Optimal Finite-Time Processes In Stochastic Thermodynamics

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For a small system like a colloidal particle or a single biomolecule embedded in a heat bath, the optimal protocol of an external control parameter minimizes the mean work required to drive the system from one given equilibrium state to another in a finite time. In general, this optimal protocol obeys an integro-differential equation. Explicit solutions both for a moving laser trap and a time-dependent strength of such a trap show finite jumps of the optimal protocol to be typical both at the beginning and at the end of the process.

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Introduction.—The concepts of classical thermodynamics like applied work and exchanged heat can be applied to soft and biomatter systems as the study of the driven dynamics of single colloidal particles and of single biomolecules has shown [1]. Since thermal fluctuations contribute substantially, work and heat acquire a stochastic contribution and must be described by probability distributions. Exact results constraining such distributions like the Jarzynski relation [2] and various generalizations thereof have been derived theoretically [3–7] and tested experimentally [8–12]. Typically, these exact relations hold for any time-dependent driving described by an external control parameter $\lambda(\tau)$.

In this Letter, we ask for the optimal protocol $\lambda^*(\tau)$ that minimizes the mean work required to drive such a system from one equilibrium state to another in a *finite* time t. The emphasis on a finite time is crucial since for infinite time, the work spent in any quasistatic process is equal to the free energy difference of the two states. For finite time, the mean work is larger and will depend on the protocol $\lambda(\tau)$. Knowing the optimal protocol $\lambda^*(\tau)$ could *inter alia* improve the extraction of free energy differences from finite-time path sampling both in various numerical schemes [13–20] and in experimental studies [21,22]. Quite generally, the smaller the mean work is, the better the statistics for free energy estimates becomes [17,23]. *A priori*, one might expect the optimal protocol connecting the given initial and final values to be smooth as it was found recently in a case study within the linear response regime [24]. In contrast, as our main result, we find here for genuine finite-time driving that the optimal protocol involves discontinuities both at the beginning and at the end of the process.

For macroscopic systems, optimal processes have been investigated under the label of finite-time thermodynamics for quite some time [25–27]. Indeed, jumps were found there as well [26] despite the significant differences both in the role of heat baths and the equations of motion between macroscopic and stochastic thermodynamics. For the former, heat reservoirs of different temperature are typically involved in a search for optimal adaptions of, e.g., Carnot-like machines to finite-time cycles. In our context, the system always remains in contact with a single heat bath of constant temperature T. Moreover, this heat bath provides thermal fluctuations which require a stochastic formulation in contrast to the deterministic description in macroscopic finite-time thermodynamics.

The model.—Paradigmatically, a Langevin equation describes the driven overdamped motion of a single degree of freedom with coordinate x in a time-dependent one-dimensional potential $V(x, \lambda(\tau))$ as

$$\dot{x} = -\mu \frac{\partial V(x, \lambda)}{\partial x} + \zeta. \tag{1}$$

Here, μ is the mobility, and time derivatives are denoted by a dot throughout the Letter. The thermal fluctuations are modeled as Gaussian white noise

$$\langle \zeta(\tau)\zeta(\tau')\rangle = 2\mu k_B T \delta(\tau - \tau'), \tag{2}$$

with k_B as Boltzmann's constant. The time evolution of the probability distribution $p(x, \tau)$ to observe the particle at position x at time τ is then governed by the Fokker-Planck equation

$$\partial_\tau p(x, \tau) = \partial_x \left[\mu \frac{\partial V}{\partial x} + \mu k_B T \partial_x \right] p(x, \tau). \tag{3}$$

Initially, the system is in thermal equilibrium in the potential $V(x, \lambda_i)$. During the time-interval $0 \le \tau \le t$, the control parameter $\lambda(\tau)$ is varied from λ_i to the final value λ_f. The mean work spent in this process

$$W[\lambda(\tau)] = \int_0^t d\tau \dot{\lambda} \left\langle \frac{\partial V}{\partial \lambda}(x(\tau), \lambda(\tau)) \right\rangle \tag{4}$$

becomes a functional of the protocol $[\lambda(\tau)]$ where the average $\langle \ldots \rangle$ is over the initial thermal distribution and over the noise history. For notational simplicity, we set $k_B T = \mu = 1$ in the following by choosing natural units for energies and times. We will first investigate two case studies motivated by previously set-up experiments on colloidal particles and then analyze the general case.

Case study I: Moving laser trap.—As an almost trivial, but still instructive introductory example, we consider a colloidal particle dragged through a viscous fluid by an optical tweezer with harmonic potential

$$V(x,\tau) = (x - \lambda(\tau))^2/2. \tag{5}$$

The focus of the optical tweezer is moved according to a protocol $\lambda(\tau)$. In previous experiments, such protocols have been used to test the fluctuation theorem [8] and the Hatano-Sasa relation [10]. The optimal protocol $\lambda^*(\tau)$ connecting given boundary values $\lambda_i = 0$ and λ_f in a time t minimizes the mean total work (4) which we express as a functional of the mean position of the particle $u(\tau) \equiv \langle x(\tau)\rangle$ as

$$W[\lambda(\tau)] = \int_0^t d\tau \dot{\lambda}(\lambda - u) = \int_0^t d\tau(\dot{u} + \ddot{u})\dot{u} = \int_0^t d\tau \dot{u}^2 + [\dot{u}^2]_0^t/2. \tag{6}$$

Here, we have used

$$\dot{u} = (\lambda - u) \tag{7}$$

which follows from averaging the Langevin equation.

The Euler-Lagrange equation corresponding to (6), $\ddot{u} = 0$, is solved by $u(\tau) = m\tau$, where $u(0) = 0$ is enforced by the initial condition. Equation (7) then requires the boundary conditions $\dot{u}(0) = \lambda_i - u(0) = 0$ and $\dot{u}(t) = \lambda_f - mt$ which can only be met by discontinuities in $\dot{u}$ at the boundaries which correspond to jumps in λ. Note that these ''kinks'' do not contribute to the integral in the second line of Eq. (6). The yet unknown parameter m follows from minimizing the mean total work

$$W = m^2 t + (\lambda_f - mt)^2/2 \tag{8}$$

which yields $m^* = \lambda_f/(t+2)$. The minimal mean work $W^* = \lambda_f^2/(t+2)$ vanishes in the quasistatic limit $t \to \infty$. The optimal protocol then follows from Eq. (7) as

$$\lambda^*(\tau) = \lambda_f(\tau + 1)/(t+2), \tag{9}$$

for $0 < \tau < t$. As a surprising result, this optimal protocol implies two distinct symmetrical jumps of size

$$\Delta\lambda \equiv \lambda(0^+) - \lambda_i = \lambda_f - \lambda(t^-) = \lambda_f/(t+2) \tag{10}$$

at the beginning and end of the process.

A priori, one might have expected a continuous linear protocol $\lambda^{\rm lin}(\tau) = \lambda_f\tau/t$ to yield the lowest work but the explicit calculation shows that

$$W^{\rm lin} = (\lambda_f/t)^2(t + e^{-t} - 1) > W^* \tag{11}$$

for any $t > 0$, with a maximal value $W^{\rm lin}/W^* \simeq 1.14$ at $t \simeq 2.69$.

In macroscopic finite-time thermodynamics, the occurrence of such jumps has previously been rationalized by pointing out the special nature of this type of variational problem where the highest derivative (here $\ddot{u}$ in Eq. (6)) occurs linearly [26]. In the present model where fluctuations are irrelevant to the mean work, these jumps have the same formal origin.

Case study II: Time-dependent strength of the trap.—In this example, fluctuations are crucial. We consider the motion of a colloidal particle in a trap whose strength becomes time dependent whereas its position remains constant. The corresponding potential reads

$$V(x,\tau) = \lambda(\tau)x^2/2 \tag{12}$$

with $\lambda(0) = \lambda_i$ and $\lambda(t) = \lambda_f > \lambda_i$ as boundary conditions. Such a potential with a sudden jump protocol has been investigated experimentally as a test of the fluctuation theorem [9]. We first derive the equation of motion for the variance $w(\tau) \equiv \langle x^2(\tau)\rangle$

$$\dot{w} = -2\lambda w + 2 \tag{13}$$

by multiplying Eq. (3) with x^2 and integrating over x. The mean work (4) can then again be cast in a local functional of the new variable w and its first derivative by solving (13) for $\dot{\lambda}$

$$W[\lambda(\tau)] = \int_0^t d\tau \dot{\lambda}\frac{w}{2} = \frac{1}{2}[\lambda w - \ln w]_0^t + \frac{1}{4}\int_0^t d\tau \frac{\dot{w}^2}{w}. \tag{14}$$

The minimization of the work functional then requires solving the Euler-Lagrange equation

$$\dot{w}^2 - 2w\ddot{w} = 0. \tag{15}$$

Its general solution

$$w(\tau) = c_1(1 + c_2\tau)^2 \tag{16}$$

contains two constants. The thermal initial distribution $w(0) = 1/\lambda_i$ fixes $c_1 = 1/\lambda_i$. The second constant c_2 follows from minimizing the total mean work

$$W = \frac{(c_2 t)^2}{\lambda_i t} - \ln(1 + c_2 t) + \frac{1}{2}(\lambda_f/\lambda_i)(1 + c_2 t)^2 - \frac{1}{2} \tag{17}$$

which leads to

$$c_2^* t = \frac{-1 - \lambda_f t + \sqrt{1 + 2\lambda_i t + \lambda_f\lambda_i t^2}}{2 + \lambda_f t}. \tag{18}$$

The optimal protocol derived from Eq. (13)

$$\lambda^*(\tau) = \frac{\lambda_i - c_2^*(1 + c_2^*\tau)}{(1 + c_2^*\tau)^2} \tag{19}$$

for $0 < \tau < t$ again implies jumps at the beginning and end of the process as shown in Fig. 1(a). Both the minimal work W^*, see Fig. 1(b), and the scaled optimal protocol $\lambda^*(\tau/t)/\lambda_i$ depend only on two parameters (λ_f/λ_i) and $\lambda_i t$.

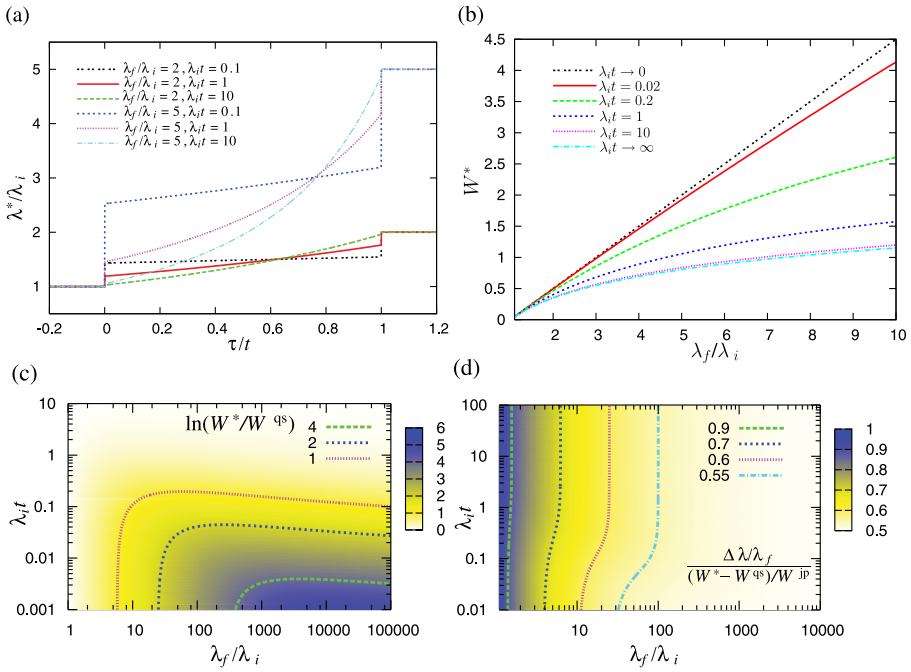

FIG. 1 (color online). Optimization results for a time-dependent strength $\lambda(\tau)$ of a laser trap for different values of (λ_f/λ_i) and $\lambda_i t$ (case study II): (a) Optimal protocols λ^*/λ_i as a function of the scaled time τ/t. (b) Minimal work W^*. (c) Logarithmic fraction $\ln(W^*/W^{qs})$ of the optimal work and the quasistatic work. (d) Relative height $\Delta\lambda/\lambda_f$ of the jump of the optimal protocol at $\tau = 0$ in units of $(W^* - W^{qs})/W^{jp}$.

For the two limiting cases of an immediate jump, $t \to 0$, and a quasistatic process, $t \to \infty$, respectively, the values of W^* also follow from general principles. For an immediate jump, the minimal work

$$W^{jp} \equiv \lim_{t\to 0} W^* = \left\langle \frac{(\lambda_f - \lambda_i)x^2}{2} \right\rangle_{\lambda_i} = \frac{1}{2}((\lambda_f/\lambda_i) - 1) \quad (20)$$

is equal to the difference in energy evaluated in the thermal initial ensemble. In this limit, the optimal protocol $\lambda^*(\tau)/\lambda_i \approx ((\lambda_f/\lambda_i) + 1)/2$ is constant for $0 < \tau < t$ but has discontinuities at $\tau = 0$ and $\tau = t$. In the quasistatic limit, the minimal work

$$W^{qs} \equiv \lim_{t\to\infty} W^* = \frac{1}{2}\ln(\lambda_f/\lambda_i) = \Delta F \quad (21)$$

is equal to the free energy difference ΔF between the final and the initial state. In this limit, the optimal protocol is continuous at $\tau = 0$ and $\tau = t$ and takes the form

$$\lambda^*(\tau/t) \approx \frac{\lambda_i}{(1 - (\tau/t) + \sqrt{(\lambda_i/\lambda_f)}(\tau/t))^2}. \quad (22)$$

For $(\lambda_f/\lambda_i) \gg 1$, the minimal work is of the order of the quasistatic work for any $\lambda_i t^* \gg 2/\ln(\lambda_f/\lambda_i)$ as a simple analysis of Eqs. (17) and (18) shows. Thus, the larger the change of the control parameter λ, the smaller is the time interval required to essentially reach the quasistatic work, as quantitatively shown in Fig. 1(c). The origin of this surprising features lies in the fact that the relaxation time scales like $1/\lambda$. For large λ, the particle can follow a larger change of the control parameter almost quasistatically. Therefore, the optimal protocol can become quite steep towards the end of the process for large λ_f.

General case.—For a general nonharmonic potential, it is not possible to express the mean work as a local functional of just one variable as we have done for the two harmonic cases. Rather, our optimization problem becomes nonlocal in time since changing the protocol at a time τ affects the mean work increments for all later times $\tau' > \tau$. This fact becomes obvious by expressing the mean work as a path integral average

$$W[\lambda(\tau)] = \int d[x(\tau)]p[x(\tau)] \int_0^t d\tau \dot{\lambda} \frac{\partial V}{\partial \lambda} \quad (23)$$

over all possible trajectories $x(\tau)$ with weight

$$p[x(\tau)] = \mathcal{N} p(x, 0) \exp\left[- \int_0^t d\tau \left(\frac{(\dot{x} + \partial_x V)^2}{4} - \frac{\partial_x^2 V}{2} \right) \right], \quad (24)$$

where $\mathcal{N}$ is a normalization constant. Minimizing the mean work (4) then requires solving the nonlocal Euler-Lagrange equation

$$\frac{d}{d\tau} \left\langle \frac{\partial V}{\partial \lambda} \right\rangle_{|\tau=\sigma} = \frac{\delta W[\lambda(\tau)]}{\delta \lambda(\sigma)} \quad (25)$$

where the right hand side can be expressed by correlation functions as

$$\frac{d}{d\tau} \left\langle \frac{\partial V}{\partial \lambda} \right\rangle_{|\tau=\sigma} = \dot{\lambda} \left\langle \frac{\partial^2 V}{\partial \lambda^2} \right\rangle_{|\tau=\sigma} + \int_\sigma^t d\tau \frac{\dot{\lambda}}{2} \left\langle \left(\frac{\partial^3 V}{\partial \lambda \partial^2 x} - (\dot{x} + \partial_x V) \frac{\partial^2 V}{\partial \lambda \partial x} \right)_{|\tau=\sigma} \cdot \left(\frac{\partial V}{\partial \lambda} \right)_{|x(\tau)} \right\rangle. \quad (26)$$

In general, this integro-differential equation solved by the optimal protocol $\lambda^*(\tau)$ looks rather inaccessible. Exploring a variational ansatz for $\lambda^*(\tau)$ allowing for jumps with numerical evaluation of the mean work seems possible but may still be a formidable task to be explored in future work.

In order to use jumps in the protocol $\lambda(\tau)$ for the efficient extraction of free energy differences from finite-time path sampling via the Jarzynski relation, one needs an estimate for the height of these jumps without knowing the underlying potential. For the moving laser trap (case study I), we get the relation $\Delta\lambda/\lambda_f = 2(W^* - W^{\mathrm{qs}})/W^{\mathrm{jp}}$. For case study II, we find numerically that the relative height of the jump $\Delta\lambda/\lambda_f$ at $\tau = 0$ is also of the order of $(W^* - W^{\mathrm{qs}})/W^{\mathrm{jp}}$, see Fig. 1(d). If such a relation gave the correct order of magnitude for the optimal jump in general cases, it could become a helpful tool for estimating the optimal jump heights. For experimentally determining the optimal protocol for an unknown potential, we envisage an adaptive procedure in which trial protocols (including estimated trial jumps) are successively improved in an iterative fashion guided by the monitored work values.

Concluding perspectives.—As a main qualitative result, our analysis of two simple but experimentally realizable model cases has revealed that the optimal protocol minimizing the mean work required to drive the system from one equilibrium state to another involves jumps of the external control parameter both at the beginning and at the end of the finite-time process. We expect such jumps to be a generic feature of the optimal protocol for arbitrary potentials. Even though we have investigated only a single degree of freedom, the extension to many coupled degrees of freedom involves only minor notational complexity but poses no further conceptual challenge.

We have focused on optimal protocols connecting two different equilibrium states. An optimal protocol for transitions in finite time between two different nonequilibrium stationary states could be investigated along similar lines in the context of steady-state thermodynamics [4]. Likewise, one can ask for the optimal protocol of cyclic processes combining mechanical steps with chemical reactions given a finite cycle time. These perspectives to be investigated in future work demonstrate that the optimization problem introduced here for stochastic thermodynamics has not only a broad fundamental significance. Its ramifications could ultimately also lead to the construction of ''optimal'' nanomachines. Finally, it is tempting to speculate which, if any, biological processes on the cellular and subcellular level have been optimized during evolution for their finite-time performance in the noisy cellular environment.

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