that relate currents with forces is symmetric, in accordance with the Onsager relations. The total entropy production [Eq. (28)] can be written in the usual way as the product of currents and forces;

$$T\sigma_T = -\mathbf{J}\cdot\nabla\mu_f - \mathbf{J}_{s,T}\cdot\nabla T - \mathbf{J}_e\cdot\nabla\phi. \tag{36}$$

If the Soret effect is considered, the energy per particle includes an additional term equal to ks_oT^2 [25], where s_o is the Soret coefficient (in Ref. [25] experimental results show that the local thermal equilibrium assumption is appropriate for describing the Soret effect). Considering that there is no electric field, the particle current is

$$\mathbf{J} = -D\nabla f - fDs_o\nabla T, \tag{37}$$

giving the known factor multiplying ∇T that represents the thermal diffusion.

Many explicit relations among transport coefficients can be obtained with this procedure. Some of them are well known, such as the relation that appears in Eq. (35), between electric conductivity κ and diffusion coefficient: $\kappa = fDq^2/kT$ ([19], p. 584).

VII. MULTICOMPONENT SYSTEM

In this section, I will analyze a system composed by a mixture of n different kinds of particles and will consider that $\mathbf{x}$ represents position in real space. There are N_j particles of each type. I assume that, since the solutions are dilute, the presence of different type of particles does not interfere in the diffusion (represented by a different continuous Markov process for each kind of particle) and that the different kinds of particles interact only through reactions. There are r possible reactions with stoichiometric coefficients $\nu_{\alpha j}$, where index α refers to the reaction and index j to the type of particle. The evolution of the density of particle number i of type j, in position $\mathbf{x}_{ij}$ at time t, is

$$\frac{\partial p_{ij}(\mathbf{x}_{ij},t)}{\partial t} = M_j[p_{ij}(\mathbf{x}_{ij},t)] + p_{ij}(\mathbf{x}_{ij},t)\sum_{\alpha=1}^{r} \nu_{\alpha j}J_\alpha/f_j, \quad (38)$$

where $J_\alpha = \frac{1}{V}\frac{d\xi_\alpha}{dt}$ (with V equal to the system's volume and ξ_α equal to the degree of reaction), f_j is the number density of type j, and M_j is a linear operator that represents the Fokker-Planck equation for particles of type j. The factor J_α/f_j is interpreted as the source (or sink) term per particle of type j due to the reaction α. J_α can depend on the number densities of the types involved in reaction α. The dependence of f_j on the density of one particle, p_{ij}, can be neglected because it is assumed that the number of particles N_j is large. Therefore, Eq. (38) is linear. Following the same process as in Sec. II, we obtain

$$\frac{\partial f_j(\mathbf{x},t)}{\partial t} = M_j[f_j(\mathbf{x},t)] + \sum_{\alpha=1}^{r} \nu_{\alpha j}J_\alpha, \quad (39)$$

Equation (39) is, in general, nonlinear.

The reservoir has constant chemical potentials μ_{ej} (the characteristic of a particle reservoir is that when some particles are added to it, the chemical potentials do not change). In equilibrium, we have $\mu_j = \mu_{ej}$. Following the steps of Sec. III, we get the entropy densities of system, reservoir, and combination of both:

$$s(\mathbf{x},t) = k\sum_j [f_j - f_j \ln(z_j f_j/N_j)], \quad (40)$$

$$s_R(\mathbf{x},t) = k\sum_j f_j \ln(z_j f_{ej}/N_j), \quad (41)$$

$$s_T(\mathbf{x},t) = k\sum_j [f_j - f_j \ln(f_j/f_{ej})], \quad (42)$$

where $f_{ej} = N_j \exp[-(e_j - \mu_{ej})/kT]/z_j$ and $z_j = \int d\mathbf{x} \exp[-(e_j - \mu_{ej})/kT]$, with e_j being equal to the energy per particle of type j. The chemical potentials are

$$\mu_j = \mu_{ej} + kT \ln(f_j/f_{ej}). \quad (43)$$

Now, we can derive the entropy balance equation as we did for a one component system in Sec. IV. The most important result is the entropy production term of the combination of system and reservoir that becomes

$$\sigma_T = \frac{k}{2}\sum_j f_j[\nabla \ln(f_j/f_{ej})]^T \cdot \mathbf{B}_j \cdot \nabla \ln(f_j/f_{ej}) - k\sum_j \ln(f_j/f_{ej})\sum_{\alpha=1}^{r} \nu_{\alpha j}J_\alpha. \quad (44)$$

The last term that involves the reactions can be rewritten as $-\Sigma_{\alpha=1}^{r} J_\alpha A_\alpha/T$, where $A_\alpha = \Sigma_j \nu_{\alpha j}\mu_j$ are the affinities, and the equilibrium condition $\Sigma_j \nu_{\alpha j}\mu_{ej} = 0$ is used (see, e.g., [19], Sec. 10.F).

The state f_{ei} is the maximum entropy solution for given values of N_i (this constraint is included though Lagrange multipliers). If the total number of particles did not reach their equilibrium values, then f_{ei} is not stationary since $f_{ei} \sim N_i$ and the total number of particles of each species can vary due to reactions. This possible dependence of N_i on time was not considered in the derivation of Eq. (44), and therefore, it should be applied to situations where the numbers N_i have reached their equilibrium values, and the deviations of f_i respect to f_{ei} do not modify the values of N_i.

I will use the result of Eq. (44) in a general reaction diffusion system and reproduce the result of the Prigogine theorem. The theorem demonstrates that if a system is maintained in a stable stationary state that is different from, but close to, equilibrium by an external thermodynamic force, this state is characterized by a minimum entropy production [26].

A reaction diffusion system is defined by

$$\frac{\partial \mathbf{f}}{\partial t} = \mathbf{D}\nabla^2\mathbf{f} + \mathbf{F}(R,\mathbf{f}), \quad (45)$$

where $\mathbf{f} = (f_1, \ldots, f_n)$, $\mathbf{D}$ is a diagonal matrix with diffusion coefficients D_i for each kind of particle, and $\mathbf{F}$ is a set of nonlinear real functions of $\mathbf{f}$ and of the control parameter R (there can be more than one control parameter, in that case R can be interpreted as a set of parameters). All densities must be real and positive. Parameter R represents the external force that drives the system out of equilibrium. The way a reaction diffusion system can be forced in an experiment is by fixing the values of the densities of a group of species that are involved in the reactions. Since these densities are fixed, they are not included in the description of Eq. (45), but their effect on $\mathbf{f}$ is represented by parameter R. This external forcing is not only external to the system but also to the reservoir so that the combination of system and reservoir is not closed and isolated. The consequence is that the total entropy of system and reservoir can decrease.

I will assume that there is a range of values of R for which there is a unique stationary and homogeneous solution that is stable. These solutions form what is called the thermodynamic branch and are the maximum entropy solutions, i.e., they are equal to $\mathbf{f}_e$. The maximum entropy solution is always stable at equilibrium, but as the control parameter R is modified, the external force can destabilize this solution. Let us suppose that R takes a value in the mentioned range; the corresponding stable homogeneous and stationary solution is $\mathbf{f}_e$, and $\mathbf{F}(R,\mathbf{f}_e)=0$. It is convenient to make the following change in variables: $f_i'=f_i/f_{ei}$. Now, the maximum entropy solution is $\mathbf{f}_e'=1$, and $\mathbf{F}'(R,1)=0$. The primes will be removed to simplify the notation. Let us consider the perturbed solution $\mathbf{f}(\mathbf{x},t)=1+\varepsilon(t)\cos(\mathbf{q}\cdot\mathbf{x})$, where $\mathbf{q}$ is the wave vector of the perturbation. The perturbation amplitudes behave as

$$\frac{d\varepsilon}{dt}=\mathsf{M}\varepsilon, \tag{46}$$

with

$$\mathsf{M}=-q^2\mathsf{D}+\left.\frac{\partial\mathbf{F}}{\partial\mathbf{f}}\right|_1. \tag{47}$$

Since 1 is a stable solution, $\frac{\partial\mathbf{F}}{\partial\mathbf{f}}|_1$ has eigenvalues with negative real part.

The entropy production for system (45) is

$$\sigma_T(\mathbf{f},\nabla\mathbf{f})=k\sum_i\frac{D_i}{f_i}(\nabla f_i)^2-k\sum_i\ln(f_i)F_i(R,\mathbf{f}). \tag{48}$$

The first and second derivatives are

$$\left.\frac{\partial\sigma_T}{\partial\mathbf{f}}\right|_1=0, \tag{49}$$

$$\left.\frac{\partial\sigma_T}{\partial\nabla\mathbf{f}}\right|_1=0, \tag{50}$$

$$\left.\frac{\partial^2\sigma_T}{\partial\mathbf{f}^2}\right|_1=-k\left[\left.\frac{\partial\mathbf{F}}{\partial\mathbf{f}}\right|_1+\left(\left.\frac{\partial\mathbf{F}}{\partial\mathbf{f}}\right|_1\right)^T\right], \tag{51}$$

$$\left.\frac{\partial^2\sigma_T}{\partial(\nabla\mathbf{f})^2}\right|_1=k2\mathrm{D}. \tag{52}$$

Since the real part of the eigenvalues of $\frac{\partial\mathbf{F}}{\partial\mathbf{f}}|_1$ is negative, $\frac{\partial^2\sigma_T}{\partial\mathbf{f}^2}|_1$ is positive definite; $\frac{\partial^2\sigma_T}{\partial(\nabla\mathbf{f})^2}|_1$ is also positive definite since D is a diagonal matrix of positive diffusion coefficients. Therefore, state 1 has minimum entropy production, in accordance with the Prigogine theorem.

It is possible to prove that the global entropy production, $P=\int d\mathbf{x}\sigma_T$, is a Lyapunov functional of (1). To show this, let us consider the entropy production evaluated in the perturbed state $\mathbf{f}=1+\varepsilon\cos\mathbf{q}\cdot\mathbf{x}$,

$$\sigma_T=k\varepsilon^T\left(q^2\mathsf{D}\sin^2(\mathbf{q}\cdot\mathbf{x})-\left.\frac{\partial\mathbf{F}}{\partial\mathbf{f}}\right|_1\cos^2(\mathbf{q}\cdot\mathbf{x})\right)\varepsilon. \tag{53}$$

Using this result, we can calculate the global entropy production [since $\sigma_T(1)=0$, it coincides with what is called the excess entropy production],

$$P=-k\frac{V}{2}\varepsilon^T\mathsf{M}\varepsilon\geq 0, \tag{54}$$

where V is the volume of the system and the inequality $P\geq 0$ comes from the stability conditions of Eq. (46); $P=0$ for $\varepsilon=0$. If M is symmetric, the time derivative of P is

$$\frac{dP}{dt}=-kV\left(\frac{d\varepsilon}{dt}\right)^2<0. \tag{55}$$

In general, M is not symmetric. In this case, rewriting Eq. (54) as $P=-k\frac{V}{4}\varepsilon^T(\mathsf{M}+\mathsf{M}^T)\varepsilon$ [take the transpose of Eq. (54), sum to Eq. (54), and divide by 2], the time derivative of P is

$$\frac{dP}{dt}=-k\frac{V}{4}\varepsilon^T(2\mathsf{M}^T\mathsf{M}+\mathsf{M}^{T^2}+\mathsf{M}^2)\varepsilon. \tag{56}$$

The eigenvectors and eigenvalues of M are $\mathbf{e}_j$ and $\lambda_j=\lambda_j'+i\lambda_j''$, where λ_j' and λ_j'' are the real and imaginary parts. The perturbations can be written as $\varepsilon=\Sigma_j a_j\mathbf{e}_j$ and $\varepsilon^T=\Sigma_j a_j^*\mathbf{e}_j^T$; replacing in Eq. (56) we obtain

$$\frac{dP}{dt}=-kV\sum_j|a_j|^2\lambda_j'^2<0. \tag{57}$$

These results prove that P satisfies the conditions to be a Lyapunov functional of 1.

To illustrate the calculation of the entropy, I will use the Brusselator [27], a classical reaction diffusion system used as a model of the Belousov-Zhabotinski reaction. The model describes the evolution of the densities of two species, f_1 and f_2, that have diffusion coefficients D_1 and D_2, respectively,

$$\frac{\partial f_1}{\partial t}=D_1\nabla^2 f_1+A-(B+1)f_1+f_1^2f_2, \tag{58}$$

$$\frac{\partial f_2}{\partial t}=D_2\nabla^2 f_2+Bf_1-f_1^2f_2. \tag{59}$$

Parameter A is fixed, and parameter B is used as the control parameter. Figure 2 shows the total entropy $\Delta S_T=S_T-S'$ as a function of B in a stationary situation, where $S_T=\int d\mathbf{x}s_T(\mathbf{x})$ and $S'=k\Sigma_jN_j$. The sudden change in ΔS_T shows the point where a nonequilibrium phase transition takes place. In the parameter region where ΔS_T becomes negative, the system converges to a dissipative structure composed by a steady-state pattern. The evaluation of S_T allows a classification of nonequilibrium patterns in terms of their order or disorder.

VIII. CONCLUSIONS

Equations (11)–(13) allow the calculation of the entropy of systems in local thermal equilibrium. This result is valid for continuous or discontinuous Markov processes and the total entropy $S_T=\int d\mathbf{x}s_T$ has the same form as the Lyapunov functionals used to demonstrate the H theorem.

Equations (26)–(29) determine the entropy balance equation for a continuous Markov process that satisfies detailed balance and that is described by a Fokker-Planck equation with coefficients independent of time. All transport coeffi-

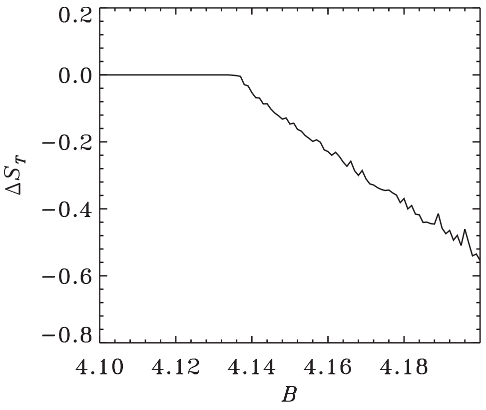

FIG. 2. Total entropy change ΔS_T, versus control parameter B, for the Brusselator model in one dimension with periodic boundary conditions. The thermodynamic branch, where $\Delta S_T=0$, is stable up to $B_c \simeq 4.14$. For $B > B_c$, the system evolves to a steady-state periodic structure with negative ΔS_T. The initial condition is random noise around the homogeneous solution $x_0=A$ and $y_0=B/A$. Parameters: $A=2$, $D_1=0.0016$, $D_2=0.006$, system length $L=40$, time used to reach stationary state: 1000, units of the vertical axis: k.

cients can be obtained from the entropy production term [Eq. (29)]. They are directly related to the diffusion matrix $\mathbf{B}$ and satisfy the Onsager relations.

The derivation of known relations among transport coefficients is a result that supports the validity of the procedure to derive them and the validity of the Boltzmann entropy for systems in local thermal equilibrium.

Multicomponent systems, with particles that can react with probabilities that depend on the densities, were analyzed in Sec. VII. The entropy production term [Eq. (44)] of the entropy balance equation was derived. It was used to study entropy production in reaction diffusion systems. It was proved that the thermodynamic branch (the set of stable homogeneous and stationary solutions that appear as the control parameter is varied) has minimum entropy production, in accordance to the Prigogine theorem.

The framework used for the derivation of the entropy balance equation is proposed as a tool for a deeper understanding of the thermodynamic meaning of concepts used in nonequilibrium diffusion systems. In particular, the Prigogine's principle of minimum entropy production is still an active subject of interesting analysis and research; see, for example, [16–18].

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