Extended forms of the second law for general time-dependent stochastic processes

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The second law of thermodynamics represents a universal principle applicable to all natural processes, physical systems, and engineering devices. Hatano and Sasa have recently put forward an extended form of the second law for transitions between nonequilibrium stationary states [Phys. Rev. Lett. **86**, 3463 (2001)]. In this paper we further extend this form to an instantaneous interpretation, which is satisfied by quite general time-dependent stochastic processes including master-equation models and Langevin dynamics without the requirements of the stationarity for the initial and final states. The theory is applied to several thermodynamic processes, and its consistence with the classical thermodynamics is shown.

I. INTRODUCTION

Equilibrium thermodynamics emerges when Carnot proposed the first theoretical treatise on mechanical work and efficiency in heat engines in the early nineteenth century. However, 150 years after its formulation, the second law of thermodynamics still appears more as a program than a well defined theory, and all the thermodynamic potentials could be well defined only in equilibrium states. This is one of the main reasons why the classic thermodynamics could not be applied to living biochemical systems: living cells must continually extract energy from their surroundings in order to sustain the characteristic features of life such as growth, cell division, intercellular communication, movement, and responsiveness to their environment.

The researches on irreversible systems far from equilibrium began with the works by Haken [1,2] about laser and Prigogine, etc. [3,4] about oscillations of chemical reactions. Prigogine and his collaborators also provided explicit expressions for entropy production in various situations, and regarded a nonequilibrium steady state as a stationary open system with positive entropy production rate [4].

In 1998, Oono and Paniconi [5] proposed a framework of steady-state thermodynamics, and distinguished the steadily generated heat which is generated even when the system remains in a single steady state and the total heat. They called the former the "housekeeping heat," which is equal to the entropy production in steady state and may come from the chemical driven force in biochemical systems [6,7]. The key point of their work is that "if we can carefully remove the steadily produced heat due to housekeeping dissipation, then the state should not be very different from equilibrium." Moreover, they also put forward a phenomenological extended form of the second law: "a process converting work into excess heat is irreversible. And "reversibility" is modulo house-keeping heat, which is produced anyway."

On the other hand, it has been known for several decades that one can use stochastic processes as mathematical representations for nonequilibrium states and steady cycle fluxes. In 1953, Onsager and Machlup [8,9] proposed the Onsager-Machlup principle, which is actually a functional, i.e., path integral, formula about the probability density of a stochastic process close to equilibrium. Hill [10–13] and Schnakenberg [14] successfully constructed a general mesoscopic master-equation model for biochemical systems and investigated its properties far from equilibrium. Since then, a rather complete mathematical theory for nonequilibrium steady states has been developed for stochastic, Markov processes [15].

In recent years, a few interesting relations that describe the statistical dynamics of driven systems even far from equilibrium have been discovered, including the fluctuation theorems of sample entropy production [16–19], Jarzynski's equality [20–22], Hatano-Sasa equality [23], etc. The main contribution of Hatano and Sasa's work [23] is to derived the first explicit expression for the extended form of the second law of thermodynamics, namely, $T\Delta S \geq Q_{ex}$, where S is the general entropy defined in their paper, and Q_{ex} is the excess heat.

However, they only derived this form for transitions between nonequilibrium stationary states, and the proof is based on a generalized version of the Jarzynski's equality. Their derivation is not so straightforward; furthermore, we believe that second law is a much more universal principle that should be satisfied by not only the specified processes. Indeed, an instantaneous form can be developed.

In the present paper, we extend the extended form of the second law for the first time to an instantaneous interpretation, which is satisfied by quite general time-dependent stochastic processes including master-equation models and Langevin dynamics without the requirements of the stationarity for the initial and final states. It says that the entropy production rate after subtracting the house-keeping heat is still non-negative, namely, $T e_p(t) - Q_{hk}(t) \geq 0$, which consequently gives rise to the extended form of the Clausius inequality, and takes Hatano-Sasa's work as a special example. Then the theory is carefully applied to several thermodynamic processes, and its consistence with the classical thermodynamics is clearly shown.

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II. THEORY

A. Master-equation processes

Stochastic models are widely used in physics, chemistry, biology, and even in economics. The master-equation process discussed here could be applied to model chemical reactions, which are of special interest in biology, in relation with their coupling with active transport across membrane [12,24] and also recent mechanisms of molecular motors [25]. Furthermore, in real biochemical systems, the external parameters such as the concentrations of external signal proteins can oscillate or fluctuates. These considerations motivate the necessity for the analysis of time-dependent processes.

In physics, master equation is a set of first-order differential equations of the mesoscopic system:

$$\frac{d}{dt} p_i(t) = \sum_{j=1}^{N} [q_{ji}(t) p_j(t) - q_{ij} p_i(t)], \qquad (1)$$

describing the dynamical evolution of a probability distribution $p_i(t)$ over states $i = 1, 2, \ldots, N$. The quantity $q_{ij}(t)$ is the transition density (probability per time) to state j from state i. It contains internal rate constants as well as external conditions imposed by the coupling to the reservoir systems. The basic properties of this model have been recently established [26].

One could take a stationary Markov chain, in which the probability transition density $Q(t)$ is invariant, as the mathematical model of the combination and transformation of biochemical polymers [11,12]. Each state of the Markov chain corresponds to a mesoscopic state of polymers.

Let us also mention that the number N need not to be finite, and the system could also be regarded as the stochastic model of coupled chemical reactions (chemical master equation) [14,27,28].

1. Essential notations and fundamental relations

Unlike the traditional approach of equilibrium thermodynamics, we should start with the general definition of entropy. The common definition of Gibbs entropy associated with any discrete probability distribution $\{p_i\}$ is

$$S[\{p_i\}] = -k \sum_i p_i \log p_i,$$

where k is the Boltzmann constant.

In statistical mechanics, it gives the entropy for a canonical ensemble of a molecular system at constant temperature, and is a generalization of Boltzmann's formula to a situation with nonuniform probability distribution.

Denote the real distribution at time t is $p(t) = \{p_i(t)\}$, and we define the *general entropy* at time t as $S(t) = -k\Sigma_i p_i(t) \log p_i(t)$.

It is widely known that the entropy change dS could be to distinguished in two terms [4,6,29]: the first, $d_e S$ is the transfer of entropy across the boundaries of the system, and the second $d_i S$ is the entropy produced within the system.

Here, it is easy to derive that [6,29]

$$\frac{dS(t)}{dt} = d_i S + d_e S = e_p(t) - h_d(t), \qquad (2)$$

where

$$e_p(t) = d_i S = \frac{1}{2} k \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{p_i(t) q_{ij}(t)}{p_j(t) q_{ji}(t)}$$

is just the instantaneous entropy production rate [26], and

$$h_d(t) = d_e S = \frac{1}{2} k \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{q_{ij}(t)}{q_{ji}(t)}$$

is due to the exchange of heat with the exterior, called the heat dissipation rate.

The heat dissipation $h_d(t)$ could be regarded as the total heat conduction $Q_{tot}(t)$ with the medium, i.e.,

$$Q_{tot}(t) = T h_d(t).$$

By convention, we take the sign of heat to be positive when it flows from the system to the heat bath.

The idea of decomposing the total heat into a "housekeeping" part and another "excess" part was put forward by Oono and Paniconi [5], and made explicit in Langevin systems by Hatano and Sasa [23].

For any fixed t, there is a steady distribution $\pi(t) = \{\pi_i(t)\}$ corresponding to $Q(t)$ satisfying $\pi(t) Q(t) = 0$, which need not obey the detailed balance condition $\pi_i(t) q_{ij}(t) = \pi_j(t) q_{ji}(t)$.

Then we could define the other two kinds of heat: the housekeeping heat and excess heat

$$Q_{hk}(t) = \frac{1}{2} k T \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{\pi_i(t) q_{ij}(t)}{\pi_j(t) q_{ji}(t)},$$

$$Q_{ex}(t) = \frac{1}{2} k T \sum_{i,j} [p_i(t) q_{ij}(t) - p_j(t) q_{ji}(t)] \log \frac{\pi_j(t)}{\pi_i(t)},$$

and obviously $Q_{tot}(t) = Q_{ex}(t) + Q_{hk}(t)$.

More importantly, the housekeeping heat is always nonnegative, which implies the nonequilibrium essence of the system,

$$Q_{hk}(t) = k T \sum_{i,j} p_i(t) q_{ij}(t) \log \frac{\pi_i(t) q_{ij}(t)}{\pi_j(t) q_{ji}(t)} \geq -k T \sum_{i,j} p_i(t) q_{ij}(t)$$

$$\times \left(\frac{\pi_j(t) q_{ji}(t)}{\pi_i(t) q_{ij}(t)} - 1 \right) = -k T \sum_i \frac{p_i(t)}{\pi_i(t)} \sum_j \pi_j(t) q_{ji}(t)$$

$$+ k T \sum_{i,j} p_i(t) q_{ij}(t) = 0,$$

by making use of a simple inequality $\log x \leq x - 1$ for $x > 0$, and the identity $\Sigma_j q_{ij}(t) \equiv 0$. Similar results have been derived by Speck and Seifert [30].

For equilibrium system, Q_{ex} reduces to the total heat Q_{tot}, because in this case $Q_{hk} \equiv 0$ due to $\pi_i(t) q_{ij}(t) = \pi_j(t) q_{ji}(t)$.

2. Second law of thermodynamics

Traditional second law of thermodynamics has two kinds of statements [31]: The Kelvin-Planck statement "No process

is possible whose sole result is the complete conversion of heat into work" and the Clausius statement "No process is possible whose sole result is the transfer of heat from a colder to a hotter body."

Then how does these thermodynamic laws apply to such a nonequilibrium time-dependent process? Although all the thermodynamic quantities in the previous sections could be defined along the sample trajectory, the Clausius inequality and many other thermodynamic constrains related to the second law should be interpreted statistically through ensemble average.

Traditional second law is built on the non-negativity of the entropy production rate. To be more precise, notice that every term in the expression of the entropy production rate, i.e.,

$$e_p(t) = \frac{1}{2} k \sum_{i,j} [p_i(t)q_{ij}(t) - p_j(t)q_{ji}(t)] \log \frac{p_i(t)q_{ij}(t)}{p_j(t)q_{ji}(t)}$$

is non-negative, and the equality holds if and only if $p_i(t)q_{ij}(t) = p_j(t)q_{ji}(t)$ for each pair of states i and j.

Then according to Eq. (2), we derived that

$$T\frac{dS(t)}{dt} + Q_{tot}(t) = Te_p(t) \geq 0, \qquad (3)$$

Equation (3) is just the well-known Clausius inequality ($dS \geq -\frac{Q_{tot}}{T}$), which is rectified to obtain expressions for the entropy produced (dS) as the result of heat exchanges (Q_{tot}).

It is well-known that "only irreversible processes contribute to entropy production," so here we need to check the condition for which the entropy production vanishes and try to answer a fundamental question "what is precisely the reversible process that connects two different equilibrium states?"

For the time-dependent process discussed in the present paper, let $e_p(t) = 0$ for each time t, then we find that all the steady distributions $\{\pi(t)\}$ must be independent with time t (i.e., $\pi(t) \equiv$ some fixed distribution π) and the detailed balance condition holds, i.e., $\pi_i q_{ij}(t) = \pi_j q_{ji}(t)$. Therefore, during this process, the transient state at each time t is just the real equilibrium state corresponding to the transition law $Q(t)$. It is just equivalent to the new concept "instantaneous reversibility" [26], which actually corresponds to the ideal reversible process involved in the classic theory of equilibrium thermodynamics. But unfortunately, these equilibrium states are all essentially the same as the initial one, only with different time scales, i.e., $Q(t) = f(t)Q(0)$ for some function f. In other words, there is no real reversible process between two different equilibrium states, which confirms the well-known belief in equilibrium thermodynamics.

Note that, all the fundamental equations in classic equilibrium thermodynamics, such as $dU = TdS - pdV$, requires that initial and final equilibrium states be defined and that there is some reversible path between them [31]. But unfortunately it is not true, and this is just why equilibrium thermodynamics could not be directly generalized to the far-from-equilibrium case.

Now it is time to derive the extended quantitative form of the Second Law of Thermodynamics. Here we give a rather different but much more general derivation from Hatano-Sasa's, only need to notice that the quantity $Te_p(t) - Q_{hk}(t) \geq 0$ again due to the simple inequality $\log x \leq x - 1$ for $x > 0$,

$$Te_p(t) - Q_{hk}(t) = \sum_{ij} p_i(t)q_{ij}(t) \log \frac{p_i(t)\pi_j(t)}{p_j(t)\pi_i(t)} \geq \sum_{ij} p_i(t)q_{ij}(t)$$

$$\times \left(\frac{p_j(t)\pi_i(t)}{p_i(t)\pi_j(t)} - 1 \right) = \sum_j \frac{p_j(t)}{\pi_j(t)} \sum_i \pi_i(t)q_{ij}(t)$$

$$- \sum_i p_i(t) \sum_j q_{ij}(t) = 0, \qquad (4)$$

Then according to Eqs. (2), we have

$$T\frac{dS(t)}{dt} + Q_{ex}(t) = Te_p(t) - Q_{hk}(t) \geq 0, \qquad (5)$$

followed by its corresponding integral forms

$$T \triangle S + \int Q_{ex}(t)dt \geq 0, \qquad (6)$$

Equation (6) is the extended form of Clausius inequality during any nonequilibrium time-dependent process, whose special case is included in Hatano and Sasa's work [23].

For equilibrium case, $Q_{ex} = Q_{tot}$, then they both return back to Eq. (3) actually. And then if in steady state, then $Te_p(t) - Q_{hk}(t) \equiv 0$, and this form of the Second Law completely disappears.

B. Langevin dynamics

Here we consider the dynamics of a Brownian particle in a circuit driven by an external force, i.e.,

$$\gamma \dot{X}(t) = - \left. \frac{\partial V(x;t)}{\partial x} \right|_{x=X(t)} + f(X(t),t) + \xi(t),$$

where $\xi(t)$ represents Gaussian white noise whose intensity is $2\gamma kT$ according to the Einstein's relation. We employ periodic conditions as Kurchan and Hatano-Sasa have done in their previous works [18,23]. This time-dependent system is realized by changing the time-dependent potential $V(x,t)$ and nonconservative force f.

Langevin differential equations which govern a random variable X can also be reformulated as "Fokker-Planck differential equations," which govern the real probability distribution $p(x,t)$ of $X(t)$. Denote the drift coefficient $b(x,t) = \frac{-\frac{\partial V(x;t)}{\partial x} + f(x,t)}{\gamma}$, it reads

$$\frac{\partial p(x,t)}{\partial t} = - \frac{\partial j(x,t)}{\partial x}, \qquad (7)$$

where the current $j(x,t) = b(x,t)p(x,t) - \frac{kT}{\gamma} \frac{\partial p(x,t)}{\partial x}$.

We write the steady-state probability distribution function as $\pi(x,t)$ for which the right-side of Eq. (7) vanishes for any fixed t, i.e.,

$$\frac{\partial\left[b(x,t)\pi(x,t) - \frac{kT}{\gamma}\frac{\partial\pi(x,t)}{\partial x}\right]}{\partial x} = 0.$$

Let us introduce the *general entropy* at time t as

$$S(t) = -k\int p(x,t)\log p(x,t)dx.$$

Here, it is easy to derive that [6,29]

$$\frac{dS(t)}{dt} = d_i S + d_e S = e_p(t) - h_d(t), \tag{8}$$

where $e_p(t) = d_i S = \int \frac{\gamma j(x,t)^2}{Tp(x,t)}dx$ is the entropy production rate at time t, and $h_d(t) = -d_e S = \frac{\gamma}{T}\int b(x,t)j(x,t)dx$ is due to the exchange of heat with the exterior, called the heat dissipation rate.

The heat dissipation $h_d(t)$ could be regarded as the total heat conduction $Q_{tot}(t)$ with the medium, i.e.,

$$Q_{tot}(t) = Th_d(t).$$

The housekeeping heat is always non-negative.

$$Q_{hk}(t) = \int \gamma\left(b(x,t) - \frac{kT}{\gamma}\frac{\partial\log\pi(x,t)}{\partial x}\right)j(x,t)dx$$

$$= \int \gamma\left(b(x,t) - \frac{kT}{\gamma}\frac{\partial\log\pi(x,t)}{\partial x}\right)^2 p(x,t)dx \geq 0.$$

And the excess heat

$$Q_{ex}(t) = kT\int \frac{\partial\log\pi(x,t)}{\partial x}j(x,t)dx$$

$$= kT\int \frac{\partial p(x,t)}{\partial t}\log\pi(x,t)dx,$$

due to the Fokker-Planck Eq. (7).

Finally, it is not difficult to compute in this case that

$$Te_p(t) - Q_{hk}(t) = (kT)^2\int p(x,t)\left(\frac{\partial\log\frac{\pi(x,t)}{p(x,t)}}{\partial x}\right)^2 dx \geq 0.$$

III. APPLIED TO CLASSIC THERMODYNAMIC PROCESSES

A. Time-independent case

For stationary states, we have the important relations

$$Th_d = Te_p = Q_{hk} = Q_{tot} \geq 0,$$

and the equality holds if and only if at equilibrium states [15].

1. Relaxation process toward equilibrium state

For systems approaching to equilibrium, the free energy could be defined as

$$F(t) = kT\sum_i p_i(t)\log\frac{p_i(t)}{\pi_i(t)}$$

in the master-equation model and

$$F(t) = kT\int p(x,t)\log\frac{p(x,t)}{\pi(x,t)}dx$$

in Langevin systems. It is just the Gibbs free energy in a spontaneously occurring chemical reaction at constant pressure p and temperature T, and also the Helmholtz free energy for systems at constant V and T [32]. Its change gives the maximum work, other than pV work. Therefore, it is called a "hybrid free energy" by Ross [32].

From a mathematical point of view, it is just the relative entropy of the distribution $\{p_i(t)\}$ [or $\{p(x,t)\}$] with respect to another one $\{\pi_i(t)\}$ [or $\{\pi(x,t)\}$]. Hong Qian [33] has proved that this relative entropy from information theory could be identified as the free energy difference associated with a fluctuating density in equilibrium, and is also associated with the distribution deviate from the equilibrium sate in nonequilibrium relaxation.

Due to the Jensen's equality for the convex function $-\log x$, we have $F(t) \geq 0$, and the equality holds if and only if it reaches the final stationary state, i.e., $p_i(t) = \pi_i(t)$ for each state i.

The extended form of the second law now gives

$$\frac{dF(t)}{dt} = -Te_p(t) \leq 0,$$

thus $F(t)$ serves as a Lyapunov function for the relaxation process toward equilibrium state [14].

2. Relaxation process toward nonequilibrium steady state

The relaxation process toward nonequilibrium steady states has been extensively discussed by Glansdorff and Prigogine [3,4], and then by Schnakenberg for the master-equation systems [14].

The extended form of the second law in this case could be reformulated as

$$\frac{dF(t)}{dt} = -Te_p(t) + Q_{hk}(t) \leq 0,$$

thus we know $F(t)$ could also serve as a Lyapunov function for this relaxation process toward nonequilibrium steady state. Until now we know that this Lyapunov property is just a directly corollary of the extended form of the second law, and we have already extended Schnakenberg's result [14] to Langevin systems.

B. Time-dependent case

Time-dependent processes are causing more and more interests from physicists nowadays [23,34–36], and it will uncover many important thermodynamic properties that originally hidden behind the stationary time-independent case.

1. Cyclic process

Second, the thermodynamic cyclic process. In equilibrium thermodynamics, a thermodynamic cycle is a series of ther-

modynamic processes which returns a system to its initial state. As a conclusion of cyclic process, all the state variables should have the same value as they had at the beginning, thus $\Delta S = 0$.

But variables such as heat are not zero over a cycle, but rather are process dependent. Hence in this case, the traditional form of the second law (3) gives $\int Q_{tot}(t)dt \geq 0$, then it is just the familiar statement of traditional second law of thermodynamics "the conversion from work to total heat is irreversible."

Then, the extended form (6) gives

$$\int Q_{ex}(t)dt \geq 0,$$

which explicitly confirms the claim that "the conversion from work to excess heat is irreversible" [5]. In other words, during a cyclic process, not only the total heat but also the excess heat could only be from the system into the heat bath rather than follow the opposite direction.

2. Transitions between equilibrium states

Jarzynski provided an expression for the equilibrium free energy difference between two configurations of a system, in terms of an ensemble of finite-time measurements of the work performed through switching from one configuration to the other (see a recent review [35] and references in).

In the stochastic-process approach [21,37,38], we consider the transition between two equilibrium states realized in the time interval $[0, T]$ where the detailed balance condition is satisfied., i.e., $Q_{hk}(t) \equiv 0$.

Here we could define an thermodynamic quantity "dissipative work" called by Jarzynski and Crooks [20–22,39–41], and rigorously formulated by Min Qian and the author [38]. To be more precise, it is just

$$W(t) = -kT \sum_i p_i(t) \frac{d \log \pi_i(t)}{dt}$$

in the master-equation models and

$$W(t) = -kT \int p(x,t) \frac{\partial \pi(x,t)}{\partial t} dx$$

for the Langevin systems.

Notice that when one finishes the task of driving the process from time 0 to time T through modulating the time-dependent transition density matrix $Q(t)$ (denoted as process 1), the system has not reached the final equilibrium state yet. Then we should wait until it really arrives (denoted as process 2), which is just the "relaxation process toward equilibrium state" with the fixed transition density $Q(T)$ described in the previous subsections.

It is easy to derive that for equilibrium systems

$$\frac{dF(t)}{dt} = W(t) - Te_p(t).$$

Therefore, we have $\Delta F_1 \leq \int_1 W(t)dt$, and $\Delta F_2 \leq \int_2 W(t)dt$ for process 1 and 2, respectively.

Finally, since $\int_2 W(t) = 0$, and $\Delta F = \Delta F_1 + \Delta F_2$ is just the free energy difference between the initial and final equilibrium states, we conclude $\Delta F \leq \int_1 W(t)dt$. It is just why we could neglect process 2 when applying Jarzynski's work relation in experiments.

Note that the situation is quite different when regarding Hitano-Sasa's equality for transitions between steady states [23]. It has not been explicitly pointed out in previous works [23,35,37,38]. See below for details.

3. Transitions between steady states

The previous steady-state thermodynamics of Langevin systems [23] is based on a generalized version of the Jarzynski work relation [20,21,35], and concluded that Q_{ex} should correspond to the change of a generalized entropy S in an appropriate limit. In fact, the extended form of the second law derived by Hatano and Sasa [23] is just a straightforward consequence of Eq. (6), which is satisfied by any transient state.

However, what they defined is just the general internal energy consistent with the first law of thermodynamics rather than the general Gibbs entropy in the present paper and also in Seifert's recent work [34]. Note that the two quantities are always different except for steady states, hence the extend form of second law of thermodynamics during the course of transition between two steady states derived by Hatano and Sasa is not flawed.

Similar to the preceding transition process between two equilibrium states, when one finishes driving the process from time 0 to T (also denoted as process 1) through varying the time-dependent transition density $Q(t)$, the system has not reached the final steady state yet, and we should wait until it arrives (denoted as process 2), which is just the "relaxation process toward steady state" where the transition density is fixed at $Q(T)$.

According to Eq. (6), we get $\int_1 Q_{ex}(t)dt \geq -\Delta S_1$, and $\int_2 Q_{ex}(t)dt \geq -\Delta S_2$ for processes 1 and 2, respectively.

Finally, since $\Delta S = \Delta S_1 + \Delta S_2$ representing the energy (entropy) difference between the initial and final steady states, we derive that

$$\int Q_{ex}(t)dt = \int_1 Q_{ex}(t)dt + \int_2 Q_{ex}(t)dt \geq -\Delta S.$$

Hatano and Sasa [23] concluded that the equality held for an infinitely slow operation in which the system is in a steady state at each time during a transition ("slow process").

It is indispensable to emphasize that we could not neglect process 2 this time when applying Hitano-Sasa's identity, because here $\int_2 Q_{ex}(t)dt$ may not be zero, which implies that the relaxation process toward the final steady state will also contribute to the heat dissipation. This critique has already be pointed out by Cohen and Mauzerall [42], but unfortunately what they criticized is the Jarzynski's equality rather than Hatano-Sasa equality. In real experiment, this relaxation process may be rapid enough and could somehow be omitted.

TABLE I. The signs of important thermodynamic quantities. Process 1: equilibrium state; process 2: nonequilibrium steady state; process 3: relaxation process toward equilibrium state; process 4: relaxation process toward nonequilibrium steady state; process 5: transition between equilibrium states; process 6: transition between steady states. "0" for zero, "+" for positive, "−" for negative, and "?" for uncertainty.

	Process 1	Process 2	Process 3	Process 4	Process 5	Process 6
Excess heat	0	0	?	?	?	?
Housekeeping heat	0	+	0	+	0	+
Entropy production	0	+	+	+	+	+
$Te_p(t) - Q_{hk}(t)$	0	0	+	+	+	+

C. Summary

The essential difference between these typical processes relies mainly on the signs of the three key thermodynamic quantities: the housekeeping heat, entropy production, and $Te_p(t) - Q_{hk}(t)$. And also the dissipative work would disappear for time-independent processes. See Table I for details.

IV. DISCUSSION

Various kinds of approaches have been put forward to nonequilibrium thermodynamics in the last several decades [43,44], but in contrast to equilibrium systems, with their elegant theoretical framework, the understanding of nonequilibrium systems is still primitive.

It is the main thesis of this paper that we are only at the beginning of a development of theoretical chemistry and physics in which thermodynamic concepts may play an even more basic role. "In any case, the number of thermodynamic or macroscopic variables is much less than the large number of the microscopic degrees of freedom. Hence, the transition from a microscopic to a macroscopic description involves a drastic reduction of the information about the system"[45].

However, the study of thermodynamics before is largely confined to equilibrium states. Although the field of "non-equilibrium thermodynamics" has successfully extended the 19th century concepts of equilibrium thermodynamics to the systems that are close to, or near equilibrium, the understanding of far-from-equilibrium systems is still poor.

To investigate these points, stochastic thermodynamics has advanced much further than other approaches during the last two decades [34,46–48]. For stochastic systems, the central problem is around the extension of the second law, which originally describes the fundamental limitation on possible transitions between equilibrium states. The main purpose of the present paper is to investigate the extended form of the second law, up to a degree of universality as general as possible.

It would be interesting to test experimentally all the quantities and relations. Although here we only study the stochastic process, the extended form of the second law derived here may be valid for many other real physical processes, since these thermodynamic quantities involved could be obtained phenomenologically [5].

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