Path Integral Approach to Quantum Thermodynamics

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(Received 22 August 2017; revised manuscript received 4 April 2018; published 26 July 2018)

Work belongs to the most basic notions in thermodynamics but it is not well understood in quantum systems, especially in open quantum systems. By introducing a novel concept of the work functional along an individual Feynman path, we invent a new approach to study thermodynamics in the quantum regime. Using the work functional, we derive a path integral expression for the work statistics. By performing the $\hbar$ expansion, we analytically prove the quantum-classical correspondence of the work statistics. In addition, we obtain the quantum correction to the classical fluctuating work. We can also apply this approach to an open quantum system in the strong coupling regime described by the quantum Brownian motion model. This approach provides an effective way to calculate the work in open quantum systems by utilizing various path integral techniques. As an example, we calculate the work statistics for a dragged harmonic oscillator in both isolated and open quantum systems.

DOI: 10.1103/PhysRevLett.121.040602

The path integral formalism of quantum mechanics and quantum field theory [1] has greatly influenced the theoretical developments of physics. It has an elegant structure for treating gauge-invariant theories. The semiclassical limit of quantum mechanics and instantons [2] (the tunneling effect) can be intuitively understood in this formalism. Quantum anomalies (e.g., chiral anomaly) naturally arise from the path integral measure [3]. The path integral allows us to understand continuous quantum phase transitions in a d-dimensional system from a mapped $(d+1)$-dimensional classical system [4]. A path integral description of open quantum systems [5] has been used to study the dissipative dynamics of the quantum systems, known as the Caldeira-Leggett model of the quantum Brownian motion [6].

Quantum thermodynamics [7–12] is an emergent field studying the nonequilibrium statistical mechanics of the quantum dissipative systems [13–15]. Topics in this field include the role of coherence and entanglement in the heat transfer in quantum devices [16–18] and in the quantum heat engines [19,20] and refrigerators [21]. Quite recently, experimental studies have been put forward, such as the experimental verification of the exact nonequilibrium relations [22] and the implementation of the quantum Maxwell demon [23,24]. Connections to the quantum information theory have been explored extensively in the studies of the Maxwell demon [25] and resource theories [26]. Previous efforts of constructing a framework of quantum thermodynamics were mainly based on operator formalisms. For example, in Refs. [9,27], the composite system is treated as an isolated system, but the definition of fluctuating work via two-point energy measurements over the composite system is thought to be *ad hoc*. In Refs. [28–31], a framework based on the quantum jump method, which was borrowed from quantum optics, is established. However, this framework is restricted to very limited cases: the weak-coupling, Markovian, and rotating-wave approximation (RWA) regime. Hence, how to understand quantum work [7] (including relations to its classical counterpart) and how to calculate its distributions in generic open quantum systems have become the most challenging problems in this field.

Classical stochastic thermodynamics [32–35], on the other hand, is a framework established in the past two decades, which extends the principles of thermodynamics from ensemble level to individual trajectory level. For example, work, heat, and entropy production are identified as trajectory functionals. The first law is reformulated on the trajectory level, and the second law is refined from inequalities to equalities, known as fluctuation theorems (FT) [36–40]. The Onsarger-Machlup "path integral" approach [41] in formulating the FT [42–45] in classical stochastic thermodynamics is an analogue [46] of Feynman's path integral formalism in quantum mechanics [1]. Thus, when extending the classical stochastic thermodynamics to the quantum regime, a natural idea is to do it based on path integral methods. Nevertheless, no attempt to reformulate quantum FT through Feynman's path integral formalism has succeeded so far (see Fig. 1 for historical developments in relevant fields).

In this Letter, we introduce a quantum work functional along an individual Feynman path in quantum systems and study quantum work statistics. For isolated quantum systems we reformulate the FT (the Jarzynski equality) [47,48] through the path integral approach. For the open quantum system, we study work statistics and FT based on path integral methods [49–51] (see Fig. 1). In particular, we can

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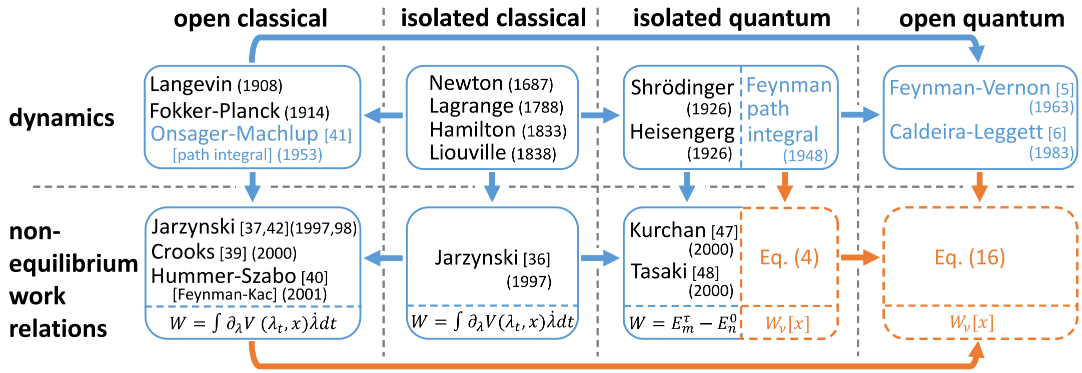

FIG. 1. Summary of historical developments of theories of dynamics and nonequilibrium work relations. The arrow between every two boxes indicates the order in which the theories were developed. The fluctuating work W along individual trajectories is defined differently in different contexts (see the bottom line of every column). We introduce the quantum work functional $W_\nu[x]$ Eq. (5) along individual Feynman paths and invent a path integral approach to study quantum thermodynamics (orange dashed box). Note that Feynman's path [1] is an analogue of the Onsager-Machlup's stochastic trajectory [41] (blue color). Similarly, our definition of the work functional along an individual Feynman path is an analogue of the definition of Sekimoto and Jarzynski of the work functional as an integral of the supplied power [7].

study the non-Markovian, non-RWA, and strong-coupling regime without making any approximations [52]. This is intriguing since stochastic thermodynamics [53–56] and quantum thermodynamics [57–61] with strong coupling have attracted much attention recently. We utilize the semiclassical approximation technique of the path integral and show the quantum-classical correspondence of the work statistics. Furthermore, quantum corrections to the classical work functional are obtained, bringing new insights into our understandings about quantum effects in thermodynamics.

Two-point measurement scheme.—We first consider an isolated system with the system Hamiltonian given by $H_S(\lambda_t) = \hat{p}^2/(2M) + \hat{V}(\lambda_t, \hat{x})$, where M is the mass and $\hat{V}(\lambda_t, \hat{x})$ is an arbitrary potential, whose time dependence is specified by λ_t. This external control of the potential drives the system out of equilibrium and injects work into the system. The fluctuating work in an isolated system is defined via the so-called two-point measurement scheme [47,48]. By measuring the energy of the system twice (E_n^0 and E_m^τ) at $t = 0$ and $t = \tau$, we define the quantum fluctuating work as the difference in the measured energies: $W_{m,n} \coloneqq E_m^\tau - E_n^0$. The joint probability about observing such measured energies is given by $p(n,m) \coloneqq p_n |\langle m(\tau)|U_S|n(0)\rangle|^2$, where $p_n \coloneqq \langle n(0)|\rho_S(0)|n(0)\rangle$, $\rho_S(0) \coloneqq e^{-\beta H_S(\lambda_0)}/Z_S(\lambda_0)$ is the initial canonical density matrix of the system at the inverse temperature β, $|n(t)\rangle$ is the nth instantaneous energy eigenstate of the system at time t, and $U_S \coloneqq \hat{T}\{\exp[(-i/\hbar)\int_0^\tau dt H_S(\lambda_t)]\}$ is the unitary operator describing the time evolution of the system. The work probability distribution is given by $P(W) \coloneqq \sum_{m,n}\delta(W - W_{m,n})p(m,n)$. Taking the Fourier transformation of the work probability distribution, we define the characteristic function of work [62] by $\chi_W(\nu) \coloneqq \int dW P(W) e^{i\nu W}$. This can be expressed as

$$\chi_W(\nu) = \mathrm{Tr}[U_S e^{-i\nu H_S(\lambda_0)}\rho_S(0)U_S^\dagger e^{i\nu H_S(\lambda_\tau)}]. \tag{1}$$

Quantum work functional and work statistics in the path integral formalism.—To obtain the path integral expression of Eq. (1), we note the following relations: $\langle x_f|U_S e^{-i\nu H_S(\lambda_0)}|x_i\rangle = \int Dx e^{(i/\hbar)S_1^\nu[x]}$ and $\langle y_i|U_S^\dagger e^{i\nu H_S(\lambda_\tau)}|y_f\rangle = \int Dy e^{-(i/\hbar)S_2^\nu[y]}$, where the actions $S_1^\nu[x]$ and $S_2^\nu[y]$ are defined as

$$S_1^\nu[x] \coloneqq \int_0^{\hbar\nu} dt \mathcal{L}[\lambda_0, x(t)] + \int_{\hbar\nu}^{\tau+\hbar\nu} dt \mathcal{L}[\lambda_{t-\hbar\nu}, x(t)],$$

$$S_2^\nu[y] \coloneqq S[y] + \int_\tau^{\tau+\hbar\nu} ds \mathcal{L}[\lambda_\tau, y(s)]. \tag{2}$$

Here, $S[y] \coloneqq \int_0^\tau ds \mathcal{L}[\lambda_s, y(s)]$ is the usual action and $\mathcal{L}[\lambda_s, y(s)] \coloneqq (M/2)\dot{y}^2(s) - V[\lambda_s, y(s)]$ is the Lagrangian. As a result, we can rewrite Eq. (1) as

$$\chi_W(\nu) = \int e^{(i/\hbar)(S_1^\nu[x] - S_2^\nu[y])}\rho(x_i, y_i), \tag{3}$$

where $\rho(x_i, y_i) \coloneqq \langle x_i|\rho_S(0)|y_i\rangle$ and the integration in Eq. (3) is performed over $\int dx_i dy_i dx_f dy_f \delta(x_f - y_f)\int Dx \int Dy$. In Eq. (3), the time dependence of the controlling parameter λ_t between the forward $x(t)$ and the backward $y(s)$ paths is shifted by $\hbar\nu$, which is relevant to the Ramsey interferometry scheme proposed in Ref. [63] [see also Fig. 2(a)]. Next, we use the identity $(i/\hbar)S_1^\nu[x] = (i/\hbar)S_2^\nu[x] + i\nu W_\nu[x]$ [64] and rewrite Eq. (3) as

$$\chi_W(\nu) = \int e^{(i/\hbar)(S_2^\nu[x] - S_2^\nu[y])}\rho(x_i, y_i)e^{i\nu W_\nu[x]}. \tag{4}$$

Here, we introduce the quantum work functional along the forward path $x(t)$ [65]:

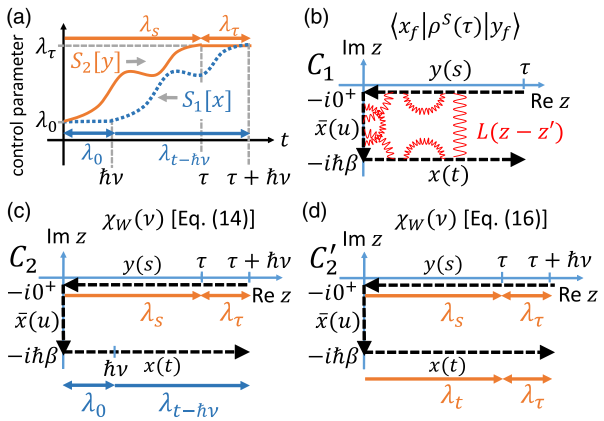

FIG. 2. Contours used in the path integral and the time dependence of the actions. (a) Time dependence of the external control used in $S_1^\nu[x]$ (dotted blue curve) and $S_2^\nu[y]$ (solid orange curve). (b) Contour used in Eq. (12). Red wavy lines show the correlation function $L(z-z')$ in $F_{\rm FV}[x,y,\bar{x}]$. (c),(d) Contour used in the characteristic function of work. Time dependences of the external control are different in Eqs. (14) and (16).

$$W_\nu[x] := \int_0^\tau dt \frac{1}{\hbar\nu}\int_0^{\hbar\nu} ds \dot{\lambda}_t \frac{\partial V[\lambda_t, x(t+s)]}{\partial\lambda_t}. \tag{5}$$

It can be regarded as a quantum extension of the classical work defined as the integral of the supplied power [32,36]:

$$W_{\rm cl}[x] := \int_0^\tau dt \dot{\lambda}_t \frac{\partial V[\lambda_t, x(t)]}{\partial\lambda_t}. \tag{6}$$

Both $W_\nu[x]$ and $W_{m,n}$ lead to the same work statistics [Eqs. (1) and (4) are identical]. In Ref. [7], it is pointed out that the equivalence of power and two-point measurement based work definitions fails to hold in quantum mechanics. We would like to emphasize that their conclusion is due to the fact that they did not obtain the proper quantum extension of Eq. (6). From Eq. (5), we find that a time average $(\hbar\nu)^{-1}\int_0^{\hbar\nu} ds\cdots$ is required to circumvent the uncertainty relation and obtain the high-frequency component ν of the work functional.

By performing the $\hbar$ expansion (or the ν expansion) in the quantum work functional Eq. (5), we can systematically obtain the quantum corrections to the classical expression of the work functional:

$$W_\nu[x] = W_{\rm cl}[x] + \frac{i\nu}{2}W_q^{(1)}[x] - \frac{\nu^2}{3!}W_q^{(2)}[x] + \cdots, \tag{7}$$

where

$$W_q^{(1)}[x] := -i\hbar\int_0^\tau dt \dot{x}(t)\dot{\lambda}_t \frac{\partial^2 V[\lambda_t, x(t)]}{\partial\lambda_t \partial x(t)} \tag{8}$$

is the first-order quantum correction to Eq. (6). Further quantum corrections can be obtained by Taylor expanding Eq. (5). Using the formula $\langle W^n\rangle := (-i)^n\partial_\nu^n\chi_W(\nu)|_{\nu=0}$, we can calculate the moments of work as follows [66]:

$$\langle W^n\rangle = \int e^{(i/\hbar)(S[x]-S[y])}\rho(x_i,y_i)(-i)^n\partial_\nu^n e^{i\nu W_\nu[x]}\Big|_{\nu=0}. \tag{9}$$

The expansion Eq. (7) is useful for calculating the nth moment of work distribution via Eq. (9). An important observation in this path integral expression is that the quantum corrections to the classical work functional can be found starting from the second moment of work distribution:

$$\langle W\rangle = \langle W_{\rm cl}\rangle_{q\rm path}, \quad \langle W^2\rangle = \langle W_{\rm cl}^2\rangle_{q\rm path} + \langle W_q^{(1)}\rangle_{q\rm path}, \tag{10}$$

where $\langle\bullet\rangle_{q\rm path}$ means average over all Feynman quantum paths; $\langle f\rangle_{q\rm path} := \int e^{(i/\hbar)(S[x]-S[y])}\rho(x_i,y_i)f[x]$. In general, the nth-order quantum correction appears in the $(n+1)$th moment of the work distribution.

In the semiclassical limit ($\hbar\to 0$), the quantum work functional Eq. (5) reduces to the classical fluctuating work Eq. (6), and the center coordinate $X(t) := [x(t)+y(t)]/2$ behaves as the classical position of the system [49]. By taking the stationary phase approximation, Eq. (4) converges to its classical counterpart $\langle e^{i\nu W_{\rm cl}}\rangle_{\rm clpath}$ [67]. Here, $\langle f\rangle_{\rm clpath} = \int\delta(M\ddot{X}(t) + V'[X(t)])p(X_i,\dot{X}_i)f[X]$ means average over all classical paths obeying Newton's equation, and $p(X_i,\dot{X}_i)$ is the initial phase-space distribution. Therefore, we analytically prove the quantum-classical correspondence of the characteristic function of work distribution in isolated systems. Relevant results have been obtained in Refs. [68,69] using a different technique.

Path integral formalism for an open system.—Having established a path integral formalism for an isolated system, we generalize it to the open system (see Fig. 1)—quantum Brownian motion described by the Caldeira-Leggett model [6,13]. We use the Caldeira-Leggett model for two reasons. First, the semiclassical limit of this model reproduces the Langevin equation with inertia term [6,13], which is a prototype model in the study of classical stochastic thermodynamics [32–35]. Second, we can analytically integrate out the degrees of freedom (d.o.f.) of the heat bath, which brings important insights into the understanding of the work statistics in the open quantum system. The Hamiltonian of the composite system is given by $H_{\rm tot}(\lambda_t) = H_S(\lambda_t) + H_B + H_{SB}$, with

$$H_S(\lambda_t) = \frac{\hat{p}^2}{2M} + \hat{V}(\lambda_t,\hat{x}), \quad H_B = \sum_k\left(\frac{\hat{p}_k^2}{2m_k} + \frac{m_k\omega_k^2}{2}\hat{q}_k^2\right),$$

$$H_{SB} = -\hat{x}\otimes\sum_k c_k\hat{q}_k + \sum_k\frac{c_k^2}{2m_k\omega_k^2}\hat{x}^2, \tag{11}$$

where we have included the counterterm $\sum_k(c_k^2/2m_k\omega_k^2)\hat{x}^2$ in the interaction Hamiltonian to cancel the negative frequency shift of the potential [70]. Here, $H_S(\lambda_t)$ is the same Hamiltonian we use for an isolated system, and m_k, ω_k, c_k, $\hat{q}_k$, and $\hat{p}_k$ are the mass, frequency, coupling strength, position, and momentum of the kth mode of the bath, respectively.

The reduced density matrix of the system at time τ is given by $\rho_S(\tau) = \mathrm{Tr}_B[U_{SB}\rho(0)U_{SB}^\dagger]$, where $U_{SB} = \hat{T}\{\exp[-(i/\hbar)\int_0^\tau dt H_{\rm tot}(\lambda_t)]\}$ is the unitary time-evolution operator for the composite system and we choose the initial state to be $\rho(0) = \exp[-\beta H_{\rm tot}(\lambda_0)]/Z_{\rm tot}(\lambda_0)$. Using the path integral technique, the reduced density matrix takes the form [49–52]

$$\begin{aligned}\langle x_f|\rho_S(\tau)|y_f\rangle &= Z_{\lambda_0}^{-1}\int dx_i dy_i \int_{x(0)=x_i}^{x(\tau)=x_f} Dx \int_{y(0)=y_i}^{y(\tau)=y_f} Dy \\ &\times \int_{\bar{x}(0)=y_i}^{\bar{x}(\hbar\beta)=x_i} D\bar{x} e^{(i/\hbar)(S[x]-S[y])-(1/\hbar)S^E[\bar{x}]} F_{\rm FV}[x,y,\bar{x}], \quad (12)\end{aligned}$$

where $F_{\rm FV}[x,y,\bar{x}]$ is the generalized Feynman-Vernon influence functional [50,51], and x, y, $\bar{x}$ are the forward, backward, and imaginary time coordinates of the system, respectively [see also the contour $\mathcal{C}_1$ in Fig. 2(b)]. Here, $S[x]$ is the action, $S^E[\bar{x}] := \int_0^{\hbar\beta} du\{(M/2)\dot{\bar{x}}^2(u) + V[\lambda_0, \bar{x}(u)]\}$ is the Euclidian version of the action, and $Z_{\lambda_0} := \mathrm{Tr}[e^{-\beta H_{\rm tot}(\lambda_0)}]/\mathrm{Tr}[e^{-\beta H_B}]$ is the reduced partition function of the system.

Work statistics for the Caldeira-Leggett model.—By generalizing Eq. (1) to the case of the composite system, the characteristic function of work distribution is given by

$$\chi_W(\nu) = \mathrm{Tr}[U_{SB}e^{-i\nu H_{\rm tot}(\lambda_0)}\rho(0)U_{SB}^\dagger e^{i\nu H_{\rm tot}(\lambda_\tau)}]. \quad (13)$$

We can integrate out the bath d.o.f. and obtain the path integral expression of Eq. (13) by adapting a similar technique we use for the isolated system:

$$\chi_W(\nu) = Z_{\lambda_0}^{-1}\int e^{(i/\hbar)(S_1^\nu[x]-S_2^\nu[y])-(1/\hbar)S^E[\bar{x}]} F_{\rm FV}^\nu[x,y,\bar{x}]. \quad (14)$$

Here, the integration is performed over $\int \delta(x_f - y_f) dx_i dy_i dx_f dy_f DxDyD\bar{x}$ and the influence functional is given by

$$\begin{aligned}F_{\rm FV}^\nu[x,y,\bar{x}] = \exp\Bigg[&-\frac{1}{\hbar}\int_0^{\tau+\hbar\nu} dt \int_0^t ds[x(t)-y(t)][L(t-s)x(s) - L^*(t-s)y(s)] + \frac{i\mu}{\hbar}\int_0^{\tau+\hbar\nu} dt[x^2(t)-y^2(t)] \\ &+ \frac{i}{\hbar}\int_0^{\tau+\hbar\nu} dt \int_0^{\hbar\beta} du[x(t)-y(t)]L^*(t-iu)\bar{x}(u) + \frac{1}{\hbar}\int_0^{\hbar\beta} du \int_0^u du' L(-iu+iu')\bar{x}(u)\bar{x}(u') - \frac{\mu}{\hbar}\int_0^{\hbar\beta} du\bar{x}^2(u)\Bigg], \quad (15)\end{aligned}$$

where $L(t-iu) := \sum_k(c_k^2/2m_k\omega_k)[\cosh(\hbar\omega_k\beta/2) \times \cosh\omega_k(u+it) - \sinh\omega_k(u+it)]$ is the complex bath correlation function, and $\mu := \sum_k c_k^2/(2m_k\omega_k^2)$. See Fig. 2(c) for the contour $\mathcal{C}_2$ we use in Eq. (14). Also note that by taking $\nu = 0$, Eq. (15) reproduces $F_{\rm FV}[x,y,\bar{x}]$. The actions $S_1^\nu[x]$ and $S_2^\nu[y]$ are the same as what we use for the isolated system Eq. (2). Using again the identity in Ref. [64], the path integral expression of the characteristic function of work distribution for an open system is given by [see Fig. 2(d) for the contour]

$$\begin{aligned}\chi_W(\nu) = Z_{\lambda_0}^{-1}&\int dx_f dy_f dx_i dy_i \delta(x_f - y_f)\int DxDyD\bar{x} \\ &\times e^{(i/\hbar)(S_2^\nu[x]-S_2^\nu[y])-(1/\hbar)S^E[\bar{x}]} F_{\rm FV}^\nu[x,y,\bar{x}] e^{i\nu W_\nu[x]}, \quad (16)\end{aligned}$$

where the quantum work functional is given by Eq. (5). We note that Eq. (16) is valid for the strong-coupling, non-Markovian, and non-RWA regime, and it allows us to calculate work statistics of the quantum Brownian model. The moments of work can be calculated by using Eq. (9), but the average is over all Feynman paths for the open system dynamics Eq. (12): $\langle f\rangle_{q\mathrm{path}} = Z_{\lambda_0}^{-1}\int e^{(i/\hbar)(S[x]-S[y])-(1/\hbar)S^E[\bar{x}]} F_{\rm FV}[x,y,\bar{x}] f[x]$. In particular, Eq. (10) also holds for an open system using the above path integral average. We can show the Jarzynski equality using the path integral expression by using Eq. (16) [71].

To show the quantum-classical correspondence of the characteristic function of work in the Brownian motion model, we take $\hbar \to 0$ and $\beta \to 0$ and introduce $X(t) = [x(t) + y(t)]/2$. We follow the standard treatment [49,52] to obtain the quasiclassical (non-Markovian) Langevin equation by introducing the noise function $\Omega(t) := i\int_0^t ds[x(s) - y(s)]\mathrm{Re}[L(t-s)]$. Using a method similar to that of the isolated system, we prove that in the classical limit, Eq. (16) converges to its classical counterpart $\langle e^{i\nu W_{\rm cl}}\rangle_{\rm clpath}$ [67]. Here, $\langle f\rangle_{\rm clpath}$ is the average over all classical paths satisfying the non-Markovian Langevin equation $M\ddot{X}(t) + V'[X(t)] + \int_0^t ds K(t-s)\dot{X}(s) = \Omega(t)$, where $K(t) := \sum_k(c_k^2/m_k\omega_k^2)\cos\omega_k t$ is the classical bath-correlation function. We emphasize that the introduction of the work functional along an individual Feynman path enables us for the first time to show the quantum-classical

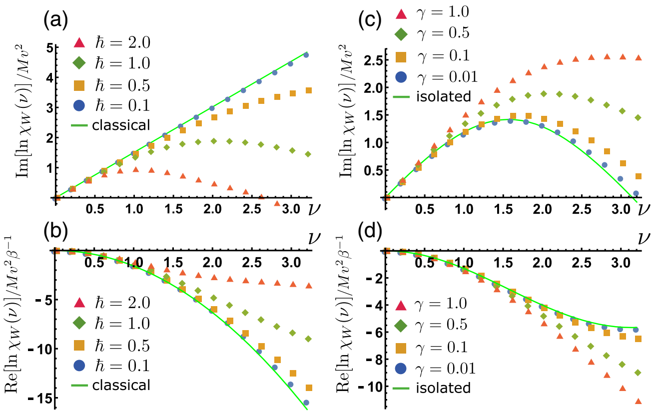

FIG. 3. Plot of the characteristic function of work distribution for a dragged harmonic oscillator using the Caldeira-Leggett model Eq. (11). The analytical expression of $\chi_W(\nu)$ is given in Ref. [74]. For simplicity, we choose the high-temperature regime and choose the following parameters: $M = \omega = v = 1$, $\tau = 2$, $\beta = 0.01$. We choose the Ohmic spectrum $J(\omega) := \sum_k (\pi c_k^2/2m_k\omega_k)\delta(\omega - \omega_k) = M\gamma\omega$ with a high-frequency cutoff ω_D, where γ is the friction coefficient. (a),(b) Plot of $\mathrm{Im}[\ln \chi_W(\nu)]$ and $\mathrm{Re}[\ln \chi_W(\nu)]$ for different values of $\hbar$ (we set $\gamma = 0.5$). (c),(d) Plot of $\mathrm{Im}[\ln \chi_W(\nu)]$ and $\mathrm{Re}[\ln \chi_W(\nu)]$ for different values of γ (we set $\hbar = 1$).

correspondence of the work statistics in open systems (see Fig. 1).

Example: Dragged harmonic oscillator.—In order to demonstrate the effectiveness of our approach in calculating work statistics, let us consider a potential given by $V[\lambda_t, x(t)] = (M\omega^2/2)[x(t) - \lambda_t]^2$. Here, λ_t describes the time dependence of the center of the harmonic potential, and we consider a linear protocol $\lambda_t = vt$. We note that the characteristic function of work for an isolated system is analytically calculated in Ref. [72] by utilizing the concept of work based on a two-point measurement. In Ref. [73], we obtain the same result by using our path integral approach.

For an open system described by the Caldeira-Leggett model Eq. (11), we cannot apply the two-point measurement approach in practice because of the huge number of d.o.f. of the bath. However, the introduction of the work functional Eq. (5) enables us to analytically calculate the characteristic function of work distribution Eq. (16) by using techniques [75] developed in the field of path integral for open quantum systems [73]. We plot $\chi_W(\nu)$ in Fig. 3.

Summary.—Before concluding the Letter, we would like to give the following remarks. The usual two-point measurement based quantum work is good for demonstrating the Jarzynski equality [27] but practically cannot be used to studying work statistics in an open quantum system because we have to deal with a huge number of d.o.f. of the bath. By contrast, with the work functional along an individual Feynman path, we can not only demonstrate the Jarzynski equality, but we can also calculate the work statistics and show the convergence of the quantum work statistics to its classical counterpart. In addition, the work functional along an individual Feynman path provides important insights into our understandings about work in quantum systems. Thus, the path integral approach to quantum work has both conceptual and technical advantages over the two-point measurement approach to quantum work.

In this Letter, we invented a path integral approach to study the quantum work and its statistics in the non-Markovian, non-RWA, and strong-coupling regime using the quantum Brownian motion model. In comparison with the definition of work based on two-point measurement, the work functional along an individual Feynman path Eq. (5) introduced in our Letter offers conceptually different interpretations and physical intuitions about work in quantum systems. Through the $\hbar$ expansion, we can systematically obtain quantum corrections to the classical work. In the strong-coupling quantum Brownian model, this work functional enables us to calculate the work statistics and prove analytically the quantum-classical correspondence of both the work functional and the work statistics, which has not been reported in open systems so far. In addition, we use a dragged harmonic oscillator as an example to show the corrections and the convergence of the quantum work statistics to its classical counterpart in an open quantum system.

The authors thank Professor Christopher Jarzynski, Professor Amir Ordacgi Caldeira, Professor Erik Aurell and Professor Peter Hänggi for helpful discussions and comments. This work was supported by the National Science Foundation of China under Grants No. 11775001, No. 11375012, and No. 11534002, and The Recruitment Program of Global Youth Experts of China.

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[1] R. P. Feynman and A. R. Hibbs, in *Quantum Mechanics and Path Integrals,* edited by D. F. Styer (Dover, New York, 2010).
[2] R. Rajaraman, *Solitons and Instantons* (North-Holland, Amsterdam, 1987).
[3] K. Fujikawa, Path-Integral Measure for Gauge-Invariant Fermion Theories, Phys. Rev. Lett. **42**, 1195 (1979).
[4] S. L. Sondhi, S. M. Girvin, J. P. Carini, and D. Shahar, Continuous quantum phase transitions, Rev. Mod. Phys. **69**, 315 (1997).
[5] R. P. Feynman and F. L. Vernon, Jr., The theory of a general quantum system interacting with a linear dissipative system, Ann. Phys. (N.Y.) **24**, 118 (1963).
[6] A. O. Caldeira and A. J. Leggett, Path integral approach to quantum Brownian motion, Physica (Amsterdam) **121A**, 587 (1983).
[7] P. Talkner and P. Hanggi, Aspects of quantum work, Phys. Rev. E **93**, 022131 (2016).
[8] M. Esposito, U. Harbola, and ad S. Mukamel, Nonequilibrium fluctuations, fluctuation theorems, and counting

statistics in quantum systems, Rev. Mod. Phys. **81**, 1665 (2009).

[9] M. Campisi, P. Hänggi, and P. Talkner, Colloquium: Quantum fluctuation relations: Foundations and applications, Rev. Mod. Phys. **83**, 771 (2011); Colloquium: Quantum fluctuation relations: Foundations and applications, Rev. Mod. Phys. **83**, 1653(E) (2011).

[10] J. P. Pekola, Towards quantum thermodynamics in electronic circuits, Nat. Phys. **11**, 118 (2015).

[11] S. Vinjanampathy and J. Anders, Quantum thermodynamics, Contemp. Phys. **57**, 545 (2016).

[12] P. Strasberg, G. Schaller, T. Brandes, and M. Esposito, Quantum and Information Thermodynamics: A Unifying Framework Based on Repeated Interactions, Phys. Rev. X **7**, 021003 (2017).

[13] A. O. Caldeira, *An Introduction to Macroscopic Quantum Phenomena and Quantum Dissipation* (Cambridge University Press, Cambridge, England, 2014).

[14] L. H. Yu and C. P. Sun, Evolution of the wave function in a dissipative system, Phys. Rev. A **49**, 592 (1994).

[15] P. Hanggi and G.-L. Ingold, Fundamental aspects of quantum Brownian motion, Chaos **15**, 026105 (2005).

[16] M. Ueda, Transmission spectrum of a tunneling particle interacting with dynamical fields: Real-time functional-integral approach, Phys. Rev. B **54**, 8676 (1996).

[17] K. Saito and A. Dhar, Fluctuation Theorem in Quantum Heat Conduction, Phys. Rev. Lett. **99**, 180601 (2007).

[18] A. Kato and Y. Tanimura, Quantum heat current under non-perturbative and non-Markovian conditions: Applications to heat machines, J. Chem. Phys. **145**, 224105 (2016).

[19] M. O. Scully, M. S. Zubairy, G. S. Agarwal, and H. Walther, Extracting work from a single heat bath via vanishing quantum coherence, Science **299**, 862 (2003).

[20] Y. Dong, K. Zhang, F. Bariani, and P. Meystre, Work measurement in an optomechanical quantum heat engine, Phys. Rev. A **92**, 033854 (2015).

[21] B. Karimi and J. P. Pekola, Otto refrigerator based on a superconducting qubit: Classical and quantum performance, Phys. Rev. B **94**, 184503 (2016).

[22] S. An, J.-N. Zhang, M. Um, D. Lv, Y. Lu, J. Zhang, Z.-Q. Yin, H. T. Quan, and K. Kim, Experimental test of the quantum Jarzynski equality with a trapped-ion system, Nat. Phys. **11**, 193 (2015).

[23] N. Cottet, S. Jezouin, L. Bretheau, P. C. Ibarcq, Q. Ficheux, J. Anders, A. Auffèves, R. Azouit, P. Rouchon, and B. Huard, Observing a quantum Maxwell demon at work, Proc. Natl. Acad. Sci. U.S.A. **114**, 7561 (2017).

[24] Y. Masuyama, K. Funo, Y. Murashita, A. Noguchi, S. Kono, Y. Tabuchi, R. Yamazaki, M. Ueda, and Y. Nakamura, Information-to-work conversion by Maxwell's demon in a superconducting circuit-QED system, Nat. Commun. **9**, 1291 (2018).

[25] J. M. R. Parrondo, J. M. Horowitz, and T. Sagawa, Thermodynamics of information, Nat. Phys. **11**, 131 (2015).

[26] M. Horodecki and J. Oppenheim, Fundamental limitations for quantum and nanoscale thermodynamics, Nat. Commun. **4**, 2059 (2013).

[27] M. Campisi, P. Talkner, and P. Hänggi, Fluctuation Theorem for Arbitrary Open Quantum Systems, Phys. Rev. Lett. **102**, 210401 (2009).

[28] J. M. Horowitz, Quantum-trajectory approach to the stochastic thermodynamics of a forced harmonic oscillator, Phys. Rev. E **85**, 031110 (2012).

[29] F. W. J. Hekking and J. P. Pekola, Quantum Jump Approach for Work and Dissipation in a Two-Level System, Phys. Rev. Lett. **111**, 093602 (2013).

[30] F. Liu, Calculating work in adiabatic two-level quantum Markovian master equations: A characteristic function method, Phys. Rev. E **90**, 032121 (2014).

[31] S. Suomela, A. Kutvonen, and T. Ala-Nissila, Quantum jump model for a system with a finite-size environment, Phys. Rev. E **93**, 062106 (2016).

[32] K. Sekimoto, *Stochastic Energetics*, Lecture Notes in Physics, Vol. 799 (Springer-Verlag, Berlin, 2010).

[33] K. Sekimoto, Langevin equation and thermodynamics, Prog. Theor. Phys. Suppl. **130**, 17 (1998).

[34] U. Seifert, Stochastic thermodynamics, fluctuation theorems and molecular machines, Rep. Prog. Phys. **75**, 126001 (2012).

[35] *Nonequilibrium Statistical Physics of Small Systems: Fluctuation Relations and Beyond*, edited by R. Klages, W. Just, and C. Jarzynski (Wiley-VCH, New York, 2013).

[36] C. Jarzynski, Nonequilibrium Equality for Free Energy Differences, Phys. Rev. Lett. **78**, 2690 (1997).

[37] C. Jarzynski, Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach, Phys. Rev. E **56**, 5018 (1997).

[38] G. E. Crooks, Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences, Phys. Rev. E **60**, 2721 (1999).

[39] G. E. Crooks, Path-ensemble averages in systems driven far from equilibrium, Phys. Rev. E **61**, 2361 (2000).

[40] G. Hummer and A. Szabo, Free energy reconstruction from nonequilibrium single-molecule pulling experiments, Proc. Natl. Acad. Sci. U.S.A. **98**, 3658 (2001).

[41] L. Onsager and S. Machlup, Fluctuations and irreversible processes, Phys. Rev. **91**, 1505 (1953).

[42] C. Jarzynski, Equilibrium free energies from nonequilibrium processes, Acta Phys. Pol. B **29**, 1609 (1998), http://www.actaphys.uj.edu.pl/fulltext?series=Reg&vol=29&page=1609.

[43] V. Y. Chernyak, M. Chertkov, and C. Jarzynski, Path-integral analysis of fluctuation theorems for general Langevin processes, J. Stat. Mech. (2006) P08001.

[44] T. Taniguchi and E. G. D. Cohen, Inertial effects in nonequilibrium work fluctuations by a path integral approach, J. Stat. Phys. **130**, 1 (2008).

[45] D. D. L. Minh and A. B. Adib, Path integral analysis of Jarzynski's equality: Analytical results, Phys. Rev. E **79**, 021122 (2009).

[46] M. Kac, Wiener and integration in function spaces, Bull. Am. Math. Soc. **72**, 52 (1966).

[47] J. Kurchan, A quantum fluctuation theorem, arXiv:cond-mat/0007360.

[48] H. Tasaki, Jarzynski relations for quantum systems and some applications, arXiv:cond-mat/0009244.

[49] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 2012).

[50] C. M. Smith and A. O. Caldeira, Generalized Feynman-Vernon approach to dissipative quantum systems, Phys. Rev. A **36**, 3509 (1987).
[51] H. Grabert, P. Schramm, and G.-L. Ingold, Quantum Brownian motion: The functional integral approach, Phys. Rep. **168**, 115 (1988).
[52] Y. Tanimura, Stochastic Liouville, Langevin, Fokker-Planck, and master equation approaches to quantum dissipative systems, J. Phys. Soc. Jpn. **75**, 082001 (2006).
[53] C. Jarzynski, Nonequilibrium work theorem for a system strongly coupled to a thermal environment, J. Stat. Mech. (2004) P09005.
[54] U. Seifert, First and Second Law of Thermodynamics at Strong Coupling, Phys. Rev. Lett. **116**, 020601 (2016).
[55] C. Jarzynski, Stochastic and Macroscopic Thermodynamics of Strongly Coupled Systems, Phys. Rev. X **7**, 011008 (2017).
[56] P. Talkner and P. Hänggi, Open system trajectories specify fluctuating work but not heat, Phys. Rev. E. **94**, 022143 (2016).
[57] Y. Subasi and B. L. Hu, Quantum and classical fluctuation theorems from a decoherent histories, open-system analysis, Phys. Rev. E **85**, 011112 (2012).
[58] M. Carrega, P. Solinas, A. Braggio, M. Sassetti, and U. Weiss, Functional integral approach to time-dependent heat exchange in open quantum systems: General method and applications, New. J. Phys. **17**, 045030 (2015).
[59] M. Carrega, P. Solinas, M. Sassetti, and U. Weiss, Energy Exchange in Driven Open Quantum Systems at Strong Coupling, Phys. Rev. Lett. **116**, 240403 (2016).
[60] E. Aurell and R. Eichhorn, On the von Neumann entropy of a bath linearly coupled to a driven quantum system, New. J. Phys. **17**, 065007 (2015).
[61] E. Aurell, On work and heat in time-dependent strong coupling, Entropy **19**, 595 (2017).
[62] P. Talkner, E. Lutz, and P. Hänggi, Fluctuation theorems: Work is not an observable, Phys. Rev. E **75**, 050102 (2007).
[63] R. Dorner, S. R. Clark, L. Heaney, R. Fazio, J. Goold, and V. Vedral, Extracting Quantum Work Statistics and Fluctuation Theorems by Single-Qubit Interferometry, Phys. Rev. Lett. **110**, 230601 (2013).
[64] The identity $(i/\hbar)S_1^\nu[x] = (i/\hbar)S_2^\nu[x] + i\nu W_\nu[x]$ can be easily shown by noting that $\partial_\tau S_1^\nu[x] = \partial_\tau S_2^\nu[x] + \hbar\nu\partial_\tau W_\nu[x]$ and $S_1^\nu[x]|_{\tau=0} = S_2^\nu[x]|_{\tau=0} + \hbar\nu W_\nu[x]|_{\tau=0}$.
[65] The work functional Eq. (5) vanishes when $\dot{\lambda}_t = 0$ because the work should only depend on the energy supplied from the time-dependent variation of the external control. Apart from this constraint, there is a freedom of choosing the form of the phase and the work functional in Eq. (4). However, when calculating the quantity $\langle W^n \rangle$ in Eq. (9), the choice does not influence the result.
[66] The ν derivative acting on $e^{(i/\hbar)(\Delta S_2^\nu[x] - \Delta S_2^\nu[y])}$ with $\Delta S_2^\nu[y] := \int_\tau^{\tau+\hbar\nu} ds\mathcal{L}[\lambda_\tau, y(s)]$ will vanish because of the delta function $\delta(x_f - y_f)$ in $\chi_W(\nu)$. Also note that $\Delta S_2^\nu|_{\nu=0} = 0$. Therefore, ΔS_2^ν does not appear in the formula for $\langle W^n \rangle$.
[67] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.040602, Sec. I, for details of the classical limit of the characteristic function of work.
[68] C. Jarzynski, H. T. Quan, and S. Rahav, Quantum-Classical Correspondence Principle for Work Distributions, Phys. Rev. X **5**, 031038 (2015).
[69] L. Zhu, Z. Gong, B. Wu, and H. T. Quan, Quantum-classical correspondence principle for work distributions in a chaotic system, Phys. Rev. E **93**, 062108 (2016).
[70] A. O. Caldeira and A. J. Leggett, Quantum tunnelling in a dissipative system. Ann. Phys. (N.Y.) **149**, 374 (1983).
[71] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.040602, Sec. II, for the derivation of Jarzynski's equality using the path integral expression.
[72] P. Talkner, P. S. Burada, and P. Hanggi, Statistics of work performed on a forced quantum oscillator, Phys. Rev. E **78**, 011115 (2008).
[73] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.121.040602, Sec. III, for the details of the analytical calculation for a dragged harmonic oscillator, which includes Ref. [74].
[74] R. Pan, T. M. Hoang, Z. Fei, T. Qiu, J. Ahn, T. Li, and H. T. Quan, The validity and breakdown of the overdamped approximation in stochastic thermodynamics: Theory and experiment, arXiv:1805.09080.
[75] C. M. Smith and A. O. Caldeira, Application of the generalized Feynman-Vernon approach to a simple system: The damped harmonic oscillator, Phys. Rev. A **41**, 3103 (1990).