High-Efficiency Free Energy Estimates Based on Variational Shortcuts to Isothermality

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The mean work in an isothermal process is widely acknowledged as an accurate estimator of the free energy difference, but the high time cost limits its practical applications. Here, enlightened by the Gauss principle of least constraint, we develop a variational method for approximately accelerating isothermal processes and thereby estimating the free energy difference by using an equality between the free energy difference and the mean work related to the original Hamiltonian. The saddle-point approximation is applied to calculate the nonequilibrium “constraint” of the accelerated isothermal process. The simulations confirm that our method can efficiently estimate the free energy difference with high accuracy. Especially during fast driving processes, where dissipation is expected to be high, the estimates given by our method largely outperforms the estimates given by the mean work and the Jarzynski equality.

Introduction. – Free energies play a critical role in understanding the thermodynamic properties of physical, chemical, and biological systems. The fast and accurate estimation of the free energy difference between equilibrium states is a challenge problem motivating researchers to develop novel methods. The mean work in an isothermal process is widely acknowledged as an accurate estimator of the free energy difference, but the high time cost limits its practical applications. As one of the most famous methods developed in recent decades, the Jarzynski equality \cite{1} establishes a rigorous relation between the free energy difference and the exponential average over the work done on individual trajectories. This equality represents a refinement of the second law of thermodynamics in nonequilibrium driving processes. However, the free energy estimator based on the Jarzynski equality was later found to converge slowly since it is dominated by rare realizations where the trajectory work is smaller than the free energy difference \cite{2,3}. The second law of thermodynamics and its refined version (the Jarzynski equality) imply an inequality between the free energy difference and the mean work done in a nonequilibrium driving process. An illuminating question is whether there is a more concise nonequilibrium equality between the free energy difference and the mean work that can help us estimate the free energy difference.

Recently, the present authors and their coworker proposed a concept of shortcuts to isothermality and found an equality (see Eq. (1) below) between the free energy difference and the intrinsic work \cite{4}. Shortcuts to isothermality have been successfully verified in experiment \cite{5,6} and further extended to the optimization of finite-time heat engines \cite{7,8} and the control of biological evolutions \cite{10}. A key step in shortcuts to isothermality is to apply an auxiliary potential to the system of interest, such that the system evolves along the “isothermal” line corresponding to the original Hamiltonian. The intrinsic work equality can estimate the free energy difference with high accuracy, so it provides a new scheme for the free energy estimation in complex systems. Unfortunately, there is a obstacle that the process of solving the auxiliary potential requires information about the system free energy. Similar obstacles are prevalent in many schemes for estimating the free energy difference \cite{11,12}. It will be of great value to the free energy estimation if we could find a method to calculate the auxiliary potential without using the the free energy information.

In this work, we develop a variational method to overcome the above mentioned difficulty and to approximately realize shortcuts to isothermality. Enlightened by the idea of the Gauss principle of least constraint, a nonequilibrium “constraint” is defined as a measure of the distance between the accurate shortcut to isothermality and the approximate counterpart. Solving a variational equation of the nonequilibrium constraint, we can obtain the best possible auxiliary potential for realizing shortcuts to isothermality. Specifically, for an underdamped Brownian particle system, we propose a trial form of the auxiliary potential that is experimentally realizable. As an illustrative example, we check our method by considering an underdamped Brownian particle moving in a double-well potential. Combined with the intrinsic work equality, the variational method can be used to efficiently estimate the free energy difference with high accuracy. Such a variational scheme is expected to overcome the difficulties of the free energy estimation in complex systems.

Shortcuts to isothermality. – Shortcut to isothermality \cite{4} is a unified framework to accelerate isothermal processes and thereby realize finite-rate transitions between two equilibrium states at the same temperature. In the following, we briefly introduce the strategy of shortcuts to isothermality. Consider a system described by the Hamiltonian \( H_o(x,\lambda(t)) \) with \( x = (x_1, x_2, \cdots, x_N) \).
representing the microstate of the system and $\lambda(t)$ being an externally controlling parameter. The system is coupled to a thermal reservoir with a constant temperature $T$. The motion of the system is governed by the following equation

$$\dot{x}_i = f_i^o(x, t).$$  \hfill (1)

In this work, the dot above a variable represents the time derivative of that variable. $f^o = (f_1^o, f_2^o, \cdots, f_N^o)$ represents a generalized “force” field that depends on the Hamiltonian $H_o(x, \lambda(t))$ and the specific dynamics we are considering.

We introduce an auxiliary potential $U_o(x, t)$ to the original Hamiltonian $H_o(x, \lambda(t))$ so that the system distribution $\rho(x, t)$ is always in the instantaneous canonical distribution of the original Hamiltonian

$$\rho(x, t) = e^{\beta[F(\lambda(t)) - H_o(x, \lambda(t))]},$$  \hfill (2)

where $\beta = 1/k_B T$ with $k_B$ being the Boltzmann factor.

$$F(\lambda) \equiv -\beta^{-1} \ln \left[ \int dx e^{-\beta H_o(x, \lambda)} \right]$$  \hfill (3)

denotes the free energy of the original system in equilibrium for fixed $\lambda$. With additional requirements that $U_o(x, t)$ vanishes at two endpoints of the driving process, the system of interest will appear to evolve along the isothermal line in a finite rate. Along this “isothermal” line, we can derive an equality between the free energy difference and the mean work related to the original Hamiltonian (which is called the intrinsic work) $\mathcal{I}$:

$$\Delta F = \langle \mathcal{I}_i \rangle \equiv \int_0^T \left\langle \frac{\partial H_o}{\partial t} \right\rangle dt,$$  \hfill (4)

where $\langle \cdots \rangle$ denotes the ensemble average over trajectories. In addition to shortcuts to isothermality, many researchers have also discussed the realization of finite-rate transitions from an equilibrium state to another one with the same temperature. Martinez et al. [13] designed a protocol of engineered swift equilibration to achieve fast switches between equilibrium states of a Brownian particle system, see also [16, 17]. Since the intermediate state of the system in engineered swift equilibration is not always guaranteed in the instantaneous canonical state $\mathcal{I}$, the intrinsic work equality $\mathcal{I}$ can not be derived from engineered swift equilibration.

Within the framework of shortcuts to isothermality, the motion equation (1) is modified to the form:

$$\dot{x}_i = f_i^o(x, t) + f_i^a(x, t),$$  \hfill (5)

with $f^a = (f_1^a, f_2^a, \cdots, f_N^a)$ representing the auxiliary field induced by $U_o(x, t)$. The form of $f^a(x, t)$ also depends on the specific dynamics we are considering. The evolution equation of the system distribution $\rho(x, t)$ can be formally written as (see the Supplemental Material [18] for details)

$$\frac{\partial \rho}{\partial t} = \hat{L}_o \rho - \frac{\partial}{\partial x_i}(f_i^a \rho),$$  \hfill (6)

where $\hat{L}_o$ represents the evolution operator related to the original field $f^o(x, t)$. Throughout this paper, the repeated subscripts abide by the Einstein summation convention. We assume that when $\lambda$ is fixed, the system will relax toward a unique equilibrium state $\rho^{eq} \propto e^{-\beta H_o(x, \lambda)}$. Hence, we can obtain $\hat{L}_o e^{-\beta H_o(x, \lambda)} = 0$. Substituting the instantaneous canonical distribution $\mathcal{I}$ into the evolution equation (6), we can derive that

$$f_i^a \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f_i^a}{\partial x_i} = \frac{dF}{dt} - \frac{\partial H_o}{\partial t}.$$  \hfill (7)

Similar equation was also derived by Vaikuntanathan and Jarzynski [12]. They did not provide a general strategy to solve for the auxiliary field $f^a(x, t)$, but suggested to construct the auxiliary field according to physical insight, experience, and prior knowledge of the system.

Equation (7) highlights the difficulty of finding the auxiliary field $f^a(x, t)$ (or the auxiliary potential $U_o(x, t)$) precisely: before solving the equation, we need to know in advance the time-dependence of the free energy, which is usually hard to obtain for most complex systems. Thus, our goal is to propose a variational method that allows one to circumvent the requirement relating to the free energy and determine the best possible $f^a(x, t)$ under some restrictions, such as some specific boundary conditions or just experimental feasibility.

Variational shortcuts to isothermality. Based on Eq. (7), we can define a function

$$\mathcal{D}(f) \equiv \int f_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f_i}{\partial x_i} + \frac{\partial H_o}{\partial t} + \frac{dF}{dt} - \frac{\partial H_o}{\partial t},$$  \hfill (8)

where $f = (f_1, f_2, \cdots, f_N)$ represents an approximation to the exact auxiliary field $f^a(x, t)$. If $f = f^o$, then $\mathcal{D}(f) = 0$.

The Gauss principle of least constraint [13] provides a clue to seek the best possible $f^a(x, t)$. The Gauss principle states that the difference between the trajectory of a restricted system and its unrestricted Newtonian counterpart can be evaluated by the least value of the so-called “constraint”. Various efforts have been made to extend the idea of the Gauss principle to other similar problems, such as the development of time reversible deterministic thermostats [20, 21] and local quantum counterdiabatic driving protocols [22, 23]. Despite the fundamental status of the Gauss principle, there are few reports about the extension of the principle in nonequilibrium driving processes.

Enlightened by the Gauss principle of least constraint, we can define a functional

$$\mathcal{G}(f) \equiv \int dx \mathcal{D}^2(f) e^{-\beta H_o},$$  \hfill (9)

as a nonequilibrium “constraint” on the approximate auxiliary field $f(x, t)$. Here we have multiplied the local constraint $\mathcal{D}^2(f)$ by a function $e^{-\beta H_o}$ and then taken an integral over the whole phase space. In principle, the function $e^{-\beta H_o}$ can be replaced by any positive function.
We will find that the function $e^{-\beta H_o}$ can help eliminate the free energy information in the nonequilibrium constraint \[13\]. We can prove that finding the exact auxiliary field in Eq. \[14\] is equivalent to solving the variational equation \[15\]

$$\frac{\delta G(f)}{\delta f} = 0.$$ \[10\]

Substituting Eq. \[15\] into the nonequilibrium constraint \[18\], we can derive

$$G(f) = \int dx \left( f_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f_i}{\partial t} \right)^2 e^{-\beta H_o} - \frac{2}{\beta} \int dx \left( f_i \frac{\partial H_o}{\partial t} - \frac{dF}{dt} \right) \frac{\partial}{\partial x_i} (f_i e^{-\beta H_o}) + \int dx \left( f_i \frac{\partial H_o}{\partial t} - \frac{dF}{dt} \right)^2 e^{-\beta H_o}.$$ \[11\]

which reveals that the nonequilibrium constraint is closely related to the time derivative of the system free energy, $dF/dt$. The third term of Eq. \[11\] does not affect the variation in Eq. \[10\] since it is independent of $f(x,t)$. By using integration by parts, we can eliminate $dF/dt$ in the second term of the constraint \[11\]:

$$-\frac{2}{\beta} \int dx \left( \frac{\partial H_o}{\partial t} - \frac{dF}{dt} \right) \frac{\partial}{\partial x_i} (f_i e^{-\beta H_o})$$

$$= \frac{2}{\beta} \int dx f_i \frac{\partial^2 H_o}{\partial x_i \partial t} e^{-\beta H_o}.$$ \[12\]

Here we have assumed that the boundary term vanishes at infinity. According to the above analysis, we can finally reduce the nonequilibrium constraint \[11\] into the following simplified form:

$$G_s(f) = \int dx \left( f_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f_i}{\partial t} \right)^2 e^{-\beta H_o} + \frac{2}{\beta} \int dx f_i \frac{\partial^2 H_o}{\partial x_i \partial t} e^{-\beta H_o},$$ \[13\]

which is our first central result. Here the requirement about the free energy information has been eliminated. According to different restrictions on the auxiliary field, we first choose a proper trial function $f(x,t)$. Then, substituting the trial function into the nonequilibrium constraint \[13\] and applying the variational procedure, we can find the best possible auxiliary field $f^a(x,t)$ and thereby approximately realize shortcuts to isothermality. We dub such a variational scheme the "variational shortcut to isothermality".

For simple forms of $H_o(x,\lambda(t))$, the integral in the constraint \[13\] is very straightforward. However, for complex systems where the integral in the nonequilibrium constraint \[13\] can not be accurately calculated, we can refer to some techniques for approximating the integral, such as the saddle-point approximation \[25\]. In order to get better approximation, we make further transformations to the nonequilibrium constraint \[13\]. By using integration by parts, we can derive that \[18\]

$$G_s(f) = \int dx W e^{-\beta H_o},$$ \[14\]

with

$$W(x,t) = \frac{1}{\beta^2} \frac{\partial f_i}{\partial x_i} \frac{\partial f_j}{\partial x_j} + \frac{1}{\beta} \frac{\partial^2 H_o}{\partial x_i \partial x_j} + \frac{2}{\beta} \frac{\partial H_o}{\partial x_i \partial t}.$$ \[15\]

Then, applying the saddle-point approximation to the integral \[14\], we can obtain \[18\]

$$G_s(f) \approx \sum_m W(x^m, t) e^{-\beta H_o(x^m, \lambda)} \prod_{i=1}^N \sqrt{\frac{2\pi}{\beta A_i(x^m, t)}},$$ \[16\]

where $A_i$ is an eigenvalue of the Hessian matrix $D$ with $D_{jk} \equiv \langle \partial^2 H_o/\partial x_i \partial x_j \rangle|_{x=x^m}$. Here $x^m$ represents one of the minimum points of the function $H_o(x, \lambda)$. Equation \[10\] is our second central result.

**Application.**—Considering an underdamped Brownian particle controlled by an original potential $U_o(q, \lambda(t))$ and a momentum-dependent auxiliary potential $U_o(q, p, t)$ with $q = (q_1, q_2, \cdots, q_N)$ and $p = (p_1, p_2, \cdots, p_N)$ denoting coordinate and momentum of the particle, respectively. The motion of the particle is governed by the modified Langevin equation \[1\]

$$\dot{q}_i = \frac{p_i}{m} + \frac{\partial U_o}{\partial q_i},$$

$$\dot{p}_i = -\frac{\partial U_o}{\partial q_i} - \frac{\partial U_o}{\partial \lambda_i} - \gamma \left( \frac{p_i}{m} + \frac{\partial U_o}{\partial p_i} \right) + \xi_i(t),$$ \[17\]

with $m$ being the mass of the particle. $\gamma$ represents the coefficient of friction and $\xi = (\xi_1, \xi_2, \cdots, \xi_N)$ denotes the standard Gaussian white noise satisfying $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = 2\gamma k_B T \delta_{ij} \delta(t-t')$. We propose the following trial form for the auxiliary potential

$$U_o(q, p, t) = \lambda(t) \{ s(\lambda(t))q_i + u_i(\lambda(t))p_i + v(q, \lambda(t)) \},$$ \[18\]

where $s(\lambda(t))$, $u(\lambda(t))$, and $v(q, \lambda(t))$ are undetermined functions. To ensure that $U_o$ vanishes at the beginning and end of the driving process, we impose the boundary conditions $\lambda(0) = \lambda(\tau) = 0$. The cross term $q_i p_i$ in the auxiliary potential \[18\], which is very hard to be realized in experiment \[12\] \[20\], can be eliminated by introducing a change of variables \[18\].

As an illustrative example, we consider an one-dimensional double-well potential

$$U_o(q, \lambda(t)) = k q^4 - \lambda(t) q^2,$$ \[19\]

where $k$ is a constant coefficient. The Brownian motion of a particle in the double-well potential \[19\] is widely used to describe noise-driven motion in a variety of bistable physical and chemical systems \[27\] \[30\]. Substituting the original potential \[19\] and the trial form of the auxiliary potential \[18\] into the nonequilibrium constraint \[10\]
and then implementing the variational procedure, we can derive that [18]

\[ U_a(q, p, t) = \frac{\beta \lambda}{8 \beta \lambda^2 + 12k} \left( 4 \lambda \gamma q \pi k - 3 \gamma \lambda q^2 \right) . \]  

![Image](image1.png)

**FIG. 1.** Comparison of estimates of \( \Delta F \) for \( \alpha = 1.0 \). \( \langle w_i \rangle \) (squares) and \( \Delta F_0 \) (diamonds) represent the estimates from the mean work and the Jarzynski equality in the process driven by \( U_o \) only. \( \langle w_i \rangle \) (circles), \( \Delta F_t \) (upper triangles), and \( \langle w_i \rangle \) (lower triangles) represent the estimates from the mean work, the Jarzynski equality, and the intrinsic work [11] in the process driven by \( U_o \) and \( U_a \). See the Supplemental Material [18] for details of each estimation method. The solid line represents the theoretical value, \( \Delta F = 62.94 \) [28]. The estimates of \( \Delta F \) are shown on a logarithmic scale.

We simulate the motion of an underdamped Brownian particle in the potential [19] and add the auxiliary potential [20] to approximately realize shortcuts to isothermality. The dimensionless driving protocol is chosen to be \( \lambda(t) = 8[1 + \cos(\pi t/\tau)] \) with \( \lambda = \lambda/\sqrt{k_B T} \). The influence of the particle inertia is determined by a parameter \( \alpha = \tau_p/\tau \) with \( \tau_p \equiv m/\gamma \) and \( \tau_{\rho} \equiv \gamma/\sqrt{k_B T} \) denoting two characteristic times of the system. The simulations are performed for dimensionless driving times \( \tilde{\tau} \equiv \tau/\tau_p \) ranging from 0.1 to 3.0. Details of the simulation are attached in the Supplemental Material [18]. We use Eq. [4] to estimate the free energy difference \( \Delta F \). The results are compared with the estimates given by the mean work and the Jarzynski equality in Fig. 1. It needs to be noted that there are two different definitions of the trajectory work for shortcuts to isothermality [31]. Here we choose to follow the definition from the thermodynamic interpretation of the Langevin dynamics [32] and take the form

\[ w_i \equiv \int_0^\tau \left( \frac{\partial U_a}{\partial t} + \frac{\partial U_o}{\partial t} \right) dt . \]  

![Image](image2.png)

**FIG. 2.** Comparison of estimates of \( \Delta F \) for \( \alpha = 0.1 \). The caption for Fig. 1 applies here.

The dimensionless driving protocol is chosen to be \( \lambda(t) = 8[1 + \cos(\pi t/\tau)] \) with \( \lambda = \lambda/\sqrt{k_B T} \). The influence of the particle inertia is determined by a parameter \( \alpha = \tau_p/\tau \) with \( \tau_p \equiv m/\gamma \) and \( \tau_{\rho} \equiv \gamma/\sqrt{k_B T} \) denoting two characteristic times of the system. The simulations are performed for dimensionless driving times \( \tilde{\tau} \equiv \tau/\tau_p \) ranging from 0.1 to 3.0. Details of the simulation are attached in the Supplemental Material [18]. We use Eq. [4] to estimate the free energy difference \( \Delta F \). The results are compared with the estimates given by the mean work and the Jarzynski equality in Fig. 1. It needs to be noted that there are two different definitions of the trajectory work for shortcuts to isothermality [31]. Here we choose to follow the definition from the thermodynamic interpretation of the Langevin dynamics [32] and take the form

\[ w_i \equiv \int_0^\tau \left( \frac{\partial U_a}{\partial t} + \frac{\partial U_o}{\partial t} \right) dt . \]  

![Image](image3.png)

**FIG. 3.** Comparison of different work distributions for \( \alpha = 1.0 \). The driving time is 0.1. \( \rho(w_o) \) (crosses) denotes the distribution of the total trajectory work \( w_o \) in the process driven by \( U_o \) only. \( \rho(w_i) \) (open circles) and \( \rho(w_i) \) (asterisks) denote the distributions of the total trajectory work \( w_i \) and the intrinsic trajectory work \( w_i \) in the process driven by \( U_o \) and \( U_a \).

Figure 3 shows the comparison of different trajectory work distributions for \( \alpha = 1.0 \). Here we choose a short driving time, \( \tilde{\tau} = 0.1 \). As shown in Fig. 3 the distribution of the intrinsic trajectory work \( \rho(w_i) \) is sharply centered around the theoretical value of \( \Delta F \) while the peaks of the total trajectory work distributions \( \rho(w_o) \) and \( \rho(w_i) \) deviate far from the theoretical value of \( \Delta F \). Besides, \( \rho(w_o) \) and \( \rho(w_i) \) take much broader forms than \( \rho(w_i) \). These observations imply that compared with the mean work and the Jarzynski equality, the intrinsic work equality [4] allows us to obtain a reliable estimate of the free energy difference with a small number of trajec-
ries. This is a superiority for the intrinsic work equality \([4]\) when we are dealing with practical systems in which only a small number of samples are available.

**Conclusion and discussion.**—Enlightened by the idea of the Gauss principle of least constraint, we have developed the variational shortcut to isothermality, which can approximately realize finite-rate isothermal transitions between equilibrium states for complex systems. A key advantage of this variational method is that it allows us to obtain the best possible auxiliary potential for shortcuts to isothermality without requiring the information of the system free energy. Combined with the intrinsic work equality \([4]\), the variational method can be used to efficiently estimate the free energy difference with high accuracy.

Considering the experimental feasibility, we have proposed a trial form \([15]\) for the auxiliary potential of the underdamped Brownian particle system. In numerical simulations, we can assume a trial form with high-order couplings between the coordinate and the momentum. The variational shortcut to isothermality is still applicable in this situation and may provide a more accurate estimate of the free energy difference.

Here we have stressed the application of our variational method in accelerating the isothermal process and estimating the free energy difference. Similar calculations are promising to be extended to other nonequilibrium driving processes, such as the shortcut to stochastic near-adiabatic pumping \([33, 34]\), the preprocessing strategies before heating and cooling \([35, 36]\), and the thermodynamic control \([38]\).

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Supplemental Material for the manuscript: High-Efficiency Free Energy Estimates Based on Variational Shortcuts to Isothermality

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I. DERIVATION OF THE EVOLUTION EQUATION FOR THE AUXILIARY FIELD, EQ. (7)

Consider a system following the motion equation

$$\dot{x}_i = f^o_i(x, t).$$  \hfill (I.1)

The evolution equation of the system distribution $\rho(x, t)$ can be formally written as

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x_i}(\dot{x}_i \rho) = -\frac{\partial}{\partial x_i}(f^o_i \rho).$$  \hfill (I.2)

If we consider $f^o(x, t)$ containing both deterministic and stochastic parts (such as the Langevin dynamics), the time evolution equation (I.2) will be different for each realization of the stochastic parts [1]. After averaging over the stochastic parts, we can formally derive the evolution equation of the observable probability:

$$\frac{\partial \rho}{\partial t} = \hat{L}_o \rho,$$  \hfill (I.3)

where $\hat{L}_o \equiv \hat{L}_o(x, t)$ represents the evolution operator. If we add an auxiliary potential $U_a(x, t)$ to the original Hamiltonian, the motion equation is modified to the form

$$\dot{x}_i = f^o_i(x, t) + f^a_i(x, t),$$  \hfill (I.4)

where the auxiliary field $f^a(x, t)$ depends on $U_a(x, t)$ and the dynamics we are considering. Since the ensemble average over the stochastic parts of $f^o(x, t)$ does not affect the deterministic field $f^a(x, t)$, we can formally derive the modified evolution equation as

$$\frac{\partial \rho}{\partial t} = \hat{L}_o \rho - \frac{\partial}{\partial x_i}(f^a_i \rho),$$  \hfill (I.5)

which is just Eq. (6) in the main text. When we adopt the strategy of shortcuts to isothermality, the system distribution will always stay in the instantaneous canonical distribution of $H_o(x, \lambda(t))$:

$$\rho^{eq}(x, \lambda(t)) = e^{\beta[F(\lambda(t)) - H_o(x, \lambda(t))]}.$$  \hfill (I.6)

Substituting the instantaneous canonical distribution (I.6) into the modified evolution equation (I.5), we can derive

$$f^a_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f^a_i}{\partial x_i} = \frac{dF}{dt} - \frac{\partial H_o}{\partial t},$$  \hfill (I.7)

which corresponds to Eq. (7) in the main text.
Since both $F(\lambda(t))$ and $H_o(x, \lambda(t))$ depend explicitly on time through the controlling parameter $\lambda(t)$, we can further derive

$$f^a_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f^a_i}{\partial x_i} = \left( \frac{dF}{d\lambda} - \frac{\partial H_o}{\partial \lambda} \right) \dot{\lambda}. \tag{I.8}$$

Comparing two sides of Eq. (I.8), we find that $f^a$ can be preassumed to take the form

$$f^a(x, t) = \dot{\lambda}(t) \nu(x, \lambda(t)), \tag{I.9}$$

with $\nu(x, \lambda(t))$ being an undetermined function.

II. EQUIVALENCE BETWEEN THE EVOLUTION EQUATION (7) AND THE VARIATIONAL EQUATION (10)

We start from the definition of the function

$$\mathcal{D}(f) \equiv f_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f_i}{\partial x_i} + \frac{\partial H_o}{\partial t} - \frac{dF}{dt}, \tag{II.1}$$

where $f \equiv f(x, t)$ represents an approximation to the exact auxiliary field $f^a(x, t)$. If $f = f^a$, then $\mathcal{D}(f) = 0$. For any forms of $f$, we can derive that

$$\int dx \mathcal{D}(f)e^{-\beta H_o} = -\frac{1}{\beta} \int dx \frac{\partial}{\partial x_i} (f_i e^{-\beta H_o}) + \int dx \left( \frac{\partial H_o}{\partial t} - \frac{dF}{dt} \right) e^{-\beta H_o} = 0. \tag{II.2}$$

Referring to the Gauss principle of least constraint [2], we define a functional

$$\mathcal{G}(f) \equiv \int dx \mathcal{D}^2(f)e^{-\beta H_o}, \tag{II.3}$$

as a nonequilibrium “constraint” on the auxiliary field $f$. If the form of the auxiliary field is free from restrictions, the nonequilibrium constraint (II.3) will be minimized whenever $f$ satisfies:

$$\frac{\delta \mathcal{G}}{\delta f} = 0 \Rightarrow \nabla \mathcal{D}|_{f=f^a} = 0, \tag{II.4}$$

which then implies

$$\mathcal{D}|_{f=f^a} = C(t) \tag{II.5}$$

with $C(t)$ being a time-dependent parameter. Because of the property (II.2), we can derive $C(t) = 0$, i.e.,

$$\mathcal{D}|_{f=f^a} = f^a_i \frac{\partial H_o}{\partial x_i} - \frac{1}{\beta} \frac{\partial f^a_i}{\partial x_i} + \frac{\partial H_o}{\partial t} - \frac{dF}{dt} = 0, \tag{II.6}$$
which, as anticipated, is just Eq. (7) in the main text. Therefore, unrestricted minimization of the nonequilibrium constraint (II.3) is mathematically equivalent to solving Eq. (7). If restrictions prevent the free choice of \( f \), we can still minimize the nonequilibrium constraint (II.3) under the given restrictions.

### III. Applying the Saddle-Point Approximation to the Nonequilibrium Constraint

Consider an integral of the form

\[
\int_{y_0}^{y_1} dy w(y) e^{Ag(y)},
\]

where \( w(y) \) and \( g(y) \) are some real functions and \( A > 0 \) is a parameter. For large values of \( A \), the integral (III.1) is completely dominated by the peaks with each peak located at a maximum of \( g(y) \). Without loss of generality, let us first assume that \( y_m \) is the only maximum point of \( g \) in the interval \((y_0, y_1)\). Changing the integral variable according to \( y = y_m + z/\sqrt{A} \) and then expanding \( Ag(y) \) in power of \( z \), we have

\[
Ag(y) = Ag(y_m) + \frac{z^2}{2} \frac{d^2 g(y)}{dy^2} \bigg|_{y=y_m} + O \left( \frac{1}{\sqrt{A}} \right).
\]

Here the first-derivative term is missing because \( y_m \) is the maximum of \( g \). In the exponential form, we can further derive that

\[
\exp(Ag(y)) = \exp \left( Ag(y_m) + \frac{z^2}{2} \frac{d^2 g(y)}{dy^2} \bigg|_{y=y_m} \right) \left( 1 + O \left( \frac{1}{\sqrt{A}} \right) \right).
\]

Assuming that \( w(y_m) \neq 0 \), we can similarly expand \( w(y) \) in power of \( z \):

\[
w(y) = w(y_m) \left( 1 + O \left( \frac{1}{\sqrt{A}} \right) \right).
\]

Substituting Eqs. (III.3) and (III.4) into (III.1), we have

\[
\int_{y_0}^{y_1} dy w(y) e^{Ag(y)} = \frac{w(y_m) e^{Ag(y_m)}}{\sqrt{A}} \int_{z_0}^{z_1} dz \left[ \exp \left( \frac{z^2}{2} \frac{d^2 g(y)}{dy^2} \bigg|_{y=y_m} \right) \left( 1 + O \left( \frac{1}{\sqrt{A}} \right) \right) \right].
\]

In the large \( A \) limit, \( z_0 \) and \( z_1 \) will tend to \(-\infty\) and \(+\infty\), respectively. Therefore, we can give the saddle-point approximation:

\[
\int_{y_0}^{y_1} dy w(y) e^{Ag(y)} \approx w(y_m) e^{Ag(y_m)} \sqrt{\frac{2\pi}{-A d^2 g(y)/dy^2 |_{y=y_m}}}. \tag{III.6}
\]
If there are multiple maxima of \( g(y) \) in the integral interval \((y_0, y_1)\), we can divide the interval into smaller intervals according to the location of each maximum point. The integral (III.1) equals to the sum of the approximation in each small interval.

In the following, we apply the saddle-point approximation to the integral in the nonequilibrium constraint. Starting from the nonequilibrium constraint (13), we can derive that

\[
G_s(f) = \int d\mathbf{x} f_i \frac{\partial H_o}{\partial x_i} e^{-\beta H_o} + \frac{1}{\beta^2} \int d\mathbf{x} \frac{\partial f_i}{\partial x_i} \frac{\partial f_j}{\partial x_j} e^{-\beta H_o} - \frac{2}{\beta} \int d\mathbf{x} f_i \frac{\partial H_o}{\partial x_i} \frac{\partial f_j}{\partial x_j} e^{-\beta H_o} + \frac{2}{\beta} \int d\mathbf{x} f_i \frac{\partial^2 H_o}{\partial x_i \partial t} e^{-\beta H_o}.
\]

(III.7)

If we apply the saddle-point approximation directly to the integral in the nonequilibrium constraint (III.7), the first term and the third term will vanish since there are first-order derivative of \( H_o \) in them. In order to get a better approximation, we make further transformations to the nonequilibrium constraint (III.7). Applying integration by parts to the first term, we can derive that

\[
\int d\mathbf{x} f_i \frac{\partial H_o}{\partial x_i} \frac{\partial H_o}{\partial x_j} e^{-\beta H_o} = -\frac{1}{\beta} \int d\mathbf{x} f_i \frac{\partial H_o}{\partial x_i} \frac{\partial (e^{-\beta H_o})}{\partial x_j} e^{-\beta H_o} = \frac{1}{\beta} \int d\mathbf{x} \left( \frac{\partial f_j}{\partial x_j} \frac{\partial H_o}{\partial x_i} + f_i \frac{\partial^2 H_o}{\partial x_i \partial x_j} + f_i \frac{\partial H_o}{\partial x_i} \frac{\partial f_j}{\partial x_j} \right) e^{-\beta H_o}.
\]

(III.8)

Here we have also assumed that the boundary terms vanish at infinity. We can similarly obtain that

\[
\frac{1}{\beta} \int d\mathbf{x} f_i \frac{\partial f_j}{\partial x_j} \frac{\partial H_o}{\partial x_i} e^{-\beta H_o} = \frac{1}{\beta^2} \int d\mathbf{x} \left( \frac{\partial f_i}{\partial x_i} \frac{\partial f_j}{\partial x_j} + f_j \frac{\partial^2 H_o}{\partial x_i \partial x_j} + f_i \frac{\partial H_o}{\partial x_i} \frac{\partial f_j}{\partial x_j} \right) e^{-\beta H_o},
\]

(III.9)

and

\[
\frac{1}{\beta} \int d\mathbf{x} f_i \frac{\partial H_o}{\partial x_i} \frac{\partial^2 H_o}{\partial x_j \partial x_j} e^{-\beta H_o} = \frac{1}{\beta^2} \int d\mathbf{x} \left( \frac{\partial f_i}{\partial x_i} \frac{\partial f_j}{\partial x_j} + f_j \frac{\partial^2 H_o}{\partial x_i \partial x_j} + f_i \frac{\partial H_o}{\partial x_i} \frac{\partial f_j}{\partial x_j} \right) e^{-\beta H_o}.
\]

(III.10)

Substituting Eqs. (III.8), (III.9), and (III.10) into (III.7), we can finally derive that

\[
G_s(f) = \frac{1}{\beta^2} \int d\mathbf{x} \frac{\partial f_i}{\partial x_j} \frac{\partial f_j}{\partial x_i} e^{-\beta H_o} + \frac{1}{\beta} \int d\mathbf{x} f_i f_j \frac{\partial^2 H_o}{\partial x_i \partial x_j} e^{-\beta H_o} + \frac{2}{\beta} \int d\mathbf{x} f_i \frac{\partial^2 H_o}{\partial x_i \partial t} e^{-\beta H_o} = \int d\mathbf{x} W e^{-\beta H_o},
\]

(III.11)

with

\[
W(x, t) = \frac{1}{\beta^2} \frac{\partial f_i}{\partial x_j} \frac{\partial f_j}{\partial x_i} + \frac{1}{\beta} f_i f_j \frac{\partial^2 H_o}{\partial x_i \partial x_j} + \frac{2}{\beta} f_i \frac{\partial^2 H_o}{\partial x_i \partial t}.
\]

(III.12)
Here we have cancelled out the terms containing the first-order derivative of \( H_o \) in the nonequilibrium constraint.

Without loss of generality, we assume that the Hamiltonian function \( H_o \) has only one minimum located at \( \mathbf{x}^m \). We use \( \Delta \equiv E_{\text{min}} - E_{\text{max}} \) to denote the difference between the minimum \( E_{\text{min}} \) of the function \( H_o \) and its adjoining maximum \( E_{\text{max}} \). Then the exponential term \(-\beta H_o\) can be transformed into

\[
-\beta H_o = A \tilde{H}_o, \quad (\text{III.13})
\]

where \( A \equiv -\beta \Delta \) and \( \tilde{H}_o \equiv H_o/\Delta \). When \( A \gg 1 \), the saddle-point approximation can be applied to the integral (III.11). Changing the integral variable according to \( \mathbf{x} = \mathbf{x}^m + z/\sqrt{A} \), we can expand \( A \tilde{H}_o \) in power of \( z \):

\[
A \tilde{H}_o(\mathbf{x}, \lambda) = A \tilde{H}_o(\mathbf{x}^m, \lambda) + \frac{z_i z_j}{2} \left. \frac{\partial^2 \tilde{H}_o}{\partial x_i \partial x_j} \right|_{\mathbf{x} = \mathbf{x}^m} + O\left(\frac{1}{\sqrt{A}}\right). \quad (\text{III.14})
\]

Similarly, we can derive that

\[
\exp(A \tilde{H}_o) = \exp \left( A \tilde{H}_o(\mathbf{x}^m, \lambda) + \frac{z_i z_j}{2} \frac{\partial^2 \tilde{H}_o}{\partial x_i \partial x_j} \bigg|_{\mathbf{x} = \mathbf{x}^m} \right) \left(1 + O\left(\frac{1}{\sqrt{A}}\right)\right), \quad (\text{III.15})
\]

and

\[
W(\mathbf{x}, t) = W(\mathbf{x}^m, t) \left(1 + O\left(\frac{1}{\sqrt{A}}\right)\right). \quad (\text{III.16})
\]

Substituting Eqs. (III.15) and (III.16) into (III.11), we have

\[
G_s(f) = \frac{W(\mathbf{x}^m, t) e^{A \tilde{H}_o(\mathbf{x}^m, \lambda)}}{\sqrt{A}} \int dz \left[ \exp \left( \frac{z_i z_j}{2} \frac{\partial^2 \tilde{H}_o}{\partial x_i \partial x_j} \bigg|_{\mathbf{x} = \mathbf{x}^m} \right) \left(1 + O\left(\frac{1}{\sqrt{A}}\right)\right) \right]. \quad (\text{III.17})
\]

In the large \( A \) limit, we can give the saddle-point approximation:

\[
G_s(f) \approx W(\mathbf{x}^m, t) e^{-\beta H_o(\mathbf{x}^m, \lambda)} \prod_{i=1}^{n} \sqrt{\frac{2\pi}{\beta \Lambda_i(\mathbf{x}^m, t)}}, \quad (\text{III.18})
\]

where \( \Lambda_i \) is an eigenvalue of the Hessian matrix

\[
D = \begin{pmatrix}
\frac{\partial^2 H_o}{\partial x_1^2} & \frac{\partial^2 H_o}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 H_o}{\partial x_1 \partial x_n} \\
\frac{\partial^2 H_o}{\partial x_2 \partial x_1} & \frac{\partial^2 H_o}{\partial x_2^2} & \cdots & \frac{\partial^2 H_o}{\partial x_2 \partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial^2 H_o}{\partial x_n \partial x_1} & \frac{\partial^2 H_o}{\partial x_n \partial x_2} & \cdots & \frac{\partial^2 H_o}{\partial x_n^2}
\end{pmatrix} \bigg|_{\mathbf{x} = \mathbf{x}^m}. \quad (\text{III.19})
\]

Similarly, if the Hamiltonian function \( H_0 \) has multiple minima \( \{\mathbf{x}^m\} \) with \( m = 1, 2, \cdots \), the integral (III.11) will be the sum of the approximation around each minimum point:

\[
G_s(f) \approx \sum_{m} W(\mathbf{x}^m, t) e^{-\beta H_o(\mathbf{x}^m, \lambda)} \prod_{i=1}^{n} \sqrt{\frac{2\pi}{\beta \Lambda_i(\mathbf{x}^m, t)}}, \quad (\text{III.20})
\]
IV. FAST-FORWARD PROTOCOL IN SHORTCUTS TO ISOTHERMALITY

We start from the modified Langevin equation

\[ \dot{q}_i = \frac{p_i}{m} + \frac{\partial U_a}{\partial p_i}, \]
\[ \dot{p}_i = -\frac{\partial U_o}{\partial q_i} - \frac{\partial U_a}{\partial q_i} - \gamma \left( \frac{p_i}{m} + \frac{\partial U_o}{\partial p_i} \right) + \xi_i(t), \tag{IV.1} \]

where the auxiliary potential takes the trial form

\[ U_a(q, p, t) = \dot{\lambda}(t) \left\{ [s(\lambda(t))q_i + u_i(\lambda(t))]p_i + v(q, \lambda(t)) \right\} . \tag{IV.2} \]

Similar to the nonlocal term in shortcuts to adiabaticity, the cross term \( q_ip_i \) in the auxiliary potential (IV.2) is hard to be realized in experiment [3, 4]. We now introduce a change of variables that can effectively eliminate the cross term.

Substituting Eq. (IV.2) into Eq. (IV.1), we can obtain

\[ \dot{q}_i = \frac{p_i}{m} + \dot{\lambda}(s_q i + u_i), \]
\[ \dot{p}_i = -\frac{\partial U_o}{\partial q_i} - \dot{\lambda} \left( s p_i + \frac{\partial v}{\partial q_i} \right) - \gamma \left[ \frac{p_i}{m} + \dot{\lambda}(s_q i + u_i) \right] + \xi_i(t). \tag{IV.3} \]

Consider the evolution of the observables

\[ Q_i = q_i, \quad P_i = p_i + m\dot{\lambda}(s_q i + u_i), \tag{IV.4} \]

along a trajectory governed by the Langevin equation (IV.3). Taking time derivative of the observables, we obtain

\[ \dot{Q}_i = \dot{q}_i, \]
\[ \dot{P}_i = \dot{p}_i + m\ddot{\lambda}(s_q i + u_i) + m\dot{\lambda}^2 \left( \frac{\partial s}{\partial \lambda} q_i + \frac{d u_i}{d \lambda} \right) + \dot{\lambda} s p_i. \tag{IV.5} \]

By applying the mapping relations (IV.4) and (IV.5) into Eq. (IV.3), we get

\[ \dot{Q}_i = \frac{P_i}{m}, \]
\[ \dot{P}_i = -\frac{\partial U_o}{\partial Q_i} + F^a_i - \gamma \frac{P_i}{m} + \xi_i(t), \tag{IV.6} \]

with the auxiliary force

\[ F^a_i(Q, t) = -\dot{\lambda} \frac{\partial v}{\partial Q_i} + m\ddot{\lambda}(s Q_i + u_i) + m\dot{\lambda}^2 \left( \frac{\partial s}{\partial \lambda} Q_i + \frac{d u_i}{d \lambda} \right). \tag{IV.7} \]
Here $\ddot{\lambda}$ represents the second time derivative of $\lambda$.

Similar to the fast-forward protocol in shortcuts to adiabaticity\cite{5,6,7,8}, Eq. (IV.6) can approximately realize a transition between two equilibrium states at the same temperature in finite time. Additional boundary conditions $\ddot{\lambda}(0) = \ddot{\lambda}(\tau) = 0$ need to be satisfied by the driving protocol. In the intermediate driving process, the system will depart from the instantaneous equilibrium state. Since $F^a$ is an explicit function of $Q$ and $t$, it will generically be easier to implement in experiment than the momentum-dependent auxiliary potential (IV.2).

V. APPLYING THE VARIATIONAL SHORTCUT TO ISOHERMALITY TO A BROWNIAN PARTICLE MOVING IN A DOUBLE-WELL POTENTIAL

Consider a Brownian particle moving in an one-dimensional potential

$$U_o(q, \lambda(t)) = kq^4 - \lambda(t)q^2. \quad (V.1)$$

In the following, we will show how to solve for the corresponding auxiliary potential by using the variational shortcut to isothermality. Both the overdamped situation and the underdamped situation have been discussed.

A. Overdamped situation

In the overdamped situation, the motion of the Brownian particle is governed by the Langevin equation

$$\dot{q} = -\frac{1}{\gamma} \frac{\partial U_o}{\partial q} - \frac{1}{\gamma} \frac{\partial U_o}{\partial q} + \frac{1}{\gamma} \xi(t). \quad (V.2)$$

Comparing Eq. (V.2) with the general motion equation (I.4), we can obtain the corresponding relations

$$f^o(q, t) = -\frac{1}{\gamma} \frac{\partial U_o}{\partial q} + \frac{1}{\gamma} \xi(t), \quad (V.3)$$

and

$$f^a(q, t) = -\frac{1}{\gamma} \frac{\partial U_o}{\partial q}. \quad (V.4)$$

Note that $f^o(q, t)$ contains both the deterministic part $-\gamma^{-1}\partial U_o/\partial q$ and the stochastic part $\gamma^{-1}\xi(t)$ while $f^a(q, t)$ is presupposed to be deterministic.
In the one-dimensional overdamped Brownian particle system, the nonequilibrium constraint (16) can be simplified to the form

\[ G_\ast \approx \sum_m W(q_m, t)e^{-\beta U_0(q_m, \lambda)} \sqrt{\frac{2\pi}{\beta \Lambda(q_m, \lambda)}}, \]  

(V.5)

with

\[ W(q, t) = \frac{1}{\beta^2} \left( \frac{\partial f}{\partial q} \right)^2 + \frac{1}{\beta} f^2 \frac{\partial^2 U_0}{\partial q^2} + \frac{2}{\beta} f \frac{\partial^2 U_0}{\partial q \partial t}. \]  

(V.6)

Here \( \Lambda(q_m, \lambda) = (\partial^2 U_0/\partial q^2)|_{q=q_m} \) with \( q_m \) representing one of the minimum points of the function \( U_0 \). Considering the double-well potential (V.1), we can derive that there are two minimum points \( q_1 = \sqrt{\lambda/2k} \) and \( q_2 = -\sqrt{\lambda/2k} \). According to the form of the original potential (V.1), we assume that the auxiliary potential takes the form

\[ U_0(q, t) = \dot{\lambda}(t)[a_4^*(t)q^4 + a_3^*(t)q^3 + a_2^*(t)q^2 + a_1^*(t)q], \]  

(V.7)

where \( a_1^*(t), a_2^*(t), a_3^*(t), \) and \( a_4^*(t) \) are undetermined parameters. Therefore, the approximate auxiliary field should take the form

\[ f(x, t) = -\frac{\dot{\lambda}(t)}{\gamma} [4a_4(t)q^3 + 3a_3(t)q^2 + 2a_2(t)q + a_1(t)], \]  

(V.8)

where \( a_1(t), a_2(t), a_3(t), \) and \( a_4(t) \) are approximations to the corresponding parameters \( a_1^*(t), a_2^*(t), a_3^*(t), \) and \( a_4^*(t) \). Substituting the trial form (V.8) into the nonequilibrium constraint (V.5) and then minimizing it over the parameters, we obtain

\[ M \begin{pmatrix} a_4^* \\ a_3^* \\ a_2^* \\ a_1^* \end{pmatrix} = \begin{pmatrix} -\gamma q^4 \\ -\gamma q^3 \\ -\gamma q^2 \\ -\gamma q^1 \end{pmatrix}, \]  

(V.9)

where

\[ M = \begin{pmatrix} 24kq^5 - 4\lambda q^3 & 18kq^4 - 3\lambda q^2 & 12kq^3 - 2\lambda q^1 & 6kq^2 - \lambda q^0 \\ 24kq^6 - 4\lambda q^4 + \frac{6}{\beta^2} q^2 & 18kq^5 - 3\lambda q^3 + \frac{3}{\beta^2} q^1 & 12kq^4 - 2\lambda q^2 + \frac{2}{\beta^2} q^0 & 6kq^3 - \lambda q^1 \\ 24kq^7 - 4\lambda q^5 + \frac{12}{\beta^2} q^3 & 18kq^6 - 3\lambda q^4 + \frac{6}{\beta^2} q^2 & 12kq^5 - 2\lambda q^3 + \frac{4}{\beta^2} q^1 & 6kq^4 - \lambda q^2 \\ 24kq^8 - 4\lambda q^6 + \frac{16}{\beta^2} q^4 & 18kq^7 - 3\lambda q^5 + \frac{9}{\beta^2} q^3 & 12kq^6 - 2\lambda q^4 + \frac{2}{\beta^2} q^2 & 6kq^5 - \lambda q^3 \end{pmatrix} \]  

(V.10)

Here

\[ \overline{q^m} \equiv \sqrt{\frac{2\pi}{4\beta \lambda}} \left[ q_1^m e^{-\beta(kq_1^1 - \lambda q_1^1)} + q_2^m e^{-\beta(kq_2^2 - \lambda q_2^2)} \right], \quad n = 0, 1, 2, \ldots \]  

(V.11)
Solving Eq. (V.9), we can derive that
\[ a_1^* = a_3^* = 0, \quad a_2^* = -\frac{3\gamma}{8\lambda}, \quad a_4^* = \frac{\gamma k}{8\lambda^2}. \]  

(V.12)

Therefore, the best possible auxiliary potential takes the form
\[ U_a(q,t) = \frac{\gamma \dot{\lambda}}{8\lambda^2} (kq^4 - 3\lambda q^2). \]

(V.13)

Note that the saddle-point approximation (V.5) applies when the distance between the maximum and the minimum of \( \beta U_0 \), i.e., \( A \equiv \beta \lambda^2/(4k) \), is much larger than 1. Therefore, the auxiliary potential (V.13) only works when the controlling parameter satisfies \( \lambda(t) \gg \sqrt{4k/\beta} \). We will discuss the case in which \( \lambda \to 0 \) at the end of this section.

B. Underdamped situation

In the underdamped situation, the evolution of the Brownian particle trajectory \( \mathbf{x} = \{q, p\}^T \) is described by the modified Langevin equation
\[
\dot{q} = \frac{p}{m} + \frac{\partial U_a}{\partial p},
\]
\[
\dot{p} = -\frac{\partial U_o}{\partial q} - \frac{\partial U_a}{\partial q} - \gamma \left( \frac{p}{m} + \frac{\partial U_a}{\partial p} \right) + \xi(t),
\]

(V.14)

where we have assumed that the auxiliary potential \( U_a \) is momentum-dependent. Comparing it with the general motion equation (I.4), we obtain the corresponding relations
\[ f_o(q, p, t) = \left\{ \frac{p}{m} - \frac{\partial U_o}{\partial q} - \frac{\gamma}{m} p + \xi(t) \right\}^T, \]

(V.15)

and
\[ f_a(q, p, t) = \left\{ \frac{\partial U_a}{\partial p} - \frac{\partial U_a}{\partial q} - \gamma \frac{\partial U_a}{\partial p} \right\}^T. \]

(V.16)

In the one-dimensional underdamped Brownian particle system, the nonequilibrium constraint (16) can be simplified to the form
\[
\mathcal{G}_s \approx \sum_m W'(q_m, t)e^{-\beta U_0(q_m, \lambda)} \sqrt{\frac{2\pi}{\beta \Lambda(q_m, \lambda)}},
\]

(V.17)

with
\[
W'(q,t) = \frac{1}{\beta^2} \left\langle \left( \frac{\partial f_q}{\partial q} \right)^2 \right\rangle_p + \frac{1}{\beta^2} \left\langle \left( \frac{\partial f_p}{\partial p} \right)^2 \right\rangle_p + \frac{2}{\beta^2} \left\langle \frac{\partial f_p}{\partial q} \frac{\partial f_q}{\partial p} \right\rangle_p + \frac{1}{\beta} \left\langle \frac{\partial^2 U_o}{\partial q^2} f_q^2 \right\rangle_p + \frac{1}{\beta} \left\langle f_p^2 \right\rangle_p + \frac{2}{\beta} \left\langle f_q \frac{\partial^2 U_o}{\partial q \partial t} \right\rangle_p.
\]

(V.18)
Here $(\cdots)_p \equiv \int_{-\infty}^{+\infty} \cdots e^{-\beta p^2/2} dp$ represents the integral in the momentum space. It can be calculated directly without using the saddle-point approximation. $f \equiv \{f_q\ f_p\}^T$ denotes an approximation to $f^a \equiv \{f_q^a\ f_p^a\}^T$. According to the trial form (18), we assume that the auxiliary potential takes the form

$$U_a(q, p, t) = \dot{\lambda}(t) [b_0^*(t)qp + b_0^*(t)p + b_4^*(t)q^4 + b_5^*(t)q^3 + b_7^*(t)q^2 + b_1^*(t)q],$$  
(V.19)

where $b_1^*(t), b_2^*(t), b_3^*(t), b_4^*(t), b_5^*(t), b_6^*(t)$, and $b_7^*(t)$ are undetermined parameters. Therefore, the approximate auxiliary field should take the form

$$f = \left\{ \dot{\lambda}(b_0q + b_3) - \dot{\lambda}[b_0(p + \gamma q) + \gamma b_5 + 4b_4q^3 + 3b_3q^2 + 2b_2q + b_1] \right\}^T,$$  
(V.20)

with $b_1(t), b_2(t), b_3(t), b_4(t), b_5(t), b_6(t)$ being approximations to the corresponding parameters $b_1^*(t), b_2^*(t), b_3^*(t), b_4^*(t), b_5^*(t), b_7^*(t)$, and $b_6^*(t)$. Substituting the form (V.20) into the nonequilibrium constraint (V.17) and then minimizing it over the parameters, we can derive that the best possible auxiliary potential follows

$$U_a(q, p, t) = \dot{\lambda} \left( \frac{\beta \lambda}{2\beta \lambda^2 + 3k}qp + b_4^*q^4 + b_5^*q^3 \right),$$  
(V.21)

where the undetermined parameters $b_5^*$ and $b_4^*$ should satisfy the relation

$$b_5^* + \frac{\lambda}{k} b_4^* = -\frac{\gamma \beta \lambda}{4\beta \lambda^2 + 6k}.$$  
(V.22)

So far the parameters $b_2^*$ and $b_4^*$ are still undetermined. In addition, let us recall that the overdamped auxiliary potential (V.13) fails when $\lambda \to 0$. Comparing Eq. (V.21) with Eq. (V.13), we find that both problems can be reconciled if assuming that the auxiliary potential takes the form

$$U_a(q, p, t) = \frac{\beta \dot{\lambda}}{8\beta \lambda^2 + 12k} \left( 4\lambda qp + \gamma kq^4 - 3\gamma \lambda q^2 \right),$$  
(V.23)

in the underdamped situation and

$$U_a(q, t) = \frac{\gamma \beta \dot{\lambda}}{8\beta \lambda^2 + 12k} \left( kq^4 - 3\lambda q^2 \right),$$  
(V.24)

in the overdamped situation. In this way, the parameters in Eq. (V.21) take the forms $b_2^* = -3\gamma \beta \lambda/(8\beta \lambda^2 + 12k)$ and $b_4^* = \gamma \beta k/(8\beta \lambda^2 + 12k)$, which can be verified to satisfy the relation (V.22). Besides, the denominator in Eq. (V.13) is amended to avoid divergence of the auxiliary potential in the limit $\lambda \to 0$. Note that Eq. (V.23) will reduce to Eq. (V.24) in the overdamped limit $m/\gamma \to 0$, which can support our assumptions about the form of the auxiliary potentials (V.23) and (V.24).
VI. ESTIMATING THE FREE ENERGY DIFFERENCE BY USING NONEQUILIBRIUM WORK RELATIONS

Consider a Brownian particle driven by the potential $U_o(x, \lambda(t))$ within the time interval $[0, \tau]$. The work performed on the system along an individual stochastic trajectory can be written as [10, 11]

$$w_o \equiv \int_0^\tau \frac{\partial U_o(x, t)}{\partial t} dt.$$  \hspace{1cm} (VI.1)

When the controlling parameter $\lambda(t)$ changes slowly, the free energy difference can be estimated by using the mean work

$$\langle w_o \rangle = \int_0^\tau \left\langle \frac{\partial U_o(x, t)}{\partial t} \right\rangle dt.$$  \hspace{1cm} (VI.2)

The Jarzynski equality provides an exact connection between the free energy difference and the trajectory work [10]:

$$\Delta F_o = -\beta^{-1} \ln \langle e^{-\beta w_o} \rangle,$$  \hspace{1cm} (VI.3)

which can estimate the free energy difference for a system that is initially in equilibrium state and then driven away by varying the controlling parameter $\lambda(t)$ in finite rate.

When we adopt shortcuts to isothermality, an auxiliary potential $U_a(x, t)$ is introduced to the original Hamiltonian. There are two different definitions of the stochastic work in this situation [12]. We choose to follow the thermodynamic interpretation of the Langevin dynamics [11] and take the definition

$$w_t \equiv \int_0^\tau \left( \frac{\partial U_o(x, t)}{\partial t} + \frac{\partial U_a(x, t)}{\partial t} \right) dt.$$  \hspace{1cm} (VI.4)

Then, the mean work takes the form

$$\langle w_t \rangle = \int_0^\tau \left( \left\langle \frac{\partial U_o(x, t)}{\partial t} \right\rangle + \left\langle \frac{\partial U_a(x, t)}{\partial t} \right\rangle \right) dt.$$  \hspace{1cm} (VI.5)

It was shown that the Jarzynski equality still holds when we consider shortcuts to isothermality [12], which leads to

$$\Delta F_t = -\beta^{-1} \ln \langle e^{-\beta w_t} \rangle.$$  \hspace{1cm} (VI.6)

With the adoption of shortcuts to isothermality, we can prove another nonequilibrium work relation [3]:

$$\Delta F = \langle w_t \rangle \equiv \int_0^\tau \left\langle \frac{\partial U_o(x, t)}{\partial t} \right\rangle dt,$$  \hspace{1cm} (VI.7)

which connects the free energy difference with the intrinsic work.
VII. DETAILS OF THE SIMULATION

We simulate an underdamped Brownian particle moving in the double-well potential (V.1) and add the auxiliary potential (V.23) to approximately realize shortcuts to isothermality. The motion of the Brownian particle is governed by the modified Langevin equation (V.14). There are two characteristic times \( \tau_p \equiv m/\gamma \) and \( \tau_q \equiv \gamma/\sqrt{k_B T} \) in the system. Through introducing the characteristic length \( l_c \equiv (k_B T/k) \) \( 1/4 \), we can reduce the coordinate \( \tilde{q} \equiv q/l_c \), the momentum \( \tilde{p} \equiv p\tau/ml_c \), the time \( s \equiv t/\tau \), and the driving protocol \( \tilde{\lambda} \equiv \lambda/(kl_c^2) \). The modified Langevin equation (V.14) can be transformed into the dimensionless form:

\[
\begin{align*}
\tilde{q}' &= \tilde{p} + \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{p}}, \\
\tilde{p}' &= -\alpha \tau^2 \frac{\partial \tilde{U}_o}{\partial \tilde{q}} - \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{q}} - \tau \left( \tilde{p} + \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{p}} \right) + \tau \sqrt{2\alpha \tau} \zeta(s),
\end{align*}
\] (VII.1)

where \( \tilde{\tau} \equiv \tau/\tau_p \) and \( \alpha \equiv \tau_p/\tau_q \). The prime on a variable represents the derivative of that variable with respect to the time \( s \). \( \zeta(s) \) represents Gaussian white noise that satisfies \( \langle \zeta(s) \rangle = 0 \) and \( \langle \zeta(s_1)\zeta(s_2) \rangle = \delta(s_1 - s_2) \). The dimensionless form of the auxiliary potential takes

\[
\tilde{U}_a(\tilde{q}, \tilde{p}, s) = \frac{\tilde{\lambda}}{\alpha \tau^2 (8\lambda^2 + 12)} (4\tilde{\lambda}\tilde{q}\tilde{p} + \tilde{\tau} \tilde{q}^4 - 3\tilde{\tau}\lambda^2). \quad (VII.2)
\]

Equation (VII.2) is solved by using the Euler algorithm

\[
\begin{align*}
\tilde{q}(s + \delta s) &= \tilde{q}(s) + \tilde{p}\delta s + \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{p}} \delta s, \\
\tilde{p}(s + \delta s) &= \tilde{p}(s) - \alpha \tau^2 \frac{\partial \tilde{U}_o}{\partial \tilde{q}} \delta s - \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{q}} \delta s - \tau \left( \tilde{p} + \alpha \tau^2 \frac{\partial \tilde{U}_a}{\partial \tilde{p}} \right) \delta s + \tau \sqrt{2\alpha \tau} \delta s \theta(s) \quad (VII.3)
\end{align*}
\]

where \( \delta s \) is the time step and \( \theta(s) \) is a random number sampled from Gaussian distribution with zero mean and unit variance.

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