

Microscopic work distribution of small systems in quantum isothermal processes and the minimal work principle

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For a two-level quantum mechanical system, we derive microscopically the exact expression for the fluctuation of microscopic work in a multistep nonequilibrium process, and we rigorously prove that in an isothermal process, the fluctuation is vanishingly small and the most probabilistic work is just equal to the difference of the free energy. Our study demonstrates that the convergence of the microscopic work in the isothermal process is due to the nature of the isothermal process rather than the usual thermodynamic limit condition. Our investigation justifies the validity of a “minimum work principle” formulation of the second law even for a small system far from the thermodynamic limit.

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I. INTRODUCTION

Thermodynamics usually deals with the systems of an infinite number of degrees of freedoms, in which relative fluctuations of the observable—e.g., energy, particle number—are inversely proportional to the square root of the numbers of the particles of the system [1]. Hence, for a macroscopic system consisting of an infinite number of particles, the fluctuations are vanishingly small and the ensemble average can describe thermodynamic phenomena completely. However, concerning small systems, usually the fluctuations of the microscopic values of thermodynamic observable will become appreciable and the ensemble average alone can no longer give a complete description [2]. In recent years, increasing interest has been drawn to the study of the thermodynamics of small systems and the emphasis has been put on fluctuations of the microscopic value of the observable, instead of their ensemble average. Some notable progress has been made, examples including the Jarzynski equality [3,4] and the fluctuation theorem [5]. The former connects the free-energy difference of two equilibrium states with an ensemble average of microscopic work in nonequilibrium processes, while the latter illustrates the probabilistic “entropy decrease” of a closed system within a short time, or transient “violation” of the second law. These studies shed new light on the understanding of nonequilibrium thermodynamical processes of biological motors in cells and promise important applications to the design of small-size machines. In all these studies, for small systems, although fluctuations of most observables are appreciable, there exists an exception—the work done during a slowest reversible equilibrium process (we use isothermal processes to replace the slowest reversible processes hereafter). It has been pointed out that the fluctuation of microscopic work done by or on a small system during a slowest reversible process is vanishingly small [3,6]. Nevertheless, although the fluctuations of the microscopic work of small systems in finite-time irreversible processes have been extensively studied [7] and the vanishing fluctuations of the microscopic work of classical small systems especially concerning the thermodynamic isothermal process have been pointed out, to our best knowledge, a rigorous proof of the above result from the microscopic point

of view is still lacking, and its quantum mechanical generalization has not been studied yet.

In this paper, we will investigate this problem by simulating a quantum isothermal process with an infinite number of infinitesimal quantum adiabatic processes (QAPs) and quantum isochoric processes (QIPs) [8–10]. We prove rigorously from a microscopic point of view the above result that, for a two-level system, the fluctuations of the microscopic work during an quantum isothermal process [10] is vanishingly small. We emphasize that, different from most cases in conventional statistical mechanics, where fluctuations vanish in the thermodynamic limit, the vanishing work fluctuations for a small system in an isothermal process are due to the intrinsic nature of the isothermal process. Our study also verifies the universal validity of the “minimum work principle” formulation of the second law: it holds even for a small system.

II. THERMODYNAMIC PROCESS IN PARAMETER SPACE

We consider a two-level quantum mechanical system with excited (ground) states $|e\rangle$ ($|g\rangle$) with instantaneous eigenenergy $E_e(t)$ [$E_g(t)$] depending on time t . This two-level system can be modeled as a spin-1/2 in an external magnetic field. It interacts with a heat bath of inverse temperature β , which can be universally modeled as a collection of many bosons with creation (annihilation) operators a_q^\dagger [a_q] [11]. The model Hamiltonian reads [12,13].

$$H = \Delta(t)\sigma_z + \sum_q \omega_q a_q^\dagger a_q + \sum_q (\lambda_q \sigma_- a_q^\dagger + \text{H.c.}), \quad (1)$$

where $\sigma_- = |g\rangle\langle e| = (\sigma_x - i\sigma_y)/2$ and $\sigma_z = (|e\rangle\langle e| - |g\rangle\langle g|)/2$. Initially, let the two-level system be thermalized to equilibrium. Then we alter the magnetic field slowly so that the energy level spacing $\Delta(t)$ slowly changes from Δ_A to Δ_B . During the controlling process illustrated by the smooth curve $\hat{A}\hat{B}$ in Fig. 1, the work is done on the system. In the infinitely slow process, which can be alternatively regarded as a quantum isothermal process [10], the two-level system is in the thermal equilibrium at every instant, which is described by the diagonal reduced density matrix $\rho_S(t) = P_e(t)|e\rangle\langle e| + [1$

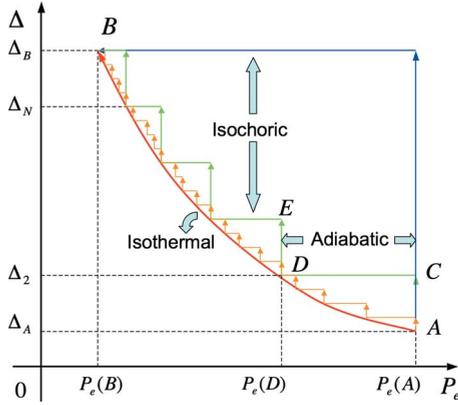


FIG. 1. (Color online) Schematic illustration of a quantum isothermal process [10] $\hat{A}\hat{B}$. Here the horizontal axis P_e is the occupation probability in the excited state of the two-level system and the vertical axis indicates the level spacing of the two-level system. The smooth curve $\hat{A}\hat{B}$ represents the isothermal process, whose “equation of state” can be expressed as $\Delta(t) = -\beta^{-1} \ln(P_e^{-1} - 1)$. The horizontal and vertical lines represent QICs and QAPs [10]. We can use many small QAPs and QIPs to model the quantum isothermal process. For example, we use a “five-step stair” path (green) $A \rightarrow C \rightarrow D \rightarrow \dots \rightarrow B$ to simulate the smooth curve $\hat{A}\hat{B}$. The “one-step” path (blue) and “20-step” path (orange) are also illustrated.

$-P_e(t)|g\rangle\langle g|$, where $P_e(t) = \exp[-\Delta(t)] / \{1 + \exp[-\beta\Delta(t)]\}$ satisfies the Gibbs distribution. It should be pointed out that, during the isothermal process, there is a heat exchange between the two-level system and the heat bath.

For such an isothermal process, it is difficult to calculate the microscopic work distribution directly. According to Refs. [8–10], however, this process can be simulated by a series of QAPs and QIPs. In QAP [QIC] processes, there is only work done (heat exchange). Hence, using the changes of eigenenergies of the microscopic state at instant $t = A, C, D$, we can indirectly calculate the microscopic work done (heat exchange) [3,4], $dW = E_\alpha(C) - E_\alpha(A)$ [$dQ = E_\alpha(D) - E_\beta(C)$], for $\alpha, \beta = e, g$. In the parameter space, these QAP and QIP series processes are represented by the “stair” path ($A \rightarrow C \rightarrow D \rightarrow \dots \rightarrow B$) in Fig. 1. When every step of the stair path becomes infinitesimal, the stair path becomes equivalent to the isothermal process $\hat{A}\hat{B}$. In this way we simulate the quantum isothermal process with N equal-height steps (see Fig. 1) with small height $\Delta = (\Delta_B - \Delta_A) / N$, where Δ_A and Δ_B are the level spacings at points A and B , respectively. The level spacings of the two-level system after the $(j-1)$ th QIC is

$$\Delta_j = \Delta_A + (j-1)\Delta, \quad (2)$$

for $j=1, 2, \dots, N+1$. The initial and final points A and B correspond to $j=1$ and $j=N+1$, respectively. When we fix the initial point A and the final point B , the jump Δ in every step decreases with the increase of the step number N and Δ approaches zero when N becomes infinity. Obviously, when $N \rightarrow \infty$, the stair path approaches its asymptotic behavior—the isothermal path (see Fig. 1). When the system reaches

thermal equilibrium, the occupation probabilities obey the Gibbs distribution defined by

$$P_e^j = e^{-\beta\Delta_j} [1 + e^{-\beta\Delta_j}]^{-1}, \quad P_g^j = P_e^j e^{\beta\Delta_j}. \quad (3)$$

We remark that there are three time scales in our process: τ_a , the time of the quantum adiabatic approximation; τ_c , the control time of changing the magnetic field, hence the level spacing; and τ_r , the relaxation of the two-level system. According to Ref. [13], τ_r is determined by the coupling strength λ_q , Eq. (1). We consider the case that $\tau_a \ll \tau_c \ll \tau_r$ for a quantum adiabatic process where we can define the microscopic work in every realization of the process.

III. MICROSCOPIC WORK DISTRIBUTION

Having defined the “path” in the parameter space ($\Delta - P_e$) space, we can further introduce the microscopic work and its corresponding probabilities for a given path. Actually, the definition of microscopic work is very similar to that in Ref. [4]. In the above path divided into many “steps,” the first step $A \rightarrow C \rightarrow D$ consists of a QAP $A \rightarrow C$ and a QIP $C \rightarrow D$. At the beginning (point A of Fig. 1), the system is initially in a thermal equilibrium state $\rho_S(A)$, which implies that the system is either in its microscopic state $|g\rangle$ or $|e\rangle$ with probabilities P_g^1 and P_e^1 , respectively. We choose the ground state in the energy reference point so that the microscopic energy $E(A)$ of the system at initial point A can take $E_e(A) = \Delta_A$ or $E_g(A) = 0$, with probability P_e^1 and $1 - P_e^1$, respectively. In the first QAP $A \rightarrow C$, the system remains in its microscopic state $|g\rangle$ ($|e\rangle$) if the system is initially in its microscopic state $|g\rangle$ ($|e\rangle$). As there is no heat exchange in the QAP, the work done by an external controller is just the change of the microscopic energy $W_\alpha = E_\alpha(C) - E_\alpha(A)$ for $\alpha = e, g$. Correspondingly the work done during $A \rightarrow C$ can be either $\Delta_C - \Delta_A$ or 0 with probabilities P_e^1 or $1 - P_e^1$, respectively. This also agrees with the definition of work in quantum mechanical systems: work is associated with the change of the level spacing [9,10,14].

After the QAP, a quantum isochoric process $C \rightarrow D$ (see Fig. 1) follows. Here, there is no work done according to the definition of work in quantum mechanical systems [9,10,14], because there is no change in the eigenenergies. Nevertheless, there is heat exchange between the system and bath. The QIPs last long enough ($\gg \tau_r$) so that the system can reach thermal equilibrium with the heat bath. After a thermalization for a long time, the two-level system reaches thermal equilibrium with the heat bath again, Eqs. (3), at instant D indicated in Fig. 1. Then a second step $D \rightarrow E \rightarrow F$ begins. Similarly, the microscopic work 0 or $\Delta_3 - \Delta_2$ is done in this step with probabilities $1 - P_e^2$ or P_e^2 . The microscopic work done and their probabilities for the remaining steps can be obtained through a similar analysis. Because in every QIP the system is independently thermalized by the heat bath, then there should be no correlations of the probabilities distributions in every two neighbor steps, or alternatively, this process is a Markovian process. Hence, the total microscopic work done after N steps is a sum of microscopic work done in all steps and the joint probabilities for N steps as a whole is the product of that of all steps.

For a special example that the microscopic work done during the whole process is $W=N\Delta$, where Δ is that for each QIP step, the joint probabilities for the system keeping in $|e\rangle$ in every QIP are $P[N\Delta]=P_e^1 P_e^2 \cdots P_e^N$. The more general case with microscopic work $W=(N-k)\Delta$ corresponds to a microscopic process, in which k out of N QIPs ends with the system in its microscopic state $|g\rangle$. The probability $P(k) := P[(N-k)\Delta]$ with the microscopic work $W=(N-k)\Delta$ in the N -step path is given by the following equation:

$$P(k) = \left(\prod_{j=1}^N P_e^j \right) \left(\prod_{l=0}^{k-1} \frac{e^{\beta\Delta_B} - e^{\beta(\Delta_A+l\Delta)}}{e^{\beta(l+1)\Delta} - 1} \right). \quad (4)$$

To prove the above result, we first consider the case with $k=1$. For this case, there is one and only one out of N QIPs, in which the system ends up in the microscopic state $|g\rangle$. Then the corresponding probability can be calculated as $P(1) = (1 - P_e^1)P_e^2 \cdots P_e^N + P_e^1(1 - P_e^2) \cdots P_e^N + \cdots + P_e^1 P_e^2 \cdots (1 - P_e^N)$ or $P(1) = (\prod_{j=1}^N P_e^j) e^{\beta\Delta_B} \sum_{x_1=1}^N e^{-\beta\Delta x_1}$ or

$$P(1) = \left(\prod_{j=1}^N P_e^j \right) \frac{(e^{\beta\Delta_B} - e^{\beta\Delta_A})}{e^{\beta\Delta} - 1}. \quad (5)$$

That means that Eq. (4) holds for $k=1$. Similarly we can check the case with $k=2$. For this case, there are two out of N QIPs, in which the system ends up in the microscopic state $|g\rangle$. Hence its probability can be expressed as

$$\begin{aligned} P(2) &= (1 - P_e^1)(1 - P_e^2)P_e^3 \cdots P_e^N + (1 - P_e^1)P_e^2(1 - P_e^3) \cdots P_e^N \\ &\quad + \cdots + P_e^1 P_e^2 \cdots (1 - P_e^{N-1})(1 - P_e^N) \\ &= \left(\prod_{j=1}^N P_e^j \right) e^{2\beta\Delta_B} \sum_{x_1=1}^N \sum_{x_2=1}^{x_1-1} e^{-\beta\Delta(x_1+x_2)} \end{aligned}$$

or

$$P(2) = \left(\prod_{j=1}^N P_e^j \right) \frac{[e^{\beta\Delta_B} - e^{\beta\Delta_A}][e^{\beta\Delta_B} - e^{\beta(\Delta_A+\Delta)}]}{(e^{\beta\Delta} - 1)(e^{2\beta\Delta} - 1)}. \quad (6)$$

Hence Eq. (4) also holds for the $k=2$ case. In general, for an arbitrary k , the corresponding probability can be expressed as

$$P(k) = \left(\prod_{j=1}^N P_e^j \right) e^{k\beta\Delta_B} \chi(k), \quad (7)$$

where $\chi(k) = \sum_{x_1=1}^N \sum_{x_2=1}^{x_1-1} \cdots \sum_{x_k=1}^{x_{k-1}-1} e^{-\beta\Delta(x_1+\cdots+x_k)}$. As $\chi(k)$ ($k=1, 2, \dots, N$) satisfy

$$\begin{aligned} \chi(k) &= \sum_{i=1}^{k-1} \left[\left(\prod_{j=1}^i \frac{-1}{1 - e^{-j\Delta}} \right) (-e^{-i\Delta}) \chi(k-i) \right] + \left(\prod_{j=1}^k \frac{-1}{1 - e^{-j\Delta}} \right) \\ &\quad \times [e^{-k(N+1)\Delta} - e^{-k\Delta}], \end{aligned} \quad (8)$$

we can use the complete induction method to prove that the $\chi(k)$ can be generally expressed as

$$\chi(k) = \prod_{l=0}^{k-1} \frac{e^{-\beta N \Delta} [e^{\beta N \Delta} - e^{\beta l \Delta}]}{e^{\beta(l+1)\Delta} - 1}. \quad (9)$$

Substituting Eq. (9) into Eq. (7), we obtain Eq. (4). Hence, by now we prove the general result given by Eq. (4).

IV. MOST PROBABILISTIC DISTRIBUTION AND FLUCTUATION

The above equation (4) can result in the main conclusion in this paper. From the above microscopic work distribution function (4), we obtain the ratio $R(k) = P(k+1)/P(k)$ of distributions for two close microscopic works—i.e.,

$$R(k) = \frac{e^{\beta\Delta_B} - e^{\beta\Delta_A+k\beta\Delta}}{e^{\beta(k+1)\Delta} - 1}. \quad (10)$$

Let \tilde{k} maximize the probability distribution $P(k)$ for the microscopic work $[N - (\tilde{k} + 1)\Delta]$. Then $P(\tilde{k}) \geq P(\tilde{k} \pm 1)$, or $R(\tilde{k}) \leq 1$ and $R(\tilde{k} - 1) \geq 1$. For very large N , $R(\tilde{k}) \simeq 1$ such that

$$\tilde{k}\Delta = \frac{1}{\beta} \ln \left[\frac{1 + \exp[\beta\Delta_B]}{\exp[\beta(\Delta_B - \Delta_A)/N] + \exp[\beta\Delta_A]} \right]. \quad (11)$$

In the large- N limit, the above equation determines the microscopic work $\tilde{W} = (N - \tilde{k})\Delta$ with most probabilistic distribution

$$\tilde{W} = \frac{1}{\beta} \ln \left(\frac{1 + e^{\beta\Delta_B}}{1 + e^{\beta\Delta_A}} \right), \quad (12)$$

which is just the free-energy difference $\Delta F_{AB} = F_B - F_A$, where $F_j = \ln[1 + \exp(\beta\Delta_j)]/\beta$ for $j=A, B$.

Next let us give a heuristic analysis of the dispersion of the work distribution (4). Because all steps in the stair path are independent of each other, thus the whole process can be regarded as Markovian. So the variance of the total microscopic work done during the whole process is equal to the sum of the variance of the local microscopic work in every step—i.e., $\langle W_{AB}^2 \rangle - \langle W_{AB} \rangle^2 = \sum_{j=1}^N (\langle W_j^2 \rangle - \langle W_j \rangle^2)$, where W_j is the microscopic work done during the j th QAP and the local fluctuations

$$\langle W_j^2 \rangle - \langle W_j \rangle^2 = \Delta^2 [P_e^j - (P_e^j)^2] \quad (13)$$

for different j are similar. Here Δ is inversely proportional to N , and $\langle W_{AB} \rangle$ being independent of N , the relative variance of W_{AB} is inversely proportional to

$$\sqrt{\frac{\langle W_{AB}^2 \rangle - \langle W_{AB} \rangle^2}{\langle W_{AB} \rangle}} \propto \frac{1}{\sqrt{N}}. \quad (14)$$

We numerically plot the work distribution function (see Fig. 2) based on the above analytical result (4) to test the above analysis. Here we choose the step number N from 1 to 10 000. For $N=1$, the stair path becomes a “one-step” path consisting of an QAP and an QIP (see Fig. 1). The microscopic work corresponding to the one-step path is either $\Delta_B - \Delta_A$ or 0 with the probability $P(W = \Delta_B - \Delta_A) = P_e^1$ or $P(W = 0) = 1 - P_e^1$. In the above figures, we choose $\exp(-\beta\Delta_A) = 1/2$, $(P_e^1 = 1/3)$, and the numerical result agrees well with our analysis. For $N=5$ (see Fig. 1), the possible microscopic work can be $W = i(\Delta_B - \Delta_A)/5$, $i=0, 1, 2, \dots, 5$. The numerical result indicates vanishing probability for $W = \Delta_B - \Delta_A$. For $N=20$ (see Fig. 1), the numerical result shows even more vanishing probabilities of the microscopic work. That is, the dispersion (fluctuation) of microscopic work de-

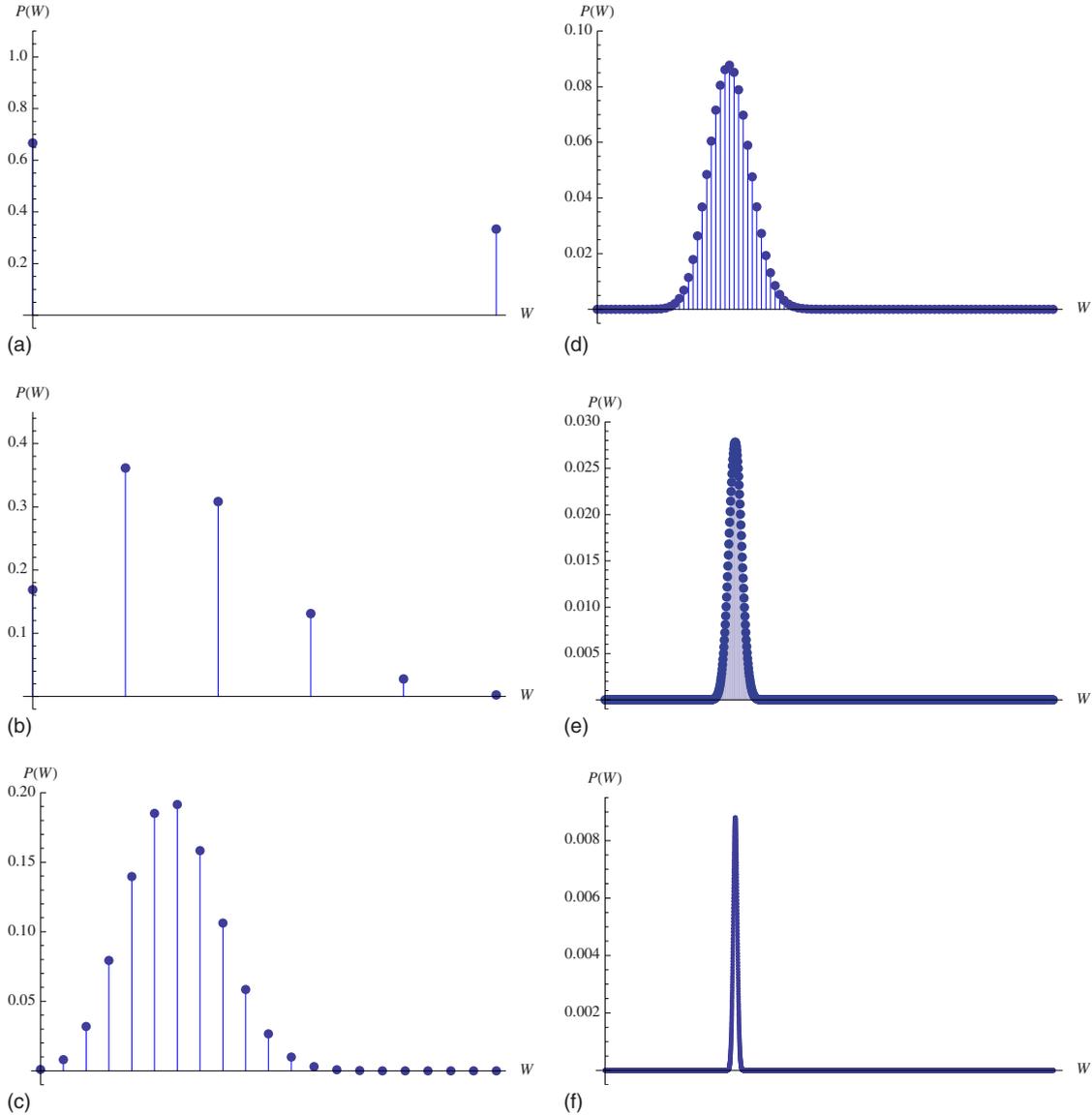


FIG. 2. (Color online) Microscopic work distribution of an N -step stair process. The horizontal axis indicates the possible microscopic work ranging from 0 to $\Delta_B - \Delta_A$, and the vertical axis is their probabilities. Here, $\exp(-\beta\Delta_A) = 1/2$, and $\exp(-\beta\Delta_B) = 1/3$. The steps are chosen to be $N = 1, 5, 20, 100, 1000$, and 10000 , respectively. The paths corresponding to $N = 1, 5, 20$ are given in Fig. 1. From these figures it can be inferred that when N is small the process is irreversible, and the fluctuation is appreciable. The relative fluctuation of the microscopic work vanishes when $N \rightarrow \infty$, or the fluctuation of an isothermal process approaches zero. Besides, the most probabilistic work from the (numerical) figures $\tilde{W} = 0.29(\ln 3 - \ln 2)k_B T$ agrees well with the (analytical) free energy difference $\Delta F_{AB} = [\ln(1 + 1/2) - \ln(1 + 1/3)]k_B T$.

crease with the increase of N . Actually, from the above numerical figures, it is not difficult to find that the dispersion of the microscopic work distribution is inversely proportional to the square root of N . For example, the dispersion for $N = 100$ is 10 times that for the $N = 10\,000$ case (see Fig. 2). Hence, numerical results agree well with our heuristic analysis and both verify our main result: when $N \rightarrow \infty$, the fluctuations of microscopic work vanish.

V. MINIMUM WORK PRINCIPLE FOR A TWO-LEVEL SYSTEM

As we have mentioned before, for small systems and within a short time, the formulation “entropy never decreases

for a closed system” of the second law may be transiently “violated” probabilistically due to appreciable fluctuations [5]. A straightforward question is, will the other formulations of the second law—e.g., the minimum work principle [6,15]—also be transiently violated probabilistically for small systems? The minimum work principle states that “when varying the speed of a given process for an initially equilibrium system, the work is minimal for the slowest realization of the process” [6,15]. In the following we will test the validity of the minimum work principle for a two-level system by utilizing formula (4) derived above. The average work over all possible realizations for a given N -step path can be expressed as

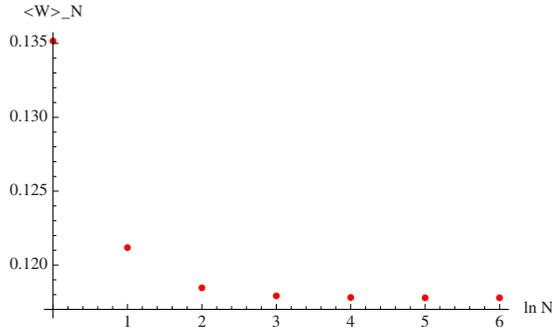


FIG. 3. (Color online) Averaged work $\langle W \rangle_N$ as a function of N , Eq. (15). The steps N chosen here are $5^0=1$, $5^1=5$, $5^2=25$, $5^3=125$, $5^4=625$, $5^5=3125$, and $5^6=15625$. It can be seen that the averaged work is a monotonically decreasing function of N . In the one-step path ($N=1$), the averaged work is equal to $\langle W \rangle_1 = (\ln 2 - \ln 3)/3 \approx 0.135155 k_B T$. In the 15625-step path, the averaged work is equal to $\langle W \rangle_{5^6} \approx 0.11784 k_B T$, which is very close to its asymptotic value $\Delta F_{AB} = [\ln(1+1/2) - \ln(1+1/3)] k_B T \approx 0.11783 k_B T$. Thus, it can be inferred that the minimum work principle still holds for a two-level system.

$$\langle W \rangle_N = \sum_{k=0}^N \left(\prod_{j=1}^N P_e^j \right) \left(\prod_{l=0}^{k-1} \frac{e^{\beta \Delta_B} - e^{\beta(\Delta_A + l \Delta)}}{e^{\beta(l+1)\Delta} - 1} \right) (N - k) \Delta. \tag{15}$$

In Fig. 3 we plot the averaged work $\langle W \rangle_N$ as a function of N , Eq. (15). It can be seen that for the two-level system, $\langle W \rangle_N$ is a monotonically decreasing function of N (time t), and when $N \rightarrow \infty$ ($t \rightarrow \infty$), the averaged work $\langle W \rangle_N$ approaches an asymptotic value and its minimum value—the difference of the free energy. Thus, from the numerical result it can be inferred that the minimum work principle still holds for a two-level system.

The above proof of the minimum work principle can be alternatively understood in the following way. From the above analytical and numerical result, we observed that the fluctuation of microscopic work in an isothermal process vanishes, and then the work of the most probabilistic distribution is equal to the difference of the free energy, $\tilde{W} = \Delta F$. According to Ref. [3], $\langle W_{\text{irre}} \rangle \geq \Delta F$, where $\langle W_{\text{irre}} \rangle$ is the average work done during an irreversible process. Combining the two results, we have $\langle W_{\text{irre}} \rangle \geq \tilde{W}$. Thus we proved the minimum work principle for small systems.

VI. DISCUSSION AND CONCLUSION

Before concluding this paper, we would like to emphasize the following points: First, the technique of simulating isothermal processes with adiabatic processes and isochoric processes is important to our proof, which enables us to establish the connection between the large-time limit and large- N limit. Second, the calculation of the exact expression of microscopic work in our paper is nontrivial because the work contributions in the different steps are not identically

distributed. Hence, it is different from the law of large numbers, with time as the large number [6]. Third, we proved that the minimum work principle formulation of the second law stands for even small systems, though other formulations may be transiently violated probabilistically [5]. This is not surprising because the minimum work principle is concerned with infinite-long-time processes, which has no contradiction with the transient violation of the second law for small systems predicted by the fluctuation theorem. Actually, the fluctuation theorem does not constitute a real violation of the second law, which is a statistical law and holds when averaged over different realization of the process. Fourth, the isothermal process is reversible, but the finite- N step path is irreversible, due to the QIP (thermalization) being irreversible. We can thus expect that the work dissipation [7,6] for the finite- N step path will be finite and will decrease with the increase of N and finally vanish when N approaches infinity.

In summary, by simulating a quantum isothermal process with infinitely many infinitesimal QAPs and QIPs, we obtain the analytical expressions of microscopic work distribution in an isothermal process. Through both analytical and numerical analyses, we rigorously verify that the fluctuations of the microscopic work distribution vanish even for a small system in an isothermal process. This result is different from the usual fluctuations in statistical mechanics—e.g., the energy fluctuation and particle number fluctuation in canonical ensembles and grand canonical ensembles, where the fluctuations of energy and particle numbers approach zero when the system approaches the thermodynamic limit (particle number approaches infinity $N_p \rightarrow \infty$). Here, however, even for a single-particle system, we microscopically demonstrate the vanishing of microscopic work fluctuations. Because $N \rightarrow \infty$ is necessary to simulate an isothermal process, we conclude that the vanishing of microscopic work fluctuations is due to the intrinsic nature of isothermal processes, rather than the thermodynamic limit of the system size. We also prove that for a small system, the minimum work principle formulation of the second law holds though other formulations maybe transiently violated probabilistically. Finally we would like to point out that our result is universal and does not depend on the specific model used here, because the technique of simulating the isothermal process with the isochoric process and the adiabatic process can be applied to any systems. Generalizations of our current discussion to other models will be given in the future.

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