Possible extended forms of thermodynamic entropy

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Abstract. Thermodynamic entropy is determined by a heat measurement through the Clausius equality. The entropy then formalizes a fundamental limitation of operations by the second law of thermodynamics. The entropy is also expressed as the Shannon entropy of the microscopic degrees of freedom. Whenever an extension of thermodynamic entropy is attempted, we must pay special attention to how its three different aspects just mentioned are altered. In this paper, we discuss possible extensions of the thermodynamic entropy.

Keywords: driven diffusive systems (theory), stochastic particle dynamics (theory), stationary states
1. Introduction

Equilibrium entropy was introduced as a state variable associated with quasi-static heat [1]. We here review a construction method by Caratheodory [2], where quasi-static heat \( d'Q \) is first defined along a path element in a state space. For example, for a simple fluid characterized by the internal energy \( U \) and the volume \( V \), we start with \( d'Q \equiv dU - p\,dV \) in the state space consisting of equilibrium states represented by \( A = (U, V) \), where \( p(A) \) is the pressure. Then, under the assumption that \( d'Q = 0 \) defines curves in the two-dimensional state space (or generally \( d-1 \)-dimensional surfaces in a \( d \)-dimensional state space), it turns out that there exists a state variable \( S \) with an integration factor \( T \) that satisfies \( dS = d'Q/T \), where \( S \) and \( T \) are determined in an essentially unique manner. This means that, for two different equilibrium states \( A \) and \( B \),

\[
S(B) - S(A) = \int_A^B \frac{d'Q}{T}
\]

holds for any paths from \( A \) to \( B \) in the state space. The state variable \( S \) determined by this procedure is the thermodynamic entropy, and \( T \) the temperature. It should be noted that paths in the state space, which are referred to as quasi-static processes, can be realized by controlling thermodynamic parameters quite slowly. With the introduction of the entropy, the fundamental relation in thermodynamics

\[
dU = T\,dS - p\,dV
\]

is obtained. The relation describes material properties in a unified manner so that we can easily understand a non-trivial fact that the volume dependence of a heat capacity with \( T \) fixed is determined from the temperature dependence of a pressure with the volume fixed.

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For more general time-dependent processes from an equilibrium state $A$ to another equilibrium state $B$, the inequality

$$S(B) - S(A) \geq \int dt \frac{J(t)}{T(t)}$$

(3)

holds, where $T(t)$ is the temperature of a single heat bath in contact with a system, and $J(t)$ is a heat flux (i.e. the energy transfer from the heat bath) at time $t$. The inequality describes a fundamental limitation of operations, which is one expression of the second law of thermodynamics. Furthermore, let $P_{eq}(\Gamma)$ be a probability density of microscopic state $\Gamma$ in an equilibrium state $A$. Then, according to statistical mechanics, $S(A)$ is equal to the Shannon entropy of $P_{eq}(\Gamma)$ defined by

$$S(A) \equiv - \int d\Gamma P_{eq}(\Gamma) \log P_{eq}(\Gamma).$$

(4)

The entropy in the elegant formulation described above is defined for equilibrium states. It is quite natural to question the possibility of entropy extended to non-equilibrium states. Indeed, several attempts were proposed in the twentieth century [3]–[8]. Here, although we can define our entropy as we like, the heart of the problem is to study whether or not the entropy by some definition exhibits other (apparently unrelated) aspects, as for the standard thermodynamic entropy. For example, if an extended entropy is defined from statistical properties, it is not obvious at all to have a relation with heat, which may be interpreted as an extended Clausius relation.

In any case, if we attempt to extend the thermodynamic entropy, we first have to consider an extension of the state space so that it involves non-equilibrium steady states in addition to equilibrium states. As the simplest case, we assume that a driving force is applied to a system in contact with a single heat bath of temperature $T$ fixed. In this case, the non-equilibrium axis $X$ (e.g. driving force, shear rate, or current) is added to the state space of equilibrium states. We then assume that $A = (A, X)$ represents a steady state and we consider a collection of $A$ as the extended state space. That is, time-dependent states are excluded from the state space. Our question is now expressed as follows. **Find a state variable $S(A)$ satisfying a natural extension of the relations (1)–(4).**

Along with a naive expectation that the Shannon entropy still plays an important role in non-equilibrium steady states, we assume that $S$ is given by the Shannon entropy,

$$S(A) = - \int d\Gamma P_{st}(\Gamma) \log P_{st}(\Gamma).$$

(5)

Then, it can be shown that

$$S(B) - S(A) \geq \int dt \frac{J(t)}{T}.$$ 

(6)

Indeed, such inequality has been understood well since the discovery of the fluctuation theorem [9]–[14] and the Jarzynski equality [15]–[18]. However, the equality in (6) does not hold even for processes realized by quasi-static operations, simply because the entropy production is positive in non-equilibrium steady states. In other words, $d'Q$ is not defined.
Possible extended forms of thermodynamic entropy

Therefore, the Shannon entropy in non-equilibrium steady states is not directly related to the heat.

In order to have an extended Clausius equality for quasi-static operations, we consider a modified heat or a renormalized heat $Q_{\text{ren}}$ such that $d'Q_{\text{ren}}$ is well-defined along a path in the extended state space. Among several possibilities, the simplest choice of $Q_{\text{ren}}$ may be the excess heat $Q_{\text{ex}}$ defined by

$$Q_{\text{ex}} = \int dt [J(t) - J_{\text{st}}(\alpha(t))],$$

(7)

where $J_{\text{st}}(\alpha)$ is the expectation value of the heat flux in the steady state of the system with the fixed parameter $\alpha$ (such as volume, temperature, and external force). By changing the parameter quite slowly, we expect that $d'Q_{\text{ex}}$ can be defined. Indeed, by considering an infinitely small step operation for specific mathematical models, we can confirm that $d'Q_{\text{ex}}$ is well-defined. Then, if this $d'Q_{\text{ex}}$ is a proper extension of $d'Q$, it could be expected that there exists a state variable $S$ satisfying

$$S(B) - S(A) = \int_A^B \frac{d'Q_{\text{ex}}}{T},$$

(8)

for any quasi-static operation.

The phenomenological framework of thermodynamics on the basis of $d'Q_{\text{ex}}$ was investigated by Oono and Paniconi [8]. The validity of this proposal can be confirmed by calculating the value of $\int d'Q_{\text{ex}}/T$ along closed paths in the extended state space. If the integration value is always zero, which corresponds to the integrability condition, $d'Q_{\text{ex}}/T$ can define a state variable by its integration along a path. This mathematical proposition was addressed by Ruelle [19] who studied an isokinetic model, independently of Oono and Paniconi. He pointed out that if the system is in the linear response regime, the integrability condition is satisfied and the state variable defined through the condition is equivalent to (5). After that, for a very wide class of systems, but still near equilibrium, the state variable can be constructed by this type of extended Clausius equality [20]–[22], while the statistical expression of the entropy is modified as the symmetrized Shannon entropy for general cases. (See (61) for its expression.) The integrability condition becomes more evident in the geometrical formulation for Markov jump processes [24, 25].

Formally speaking, there is no particular reason for the claim that $d'Q_{\text{ex}}$ is a proper extension of $d'Q$. Recently, new types of extended Clausius inequality have been proposed [26, 27] without employing the excess heat (7). With regard to such modification, it should be recalled that Hatano and Sasa introduced a renormalized heat, which was referred to as ‘excess heat’, but takes a different form from (7), and that they formulated a generalized second law on the basis of the renormalized heat [28]. In this paper, we discuss possible extensions of thermodynamic entropy from a viewpoint of the Hatano–Sasa relation.

This paper is organized as follows. In section 2, for simplicity, we introduce a simple Langevin model that describes non-equilibrium Brownian motion. Note however that our arguments can apply to general Markov processes. After quickly reviewing the second law of equilibrium thermodynamics, we address the question explicitly in the model.
section 3, we derive the Hatano–Sasa relation with emphasis of a role of the dual system. A non-trivial nature of systems with odd parity variables is also understood from the argument, and the extended Clausius equality with the excess heat is re-derived in a straightforward manner.

2. Question

If there exists an extension of the thermodynamic framework, it should apply to a wide class of non-equilibrium systems such as heat conduction systems, sheared systems, molecular motors, and so on. The description depends on the systems we study. For example, heat conduction systems are described by Hamiltonian equations supplemented with stochastic reservoirs, and molecular motors are described by Langevin equations with Markov processes for chemical reaction. Thus, an extension of the thermodynamic framework should be considered at least for these systems in a universal manner. Keeping such a universal feature in mind, however, we focus on the simplest example: a Langevin equation

\[ \gamma \dot{x} = f - \frac{\partial U(x; \nu)}{\partial x} + \xi \]  

that describes a non-equilibrium Brownian motion on a circuit of length \( L \), where the dot symbol on the top of \( x \) represents the time derivative, \( \gamma \) a friction constant, \( f \) a uniform driving force, \( U(x; \nu) \) an \( L \)-periodic potential with a parameter \( \nu \) that characterizes the shape of the potential, and \( \xi \) noise that satisfies

\[ \langle \xi(t) \xi(t') \rangle = 2\gamma T \delta(t - t'). \]  

We set \( \alpha = (f, \nu) \) and change the value of \( \alpha \) in time. We express the protocol as a function of time \( \dot{\alpha} \equiv (\alpha(t))'_{t=-\tau} \), setting \( \alpha(-\tau) = \alpha_i \) and \( \alpha(\tau) = \alpha_f \). Here, we assume that the external operation is performed only in the interval \( [-\tau', \tau'] \) with \( 0 \leq \tau' \ll \tau \). More precisely, \( \tau - \tau' \) is chosen to be much longer than the relaxation time of the system.

Although we mainly analyze (9) in this paper, the argument is not restricted to the specific model. Indeed, it is easy to replace the argument so as to investigate general Markov processes. In order to see the correspondence with general cases, we introduce a discrete time as \( t_k = -\tau + 2k\tau/K, \ 0 \leq k \leq K \). We assume the protocol as \( \alpha(t) = \alpha_k \) for \( t_k \leq t \leq t_{k+1} \) with \( 0 \leq k \leq K - 1 \). Let \( \Psi(x_k \rightarrow x_{k+1}; \alpha_k) \) be a transition probability to \( x_{k+1} \) from \( x_k \) in a time interval \( [t_k, t_{k+1}] \). (See equation (35) for the Langevin equation (9).) Suppose that the heat \( Q(x_k \rightarrow x_{k+1}; \alpha_k) \) is determined from an energetic consideration. (See equation (26) for the Langevin equation (9).) The results presented below are derived for models that satisfy

\[ -\beta Q(x_k \rightarrow x_{k+1}; \alpha_k) = \log \frac{\Psi(x_k \rightarrow x_{k+1}; \alpha_k)}{\Psi(x_{k+1} \rightarrow x_k; \alpha_k)}, \]  

which is called the local detailed balance condition [29]. It can be confirmed that the Langevin equation with the energetic interpretation satisfies the local detailed balance

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condition. For other interesting non-equilibrium steady states for systems in contact with multiple heat baths, (11) should be replaced by a different form. Corresponding to this replacement, the argument below also should be modified.

We first review the second law of thermodynamics for the model (9) with \( f = 0 \). The stationary probability density of \( x \), \( P_{\text{st}}(x; \nu) \), is expressed as

\[
P_{\beta}^{\text{can}}(x; \nu) = \exp[-\beta(U(x; \nu) - F(\beta, \nu))],
\]

(12)

where \( F \) corresponds to the free energy determined from the normalization of probability and \( \beta = 1/T \). The Boltzmann constant is set to unity. The Shannon entropy \( S \) in the equilibrium state is defined as

\[
S(\nu) \equiv -\int dx P_{\beta}^{\text{can}}(x; \nu) \log P_{\beta}^{\text{can}}(x; \nu).
\]

(13)

Since \( f = 0 \), \( \hat{\nu} = (\nu(t))_{t=\tau}^{\infty} \) with \( \nu(-\tau) = \nu_i \) and \( \nu(\tau) = \nu_f \) is used for the representation of the protocol. From the Langevin equation, we have the energy balance equation

\[
U(x(\tau); \nu_f) - U(x(-\tau); \nu_i) = \int_{-\tau}^{\tau} dt \dot{x} \int dt \circ \frac{\partial U(x; \nu)}{\partial x},
\]

(14)

where \( \circ \) represents the Stratonovich rule of the multiplication. The first term is interpreted as the work associated with the change in the parameter and the second term corresponds to the heat from the environment, which is denoted by \( Q \). That is, for a given trajectory \( \hat{x} \equiv (x(t))_{t=0}^{\tau} \), we define the heat as

\[
Q(\hat{x}; \hat{\nu}) \equiv \int_{-\tau}^{\tau} dt \dot{x} \circ \frac{\partial U(x; \nu)}{\partial x},
\]

(15)

which was first pointed out in [30]. Now, suppose that the system is in the equilibrium state at \( t = 0 \). It is then shown that

\[
S(\nu_f) - S(\nu_i) \geq \beta \langle Q(\hat{\nu}) \rangle,
\]

(16)

where \( \langle \rangle \) represents the average of many realizations for the given protocol \( \hat{\nu} \).

We present a proof of (16) by using the transition probability \( \Psi \). We notice the identity of the type

\[
\int dx_0 \int dx_1 \cdots \int dx_K G(\hat{x}; \hat{\alpha}) \prod_{k=0}^{K-1} \Psi(x_{k+1} \rightarrow x_k; \alpha_k) P_{\text{st}}(x_0; \alpha_0) = 1.
\]

(17)

As one example of such \( G \), we can choose

\[
G = \frac{P_{\text{st}}(x_K; \alpha_f)}{P_{\text{st}}(x_0; \alpha_i)} \prod_{k=0}^{K-1} \frac{\Psi(x_{k+1} \rightarrow x_k; \alpha_k)}{\Psi(x_k \rightarrow x_{k+1}; \alpha_k)}.
\]

(18)

Indeed, by substituting (18) into the left-hand side of (17), we can confirm the identity (17), which is expressed as

\[
\langle e^{-\Sigma} \rangle = 1
\]

(19)

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in terms of the total entropy production $\Sigma$ defined by

$$\Sigma \equiv -\log P_{\text{st}}(x(\tau); \alpha) + \log P_{\text{st}}(x(-\tau); \alpha_i) - \beta Q(\hat{x}; \hat{\alpha}).$$  \hspace{1cm} (20)

From $e^{-x} \geq 1 - x$, (19) leads to (16). The identity (19) is equivalent to the Jarzynski equality and it is also called an integral fluctuation theorem.

Here, from (12), we have the adiabatic theorem

$$\frac{\partial F}{\partial \nu} = \left\langle \frac{\partial U}{\partial \nu} \right\rangle$$  \hspace{1cm} (21)

in equilibrium states. Since this can be rewritten as

$$\frac{\partial S}{\partial \nu} = \beta \left[ \frac{\partial \langle U \rangle}{\partial \nu} - \left\langle \frac{\partial U}{\partial \nu} \right\rangle \right],$$  \hspace{1cm} (22)

we can derive

$$S(\nu_f) - S(\nu_i) = \beta \langle Q(\hat{\nu}) \rangle,$$  \hspace{1cm} (23)

for quasi-static operations $\hat{\nu}$ which are realized by a chain of infinitely small step operations. It should be noted that the equality (23) is related to the reversibility, because for the time-reversed protocol of $\hat{\nu}$, which is defined by $\hat{\nu}^\dagger(t) = \nu(-t)$, (23) leads to the reversibility

$$\langle Q(\hat{\nu}^\dagger) \rangle = -\langle Q(\hat{\nu}) \rangle$$  \hspace{1cm} (24)

for quasi-static operations $\hat{\nu}$. Without the reversibility (24), the equality part in (16) does not hold.

Although we have focused on the case that $\beta$ is constant in time, it is easy to extend the argument so as to derive the Clausius relation for the protocol in which $\beta$ is changed as a function of time.

Now, we consider the case $f \neq 0$. In this case, the stationary distribution $P_{\text{st}}(x; \alpha)$ is not canonical. Nevertheless, suppose that the entropy $S$ is given by the Shannon entropy of $P_{\text{st}}(x; \alpha)$:

$$S(\alpha) \equiv -\int dx P_{\text{st}}(x; \alpha) \log P_{\text{st}}(x; \alpha).$$  \hspace{1cm} (25)

The heat, the energy transfer from the bath, is given by

$$Q(\hat{x}; \hat{\alpha}) \equiv \int_{-\tau}^\tau dt \dot{x} \circ \left( \frac{\partial U(x; \nu)}{\partial x} - f \right).$$  \hspace{1cm} (26)

Since we can derive (19) even for this case by using the same method, we obtain

$$S(\alpha_f) - S(\alpha_i) \geq \beta \langle Q(\hat{\alpha}) \rangle$$  \hspace{1cm} (27)

for general cases. This implies the second law of thermodynamics for non-equilibrium states. However, since $\langle Q(\hat{\alpha}^\dagger) \rangle \neq -\langle Q(\hat{\alpha}) \rangle$ for general quasi-static operations $\hat{\alpha}$, the
equality in (27) does not hold for any quasi-static operations with \( f \neq 0 \). Therefore, the entropy in non-equilibrium steady states with \( f \neq 0 \) cannot be determined from the heat as Clausius did.

These considerations lead to the following explicit question for models that satisfy (11). (i) Find a renormalized heat \( Q^{\text{ren}} \) that satisfies

\[
\int d'Q^{\text{ren}} = 0
\]  

(28)

along closed paths in the extended state space with \( \beta \) fixed. (ii) Investigate whether or not the state variable \( S \) defined by \( Q^{\text{ren}} \) satisfies the inequality

\[
S(\alpha_f) - S(\alpha_i) \geq \beta \langle Q^{\text{ren}}(\hat{\alpha}) \rangle
\]  

(29)

for any processes given by \( \hat{\alpha} \). (iii) Derive a statistical expression of \( S(\alpha) \).

3. Result

3.1. Dual system

A key step in solving the question is to find a new identity, which may be similar to (19), but may be defined for a quantity reversible in quasi-static operations. Recall that the irreversibility \( \langle Q(\hat{\alpha}^\dagger) \rangle \neq -\langle Q(\hat{\alpha}) \rangle \) for general quasi-static operations \( \hat{\alpha} \) originates from the persistent heat generation (entropy production) in non-equilibrium steady states. We thus need to remove this persistent contribution. Our basic strategy, which was proposed in [28], is to employ the decomposition of the force

\[
F(x; \alpha) = f - \frac{\partial U(x; \nu)}{\partial x}
\]  

(30)

in the form

\[
F(x; \alpha) = b(x; \alpha) - T \frac{\partial \phi(x; \alpha)}{\partial x}
\]  

(31)

using the individual entropy

\[
\phi(x; \alpha) \equiv -\log P_{\text{st}}(x; \alpha).
\]  

(32)

That is, we rewrite (9) as

\[
\gamma \dot{x} = b(x; \alpha) - T \frac{\partial \phi(x; \alpha)}{\partial x} + \xi.
\]  

(33)

One may see that (31) is nothing but the definition of \( b(x; \alpha) \), but as described in [28], \( b(x; \alpha) \) and \( -T \partial_x \phi(x; \alpha) \) in (31) correspond to the irreversible and reversible parts of the force, respectively. We shall explain the origin of these names.

As a basic property of fluctuation, we review the concept of ‘duality’. We consider the ensemble of trajectories \( \hat{x} = \{x(t)\}_{t=-\tau}^\tau \) in non-equilibrium steady states with the
parameter fixed. We denote the probability measure of trajectories as $\mathcal{P}(\hat{x})$. For this ensemble, we can consider the ensemble consisting of time-reversed trajectories $\hat{x}^\dagger$ such that $x^\dagger(t) = x(-t)$. We then ask for a stochastic process that yields the ensemble of $\hat{x}^\dagger$. Formally, such a stochastic process, which is called a dual process, generates the probability measure of trajectories $\mathcal{P}^\dagger(\hat{x}) = \mathcal{P}(\hat{x}^\dagger)$. We can prove that for the Langevin equation (9), the dual process is given by the Langevin equation in the form

$$\gamma \dot{x} = -b(x; \alpha) - T \frac{\partial \phi(x; \alpha)}{\partial x} + \xi.$$  (34)

By comparing (33) and (34), one finds that $b(x)$ and $-T \partial_x \phi(x)$ in the force decomposition (31) correspond to the irreversible and reversible parts, respectively.

We present a proof. For the Langevin equation (33), the probability density of trajectories with $x(-\tau)$ fixed is written as

$$\Psi(\hat{x}) = C e^{-\frac{\beta}{4\gamma} \int_{-\tau}^{\tau} dt \left[ (\gamma \dot{x} - b + T \partial_x \phi)^2 - \frac{2}{\beta} \partial_x (T \partial_x \phi - b) \right]},$$  (35)

where $C$ is the normalization constant. (See the appendix in [31] for a derivation through the naive discretization of time.) Let $\tilde{\Psi}$ be the probability of trajectories for the Langevin equation (34). That is,

$$\tilde{\Psi}(\hat{x}) = C e^{-\frac{\beta}{4\gamma} \int_{-\tau}^{\tau} dt \left[ (\gamma \dot{x} + b + T \partial_x \phi)^2 - \frac{2}{\beta} \partial_x (T \partial_x \phi + b) \right]}.$$  (36)

By taking the ratio of $\Psi(\hat{x})$ and $\tilde{\Psi}(\hat{x}^\dagger)$, we obtain

$$\frac{\Psi(\hat{x})}{\tilde{\Psi}(\hat{x}^\dagger)} = e^{-\int_{-\tau}^{\tau} dt \left[ \partial_x \phi + (b + T \partial_x \phi)/\gamma \right]}.$$  (37)

From the steady state condition $b e^{-\phi} = \gamma J = \text{const}$, we have $\partial_x b = b \partial_x \phi$. Thus,

$$\Psi(\hat{x}) P_{st}(x(-\tau)) = \tilde{\Psi}(\hat{x}^\dagger) P_{st}(x(\tau)).$$  (38)

This relation indicates that $\tilde{\Psi}$ is the dual transition probability of $\Psi$, because $\mathcal{P}^\dagger(\hat{x}) = \tilde{\Psi}(\hat{x}) P_{st}(x(-\tau))$. We thus conclude that (34) is the Langevin equation describing the dual process. As seen in the proof, the so-called Jacobian term $2\partial_x (T \partial_x \phi - b)/\beta$ in the path integral expression (35) is inevitable to obtain (38).

### 3.2. Extended Clausius relation

Now, we consider an external operation with a protocol $\hat{\alpha}$. For a given trajectory $\hat{x}$, the heat (from the heat bath) is given by

$$Q(\hat{x}; \hat{\alpha}) \equiv \int_{-\tau}^{\tau} dt \dot{x} \circ \left( T \frac{\partial \phi(x; \alpha)}{\partial x} - b \right).$$  (39)

Suppose that this trajectory $\hat{x}$ is also observed in the dual Langevin equation. Then, the heat is

$$Q^\dagger(\hat{x}; \hat{\alpha}) \equiv \int_{-\tau}^{\tau} dt \dot{x} \circ \left( T \frac{\partial \phi(x; \alpha)}{\partial x} + b \right).$$  (40)

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By expressing the Shannon entropy of $P_{st}$ as

$$S(\alpha) = \int dx \phi(x;\alpha)P_{st}(x;\alpha),$$

we can prove

$$S(\alpha_f) - S(\alpha_i) \geq \beta(\langle Q \rangle + \langle Q^\dagger \rangle)/2,$$

(42)

where the equality holds for the quasi-static processes. This is the extended Clausius inequality which is valid even far from equilibrium. The result gives the answer to (29) by setting $Q_{ren} = (Q + Q^\dagger)/2$ and $S(\alpha) = S(\alpha)$. The proof of (42) is the following. We first define

$$Y \equiv \int dt \dot{\alpha} \frac{\partial \phi(x;\alpha)}{\partial \alpha}.$$

(43)

From (39) and (40), we immediately obtain

$$\beta(Q + Q^\dagger)/2 = \phi(x(\tau);\alpha_f) - \phi(x(-\tau);\alpha_i) - Y.$$

(44)

This may be interpreted as a balance equation of the individual entropy $\phi$. Next, by substituting

$$G = \frac{P_{st}(x_K;\alpha_f)}{P_{st}(x_0;\alpha_i)} \prod_{k=0}^{K-1} \frac{P_{st}(x_k;\alpha_k)}{P_{st}(x_{k+1};\alpha_k)}$$

(45)

into the right-hand side of (17) we can confirm the identity (17). This is expressed as a non-equilibrium identity

$$\langle e^{-Y} \rangle = 1,$$

(46)

which leads to a generalized second law

$$\langle Y \rangle \geq 0.$$

(47)

Since the adiabatic theorem in this case leads to $\langle Y \rangle = 0$ for quasi-static operations, the equality in (47) holds for quasi-static processes. By combining (44) with (47), we obtain (42).

In the proof described above, one may doubt that (44) is also valid for non-Langevin cases. We thus present another proof so that we can consider general Markov processes. By using the steady state distribution $P_{st}(x;\alpha_k)$, the dual transition probability $\Psi^\dagger(x_k \rightarrow x_{k+1};\alpha_k)$ is defined as

$$\Psi^\dagger(x_{k+1} \rightarrow x_k;\alpha_k) = \frac{\Psi(x_k \rightarrow x_{k+1};\alpha_k)P_{st}(x_k;\alpha_k)}{P_{st}(x_{k+1};\alpha_k)}.$$

(48)

From (11) and (48), we obtain

$$\beta[Q(x_k \rightarrow x_{k+1};\alpha_k) + Q^\dagger(x_k \rightarrow x_{k+1};\alpha_k)]/2 = -\log \frac{P_{st}(x_{k+1};\alpha_k)}{P_{st}(x_k;\alpha_k)}.$$

(49)
Possible extended forms of thermodynamic entropy

The right-hand side is rewritten as

\[ - \log P_{st}(x_{k+1}; \alpha_k) + \log P_{st}(x_{k+1}; \alpha_{k+1}) - \log P_{st}(x_{k+1}; \alpha_{k+1}) + \log P_{st}(x_k; \alpha_k). \]

By taking the limit \( K \to \infty \), we obtain (44).

We can rewrite (42) as another form. Let us define \( Q_{hk} \) as

\[ Q_{hk} \equiv (Q - Q^\dagger)/2, \]

which is interpreted as an intrinsic part of irreversible heat. Then, (42) becomes

\[ S(\alpha_1) - S(\alpha_0) \geq \beta(\langle Q \rangle - \langle Q_{hk} \rangle). \]

This is the expression proposed in [28]. Motivated by [8], \( Q_{hk} \) was referred to as the house-keeping heat and \( Q - Q_{hk} \) was called the ‘excess heat’. However, this excess heat is different from the more naive one given in (7). More explicitly, we can write \( \langle Q_{hk} \rangle = -\int dt \langle \dot{x}(t) \circ b(x(t)) \rangle \) whose integrand is different from the steady state heat flux \( -J_{st} = \langle \dot{x}(t) \circ b(x(t)) \rangle_{st} \), where \( \langle \rangle_{st} \) represents the expectation value in the steady state of the system with \( \alpha(t) \) fixed virtually. It should be noted that there is no difference when we do not change the parameter \( \alpha \) in time. Since we did not have any knowledge on the nature of the house-keeping heat for time-dependent cases, we identified (51) to be a mathematical expression of the house-keeping heat in the phenomenological proposal.

The identity (46) takes the same form as (19). Interestingly, when we consider the decomposition

\[ \Sigma = Y + Z, \]

\( Z \) is equal to \(-Q_{hk} = -(Q - Q^\dagger)/2 \), and \( Z \) also satisfies

\[ \langle e^{-Z} \rangle = 1, \]

which was presented by Speck and Seifert [32]. See also [33]. The identity is obtained by choosing

\[ G = \prod_{k=0}^{K-1} \frac{\Psi(x_{k+1} \rightarrow x_k; \alpha_k) P_{st}(x_{k+1}; \alpha_k)}{\Psi(x_k \rightarrow x_{k+1}; \alpha_k) P_{st}(x_k; \alpha_k)}, \]

in (17). The decomposition (53) that satisfies relations (19), (46), and (54) seems to be rather surprising, but we do not understand the physical principle behind this fact.

3.3. Cases with odd parity variables

The inequality (42) can be derived for a wide class of systems, as is understood from the derivation method. However, unfortunately, there is a restriction of the application. The inequality (42) does not hold for systems with odd parity variables. In order to demonstrate the difficulty, we consider the under-damped version of the Langevin equation (9), which takes the form

\[ m\ddot{x} + \gamma \dot{x} = f - \frac{\partial U(x; \nu)}{\partial x} + \xi, \]

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where \( m \) is the mass. The dynamical variable in this model is \( z = (x, p) \) with \( p = m \dot{x} \). Since \( z \) becomes \( z^* = (x, -p) \) for the time reversal operation, \( z \) contains the odd parity variable. For the trajectory \( \hat{z} = (z(t))_{t=-\tau}^{\tau} \), the time-reversed trajectory \( \hat{z}^\dagger \) is given by \( \hat{z}^\dagger(t) = z^*(-t) \). For this model, we have a transition probability \( \Psi(z_k \to z_{k+1}; \alpha_k) \) in the discrete time description. Then, the local detailed balance condition (11) is replaced by

\[
-\beta Q(z_k \to z_{k+1}; \alpha_k) = \log \frac{\Psi(z_k \to z_{k+1}; \alpha_k)}{\Psi(z_{k+1}^* \to z_k^*; \alpha_k)}.
\]

(57)

All the arguments in this subsection apply to general Markov processes satisfying (57).

Even in this case, the non-equilibrium equality (46) is valid, and this leads to the generalized second law (47). However, its energetic interpretation is not clearly obtained, as pointed out by [34, 35]. Following our basic strategy respecting the reversible part of heat, we expect that \( Q + Q^\dagger \) is related to the existence of a state variable. Here, the dual system is defined as that yielding the ensemble of the reversed path \( \hat{z}^\dagger \) starting from \( z^* \), where \( z \) is taken from the stationary distribution of the system with \( \alpha_f \). That is, the transition probability of the dual system is defined as

\[
\Psi^\dagger(z_{k+1}^* \to z_k^*; \alpha_k) \equiv \frac{\Psi(z_k \to z_{k+1}; \alpha_k) P_{st}(z_k; \alpha_k)}{P_{st}(z_{k+1}; \alpha_k) P_{st}(z_k^*; \alpha_k)}.
\]

(58)

Then, (49) is replaced by

\[
\beta[Q(z_k \to z_{k+1}; \alpha_k) + Q^\dagger(z_k \to z_{k+1}; \alpha_k)] = -\log \frac{P_{st}(z_{k+1}; \alpha_k) P_{st}(z_k^*; \alpha_k)}{P_{st}(z_k; \alpha_k) P_{st}(z_{k+1}^*; \alpha_k)}.
\]

(59)

It should be noted that \( P_{st}(z) \neq P_{st}(z^*) \) in this example and that this property holds for many systems. Obviously, (49) holds for some examples that satisfy \( P_{st}(z) = P_{st}(z^*) \). By setting

\[
\phi_{sym}(z, \alpha) \equiv -\frac{1}{2} [\log P_{st}(z; \alpha) + \log P_{st}(z^*; \alpha)],
\]

(60)

we define

\[
S_{sym}(\alpha) \equiv \int dz P_{st}(z) \phi_{sym}(z; \alpha)
\]

(61)

and

\[
Y_{sym} \equiv \int d\alpha \frac{\partial \phi_{sym}(z; \alpha)}{\partial \alpha}.
\]

(62)

Now, taking the limit \( K \to \infty \) in (59), we obtain

\[
\beta(\langle Q \rangle + \langle Q^\dagger \rangle)/2 = S_{sym}(\alpha_f) - S_{sym}(\alpha_i) - \langle Y_{sym} \rangle.
\]

(63)

Since \( Y_{sym} \) is not related to \( Y \), we cannot combine the generalized second law (47) with (63).

Nevertheless, when we focus on quasi-static processes near equilibrium, we can rewrite (63) as a stimulating form. Explicitly, we consider a step process \( \alpha(t) = \alpha_0 + \delta \alpha_1 \theta(t) \),
where $\alpha_0$ and $\alpha_1$ are two parameter values, and $\theta(\ )$ is the Heaviside step function. We also set $\epsilon = \beta fL$. We then assume that the dimensionless quantities $\epsilon$ and $\delta$ are small. In the step process, we have

$$\langle Y^{\text{sym}} \rangle = \delta \alpha_1 \int dz \, P_{\text{st}}(z; \alpha) \frac{\partial \phi^{\text{sym}}(z; \alpha)}{\partial \alpha}. \quad (64)$$

By using the equality

$$\int dz \, P_{\text{st}}(z; \alpha) \frac{\partial \phi(z; \alpha)}{\partial \alpha} = 0, \quad (65)$$

we obtain

$$\langle Y^{\text{sym}} \rangle = \frac{\delta \alpha_1}{4} \int dz \left[ P_{\text{st}}(z; \alpha) \frac{\partial \phi(z^*; \alpha)}{\partial \alpha} + (z \leftrightarrow z^*) \right]. \quad (66)$$

By noting $P_{\text{st}}(z^*; \alpha) - P_{\text{st}}(z; \alpha) = O(\epsilon)$, we find that

$$\phi(z^*; \alpha) = - \log[P_{\text{st}}(z; \alpha) + P_{\text{st}}(z^*; \alpha) - P_{\text{st}}(z; \alpha)]$$
$$= - \log P_{\text{st}}(z; \alpha) - \log \left[ 1 + \frac{P_{\text{st}}(z^*; \alpha) - P_{\text{st}}(z; \alpha)}{P_{\text{st}}(z; \alpha)} \right]$$
$$= \phi(z; \alpha) - \frac{P_{\text{st}}(z^*; \alpha) - P_{\text{st}}(z; \alpha)}{P_{\text{st}}(z; \alpha)} + O(\epsilon^2). \quad (67)$$

This gives

$$\int dz \, P_{\text{st}}(z; \alpha) \frac{\partial \phi(z^*; \alpha)}{\partial \alpha} = - \int dz \, P_{\text{st}}(z; \alpha) \frac{\partial}{\partial \alpha} \frac{P_{\text{st}}(z^*; \alpha)}{P_{\text{st}}(z; \alpha)} + O(\epsilon^2)$$
$$= - \int dz \, P_{\text{st}}(z^*; \alpha) \frac{\partial \phi(z; \alpha)}{\partial \alpha} + O(\epsilon^2). \quad (68)$$

By substituting (68) into (66), we obtain

$$\langle Y^{\text{sym}} \rangle = O(\epsilon^2 \delta). \quad (69)$$

Here, we rewrite $\langle \rangle$ as $\langle \rangle_{\hat{a}}$ in order to explicitly express the protocol dependence. We then denote the expectation value with respect to $P^1(\ ; \hat{a})$ by $\langle \rangle_{\hat{a}}^{1 \dagger}$. From the definitions, we have $\langle Q^1 \rangle_{\hat{a}} = - \langle Q^1 \rangle_{\hat{a}}^{1 \dagger}$. Noting $\langle Q^1 \rangle_{\hat{a}}^{1 \dagger} = O(\epsilon^2)$ in steady states, we see $\langle Q^1 \rangle_{\hat{a}} = \langle Q^1 \rangle_{\hat{a}}^{1 \dagger} = O(\epsilon^2 \delta)$. These estimations lead to

$$\langle Q^1 \rangle_{\hat{a}} = - \langle Q \rangle_{\hat{a}}^{1 \dagger} + O(\epsilon^2 \delta). \quad (70)$$

By substituting (69) and (70) into (63), we obtain

$$S_{\text{sym}}(\alpha_1) - S_{\text{sym}}(\alpha_0) = \beta(\langle Q \rangle_{\hat{a}} - \langle Q \rangle_{\hat{a}}^{1 \dagger})/2 + O(\epsilon^2 \delta). \quad (71)$$

This extended Clausius relation has the advantage that the right-hand side can be obtained by a heat measurement in experiments without knowing the details of a system. It should be noted that

$$\langle Q \rangle_{\hat{a}} - \langle Q \rangle_{\hat{a}}^{1 \dagger}/2 = Q^{\text{ex}} + O(\delta^2). \quad (72)$$

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Therefore, (71) is rewritten as
\[ dS^{\text{sym}} = \beta d'Q^{\text{ex}} + O(\epsilon^2), \]
which gives the solution to (28) and the equality part in (29) by setting \( S = S^{\text{sym}} \) and \( Q^{\text{ren}} = Q^{\text{ex}} \) near equilibrium. However, the inequality in (29) is not valid in this formulation. It should be noted that (73) holds for over-damped cases, where \( S^{\text{sym}} \) becomes the Shannon entropy.

The relation (71) with the symmetrized Shannon entropy was proposed in [20, 21] and developed further in [22]. (See also [23] for the mathematically rigorous derivation for Markov jump processes.) The relation (71) can be derived for (maybe) all non-equilibrium steady state systems near equilibrium including heat conduction systems and sheared systems.

4. Concluding remarks

In this paper, we have discussed a possible framework of steady state thermodynamics on the basis of a review of the Hatano–Sasa relation. In particular, a technically important message is that the extended Clausius relation in the form (42) can be understood from two identities, the balance equation (44) and the generalized Jarzynski equality (46). When we consider systems with odd parity variables, (46) is still valid, but (44) is modified as (63) which contains \( Y^{\text{sym}} \) that cannot be connected to (46). Nevertheless, for quasi-static processes near equilibrium, only the condition (63) gives the definition of the state variable in terms of the excess heat that can be measured in a calorimetric experiment.

Recently, Bertini et al have proposed a different type of extension of the Clausius inequality by studying fluctuating hydrodynamics for a density field. Their formulation utilizes a decomposition similar to (31) and the work associated with the anti-symmetric current is subtracted. Although it shares common concepts with our formulation, there might be essential difference in the origin of the inequality. For the moment, their inequality can be derived only for a special type of fluctuating hydrodynamics. It might be interesting to uncover a universal structure behind their formulation.

As a different recent approach, Maes and Netočný have formulated an extended Clausius relation in connection with dynamical fluctuation theory [26]. Their key concept is a modified system in which a time-dependent distribution becomes stationary. Since a framework using such a modified system often appears in recent non-equilibrium statistical mechanics [36, 37], this might be one direction which we should consider seriously.

Furthermore, by considering an extension of the axiomatic formulation of the thermodynamic entropy [38], Lieb and Yngvason have argued non-equilibrium entropy from the viewpoint of adiabatic accessibility [39]. Here, it should be noted that a set of axioms of ‘adiabatic processes’ formulated in [38] precisely specifies real adiabatic processes, while a set of axioms of ‘adiabatic processes’ formulated in non-equilibrium state spaces might allow us to make different models of ‘adiabatic processes’.

What is the most promising approach? At present, we do not have an answer. Nevertheless, if we respect the operational determination of the entropy, the Hatano–Sasa formulation using \( Q^1 \), the result by Bertini et al, and the approach by Maes–Netočný
have serious difficulties. The only possible way in the operational framework may be to employ $d'Q^{ex}$, but we know that the thermodynamic framework on the basis of $d'Q^{ex}$ may be restricted to a class of systems near equilibrium. If we assume that $d'Q^{ex}$ plays an essential role, we should have another method. One possible extension in this direction is to introduce the integration factor such that

$$dS = d'Q^{ex}/T_{eff}. \quad (74)$$

The previous result indicates that $T_{eff} = T$ and $S = S^{sym}$ near equilibrium. As far as we know, $T_{eff}$ and $S$ have not been calculated in this approach. It would be interesting if one could find the physical significance of $T_{eff}$.

All the arguments in this paper are too formal. The most important question to be solved may be to find phenomena for which an extended form of the entropy provides a useful understanding. As one example, Sasa and Tasaki studied the force arising from a change in the statistical weight in non-equilibrium steady states on the basis of a phenomenological framework of steady state thermodynamics [40]. Although this proposal was too naive, the direction of thinking might be correct. It would be amazing to find an experimental configuration that extracts purely statistical mechanical effects in non-equilibrium steady states.

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Possible extended forms of thermodynamic entropy

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