Steady-State Thermodynamics of Langevin Systems

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We study Langevin dynamics describing nonequilibirum steady states. Employing the phenomenological framework of steady-state thermodynamics constructed by Oono and Paniconi [Prog. Theor. Phys. Suppl. **130**, 29 (1998)], we find that the extended form of the second law which they proposed holds for transitions between steady states and that the Shannon entropy difference is related to the excess heat produced in an infinitely slow operation. A generalized version of the Jarzynski work relation plays an important role in our theory.

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The second law of thermodynamics describes the fundamental limitation on possible transitions between equilibrium states. In addition, it leads to the definition of entropy, in terms of which the heat capacity and equations of state can be treated in a unified way.

In contrast to equilibrium systems, with their elegant theoretical framework, the understanding of nonequilibrium steady-state systems is still primitive. The broad goal with which we are concerned in this paper is to establish the connection between the phenomena displayed by nonequilibrium steady states and thermodynamic laws. We expect that a unified framework that describes both equilibrium and nonequilibrium phenomena can be obtained by extending the second law to the state space consisting of equilibrium and nonequilibrium steady states. There have been several attempts to construct such a framework [1–4]. Among them, a phenomenological framework proposed by Oono and Paniconi seems most sophisticated, and their framework has been named "steady-state thermodynamics" (SST) [4].

Oono and Paniconi focused on transitions between steady states and distinguished steadily generated heat, which is generated even when the system remains in a single state in the state space and the total heat. They call the former the "housekeeping heat." Subtracting the housekeeping heat from the total heat defines the excess heat, which reflects the change of the system in the state space:

$$Q_{\rm ex} \equiv Q_{\rm tot} - Q_{\rm hk} \,. \tag{1}$$

Here $Q_{\rm tot}$ and $Q_{\rm hk}$ denote the total heat and the housekeeping heat, respectively. By convention, we take the sign of heat to be positive when it flows from the system to the heat bath.

For equilibrium systems, $Q_{\rm ex}$ reduces to the total heat $Q_{\rm tot}$, because in this case $Q_{\rm hk} = 0$. Because any proper formulation of SST should reduce to equilibrium thermodynamics in the appropriate limit, $Q_{\rm ex}$ should correspond to the change of a generalized entropy S within the SST. Here we treat systems in contact with a single heat bath whose temperature is denoted by T, so that the second law of SST reads [4]

$$T\Delta S \geq -Q_{\rm ex} \,. \tag{2}$$

The equality here holds for an infinitely slow operation in which the system is in a steady state at each time during a transition. (We call such a process a "slow process.") That is, the generalized entropy difference ΔS between two steady states can be measured as $-Q_{\rm ex}/T$ resulting from a slow process connecting these two states. This allows us to define the generalized entropy of nonequilibrium steady states experimentally, by measuring the excess heat obtained in a slow process between any nonequilibrium steady state and an equilibrium state, whose entropy is known.

These are phenomenological considerations and they should ultimately be confirmed through experiments. As a preliminary step toward this confirmation, in this Letter, we find support for the validity of the above discussion by studying a simple stochastic model. With the same motivation, Sekimoto and Oono considered a simple Langevin system and defined the quantity $Q_{\rm ex}$ [5,6]. However, this nonequilibrium system reduces to an equilibrium system through a suitable transformation of variables and hence lacks generality. Also, one of the present authors has found that the minimum work principle holds for certain types of transitions between steady states [7], with some assumption regarding the steady-state measure. In this Letter, we derive the inequality (2) in a more general context and show that the equality holds for slow processes. This result relates the excess heat to the generalized entropy.

We consider the dynamics of a Brownian particle in a circuit driven by an external force. These dynamics are described by the Langevin equation

$$\gamma \dot{x} = -\frac{\partial U(x;\lambda)}{\partial x} + f + \xi(t) \,, \tag{3}$$

where $\xi(t)$ represents Gaussian white noise whose intensity is $2\gamma k_{\rm B}T$. We employ periodic boundary conditions, and thus the particle flows due to the nonconservative force f. This simple nonequilibrium system was investigated by Kurchan with regard to the fluctuation theorem [8]. Transitions between steady states are realized by changing the parameters λ and f. We assume that if the system is left unperturbed, it eventually reaches a steady state which is uniquely determined by the parameter values. Although we consider an explicitly one-dimensional system for simplicity, multidimensional cases, including many-particle systems, are essentially the same.

We write the steady-state probability distribution function as $\rho_{ss}(x;\alpha)$, where α denotes the set of control parameters of the system, λ and f. Then we manipulate the system by changing the value of α during the interval from $t = 0$ to $t = \tau^*$. We assume that the system is initially in a steady state, and after the completion of the manipulation it converges to a new steady state. Let τ denote the time at which the system reaches the new steady state ($0 < \tau^* < \tau$). We discretize $[0, \tau]$ as $[t_0, t_1, \ldots, t_N]$. We denote the value of α at the ith time step by α_i. This value changes at each time step from time t_0 until time $t_M = \tau^*$, while after this time it remains fixed: $\alpha_i = \alpha_M$ for $i \geq M$. We also write $x(t_i)$ as x_i. We consider the limit of an infinitely fine discretization by keeping τ^* and τ fixed and taking $N \to \infty$.

Let us introduce a new quantity $\phi(x;\alpha)$ defined by

$$\phi(x;\alpha) = -\log\rho_{ss}(x;\alpha), \tag{4}$$

where $\rho_{ss}(x;\alpha)$ is the probability distribution function of the steady state corresponding to α. Let $P(x' \mid x;\alpha)$ be the transition probability from x to x' in one time step (whose length is $\Delta t = \tau/N$) for a given value of α. Note that by definition

$$\int dx' \, P(x \mid x';\alpha)\rho_{ss}(x';\alpha) = \rho_{ss}(x;\alpha). \tag{5}$$

Then for a given sequence $(x_0, x_1, \ldots, x_N)$, which is collectively denoted by $[x]$, the average of a quantity $g([x])$ is written as

$$\langle g\rangle \simeq \int \prod_{i=0}^{N} dx_i \left(\prod_{i=0}^{N-1} P(x_{i+1} \mid x_i;\alpha_i)\right)\rho_{ss}(x_0;\alpha_0)g([x]), \tag{6}$$

where the symbol $\simeq$ expresses that this is an approximate equality that becomes exact in an appropriate, infinitely fine discretization limit of $N \to \infty$.

Now, in order to derive Eq. (2) for the system described by Eq. (3), we utilize a Jarzynski-type equality. For transitions between isothermal equilibrium states, it is known that the following equality holds between the work done to the system W and the equilibrium Helmholtz free energy difference ΔF [9]:

$$\langle e^{-\beta W}\rangle_c = e^{-\beta \Delta F}. \tag{7}$$

Here $\beta = 1/k_B T$ and $\langle\cdot\rangle_c$ denotes the average over all possible histories with respect to equilibrium fluctuations. Note that the minimum work principle $\langle W\rangle_c \geq \Delta F$ immediately follows from this relation, due to the Jensen inequality $\langle e^x\rangle \geq e^{\langle x\rangle}$. In a similar way, we now set out to derive Eq. (2) through the somewhat generalized version of Eq. (7)

$$\langle \exp[-\beta Q_{ex} - \Delta\phi]\rangle = 1, \tag{8}$$

where $\Delta\phi = \phi(x_N;\alpha_N) - \phi(x_0;\alpha_0)$.

We start with the identity

$$\left\langle\left[\prod_{i=0}^{N-1} \frac{\rho_{ss}(x_{i+1};\alpha_{i+1})}{\rho_{ss}(x_{i+1};\alpha_i)}\right]\right\rangle \simeq 1. \tag{9}$$

This follows from Eqs. (5) and (6). Rewriting Eq. (9) using ϕ, we have

$$\left\langle \exp\left[\sum_{i=0}^{N-1}\{-\phi(x_{i+1};\alpha_{i+1}) + \phi(x_{i+1};\alpha_i)\}\right]\right\rangle \simeq 1. \tag{10}$$

Taking the limit $N \to \infty$, Eq. (10) becomes

$$\left\langle \exp\left[-\int_0^\tau dt\, \dot\alpha \,\frac{\partial\phi(x;\alpha)}{\partial\alpha}\right]\right\rangle = 1. \tag{11}$$

It can be easily seen that Eq. (11) reduces to the equilibrium Jarzynski equality (7) when we set $\phi = -\beta(F - U)$.

Now we express the left-hand side of Eq. (11) in terms of heat, so that we can find the correspondence with Eq. (8). First, for Langevin systems, the total heat flowing into the heat bath, Q_{tot}, is defined by

$$Q_{tot} = \int_0^\tau dt\,[\gamma\dot x(t) - \xi(t)]\dot x(t). \tag{12}$$

Note that the products of $\dot x(t)$ and the other quantities are of the Stratonovich type. This interpretation of the heat was proposed and investigated by Sekimoto [10]. In addition, we note that βQ_{tot} satisfies the fluctuation theorem if the system remains in a steady state [8].

Next we rewrite Eq. (3) as

$$\gamma\dot x = b(x) - \beta^{-1}\frac{\partial\phi(x;\alpha)}{\partial x} + \xi(t), \tag{13}$$

where

$$b(x) = f - \frac{\partial U(x;\alpha)}{\partial x} + \beta^{-1}\frac{\partial\phi(x;\alpha)}{\partial x}. \tag{14}$$

Equation (13) corresponds to the decomposition of the flux $\dot x$ into an irreversible part $b(x)$ and a reversible part $\partial\phi/\partial x$, in the sense of Refs. [11,12]. Multiplying Eq. (13) by $\dot x(t)dt$ and integrating with respect to t from $t = 0$ to $t = \tau$, we get

$$\beta Q_{tot} = \int_0^\tau dt\,\beta b(x)\dot x(t) - \Delta\phi + \int_0^\tau dt\,\frac{\partial\phi(x;\alpha)}{\partial\alpha}\dot\alpha(t). \tag{15}$$

Here we define the housekeeping heat as [13]

$$Q_{hk} = \int_0^\tau dt\, b(x)\dot x(t). \tag{16}$$

We discuss a physical meaning of this expression later; e.g., see Eq. (27). Using $Q_{ex} = Q_{tot} - Q_{hk}$, we can rewrite Eq. (11) as the generalized Jarzynski equality (8).

Now we derive the second law for SST. From Eq. (8) and the Jensen inequality, we obtain

$$\beta\langle Q_{\rm ex}\rangle + \Delta\langle\phi\rangle \geq 0\,. \tag{17}$$

The quantity $\Delta\langle\phi\rangle$ is the difference between the averages of $\phi(x;\alpha)$ with respect to the initial and the final steady-state measures. Now, note that with the information-theoretic (Shannon) entropy given as

$$S(\alpha) = -\int dx\,\rho_{\rm ss}(x;\alpha)\log\rho_{\rm ss}(x;\alpha)\,, \tag{18}$$

the quantity $\langle\Delta\phi\rangle$ is equal to ΔS. Equation (17) then becomes

$$T\Delta S \geq -\langle Q_{\rm ex}\rangle\,. \tag{19}$$

Thus if we identify the Shannon entropy with the generalized entropy S, we obtain the second law for SST, Eq. (2).

We next consider a slow process in which the distribution function of the system can be regarded as $\rho_{\rm ss}(x_i;\alpha_i)$ at each time t_i. We then have

$$\left\langle\int d\alpha\,\frac{\partial\phi(x;\alpha)}{\partial\alpha}\right\rangle = \iint d\alpha\,dx\,\rho_{\rm ss}(x;\alpha)\,\frac{\partial\phi(x;\alpha)}{\partial\alpha} \tag{20}$$

$$= 0\,. \tag{21}$$

Recalling that

$$\int d\alpha\,\frac{\partial\phi(x;\alpha)}{\partial\alpha} = \Delta\phi + Q_{\rm ex}\,, \tag{22}$$

we can prove that the equality holds in Eq. (19) for a slow process.

Equation (17), together with the discussion following it, constitutes the main result of this Letter. In the following we discuss five important points that are peripherally related to this main result.

First, because we have been able to define a generalized entropy, we can also define a generalized Helmholtz free energy F valid for nonequilibrium steady states.

$$F(\alpha) = \int dx\,\rho_{\rm ss}(x;\alpha)U(x;\lambda) - TS(\alpha)\,. \tag{23}$$

From the second law for SST, Eq. (19), if we define the excess work by

$$W_{\rm ex} = Q_{\rm ex} + \Delta U\,, \tag{24}$$

the minimum work principle for SST immediately follows:

$$\langle W_{\rm ex}\rangle - \Delta F \geq 0\,. \tag{25}$$

The equality here holds for slow processes, as in the case of Eq. (19).

The next point we wish to discuss regards the function $b(x)$. The physical meaning of this function as defined by Eq. (14) is somewhat unclear. Because this quantity also appears in the definition of the housekeeping heat, it would be helpful if we could obtain a more intuitive expression for it. We now derive such an expression. We consider the local probability current, $j_{\rm ss}$, for a given steady state.

$$\gamma j_{\rm ss} = -\beta^{-1}\,\frac{\partial\rho_{\rm ss}(x;\alpha)}{\partial x} + \left[f - \frac{\partial U(x;\alpha)}{\partial x}\right]\rho_{\rm ss}(x;\alpha)\,. \tag{26}$$

This value is independent of x for the one-dimensional case. Using Eqs. (4) and (14), Eq. (26) becomes

$$b(x) = \frac{\gamma j_{\rm ss}}{\rho_{\rm ss}(x;\alpha)}\,, \tag{27}$$

which is propotional to the local average velocity.

As the third point of interest, we now discuss the relation between the generalized Jarzynski equality and the fluctuation theorem [8,14–17]. Our argument is the generalization of the Crooks argument [18], which focuses on transitions between equilibrium states.

We first review the fluctuation theorem, following Ref. [16]. Let $\sigma([x])$ be defined according to

$$\exp[-\tau\sigma([x])] = \left[\prod_{i=0}^{N-1}\frac{P(\tilde{x}_{i+1}\,|\,\tilde{x}_i;\tilde{\alpha}_i)}{P(x_{i+1}\,|\,x_i;\alpha_i)}\right]\frac{\rho_{\rm ss}(\tilde{x}_0;\tilde{\alpha}_0)}{\rho_{\rm ss}(x_0;\alpha_0)}\,, \tag{28}$$

where $\tilde{x}_i = x_{N-i}$ and $\tilde{\alpha}_i = \alpha_{N-i}$. Note that we can express $\tau\sigma$ as

$$\tau\sigma = \beta Q_{\rm tot} - \Delta\phi \tag{29}$$

by using an explicit form of $P(x_{i+1}\,|\,x_i;\alpha_i)$ [19]. By a straightforward calculation, we find that the probability distribution of $\sigma([x])$, which is denoted by $\Pi_\sigma(z)$, satisfies

$$\Pi_\sigma(z) = \exp(\tau z)\tilde{\Pi}_\sigma(-z)\,, \tag{30}$$

where the function $\tilde{\Pi}_\sigma$ is the probability distribution of $\sigma([x])$ for the system with the parameter set $\tilde{\alpha}$ obtained from α under time reversal. Equation (30) leads to

$$\langle\exp(-\tau\sigma)\rangle = 1\,. \tag{31}$$

We remark that for the case of time-independent α, Eq. (30) reduces to the relation referred to as the fluctuation theorem.

As Crooks demonstrated [18], Eq. (31) yields the Jarzynski equality (7) if we are concerned with transitions between equilibrium states. However, for transitions between nonequilibrium steady states, Eqs. (29) and (31) with the Jensen inequality do not provide our result Eq. (8), but rather $T\Delta S \geq -\langle Q_{\rm tot}\rangle$. Although this inequality does hold, the equality cannot be realized since $-\langle Q_{\rm tot}\rangle$ is negative infinite for slow processes. Thus we cannot define the generalized entropy through Eq. (31).

In order to clarify the difference between Eqs. (8) and (31), we rewrite Eq. (9) as

$$\left\langle\frac{\rho_{\rm ss}(x_N;\alpha_N)}{\rho_{\rm ss}(x_1;\alpha_0)}\left[\prod_{i=1}^{N-1}\frac{P^\dagger(x_i\,|\,x_{i+1};\alpha_i)}{P(x_{i+1}\,|\,x_i;\alpha_i)}\right]\right\rangle = 1\,, \tag{32}$$

where $P^\dagger(x_i\,|\,x_{i+1};\alpha_i)$ is the dual transition probability

[20] defined by

$$P^{\dagger}(x_i \,|\, x_{i+1}; \alpha_i)\rho_{\rm ss}(x_{i+1}; \alpha_i) = P(x_{i+1} \,|\, x_i; \alpha_i) \times \rho_{\rm ss}(x_i; \alpha_i)\,. \quad (33)$$

When the detailed balance condition is satisfied, Eq. (32) together with Eq. (28) leads to Eq. (31), due to the equality $P^{\dagger} = P$. However, the detailed balance condition is violated in nonequilibrium steady states, and thus the generalized Jarzynski equality is not directly related to the fluctuation theorem.

The above discussion leads us to the fourth important point we wish to discuss here, regarding the extent to which detailed balance is violated. For this purpose, we define the quantity B as

$$\exp[-B(x_{i+1}, x_i; \alpha_i)] = \frac{P(x_i \,|\, x_{i+1}; \alpha_i)\rho_{\rm ss}(x_{i+1}; \alpha_i)}{P(x_{i+1} \,|\, x_i; \alpha_i)\rho_{\rm ss}(x_i; \alpha_i)}\,. \quad (34)$$

Then using Eqs. (8), (32), and (33), we obtain an alternative expression of the housekeeping heat $Q_{\rm hk}$:

$$\beta Q_{\rm hk} \simeq \sum_{i=1}^{N-1} B(x_{i+1}, x_i; \alpha_i)\,. \quad (35)$$

The fifth point we wish to discuss here is the relation between our present results and those previously presented by one of the authors [7]. Note that if we can decompose ϕ as

$$\phi = -\beta[F^{*} - \chi(x; f) - U(x; \lambda)]\,, \quad (36)$$

the following equality holds:

$$\left\langle \exp\left[-\beta \int d\lambda \, \frac{\partial U(x; \lambda)}{\partial \lambda}\right]\right\rangle = \exp[-\beta \Delta F^{*}]\,. \quad (37)$$

We point out that F^{*} here is different from the free energy F defined by Eq. (23). It is seen that Eq. (37) is a special case of Eq. (11), since here the only control parameter is λ, and the assumption implicit in the decomposition of Eq. (36) is necessary for its derivation.

In conclusion, by defining the excess heat, we have derived the second law for SST, Eq. (19), in the case of a simple stochastic model. The corresponding thermodynamic function, the generalized entropy, is found to be the Shannon entropy. Also, it is found that for a slow process, the change in this entropy is identical to the excess heat divided by the temperature.

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