Irreversibility resulting from contact with a heat bath caused by the finiteness of the system

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When a small dynamical system that is initially in contact with a heat bath is detached from this heat bath and then caused to undergo a quasi-static adiabatic process, the resulting statistical distribution of the system's energy differs from that of an equilibrium ensemble. Subsequent contact of the system with another heat bath is inevitably irreversible, hence the entire process cannot be reversed without a net energy transfer to the heat baths.

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I. INTRODUCTION

Ordinary thermodynamics assumes the extensivity of the system in question, and it is not applicable directly to finite systems. Hill [1] developed a framework to deal with systems that are moderately large and homogeneous, except for their boundaries. In this framework, the corrections to the thermodynamic behavior due to the the effect of the surfaces and the edges of the system are incorporated in the form of an expansion in the number of the constituent atoms, N. Our interest here is in systems further removed from the thermodynamic limit, such as mesoscopic devices and molecular motors, which are intrinsically small and heterogeneous and for which the method of Ref. [1] is not sufficient. Hereafter, we call such systems "small systems."

In this paper our purpose is to elucidate the distinctive nature of small systems by considering the following process, which we denote by $\{T_1, a_1; T_2, a_2\}$ (see Fig. 1).

(i) First, a small system is in thermal contact with a heat bath of temperature T_1. (Throughout this paper we assume that both the interaction energy associated with the thermal contact and the work required to change this contact are negligibly small [2].)

(ii) We then gradually remove the thermal contact between the system and the heat bath.

(iii) Next, we change some arbitrary control parameter of the system, a, from its initial value a_1 to a new value a_2 *quasistatically*. We measure the work required to make this change as the increase of the energy of the small system.

(iv) Finally, we gradually establish a thermal contact between the system and the second heat bath of temperature T_2.

We now introduce the concept of the "reversibility" associated with the process $\{T_1, a_1; T_2, a_2\}$.

Definition. The process $\{T_1, a_1; T_2, a_2\}$ is called "reversible" if no net energy is transferred, on the statistical average over infinite number of repetitions, from or to either heat bath through the composite processes of $\{T_1, a_1; T_2, a_2\}$ followed by $\{T_2, a_2; T_1, a_1\}$. If the process $\{T_1, a_1; T_2, a_2\}$ is

not reversible, it is called "irreversible."

Reversibility, therefore, implies that the statistical average of the work needed for the process $\{T_1, a_1; T_2, a_2\}$ is the opposite of that for the process $\{T_2, a_2; T_1, a_1\}$. In macroscopic systems, reversibility holds if and only if T_2 is equal to the temperature of the (macroscopic) system after operation (iii). This fact is a prerequisite for the existence of thermodynamics, in which the Helmholtz free energy can be used to relate equilibrium states at different temperatures. For small systems, however, the situation is completely different:

Statement. The processes $\{T_1, a_1; T_2, a_2\}$ for small systems are irreversible, except for some "special" cases.

It is important to note that for small systems we cannot define the temperature unambiguously, at least when they are isolated, and the energy of the system at the end of operation (ii) is a strictly statistical quantity. (This is related to the fact that the operation of removing the thermal contact is intrinsically irreversible, however small the work associated with this operation.) In order to understand intuitively how these features of small systems lead to irreversibility, we first describe qualitatively what happens in the processes (i)–(iv).

In (i), the energy E of the small system fluctuates, and its statistics obey the canonical ensemble at temperature T_1. In (ii), the energy of the system is fixed at a particular value. This energy E is a stochastic variable, and its distribution is given by the canonical ensemble at temperature T_1, as long as the removal of the thermal contact with the heat bath is sufficiently gentle [2]. In (iii), the energy of the small system changes in such a manner that the phase volume enclosed by a constant energy surface, $J(E, a)$, [see Eq. (22) in the text] is invariant. This follows from the ergodic invariant theorem [3]. With the exception of those systems for which $J(E, a)$ has a special functional property, the statistical distribution of E at the end of this adiabatic process is no longer consistent with the canonical ensemble at *any* temperature. In (iv), this noncanonical distribution of the energy relaxes *irreversibly* (in the ordinary sense) to the canonical distribution at the temperature T_2, whether or not, on statistical average, the
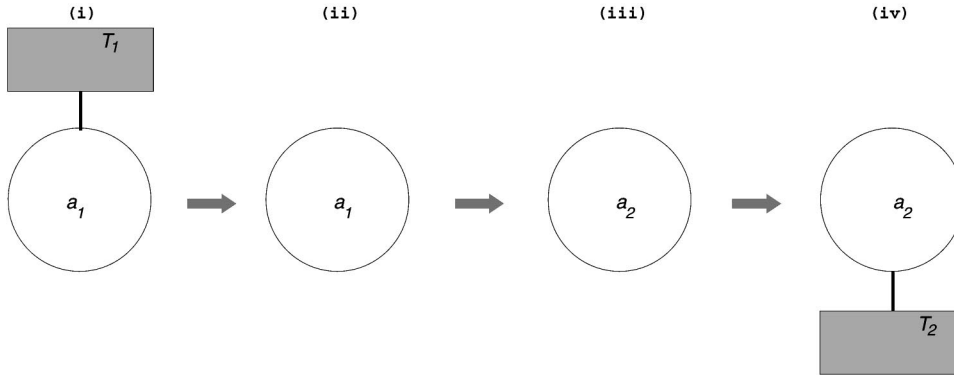
FIG. 1. The process $\{T_1,a_1;T_2,a_2\}$ is schematically depicted as (i)$\Rightarrow$(ii)$\Rightarrow$(iii)$\Rightarrow$(iv). The gray boxes represent the heat baths at the temperatures indicated therein, and the circles represent the small system. The thick solid lines in (i) and (iv) denote the thermal contact between the small system and the two heat baths.

net energy transfer between the system and the heat bath is zero. We note that the essential feature distinguishing small systems from macroscopic systems is the distortion of the energy distribution in (iii), which can be neglected in macroscopic thermodynamics.

In the following sections we prove the above statement with an argument based on the ergodicity hypothesis of Hamiltonian dynamical systems. The outline of the proof is as follows. In Sec. II we prove the three lemmas as preparatory steps for the main statement. In Sec. III we prove the main statement. In Sec. IV we discuss the physical meaning of the Statement. We also show there the necessary condition for the process $\{T_1,a_1;T_2,a_2\}$ to be reversible.

II. THREE LEMMAS

In order to prove the Statement, we first introduce three lemmas.

Lemma 1—The entropy S (see below) remains invariant in the process (iii).

Proof. We consider an ensemble of the mechanical system which is described by a time-dependent Hamiltonian H. Let us denote by $P(\Gamma,t)$ the normalized distribution function of the ensemble at time t, where Γ is the phase coordinates of the system, i.e., the position coordinates and the momenta of the system. The entropy S is defined as, a functional of the normalized distribution P,

$$S[P(\cdot,t)]\equiv -\int_{\{\Gamma\}}P(\Gamma,t)\ln P(\Gamma,t)d\Gamma, \qquad (1)$$

where the symbol $\{\Gamma\}$ indicates that the integral is taken over the whole phase space.

Let us now examine the behavior of the entropy S with time. First, we note that the time evolution of the distribution function is described by the so-called Liouville's equation,

$$\frac{\partial P(\Gamma,t)}{\partial t}=-\left(\frac{\partial}{\partial q}\frac{\partial H(\Gamma,t)}{\partial p}-\frac{\partial}{\partial p}\frac{\partial H(\Gamma,t)}{\partial q}\right)P(\Gamma,t)$$

$$\equiv -\frac{\partial}{\partial\Gamma}[V_{(\Gamma,t)}P(\Gamma,t)],$$

where q and p are the position coordinates and the momenta of the system, respectively, and we have introduced here the velocity of the system point in the phase space, $V_{(\Gamma,t)}$. The velocity $V_{(\Gamma,t)}$ satisfies

$$\frac{\partial}{\partial\Gamma}V_{(\Gamma,t)}=0, \qquad (2)$$

which can be checked by the equation of motion of the mechanical system.

Using Eq. (2), we evaluate the time derivative of the entropy S,

$$\frac{\partial S[P(\cdot,t)]}{\partial t}=-\int_{\{\Gamma\}}\frac{\partial P(\Gamma,t)}{\partial t}\frac{d(x\ln x)}{dx}\bigg|_{x=P(\Gamma,t)}d\Gamma$$

$$=\int_{S_\Gamma}V_{(\Gamma,t)}P(\Gamma,t)\ln P(\Gamma,t)dS_\Gamma,$$

where the symbol S_Γ represents the surface integral over the surface enclosing the phase space and we have used Eq. (2) and performed the integration by parts. As we are interested in a mechanical system such that all particles are confined in a finite region in position space and that the Hamiltonian involves the kinetic energy terms $p^2/2m$, $P(\Gamma,t)$ vanishes at any point on $S_{\{\Gamma\}}$. The lemma applies to the process (iii), since a quasistatic adiabatic process is realized by a time-dependent Hamiltonian.

Lemma 2—A canonical distribution is the distribution to maximize the entropy S subject to the constraint that the ensemble average of the energy is E, i.e.,

$$\int_{\{\Gamma\}}H(\Gamma)P(\Gamma)d\Gamma=E, \qquad (3)$$

where the canonical distribution characterized by the Hamiltonian H and the temperature T is defined as

$$P_c(\Gamma;T,H)\equiv\frac{e^{-[H(\Gamma)]/T}}{Z(T,H)}, \qquad (4)$$

with $Z(T,H)$ being the normalization constant,

$$Z(T,H)=\int_{\{\Gamma\}}e^{-[H(\Gamma)]/T}d\Gamma. \qquad (5)$$

Proof. Let us examine the difference between the entropies of two distributions, the canonical distribution P_c and any other distribution P, both being normalized and satisfying the constraint condition (3). We find

$$S[P_c] - S[P] = \int_{\{\Gamma\}} P(\Gamma) \ln \frac{P(\Gamma)}{P_c(\Gamma)} d\Gamma, \qquad (6)$$

where we have used Eq. (4) and the conditions

$$\int_{\{\Gamma\}} P_c(\Gamma) d\Gamma = \int_{\{\Gamma\}} P(\Gamma) d\Gamma = 1,$$

$$\int_{\{\Gamma\}} H(\Gamma) P_c(\Gamma) d\Gamma = \int_{\{\Gamma\}} H(\Gamma) P(\Gamma) d\Gamma = E.$$

We have written here the canonical distribution as $P_c(\Gamma)$ for the simplicity of notation, though precisely it implies $P_c(\Gamma; T, H)$ in our notation. The right-hand side of Eq. (6) is known as the *relative entropy* and has been known to be non-negative, as we easily demonstrate as follows:

$$\int_{\{\Gamma\}} P(\Gamma) \ln \frac{P(\Gamma)}{P_c(\Gamma)} d\Gamma$$

$$= \int_{\{\Gamma\}} P(\Gamma) \ln \frac{P(\Gamma)}{P_c(\Gamma)} d\Gamma - \int_{\{\Gamma\}} [P(\Gamma) - P_c(\Gamma)] d\Gamma$$

$$= \int_{\{\Gamma\}} P_c(\Gamma) \left(\frac{P(\Gamma)}{P_c(\Gamma)} \ln \frac{P(\Gamma)}{P_c(\Gamma)} - \frac{P(\Gamma)}{P_c(\Gamma)} + 1 \right) d\Gamma \geqslant 0. \qquad (7)$$

The inequality in the last line follows from the fact that $x \ln x - x + 1 \geqslant 0$ for $x \geqslant 0$. The equality holds if and only if $x = 1$, so that only the canonical distribution realizes the maximum value of S. Thus the lemma is proved.

Lemma 3—Let $\langle H \rangle_{(T,H)}$ be the ensemble average of the Hamiltonian H over the canonical distribution $P_c(\Gamma; T, H)$. (Hereafter we shall denote, in general, the canonical average using the distribution $P_c(\Gamma; T, H)$ by $\langle \cdot \rangle_{(T,H)}$, that is, for an arbitrary physical quantity A defined on the phase space: $\langle A \rangle_{(T,H)} \equiv \int_{\{\Gamma\}} A(\Gamma) P_c(\Gamma; T, H) d\Gamma$). Then $\langle H \rangle_{(T,H)}$ is monotonically increasing with T. The entropy $S[P_c(\cdot; T, H)]$ is also monotonically increasing with T.

Proof. Differentiating $\langle H \rangle_{(T,H)}$ with respect to T, we obtain

$$\frac{\partial \langle H \rangle_{(T,H)}}{\partial T} = \frac{\langle (H - \langle H \rangle_{(T,H)})^2 \rangle_{(T,H)}}{T^2}. \qquad (8)$$

Since the value of H is indeed distributed under the canonical distribution, the right-hand side of Eq. (8) is positive.

Likewise, differentiating $S[P_c(\cdot; T, H)]$ with respect to T, we obtain

$$\frac{\partial S[P_c(\cdot; T, H)]}{\partial T} = \frac{1}{T} \frac{\partial \langle H \rangle_{(T,H)}}{\partial T}. \qquad (9)$$

We note that the temperature T is positive in most physical situations. Indeed, for the Hamiltonian involving the kinetic terms, T must be positive to satisfy the normalization condition of the canonical distribution. Thus, the right-hand side of Eq. (9) is positive.

III. PROOF OF THE STATEMENT

Let us consider an ensemble of the small systems whose Hamiltonian is H_a, where a is a parameter controlled from the outside. We shall analyze the two processes for the ensemble, $\{T_1, a_1; T_2, a_2\}$ and its inverse $\{T_2, a_2; T_1, a_1\}$ with given the values of the temperature T_1 and parameters a_1 and a_2. A temperature T_2 is to be determined so that the heat bath of the temperature T_2 receives no energy from the ensemble of the small systems during the process (iv) of $\{T_1, a_1; T_2, a_2\}$. First, we consider the process $\{T_1, a_1; T_2, a_2\}$. When detached from the heat bath of the temperature T_1 [the process (ii)], the ensemble is the canonical ensemble characterized by T_1 and H_{a_1}. The ensemble average of the energy, $\bar{E}_1$, is then given by

$$\bar{E}_1 = \langle H_{a_1} \rangle_{(T_1, H_{a_1})}. \qquad (10)$$

When the parameter a of the system is quasistatically changed along the process (iii), the distribution of the systems, in general, changes. The final distribution is uniquely determined by the adiabatic theorem. (We will not write down the explicit form of the distribution, since our proof does not depend on the concrete form of the distribution.) We will write the distribution of the ensemble at a as $P_a(\Gamma; T_1, H_{a_1})$, where T_1 and H_{a_1} are the arguments reminding us of the fact that the ensemble at $a = a_1$ was the canonical ensemble with T_1 and H_{a_1}. By our definition, P_a at any temperature T and for any value of a satisfies

$$P_a(\Gamma; T, H_a) = P_c(\Gamma; T, H_a). \qquad (11)$$

According to Lemma 1, the entropy S remains invariant during the process (iii),

$$S[P_{a_1}(\cdot; T_1, H_{a_1})] = S[P_{a_2}(\cdot; T_1, H_{a_1})]. \qquad (12)$$

At the end of (iii) the ensemble average of the energy $\bar{E}_2$ is expressed as

$$\bar{E}_2 = \int_{\{\Gamma\}} H_{a_2}(\Gamma) P_{a_2}(\Gamma; T_1, H_{a_1}) d\Gamma. \qquad (13)$$

For the process (iv), we choose the temperature T_2 so that the average energy of the ensemble does not change upon the contact with the heat bath of the temperature T_2. It is because our aim is to know whether or not the process $\{T_1, a_1; T_2, a_2\}$ can be made reversible. T_2 must, therefore, satisfy

$$\bar{E}_2 = \langle H_{a_2} \rangle_{(T_2, H_{a_2})}. \qquad (14)$$

According to Lemma 2, the relations (13) and (14) imply

$$S[P_{a_2}(\cdot;T_1,H_{a_1})] \leq S[P_c(\cdot;T_2,H_{a_2})], \qquad (15)$$

where the equality holds only if the ensemble at the end of (iii) is the canonical ensemble. If our system is such that the canonical distribution is transformed into the canonical one through the process (iii) of $\{T_1,a_1;T_2,a_2\}$, then it is also true for the process (iii) of $\{T_2,a_2;T_1,a_1\}$, since (iii) is a quasistatic adiabatic and is, therefore, reversible process.

Next, we examine the process $\{T_2,a_2;T_1,a_1\}$. As above, the process (iii) yields the relation

$$S[P_{a_2}(\cdot;T_2,H_{a_2})] = S[P_{a_1}(\cdot;T_2,H_{a_2})]. \qquad (16)$$

The ensemble average of the energy at the end of (iii), $\bar{E}'_1$, is

$$\bar{E}'_1 = \int_{\{\Gamma\}} H_{a_1}(\Gamma) P_{a_1}(\Gamma;T_2,H_{a_2}) d\Gamma. \qquad (17)$$

Now we ask if there is a nonzero flow of energy into the heat bath of the temperature T_1 at the end of (iii) of the process $\{T_2,a_2;T_1,a_1\}$ when we put the ensemble in contact with that heat bath. To answer this we only need to compare the value of $\bar{E}'_1$ with that of $\bar{E}_1$ since the contact with the heat bath forces the ensemble to obey the canonical distribution with the average energy $\bar{E}_1$. If $\bar{E}'_1 > \bar{E}_1$, then the positive energy, $\bar{E}'_1 - \bar{E}_1$, flows from the ensemble to the heat bath.

To see if this is the case, it is convenient to introduce the temperature T'_1 which satisfies

$$\bar{E}'_1 = \langle H_{a_1} \rangle_{(T'_1,H_{a_1})}, \qquad (18)$$

that is, we temporally introduce the canonical ensemble whose the ensemble energy is equal to $\bar{E}'$. The Eqs. (17) and (18) imply, with Lemma 2, that

$$S[P_{a_1}(\cdot;T_2,H_{a_2})] \leq S[P_c(\cdot;T'_1,H_{a_1})]. \qquad (19)$$

Combining Eqs. (12), (15), (16), and (19), we arrive at the inequality

$$S[P_c(\cdot;T_1,H_{a_1})] \leq S[P_c(\cdot;T'_1,H_{a_1})], \qquad (20)$$

where we have used the property (11) of P_a. According to Lemma 3, this inequality (20) implies

$$T_1 \leq T'_1$$

and

$$\bar{E}_1 \leq \bar{E}'_1. \qquad (21)$$

Thus we now complete the proof of the Statement: Given the temperature T_1 and the parameters a_1 and a_2, no matter what we choose as the temperature T_2, the process $\{T_1,a_1;T_2,a_2\}$ or $\{T_2,a_2;T_1,a_1\}$ generally requires some non-negative energy to move from the ensemble of the small systems to the heat baths. The special case with no energy transfer is the

reversible case as mentioned below in Eq. (15), that is, the only case that the canonical distribution form of the ensemble is preserved in the quasistatic adiabatic process (iii). We will discuss the condition for this to occur in the following section.

IV. DISCUSSION

We first note that the inequality (21) is fundamental in the sense that if it were violated, we could construct a perpetual machine of the second kind with the following hypothetical protocol.

(1) We start from an ensemble of the small systems in contact with a heat bath at temperature T_1.

(2) We detach these systems *gently* from the heat bath, and change the parameter a from a_1 to a_2 quasistatically. The work necessary to make this change is $\bar{E}_2 - \bar{E}_1$ per system.

(3) We now fix the parameter a at a_2, and introduce the interactions among these system. We assume that these interactions are sufficiently smaller than the systems energy, but at the same time large enough for the repartition of the energy within a certain time.

(4) We remove these interactions: the ensemble of the systems obeys the canonical distribution characterized by T_2 and H_{a_2}. (Note that we have not used any heat bath other than the initial one at the temperature T_1.)

(5) We then slowly change the parameter a from a_2 back to a_1. The required work here is $\bar{E}'_1 - \bar{E}_2$.

(6) Finally, we close the cycle by bringing these small systems into contact with the heat bath at temperature T_1.

If the inequality $(\bar{E}_2 - \bar{E}_1) + (\bar{E}'_1 - \bar{E}_2) < 0$ were to hold in this cycle, we could obtain the positive work $\bar{E}_1 - \bar{E}'_1$ through the cycle, where the only resource of the energy is the heat bath at temperature T_1.

Below we will derive briefly the condition that the cycle of processes discussed above become reversible. This condition requires that the distribution remains to be the canonical one upon quasistatic adiabatic processes, see the paragraph below (15). The change of the distribution in those processes is governed by the adiabatic theorem [3]: If we denote by E_1 and E_2 the energy of the system before and after a quasistatic adiabatic process, through which the parameter changes from a_1 to a_2, respectively, the "action" $J(E,a)$ defined by

$$J(E,a) \equiv \int_{\{\Gamma\}} \theta(E - H_a(\Gamma)) d\Gamma \qquad (22)$$

satisfies the following relationship:

$$J(E_1,a_1) = J(E_2,a_2). \qquad (23)$$

Using Eq. (23) we can see how the energy distribution of the system's ensemble changes through such process. The energy distribution before the process, $P(E_1)$, is given by construction as

$$P(E_1)dE_1 = \frac{e^{-(E_1)/(T_1)}}{Z(T_1,H_{a_1})} W(E_1,a_1)dE_1,$$

where Z has been defined below (5) and $W(E,a)$ is defined by $W(E,a) \equiv [\partial J(E,a)]/\partial E$. Noting that Eq. (23) and the above definition of $W(E,a)$ give

$$W(E_1,a_1)dE_1 = W(E_2,a_2)dE_2,$$

the energy distribution after the process, $P'(E_2)$ is given as

$$P'(E_2)dE_2 = \frac{e^{-E_1/T_1}}{Z(T_1,H_{a_1})} W(E_2,a_2)dE_2.$$

This distribution corresponds to the canonical one at some temperature, say T_2, if and only if

$$\frac{E_1}{T_1} = \frac{E_2}{T_2}$$

is satisfied. Thus, we reach the condition for the reversibility: the adiabatic theorem (23) applied for a quasistatic adiabatic process of the system should yield the relationship

$$E_2 = \phi(a_1,a_2)E_1 \tag{24}$$

with $\phi(a_1,a_2)$ being a function of the parameter values before and after the process.

An example of the systems satisfying Eq. (24) is a harmonic oscillator with the Hamiltonian, $H_a = p^2/2 + aq^2/2$. When the spring constant a is changed quasistatically, the process $\{T_1,a_1;T_2,a_2\}$ is reversible. By constrast, an example that does not satisfy Eq. (24) is given by the following Hamiltonian:

$$H_a = p^2/2 + \exp\left\{\frac{|q|}{a}\right\}.$$

The proof, not shown here, is easy.

Our proof of Eq. (21) is for the systems obeying classical dynamics. After our work, H. Tasaki has shown that essentially the same mechanism of irreversibility is found for the systems obeying quantum mechanics [4]. There, the proof has been done, just we did here, using the fact that the canonical ensemble realizes the maximum entropy among those ensembles with the same average energy. We could say that it is this property of the canonical ensemble that leads to the inequality (21).

In order to obtain a deeper physical insight of the inequality (21), let us compare the system that consists of infinitely many small subsystems connected among each other with the system of the ensemble of mutually isolated small systems. We shall call these two systems the "connected system" and the "disconnected system," respectively. As the former system is macroscopic, we can apply to it the ordinary thermodynamics and therefore the process $\{T_1,a_1;T_2,a_2\}$ can be made reversible for such system. To assure it we must assume that the interaction energy assigned to the coupling among the small subsystems is assumed to be ignorably small while it is effective enough to attain the ther-
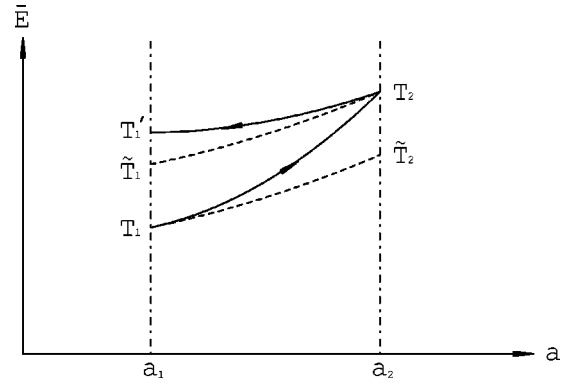

FIG. 2. Thick solid curves: The average energy of the small system, $\bar{E}$, as a function of the parameter a, along quasistatic adiabatic processes. The arrows indicate the direction of the processes. Dotted curves: The energy of the combined system per constituent small system along quasistatic adiabatic processes. At each extreme point of the curves, the value of the average energy is indicated by the corresponding temperature of the canonical ensemble. For example, T_1' indicates that $\bar{E} = \langle H_{a_1}\rangle_{(T_1',H_{a_1})}$. At the point indicated by T_2, the upper solid curve and the upper dotted curve are tangent, and at the point indicated by T_1, the lower solid curve and the lower dotted curve are tangent.

mal equilibrium of the whole connected system. Under this assumption we can prove (not shown) that the energy distribution of the small subsystems belonging to the connected system remains to be the canonical one throughout the process (iii).

Furthermore the entropy related to this distribution, whose definition has been given in Eq. (1), is conserved during the process (iii), as we can show easily by using the fact that the distribution is kept to be canonical throughout this process. That is, along the process (iii) the canonical distribution $P_c(\Gamma;\tilde{T},H_a)$ of the connected system at the parameter value a satisfies the following relationship:

$$S[P_c(\cdot;T_1,H_{a_1})] = S[P_c(\cdot;\tilde{T},H_a)].$$

This equality combined with Lemma 2 implies that, at any point along the process (iii), the average energy of the small systems in the disconnected system is generally not smaller than the average energy of the small subsystems in the connected system (see Fig. 2 for the schematic illustration). This figure gives us the intuitive picture that the irreversibility of the disconnected system is caused by its excess energy in reference to the connective system which is reversible.

It is a future topic of investigation to determine if we can construct a thermodynamic framework of small systems that can describe adiabatic processes as well as isothermal processes for systems in contact with heat baths. Our results imply that, in such framework, if there exists a thermodynamic function whose difference calculated with respect to two states is the quasistatic adiabatic work $\bar{E}_2 - \bar{E}_1$, then it cannot be the case that this function depends on only T and a. (This is in contrast to the case of isothermal processes for a small system in contact with a heat bath. For such pro-

cesses, using the formalism of stochastic energetics [5–7] it has been shown that the Helmholtz free energy can be used to determine the work necessary to move between two states by changing the value of a sufficiently slowly so that the small system evolves quasistatically.)

To construct the thermodynamic framework of a small system, it is desirable to find a method of characterizing in terms of work the process through which the distribution changes from a noncanonical form $P_{a_2}(\cdot;T_1,H_{a_1})$ to the canonical form $P_c(\cdot;T_2,H_{a_2})$. If this is possible, it is natural to expect that the maximum of such extracted work to be $T_2(S[P_c(\cdot;T_2,H_{a_2})] - S[P_{a_2}(\cdot;T_1,H_{a_1})])$ [see Eq. (15)]. In any case, the quantity $S[P_c(\cdot;T_2,H_{a_2})] - S[P_{a_2}$

$(\cdot;T_1,H_{a_1})]$ is a strong measure of the distance from the corresponding reversible process since this is nonvanishing unless the functions $P_{a_2}(\cdot;T_1,H_{a_1})$ and $P_c(\cdot;T_2,H_{a_2})$ are identical.

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