

Dynamical generalization of nonequilibrium work relation

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The evolution of systems in contact with thermal, chaotic, or turbulent surroundings—often modeled with stochastic equations of motion—can be particularly complex when these equations of motion are nonautonomous, that is, when external parameters of the surroundings are varied with time. In this paper we establish a rigorous equality relating the nonautonomous behavior of such a system, to solutions of the corresponding autonomous equations of motion, for arbitrary initial conditions. If the system is initially in thermal equilibrium, we recover previously known results relating nonequilibrium work values to equilibrium probability distributions. We discuss specific examples of our result, and suggest an experimental setting in which it might be verified.

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Consider a system that is coupled to both a heat bath at temperature $T = \beta^{-1}$, and an externally controlled work parameter μ , and imagine that we subject this system to a process during which the work parameter is varied in time. For such a process the following equality holds [Ref. [1], Eq. (18)]:

$$\langle \delta[x(t) - x] \exp[-\beta w(t)] \rangle = \frac{1}{Z_0} \exp[-\beta H(\mu(t), x)], \quad (1)$$

where $w(t) \equiv \int_0^t dt' \dot{\mu}(t') \partial_{\mu} H(\mu(t'), x(t'))$ is the work performed on the system, up to time t , by the variation of the parameter μ . Here $H(\mu, x)$ is the microscopic Hamiltonian for the system of interest, expressed as a function of the system's microstate x and the work parameter μ ; $\mu(t')$ specifies the externally imposed schedule for varying this parameter (and $\dot{\mu} = d\mu/dt'$); and $x(t')$ gives the microscopic evolution of the system during a single realization of this process. The angular brackets denote an average over all possible trajectories $x(t')$ —equivalently, an average over realizations of the thermal noise generated by the heat bath—and the independent variable x appearing on both sides of the equation is an arbitrary point in the phase space of the system. Finally, $Z_0 = \int dx \exp[-\beta H(\mu(0), x)]$ is the partition function for the equilibrium state associated with the initial value of the work parameter. In Ref. [1] it was assumed that (a) the noise driving the system is thermal in origin, generated by a heat bath at equilibrium, and (b) at the initial time $t' = 0$ the system is in equilibrium with the bath, and therefore described statistically by the Boltzmann-Gibbs distribution.

The left side of Eq. (1) is a *weighted distribution function* (WDF), which is analogous to an ordinary *probability distribution function* (PDF), except that each realization in the ensemble carries a time-dependent statistical weight, $\exp[-\beta w(t)]$. (If we picture the ensemble of realizations as a swarm of particles evolving in x space, and imagine that each particle has a time-dependent “mass” $\exp[-\beta w(t)]$, then the WDF is analogous to a mass density, whereas the PDF is like a number density [1].) Equation (1) tells us that the WDF evolves in a very simple manner: apart from normalization, it

is identical to the equilibrium distribution corresponding to the current value of the work parameter [right side of Eq. (1)]. This remains true even if μ is varied rapidly and violently, so that the system gets driven substantially out of equilibrium during a typical realization of the process. Hummer and Szabo [2] have drawn attention to a close connection between Eq. (1) and the Feynman-Kac theorem.

By integrating both sides of Eq. (1) with respect to x , one arrives at an equality relating nonequilibrium work values and equilibrium free energy differences [1–6]. These results are closely related to a class of *fluctuation theorems* for entropy production, which can be formulated either for nonequilibrium steady states [7–12], or for systems driven away from an initial state of equilibrium [13–16]. Moreover, it has been shown [16–19] that the results of Refs. [1–6] can be generalized to apply to situations in which the thermal bath is replaced by another source of noise, such as a stochastic bath that drives the system to a nonequilibrium steady state (when μ is held fixed), or a chaotic or turbulent bath [20]. In recent years, a number of optical micromanipulation experiments have provided confirmation of a number of these theoretical predictions [21–25].

Equation (1) establishes a relationship between the behavior of the system when the parameter μ is varied with time [on the left-hand side (lhs)] and the equilibrium distribution at fixed μ [on the right-hand side (rhs)]. In effect, this result asserts that equilibrium information is encoded in the nonequilibrium dynamics of the system. The quantity $\exp[-\beta w(t)]$ provides the key to decoding this information; by endowing each nonequilibrium realization with a statistical weight $\exp[-\beta w(t)]$, we recover the equilibrium distribution. More formally, Eq. (1) relates the *nonautonomous* evolution of the system, to stationary solutions of corresponding *autonomous* equations of motion [26], provided the system begins in a stationary state.

It is natural to wonder whether Eq. (1) can be generalized by relaxing either or both of the two conditions mentioned above. The investigations initiated by Hatano and Sasa's research [16–19] represent a relaxation of condition (a). In this Rapid Communication we relax condition (b), and show that

Eq. (1) can be generalized to accommodate arbitrary distributions of initial conditions. Our central results then relate the system's nonautonomous evolution [lhs, Eqs. (7) and (9)] to general solutions—e.g., Green functions—of the autonomous evolution [rhs, Eqs. (7) and (9)]. In other words, we establish a link between the evolution of the system when the parameter μ is held fixed, and its response to arbitrary variations of that parameter. As with Eq. (1), the crucial element of this link is a statistical reweighting procedure: by assigning a weight of the form $\exp[-A(t)]$ to each nonautonomous realization, we reconstruct the autonomous evolution.

As in Ref. [1], we assume that the dynamics of our system are described by a Markov process,

$$\dot{x} = \zeta(x, \mu),$$

where $\zeta(x, \mu)$ generally includes both deterministic and stochastic terms, the latter generated by a heat bath or other source of noise. Note that the work parameter μ appears in the equations of motion as a control parameter. We will be interested in a process during which the system evolves in time as μ is varied externally, according to some arbitrary (not necessarily quasistatic) schedule $[\mu] \equiv \{\mu(t'), 0 \leq t' \leq t\}$. Under these assumptions, the probability distribution function (PDF) $P(x, t) = \langle \delta[x - x(t)] \rangle$, describing a statistical ensemble of realizations of this process, evolves under a master equation,

$$\partial_t P = \hat{\mathcal{L}}_{\mu(t)} P,$$

where the transition operator $\hat{\mathcal{L}}_{\mu}$ specifies the parameter-dependent stochastic dynamics.

Let us define the Green function $G(x, t|x^0, [\mu])$ to be the probability of observing the system in microstate x at time t , given an initial microstate x^0 at time 0

$$\partial_t G - \hat{\mathcal{L}}_{\mu(t)} G = \delta(t) \delta(x - x^0).$$

Note the explicit dependence of G on the schedule $[\mu]$. We next introduce an autonomous Green function, \bar{G} (along with a related function $\varphi \equiv -\ln \bar{G}$), describing the evolution of the system when μ is held fixed

$$\bar{G}(x, t|x^0, \mu) = \exp[-\varphi(x, t|x^0, \mu)] = \exp(\hat{\mathcal{L}}_{\mu} t) \delta(x - x^0). \quad (2)$$

Now returning to the general case of an arbitrary schedule $[\mu]$, let us define an observable

$$A(t) \equiv \int_0^t dt' \dot{\mu}(t') \partial_{\mu} \varphi(x(t')|x^0, t'; \mu(t')). \quad (3)$$

We can think of A as an auxiliary variable, analogous to $w(t)$ in Eq. (1), evolving under the equation of motion $\dot{A} = \dot{\mu} \partial_{\mu} \varphi$. (Note that information about the autonomous evolution enters the definition of A , through the function φ .) Now consider a joint Green function $\mathcal{G}(x, A, t|x^0, [\mu])$, which is the probability for reaching a microstate x and a specific value A at time t , given initial conditions $x(0) = x^0$ and $A(0) = 0$. This function satisfies the master equation

$$\partial_t \mathcal{G} - \hat{\mathcal{L}}_{\mu(t)} \mathcal{G} + \dot{\mu} \frac{\partial \varphi}{\partial \mu} \frac{\partial \mathcal{G}}{\partial A} = \delta(t) \delta(A) \delta(x - x^0), \quad (4)$$

where the last term on the left side is simply a continuity term accounting for the evolution of $A(t)$. Let us finally introduce the convolution of $\exp(-A)$ with the joint Green function:

$$\begin{aligned} \mathcal{Q}(x, t|x^0, [\mu]) &\equiv \int dA \exp[-A] \mathcal{G}(x, A, t|x^0, [\mu]) \\ &= \langle \delta(x(t) - x) \exp[-A(t)] \rangle_{x^0}, \end{aligned} \quad (5)$$

where $\langle \cdots \rangle_{x^0}$ indicates an average over realizations launched from initial conditions x^0 . The function \mathcal{Q} that we have constructed is a WDF, in which each realization carries a statistical weight $\exp[-A(t)]$. From Eqs. (4) and (5) we get an evolution equation for \mathcal{Q} after a single integration by parts

$$\partial_t \mathcal{Q} - \hat{\mathcal{L}}_{\mu(t)} \mathcal{Q} + \dot{\mu} \frac{\partial \varphi}{\partial \mu} \mathcal{Q} = \delta(t) \delta(x - x^0). \quad (6)$$

For an arbitrary schedule $[\mu]$ the solution of Eq. (6) is given by $\mathcal{Q} = \exp[-\varphi(x, t|x^0, \mu(t))]$. This can be verified by direct substitution, using the fact that for constant μ the solution of Eq. (6) is given by Eq. (2). We thus finally arrive at

$$\langle \delta(x(t) - x) \exp[-A(t)] \rangle_{x^0} = \bar{G}(x, t|x^0, \mu(t)), \quad (7)$$

with no restrictions on the time dependence of $\mu(t)$.

While Eq. (7) pertains to a δ -function distribution of initial conditions, we can easily generalize this result. Consider a parameter-dependent family of distributions, $\rho(x, \mu)$, and now define \bar{G} and φ by

$$\bar{G}(x, t|[\rho], \mu) = \exp\{-\varphi(x, t|[\rho], \mu)\} = \exp(\hat{\mathcal{L}}_{\mu} t) \rho(x, \mu), \quad (8)$$

analogous to Eq. (2). Then by following exactly the same procedure as led to Eq. (7), we arrive at

$$\langle \delta(x(t) - x) \exp[-A(t)] \rangle_{[\rho]} = \bar{G}(x, t|[\rho], \mu(t)), \quad (9)$$

where $\langle \cdots \rangle_{[\rho]}$ denotes an average over an ensemble of realizations with initial conditions sampled from $\rho[x, \mu(0)]$, and $A(t)$ is defined as in Eq. (3), but with $[\rho]$ rather than x^0 appearing as the argument of $\partial_{\mu} \varphi$. For the special choice $\rho(x, \mu) = \delta(x - x^0)$, we recover Eq. (7). On the other hand, if we take $\rho(x, \mu) = \rho^S(x, \mu)$, where ρ^S is the stationary distribution corresponding to a fixed value of μ (i.e., $\hat{\mathcal{L}}_{\mu} \rho^S = 0$), then we get $\bar{G}(x, t|[\rho], \mu) = \rho^S(x, \mu)$, which is the situation considered in Refs. [1, 2, 14–19].

Equation (7) and its generalization, Eq. (9), constitute the central results of this paper. As mentioned earlier, the left side in each case pertains to nonautonomous equations of motion; the average is defined over trajectories evolving as μ is varied with time. By contrast, the right side pertains to autonomous equations of motion; \bar{G} describes evolution with μ held fixed. Equations (7) and (9) show that, by assigning an evolving weight $\exp[-A(t)]$ to every member of the non-

autonomous ensemble, we recover the autonomous solution.

These results can be generalized further, as follows. Let us refer to $\dot{\mu}\partial_{\mu}\varphi$ as the *generator* of the statistical weight $\exp[-A(t)]$ appearing in Eqs. (7) and (9), i.e., $\dot{\mu}\partial_{\mu}\varphi$ is the quantity whose time integral determines the weight assigned to a trajectory by Eq. (3). Now consider a WDF constructed with a different (as yet unspecified) generator, $\Omega(x, t)$

$$\mathcal{P}(x, t) = \langle \delta[x(t) - x] \exp[-B(t)] \rangle, \quad (10)$$

$$B(t) \equiv B_0 + \int_0^t dt' \Omega[x(t'), t'],$$

where $B_0 = -\ln \int dx \mathcal{P}(x, 0)$ simply allows for an arbitrary initial normalization of \mathcal{P} . Furthermore, suppose we want $\mathcal{P}(x, t)$ to evolve according to the equation

$$\dot{\mathcal{P}}(x, t) = \exp[-\psi(x, t)], \quad (11)$$

for a particular (but arbitrary) function ψ . We now show how we can choose Ω so that Eq. (11) is satisfied. The WDF defined by Eq. (10) evolves according to

$$\frac{\partial \mathcal{P}}{\partial t} = (\hat{\mathcal{L}}_{\mu} - \Omega)\mathcal{P}. \quad (12)$$

[This result can be obtained by following the steps that led to Eq. (6).] Since we want Eq. (11) to solve this equation, we replace \mathcal{P} with $\exp(-\psi)$ in Eq. (12), then rearrange terms to get

$$\Omega(x, t) = \frac{\partial \psi}{\partial t} + e^{\psi} \hat{\mathcal{L}}_{\mu} e^{-\psi}. \quad (13)$$

This result gives a prescription for choosing a generator $\Omega(x, t)$, such that the corresponding WDF [given by Eq. (10)] has the desired time dependence, $\mathcal{P} = \exp(-\psi)$, Eq. (11).

It is easy to reproduce Eqs. (7) and (9) within the framework of the previous paragraph. For instance, if we choose $\psi(x, t) = \varphi[x, t | x^0, \mu(t)]$ then Eq. (13) becomes

$$\Omega = \frac{\partial \varphi}{\partial t} + \dot{\mu} \frac{\partial \varphi}{\partial \mu} + e^{\varphi} \hat{\mathcal{L}}_{\mu} e^{-\varphi} = \dot{\mu} \frac{\partial \varphi}{\partial \mu}, \quad (14)$$

which leads immediately [via Eq. (10)] to Eq. (7). Similarly the choice $\psi(x, t) = \varphi(x, t | [\rho], \mu(t))$ leads to Eq. (9). We now briefly discuss two further examples within this framework, which lead to generalizations of Eq. (1).

Example 1. Given a Hamiltonian $H(\mu, x)$, Markovian dynamics $\hat{\mathcal{L}}_{\mu}$, and a particular schedule $[\mu]$ for varying the work parameter, suppose we want to construct a WDF that evolves as an unnormalized Boltzmann-Gibbs distribution, $\mathcal{P}(x, t) = \exp[-\beta H(\mu(t), x)]$, that is, $\psi(x, t) = \beta H(\mu(t), x)$. Equation (13) then gives us the generator

$$\Omega(x, t) = \beta \dot{\mu} \frac{\partial H}{\partial \mu} + e^{\beta H} \hat{\mathcal{L}}_{\mu} e^{-\beta H}. \quad (15)$$

Hence,

$$B(t) = -\ln Z_0 + \beta w(t) + \int_0^t dt' \eta(x(t'), t'), \quad (16)$$

where $w(t)$ and Z_0 are defined as for Eq. (1), and $\eta = e^{\beta H} \hat{\mathcal{L}}_{\mu} e^{-\beta H}$. Combining these results gives us

$$\langle \delta[x(t) - x] \exp[-\beta w(t) + \int_0^t dt' \eta] \rangle = \frac{\exp[-\beta H(\mu(t), x)]}{Z_0}. \quad (17)$$

Note that if the autonomous (i.e., fixed μ) dynamics are *balanced*—that is, if they preserve the canonical distribution ($\hat{\mathcal{L}}_{\mu} e^{-\beta H} = 0$)—then $\eta = 0$ and we recover Eq. (1). [Indeed, Eq. (1) was derived in Ref. [1] under the explicit assumption (a) that this condition is satisfied.] With this in mind, we can view Eq. (17) as a stronger version of Eq. (1), which reveals how to construct equilibrium distributions from averages over nonequilibrium trajectories, even when the autonomous dynamics are not balanced, $\hat{\mathcal{L}}_{\mu} e^{-\beta H} \neq 0$. By integrating both sides with respect to x , we obtain

$$\langle \exp[-\beta w(t) + \int_0^t dt' \eta] \rangle = \exp[-\beta \Delta F(t)], \quad (18)$$

where $\Delta F(t) = F_{\mu(t)} - F_{\mu(0)}$ is the free-energy difference between the equilibrium states corresponding to parameter values $\mu(0)$ and $\mu(t)$. This is a generalization of the nonequilibrium work theorem, $\langle e^{-\beta w} \rangle = e^{-\beta \Delta F}$, derived previously for the case when the autonomous dynamics are balanced [1–6].

Example 2. Suppose that we have some dynamics $\dot{x} = \zeta^0(x, \mu)$ that are balanced, i.e., $\hat{\mathcal{L}}_{\mu}^0 \exp[-\beta H(\mu, x)] = 0$. Now suppose that when μ is varied with time, the system obeys the following dynamics:

$$\dot{x} = \zeta(x, \mu, \dot{\mu}) = \zeta^0(x, \mu) + \dot{\mu} v(x, \mu), \quad (19)$$

$$\text{i.e., } \frac{\partial P}{\partial t} = \hat{\mathcal{L}}_{\mu} P = \hat{\mathcal{L}}_{\mu}^0 P - \dot{\mu} \frac{\partial}{\partial x} [v(x, \mu) P],$$

where $v(x, \mu)$ is an arbitrary vector field. Under these dynamics, every infinitesimal change $d\mu$ in the external parameter induces a change $dx = v(x, \mu) d\mu$ in the microstate of the system, in addition to the autonomous dynamics ζ^0 . Now imagine an ensemble evolving under these equations of motion, and suppose that we want to construct a WDF that evolves according to $\mathcal{P}(x, t) = \exp[-\beta H(\mu(t), x)]$ (as in Example 1). Equation (13) then gives us

$$\Omega(x, t) = \beta \dot{\mu} \frac{\partial H}{\partial \mu} + e^{\beta H} \hat{\mathcal{L}}_{\mu} e^{-\beta H} = \dot{\mu} \left(\beta \frac{\partial H}{\partial \mu} + \beta v \nabla H - \nabla v \right),$$

where $\nabla = \partial / \partial x$. This result shows us how to extend Eq. (1) to dynamics of the sort given by Eq. (19), and is applicable to numerical simulations in which nonphysical “metric scaling” terms of the form $\dot{\mu} v(x, \mu)$ are added to the equations of motion so as to keep the system close to thermal equilibrium [27].

Finally, our central result can be illustrated by the following gedanken experiment. Consider a single polymer mol-

ecule attached to two micron-sized beads, immersed in a statistically steady chaotic and/or turbulent flow. Furthermore, imagine that the beads are initially ($t < 0$) held in place with micropipettes and/or tightly focused optical tweezers, so that the initial bead-to-bead distance takes on a fixed value, x^0 . Now at $t=0$ we release one of the beads and we monitor its subsequent dynamics, which will be driven by a combination of thermal fluctuations and chaotic flow. By repeating such a measurement many times, we can, in principle, determine the autonomous Green function $\bar{G}(x, t | x^0, \mu)$ to a desired level of accuracy, simply by constructing a histogram of the observed bead-to-bead distance at a time t after the release of the bead. Here μ is some external parameter (perhaps the temperature or mean flow of the turbulent fluid, or the strength of an externally applied electric or magnetic field that acts on the released bead) that is held constant during the above “calibration” procedure. Now imagine that we repeat this calibration for a number of fixed values of μ , thus obtaining $\bar{G}(x, t | x^0, \mu)$ over a range of parameter values. With this information under our belt, we

now imagine a measurement during which: (a) we vary the parameter μ after releasing the bead, (b) we monitor the bead-to-bead distance $x(t)$, and (c) we construct the quantity $A(t)$ from Eq. (3), using the tabulated function \bar{G} obtained from the calibration runs. We repeat this measurement many times, always following the same protocol for varying the parameter μ , and at the end we construct the weighted histogram $\langle \delta[x(t) - x] \exp[-A(t)] \rangle_{x^0}$, at some time t . According to Eq. (7) this weighted histogram should coincide with the previously tabulated Green function $G_{\mu(t)}(x | x^0, t)$, where $\mu(t)$ denotes the values of the external parameter at time t during the protocol. In view of single-molecule pulling experiments such as those of Refs. [21,25] an experiment along the lines outlined above might well be feasible, and would provide a direct test of our predictions.

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