PHYSICAL REVIEW E **79**, 010102(R) (2009)

# Generalized Clausius relation and power dissipation in nonequilibrium stochastic systems

B. Gaveau,[1] M. Moreau,[2] and L. S. Schulman[3]
[1]Department of Mathematics, University Pierre et Marie Curie, 75252 Paris Cedex 05, France
[2]LPTMC (UMR 7600), University Pierre et Marie Curie, CNRS, case 121, 75252 Paris Cedex 05, France
[3]Department of Physics, Clarkson University, Potsdam, New York 13699-5820, USA

(Received 17 April 2008; revised manuscript received 2 December 2008; published 23 January 2009)

In the framework of the stochastic dynamics of open Markov systems, we derive an extension of the Clausius inequality for transitions between states of the system. We give a formula for the power produced when the system is in its stationary state and relate it to the dissipation of energy needed to maintain the system out of equilibrium. We deduce that, near equilibrium, maximal power production requires an energy dissipation of the same order of magnitude as the power production.

DOI: 10.1103/PhysRevE.79.010102 PACS number(s): 05.90.+m, 05.40.−a

Calculations and bounds on work production, Carnot efficiency, heat exchange, and the Clausius inequality are at the core of thermodynamics. In this context, two kinds of situations typically occur: the cyclic functioning of a motor, and relaxation from a displaced nonequilibrium macroscopic state to an equilibrium state, possibly under the control of an external parameter. In both cases, it has long been realized that maximal work can be produced only by a system operating reversibly and infinitely slowly, so there is neither power production nor dissipation [1]. More realistic situations have been studied from many viewpoints, and the results are often controversial. In the context of nonequilibrium thermodynamics and kinetic theories, this has led to the definitions of generalized state potentials, principles of minimum entropy production, and various fluctuation-dissipation relations [2–5]. Recently, Gallavotti and Cohen [6] studied entropy fluctuations and their probability distributions in nonequilibrium systems starting from Hamiltonian dynamics. Jarzynski [7] has proved a new relation for work production in an isothermal system performing externally controlled transitions between two states, but there is still debate at the level of Hamiltonian dynamics [8,9]. These results were extended to Langevin dynamics and to stochastic differential systems. Again one considers spontaneous relaxation of the state of a system to the stationary state or its forced evolution under an external control, and studies entropy production, efficiency of work production, and optimal control [10–15]. Results of this sort were also obtained for the dynamics of discrete Markov systems [11,15–19] as described, in particular, in the work of Schnakenberg [16].

Nevertheless, natural complex systems, in particular biological or economic, evolve spontaneously: either they remain in a stationary nonequilibrium state where they evolve according to generalized cycles and probability currents while producing, consuming, or recycling resources, or they relax to their stationary state spontaneously, without externally controlled intervention, after displacement by a natural perturbation [18]. We have developed a stochastic framework for these more general systems. The general idea is that the forces controlling the evolution of these systems are entropic; they are caused by the variation of the volume of the state space regions between which the system transits. [See Eq. (3) below.] On the other hand, during its evolution the system produces and consumes various resources, which define coordinates of its state space, and are thus related to the entropic volume [18]. These methods were applied to a derivation of the Jarzynski equality for isothermal physical or chemical systems [20].

The present Rapid Communication has two goals. First we extend the celebrated Clausius inequality to nonisothermal systems in the transient regime [see Eq. (11) below]. Second, we consider power production—necessarily in a context involving *time* dependence—and observe that maximal efficiency and optimal power production are in conflict, since to achieve the best Carnot efficiency the system must move infinitely slowly [see Eqs. (17)–(19)]. We here calculate spontaneous power production in a stationary nonequilibrium state and provide an upper bound. The time-dependent context necessarily goes beyond traditional thermodynamics.

Consider the stochastic dynamics of a discrete system $\mathbf{s}$ undergoing a discrete time process. The elementary time step $\tau$ is taken as the time unit. The dynamics is defined by the stochastic matrix $\mathbf{R}\equiv(R_{xy})$, where $R_{xy}\equiv p(x,t+\tau|y,t)$ is the transition probability from $y$ to $x$ in time $\tau$. Let $\gamma=(y_0,u_1,u_2,u_{N-1},x_0)$ be an $N$-step path from $y_0$ to $x_0$. The weight of this path is

$$W(\gamma)=R_{x_0u_{N-1}}R_{u_{N-1}u_{N-2}}\cdots R_{u_1y_0}. \tag{1}$$

The conditional average of a function $F(\gamma,t)$, given the initial and final states $y_0$ and $x_0$, is

$$\langle F(\gamma,t=N\tau)\rangle_{x_0y_0}=\frac{\sum_{\gamma:y_0\to x_0;|\gamma|=N}W(\gamma)F(\gamma,t)}{\sum_{\gamma:y_0\to x_0;|\gamma|=N}W(\gamma)}, \tag{2}$$

where $|\gamma|$ is the number of steps of trajectory $\gamma$. For each elementary transition $y\to x$, defined by the fact that $R_{yx}$ and $R_{xy}$ differ from 0, we suppose that the following relation holds:

$$R_{xy}/R_{yx}=\exp\,(\delta S^{\mathrm{tot}})_{xy}, \tag{3}$$

where $(\delta S^{\mathrm{tot}})_{xy}$ is the total entropy variation of the system of interest $\mathbf{s}$ and of the other systems which are implied in the transition. Relation (3) was introduced and used in previous papers [18,20]. Its meaning is the following. The entire "universe," system $\mathbf{s}$ plus reservoirs, satisfies detailed balance. Denoting reservoir states by $\xi$ and $\eta$, this means that

 

$$\frac{R_{x\xi,y\eta}}{R_{y\eta,x\xi}} = \exp(\delta S^{\mathrm{tot}})_{x\xi,y\eta}. \tag{4}$$

However, the nature of a proper reservoir is such that neither the left- nor the right-hand side of this equation depends on the specific $\xi$ and $\eta$. Of course, not all pairs of reservoir states $\eta$ and $\xi$ allow the $y\to x$ transition, but when they do, the rates are independent of the choices. In fact

$$(\delta S^{\mathrm{tot}})_{xy} \equiv S^{\mathrm{tot}}(x,\xi) - S^{\mathrm{tot}}(y,\eta) = s(x) - s(y) + S(\xi) - S(\eta),$$

where $S$ is the reservoir entropy. Note that (from the definition of "reservoir") the change in reservoir entropy is determined by the change in the system state, as is explicitly shown below, and we can write $S(\xi)-S(\eta)\equiv\delta S_{xy}$ (but in general this is *not* the variation from $y$ to $x$ of any function of the system state alone). Therefore we drop $\xi$ and $\eta$ from (4) and obtain Eq. (3), which is the analog for discrete Markov dynamics of the time reversal asymmetry found in [6] and later developed by several authors [10,19,21–23].

We assume that the system **s** can exchange energy with several reservoirs $\mathbf{S}^\nu$, labeled by the index $\nu=1,2,\ldots$. Reservoir $\mathbf{S}^\nu$ is characterized by its temperature $T_\nu$ or its inverse temperature $\beta_\nu=1/T_\nu$, the Boltzmann factor $k_B$ being always taken to be unity. The entropy variation of $\mathbf{S}^\nu$ is $-\beta_\nu\delta q_\nu$ when it supplies energy (i.e., heat) $\delta q_\nu$ to the system. The system can also receive energy (i.e., work) $\delta w\equiv\delta q_0$ from a mechanical system $\mathbf{S}^0$ whose entropy, by definition, does not change in time. For the mechanical system we take $\beta_0=0$.

During an elementary transition $y\to x$, we assume that the system can receive heat $\delta q_{xy}$ from *at most one of the reservoirs*, and work $\delta w_{xy}$ from the mechanical system. For any function $h$ of the system state $x$, we write $\delta_{xy}h=h(x)-h(y)$; thus the energy variation of the system is $\delta_{xy}e=\delta q_{xy}+\delta w_{xy}$. We suppose, as currently done, that during an elementary transition $y\to x$ the mechanical work $\delta w_{xy}$ can be expressed as a function of $x$ and $y$ alone: then the same property holds for $\delta q_{xy}$ and for the entropy variation of the reservoir which interacts with $s$ during $y\to x$. Then, the total entropy variation $\delta S^{\mathrm{tot}}(\gamma,t=N\tau)$ along an $N$-step trajectory $\gamma$ from $y_0$ to $x_0$ is

$$\begin{aligned}\delta S^{\mathrm{tot}}(\gamma,t=N\tau) &= \sum_{n=0}^{N-1}(\delta_{u_n u_{n+1}}s + \delta S_{u_n u_{n+1}})\\ &= \delta_{x_0 y_0}s + \sum_{n=0}^{N-1}(-\beta_{u_{n+1}u_n}\delta q_{u_{n+1}u_n}).\end{aligned} \tag{5}$$

Define $\bar{\gamma}$ to be the time reversal of trajectory $\gamma$. Then, using relations (1)–(4) it is straightforward to show that

$$\langle\exp(-\delta S^{\mathrm{tot}}(\gamma,t=N\tau))\rangle_{x_0y_0} = \frac{\sum_{\bar{\gamma}:x_0\to y_0;|\bar{\gamma}|=N} W(\bar{\gamma})}{\sum_{\gamma:y_0\to x_0;|\gamma|=N} W(\gamma)} = \frac{p(y_0,t|x_0,0)}{p(x_0,t|y_0,0)}, \tag{6}$$

$p(x,t|y,0)$ being the transition probability from $y$ to $x$ during time $t$.

In the long-time limit, $t/\tau=N\gg1$, $p(x,t|y,0)\sim p^0(x)$. Assuming that this limit is attained and defining [8] the information potential of $x$ by $\phi(x)=-\ln p^0(x)$, we obtain by (6)

$$\begin{aligned}\langle\exp(-\delta S^{\mathrm{tot}}(\gamma,t=N\tau))\rangle_{x_0y_0} &= \exp[\phi(x^0)-\phi(y^0)]\\ &\equiv \exp(\delta_{x_0y_0}\phi),\end{aligned} \tag{7}$$

which, using the expression of $\delta S^{\mathrm{tot}}$, yields our first result, the *generalized Clausius relation*

$$\begin{aligned}\left\langle\exp\left(\sum_{\nu>0}\beta^\nu\delta q^\nu\right)\right\rangle_{x_0y_0} &\equiv \left\langle\exp\left(\sum_{n=0}^{N-1}\beta_{u_{n+1}u_n}\delta q_{u_{n+1}u_n}\right)\right\rangle_{x_0y_0}\\ &= \exp[\delta_{x_0y_0}(s+\phi)],\end{aligned} \tag{8}$$

where $\delta q^\nu$ is the total heat received by the system from thermostat $\mathbf{S}^\nu$ during the transition $y_0\to x_0$. From relation (8) we obtain in the long-time limit, by Jensen's inequality,

$$\left\langle\sum_{\nu>0}\beta^\nu\delta q^\nu\right\rangle_{x_0y_0} \leqslant \delta_{x_0y_0}(s+\phi), \tag{9}$$

which is a mesoscopic version of the Clausius inequality.

Inequality (9) is changed into an equality if and only if in each elementary transition $y\to x$ we have $\beta_{xy}\delta q_{xy}=\delta_{xy}(s+\phi)\equiv(s+\phi)(x)-(s+\phi)(y)$, which is easily shown to be equivalent to detailed balance. Thus, detailed balance is the mesoscopic counterpart of thermodynamic reversibility. Equations (8) and (9) can be compared with the generalizations of the Clausius inequality obtained in very different contexts by Refs. [21,25,26].

Specializing to an isothermal system, $\beta_\nu=\beta$ for any $\nu$, we easily recover the result of Ref. [20] in the long-time limit

$$\left\langle\exp\left(-\beta\sum_{n=0}^{N-1}\delta w_{u_n u_{n+1}}\right)\right\rangle_{x_0y_0} = \exp[\delta_{x_0y_0}(-\beta f+\phi)], \tag{10}$$

where $f(x)=e(x)-Ts(x)$ is the mesoscopic free energy in state $x$. From (10) one can recover the Jarzynski equality [7], which has given rise to a very large literature (see [7,8,11,15,27] and references therein).

We now come back to the transient situation and to Eq. (6), which is valid at any time. Taking its logarithm, we multiply it by the joint probability $p(y_0,0;x_0,t)$ and sum over $x_0$ and $y_0$. After manipulations using Jensen's inequality and the properties of relative entropy, we eventually obtain [24] the extended Clausius inequality

$$\left\langle \sum_{\nu>0} \beta^{\nu} \delta q^{\nu} \right\rangle \leqslant \delta_t \bar{s}, \tag{11}$$

where $\langle\ \rangle$ denotes the global average over all paths between times 0 and $t$, and $\delta_t\bar{s} \equiv \bar{s}(t) - \bar{s}(0)$ is the variation of the generalized macroscopic entropy $\bar{s}$ of the systems between times 0 and $t$, with

$$\bar{s}(t) = \langle s(x) - \ln[p(x,t)] \rangle = \sum_x s(x)p(x,t) - \sum_x p(x,t)\ln p(x,t). \tag{12}$$

Note that the entropy $\bar{s}(t)$ contains not only the expectation of the usual mesoscopic entropy, but information about the transient state of the system as well. If the system **s** is isolated $\bar{s}(t)$ can be proved [15] to be an increasing function of time, as it should be, although the quantity $-\Sigma_x p(x;t)\ln p(x,t)$ can increase or decrease as a function of time. Relation (10) is an extension of the classical Clausius inequality [8], valid in the transient situation, which is thus derived in the framework of stochastic dynamics.

The previous results can be extended straightforwardly to inhomogeneous systems consisting in $n$ homogeneous cells, provided that during each elementary transition $x \rightarrow y$, each cell $k$ of the system **s** interacts with (at most) one of the reservoirs, $\mathbf{S}^{\nu}$, whereas it receives work from the mechanical system and energy from the other cells.

We now consider bounds related to power production. Recall that Carnot's theorem gives the maximum efficiency for a motor operating between two heat sources, which is attained if all transitions are reversible. As remarked earlier, this takes infinite time and power production vanishes. In practice, *power* is often the most relevant quantity and maximum efficiency is less important. To address this, we consider power and entropy production per unit time when the stochastic system **s** is in its stationary state. The probability current corresponding to the elementary transition $y \rightarrow x$ is then $J_{xy} = R_{xy}p_0(y) - R_{yx}p_0(x)$. The stationary *total entropy production* per unit time [16,18] can be written, thanks to (3),

$$\begin{aligned}\mathcal{D} &= \frac{1}{2}\sum_{x,y} J_{xy}\delta_{xy}S^{\text{tot}} \\ &= \frac{1}{2}\sum_{x,y} [R_{xy}p_0(y) - R_{yx}p_0(x)]\ln \frac{R_{xy}p_0(y)}{R_{yx}p_0(x)} \geqslant 0.\end{aligned} \tag{13}$$

This is the analog, in our context, of the entropy production defined in [2,3]. Equation (13) expresses the well-known fact [16–18] that entropy production vanishes if and only if the stationary state satisfies detailed balance. Defining

$$\mathcal{D}_{xy} = J_{xy} \ln \frac{R_{xy}p_0(y)}{R_{yx}p_0(x)} \geqslant 0, \tag{14}$$

we have

$$\begin{aligned}\mathcal{D} &= \frac{1}{2}\sum_{x,y} \mathcal{D}_{xy} = \frac{1}{2}\sum_{x,y} J_{xy}\delta_{xy}(s+\phi) + \frac{1}{2}\sum_{x,y} J_{xy}\delta S^{\nu}_{xy} \\ &= \frac{1}{2}\sum_{\beta_{xy}>0} J_{xy}\delta S^{\nu}_{xy},\end{aligned} \tag{15}$$

so that $\mathcal{D}$ vanishes if $J_{xy}=0$ for each transition during which **s** actually interacts with one of the reservoirs. Since $\mathcal{D}$ vanishes if and only if $J_{xy}=0$ for *all* elementary transitions, it follows that if $J_{xy}=0$ for each transition during which **s** actually interacts with a reservoir ($\beta_{xy} \neq 0$), then $J_{xy}=0$ for all elementary transitions, a result that was derived in terms of networks by Schnakenberg [16]. It is found from (3) and (14) that

$$\mathcal{D}_{xy} = J_{xy}[\delta_{xy}(s+\phi) - \beta_{xy}\delta_{xy}e + \beta_{xy}\delta w_{xy}]. \tag{16}$$

From (16) we deduce that the power received by **s** is

$$\mathcal{P} = \frac{1}{2}\sum_{x,y} J_{xy}\delta w_{xy} = \frac{1}{2}\sum_{x,y,\beta_{xy}>0}\left(\frac{1}{\beta_{xy}}\mathcal{D}_{xy} - \frac{1}{\beta_{xy}}J_{xy}\delta_{xy}(s+\phi)\right). \tag{17}$$

The first term in the large parentheses on the right-hand side is always non-negative. This allows us to give a general, explicit definition of the *power dissipation* $\mathcal{D}_{\mathcal{W}}$,

$$\mathcal{D}_W = \frac{1}{2}\sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}}\mathcal{D}_{xy} = \frac{1}{2}\sum_{x,y,\beta_{xy}>0} J_{xy}\frac{1}{\beta_{xy}} \ln \frac{R_{xy}p_0(y)}{R_{yx}p_0(x)} \geqslant 0. \tag{18}$$

This relation reduces to the equality $\mathcal{D}_{\mathcal{W}} = T\mathcal{D}$ when the system dissipates energy in only one reservoir at temperature $T$: then power dissipation is just proportional to entropy dissipation. In the general case, the power $-\mathcal{P}$ released by the system satisfies

$$-\mathcal{P} \leqslant -\mathcal{A} \equiv \frac{1}{2}\sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} J_{xy}\delta_{xy}(s+\phi), \tag{19}$$

which gives an upper bound for the power production.

This upper bound of $-\mathcal{P}$ is attained if and only if $\mathcal{D}_{xy}=0$ for any transition with $\beta_{xy}>0$, which implies that $J_{xy}=0$ for any transition: then detailed balance is satisfied and $\mathcal{P}$ vanishes. Thus, in order that a system can act as a motor ($-\mathcal{P}>0$), a necessary condition is that it is not in equilibrium: the power dissipation should be positive.

Moreover, it is seen that if the stochastic potential is supposed to be fixed, $-\mathcal{A}$ is a linear function of the currents whereas the power dissipation $\mathcal{D}_{\mathcal{W}}$ can be approximated by a quadratic function of the currents near detailed balance conditions. The assumption that the stationary distribution $p_0(x)$ remains unchanged seems to be rather strong. However, when complete calculations are made for maximizing the power production near detailed balance by slightly changing the transition probabilities from their equilibrium values, it turns out [24] that the optimal stationary distribution does not change at the first order, which justifies the assumption. Under such circumstances, these remarks allow us to make rough estimates of maximum power production and its relation to associated quantities. In fact, we suppose that the actual transition matrix $R_{xy}$ is a small perturbation of a detailed balance matrix $\bar{R}_{xy}$, and that $\mathbf{R}$ and $\bar{\mathbf{R}}$ have the same stationary distribution $p_0(x)$ (for characterization of the class of such matrices, see [28]). Under these circumstances a remarkable fact emerges: an upper bound of the power delivered by the system is attained if the dissipation equals the power produced. Let $K_{xy} \equiv R_{xy} p_0(y)$, with $\bar{K}$ the corresponding quantity for $\bar{R}$, so that $\bar{K}_{xy} = K_{yx}$. To lowest order in the deviation of $\mathbf{R}$ from $\bar{\mathbf{R}}$, one can easily show that $-\mathcal{D}_{\mathcal{W}} \approx -\Sigma_{x,y,\beta_{xy}>0}(J_{xy})^2/(2\beta_{xy}\bar{K}_{xy})$. Writing $B_{xy} \equiv \delta_{xy}(s+\phi)$, we have

$$-\mathcal{P} \approx \frac{1}{2} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} \left[ -\frac{1}{\bar{K}_{xy}} \left( J_{xy} - \frac{1}{2}\bar{K}_{xy} B_{xy} \right)^2 + \frac{1}{4}\bar{K}_{xy}(B_{xy})^2 \right]$$
$$\leqslant \frac{1}{8} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} \bar{K}_{xy}(B_{xy})^2. \qquad (20)$$

This upper bound is attained if $J_{xy} = \frac{1}{2}\bar{K}_{xy} B_{xy}$ for each transition, in which case the power dissipation is equal to the power produced,

$$\mathcal{D}^{\max} \approx \frac{1}{8} \sum_{x,y,\beta_{xy}>0} \frac{1}{\beta_{xy}} \bar{K}_{xy}(B_{xy})^2 = -\mathcal{P}^{\max}. \qquad (21)$$

In this situation, the power produced is half the quantity $-\mathcal{A} = -\mathcal{P} + \mathcal{D}_{\mathcal{W}}$ given by Eq. (19). It is clear that the currents must satisfy constraints that may not allow this optimization. Nevertheless, maximizing $-\mathcal{P}$ under the relevant constraints confirms [24] that, close to detailed balance, the maximum power released by the system is obtained when the power dissipation is of the same order of magnitude as the power produced.

Of course, this may be invalid far from detailed balance conditions. More accurate, quantitative results should rely on specific examples, but in principle they can be obtained from the previous formulas. In this connection we mention a tantalizing exercise [29] from an elementary mechanics text: Material drops at a constant rate onto a conveyor belt moving with constant velocity $v$ parallel to the ground. How much power is needed to drive the belt? The answer turns out to be that the optimum power to be supplied is exactly twice the kinetic energy imparted to the particles (which can be seen by going into the belt reference frame). Thus the power output (the kinetic energy of the material) exactly equals the energy dissipated by friction. Our assumptions in the foregoing derivation are too restrictive to make this result a special case, but there is very much the suggestion that the factor 1/2 that we have encountered, due to the approximation near equilibrium, is more general than our demonstration.

We thank the Max Planck Institut für Physik Komplexer Systeme in Dresden, where this paper was partly prepared.

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