Statistical mechanical derivation of the second law of thermodynamics

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Abstract

In a macroscopic (quantum or classical) Hamiltonian system, we prove the second law of thermodynamics in the forms of the minimum work principle and the law of entropy increase, under the assumption that the initial state is described by a general equilibrium distribution. Therefore the second law is a logical necessity once we accept equilibrium statistical mechanics.

Note added (December, 2000): We learned that the main observation in the present note (the inequality (8) in the case $H = H'$) is contained in A. Lenard, J. Stat. Phys. 19, 575 (1978). (See also W. Pusz and S. L. Woronowicz, Commun. Math. Phys. 58, 273 (1978), W. Thirring, Quantum Mechanics of Large Systems (Springer, 1983).) We note, however, that Lenard does not have the viewpoint of micro-macro separation (which we believe necessary for thermodynamic discussions) and do not discuss results like our Theorem 2. We do not publish the present note as an original paper, but try to discuss these (and other related) points in future publications.

To understand macroscopic irreversibility from microscopic mechanics is one of the unsolved fundamental problems in physics. One may roughly classify the problem of irreversibility into that of “equilibration” and of “operational irreversibility.” The former aims at justifying equilibrium statistical mechanics, and has a rich (but not yet satisfactory) history which goes back to Boltzmann. The latter problem of “operational irreversibility” deals with a microscopic interpretation of the second law of thermodynamics. Briefly speaking, (a version of) the second law is a statement about the fundamental limitation on the possibility of adiabatic operation bringing one equilibrium state to another. Recall that, although the initial and final states are assumed to be in perfect equilibriums, the process connecting the two can go far away from equilibrium.

Although these two problems about irreversibility are intimately connected, we here concentrate only on the second problem of “operational irreversibility” and give a solution to it. More precisely, we assume that the initial state of a macroscopic (quantum or classical) Hamiltonian system is described by a general equilibrium distribution, and rigorously derive the second law of thermodynamics in the forms of the minimum work principle and the law of entropy increase. This establishes that the second law is a logical necessity once we accept equilibrium statistical mechanics and Hamiltonian mechanics.

Setup and basic inequality: We examine an adiabatic process in thermodynamics, where an external (classical) agent performs an operation on a thermally isolated system. This may be modelled by a quantum mechanical system with an $N$-dimensional Hilbert space whose time evolution is determined by a time dependent Hamiltonian $H(t)$.

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(One imagines that the agent changes some of the parameters in the Hamiltonian.) The operation (and the period of equilibration following it) takes place in the time interval \( t_{\text{init}} \leq t \leq t_{\text{fin}} \), and we write \( H = H(t_{\text{init}}) \) and \( H' = H(t_{\text{fin}}) \). We denote by \( U \) the unitary time evolution operator for the whole operation.

For \( i = 1, \ldots, N \), let \( |\varphi_i⟩ \) and \( |\varphi'_i⟩ \) be the eigenstates of the Hamiltonians \( H \) and \( H' \), respectively, with the eigenvalues \( E_i \) and \( E'_i \). The states are numbered so that \( E_i \leq E_{i+1} \) and \( E'_i \leq E'_{i+1} \). We assume that the initial equilibrium state is described by a density matrix \( \rho_{\text{init}} = w(H) = \sum_{i=1}^{N} |\varphi_i⟩⟨\varphi_i| \), where \( w(\cdot) \) is a function of energy. We denote the initial expectation as \( \langle \cdots \rangle_{\text{init}} = \text{Tr}[\cdots\rho_{\text{init}}] \), and the final expectation (corresponding to the unitary operator \( U \)) as \( \langle \cdots \rangle_U = \text{Tr}[\cdots U \rho_{\text{init}} U^{-1}] \).

We define a special unitary transformation \( \tilde{U} \) by \( \tilde{U}|\varphi_i⟩ = |\varphi'_i⟩ \) for \( i = 1, \ldots, N \). The “adiabatic theorem” in quantum mechanics implies that the unitary operator \( \tilde{U} \) arises as the solution of the Schrödinger equation when the operation (i.e., the change of the Hamiltonian) is executed infinitely slowly. Thus we may suppose that \( \tilde{U} \) corresponds to a quasi-static operation in thermodynamics.

Our results are based on the following inequality.

Lemma — Let \( w(E) \) be nonincreasing in \( E \), and let \( F \) be an observable such that \( F|\varphi'_i⟩ = F_i|\varphi'_i⟩ \) with \( F_i \) nondecreasing in \( i \). Then, for any \( U \),

\[
\langle F \rangle_U \geq \langle F \rangle_{\tilde{U}}.
\]  

Proof: Observe that

\[
\langle F \rangle_U = \text{Tr}[FUw(H)U^{-1}]
\]

\[
= \sum_{i,j=1}^{N} \langle \varphi'_i | F | \varphi'_j \rangle \langle \varphi'_j | U | \varphi_j \rangle \langle \varphi_j | w(H) | \varphi_j \rangle \langle \varphi_j | U^{-1} | \varphi'_i \rangle
\]

\[
= \sum_{i,j=1}^{N} F_i \alpha_{i,j} w_j,
\]

where \( w_j = w(E_j) \), and \( \alpha_{i,j} = |\langle \varphi'_i | U | \varphi_j \rangle|^2 \). Since \( \alpha_{i,j} = \delta_{i,j} \) when \( U \) happens to be \( \tilde{U} \), we find \( \langle F \rangle_{\tilde{U}} = \sum_{i=1}^{N} F_i w_i \). From the unitarity, we have \( 0 \leq \alpha_{i,j} \leq 1 \) and \( \sum_i \alpha_{i,j} = \sum_j \alpha_{i,j} = 1 \). By setting \( w_{N+1} = 0 \), we have for any \( A_j \) that

\[
\sum_{j=1}^{N} A_j w_j = \sum_{j=1}^{N} (w_j - w_{j+1}) \sum_{k=1}^{j} A_k.
\]

By using this we find

\[
\sum_{i,j=1}^{N} F_i \alpha_{i,j} w_j = \sum_{j=1}^{N} (w_j - w_{j+1}) \sum_{i=1}^{j} \beta_i^{(j)} F_i,
\]

with \( \beta_i^{(j)} = \sum_{k=1}^{i} \alpha_{i,k} \), which satisfies \( 0 \leq \beta_i^{(j)} \leq 1 \), and \( \sum_{i=1}^{N} \beta_i^{(j)} = j \). Since \( F_i \) is nondecreasing, we have

\[
\sum_{i=1}^{N} \beta_i^{(j)} F_i = \sum_{i=1}^{j} \beta_i^{(j)} F_i + \sum_{i=j+1}^{N} \beta_i^{(j)} F_i
\]
\[
\sum_{i=1}^{j} \beta_i^{(j)} F_i + \left( \sum_{i=j+1}^{N} \beta_i^{(j)} \right) F_j
\]
\[
= \sum_{i=1}^{j} \beta_i^{(j)} F_i + (j - \sum_{i=1}^{j} \beta_i^{(j)}) F_j
\]
\[
\geq \sum_{i=1}^{j} \beta_i^{(j)} F_i + \sum_{i=1}^{j} (1 - \beta_i^{(j)}) F_i = \sum_{i=1}^{j} F_i
\] (5)

Substituting (5) into (4) and using (3), we get

\[
\sum_{i,j=1}^{N} F_i \alpha_{i,j} w_j \geq \sum_{j=1}^{N} (w_j - w_{j+1}) \sum_{i=1}^{j} F_i = \sum_{i=1}^{N} F_i w_i,
\] (6)

which is the desired bound.

**Physical quantities:** We consider two physical quantities. The work \( W(U) \) done by the agent to the system during the operation (described by \( U \)) is

\[
W(U) = \langle H' \rangle_U - \langle H \rangle_{\text{init}}.
\] (7)

Note that this definition follows uniquely from the energy conservation (of the system plus the agent).

We introduce the energy level operators \( \Omega \) and \( \Omega' \) for the Hamiltonians \( H \) and \( H' \), respectively, by \( \Omega | \phi_j \rangle = j | \phi_j \rangle \) and \( \Omega' | \phi'_j \rangle = j | \phi'_j \rangle \). Then we define the initial entropy as \( S_{\text{init}} = \langle \log \Omega \rangle_{\text{init}} \) and the entropy after the operation as \( S_{\text{fin}}(U) = \langle \log \Omega' \rangle_U \). Note that \( U^{-1} \Omega' U = \Omega \), and hence \( S_{\text{fin}}(U) = S_{\text{init}} \). Although there are various ways of defining entropies, these are natural extensions of the Boltzmann entropy \( \frac{1}{T} \). It is not hard to check that \( \frac{1}{T} \), for equilibrium states of a macroscopic system, the above definition agrees with other statistical mechanical entropies and hence with the thermodynamic entropy. It is when one considers non-equilibrium states, that various statistical mechanical entropies exhibit different behaviors. See below.

**Second law for nonincreasing distributions:** By setting \( F = H' \) or \( F = \log \Omega' \), we can readily apply the inequality (4) to get

**Theorem 1** — Suppose that \( w(E) \) (which determines the initial distribution) is nonincreasing in \( E \). Then we have the minimum work principle

\[
W(U) \geq W(\tilde{U}),
\] (8)

and the law of entropy increase

\[
S_{\text{fin}}(U) \geq S_{\text{fin}}(\tilde{U}) = S_{\text{init}},
\] (9)

for any \( U \) which is consistent with the Hamiltonians \( H \) and \( H' \).

Among the examples of distributions with nonincreasing \( w(E) \) are the canonical distribution with \( w_{\text{can}}^{\beta}(E) = e^{-\beta E} / \sum_i e^{-\beta E_i} \), and the extended microcanonical ensemble with
$w^{\text{emc}}_E(E) = \chi[E \leq \bar{E}] / N(\bar{E})$ where $N(\bar{E}) = \max\{i | E_i \leq \bar{E}\}$ is the number of states. (The characteristic function is defined by $\chi(\text{true}) = 1$ and $\chi(\text{false}) = 0$.) In the extended microcanonical ensemble, all the eigenstates with energies below $\bar{E}$ are given the equal weights. Although this distribution may not be popular, it is known to recover thermodynamics equally well as the standard distributions. (See, for example, [11].) We remind the reader that modern statistical physics relies fundamentally on the fact that an equilibrium state of a macroscopic system can be represented by various different statistical distributions, but the different descriptions provide us with exactly the same thermodynamics [1].

The inequality (8) represents the minimum work principle for adiabatic processes, which says that the work required for a given change of extensive parameters takes its minimum in the limit of slow operation [12]. The minimum work principle is usually stated for isothermal processes. To get this version of the principle, we consider a system which can be separated into a small (but still macroscopic) subsystem and a big heat bath. We decompose the Hamiltonian as $H = H_{\text{sub}} + H_{\text{bath}} + H_{\text{int}}$ and assume that the interaction $H_{\text{int}}$ between the subsystem and the bath is small in a certain sense. When one only changes $H_{\text{sub}}$ during the operation, we can show (by a standard estimate [8]) that $W(\tilde{U}) \simeq F(\beta, H'_{\text{sub}}) - F(\beta, H_{\text{sub}})$ where $F(\beta, H_{\text{sub}}) = -\beta^{-1} \log \text{Tr}[\exp(-\beta H_{\text{sub}})]$ is the free energy of the subsystem. Then the inequality (8) implies the minimum work principle for an isothermal process.

The inequality (8) represents the law of entropy increase, which says that the entropy never decreases when an adiabatic process is possible [13]. This may be regarded as a realization of the conventional wisdom [14] (which seems to be not rigorously founded) that a “coarse grained” entropy can measure irreversibility [15]. For the reader who worries about the arbitrariness in the definition of entropy, we remark that the law of entropy increase can also be derived from purely thermodynamic considerations [10] by using the minimum work principle (8), which does not suffer from any ambiguities in the definitions.

Therefore if we assume that the initial state is described by the canonical or the extended microcanonical (or other nonincreasing) distributions, then the second law of thermodynamics (i.e., the minimum work principle and the law of entropy increase) can be established as rigorous (and easily proved) mathematical statements [17].

**Microcanonical ensemble:** We can also treat the standard microcanonical distribution with the weight $w^{\text{mc}}_{E,\Delta E}(E) = \chi[\bar{E} \leq E \leq \bar{E} + \Delta E] / N(\bar{E}, \Delta E)$ where $N(\bar{E}, \Delta E)$ is the number of levels such that $\bar{E} \leq E_i \leq \bar{E} + \Delta E$. In this case, however, we do not have the inequality (4), but only have its weaker form [18]

$$\langle F \rangle_U \geq \langle F \rangle_{\min} \equiv \frac{1}{N(\bar{E}, \Delta E)} \sum_{i=1}^{N(\bar{E}, \Delta E)} F_i,$$

where $\langle \cdots \rangle_{\min}$ is the expectation in the distribution where the $N(\bar{E}, \Delta E)$ states with the lowest energies are given exactly the same weights. It is clear that $\langle F \rangle_{\min}$ is in general smaller than the desired $\langle F \rangle_{\tilde{U}}$. But for a normal macroscopic systems and an extensive $F$, we can prove that $\langle F \rangle_{\min}$ and $\langle F \rangle_{\tilde{U}}$ are essentially identical with each other [18]. Consequently, we get
Theorem 2 — Suppose that the model has an additional parameter $V$ (the volume), and we take a suitable thermodynamic limit $V \to \infty$ as is explained in [19]. Then we have the minimum work principle and the law of entropy increase in the forms

$$\lim \inf_{V \to \infty} \{W(U) - W(\tilde{U})\} \geq 0, \quad (11)$$

and

$$\lim \inf_{V \to \infty} \{S_{\text{fin}}(U) - S_{\text{init}}\} \geq 0, \quad (12)$$

for any $U$ consistent with the Hamiltonians $H$ and $H'$.

The discussions that follow Theorem 1 apply equally here.

**Classical systems:** All of the above results can be proved for classical Hamiltonian systems as well. Since the extension is straightforward [8], let us discuss only the basic ideas.

Consider exactly the same situation as in quantum systems. We denote a phase space point by $\Gamma$, and let $H(\Gamma)$ and $H'(\Gamma)$ be the initial and the final Hamiltonians, respectively. We assume that the initial state is sampled from a probability distribution $d\mu_{\text{init}} = w(H(\Gamma)) d\Gamma$ where $w(E)$ is a function of energy and $d\Gamma$ is the Lebesgue measure. The time evolution map for the whole operation is denoted as $\tau$, and the map corresponding to infinitely slow operation is denoted as $\tilde{\tau}$. The relevant expectation values of a function $F(\Gamma)$ are

$$\langle F \rangle_{\text{init}} = \int d\mu_{\text{init}}(\Gamma) F(\Gamma) \quad \text{and} \quad \langle F \rangle_{\tau} = \int d\mu_{\text{init}}(\Gamma) F(\tau(\Gamma)).$$

In order to make use of the argument for quantum systems, we decompose the phase space into a disjoint union $\bigcup_{i=1}^{\infty} V_i$ with $V_i = \{\Gamma \mid E_i \leq H(\Gamma) < E_{i+1}\}$. Here the sequence $E_1, E_2, \ldots$ is chosen so that $|V_i| = v$ with a constant $v > 0$ for all $i$. ($|V|$ is the Lebesgue volume of a set $V$.) We also construct a similar decomposition $\bigcup_{i=1}^{\infty} V_i'$ for $H'(\Gamma)$ using the same volume $v$. Then, for a given $\tau$, we define $\alpha_{i,j} = \delta^{-1}|V_i' \cap \tau(V_j)|$, which is the ratio of the phase space point in $V_j$ which flow into $V_i'$. By using the Liouville theorem (i.e., the conservation of the phase space volume), we see that $\sum_i \alpha_{i,j} = \sum_j \alpha_{i,j} = 1$ exactly as in quantum cases. The adiabatic theorem again implies that $\alpha_{i,j} = \delta_{i,j}$ for the map $\tilde{\tau}$.

Assume that the function $F(\Gamma)$ depends only on the energy $H'(\Gamma)$. Since $H(\Gamma) = E_j + O(v)$ for $\Gamma \in V_j$, $H'(\Gamma) = E_i' + O(v)$ for $\Gamma \in V_i'$, and $\sum_i \chi[\Gamma \in V_j, \tau(\Gamma) \in V_i'] = 1$, we find that

$$\langle F \rangle_{\tau} = \sum_{i,j} \int d\Gamma F(\Gamma) \chi[\Gamma \in V_j, \tau(\Gamma) \in V_i'] w(H(\Gamma))$$

$$\simeq v \sum_{i,j} F(E_i') \alpha_{i,j} w(E_j). \quad (13)$$

Note that the final expression becomes exact as $v \to 0$. Observing that this representation is exactly the same as the quantum one, the rest of the proof proceeds automatically.

**Discussions:** We have presented general theorems which establish the validity of the second law of thermodynamics (in the forms of minimum work principle and the law of entropy increase) under the assumption that the initial state is described by a certain
equilibrium distribution. This means that the “order theoretical” nature \cite{2} of the second law is already inherent in equilibrium statistical mechanics and Hamiltonian mechanics.

A major and essential limitation to the present approach is that the final state with the density matrix \( \rho_{\text{fin}} = U \rho_{\text{init}} U^{-1} \) in general does not correspond to an exact equilibrium distribution (while we expect it to describe an equilibrium state in a macroscopic sense). This means that our derivation of the second law is not useful if we perform yet another operation after the first one (where \( \rho_{\text{fin}} \) determines the initial state). Given the fact that thermodynamics has been verified in experiments repeated over and over in the history, we have to say that this limitation is quite serious.

A solution to this problem is simply to replace \( \rho_{\text{fin}} \) with an exact equilibrium density matrix \( \tilde{\rho}_{\text{fin}} \), where the latter is chosen so that the replacement produces no macroscopically observable effects. Then we can apply the argument of the present paper to derive the second law. Of course the main remaining issue here is to justify \cite{20} the replacement of \( \rho_{\text{fin}} \) by \( \tilde{\rho}_{\text{fin}} \), which is a part of the problem of “equilibration.”

It is a pleasure to thank Shin-ichi Sasa for various useful discussions and suggestions which have been essential for the present work, Elliott Lieb for valuable discussions and comments, and Yoshi Oono, Joel Lebowitz, and Ken Sekimoto for useful discussions on related topics.

References

[1] Since the literature is so vast, we only refer to a recent monograph; G. Gallavotti, *Statistical Mechanics: A Short Treatise*, (Springer, 1999).

[2] E. H. Lieb and J. Yngvason, Phys. Rep. 310, 1 (1999); Physics Today, April 2000, p. 32.

[3] For classical Hamiltonian systems with canonical distribution, some versions of the second law has been proved in C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997); J. Stat. Phys. 96, 415 (1999). Extensions to quantum systems is not hard.

[4] Since we are proving only inequalities, it is trivial to take the limit \( N \to \infty \). One can treat, for example, systems of particles in a continuum space by first introducing artificial “cutoffs” to make the Hilbert space finite dimensional, and carefully taking necessary limits after the proofs.

[5] 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 \( U = U(t_{\text{fin}}) \).

[6] This conclusion is not trivial as it appears. In a usual macroscopic system, the adiabatic theorem requires an operation to be done so slowly that it can never be (thermodynamically) realistic. Nevertheless we expect the theorem to provide us with information of thermodynamic quasi-static operations unless the operation contains nontrivial steps such as thermally decoupling a part of the system.
The following inequality and its implication to the second law was first discussed in H. Tasaki, unpublished note (cond-mat/0005128), where we focused on partial derivation of the second law directly from quantum dynamics in systems satisfying certain conditions. (See H. Tasaki, Phys. Rev. Lett. 80, 1373 (1998).) We then realized that the argument can be used more effectively in the present context. See [8] for a unified treatment.

Note that $W(U)$ is the expectation value of the energy difference. The actual work does fluctuate around $W(U)$, but the fluctuation must be negligible in nonpathological macroscopic states.

The Boltzmann entropy is defined as $S_B = \log W$ (we set the Boltzmann constant to be unity), where $W$ is the number of microstates with the same prescribed macroscopic characters. Now given a generic eigenstate with energy $E$ of a macroscopic quantum system, we can choose $W$ to be either the density of states at $E$ or the number of eigenstates with energies below $E$. Both give the same result in the thermodynamic limit, and our definition corresponds to the latter choice. The dependence of our entropy on Hamiltonian corresponds to a macroscopic characterization in terms of energy variables.

For the special case with $H' = H$, we have $\tilde{U} = 1$ and hence $W(\tilde{U}) = 0$. Then (8) becomes $W(U) \geq 0$, which means that the work done during an adiabatic cycle cannot be negative. This is the Planck’s principle [2].

The entropy principle states that an adiabatic process is possible when and only when the entropy does not decrease [2]. See [8] for the remaining “when” part.

Recall that the von Neuman and the Gibbs entropies are time independent. But we believe that this fact independence no significance in thermodynamics since these entropies coincide with the thermodynamic entropy only when the state corresponds to an exact equilibrium distribution. See, for example, J. Lebowitz, Physics Today, September 1993, p. 32.

Denote by $X$ and $X'$ the sets of extensive variables corresponding to $H$ and $H'$, respectively. We assume (as usual) that a thermodynamic equilibrium state is fully determined by specifying its energy and extensive variables. Let $E = \langle H \rangle_{\text{init}}$, $E' = \langle H' \rangle_U$, and $\bar{E}' = \langle H' \rangle_{\tilde{U}}$. The thermodynamic entropy should satisfy $S_{TD}(E, X) = S_{TD}(\bar{E}', X')$ because the two states are connected by a quasi-static adiabatic process. We also have $S_{TD}(E', X') \geq S_{TD}(\bar{E}', X')$ since $E' \geq \bar{E}'$ from (8), and the entropy is increasing in energy. Then we get the desired inequality $S_{TD}(E', X') \geq S_{TD}(E, X)$.  

[7] The following inequality and its implication to the second law was first discussed in H. Tasaki, unpublished note (cond-mat/0005128), where we focused on partial derivation of the second law directly from quantum dynamics in systems satisfying certain conditions. (See H. Tasaki, Phys. Rev. Lett. 80, 1373 (1998).) We then realized that the argument can be used more effectively in the present context. See [8] for a unified treatment.

[8] H. Tasaki, to be published.

[9] Note that $W(U)$ is the expectation value of the energy difference. The actual work does fluctuate around $W(U)$, but the fluctuation must be negligible in nonpathological macroscopic states.

[10] The Boltzmann entropy is defined as $S_B = \log W$ (we set the Boltzmann constant to be unity), where $W$ is the number of microstates with the same prescribed macroscopic characters. Now given a generic eigenstate with energy $E$ of a macroscopic quantum system, we can choose $W$ to be either the density of states at $E$ or the number of eigenstates with energies below $E$. Both give the same result in the thermodynamic limit, and our definition corresponds to the latter choice. The dependence of our entropy on Hamiltonian corresponds to a macroscopic characterization in terms of energy variables.

[11] R. B. Griffiths, J. Math. Phys. 6, 1447 (1965); E. H. Lieb and J. Lebowitz, Adv. Math. 9, 316 (1972).

[12] For the special case with $H' = H$, we have $\tilde{U} = 1$ and hence $W(\tilde{U}) = 0$. Then (8) becomes $W(U) \geq 0$, which means that the work done during an adiabatic cycle cannot be negative. This is the Planck’s principle [2].

[13] The entropy principle states that an adiabatic process is possible when and only when the entropy does not decrease [2]. See [8] for the remaining “when” part.

[14] See, for examples, D. N. Zubarev, Nonequilibrium Statistical Thermodynamics (Plenum, New York, 1974), Section 8.4; J. Rau and B. Müller, Phys. Rep. 272, 1 (1996), Section A.3.1.

[15] Recall that the von Neuman and the Gibbs entropies are time independent. But we believe that this fact independence no significance in thermodynamics since these entropies coincide with the thermodynamic entropy only when the state corresponds to an exact equilibrium distribution. See, for example, J. Lebowitz, Physics Today, September 1993, p. 32.

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[17] Note that the system need not be macroscopic. This fact may find applications in the discussions of “small” systems. See K. Sato, K. Sekimoto, T. Honhou, and F. Takagi, preprint (cond-mat/0008393), and H. Tasaki, unpublished note (cond-mat/0008420), where we already used the result of the present note.

[18] The inequality is almost trivial, but let us present a proof. We abbreviate $N(\bar{E})$ and $N(\bar{E}, \delta E)$ as $N_0$ and $\bar{N}$, respectively. Then $\langle F \rangle_U = \bar{N}^{-1} \sum_{j=N_0+1}^{\bar{N}} \sum_{i=1}^{N} F_i \alpha_{i,j} = \bar{N}^{-1} \sum_{j=1}^{\bar{N}} \sum_{i=1}^{N} F_i \tilde{\alpha}_{i,j}$, where we defined $\tilde{\alpha}_{i,j} = \alpha_{i,j+N_0}$ for $j = 1, \ldots, \bar{N}$. We have $\tilde{\alpha}_{i,j} \geq 0$, $\sum_{i=1}^{N} \tilde{\alpha}_{i,j} = 1$, and $\sum_{j=1}^{\bar{N}} \tilde{\alpha}_{i,j} \leq 1$. Then (10) can be proved exactly as (6).

[19] Sketch of the assumptions and proof: We assume that there is an additional parameter $V$ (the volume), and the numbers of states $N(E)$ and $N'(E')$ for $H$ and $H'$, respectively, behave as $N(E \varepsilon V) \approx e^{V \sigma(\varepsilon)}$ and $N'(E' V') \approx e^{V \sigma'(E')}$ as $V \to \infty$ with continuous increasing functions (entropies) $\sigma(\varepsilon)$ and $\sigma'(E')$. We choose the relevant energies as $\bar{E} = \varepsilon V$ and $\Delta E = \alpha V^\delta$ with constants $\varepsilon$, $\alpha > 0$, and $0 < \delta < 1$. The initial state $\langle \cdots \rangle_{\text{init}}$ is the microcanonical distribution with the energy range from $\bar{E}$ to $\bar{E} + \Delta E$, the final state $\langle \cdots \rangle_{\tilde{U}}$ is that with the range $\bar{E}'$ to $\bar{E}' + \Delta E'$, and $\langle \cdots \rangle_{\text{min}}$ is that with the range 0 to $\bar{E}'$ (where the lowest energy is set to zero). Here $\bar{E}'$, $\Delta E'$, and $\tilde{E}'$ are determined by $N'(\bar{E}') = N(\bar{E})$, $N'(\bar{E}' + \Delta E') = N(\bar{E} + \Delta E)$, and $N'(\bar{E}') = N(\bar{E}, \Delta E) = N(\bar{E} + \Delta E) - N(\bar{E}) + 1$. By using the above assumptions, we find that $\bar{E}'/V$, $(\bar{E}' + \Delta E')/V$, and $\bar{E}'/V$ converge to a single value $\varepsilon'$ as $V \to \infty$. Then if $F(E') = V f(E'/V)$, the standard estimate (based on the fact that $N'(E')$ is a rapidly increasing function) implies $\langle f(H'/V) \rangle_{\tilde{U}} \approx f(\varepsilon')$ and $\langle f(H'/V) \rangle_{\text{min}} \approx f(\varepsilon')$ as $V \to \infty$.

[20] Note that such a justification can only be possible for generic operations, since the entropy does decrease for the very special operation corresponding to $U^{-1}$. 