A generalization of Clausius inequality for processes between nonequilibrium steady states in chemical reaction systems

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We investigate nonequilibrium chemical reaction systems from the viewpoint of steady state thermodynamics proposed by Oono and Paniconi [Prog. Theor. Phys. Suppl. 130, 29 (1998)]. The concentrations of some compounds are operated by an external system, so that a transition from a steady state to other steady state takes place. We show that an analogue of Clausius inequality holds macroscopically for the operation processes. This implies that the second law of thermodynamics can be generalized, including nonequilibrium steady states.

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Most of the interesting and important chemical reactions take place under nonequilibrium conditions, for instance, in biological systems and in chemical plants. When the concentration of a compound is changed by an external system, how do the concentrations of the other compounds respond? What kinds of restrictions are imposed on possible physical processes? Beyond individual systems, if there is a phenomenological framework for nonequilibrium states to study such questions, it is as valuable as equilibrium thermodynamics.

A lot of efforts have been done to describe nonequilibrium systems from thermodynamic viewpoints [1]. Oono and Paniconi have proposed a phenomenological framework, steady state thermodynamics (SST) [2], for nonequilibrium steady states in a parallel form to equilibrium thermodynamics. A significant characteristic of equilibrium thermodynamics is the second law which asserts the existence of quasi-equilibrium and non-quasiequilibrium processes, that is responsible for the evolution and stability criteria. Similarly, they consider that even for the processes between nonequilibrium steady states "quasisteady" and "non-quasisteady" processes should exist. Since the system steadily generates dissipations, we need to carefully extract a quantity relevant to the operation to change the steady state. For such a quantity, they propose the "excess heat" absorption \( Q_{\text{ex}} = Q - Q_{\text{hk}} \) where \( Q \) is the heat absorbed by the system, and \( Q_{\text{hk}} \) is the "house-keeping" heat absorption to maintain the steady state. In an appropriate "quasisteady" limit, the quantity should be equal to the difference of a pertinent "thermodynamic function" of SST.

 Whereas ultimate justification of the framework remains with its experimental analysis, it may be worthwhile to explore several models for the validity of SST. Sekimoto and Oono studied a simple Langevin system so that they found the house-keeping heat and a thermodynamic function for the system [3]. Then Hatano and Sasa investigated a Brownian particle driven by an external force [4]. For a process operated by an external system, they found the generalized Jarzynski equality [5], \( \exp \{ \beta Q_{\text{ex}} + \phi(x_f; a_f) - \phi(x_i; a_i) \} = 1 \) where \( \phi(x; a) = \log p(x; a) \) with \( p(x; a) \) the stationary probability of the steady state given a parameter \( a \), \( a_i \) and \( a_f \) are the parameters of the initial and final state of the process, \( \beta \) is the inverse temperature, and \( \langle \cdot \rangle \) indicates the ensemble average over all possible paths. Then, identifying \( S(a) = -\langle \phi(x, a) \rangle = - \int p(x; a) \log p(x; a) dx \) as the entropy function of SST, they found generalized Clausius inequality \( \beta Q_{\text{ex}} \leq S(a_f) - S(a_i) \). They also proposed that the "house-keeping" heat is related to the degree of breakdown of the detailed balance condition.

In this Letter, we investigate nonequilibrium chemical reaction systems from the viewpoint of SST. We consider "ideal" reaction systems, i.e., the mixture and reactions are homogeneous in space, the non-reactive collisions of molecules occur frequently between the successive reactions, and the time scale of the reactions and that of the internal degrees of freedom of the molecules are separated. Then the system can be described by Markov jump processes [6]. We show that the similar argument developed in [5] also holds in such systems. First we show that a generalized Jarzynski equality holds for Markov jump processes. Connecting the equality with an energetic interpretation, we show a generalized Clausius inequality, which is the manifestation of non-quasisteady processes.

Consider a vessel with its volume \( V \), in which \( M + N \) chemical compounds \( A_i \) (\( i = 1, \cdots, M \)) and \( X_j \) (\( j = 1, \cdots, N \)) exist. Among these chemical compounds, the following chemical reactions take place:

\[
\sum_{l=1}^{M} a_{l+1}^0 A_l + \sum_{j=1}^{N} c_{+lj} X_j \to \sum_{l=1}^{M} c_{l-1}^0 A_l + \sum_{j=1}^{N} c_{-lj} X_j , \tag{1}
\]

with \( l = 1, \cdots, L \). Let us call the forward reactions reaction \( +l \) while the backward reactions reaction \( -l \). We assume that both the rate constants \( k_{+l} \) and \( k_{-l} \) of the reaction \( +l \) and reaction \( -l \), respectively, are positive. The stoichiometric coefficients \( a_{l+1}^0 \) and \( c_{\pm lj} \) are non-negative integer. The concentrations of \( A_i \)'s are kept \( a_i \). The number of molecules \( X_j \) is denoted by \( n_j \). The state of the system is denoted by \( n = (n_1, \cdots, n_N) \). Let \( n_i \) be \( n_{l+1} = n_i + 1 \) and \( n_{-l} = n_i - 1 \). When the reaction \( l \in \mathbb{Z} \),
$[-L, \ldots, -1, 1, \ldots, L]$ takes place, the state jumps from $n$ to $n + \nu_l = (n_1 + \nu_{l_1}, \ldots, n_N + \nu_{l_N})$.

For $A_i$'s, one can consider that these compounds are exchanged between the vessel and its surroundings, and the exchange process is sufficiently fast so that the concentrations are well controlled. Although we neglect to consider the exchange process for simplicity, it is always possible to take the process into account. We then consider the situation where an external system operates the system in time by changing some of the concentrations $a_i$'s during the times $[0, t]$. The set of such time-dependent concentrations at time $s$ are denoted by $a(s)$, and $a(s)$ is changed according to a given operation protocol $a(s)_{0 \leq s \leq t}$.

The probability $p(n, s)$ that the system is in the state $n$ at time $s$ follows the master equation,

$$\frac{\partial p(n, s)}{\partial s} = \sum_{l=-L}^{L} \left( E_l^{ci} - 1 \right) W_l(n, n + \nu_l; a(s))p(n, s)$$

(2)

where $E_l^{ci}$ is an operator defined by its effect on an arbitrary function $f(n)$, $E_l^{ci} f(n) = f(n_1 - \nu_{l_1}, \ldots, n_N - \nu_{l_N})$, and $W_l(n, n + \nu_l; a)$ is the transition probability, given $a$, that the reaction $l$ takes place per unit time $[8]$.

$$W_l(n, n + \nu_l; a) = V k_l \prod_{i=1}^{M} \delta_{\nu_l}^{\delta_i} \prod_{j=1}^{N} \left( \frac{n_i!/(n_i - \nu_i)!}{V a_i^{n_i}} \right)$$

(3)

with $l \in [-L, \ldots, -1, 1, \ldots, L]$. We suppose that if the time-dependent parameters are virtually fixed at $a$, the probability distribution function approaches a unique stationary probability distribution function $p_s(n; a)$ that satisfies $\sum_{l=-L}^{L} \left( E_l^{ci} - 1 \right) W_l(n, n + \nu_l; a)p_s(n; a) = 0$.

Let us consider a particular state at time $s$ denoted by $n(s)$, and a particular path denoted by $n(s)_{0 \leq s \leq t}$. Starting from an initial state $n(0)$, $n(s)$ is given by

$$n_j(s) = n_j(0) + \int_{0}^{s} \sum_{l=-L}^{L} \nu_{lj} \xi_l(u) du$$

(4)

where each $\xi_l(u)$ is a sequence of $\delta$-function, located at those times when the reaction $l$ takes place.

For these processes, we consider an energetic interpretation. In the present model system, we simply suppose that a molecule of each compound has the energy $E_l^{ci}$ of $A_l$ or $E_j$ of $X_j$ and no interaction energy among molecules is taken into account. Under equilibrium conditions, the states of the system should obey the grand canonical ensemble, and the detailed balance condition should hold. This leads to a relation between rates of a transition and its reverse, as

$$k_{l+} = \sum_{l=1}^{M} \left( \nu_0 e^{\beta E_0} \right)_{-v_{l_1}} \prod_{j=1}^{N} \left( \nu_0 e^{\beta E_j} \right)_{-v_{l_j}}$$

(5)

where $\nu_0$ is a certain constant of the dimension of $V$.

For a particular state $n$, the internal energy of the system $E$ is given by $E = \sum_{j=1}^{N} E_j n_j$. The internal energy change $\Delta E(t)$ is given by

$$\Delta E(t) = E(t) - E(0) = \sum_{j=1}^{N} \int_{0}^{t} \sum_{l=-L}^{L} E_{lj} \xi_l(u) du.$$  

(6)

Here the energy of $A_i$'s is not included in $E$ for the following reason. Since in the present consideration the concentrations of $A_i$'s completely follow the parameters $a_i$'s at every moment, the role of $A_i$'s is nothing more than that of reservoirs. If one would consider this unphysical, the injection and extraction processes should be taken into account.

Next we show that the generalized Jarzynski equality, which shall be given in Eq. (3), holds in the Markov jump processes generated according to $W_i$. The idea to prove the equality has been developed first by Crooks under equilibrium conditions [3]. Then, Hatano and Sasa generalize the argument for Langevin systems under nonequilibrium conditions [3].

Consider that a particular path $n(s)_{0 \leq s \leq t}$, which is a sequence of states

$$n(0) \xrightarrow{t_1} n(t_1) \xrightarrow{t_2} \cdots \xrightarrow{t_n} n(t_n),$$

(7)

with $t_i$ a jump time when the system jumps from $n(t_{i-1})$ to $n(t_i) = n(t_{i-1}) + \nu_i$, ($i = 1, \ldots, n, t_n \leq t < t_{n+1}$).

If the system is in the state $n$ at time $s$, the probability that a transition takes place per unit time is given by $W(n; a(s)) = \sum_{l=-L}^{L} W_l(n, n + \nu_l; a(s))$. The system stays in $n$ until $s' = s + \tau$, where $\tau$ is an independent random variable distributed according to the density function $W(n; a(s + \tau)) \exp \left\{ -\int_{s'}^{s+\tau} W(n; a(u)) du \right\}$. Then, at $s'$ the system jumps to $n + \nu_i$ according to the probability $W_l(n, n + \nu_l; a(s'))/(W(n; a(s')))$. Suppose that at time 0 the system is in a steady state. Then, the probability $P[t] = P[n(s)_{0 \leq s \leq t}; a(s)_{0 \leq s \leq t}]$ that we have the path $n(s)_{0 \leq s \leq t}$ is given by

$$P[t] = p_s(n(0); a(0)) \prod_{i=1}^{n} W_i(n(t_{i-1}), n(t_i); a(t_i))$$

$$\times e^{-\int_{0}^{t} W(n(u); a(u)) du},$$

(8)

where $t_0 = 0$.

Consider the transition probability $\tilde{W}_l(n, n + \nu_l; a)$, defined by

$$\tilde{W}_l(n, n + \nu_l; a) = \frac{p_s(n + \nu_l; a)}{p_s(n; a)} W_l(n + \nu_l, n; a).$$

(9)

If the detailed balance condition holds, $\tilde{W}_l = W_l$. For a given path $n(s)_{0 \leq s \leq t}$ generated by $W_i$, consider the path $\tilde{n}(s)_{0 \leq s \leq t}$ generated by $\tilde{W}_l$ given by $\tilde{n}(s) = n(t - s)$ with a parameter protocol $\tilde{a}(s) = a(t - s)$. The jump times for $\tilde{n}(s)_{0 \leq s \leq t}$ is given by $\tilde{t}_i = t - t_{n-i+1}$ at
which the transition takes place from $\tilde{n}(\tilde{t}_{i-1})$ to $\tilde{n}(\tilde{t}_{i}) = \tilde{n}(\tilde{t}_{i-1}) + \nu_i$ with $\tilde{t}_i = -\ln_i + 1$. The probability $\tilde{P}[t] = \tilde{P}(\tilde{n}(s)_{0 \leq s \leq t}; \tilde{a}(t)_{0 \leq s \leq t})$ that we have the path $\tilde{n}(s)_{0 \leq s \leq t}$ is also calculated as is the case of $P[t]$. Here, we suppose that $\tilde{n}(s)$ also starts from a steady state. Now we compare $\tilde{P}[t]$ with $P[t]$. Let us introduce the quantity $\phi(n; a)$, 

$$p_s(n; a) = \exp \phi(n; a).$$

Using Eq. (11), and noting $\tilde{W}(n; a) = \sum_{i=-L}^{L} \tilde{W}_i(n, n + \nu_i; a) = W(n; a)$, $\tilde{P}[t]$ has a density relative to $P[t]$ as

$$\tilde{P}[t] = e^{\phi(n(t); a(t)) - \phi(n(0), a(0)) + \Phi[t]} P[t],$$

where $\Phi[t] = \Phi[n(s)_{0 \leq s \leq t}; a(s)_{0 \leq s \leq t}]$ is the quantity

$$\Phi[t] = \int_{0}^{t} \left\{ \phi(n(s^-); a(s)) - \phi(n(s); a(s)) \right\} \xi(s) ds \quad (12)$$

with $\xi(s) = \sum_{i=-L}^{L} \xi_i(s)$ and $n(s^-)$ the state just before the jump to $n(s)$ at time $s$, i.e., the state after the previous jump event. By summing Eq. (11) over all possible paths, we obtain the generalized Jarzynski equality

$$\langle \exp \{ \phi(n(t), a(t)) - \phi(n(0), a(0)) + \Phi[t] \} \rangle = 1 \quad \text{(13)}$$

with Eqs. (11) and (12), where $\langle \cdot \rangle$ indicates the ensemble average over all possible paths.

It may be worth mentioning that if one consider that the path $\tilde{n}(s)_{0 \leq s \leq t}$ is generated according to $\tilde{W}_i$ instead of $\tilde{W}_i$, then the fluctuation theorem is obtained by comparing the path probabilities $\tilde{P}[t]$ for $\tilde{P}[t]$. Eq. (13) leads to the relation

$$\langle \Phi[t] \rangle \leq -\langle \phi(t) \rangle - (-\langle \phi(0) \rangle),$$

where $-\langle \phi(s) \rangle = -\sum_n p_s(n; a(s)) \log \{ p_s(n; a(s)) \}$. When the change of $a(s)$ is so slow that $p_s(n, s)$ can be regarded as $p_s(n; a(s))$, the equality holds in Eq. (14).

Next we interpret the inequality (14) from energetic point of view and show the existence of non-quasi-steady processes. Let $\zeta_i(n, n + \nu_i; a)$ be the quantity that characterizes the degree of the breakdown of the detailed balance condition, given by

$$\frac{p_s(n, \nu_i; a) W_i(n, n + \nu_i; a)}{W_i(n + \nu_i, a)} = e^{-\zeta_i(n, n + \nu_i; a)}. \quad \text{(15)}$$

Obviously, if the detailed balance condition holds, $\zeta_i(n, n + \nu_i; a) = 0$. Substituting Eqs. (3), (2) and (12) into Eq. (13), $\Phi[t]$ can be rewritten by

$$\Phi[t] = \beta \Delta \mathcal{E}(t) + \beta \int_{0}^{t} \sum_{i=-L}^{L} \sum_{j=1}^{M} \nu_{ij} \mu_{ij}^{0}(s) \xi_i(s) ds - \int_{0}^{t} \sum_{i=-L}^{L} \zeta_i(n(s) - \nu_i, n(s); a(s)) \xi_i(s) ds$$

$$+ \int_{0}^{t} \sum_{i=-L}^{L} \log \left( \prod_{j=1}^{N} \lambda_{ij}(n_j(s) - \nu_{ij})! \right) \xi_i(s) ds \quad \text{(16)}$$

with $\mu_{ij}^{0}(s) = E_{ij} + \frac{1}{\beta} \log \{ p_i(a_i(s)) \}$, the chemical potential of $A_i$. For the first three terms on the r.h.s., we introduce the quantity $\mathcal{D}_{ex}[t] = \mathcal{D}_{ex}[n(s)_{0 \leq s \leq t}; a(s)_{0 \leq s \leq t}]$ given by

$$\mathcal{D}_{ex}[t] = \Delta \mathcal{E}(t) + \int_{0}^{t} \sum_{i=-L}^{L} \sum_{j=1}^{M} \nu_{ij} \mu_{ij}^{0}(s) \xi_i(s) ds - \mathcal{D}_{hk}[t]. \quad \text{(17)}$$

where $\mathcal{D}_{hk}[t] = \mathcal{D}_{hk}[n(s)_{0 \leq s \leq t}; a(s)_{0 \leq s \leq t}]$ is defined by

$$\mathcal{D}_{hk}[t] = \frac{1}{\beta} \int_{0}^{t} \sum_{i=-L}^{L} \xi_i(n(s) - \nu_i, n(s); a(s)) \xi_i(s) ds. \quad \text{(18)}$$

Note that the fourth term on the r.h.s. of Eq. (18) is rewritten by $\log \left\{ \prod_{j=1}^{N} \left( \frac{\nu_j}{\lambda_j} \right)^{n_j(s)} \right\}$. Substituting Eq. (10) into Eq. (14), with Eqs. (17) and (18), we obtain the main result of this Letter

$$\beta \langle \mathcal{D}_{ex}[t] \rangle \leq S(a(t)) - S(a(0)), \quad \text{(19)}$$

where $S(a)$ is the quantity defined by

$$S(a) = -\sum_n p_s(n; a) \log \left\{ \prod_{i=1}^{N} \left( \frac{\nu_i}{\lambda_i} \right)^{n_i(s)} p_i(n; a) \right\}. \quad \text{(20)}$$

In order to make $\mathcal{D}_{ex}[t]$ in (17) transparent, we introduce $A_l$ the chemical affinity of the reaction $l$ as

$$A_l = -\sum_{i=1}^{M} \nu_{il} \mu_{il}^{0} - \sum_{j=1}^{N} \nu_{lj} \mu_{lj}^{0} = -A_{-l} \quad \text{(21)}$$

with $\mu_j(s)$ the chemical potential of $X_j$. When $A_l > 0$, the reaction $l$ proceeds on average. Under equilibrium conditions, $A_l = 0$. Using Eq. (11), $\mathcal{D}_{ex}[t]$ is rewritten by

$$\mathcal{D}_{ex}[t] = \Delta \mathcal{E}(t) - \int_{0}^{t} \sum_{j=1}^{N} \mu_j \nu_{lj} \xi_j(s) ds - \int_{0}^{t} \sum_{i=-L}^{L} A_l \zeta_i(s) ds - \mathcal{D}_{hk}[t]. \quad \text{(22)}$$

Let us first see the consistency between (19) and equilibrium thermodynamics. Under equilibrium conditions $\mathcal{D}_{hk}[t] = 0$ and $A_l = 0$. Thus, the first two terms on the r.h.s. of (22) are relevant to equilibrium thermodynamics. By considering $\mathcal{D}[a]$ as the equilibrium thermodynamic entropy, (13) is nothing but Clausius inequality.

Under nonequilibrium conditions, the third term on the r.h.s. of (22) includes the continuous dissipation, even when system’s parameters are kept constants. In order to discuss the thermodynamics with respect to operations upon the system, we need to carefully extract the quantities relevant to the change in the macroscopic state. When $da/dt$ is so small that $p(n, s)$ can be regarded as $p_s(n; a(s))$, $\langle \mathcal{D}_{ex}[t] \rangle$ coincides with the difference of $\mathcal{S}(a)$ between the initial and final state of a process. Let us
then consider $\langle D_{ex}[t] \rangle$ as the quantity relevant to the operations, and $S(a)$ as the thermodynamic function that characterizes the nonequilibrium steady states. The quasi-steady process is realized in the limit $1/t \to 0$, given the parameter protocol $a(s) = \hat{a}(s/t)$ with a given parameter path $\hat{a}(\tau)$ for $0 \leq \tau \leq 1$. When $1/t$ is finite, $\langle D_{ex}[t] \rangle$ is smaller than the difference of $S(a)$ and the processes are considered to be non-quasi-steady processes. In [17], $-\langle D_{hk} \rangle$ is regarded as the dissipation called the house-keeping dissipation that keeps the system far from equilibrium [5]. In this way, we find a similar structure in nonequilibrium steady states to equilibrium thermodynamics, and consider Eq. (19) as a generalization of Clausius inequality.

In the definition of the house-keeping dissipation (18) and hence the steady state entropy (20) there is some arbitrariness. So far no systematic discussion exists in order to justify these definitions under nonequilibrium conditions. However, in some cases we identify $-\langle D_{hk}[n(s)_{0 \leq i \leq t}] \rangle$ as so-called entropy production. When $p_s(n; a)$ is a Poisson distribution or for each compound a grand canonical distribution can be supposed (local equilibrium), $D_{hk}$ is written by

$$-\langle D_{hk}[n(s)_{0 \leq i \leq t}] \rangle \simeq \left\langle \int_0^t \sum_{i=-L}^L A_i \xi_t(s) ds \right\rangle$$

(23)

where $\mu_j(s)$ in $A_i$ is defined by $\mu_j(s) = E_j + \frac{1}{\beta} \log \{v_0(n_j(a(s)))/V\}$ with $n_j(a) = \sum_n n_j p_s(n; a)$. The r.h.s. of Eq. (23) is identified as the entropy production [4]. In such cases, although the condition is nonequilibrium, $D_{ex}$ can be reduced again as

$$D_{ex}[t] = \Delta \mathcal{E}(t) - \int_0^t \sum_{j=1}^N \mu_j d n_j(s),$$

(24)

so that the same form as in equilibrium thermodynamics is obtained. This implies that at least near equilibrium the same relation with equilibrium thermodynamics can be applicable to nonequilibrium system by extending the definition of entropy.

If we compare the inequality (13) with the previous result in [7], $\beta Q_{ex} \leq S(a_f) - S(a_i)$ with $Q_{ex} = Q - Q_{hk}$, one might identify the first three terms on the r.h.s in (23) as the heat absorbed by the system. However, this is not the case, since in the present case the dissipation without heat generation can take place such as the mixing without energy conversion [3].

We note that if each molecule is described individually, $S$ is rewritten by $S = -\sum_{\{n\}} p_s(\{n\}) \log p_s(\{n\})$, where $p_s(\{n\})$ is the probability of the state $\{n\}$ where the molecules are distinguished.

In the present Letter, nonequilibrium chemical reactions have been studied from the view point of steady state thermodynamics [2]. First we have shown that the generalized Jarzynski equality holds in the Markov jump process, and then we have a generalization of Clausius inequality (19). The argument presented here can be applicable to other systems such as lattice gas systems. Our choice of the connection between the energetics and the kinetic parameters is quite simple. When the connection between them is much more complicated, how our result will be modified remains to be clarified. The experimental verification of the present result is another significant problem. Especially, how the entropy function and the house-keeping dissipation can be measured remains as a future problem.

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