# Jarzynski Relations for Quantum Systems and Some Applications

Hal Tasaki<sup>1</sup>

### 1 Introduction

In a series of papers (see [1, 2, 3] and references therein) Jarzynski proved remarkable exact relations in various dynamical systems which relate nonequilibrium quantities with equilibrium free energies. Possible relations between Jarzynski's results and the "fluctuation theorem" for steady state nonequilibrium systems has been pointed out by Crooks [4]. Piechocinska [5] and Kurchan [6] extended some of these results to quantum systems. See also [7] for a related (but different) attempt at extending Jarzynski relations to quantum systems.

In this note, we derive quantum analogues of Jarzynski's relations, and discuss two applications, namely, a derivation of the law of entropy increase for general compound systems, and a preliminary analysis of heat transfer between two quantum systems at different temperatures. We believe that the derivation of the law of entropy increase in Section 3 is new and rather important. (But the argument is essentially that in [2].)

It is likely that many of the materials presented here are known to experts in the field. We nevertheless believe that to summarize all these results in a self-contained (and, hopefully, transparent) manner can be useful for further investigation in related (more difficult) problems.

We have tried to make the present note technically self-contained. The readers are suggested to go back to the references for physical backgrounds.

# 2 Jarzynski relations for quantum systems

We concentrate here on a general quantum mechanical system with a single time-dependent Hamiltonian, and describe the derivation of quantum analogues of Jarzynski relations. Some of the results are already derived in [5, 6].

## 2.1 Setup

Let us give abstract settings without specifying physical interpretations.

Consider a quantum system with an N-dimensional Hilbert space. Take an arbitrary time-dependent Hamiltonian H(t) in the time interval  $t \in [t_{\text{init}}, t_{\text{fin}}]$ , and let  $H(t_{\text{init}}) = H$  and  $H(t_{\text{fin}}) = H'$ . For i = 1, ..., N, we denote by  $|\varphi_i\rangle$  and  $|\varphi_i'\rangle$  the normalized eigenstates

<sup>&</sup>lt;sup>1</sup> Department of Physics, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171, JAPAN electronic address: hal.tasaki@gakushuin.ac.jp

of H and H', respectively, with eigenvalues  $E_i$  and  $E'_i$ . Let U be the unitary operator for time evolution during the whole period<sup>2</sup>.

We assume that, at  $t = t_{\text{init}}$ , the system is in the Gibbs state with inverse temperature  $\beta$ , which is described by the density matrix

$$\rho_{\text{init}} = \frac{e^{-\beta H}}{Z(\beta)},\tag{2.1}$$

with  $Z(\beta) = \sum_{i=1}^{N} e^{-\beta E_i}$ . We denote by

$$\langle \cdots \rangle_{\text{init}} = \text{Tr}[(\cdots)\rho_{\text{init}}],$$
 (2.2)

the expectation at  $t = t_{\text{init}}$ , and by

$$\langle \cdots \rangle_{\text{fin}} = \text{Tr}[(\cdots)U\rho_{\text{init}}U^{-1}],$$
 (2.3)

the expectation at  $t = t_{\text{fin}}$ .

Let us define a crucial quantity

$$p_{i,j} = \frac{e^{-\beta E_i}}{Z(\beta)} |\langle \varphi_j' | U | \varphi_i \rangle|^2, \qquad (2.4)$$

which (if one wishes) can be interpreted as the probability that one finds the system in the i-th eigenstate of H at  $t = t_{\text{init}}$  and then in the j-th eigenstate of H' at  $t = t_{\text{fin}}$ . (See [5, 6] and footnote 5.) One can also think of  $p_{i,j}$  as a purely theoretical quantity without giving it any interpretations. Note that the unitarity (and the definition of  $Z(\beta)$ ) guarantees the normalization  $\sum_{i,j} p_{i,j} = 1$ . For any function f(E, E') of two energy variables E and E', we define its "classical average" by

$$\overline{f(E, E')} = \sum_{i,j=1}^{N} p_{i,j} f(E_i, E'_j).$$
(2.5)

It is crucial to note that, in a general situation where H and  $U^{-1}H'U$  do not commute, the classical average  $\overline{f(E,E')}$  does not correspond to quantum mechanical expectation in any obvious way. However, for the simplest f, we easily find

$$\overline{E} = \langle H \rangle_{\text{init}}, \quad \overline{E'} = \langle H' \rangle_{\text{fin}},$$
 (2.6)

which will be crucial for the applications of the main equality.

### 2.2 Jarzyinski's equality and inequality

From the definitions (2.5) and (2.4), we find for any  $\tilde{\beta}$  that

$$\overline{e^{\beta E - \tilde{\beta} E'}} = \sum_{i,j=1}^{N} e^{\beta E_i - \tilde{\beta} E'_j} \frac{e^{-\beta E_i}}{Z(\beta)} |\langle \varphi'_j | U | \varphi_i \rangle|^2$$

$$= \frac{1}{Z(\beta)} \sum_{j=1}^{N} e^{-\tilde{\beta} E'_j}$$

$$= \frac{Z'(\tilde{\beta})}{Z(\beta)}, \qquad (2.7)$$

Let U(t) be the solution of the Schrödinger equation  $i\partial U(t)/\partial t = H(t)U(t)$  with  $U(t_{\text{init}}) = 1$ . Then  $U = U(t_{\text{fin}})$ .

where we used the unitarity to get the second line, and introduced  $Z'(\tilde{\beta}) = \sum_{j=1}^{N} e^{-\tilde{\beta}E'_{j}}$ . We call (2.7) the Jarzynski equality.

By using the Jensen inequality  $\overline{\exp(f)} \ge \exp(\overline{f})$ , we find that

$$\exp\left(\beta \overline{E} - \tilde{\beta} \overline{E'}\right) \le \frac{Z'(\tilde{\beta})}{Z(\beta)}.$$
(2.8)

By noting the identities (2.6), this reduces to the following inequality for quantum mechanical expectation values.

$$\beta \langle H \rangle_{\text{init}} - \tilde{\beta} \langle H' \rangle_{\text{fin}} \le \log Z'(\tilde{\beta}) - \log Z(\beta),$$
 (2.9)

for any  $\tilde{\beta}$ .

**Remark:** (9/25/2000) The inequality (2.9) (as well as other inequalities such as (3.16) and (4.9)) follows directly from the wellknown property of the relative entropy as follows. (We stress, however, that the Jarzynski's basic *equality* contains much stronger information than the corresponding inequality.)

Let  $\rho_{\text{init}}$  be an arbitrary density matrix and let  $\rho_{\text{fin}} = U \rho_{\text{init}} U^{-1}$  where U is an arbitrary unitary operator. Then we have

$$\operatorname{Tr}[\rho_{\text{init}}\log\rho_{\text{init}}] = \operatorname{Tr}[\rho_{\text{fin}}\log\rho_{\text{fin}}],$$
 (2.10)

which is the well known invariance of the von Neuman entropy. Let  $\rho'$  be an arbitrary density matrix. Then the relative entropy [8] satisfies

$$S(\rho'|\rho_{\text{fin}}) = \text{Tr}[\rho_{\text{fin}}(\log \rho_{\text{fin}} - \log \rho')] \ge 0. \tag{2.11}$$

By combining (2.10) and (2.11), we get

$$\operatorname{Tr}[\rho_{\text{init}}\log\rho_{\text{init}}] \ge \operatorname{Tr}[\rho_{\text{fin}}\log\rho'].$$
 (2.12)

This inequality reduces, for example, to (3.16) by choosing both the initial density matrix  $\rho_{\text{init}}$  and the reference density matrix  $\rho'$  as Gibbs states.

### 2.3 Basic applications to thermodynamics

We now suppose that our quantum mechanical system is a macroscopic one, and imagine that the time dependent Hamiltonian H(t) models an adiabatic operation in thermodynamics. (See, for example, [12].) We further suppose that the Hamiltonian H(t) stays at H' sufficiently long time at the end of the operation, so that the system reaches a macroscopic equilibrium.

By first setting  $\tilde{\beta} = \beta$ , we get an inequality for the (expectation value of the) work W(U) done by the outside agent (who controls the Hamiltonian) to the system, i.e,

$$W(U) \equiv \langle H' \rangle_{\text{fin}} - \langle H \rangle_{\text{init}} \ge \frac{1}{\beta} \{ \log Z(\beta) - \log Z'(\beta) \}.$$
 (2.13)

Since the relation of (the classical version of) this inequality to the minimum work principle is fully discussed in [1], we do not repeat the discussion here.

Now in a thermodynamic system whose energy is known to be U, its entropy can be obtained via a Legendre transformation as<sup>3</sup>

$$S(U) = \min_{\tilde{\beta}} \tilde{\beta} \{ U - F(\tilde{\beta}) \} = \bar{\beta} \{ U - F(\bar{\beta}) \}, \tag{2.14}$$

where  $F(\beta)$  is the Helmoholtz free energy, and  $\bar{\beta}$  is the unique inverse temperature at which the minimum is attained (and which is nothing but the equilibrium value of the inverse temperature).

From the basic inequality (2.9), we have

$$\beta\{\langle H \rangle_{\text{init}} - F(\beta)\} \le \tilde{\beta}\{\langle H' \rangle_{\text{fin}} - F'(\tilde{\beta})\}$$
 (2.15)

for any  $\tilde{\beta}$ , where  $F(\beta) = -\beta^{-1} \log Z(\beta)$ , and  $F'(\tilde{\beta}) = -\tilde{\beta}^{-1} \log Z'(\tilde{\beta})$ . From (2.14), we see that the left-hand side of (2.15) is nothing but the entropy S of the initial state, and the minimum over  $\tilde{\beta}$  of the right-hand side is the entropy S' of the final state. Consequently we find from (2.15) that

$$S \le S',\tag{2.16}$$

which is the law of entropy increase in an adiabatic process<sup>4</sup>.

### 2.4 "Fluctuation theorem" like symmetry

The reader interested in the topic of Section 3 can skip the present subsection. Let a variable w take values of the form  $E'_j - E_i$  for i, j = 1, ..., N, and let

$$P_{U}(w) = \sum_{i,j=1}^{N} \chi[E'_{j} - E_{i} = w] p_{i,j}$$

$$= \sum_{i,j=1}^{N} \chi[E'_{j} - E_{i} = w] \frac{e^{-\beta E_{i}}}{Z(\beta)} |\langle \varphi'_{j} | U | \varphi_{i} \rangle|^{2}, \qquad (2.17)$$

where the characteristic function is defined as  $\chi[\text{true}] = 1$ , and  $\chi[\text{true}] = 0$ . This can be interpreted as the probability that the difference of the measured energies<sup>5</sup> at the initial and the final states is equal to w.

Now an easy calculation shows that

$$e^{-\beta w} P_{U}(w) = \sum_{i,j=1}^{N} \chi[E'_{j} - E_{i} = w] e^{-\beta E'_{j} + \beta E_{i}} \frac{e^{-\beta E_{i}}}{Z(\beta)} |\langle \varphi'_{j} | U | \varphi_{i} \rangle|^{2}$$

$$= \frac{Z'(\beta)}{Z(\beta)} \sum_{i,j=1}^{N} \chi[E_{i} - E'_{j} = -w] \frac{e^{-\beta E'_{j}}}{Z'(\beta)} |\langle \varphi_{i} | U^{-1} | \varphi'_{j} \rangle|^{2}.$$
 (2.18)

<sup>&</sup>lt;sup>3</sup> Throughout the present note, we set the Boltzmann constant to unity.

<sup>&</sup>lt;sup>4</sup> The inequality (2.15) is valid for arbitrary finite systems. But (2.16) is meaningful only for macroscopic systems, since the definition (2.14) of entropy should be used in the thermodynamic limit.

<sup>&</sup>lt;sup>5</sup> We suppose that, as in [5, 6], one first measures H at time  $t = t_{\text{init}}$ , and the state contracts to the eigenstate which corresponds to the measured energy. Then the system evolves according to U, and one measures H' at time  $t = t_{\text{fin}}$ .

With (2.17) in mind, it is natural to define

$$P_{U^{-1}}(w') = \sum_{i,j=1}^{N} \chi[E_j - E_i' = w'] \frac{e^{-\beta E_i'}}{Z'(\beta)} |\langle \varphi_j | U^{-1} | \varphi_i' \rangle|^2.$$
 (2.19)

This correspond to the inverse situation where the initial state is the Gibbs state for H', and the time evolution is given by  $U^{-1}$ . Then (2.18) implies

$$e^{-\beta w} P_U(w) = \frac{Z'(\beta)}{Z(\beta)} P_{U^{-1}}(-w).$$
 (2.20)

Consider a situation where H = H', and the time evolution is symmetric in the sense that<sup>6</sup>

$$|\langle \varphi_i | U | \varphi_i \rangle| = |\langle \varphi_i | U^{-1} | \varphi_i \rangle|. \tag{2.21}$$

Then we have  $Z(\beta) = Z'(\beta)$ , and  $P_U(w) = P_{U^{-1}}(w)$ . Thus (2.20) take the significant form [6]

$$e^{-\beta w}P_U(w) = P_U(-w),$$
 (2.22)

which (at least formally) resembles the fluctuation theorem for steady state<sup>7</sup>. But it is questionable whether this equality carries information about nonequilibrium systems (like the original fluctuation theorem). Later in Section 4, we derive another relation which also resembles the fluctuation theorem. (See (4.15).) We do not go into details about the fluctuation theorem, and just refer to recent works [9, 10], and those discuss possible relations between the fluctuation theorem and the Jarzynski relations [4, 3].

# 3 The law of entropy increase for general compound systems

### 3.1 Precise statement in thermodynamics

The law of entropy increase represents the heart of the second law of thermodynamics. In the present note, we have already discussed the law of entropy increase (2.16), but this is only for simple systems.

A simple system is a basic notion in thermodynamics, which stands for a system that can exchange energy within it, and hence always attains a uniform temperature in equilibrium. A compound system, on the other hand, consists of several distinct simple systems which do not exchange energies with each other. (In the usual language of thermodynamics, they are separated by "adiabatic walls.") An equilibrium state of a compound system is a composition of equilibrium states of each simple system that constitute it.

We assume that a thermodynamic (i.e., macroscopic) equilibrium state of simple system is completely characterized by specifying its inverse temperature  $\beta$  and a set X of extensive

This is true when H(t) is symmetric in the sense that  $H(t) = H(t_{\text{init}} + t_{\text{fin}} - t)$  for any t such that  $t_{\text{init}} \leq t \leq t_{\text{fin}}$ , and the matrix elements  $\langle \varphi_i | H(t) | \varphi_j \rangle$  is real for all t and i, j.

<sup>&</sup>lt;sup>7</sup> One finds that the derivation is quite similar (although the derivation of the present result is rather trivial). See especially [9].

variables<sup>8</sup>. In case of a fluid with M components in a container,  $X = (V, N_1, \ldots, N_M)$  where V is the volume of the container and  $N_i$  the amount of i-th substance. We denote by  $(\beta; X)$  the equilibrium states specified by  $\beta$  and X.

Then an equilibrium state of a compound system can be written as

$$\{(\beta_1; X_1) | (\beta_2; X_2) | \cdots | (\beta_n; X_n) \},$$
 (3.1)

where  $(\beta_k; X_k)$  denotes the equilibrium state of the k-th simple system constituting the whole compound system. Here the vertical bars represent adiabatic walls.

Then the strongest form of the *law of entropy increase* states that if an adiabatic operation

$$\{(\beta_1; X_1) | \cdots | (\beta_n; X_n)\} \to \{(\beta_1'; X_1') | \cdots | (\beta_m'; X_m')\},$$
 (3.2)

is possible, then one always has<sup>9</sup>

$$\sum_{k=1}^{n} S(\beta_k; X_k) \le \sum_{\ell=1}^{m} S(\beta'_{\ell}; X'_{\ell}), \tag{3.3}$$

where  $S(\beta; X)$  is the entropy of a simple system in state  $(\beta; X)$ . Note that we allowed the number of simple systems to vary in the adiabatic operation (3.2), since we can insert or remove adiabatic walls during an operation.

We stress that the law of entropy increase for compound system is much stronger than that for simple systems, and (along with additivity of the entropy) has far reaching implications. See, for example, [11].

#### 3.2 Statistical mechanical derivation

We give a statistical mechanical derivation of (3.3). We stress that what follows is an almost trivial and natural modification of the argument in [2].

We treat a model similar to Section 2 with suitable modifications necessary to represent compound systems.

We again model an adiabatic operation by a time dependent Hamiltonian H(t) with t in the range  $t_{\text{init}} \leq t \leq t_{\text{fin}}$ . We denote the initial Hamiltonian as  $H(t_{\text{init}}) = H$  and the final Hamiltonian as  $H(t_{\text{fin}}) = H'$ .

We decompose the Hilbert space  $\mathcal{H}$  of the system as

$$\mathcal{H} = \bigotimes_{k=1}^{n} \mathcal{H}_k, \tag{3.4}$$

and assume that the initial Hamiltonian has the form

$$H = \sum_{k=1}^{n} \mathbf{1}_{1} \otimes \mathbf{1}_{2} \otimes \cdots \otimes \mathbf{1}_{k-1} \otimes H_{k} \otimes \mathbf{1}_{k+1} \otimes \cdots \otimes \mathbf{1}_{n}, \tag{3.5}$$

<sup>&</sup>lt;sup>8</sup> This is not true at tricritical points, but we do not go into such details here.

<sup>&</sup>lt;sup>9</sup> The *entropy principle* states, in addition to the law of entropy increase, that the adiabatic operation (3.2) is always possible when (3.3) holds (and when the conservations of masses are satisfied). We do not discuss this additional part of the principle, and focus only on the law of entropy increase.

where  $\mathbf{1}_k$  is the identity operator on  $\mathcal{H}_k$ , and  $H_k$  acts only on  $\mathcal{H}_k$ . For each  $k = 1, \ldots, n$ , we denote by  $|\varphi_i^{(k)}\rangle$  with  $i = 1, \ldots, d_k \equiv \dim(\mathcal{H}_k)$  the normalized eigenstate of  $H_k$  with the eigenvalue  $E_i^{(k)}$ . To represent states of the whole system, we use a multi-index  $\mathbf{i} = (i_1, i_2, \ldots, i_n)$  with  $i_k = 1, \ldots, d_k$ , and define

$$|\Phi_{\mathbf{i}}\rangle = \bigotimes_{k=1}^{n} |\varphi_{i_k}^{(k)}\rangle. \tag{3.6}$$

Similarly we decompose the same Hilbert space as

$$\mathcal{H} = \bigotimes_{\ell=1}^{m} \mathcal{H}'_{\ell},\tag{3.7}$$

and assume that the final Hamiltonian has the form

$$H' = \sum_{\ell=1}^{m} \mathbf{1}_{1}' \otimes \mathbf{1}_{2}' \otimes \cdots \otimes \mathbf{1}_{\ell-1}' \otimes H_{\ell}' \otimes \mathbf{1}_{\ell+1}' \otimes \cdots \otimes \mathbf{1}_{m}', \tag{3.8}$$

where  $\mathbf{1}'_{\ell}$  is the identity operator on  $\mathcal{H}'_{\ell}$ , and  $H'_{\ell}$  acts only on  $\mathcal{H}'_{\ell}$ . For each  $\ell = 1, \ldots, m$ , we denote by  $|\varphi'_{j}^{(\ell)}\rangle$  with  $j = 1, \ldots, d'_{\ell} \equiv \dim(\mathcal{H}'_{\ell})$  the normalized eigenstate of  $H'_{\ell}$  with the eigenvalue  $E'_{j}$ . We again use a multi-index  $\mathbf{j} = (j_{1}, j_{2}, \ldots, j_{m})$  with  $j_{\ell} = 1, \ldots, d'_{\ell}$ , and define

$$|\Phi_{\mathbf{j}}'\rangle = \bigotimes_{\ell=1}^{m} |\varphi_{j_{\ell}}^{\prime(\ell)}\rangle. \tag{3.9}$$

We assume that at  $t = t_{\text{init}}$  the k-th simple system is in the Gibbs state with inverse temperature  $\beta_k$ . The whole state is then represented by the density matrix

$$\rho_{\text{init}} = \bigotimes_{k=1}^{n} \frac{e^{-\beta_k H_k}}{Z_k(\beta_k)},\tag{3.10}$$

where  $Z_k(\beta) = \sum_{i=1}^{d_k} e^{-\beta E_i^{(k)}}$ .

Then the system evolves according to the time dependent Hamiltonian H(t) until  $t = t_{\rm fin}$ . We assume that, near the end of the operation, H(t) stays at H' for sufficiently long time so that each of the m simple systems reach equilibrium. (Note that they are not necessarily described by the exact Gibbs states. See, for example, the discussion at the end of [12].) We denote by U the time evolution unitary operator for the whole process, and denote by

$$\langle \cdots \rangle_{\text{init}} = \text{Tr}[(\cdots)\rho_{\text{init}}],$$
 (3.11)

the expectation at  $t = t_{init}$ , and by

$$\langle \cdots \rangle_{\text{fin}} = \text{Tr}[(\cdots)U\rho_{\text{init}}U^{-1}],$$
 (3.12)

the expectation at  $t = t_{\text{fin}}$ .

Following (2.4), we define

$$p_{\mathbf{i},\mathbf{j}} = \left(\prod_{k=1}^{n} \frac{\exp[-\beta_k E_{i_k}^{(k)}]}{Z_k(\beta_k)}\right) |\langle \Phi_{\mathbf{j}}' | U | \Phi_{\mathbf{i}} \rangle|^2, \tag{3.13}$$

and

$$\overline{f(E^{(1)}, \dots, E^{(n)}, E'^{(1)}, \dots, E'^{(m)})} = \sum_{\mathbf{i}, \mathbf{j}} p_{\mathbf{i}, \mathbf{j}} f(E_{i_1}^{(1)}, \dots, E_{i_n}^{(n)}, E'^{(1)}_{j_1}, \dots, E'^{(m)}_{j_m}).$$
(3.14)

Then one easily finds for any  $\tilde{\beta}_1, \ldots, \tilde{\beta}_m$  that

$$\overline{\exp\left[\sum_{k=1}^{n} \beta_{k} E^{(k)} - \sum_{\ell=1}^{m} \tilde{\beta}_{\ell} E^{\prime(\ell)}\right]} = \left(\prod_{k=1}^{n} \frac{1}{Z_{k}(\beta_{k})}\right) \sum_{\mathbf{i},\mathbf{j}} \left(\prod_{\ell=1}^{m} \exp\left[-\tilde{\beta}_{\ell} E^{\prime(\ell)}_{j_{\ell}}\right]\right) |\langle \Phi_{\mathbf{j}}' | U | \Phi_{\mathbf{i}} \rangle|^{2}$$

$$= \frac{\prod_{\ell=1}^{m} Z_{\ell}'(\tilde{\beta}_{\ell})}{\prod_{k=1}^{n} Z_{k}(\beta_{k})}, \tag{3.15}$$

where  $Z'(\tilde{\beta}) = \sum_{j=1}^{d'_{\ell}} e^{-\tilde{\beta} E'^{(\ell)}_{j}}$ . By using the Jensen inequality, we have

$$\exp\left[\sum_{k=1}^{n} \beta_k \overline{E^{(k)}} - \sum_{\ell=1}^{m} \tilde{\beta}_{\ell} \overline{E^{\prime(\ell)}}\right] \le \frac{\prod_{\ell=1}^{m} Z_{\ell}'(\tilde{\beta}_{\ell})}{\prod_{k=1}^{n} Z_{k}(\beta_{k})}.$$
(3.16)

Noting that  $^{10}$ 

$$\langle H_k \rangle_{\text{init}} = \overline{E^{(k)}}, \quad \langle H'_\ell \rangle_{\text{fin}} = \overline{E^{\prime(\ell)}},$$
 (3.17)

we finally get

$$\sum_{k=1}^{n} \beta_k \{ \langle H_k \rangle_{\text{init}} - F_k(\beta_k) \} \le \sum_{\ell=1}^{m} \beta_\ell \{ \langle H'_\ell \rangle_{\text{fin}} - F'_\ell(\tilde{\beta}_\ell) \}, \tag{3.18}$$

for any  $\tilde{\beta}_1, \ldots, \tilde{\beta}_m$ , where  $F_k(\beta) = -\beta^{-1} \log Z_k(\beta)$  and  $F'_{\ell}(\tilde{\beta}) = -\tilde{\beta}^{-1} \log Z'_{\ell}(\tilde{\beta})$ . Then the desired inequality

$$\sum_{k=1}^{n} S_k \le \sum_{\ell=1}^{m} S_{\ell}',\tag{3.19}$$

follows (for a macroscopic system) as in Section 2.3

### 3.3 Remarks

It is quite remarkable that Jarzynski's method provides us with such a simple (indeed almost trivial) proof of the strongest form of the law of entropy principle.

It should be noted, however, that the present derivation works only when the initial state is a product of exact Gibbs states. The heart of modern statistical physics is that macroscopic system in equilibrium can be modelled by various different distributions, and all of them give rise to the same (true) thermodynamics. According to this spirit, we must be able to extend the present derivation to a much wider class of initial states, but it seems rather difficult for the moment. Note that for simple systems, there exists a proof of the second law of thermodynamics which works for a large class of distributions [12], but the argument there can hardly be applied to compound systems.

To be precise, the left-hand side should be  $\langle \mathbf{1}_1 \otimes \cdots \otimes \mathbf{1}_{k-1} \otimes H_k \otimes \mathbf{1}_{k+1} \otimes \cdots \otimes \mathbf{1}_n \rangle_{\text{init}}$ .

# 4 Heat transfer between two quantum systems

We briefly discuss preliminary results obtained by applying the present techniques to a highly nonequilibrium transient phenomenon. More precisely, we put two quantum system in different temperatures into a thermal contact, and wish to examine the heat flow from one system to the other. This is essentially contained in Jarzynski's work [3], but our motivation here seems less ambitious.

Consider a quantum mechanical system consisting of two systems whose Hilbert spaces are  $\mathcal{H}_1$  and  $\mathcal{H}_2$ . Then the Hilbert space for the whole system is  $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$ . We assume that the Hamiltonian of the model is time independent, and write it in the form

$$H = H_1 \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes H_2 + H_{\text{int}}, \tag{4.1}$$

where  $H_k$  acts only on  $\mathcal{H}_k$  (k = 1, 2) while  $H_{\text{int}}$  acts on the whole  $\mathcal{H}$ . For k = 1, 2, we denote by  $|\varphi_i^{(k)}\rangle$  the normalized eigenstate of  $H_k$  with the eigenvalue  $E_i^{(k)}$  where  $i = 1, \ldots, d_k \equiv \dim(\mathcal{H}_k)$ .

We assume that initially (which corresponds to t = 0) two systems are independently in equilibrium at inverse temperatures  $\beta_1$  and  $\beta_2$ , respectively. This corresponds to the density matrix

$$\rho_{\text{init}} = \frac{e^{-\beta_1 H_1}}{Z_1(\beta_1)} \otimes \frac{e^{-\beta_2 H_2}}{Z_2(\beta_2)},\tag{4.2}$$

with  $Z_k(\beta) = \sum_{i=1}^{d_k} e^{-\beta E_i^{(k)}}$ . Then the expectation at time t is given by

$$\langle \cdots \rangle_t = \text{Tr}[(\cdots)U(t)\rho_{\text{init}}U(-t)],$$
 (4.3)

where the unitary operator for time evolution is  $U(t) = e^{-iHt}$ .

In order to test for the possible heat transfer between the two systems, we examine the quantity  $^{11}$ 

$$\Delta S(t) = \beta_1 \{ \langle H_1 \rangle_t - \langle H_1 \rangle_0 \} + \beta_2 \{ \langle H_2 \rangle_t - \langle H_2 \rangle_0 \}. \tag{4.4}$$

Since  $\langle H_k \rangle_t - \langle H_k \rangle_0$  is the increase of energy in the k-th system,  $\Delta S(t)$  can be interpreted as the *increase of entropy* in the whole system, provided that the change in the inverse temperatures of the two systems are small and the contribution of  $H_{\text{int}}$  to the total entropy is negligible.

To examine  $\Delta S(t)$ , we again introduce the probability

$$p_{i,j;\ell,m}(t) = \frac{e^{-\beta_1 E_i^{(1)}}}{Z_1(\beta_1)} \frac{e^{-\beta_2 E_j^{(2)}}}{Z_2(\beta_2)} |\langle \varphi_m^{(2)} | \langle \varphi_\ell^{(1)} | U(t) | \varphi_i^{(1)} \rangle |\varphi_j^{(2)} \rangle|^2, \tag{4.5}$$

and the corresponding classical average of a function  $f(E^{(1)}, E^{(2)}, E'^{(1)}, E'^{(2)})$  as

$$[f(E^{(1)}, E^{(2)}, E'^{(1)}, E'^{(2)})]_t = \sum_{i,j,\ell,m} p_{i,j;\ell,m}(t) f(E_i^{(1)}, E_j^{(2)}, E_\ell'^{(1)}, E_m'^{(2)}), \tag{4.6}$$

<sup>&</sup>lt;sup>11</sup> To be precise,  $H_1$  and  $H_2$  should be  $H_1 \otimes \mathbf{1}_2$  and  $\mathbf{1}_1 \otimes H_2$ , respectively. We make the same abbreviation in what follows.

where we avoided the notation  $\overline{f}$  since the average depends on t. Note again that

$$[E^{(k)}]_t = \langle H_k \rangle_0, \quad [E'^{(k)}]_t = \langle H_k \rangle_t. \tag{4.7}$$

Now it is automatic to check that

$$\left[e^{\beta_1(E^{(1)}-E'^{(1)})+\beta_2(E^{(2)}-E'^{(2)})}\right]_t = 1, \tag{4.8}$$

for any t. Then the Jensen inequality  $[e^f]_t \ge e^{[f]_t}$  implies

$$\Delta S(t) \ge 0,\tag{4.9}$$

which shows the (wellknown) fact that heat never flows from the colder to the hotter. We stress that (4.9) has been *proved rigorously* (and indeed very easily) for quite general quantum systems.

To get a stronger result, let  $s = \beta_1(E'^{(1)} - E^{(1)}) + \beta_2(E'^{(2)} - E^{(2)})$ . Then  $[s]_t = \Delta S(t)$ . Since (4.8) says  $[e^{-s}]_t = 1$ , one has

$$\Delta S(t) = [s]_t = [e^{-s} - 1 + s]_t = [d(s)]_t, \tag{4.10}$$

where

$$d(x) = e^{-x} - 1 + x = \sum_{n=2}^{\infty} \frac{(-x)^n}{n!}$$
(4.11)

satisfies d(0) = 0 and d(x) > 0 for any  $x \neq 0$ . (4.10) and (4.6) lead to the expression

$$\Delta S(t) = \sum_{i,j,\ell,m} p_{i,j,\ell,m}(t) d[\beta_1 (E_{\ell}^{\prime(1)} - E_i^{(1)}) + \beta_2 (E_m^{\prime(2)} - E_j^{(2)})], \tag{4.12}$$

which is remarkable in that every term in the sum is nonnegative. This means that, when one tries to construct a rigorous lower bound for  $\Delta S(t)$  (which would rigorously establish the existence of a finite heat flow), one can freely throw away unwanted terms in (4.12), only keeping well controlled terms in the sum. (Moreover d(x) can be bounded from below by simpler functions if necessary.) Although we have no concrete estimates in this abstract setting, we hope one can construct meaningful rigorous lower bounds for  $\Delta S(t)$  by examining typical concrete models.

Let us make one more remark in connection with the fluctuation theorem. If we define

$$P_t(s) = \sum_{i,j,\ell,m} p_{i,j,\ell,m}(t) \chi \left[\beta_1 \left(E_{\ell}^{(1)} - E_i^{(1)}\right) + \beta_2 \left(E_m^{(2)} - E_j^{(2)}\right) = s\right]. \tag{4.13}$$

Then exactly as in Section 2.4, we can prove

$$e^{-s}P_t(s) = P_{-t}(-s),$$
 (4.14)

or, for models with time reversal symmetry<sup>12</sup>

$$e^{-s}P_t(s) = P_t(-s),$$
 (4.15)

In the sense that  $|\langle \varphi_m^{(2)} | \langle \varphi_\ell^{(1)} | U(t) | \varphi_i^{(1)} \rangle | \varphi_j^{(2)} \rangle| = |\langle \varphi_m^{(2)} | \langle \varphi_\ell^{(1)} | U(-t) | \varphi_i^{(1)} \rangle | \varphi_j^{(2)} \rangle|$  for any  $i, j, \ell.m$ . See footnote 6.

which has the form of "fluctuation theorem." This is a special case of Jarzynski's "detailed fluctuation theorem" [3].

It is a pleasure to thank Shin-ichi Sasa for introducing me to the whole subject, and for indispensable discussions.

## References

- [1] C. Jarzynski, A nonequilibrium equality for free energy differences, Phys. Rev. Lett. 78, 2690 (1997), cond-mat/9610209.
- [2] C. Jarzynski, Microscopic analysis of Clausius-Duhem processes, J. Stat. Phys. 96, 415 (1999), cond-mat/9802249.
- [3] C. Jarzynski, Hamiltonian derivation of a detailed fluctuation theorem, J. Stat. Phys. 98, 77 (2000), cond-mat/9908286
- [4] G. E. Crooks, The Entropy Production Fluctuation Theorem and the Nonequilibrium Work Relation for Free Energy Differences, Phys. Rev. E 60, 2721 (1999), condmat/9901352.
- [5] B. Piechocinska, Information erasure, Phys. Rev. A 61, 062314 (2000).
- [6] J. Kurchan, A Quantum Fluctuation Theorem, cond-mat/0007360.
- [7] S. Yukawa A Quantum Analogue of the Jarzynski Equality, J. Phys. Soc. Jpn. 69, 2367 (2000), cond-mat/0007456
- [8] A. Wehrl, General properties of entropy, Rev. Mod. Phys. 50, 221–260 (1978).
- [9] C. Maes, The Fluctuation Theorem as a Gibbs Property, J. Stat. Phys. **95**, 367–392 (1999).
- [10] J. L. Lebowitz and H. Spohn, A Gallavotti-Cohen-Type Symmetry in the Large Deviation Functional for Stochastic Dynamics, J. Stat. Phys. 95, 333–365 (1999).
- [11] E. H. Lieb and J. Yngvason, The Physics and Mathematics of the Second Law of Thermodynamics, Phys. Rep. 310, 1 (1999), cond-mat/9708200; A Fresh Look at Entropy and the Second Law of Thermodynamics, Physics Today, April 2000, mathph/0003028.
- [12] H. Tasaki, Statistical mechanical derivation of the second law of thermodynamics, preprint, cond-mat/0009206.