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Entropy Production in Nonequilibrium Systems at Stationary States

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We present a stochastic approach to nonequilibrium thermodynamics based on the expression of the entropy production rate advanced by Schnakenberg for systems described by a master equation. From the microscopic Schnakenberg expression we get the macroscopic bilinear form for the entropy production rate in terms of fluxes and forces. This is performed by placing the system in contact with two reservoirs with distinct sets of thermodynamic fields and by assuming an appropriate form for the transition rate. The approach is applied to an interacting lattice gas model in contact with two heat and particle reservoirs. On a square lattice, a continuous symmetry breaking phase transition takes place such that at the nonequilibrium ordered phase a heat flow sets in even when the temperatures of the reservoirs are the same. The entropy production rate is found to have a singularity at the critical point of the linear-logarithm type.

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The distinguishing feature of a system out of thermodynamic equilibrium is the continuous production of entropy. The variation of entropy per unit time is not only due to the exchange of entropy with the environment but also due to the internal entropy production [1–3], that is,

$$\frac{dS}{dt} = \Pi - \Phi, \tag{1}$$

where S is the entropy of the system, Π is the rate of entropy production and Φ is the flow of entropy per unit time *from* the system *to* the outside. Within this context, the second law of thermodynamics is equivalent to saying that the rate of entropy production is nonnegative, $\Pi \geq 0$. In the steady state, S is constant and all entropy generated is continuously been given away to the environment, $\Pi = \Phi$. If the stationary state is a nonequilibrium, that is, irreversible then $\Pi = \Phi > 0$. In the equilibrium state, $\Pi = \Phi = 0$.

In this Letter we wish to present a microscopic stochastic approach to the thermodynamics of far from equilibrium systems, that embodies the properties of the entropy production rate just stated and from which we should be able to deduce the macroscopic bilinear form for the entropy production rate for nonequilibrium systems in the steady states in terms of fluxes and forces [1–4]. To this end we assume that the system we are studying is amenable to be described by a continuous time Markovian process which amounts to assume a description in terms of a master equation [5]

$$\frac{d}{dt}P_i(t) = \sum_j \{W_{ij}P_j(t) - W_{ji}P_i(t)\}, \tag{2}$$

where W_{ij} is the transition rate from state j to state i and $P_i(t)$ is the probability of state i at time t. The deduction of the macroscopic bilinear form is performed by placing the system in contact with two reservoirs with distinct sets of thermodynamic fields and by assuming an appropriate form for the transition rate, to be explained below. We remark that the contact with two reservoirs keeps the system far from equilibrium.

To establish a microscopic approach to nonequilibrium thermodynamics one encounters two major problems concerning entropy. The first is the definition of entropy S of irreversible systems. This problem is solved if one uses the Boltzmann-Gibbs expression [6,7],

$$S(t) = -k\sum_i P_i(t)\ln P_i(t), \tag{3}$$

to represent the nonequilibrium entropy, where k the Boltzmann constant.

The second problem is the definition of entropy production rate Π. It should meet the two important properties, stated above, that represent the second law of thermodynamics. (a) It should be nonnegative and (b) it should vanish for systems in equilibrium. A system is considered to be in thermodynamic equilibrium if it exhibits microscopic reversibility [8]. For systems described by a master equation this is equivalent to the detailed balance condition $W_{ij}P_j = W_{ji}P_i$, for any pair of states i and j. An expression that meet the conditions (a) and (b), for systems described by a master equation, is the one advanced by Schnakenberg [9]

$$\Pi(t) = \frac{k}{2}\sum_{ij}\{W_{ij}P_j(t) - W_{ji}P_i(t)\}\ln\frac{W_{ij}P_j(t)}{W_{ji}P_i(t)}, \tag{4}$$

an expression that has been considered by several authors [10–22] and has a close relationship with the fluctuation theorems of Gallavotti and Cohen [23] and with the Jarzynski equality [24,25]. It is nonnegative because each term in the summation is of the form $(x - y)\ln(x/y)$ and vanishes in equilibrium, that is, when microscopic reversibility or detailed balance condition is obeyed.

In the stationary state the expression (4) reduces to the simpler expression

$$\Pi = k\sum_{ij} W_{ij} P_j \ln\frac{W_{ij}}{W_{ji}}, \tag{5}$$

where P_i is the stationary probability distribution. Expression (5) is particularly useful since it can be understood as an average over the probability distribution P_i. To deduce (5) from (4) it suffices to notice that the difference between these two expression equals dS/dt, which vanishes in the stationary state.

To proceed further we need to know the specific forms of the transition rates corresponding to a given situation. We begin by considering firstly systems that in the stationary state are found to be in thermodynamic equilibrium. In this case the system exhibits the microscopic reversibility which is equivalent to the detailed balance condition $W_{ij}/W_{ji} = P_i^e/P_j^e$, where P_i^e is the equilibrium probability distribution. The desired transition rate should then be of the general form $W_{ij} = K_{ij}[P_i^e/P_j^e]^{1/2}$ where K_{ij} is symmetric, that is, $K_{ij} = K_{ji}$. The equilibrium probability distribution P_i^e is assumed to be the Gibbs distribution describing the contact of the system with a specific reservoir. Here we consider a reservoir that exchanges heat and particles with the system so that the associated distribution is $P_i^e \propto \exp\{-\beta(E_i - \mu N_i)\}$ [26], $\beta = 1/kT$, where E_i and N_i are the energy and the number of particles of the system, and T and μ are the temperature and the chemical potential of the reservoir. The desired transition rate is then

$$W_{ij} = K_{ij} e^{-\beta[(E_i - E_j) - \mu(N_i - N_j)]/2}. \tag{6}$$

Let us imagine now the system to be in contact with two distinct reservoirs, 1 and 2. Reservoirs 1 and 2 are associated with the temperatures T_1 and T_2 and the chemical potentials μ_1 and μ_2, respectively. The transition rate associated to the rth reservoir is given by

$$W_{ij}^{(r)} = K_{ij}^{(r)} e^{-\beta_r[(E_i - E_j) - \mu_r(N_i - N_j)]/2}, \tag{7}$$

where $\beta_r = 1/kT_r$.

Each possible transition occurring in the system between two states i and j is either due to the contact with the reservoirs or is an internal transition with no relation to the reservoirs. The transitions describing the contact with the reservoirs are assumed to be caused by the contact with either one or the other reservoir so that the transition rate is either $W_{ij}^{(1)}$ or $W_{ij}^{(2)}$. The internal transitions, denoted by $W_{ij}^{(3)}$, are assumed to have the property $W_{ij}^{(3)} = W_{ji}^{(3)}$ whenever $E_i = E_j$ and $N_i = N_j$, otherwise $W_{ij}^{(3)} = 0$. Each possible transition is therefore assumed to belong to one of three mutually exclusive classes of transitions labeled 1, 2, and 3. Introducing a projection variable $\gamma_{ij}^{(r)} = \gamma_{ji}^{(r)}$ that takes the value 1 if the transition between states i and j belongs to class r and 0 otherwise then the transition rate can be written as

$$W_{ij} = \gamma_{ij}^{(1)} W_{ij}^{(1)} + \gamma_{ij}^{(2)} W_{ij}^{(2)} + \gamma_{ij}^{(3)} W_{ij}^{(3)}. \tag{8}$$

The entropy production rate becomes then

$$\Pi = k\sum_{r=1,2}\sum_{ij} \gamma_{ij}^{(r)} W_{ij}^{(r)} P_j \ln\frac{W_{ij}^{(r)}}{W_{ji}^{(r)}}. \tag{9}$$

Notice that the summation is only over the transitions associated to the two reservoirs since the transitions of class 3 give no contribution to Π. By the use of (7) it can be written as

$$\Pi = \sum_{r=1,2}\sum_{ij} \gamma_{ij}^{(r)} W_{ij}^{(r)} P_j \left[\frac{1}{T_r}(E_j - E_i) - \frac{\mu_r}{T_r}(N_j - N_i)\right]. \tag{10}$$

Since the flux of energy (actually heat) from reservoir 1 into the system is

$$\mathcal{J}_E = \sum_{ij} \gamma_{ij}^{(1)} W_{ij}^{(1)} P_j (E_i - E_j), \tag{11}$$

and the flux of particles from reservoir 1 into the system is

$$\mathcal{J}_N = \sum_{ij} \gamma_{ij}^{(1)} W_{ij}^{(1)} P_j (N_i - N_j), \tag{12}$$

and making use of the global balance equation, then expression (10) can be written in the bilinear form

$$\Pi = X_E \mathcal{J}_E + X_N \mathcal{J}_N, \tag{13}$$

where $X_E = 1/T_2 - 1/T_1$ and $X_N = \mu_1/T_1 - \mu_2/T_2$ are the thermodynamic forces conjugated to the flux of energy and particles, respectively.

We have applied the results above to a nonequilibrium interacting lattice gas model defined on a regular lattice with energy $E = -J\sum_{(\ell,\ell')} \sigma_\ell \sigma_{\ell'}$, where the summation is over the nearest neighbor sites, and number of particles $N = \sum_\ell (\sigma_\ell + 1)/2$. We are using spin variables σ_ℓ that take the values $+1$ or -1 according to whether the sites are occupied or empty. The whole configuration of the lattice is denoted by σ. The system is in contact with two reservoirs that keep the system far from equilibrium. The contact with each reservoir is described by a spin flip transition rate of the Glauber type

$$w_\ell(\sigma) = \frac{\alpha}{2}\left\{1 - \sigma_\ell \tanh\left[\beta_r\left(J\sum_\delta \sigma_{\ell+\delta} + H_r\right)\right]\right\}, \tag{14}$$

which is a particular form of (7), where H_r is related to the chemical potential by $H_r = \mu_r/2$ and α sets the time scale. To update a chosen site, we use reservoir 1 if the majority of neighboring spins is up and reservoir 2 if the majority is down. When there is a tie, one uses reservoir 1 if the site at the right of the chosen site is up and reservoir 2 if it is down. For the one-dimensional model the local configurations are $+\cdot+$ and $-\cdot+$ for reservoir 1 and $-\cdot-$ and $+\cdot-$ for reservoir 2, where the dot represents the site to be updated. For the model defined on a square lattice the local configurations associated to each reservoir are shown in Fig. 1. This model is related to models that describe the flux of molecules across a cell membrane [27]. The two reservoirs represent the inside and outside regions of a cell. Depending on the configuration of its neighborhood, a site can exchange particles with either the outside or the inside region.

Here we report results for a linear chain and for a square lattice for the case in which $T_1 = T_2 = T$ and $H_1 = -H_2 = H$. In this case the model has up-down symmetry and $X_N = (4H/T)$ and $X_E = 0$ so that $\Pi = (4H/T)\mathcal{J}_N$.

For the linear chain it follows from (14) that the spin flip transition rate can be written in the equivalent form

$$w_\ell(\sigma) = (b_0 + b_1\sigma_{\ell-1}\sigma_{\ell+1})e^{-\sigma_\ell\beta[J\sigma_{\ell-1}+(J+H)\sigma_{\ell+1}]}, \tag{15}$$

where b_0 and b_1 are known functions of βJ and βH. The stationary probability distribution $P(\sigma)$ is obtained by assuming that it has the form

$$P(\sigma) = \frac{1}{Z}e^{K\sum_\ell \sigma_\ell\sigma_{\ell+1}}, \tag{16}$$

where K is a parameter to be found. If we substitute (15) and (16) into the global balance equation

$$\sum_\ell \{w_\ell(\sigma^\ell)P(\sigma^\ell) - w_\ell(\sigma)P(\sigma)\} = 0, \tag{17}$$

where σ^ℓ denotes the configuration obtained from σ by changing the sign of σ_ℓ, we get

$$\sum_\ell \{a_0 + \sigma_\ell(a_1\sigma_{\ell-1} + a_2\sigma_{\ell+1}) + a_3\sigma_{\ell-1}\sigma_{\ell+1}\} = 0, \tag{18}$$

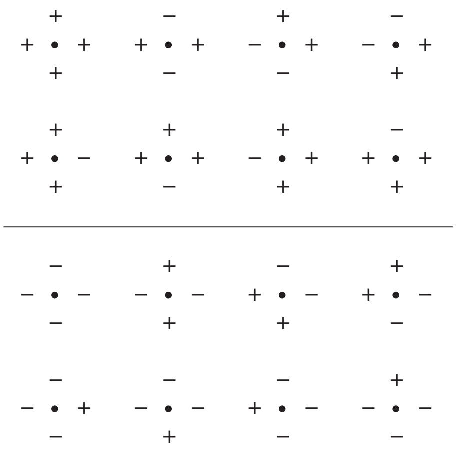

FIG. 1. Local configurations on a square lattice associated to reservoir 1 (above the line) and reservoir 2 (below the line). The dot represents the site to be updated.

where a_i are known functions of K, βJ and βH. A solution of this equation is obtained by imposing $a_0 = a_3 = 0$ and $a_1 = -a_2$. These three conditions are not all independent and can be met by just one constraint, which is found to be $K = \beta(J + H)/2$.

The production of entropy per site Π^* is also obtained exactly. Substituting (15) and (16) into the expression for the entropy production rate

$$\Pi^* = k\left\langle w_\ell(\sigma)\ln\frac{w_\ell(\sigma^\ell)}{w_\ell(\sigma)}\right\rangle, \tag{19}$$

we obtain an expression that involves the nearest neighbor and next-nearest neighbor correlations $\langle\sigma_\ell\sigma_{\ell+1}\rangle$ and $\langle\sigma_{\ell-1}\sigma_{\ell+1}\rangle$. But these two correlations can be obtained exactly from the solution of the one-dimensional model defined by (16). They are $\tanh K$ and $(\tanh K)^2$, respectively, which lead us to the following expression for the rate of entropy production:

$$\Pi^* = \frac{\alpha H\tanh\beta H}{2T(\cosh K)^2}. \tag{20}$$

The flux of heat $\mathcal{J}_E$ vanishes identically. It is worth to point out that if a temperature T_S is associated to the system through $K = J/kT_S$ then $T_S = T/(1 + H/2J)$ and the temperature of the system T_S is distinct from the temperature T of the reservoirs.

On a square lattice the entropy production rate was obtained from numerical simulations. At each time step a site of the lattice is randomly chosen and is updated according to the Glauber dynamics defined by (14). According to the local configuration, shown in Fig. 1, we use either $H_1 = H$ or $H_2 = -H$ in Eq. (14). The temperature T is the same. The simulations were performed on a square lattice of linear size $L = 160$ and periodic boundary conditions. The results obtained at the stationary state are shown in Fig. 2 in units where $k = 1$ and $J = 1$. The model exhibits a symmetry breaking phase transition at $T = 3.125(5)$ from a disordered to an ordered state. The entropy production rate per site Π^* is finite but has a singularity at the critical point which is better appreciated if we look at its derivative $d\Pi^*/dT$. This last quantity diverges at the critical point as can be seen in Fig. 2. Our results indicate a logarithmic divergence for $d\Pi^*/dT$, similar therefore to the specific heat divergence of the equilibrium Ising model on a square lattice. Similar behavior has also been found in the majority vote model [14].

The phase transition taking place in this irreversible model could be characterized, at a first thought, by the magnetization and susceptibility. However, these quantities do not grasp the irreversible character of the system. Alone they could not tell whether the system is or is not in equilibrium. The full characterization is accomplished by the currents and fluxes of various types taking place a the nonequilibrium steady state. These fluxes together with the forces make up the entropy production rate, as given

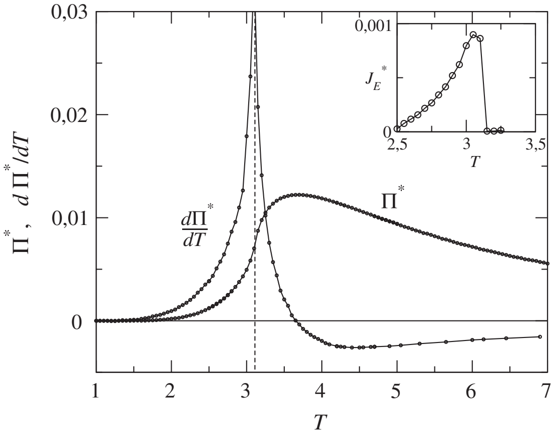

FIG. 2. Entropy production rate per site Π^*, the derivative $d\Pi^*/dT$ and the heat flux per site $\mathcal{J}_E^*$ (inset) versus temperature T obtained from numerical simulations. They exhibit singularities at the critical temperature $T_c = 3.125(5)$.

by the bilinear form, assigning to this quantity a fundamental role in describing the phase transition at nonequilibrium steady states.

The nature of the phase transition can be found from the behavior of the entropy production rate and the fluxes as functions of the external parameters. A discontinuous, or first order, phase transition takes place if these quantities display a jump at the transition point. If they are continuous, the transition is continuous, or second order. In this respect, these quantities play roles analogous to the first derivatives of the Gibbs free energy in equilibrium system. According to this framework, the phase transition of the present two-dimensional model is second order and is similar to the continuous phase transition in the equilibrium Ising model in the sense that the derivative of the continuous function diverges instead of having a jump.

Another and perhaps more meaningful characterization of the phase transition is provided by the order parameter. Since we are faced with a phase transition in which the up-down symmetry is broken at low temperatures, the order parameter has to change sign under the up-down transformation, that is, should be antisymmetric. Antisymmetric quantities vanish in the disordered phase and become nonzero in the ordered phase. This is exactly the case of the heat flux $\mathcal{J}_E$, which is an antisymmetric quantity and may therefore be identified as the order parameter, in contrast to the particle flux $\mathcal{J}_N$, which is symmetric. Above the critical temperature there is no heat flux. Below the critical temperature a nonzero heat flux sets in, as can be seen in the inset of Fig. 2, in spite of the fact that the temperatures of the reservoirs are the same. Because of the symmetry breaking there may be two coexisting phase at low temperature: one characterized by a heat flow from reservoir 1 to reservoir 2 and the other, from 2 to 1.

The one-dimensional model introduced above is an example of models lacking detailed balance but having a Boltzmann-Gibbs (BG) distribution as the stationary state [28]. In spite of being described by a BG distribution such models are out of equilibrium, with a nonzero production of entropy. In two dimension, the simplest model of this type is the North-East model defined on a square lattice by the spin flip transition rate [28,29]

$$w_\ell(\sigma) = \alpha e^{-2K\sigma_\ell(\sigma_{\ell+\hat{x}}+\sigma_{\ell+\hat{y}})}. \tag{21}$$

Employing the same reasoning used in the one-dimensional case, it is straightforward to show that the stationary probability distribution for this stochastic process is the BG distribution

$$P(\sigma) = \frac{1}{Z} e^{K\sum_{(\ell,\ell)}\sigma_\ell\sigma_{\ell'}}, \tag{22}$$

where the summation is over the nearest neighbor pair of sites of a square lattice and describes an Ising model with nearest neighbor interactions, which exhibits also a symmetry breaking phase transition at a temperature $T = 1/K$ given by $T_c = 2/\ln(1+\sqrt{2})$. The calculation of the entropy production rate for this model can be carried out exactly. Indeed, from the definition (5) of the entropy production and using the transition rate (21) we obtain the following expression for the entropy production rate per site

$$\Pi^* = a - b\langle\sigma_\ell\sigma_{\ell+\hat{x}}\rangle + a\langle\sigma_{\ell+\hat{x}}\sigma_{\ell+\hat{y}}\rangle, \tag{23}$$

where $a = 4k\alpha K \sinh 4\ \mathrm{K}$, $b = 8k\alpha K \cosh 4\ \mathrm{K}$, and $\langle\sigma_\ell\sigma_{\ell+\hat{x}}\rangle$ and $\langle\sigma_{\ell+\hat{x}}\sigma_{\ell+\hat{y}}\rangle$ are the nearest and next-nearest neighbor correlations on a square lattice. Since these two correlations can be determined exactly for the Ising model on a square lattice [30] it follows that the entropy production can also be exactly calculated. Substituting the closed forms for the correlations (from [30], pages 200–201) we get the desired expression for Π, which is too cumbersome to be written down but can be appreciated in the plot of Fig. 3. It is important to notice that these correlations are finite but have

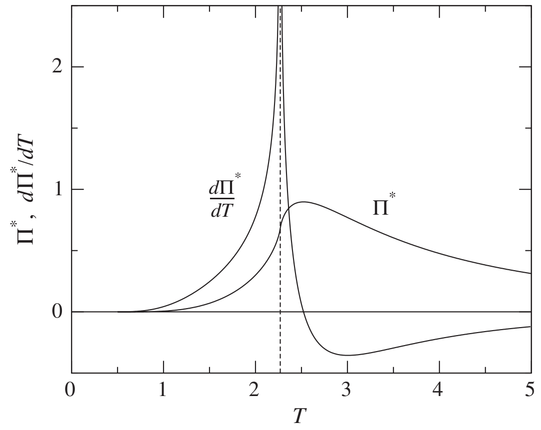

FIG. 3. Entropy production rate per site Π^* and the derivative $d\Pi^*/dT$ versus temperature according to the exact expression (23). They exhibit singularities at the critical temperature $T_c = 2/\ln(1+\sqrt{2}) = 2.269\,185$.

singularities of the type $|T - T_c| \ln|T - T_c|$ [30]. These features are reflected on the production of entropy, that is, this quantity is also finite and has the same type of singularity, as can be seen in the plot of Π^* versus T shown in Fig. 3 together with the plot of $d\Pi^*/dT$ versus T.

As a final remark, the existing examples of nonequilibrium models with stationary BG probability distribution teach us that the BG distribution is a necessary but not a sufficient condition for the thermodynamic equilibrium. Actually, the necessary and sufficient condition is detailed balance, or microscopic reversibility or, in macroscopic terms, the vanishing of entropy production rate.

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