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. Explicite 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 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, 4, 5, 6, 7] and tested experimentally [8, 9, 10, 11, 12, 13]. Typically, these exact relations hold for any time-dependent driving described by an external control parameter \( \lambda (\tau) \).

In this paper, 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 quasi-static 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, 14, 15, 10, 11, 12, 13] 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 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, 26, 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 adaption 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 co-ordinate \( x \) 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, \( \mu \) is the mobility and time-derivatives are denoted by a dot throughout the paper. The thermal fluctuations are modelled as Gaussian white noise \( \langle \zeta(\tau)\zeta(\tau') \rangle = 2\mu k_B T \delta(\tau - \tau') \), 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 \( \tau \) is then governed by the Fokker-Planck equation

\[
\partial_\tau p(x, \tau) = \partial_x \left[ \mu \frac{\partial V}{\partial x} + \mu k_B T \partial_x \right] p(x, \tau). \tag{2}
\]

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

\[
W[\lambda(\tau)] = \int_0^t d\tau \lambda \left\langle \frac{\partial V}{\partial \lambda}(x(\tau), \lambda(\tau)) \right\rangle \tag{3}
\]

becomes a functional of the protocol \( [\lambda(\tau)] \) where the average \( \langle ... \rangle \) 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

\[
V(x, \tau) = (x - \lambda(\tau))^2 / 2. \tag{4}
\]
The optimal protocol then follows from eq. (6) as
\[ W = \int_0^t d\tau \lambda (u + \dot{u}) \]
for any \( W \), which follows from averaging the Langevin equation.

Here, we have used
\[ \dot{u} = (\lambda - u) \]
(6)
which follows from averaging the Langevin equation.

The Euler-Lagrange equation corresponding to (5), \[ \dot{\lambda} = \lambda (\dot{u} + \ddot{u}) \]
for the variance \( u(\tau) \equiv \langle x(\tau) \rangle \) as
\[ W[\lambda(\tau)] = \int_0^t d\tau \lambda (u + \ddot{u}) = \int_0^t d\tau (\dot{u} + \ddot{u}) \dot{u} \]
\[ = \int_0^t d\tau \dot{u}^2 + [\dddot{u}]_0^t / 2. \]
(5)
The optimal protocol derived from eq. (12)
\[ W[\lambda(\tau)] = \int_0^t d\tau \lambda w(\tau) = \frac{1}{2} [\lambda w - \ln w]_0^t + \frac{1}{4} \int_0^t d\tau \dot{w}^2 \]
(13)
by multiplying eq. (2) with \( x^2 \) and integrating over \( x \).

The mean work \( \lambda \) can then again be cast in a local functional of the new variable \( w \) and its first derivative by solving (12) for \( \lambda \)
\[ W[\lambda(\tau)] = \int_0^t d\tau \lambda w(\tau) = \frac{1}{2} [\lambda w - \ln w]_0^t + \frac{1}{4} \int_0^t d\tau \dot{w}^2 \]
(13)
its general solution
\[ w(\tau) = c_1 (1 + c_2 \tau)^2 \]
(15)
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
\[ W = \frac{(c_2 t)^2}{\lambda_it} - \ln (1 + c_2 t) + \frac{1}{2} (\lambda_f / \lambda_i) (1 + c_2 t)^2 - \frac{1}{2} \]
which leads to
\[ c_2^2 t = -1 - \lambda_f t + \sqrt{1 + 2 \lambda_f t + \lambda_f \lambda_i t^2} \]
(17)
The optimal protocol derived from eq. (12)
\[ \lambda^*(\tau) = \frac{\lambda_i - c_2^2 (1 + c_2^2 \tau)}{(1 + c_2^2 \tau)} \]
(18)
for \( 0 < \tau < t \) again implies jumps at the beginning and end of the process as shown in Fig. 1. Both the minimal work \( W^* \), see Fig. 1, and the scaled optimal protocol \( \lambda^*(\tau)/\lambda_i \) depend only on two parameters \( (\lambda_f / \lambda_i) \) and \( \lambda_f t \).

For the two limiting cases of an immediate jump, \( t \to 0 \), and a quasi-static process, \( t \to \infty \), respectively, the values of \( W^* \) also follow from general principles. For an immediate jump, the minimal work
\[ W_{im} \equiv \lim_{t \to 0} W^* = \frac{\lambda_i - \lambda_f \lambda_i}{2 \lambda_f} \]
(19)
The origin of this surprising features lies in the fact that the relaxation time scales like $1/\lambda$. For large $\lambda$, the particle can follow a larger change of the control parameter almost quasi-statically. Therefore, the optimal protocol can become quite steep towards the end of the process for large $\lambda_f$.

**General case.** For a general non-harmonic 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 non-local in time since changing the protocol at $t > \tau'$ 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

$$W[\lambda(\tau)] = \int dx(x) p[x(\tau)] \int_0^\tau d\tau' \partial \lambda \left[ \frac{\partial V}{\partial \lambda} \right] .$$

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

$$p[x(\tau)] = N p(x, 0) \exp \left[ -\int_0^\tau d\tau \left( \frac{\dot{x} + \partial_\lambda V}{4} - \frac{\partial_\lambda^2 V}{2} \right) \right] ,$$
where $\mathcal{N}$ is a normalization constant. Minimizing the mean work requires solving the non-local Euler-Lagrange equation

$$\frac{d}{d\tau} \left( \frac{\partial V}{\partial \lambda} \right)_{\tau=\sigma} = \frac{\delta W[\lambda(\tau)]}{\delta \lambda(\sigma)}$$

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

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

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 $\Delta \lambda/\lambda_f = 2(W^* - W^0)/W^{jp}$.

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 non-equilibrium stationary states could be investigated along similar lines in the context of steady-state thermodynamics. 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” nano-machines. Finally, it is tempting to speculate which, if any, biological processes can become a helpful tool for estimating free energy differences from finite-time processes on the cellular and subcellular level have been optimized during evolution for their finite-time performance in the noisy cellular environment.