Memory effects on the convergence properties of the Jarzynski equality

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(Received 15 May 2006; revised manuscript received 10 August 2006; published 8 December 2006)

In this paper we consider solvable model systems on which finite-time work is done. For the systems and changes in state considered, there is no entropic change and the ensuing work distribution is Gaussian. We focus on the fluctuations in the work for such systems, arising from system-bath interactions and finite system recurrences, and study the resulting effect of dynamical broadening on the corresponding distribution $P(e^{-\beta_0 W})$. This allows us to describe the dependence of $P(e^{-\beta_0 W})$ on time and system-bath interactions. From the long-time behavior of the work fluctuations and $P(e^{-\beta_0 W})$, we clarify both (i) when a stochastic treatment of the dynamics may be legitimately invoked and (ii) how information on the system-bath interaction for stochastic, near-equilibrium, systems may be extracted for such processes where a final temperature is well defined.

DOI: 10.1103/PhysRevE.74.061105 PACS number(s): 05.70.Ln, 05.20.−y, 05.40.−a

I. INTRODUCTION

It was first shown by Jarzynski that, under certain circumstances, a change in free energy for a system ΔF induced by applying a force over some time τ may be computed by summing over all work cumulants for a system and bath initially equilibrated to temperature β_o^{-1} by a supersystem. More explicitly the Jarzynski equality (JE) reads [1,2]

$$e^{-\Delta F} = \langle e^{-W}\rangle_0 = e^{\sum_{n=1}^{\infty}(-)^n \langle W^n\rangle_{0,c}/n!} \quad (1)$$

where Jarzynski's work $W=W(\tau)$ is $W(\tau)=\int_0^\tau dt \partial_t \mathcal{H}$ where $\mathcal{H}$ is the system plus bath Hamiltonian and the subscript c above denotes cumulants. The average $\langle\cdots\rangle_0$ is performed with respect to the (canonical) distribution of the system plus bath initial conditions. For convenience, all quantities with units of energy are rescaled by the inverse of temperature β_0 throughout and Boltzmann's constant, $k_{\rm B}$, is set to 1.

Since the derivation of Eq. (1), experiments and simulations have verified the equality and related fluctuation theorems with varying success [3–8] while, from the theoretical standpoint, some of the conditions used to derive the JE have been relaxed and notable points have been clarified [9–24]. Alternate fluctuation theorems have also been proposed [25–34].

In previous work, we studied the effect of large phase space redistribution of the system on the convergence properties of the work cumulant expansion of Eq. (1) in the limit of a temporally diabatic process [35]. In this treatment, the system served as its own bath and the entropy difference ΔS, between the initial and final equilibrium states was $\Delta S = \sum_{n=2}^{\infty}\frac{(-)^n\langle W^n\rangle_c}{n!}$. We studied these types of processes by mapping our problem onto the reverse process, i.e., by using diabatic drops in potential in a region of the coordinate phase volume to study entropic processes. The existence of this duality between forward and reverse processes was earlier pointed out by Ritort and very recently reviewed by Jarzynski [9,36].

Since the change in potential was diabatic, time did not explicitly enter into our analysis. Instead, we dealt with the expansion of the ideal gas and the Gaussian chain both of which are exactly solvable. We were thereby able to address the subtle issue of the thermodynamic limit on sampling of higher-order work cumulants for the case where the free energy change is primarily entropic and for which an accurate determination of the free energy change relies on the tails of the work distribution.

However, the strength of Jarzynski's formalism lies in characterizing thermodynamic quantities for finite-time experiments on systems coupled to their environment. Attention has thus been drawn to the convergence of the work cumulant expansion in time [14,36–38].

There is another fundamental issue regarding the inherent time-dependence in the formulation of the JE which has received less attention in the literature. Consider the crucial step in the derivation of the JE which involves disconnecting a finite number of canonically distributed degrees of freedom, labeled as system plus bath at initial temperature β_o^{-1}, and allowing these to evolve under the action of a force from time 0 to τ. The question arises whether the final system plus bath Boltzmann weights, used in computing free energy differences according to Eq. (1), can be related to the true Boltzmann weights in the absence of disconnection from the microcanonical supersystem [2,39,40]. In general, this is not true because the temperature of a supersystem (and thus the temperature of any finite number of degree of freedom contained within the microcanonical ensemble) changes for an arbitrary variation in the total energy content.

In a related context, previous work by I. Oppenheim has demonstrated how the temperature of a microcanonical supersystem is renormalized by the application of an external force using nonlinear response theory [41,42]. This was shown for the case of an adiabatic change by an expansion in N^{-1}, where N is the number of degrees of freedom contained in the microcanonical supersystem.

For the case when the applied force only recenters the energy distribution of the system, the above difficulties do not arise. The same holds for a system with strongly dissipative dynamics where the system is near equilibrium at every step and the temperature is instead defined through a fluctuation-dissipation theorem [43].

In this paper, we consider model systems with Gaussian work distributions, $P(W)$, onto which finite-time work is done and for which the change in free energy is attributed solely to an energy change. In Sec. II we consider the case of stretching a one-dimensional harmonic chain. We study the fluctuations in the work for this model when the stretching dynamics are both deterministic and dissipative, i.e., Rouse chain. This model contains important features of the anharmonic case since the one-dimensional dynamics can be regarded as the small amplitude limit of the fully coupled dynamics along both longitudinal and transversal directions when pulling higher dimensional chains. Aspects of the nonlinear problem are relegated to future work. In Sec. III the study is extended to the multiply bonded system, i.e., the Zwanzig problem [43].

With the results derived in Secs. II and III in hand, we turn in Sec. IV to an analysis of the distribution $P(e^{-W})$. While the mean of $P(e^{-W})$, $e^{-\Delta F}$, is related to the thermodynamic changes undergone by the system, the width of $P(e^{-W})$ depends on nonequilibrium parameters including bath-system coupling. In Sec. IV we discuss when stochastic dynamics may be legitimately invoked to model the breadth of the distribution $P(e^{-W})$ and indicate how information on the system-bath interaction may be extracted from $P(e^{-W})$. We briefly conclude in Sec. V.

II. MEMORY EFFECTS FOR THE HARMONIC CHAIN

A. Deterministic case

We first consider the example of a classical harmonic chain with N subunits and coupling matrix $\mathbf{K}$ in real space with cyclic boundary conditions and further add that the Nth subunit is linearly coupled to an external force $f(t)$ which is nonzero from $[0,\tau]$. We emphasize that the total phase volume is conserved throughout. Under certain circumstances, we may exactly diagonalize $\mathbf{K}$ and compute the partition function Z after having applied a force for any given time τ, such that $\ln[Z(\tau)/Z(0)] \propto \mathbf{f}(\tau)^T \mathbf{K}^{-1}\mathbf{f}(\tau)$ where $\mathbf{f}(\tau)^T = [0,0,\ldots,f(\tau)]$. The proportionality constant is τ independent. The 0-eigenvalue mode, which arises for the case of cylic boundary conditions, can be avoided by subtracting the kinetic energy associated to the center of motion from the Hamiltonian.

The purpose of this short introduction is simply to highlight that, given $\ln[Z(\tau)/Z(0)]$, it is easily verified that the free energy difference arises from changes to the internal energy exclusively. Thus, all such models are special in the sense that no entropy is generated. On the other hand, these models can be used to single out dynamical broadening effects in the work distribution arising from system-bath interaction and finite system recurrence time. The remainder of our discussion will be restricted to such models.

For now, we will chose to compute the free energy using Jarzynski's formalism by explicitly computing all nonzero work cumulants for the case of tridiagonal $\mathbf{K}$ with Hamiltonian

$$\mathcal{H} = \sum_{m=1}^{N} \left(\frac{1}{2} p_m^2 + \frac{1}{2} K (x_m - x_{m-1})^2 - f(t) x_m \delta_{Nm} \right). \tag{2}$$

where the mass of each subunit is set to 1.

We use the Fourier representation for the set of coordinates x_m in real space in mass rescaled units $x_m = \frac{1}{\sqrt{N}} \Sigma_{k=1}^{N} e^{2\pi i m k/N} x_k$ appropriate for the case where cyclic boundary conditions are employed, such that

$$\mathcal{H} = \sum_{k=1}^{N} \left(\frac{1}{2} p_k p_{-k} + \frac{1}{2} \omega_k^2 x_k x_{-k} - \frac{f(t)}{2\sqrt{N}} (x_k + x_{-k}) \right), \tag{3}$$

where $\{p_k\}$ are the k-space momenta, $\{\omega_k^2 \equiv 4K \sin^2(\frac{\pi k}{N})\}$ are the successive eigenvalues of the coupling matrix, and the last term has been rewritten in symmetric form.

It follows from the definition of $W(\tau)$ that $W(\tau) = -\int_0^\tau dt \dot{f}(t) x_N(t) = -\Sigma_{k=1}^{N} \int_0^\tau dt \frac{\dot{f}(t)}{\sqrt{N}} x_k(t)$. The average work may be simplified to

$$\langle W(\tau) \rangle = -\sum_{k=1}^{N} \int_0^\tau dt \frac{\dot{f}(t)}{\sqrt{N}} \langle x_k^p(t) \rangle, \tag{4}$$

where the superscript p labels the particular solutions of the full $\{x_k(t)\}$, since the mean for the set $\{x_k(0), p_k(0)\}$ is 0. Furthermore, it follows from the fact that members of the set $\{x_k(0), p_k(0)\}$ are Gaussian random variables that all work cumulants above the second are identically zero so that

$$\Delta F(\tau) = \langle W(\tau) \rangle - 1/2 \langle W(\tau)^2 \rangle_c. \tag{5}$$

We may evaluate $\langle W(\tau) \rangle$ by formally inserting the particular solution of the equation of motion (EOM) for every k mode, obtained from the Hamiltonian of Eq. (3), into Eq. (4) yielding for the deterministic case

$$\langle W(\tau) \rangle_{\text{det}} = -\sum_{k=1}^{N-1} \frac{1}{N} \int_0^\tau dt \int_0^t ds \dot{f}(t) G^{\text{det}}(t-s) f(s), \tag{6}$$

where $G^{\text{det}}(t) \equiv \sin \omega_k t / \omega_k$. The summation excludes the $k=N$ mode so that $G^{\text{det}}(t)$ be well defined for all k. Integrating by parts, and using $f(0) \equiv 0$, we obtain

$$\langle W(\tau) \rangle_{\text{det}} = -\sum_{k=1}^{N-1} \frac{f(\tau)^2}{2N\omega_k^2} + \sum_{k=1}^{N-1} \int_0^\tau dt \int_0^t ds \dot{f}(t) \frac{\cos[\omega_k (t-s)]}{N\omega_k^2} \dot{f}(s). \tag{7}$$

By direct calculation from Eq. (2), the change in free energy is $\Delta F = -\Sigma_{k=1}^{N-1} \frac{f(\tau)^2}{2N\omega_k^2}$. From this change in free energy and Eq. (5) the fluctuations in the work are

$$\langle W(\tau)^2 \rangle_{\text{det},c} \to 2 \sum_{k=1}^{N-1} \int_0^\tau dt \int_0^t ds \dot{f}(s) \frac{\cos[\omega_k (t-s)]}{N\omega_k^2} \dot{f}(t). \tag{8}$$

Alternatively, we may have explicitly calculated the second work cumulant and verified the JE.

B. Rouse dynamics and comparison to Sec. II A

The above methodology is particularly useful for the Gaussian set $\{x_k(0), p_k(0)\}$, introduced in the Hamiltonian of

Eq. (3), with zero mean and may be readily adapted to treat Rouse dynamics of the harmonic chain, labeled R, by modifying the above treatment at the level of the particular EOM. The solution to the EOM for the case of Rouse dynamics is simply

$$\mathbf{x}(t) = e^{-\gamma^{-1}\mathbf{K}t}\mathbf{x}(0) + \int_0^t ds e^{\gamma^{-1}\mathbf{K}(s-t)}(\gamma^{-1}\mathbf{f}(s) + \gamma^{-1}\boldsymbol{\eta}(s)), \tag{9}$$

where $\boldsymbol{\eta}(t)$ is the random noise term with zero mean and variance $\langle \eta_m(t)\eta_n(t')\rangle = 2\delta_{mn}\delta(t-t')$ and γ is the strength of the dissipation.

The average work for the case of Rouse dynamics then follows

$$\begin{aligned}\langle W(\tau)\rangle_R &= \gamma^{-1}\int_0^\tau dt\int_0^t ds\dot{\mathbf{f}}(t)^T e^{\gamma^{-1}\mathbf{K}(s-t)}\mathbf{f}(t)\\ &= \gamma^{-1}\int_0^\tau dt\int_0^t ds\dot{f}(t)(e^{\gamma^{-1}\mathbf{K}(s-t)})_{NN}f(t).\end{aligned} \tag{10}$$

Since $\mathbf{K}$ has earlier been diagonalized, the second equality of Eq. (10) above is easily evaluated. Integrating by parts we obtain

$$\langle W(\tau)\rangle_R = -\sum_{k=1}^{N-1}\frac{f(\tau)^2}{2N\omega_k^2} + \sum_{k=1}^{N-1}\int_0^\tau dt\int_0^t ds\dot{f}(t)\frac{e^{\gamma^{-1}\omega_k^2(s-t)}}{N\omega_k^2}\dot{f}(s). \tag{11}$$

The work fluctuations follow from the above and Eq. (5)

$$\langle W(\tau)^2\rangle_{R,c} = 2\sum_{k=1}^{N-1}\int_0^\tau dt\int_0^t ds\dot{f}(s)\frac{e^{\gamma^{-1}\omega_k^2(s-t)}}{N\omega_k^2}\dot{f}(t). \tag{12}$$

The results of Eqs. (11) and (12) are consistent with the results of the insightful work of Dhar [38]. As before, it is simple but tedious to verify the JE by explicitly computing Eq. (12).

We wish to compare the results for the work for both deterministic and Rouse dynamics (7) and (11) respectively, for a general applied force of the form αt^n where α is a t-independent proportionality constant and the applied force is linearly coupled to a system coordinate. It is straightforward to do so by adopting the following convenient notation for the general form for the average work applicable to both deterministic and Rouse dynamics

$$\langle W(\tau)\rangle = -\sum_{k=1}^{N-1}\frac{1}{N}\int_0^\tau dt\int_0^t ds\dot{f}(t)G(t-s)f(s), \tag{13}$$

where $\int_0^t ds G(t-s)f(s)$ is identified with $[\partial_t^2+\omega_k^2]^{-1}f(t)$ for the deterministic chain and $[\gamma\partial_t+\omega_k^2]^{-1}$ for the Rouse chain. As a note, the inverse of the operator is guaranteed to exist because the summation over k excludes $k=N$.

It is now possible to rescale time such that $t\to\tilde{t}\tau$, where $\tilde{t}$ is a dimensionless time, and rewrite the average work of Eq. (13) as follows:

$$\langle W(\tau)\rangle_{\text{det}} = -\sum_{k=1}^{N-1}\int_0^1 d\tilde{t}\frac{\dot{\tilde{f}}(t)}{2N\omega_k^2}\left(1 - \frac{\partial_{\tilde{t}}^2}{\tau^2\omega_k^2} + \mathcal{O}(\tau^{-4})\right)f(t), \tag{14}$$

$$\langle W(\tau)\rangle_R = -\sum_{k=1}^{N-1}\int_0^1 d\tilde{t}\frac{\dot{\tilde{f}}(t)}{2N\omega_k^2}\left(1 - \frac{\partial_{\tilde{t}}}{\gamma^{-1}\tau\omega_k^2} + \mathcal{O}(\tau^{-2})\right)f(t), \tag{15}$$

where $\dot{\tilde{f}}(t)\equiv\partial_{\tilde{t}}f(t)$ and we have expanded the general $G(t)$ as a geometric series. Memory effects are unimportant when τ exceeds the relaxation time of the most sluggish of the k modes, i.e., $\tau \gg \gamma/\omega_k^2$ and it is thus possible to approximate the exact $P(W)$ beyond the first few recurrence times of the system by some dissipative approximation.

Also, it is surprising to see that even as the force grows in time, the effect of fluctuations in the work become negligible for long time implying that the distribution in W or e^{-W} eventually peaks around its thermodynamic value [44]. A note on stretching chains with open ends can be found in Ref. [45].

III. MEMORY EFFECTS FOR A SYSTEM WITH EXPLICIT BATH

We extend the analysis to an explicit bath model, the multiply bonded system MBS in which a known potential energy surface is coupled to N bath modes [43]. We show how the dependence of the work fluctuations on realistic bath parameters simplifies beyond the first few recurrence times of the system.

We begin by defining the Hamiltonian

$$\mathcal{H} = \frac{1}{2}p^2 - f(t)x + \frac{K}{2}x^2 + \sum_{j=1}^{N}\left[\frac{1}{2}p_j^2 + \frac{1}{2}\omega_j^2\left(q_j - \frac{\gamma_j}{\omega_j^2}x\right)^2\right] \tag{16}$$

with index j denoting the bath and where γ_j is a measure of the bath-system coupling strength. In order to compute both average work and fluctuations we first write coupled EOM for system and bath and eliminate bath variables to obtain an EOM depending exclusively on system variables. The resulting system EOM is often written as $\ddot{x}(t)=\sum_j F_j(t)-\int_0^t ds\sum_j M_j(t-s)\dot{x}(s)+f(t)-Kx(t)$, where the memory kernel $\sum_j M_j(t)=\sum_j\frac{\gamma_j^2}{\omega_j^2}\cos(\omega_j t)$ and the random noise term $F_j(t)=\gamma_j\Big[q_j(0)-\frac{\gamma_j}{\omega_j^2}x(0)\Big]\cos(\omega_j t)+\frac{\gamma_j}{\omega_j}p_j(0)\sin(\omega_j t)$. In the continuum limit, $\sum_j M_j(t)$ smoothly goes over to $\int_0^\infty d\omega g(\omega)\gamma(\omega)^2\cos(\omega t)/\omega^2$, where $g(\omega)$ is a bath density of states.

It is natural to solve the resulting system EOM in Laplace space. Since both system and bath degrees of freedom are initially Gaussian random variables with zero mean, the average work is simply

$$\langle W(\tau)\rangle_{\text{MBS}} = -\int_0^\tau dt\int_0^t ds\dot{f}(t)G^{\text{MBS}}(t-s)f(s), \tag{17}$$

where

$$\int_0^t ds G^{\mathrm{MBS}}(t-s)f(s) = \mathcal{L}^{-1}\left(\left[K+z^2+\sum_j z\hat{M}_j(z)\right]^{-1}\hat{f}(z)\right) = \mathcal{L}^{-1}[\hat{a}(z)\hat{f}(z)] \tag{18}$$

with $\mathcal{L}^{-1}$ denoting the inverse Laplace transform operation and $\hat{a}(z)$ is defined through the expression above. We note however that by the (inverse) Laplace convolution theorem $\mathcal{L}^{-1}(\hat{f}(z)\hat{a}(z))=\int_0^t ds f(s)a(t-s)$. It is now straightforward to integrate Eq. (18) by parts

$$\langle W(\tau)\rangle_{\mathrm{det}} = -\frac{f(\tau)^2}{2K} + \int_0^\tau dt \int_0^t ds \dot{f}(t)v(t-s)\dot{f}(s), \tag{19}$$

where $v(t)$ is implicitly defined through Eqs. (18) and (19) and depends on the pole structure of $\hat{a}(z)$. The average work is entirely analogous to the form of Eqs. (7) and (11). As expected, we verify that the bath does not contribute to the system free energy change $-\frac{f(\tau)^2}{2K}$.

By selecting, for simplicity, identically distributed $\{\gamma_j,\omega_j\}$, i.e., $g(\omega)=N\delta(\omega-\omega_0)$ with $\gamma(\omega)=\gamma$, then for arbitrary $f(t)$ we recover a closed form expression for the average work

$$\int_0^t ds v(t-s)\dot{f}(s) = \mathcal{L}^{-1}\left(z\hat{f}(z)\frac{r_1r_2+(r_1+r_2-z^2)\omega^2}{r_1r_2(r_1-z^2)(r_2-z^2)}\right), \tag{20}$$

where

$$r_{1,2} = \left(\frac{-\left(\omega^2+\frac{\gamma^2N}{\omega^2}+K\right)\pm\sqrt{\left(\omega^2+\frac{\gamma^2N}{\omega^2}+K\right)^2-4K\omega^2}}{2}\right).$$

Though we will come back to this point in the context of a discussion on a more general spectral function, it suffices to indicate for now that for sufficiently large τ the work fluctuations, expressed in Eqs. (19) and (20), considerably simplify and eventually vanish for infinite τ [46].

While identically distributed bath couplings and frequencies lead to closed form expressions for work averages and fluctuations, (20), it is straightforward to extend the analysis to more realistic bath models. By doing so, we make explicit the dependence of the work fluctuations on parameters of interest including system-bath coupling strength and as an aside obtain the expected result that the average work is indeed independent of the choice of bath spectral function for long times.

As an illustration, we select a Lorentzian density of states $g(\omega)=\frac{2}{\pi}\frac{\omega_c}{\omega_c^2+\omega^2}$ with Ohmic coupling $\gamma(\omega)=c\omega$. We identify ω_c as the bath cutoff frequency and c as a measure system-bath coupling strength with units of inverse time. Given the above, the Laplace transform of the term containing the memory kernel in Eq. (18) takes the form

$$z\sum_j \hat{M}_j(z) = z\int_0^\infty d\omega \frac{2c^2}{\pi}\frac{\omega_c}{\omega_c^2+\omega^2}\frac{z}{z^2+\omega^2}. \tag{21}$$

By repeating the arguments that lead to Eqs. (14) and (15), we first expand the denominator on the right hand side of Eq. (18) as a geometric series

$$\left[K+z^2+\sum_j z\hat{M}_j(z)\right]^{-1} = \frac{1}{K}\left[1-\left(\frac{z^2}{K}+\frac{z\sum_j\hat{M}_j(z)}{K}\right)+\cdots\right], \tag{22}$$

where by rescaling $t=\tilde{t}\tau$ such that $z=\tilde{z}\tau^{-1}$ (and $\mathcal{L}^{-1}=\tilde{\mathcal{L}}^{-1}\tau^{-1}$) terms not explicitly written are at least $\mathcal{O}(\tau^{-2})$. Since z is the Laplace variable integrated along a vertical line in the complex z plane to the right of the real part of all singularities we take $\mathrm{Re}(z)>\omega_c$ and expand the resulting integral of Eq. (21) for large τ

$$(z/K)\sum_j \hat{M}_j(z) = \frac{\tilde{z}c^2}{\tau K\omega_c}\left(1-\frac{\tilde{z}}{\tau\omega_c}+\mathcal{O}(\tau^{-2})\right). \tag{23}$$

Inserting Eq. (23) back into Eq. (22) we recover

$$\left[K+z^2+\sum_j z\hat{M}_j(z)\right]^{-1} = \frac{1}{K}\left[1-\frac{\tilde{z}c^2}{\tau K\omega_c}\left(1-\frac{\tilde{z}}{\tau\omega_c}+\mathcal{O}(\tau^{-2})\right)+\mathcal{O}(\tau^{-2})\right]. \tag{24}$$

In analogy to Eqs. (14) and (15), we recover a single condition to leading order which must be satisfied in order for work fluctuations to have small effect for long τ; $\tau \gg \sum_j \hat{M}_j(\tilde{z}\to 0)/K$. This condition, roughly interpreted, leads to the conclusion that for stretching times exceeding the typical system relaxation time, work fluctuations are subdominant. Thus, $P(W)$ and correspondingly $P(e^{-W})$ are sharply peaked around their thermodynamic mean and there is some flexibility as to how the bath system interaction may be modeled.

Additional conditions, appearing in Eq. (24) at higher order in τ^{-1}, simply arise because we have not set the inertial term of the system EOM to zero, i.e., assumed overdamped dynamics as was the case for the Rouse model presented earlier. The dependence of the width of the work distribution with the cutoff frequency and bath system coupling follows from Eq. (24).

IV. BATH DEPENDENCE AND LONG-TIME BEHAVIOR OF $P(e^{-W})$

The work distribution is defined as the expectation value of $\delta(W-W[\{q_i(0),p_i(0)\},\tau])$ over an initial distribution of phase points $\varrho[\{q_i(0),p_i(0)\}]$ as follows

$$P(W) \equiv \int \mathcal{D}[\{q_i(0),p_i(0)\}]\varrho[\{q_i(0),p_i(0)\}] \times \delta(W-W[\{q_i(0),p_i(0)\},\tau]) \tag{25}$$

with all other factors absorbed into the above defined measure. By expanding the δ function in its Fourier representation $\delta(x)=\int_{-\infty}^{\infty} dm e^{imx}$, with m as the dummy Fourier variable, it is possible to show that for all examples considered, the work distribution $P(W,\{\alpha_i\})$ is Gaussian, where $\{\alpha_i\}$ is the set of system and bath parameters. Assuming the order of integration of the variables $\{q_i(0),p_i(0)\}$ and m is interchangeable, we recover in the integrand with respect to m what is commonly referred to as the characteristic function of $P(W,\{\alpha_i\})$. In general, the dependence of first and second work cumulants on $\{\alpha_i\}$ is complicated.

From the approach we have taken to compute the fluctuations in the work for various models, we concluded that $\langle W^2\rangle_c$ is subdominant in τ for $f(\tau)$ varying as any power of τ, in the case of linear coupling to the external force. The long-time limit is obtained by subsequently integrating over m thus reducing $P(W,\{\alpha_i\})$ to the following:

$$\lim_{\tau\to\infty} P(W) = \delta(W - \langle W[\{q_i(0),p_i(0)\},\tau]\rangle) \tag{26}$$

which is a reasonable result.

We are, however, interested in the properties of the distribution of $P(x\equiv e^{-W},\{\alpha_i\})$ whose width measures the degree of accuracy of a free energy measurement using Jarzynski's prescription. Moreover, for Gaussian $P(W,\{\alpha_i\})$, $P(x,\{\alpha_i\})$ is log normal with

$$P(x,\{\alpha_i\}) = x^{-1}/\sqrt{2\pi\langle W^2\rangle_c}e^{-(\ln x + \langle W\rangle)^2/2\langle W^2\rangle_c}. \tag{27}$$

The long-time behavior of $P(x,\{\alpha_i\})$ then follows

$$\lim_{\tau\to\infty} P(e^{-W},\{\alpha_i\}) = e^{\langle W\rangle}\delta(W - \langle W[\{q_i(0),p_i(0)\},\tau]\rangle). \tag{28}$$

Given the results derived from Secs. II and III, it is possible to quantify whether certain regimes of bath parameters lead to efficient sampling of $P(x,\{\alpha_i\})$ and how these may be extracted from work distribution widths. We will show this for particular α_i appearing in the models considered earlier for the special case where $f(t)$ is linear in t.

The first such parameter considered is γ defined in part B of Sec. II, Eq. (9), as the measure of dissipation in the Rouse model. We assume for now that all parameters, aside from γ, are specified and held fixed so that $P_R(x,\{\alpha_i\})$, determined from Eqs. (11) and (12) and Eq. (27), is simply rewritten as $P_R(x,\gamma)$. This distribution plotted in Fig. 1 has a mean $e^{-\Delta F}=2.29$ which is independent of γ. Clear sharpening of the distribution around its thermodynamic mean is apparent for increasing dissipation. Note from Eq. (9) that *decreasing* γ implies stronger dissipation in this model [31].

The joint γ-τ dependence can also be probed by reconsidering an equivalent distribution to that of Fig. 1 for longer τ. The mean of $P_R(x,\gamma)$ is higher in Fig. 2 for the set of parameters selected $e^{-\Delta F}=27.8$ though all other features of interest remain unchanged. Incidentally, by comparing Eqs. (7) and (11) it is easy to verify that the approximate $P_R(x,\gamma)$ becomes indistinguishable from the deterministic $P_{\mathrm{det}}(x,\{\alpha_i\})$ when both τ and γ^{-1} are large since this is precisely the regime where the dynamical broadening effects become negligible. Extracting γ from the standard deviation

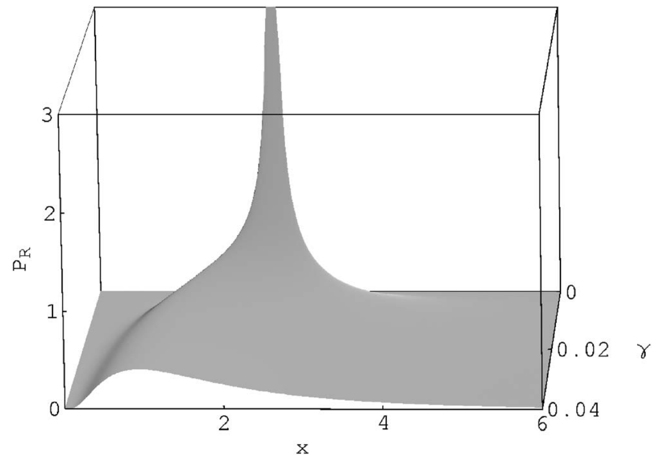

FIG. 1. Effect of dissipation on the sharpening of the distribution $P_R(x,\gamma)$ with $\{N,K,\alpha,\tau\}=\{20,1,1,1\}$ in the appropriate units.

of the work distribution is then possible in certain limits provided the system under study can be mapped onto one with Rouse dynamics.

Many of the above arguments carry over directly to the MBS though a few remarks are in order. We first consider the distribution of $P_{\mathrm{MBS}}(x,\gamma)$, constructed using Eqs. (19) and (20) and Eq. (27), in the strong coupling limit to the bath, large γ. In this limit, memory effects induced by coupling of the system to the medium are important, the resulting distribution is broad and the corresponding mean of $P_{\mathrm{MBS}}(x,\gamma)$ difficult to sample. The opposite holds true for weak coupling to the bath though for long enough τ, memory effects become subdominant as shown in Eq. (24) for the case of a more general bath spectral function. The effect of coupling to the environment on the distribution of $P_{\mathrm{MBS}}(x,\gamma)$ is reproduced in Fig. 3 for a specified set of parameters with mean $e^{-\Delta F}=8.27$.

As before, while the ease of extracting thermodynamic information is determined by the shape of $P_{\mathrm{MBS}}(x,\gamma)$, bath parameters of interest can be reliably extracted from the breadth of the work distribution provided the system can be mapped to the Zwanzig model.

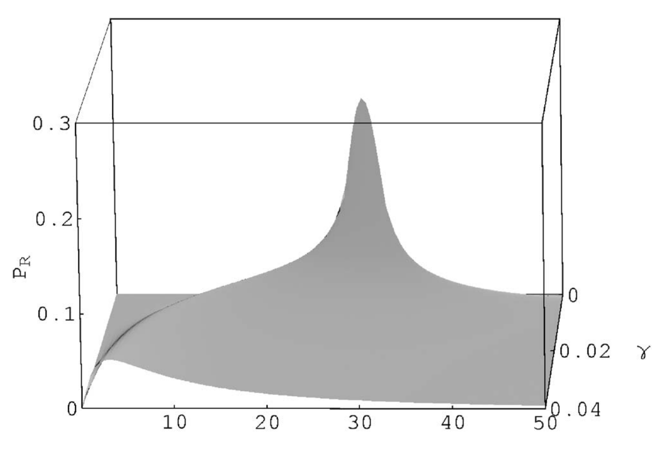

FIG. 2. Effect of dissipation on the sharpening of the distribution $P_R(x,\gamma)$ using $\{N,K,\alpha,\tau\}=\{20,1,1,2\}$ in the appropriate units.

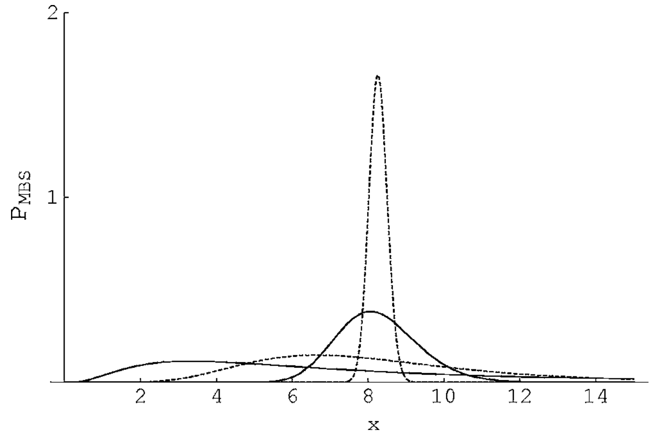

FIG. 3. Effect of coupling to the environment on the sharpening of the distribution $P_{\mathrm{MBS}}(x,\gamma)$ using $\{N,K,\alpha,\tau,\omega\}=\{10,10,0.65,10,1.5\}$ in the appropriate units. Decreasing values of γ, {5,4,0.5,0.1}, are depicted by successive solid and dashed lines, respectively. See text.

V. CONCLUSION

This paper is meant to serve a threefold purpose. We first note that the difficulty of having to deal with the notion of a general nonequilibrium temperature appropriate to the description of the final system plus bath Boltzmann weights is circumvented by dealing with systems of a special type. More specifically, our analysis is limited to stretching of a harmonic system through linear coupling to an external force, for which there is only an energy change. By extension, the case of Rouse dynamics or other strongly dissipative systems is also special by virtue of having well defined Boltzmann weights while work is applied onto the system.

Secondly, we extend our previous work on convergence properties of the JE by eliminating all sources of broadening in $P(W)$ except those arising from dynamical origins [35]. This is done by explicitly calculating work fluctuations for various harmonic models containing the essence of the more-general nonlinear problem. We relate this discussion back to how various nonequilibrium parameters of the model affect the breadth of the distribution $P(e^{-W})$ and thus how simply the mean $(e^{-\Delta F})$ is selected for various parameter regimes.

Thirdly, from the behavior of $P(W)$, alternatively $P(e^{-W})$, it is shown how important parameters relating to the bath-system interaction may be simply extracted.

For nonlinear coupling to the external force, it is possible to imagine changing the force constant of the harmonic system in time which, following arguments identical to those at the beginning of Sec. II, leads to generation of entropy. From these arguments, the dynamics of systems with slightly anharmonic potentials are equally good candidates for the study of dynamical entropy generation within the context of the JE. Additional models of interest would certainly include, though not be limited to, the dynamics of the freely jointed chains with the possibility of slight excluded volume interaction and the wormlike chain with either pure bending or bending and stretching potential.

ACKNOWLEDGMENTS

This work was partially supported by the NSF, Grant No. 0306287. One of the authors (S.P.) acknowledges financial support from NSERC and thanks Professor Irwin Oppenheim and X.G. Song for their insightful remarks.

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[44] Clearly fluctuations are not subdominant when the force is applied on resonance. This scenario, however, is not considered because assuming a closed set of trajectories for the system and bath is merely an idealization.
[45] We reconsider the Hamiltonian from Eq. (2) with the summation index, m, running from 1 to $N+1$ with open chain boundary conditions, i.e., $x_0=x_{N+1}=0$. The coupling matrix is easily diagonalized by the discrete sine transform $x_m(t)=\sqrt{\frac{2}{N+1}}\Sigma_{k=0}^{N}\sin\left(\frac{\pi mk}{N+1}\right)x_k(t)$ which satisfies the specified boundary conditions. It is important to note that the work, when applied to a single bead, is a boundary effect. As an example, if the work is applied to the last bead the analogue of Eq. (3) follows with some differences, namely, $\omega_k=2\sqrt{K}\sin\left(\frac{\pi k}{2(N+1)}\right)$ and $f(t)x_N=f(t)\Sigma_{k=1}^{N}\sqrt{\frac{2}{N+1}}\sin\left(\frac{\pi Nk}{N+1}\right)x_k(t)$. The free energy for open ends is then

$$\Delta F=-\sum_{k=1}^{N}\frac{f(\tau)^2}{N+1}\left(\frac{\sin^2\left(\frac{\pi Nk}{N+1}\right)}{4K\sin^2\left(\frac{\pi k}{2(N+1)}\right)}\right)$$
$$=-\frac{f(\tau)^2}{N+1}\left[\frac{N}{2K}+\frac{1}{2K}\cos\left(\frac{N\pi}{2(N+1)}\right)csc\left(\frac{\pi}{2(N+1)}\right)\right]$$
$$\sim -f(\tau)^2 2K+\mathcal{O}(N^{-1}).$$

This free energy difference has the same τ dependence, though different N scaling, as the free energy difference computed using cyclic boundary conditions, see Eqs. (7) and (8). On the other hand, it is also possible to compute a free energy change with open chain boundary conditions when the force is applied to a bead in the middle of the open-ended chain. In this case both τ dependence and N scaling of the free energy change are identical to the free energy change computed using cyclic boundary conditions for the chain.
[46] As a check, we expand Eq. (19) with $v(t)$ specified by Eq. (20) in the weak coupling limit $\lim_{\gamma\to 0}\langle W(\tau)\rangle_{\text{det}}=-\frac{f(\tau)^2}{2K}+\int_0^\tau dt\int_0^t ds\dot{f}(t)\frac{\cos[\sqrt{K}(t-s)]}{K}\dot{f}(s)+\mathcal{O}(\gamma^2)$ which is the correct analog of Eq. (7).