

## Dissipation of energy and of information in nonequilibrium reaction-diffusion systems

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In this paper, we prove a general inequality for the macroscopic relaxation towards a stationary nonequilibrium state. Namely, the rate of dissipation of energy in the system always exceeds the rate of dissipation of information (up to temperature). Here the information function is defined as the logarithm of the stationary probability distribution divided by the volume. The equality is achieved if and only if the stationary probability distribution is an equilibrium distribution function. This implies a lower bound for the work needed to produce a fluctuation away from the stationary state, which should have experimental consequences.

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### I. INTRODUCTION

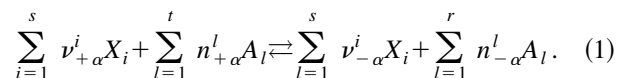
Many natural systems are not in equilibrium although they reach a stationary state. One of the main problems of out-of-equilibrium thermodynamics is to define nonequilibrium state functions and to find relations between them, as well as evolution laws, in particular far from equilibrium. This problem has been addressed by many authors (see, e.g., [1–10]). We derive a general inequality, which holds for any reaction-diffusion system, between the rate of dissipation of energy and the rate of dissipation of information (in a sense to be defined later), during the relaxation of the system from a nonstationary state to a (nonequilibrium) stationary state.

It is well known (see [1]) that for a system in an equilibrium state, the work necessary to produce a fluctuation away from this macroscopic equilibrium state is larger than the variation of the free energy of the system. Our main result concerns the work per unit time given to the system, during the macroscopic spontaneous relaxation towards a stationary state. More precisely, we consider a reaction-diffusion system, maintained at a fixed temperature by a heat bath. Certain species are also maintained at fixed concentrations by the action of external reservoirs, while other species evolve spontaneously under the chemical and diffusion processes that take place inside the system. Starting from a macroscopic state, one can also define the work given to the system by the external reservoirs of fixed species during the spontaneous relaxation towards the stationary state (which is, in general, nonequilibrium). We prove that, during the spontaneous evolution, the rate per unit time of this is always larger than the rate of variation of  $F + k_B T \ln_{10} P$ , where  $F$  is the (nonequilibrium) free energy and  $P$  is the stationary distribution probability, with equality if and only if the system evolves toward a thermal equilibrium state.

We notice that this kind of inequality cannot be obtained by the classical principles of thermodynamics alone, or even of those of generalized thermodynamics. Moreover, an inequality concerning the variation of entropy was derived in [11], but this does not relate obviously to the variation of free energy and the external work.

### II. REACTION DIFFUSION SYSTEMS

We consider a system at a fixed temperature  $T$ , with chemical species denoted by  $X_i$ ,  $i=1,\dots,s$ , and other chemical species denoted by  $A_l$ ,  $l=1,\dots,r$ , which will be kept constant by reservoirs later on. The volume of the system is  $V$ , supposed to be large, and we denote by  $x_i$  and  $a_l$  the respective concentrations of the species  $X_i$  and  $A_l$  (number of particles divided by  $V$ ). The internal evolution of the system is described by  $p$  processes, denoted  $\alpha=1,\dots,p$ , of the type



This type of process describes chemical reactions, as well as diffusion, if the total volume  $V$  is divided in cells and the  $X_i$  or  $A_l$  denote a species in a given cell. The numbers  $\nu_{\pm\alpha}^i$ ,  $n_{\pm\alpha}^l$  are positive or zero integers.

We assume that the system can be described by a non-equilibrium free energy  $F(x,a)$  (per unit volume). For a system that is in partial equilibrium,  $F(x,a)$  would be the sum of the equilibrium free energies of each species at their respective concentration, but we do not restrict ourselves to this special form. The chemical potentials are

$$\mu_i = \frac{\partial F}{\partial x_i}, \quad m_l = \frac{\partial F}{\partial a_l}.$$

The rate constants  $\omega_{\alpha}^{\pm}$  of the backwards and forward processes  $\alpha$  are given by

$$\omega_{\alpha}^{\pm} = C_{\alpha} \exp \left[ \frac{1}{k_B T} \left( \sum_i \nu_{\pm\alpha}^i \mu_i + \sum_l n_{\pm\alpha}^l m_l \right) \right], \quad (2)$$

where  $C_{\alpha}$  depends only on  $\alpha$  [14]. This assures that each process is equilibrated at thermal equilibrium. It is easily seen that this formula applies to the usual kinetic laws when the chemical potentials are given by their classical expres-

sion for ideal mixtures and perfect gases. It has been shown that it also holds in more general conditions [13]. If we define

$$\tau_\alpha^j = \nu_{-\alpha}^j - \nu_{+\alpha}^j, \quad t_\alpha^l = n_{-\alpha}^l - n_{+\alpha}^l,$$

the free evolution equations (when concentrations  $x_i$  and  $a_l$  are unconstrained) are

$$\frac{dx_i}{dt} = \sum_\alpha \tau_\alpha^i (\omega_\alpha^+ - \omega_\alpha^-), \quad \frac{da_l}{dt} = \sum t_\alpha^l (\omega_\alpha^+ - \omega_\alpha^-). \quad (3)$$

If we denote by  $\xi^\alpha(t)$  the progress variable up to time  $t$  of the process  $\alpha$ , i.e., the number of forward events  $\alpha$  minus the number of backward events  $\alpha$  up to time  $t$  (divided by  $V$ ), we have

$$x_i(t) = x_i(0) + \sum_\alpha \tau_\alpha^i \xi^\alpha(t), \quad (4a)$$

$$a_l(t) = a_l(0) + \sum_\alpha t_\alpha^l \xi^\alpha(t), \quad (4b)$$

and for given  $(x(0), a(0))$  the system evolves towards a thermal equilibrium where each process  $\alpha$  is equilibrated because of the choice of the rates in Eq. (2).

### III. NONEQUILIBRIUM SITUATION: A THERMODYNAMIC INEQUALITY

We now assume that external reservoirs control the concentration of the species  $A_l$ , and, to simplify matters, we assume that the external reservoirs maintain the concentration  $a_l$  at fixed values. Under this condition, the state space breaks up in invariant subspaces  $E(x(0))$  given by the linear equations

$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i \xi^\alpha.$$

Because by Eq. (4a), the evolution is confined to such a space. If at time 0,  $x_i(0)$  is given, Eq. (4a) gives the value of the stochastic process  $x_i(t)$  at any time. The macroscopic evolution is given by

$$\frac{dx_i}{dt} = \sum \tau_\alpha^i (\omega_\alpha^+ - \omega_\alpha^-), \quad \frac{da_l}{dt} = 0. \quad (5)$$

We will show that it is possible to define a state function  $-k_B\Phi$ , which is the analog of Einstein entropy per unit volume, usually defined for equilibrium distributions (see Sec. IV). This quantity is obtained from the stationary distribution of the stochastic theory. Before studying it in the next section, we now state our main result, which is an inequality, holding out of equilibrium, between  $dF/dt$ ,  $d\Phi/dt$ , and  $w$ , the work done per unit time by the external reservoirs in order to maintain the concentrations of the species  $A_l$  at the constant value  $a_l$ .

This thermodynamic inequality can be written as

$$-\left(\frac{dF}{dt} - w\right) \geq -k_B T \frac{d\Phi}{dt}. \quad (6)$$

Moreover,  $d\Phi/dt$  and  $dF/dt - w$  are always negative, and Eq. (6) is an equality if and only if the fixed concentrations  $a_l$  are such that the system reaches a complete thermodynamic equilibrium under the evolution given by Eq. (6), i.e., a state for which detailed balance is realized, so that each process  $\alpha$  is equilibrated.

The second principle only states that  $dF/dt - w$  is negative for nonreversible transformations. The fact that  $d\Phi/dt$  is also negative agrees with the interpretation of  $-k_B\Phi$  as an entropy intrinsic to the system (see Sec. V). Inequality (6) indicates that the total entropy production always contains other positive contributions in an open system out of equilibrium, but it cannot be deduced from the second principle alone. We now give the derivation of this inequality.

### IV. PROOF OF INEQUALITY (6)

#### A. Stochastic theory

We introduce the stochastic theory of the system described in Sec. III, in order to define the function  $\Phi$ . The state space is now specified by the number  $n_i$  of particles of species  $X_i$  and the state of the system is a probability distribution function  $P(\{n_i\}, t)$  satisfying the master equation

$$\frac{\partial P(\{x_{ij}\}, t)}{\partial t} = \sum_\delta [W_\delta(\{n_i - \delta_i\})P(\{n_i - \delta_i\}, t) - W_\delta(\{n_i\})P(\{n_i\}, t)], \quad (7)$$

where  $W_\delta(\{n_i\})$  is the probability per unit time of a transition  $\{n_i\} \rightarrow \{n_i + \delta_i\}$  and the summation in Eq. (7) is over all possible transitions  $\delta = \{\delta_i\}$  occurring in the system, due to the reactions processes (1). The hypothesis that  $P$  obeys a master equation is made by most authors (see [1–6]) and can be justified in many situations. We go to the large volume asymptotics in the usual manner (see [2]), writing

$$x_i = \frac{n_i}{V}, \quad dx_i = \frac{1}{V}, \quad P(\{n_i\}, t) = p(\{x_i\}, t) \prod_{i=1}^s dx_i,$$

$$W_\delta(\{n_i\}) = V w_\delta(\{x_i\})$$

and we obtain

$$\frac{\partial p(x, t)}{\partial t} = V \sum_\delta \left[ w_\delta \left( \left\{ x_i - \frac{\delta_i}{V} \right\} \right) p \left( \left\{ x_i - \frac{\delta_i}{V} \right\}, t \right) - w_\delta(\{x_i\}) p(\{x_i\}, t) \right]. \quad (8)$$

As it was noticed previously, because of Eq. (4), the evolution is confined to the invariant subspace  $E(x(0))$  defined by the linear equations

$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i \xi^\alpha, \quad (9)$$

where the  $\xi^\alpha$  denote the progress variable of the process  $\alpha$ . The system tends to a stationary state  $p_S(x|x(0))$  confined on the space  $E(x(0))$ . In the large volume limit we can write (see, e.g., [4,8,12])

$$p_S(x|x(0)) = U \exp[-V\Phi(x|x(0))], \quad (10)$$

where  $U$  is a normalizing factor and  $\Phi(x|x(0))$  is a certain function on  $E(x(0))$ . It is seen from Eq. (10) that  $-k_B V\Phi$  is the analog of Einstein entropy usually defined for equilibrium distributions. It can be shown (e.g., [4,8,12]) that  $\Phi$  satisfies the Hamilton Jacobi equation

$$\sum_{\delta} w_{\delta}(x) \left[ \exp \left( \sum_{i=1}^1 \delta_i \frac{\partial \Phi}{\partial x_i} \right) - 1 \right] = 0. \quad (11)$$

We have proved [12] that under certain hypotheses, there exists a unique regular solution of the Hamilton Jacobi Eq. (11) up to an additive constant [which is the normalization constant of the stationary state  $p_S(x|x(0))$ ] and we have studied there several remarkable properties of  $\Phi$ . It is clear that all the previous quantities depend on the fixed values of  $a_l$ , although this fact is not mentioned explicitly in our notations.

### B. The main inequality

We write, using the macroscopic evolution equations (5),

$$\begin{aligned} \frac{dF}{dt} &= \sum_i \frac{\partial F}{\partial x_i} \frac{dx_i}{dt} \\ &= \left( \sum_i \frac{\partial F}{\partial x_i} \frac{dx_i}{dt} + \sum_l \frac{\partial F}{\partial a_l} \left[ \frac{da_l}{dt} \right]_R \right) - \sum_l \frac{\partial F}{\partial a_l} \left[ \frac{da_l}{dt} \right]_R, \end{aligned} \quad (12)$$

where  $[da_l/dt]_R$  is the number of particles  $A_l$  (per unit volume and time) that should be exchanged with the reservoir in order to maintain  $a_l$  constant, namely

$$\left[ \frac{da_l}{dt} \right]_R = \sum_{\alpha} t_{\alpha}^l (\omega_{\alpha}^+ - \omega_{\alpha}^-).$$

The last term of Eq. (12),  $-\sum(\partial F/\partial a_l)[da_l/dt]_R$ , is exactly the work  $w$  (per unit volume and time) that should be done by the reservoir in order to maintain  $a_l$  constant:

$$w = - \sum_{\alpha,l} m_l t_{\alpha}^l (\omega_{\alpha}^+ - \omega_{\alpha}^-). \quad (13)$$

On the other hand,

$$\begin{aligned} \sum_i \frac{\partial F}{\partial x_i} \frac{dx_i}{dt} + \sum_l \frac{\partial F}{\partial a_l} \left[ \frac{da_l}{dt} \right]_R &= k_B T \sum (\omega_{\alpha}^+ - \omega_{\alpha}^-) \ln_{10} \frac{\omega_{\alpha}^-}{\omega_{\alpha}^+} \\ &\leq 0. \end{aligned} \quad (14)$$

For a given initial state  $x(0)$ , we can express  $\Phi(x)$  as a function of the progress variables  $\xi_{\alpha}$  using Eq. (9). Then, Eq. (11) can be rewritten as

$$\sum_{\alpha} \left\{ \omega_{\alpha}^+ \left[ \exp \left( \frac{\partial \Phi}{\partial \xi_{\alpha}} \right) - 1 \right] + \omega_{\alpha}^- \left[ \exp \left( - \frac{\partial \Phi}{\partial \xi_{\alpha}} \right) - 1 \right] \right\} = 0. \quad (15)$$

On the other hand, if we define  $q_{\alpha} = \ln_{10}(\omega_{\alpha}^-/\omega_{\alpha}^+)$ , we have

$$\omega_{\alpha}^+ [\exp(q_{\alpha}) - 1] + \omega_{\alpha}^- [\exp(-q_{\alpha}) - 1] = 0 \quad (\text{all } \alpha). \quad (16)$$

We subtract from Eq. (15) the sum over  $\alpha$  of Eq. (16) to obtain

$$\begin{aligned} \sum_{\alpha} \omega_{\alpha}^+ \left[ \exp \left( \frac{\partial \Phi}{\partial \xi_{\alpha}} \right) - \exp(q_{\alpha}) \right] \\ + \omega_{\alpha}^- \left[ \exp \left( - \frac{\partial \Phi}{\partial \xi_{\alpha}} \right) - \exp(-q_{\alpha}) \right] = 0, \end{aligned}$$

and use the inequality

$$e^x - e^y \geq e^y(x - y)$$

with equality if and only if  $x = y$ , to obtain

$$\sum (\omega_{\alpha}^+ e^{q_{\alpha}} - \omega_{\alpha}^- e^{-q_{\alpha}}) \left( \frac{\partial \Phi}{\partial \xi_{\alpha}} - q_{\alpha} \right) \geq 0,$$

which is rewritten as

$$\sum_{\alpha} (\omega_{\alpha}^+ - \omega_{\alpha}^-) q_{\alpha} \leq \sum_{\alpha} (\omega_{\alpha}^+ - \omega_{\alpha}^-) \frac{\partial \Phi}{\partial \xi_{\alpha}}. \quad (17)$$

But the second member of the inequality (17) is precisely  $d\Phi/dt$ , so that we have

$$\sum_{\alpha} (\omega_{\alpha}^+ - \omega_{\alpha}^-) \ln_{10} \frac{\omega_{\alpha}^-}{\omega_{\alpha}^+} \leq \frac{d\Phi}{dt} \quad (18)$$

with equality if and only if  $\partial \Phi / \partial \xi_{\alpha} = \ln_{10}(\omega_{\alpha}^-/\omega_{\alpha}^+)$ , namely, if  $\exp(-V\Phi)$  satisfies detailed balance for each  $\alpha$ , so that it is the equilibrium distribution function. Equations (12)–(14) and inequality (18) give the proof of inequality (6). The inequality  $d\Phi/dt \leq 0$  is proved by applying the inequality  $\exp x - 1 \geq x$  to Eq. (15).

### V. INTERPRETATION AND CONCLUSION

We have obtained a general inequality that is valid for any reaction-diffusion system at fixed temperature and volume. It relates the rate of the nonequilibrium free energy of the system to the rate of Einstein entropy production  $-k_B d\Phi/dt$ , and to the rate of work  $w$  done by the reservoirs to maintain this nonequilibrium distribution function during the spontaneous relaxation to the stationary state. The positive quantity  $-(dF/dt - w)$  is the rate of dissipation of energy (energy lost by the system per unit time and unit volume). On the other hand,  $-d\Phi/dt$  is the rate of dissipation of information. In fact, the function  $-\Phi(x|x(0))$  is the relative entropy of the distribution  $\delta(\cdot - x)$  with respect to the stationary distribution  $p_S$  (see [10]), namely,

$$-\Phi(x|x(0)) = - \sum_{x'} \delta(x' - x) \ln_{10} \frac{\delta(x' - x)}{p_S(x'|x(0))}.$$

Thus  $\Phi$  is a measure of the information that one gets when one knows that the system is in the state  $x$ , with respect to the knowledge of the stationary state  $p_S(x|x(0))$ . Thus, inequality (6) states that the rate of energetic dissipation is

larger than the rate of information dissipation (times the Boltzmann factor  $k_B T$ ) if the system approaches a nonequilibrium stationary state, whereas both rates of dissipation are equal if the stationary state is an equilibrium state with detailed balance.

We can reinterpret inequality (6) in a different manner: it can be written as

$$\frac{d(F - k_B T \Phi)}{dt} \leq w. \quad (19)$$

Under this form, it means that the rate of work (given by the reservoirs to the system) during the spontaneous macroscopic relaxation to the stationary state is larger than the rate of variation of  $F - k_B T \Phi$  and so it is larger than the rate of variation of  $F$  alone (because  $d\Phi/dt \leq 0$ ).

Inequality (19) leads to experimental predictions that could be verified. It is surprising that inequality (19) is an equality if and only if the stationary state is an equilibrium state. The mathematical reason is that  $e^x - e^y \geq e^y(x - y)$  with equality if and only if  $x = y$ . But there is also a physical reason for this equality. Namely, let  $\bar{x}$  be the value of the variables  $x$  at thermal equilibrium so that  $(\bar{x}, a)$  is a state of thermal equilibrium. In this case it is possible to prove (see [12]) that

$$\Phi(x) = F(x, a) - \sum_i \frac{\partial F}{\partial x_i}(\bar{x}, a) x_i$$

so that

$$\begin{aligned} \frac{d(F - k_B T \Phi)}{dt} &= \sum_i \frac{\partial F}{\partial x_i}(\bar{x}, a) \frac{dx_i}{dt} \\ &= \sum_{i, \alpha} \tau_{\alpha}^i \mu_i(\bar{x}, a) (\omega_{\alpha}^+ - \omega_{\alpha}^-). \end{aligned} \quad (20)$$

But we know that if  $(\bar{x}, a)$  is a true equilibrium state, the total variations for all processes  $\alpha$  are 0 at equilibrium so that  $\partial F / \partial \xi_{\alpha} = 0$ , or

$$\sum_i \tau_{\alpha}^i \mu_i(\bar{x}, a) + \sum_l t_{\alpha}^l m_l^{\alpha}(\bar{x}, a) = 0.$$

From Eq. (20), we deduce

$$\frac{d(F - k_B T \Phi)}{dt} = - \sum_{l, \alpha} t_{\alpha}^l m_l^{\alpha}(\bar{x}, a) (\omega_{\alpha}^+ - \omega_{\alpha}^-),$$

which is  $w$  [Eq. (12)].

Finally, we compare our result with the results of Ref. [11]. In this work, the authors considered the variation of entropy of the distribution probability

$$S(t) = - \sum_x P(x, t) \ln_{10} P(x, t),$$

where  $P(x, t)$  satisfies the master equation, and they decomposed  $dS(t)/dt$  in a positive irreversible part  $d_i S/dt$  and an exchange part  $d_e S/dt$  (which can have any sign).

We consider instead the variation of the relative entropy (which would be the free energy for an equilibrium system, see [10]), which is always negative, and we compare it to the dissipation of energy that is in principle measurable, rather than the entropy. In the present work, we consider only the variation along the deterministic trajectories of the system. In a work to appear [15], we shall extend our result to the stochastic variation and derive other inequalities.

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