Microcanonical work and fluctuation relations for an open system: An exactly solvable model

Y. Subašič1,* and C. Jarzynski2,†

1Joint Quantum Institute and Maryland Center for Fundamental Physics, University of Maryland, College Park, Maryland 20742
2Department of Chemistry and Biochemistry and Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

(Dated: November 6, 2013)

We calculate the probability distribution of work for an exactly solvable model of a system interacting with its environment. The system of interest is a harmonic oscillator with a time dependent control parameter, the environment is modeled by \( \lambda \) independent harmonic oscillators with arbitrary frequencies, and the system-environment coupling is bilinear and not necessarily weak. The initial conditions of the combined system and environment are sampled from a microcanonical distribution and the system is driven out of equilibrium by changing the control parameter according to a prescribed protocol. In the limit of infinitely large environment, i.e. \( \lambda \to \infty \), we recover the nonequilibrium work relation and Crooks’s fluctuation relation. Moreover, the microcanonical Crooks relation is verified for finite environments. Finally we show the equivalence of multi-time correlation functions of the system in the infinite environment limit for canonical and microcanonical ensembles.

I. INTRODUCTION

Recent advances in technology, like real time monitoring and control of single molecules, enable experiments where small systems can be studied under nonequilibrium conditions [1]. Alongside these advances, there has been considerable progress in our theoretical understanding of the nonequilibrium statistical mechanics of small systems. In this paper we will be concerned in particular with the nonequilibrium work relation [2, 3],

\[
\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \tag{1}
\]

and the closely related fluctuation relation, due to Crooks [4–6],

\[
\frac{P(W)}{P(-W)} = e^{\beta(W-\Delta F)}. \tag{2}
\]

Both of these relate the statistical fluctuations in the work \( W \) performed on a system during a nonequilibrium process, to a free energy difference \( \Delta F \) between two equilibrium states of the system. The angular brackets in Eq. (1) denote an average over an ensemble of realizations of the process, and \( \beta \) specifies the inverse temperature at which the system is prepared prior to each realization. In Eq. (2) the numerator and denominator denote the distributions of work values corresponding to a conjugate pair of “forward” and “reverse” processes. Eqs. (1) and (2) have been derived by various means, using a variety of equations of motion to model the microscopic dynamics – see Ref. [7] for a review with extensive references – and have been confirmed experimentally [8–13].

We will focus our attention on the formulation of these results within the framework of classical, Hamiltonian dynamics. The Hamiltonian for the system of interest is assumed to depend on a control parameter \( \lambda \), whose time dependence over an interval \( 0 \leq t \leq \tau \) is specified by a schedule, or protocol, \( \lambda(t) \). The free energy difference \( \Delta F \) refers to two different equilibrium states, corresponding to the initial and final parameter values, \( \lambda_0 \) and \( \lambda_\tau \).

Ref. [2] presents Hamiltonian derivations of Eq. (1) for two different scenarios. In the first, a system of interest is prepared in equilibrium by being placed in weak contact with a thermal reservoir, which is then removed. In this case it is natural to treat the initial conditions of the system of interest as a random sample from the canonical distribution (reflecting the method of preparation), and also to use Hamiltonian dynamics to model the subsequent evolution of the thermally isolated system as the control parameter is varied (\( 0 \leq t \leq \tau \)).

In the second scenario considered in Ref. [2], the system remains in weak thermal contact with the reservoir throughout the process. In this derivation, initial conditions for the combined system and reservoir were assumed to be sampled from a canonical distribution, and then Hamilton’s equations were used to model evolution in the full phase space. In Ref. [14] this approach was extended to a system in strong thermal contact with a reservoir, again assuming canonically sampled initial conditions in the full phase space.

In both derivations described in the previous paragraph, the use of Hamilton’s equations to model the dynamics in the full phase space implies that the combined system of interest and reservoir are being treated as a large, thermally isolated system. The assumption of a canonical distribution of initial conditions for this combined system renders the derivation of Eq. (1) (as well as Eq. (2)) straightforward. However, from a conceptual
perspective this assumption is somewhat problematic, as the equilibrium state of an isolated system is typically associated with the microcanonical ensemble. It is therefore natural to wonder whether Eqs. (1) and (2) remain valid when initial conditions are sampled microcanonically rather than canonically. In this paper we will address this question through the exact analysis of a model system, involving a harmonic oscillator (the system of interest) coupled strongly to a bath of \( N \) other harmonic oscillators (the thermal reservoir). This model has previously been studied by Hasegawa [15], who considered initial conditions sampled from the canonical ensemble. More generally, the study of model systems for which exact results can be obtained has illustrated and illuminated a variety of issues related to Eqs. (1) and (2). [16–37]

It is widely believed that in the thermodynamic limit, the average thermodynamic properties of a physical system are independent of the choice of the ensemble. This is the idea of ensemble equivalence [38]. However, the situation is quite different when fluctuations are considered [39]. (As a simple example note that the variance of the total energy is proportional to heat capacity in the canonical ensemble, but vanishes identically in the microcanonical ensemble.) This suggests that the validity of Eqs. (1) and (2), for microcanonically sampled initial conditions, does not follow immediately from the equivalence of ensembles, even when the thermal reservoir is assumed to be macroscopic. This issue is especially relevant since large fluctuations with very small probabilities play a dominant role in the nonequilibrium work relation [40] whereas standard ensemble equivalence results do not make any claim about or depend on such low probability events. Moreover, the work \( W \) is not simply a function of the phase space variables, but rather a functional of the phase space trajectory, and its fluctuations may be more complex than that of typically considered phase space functions.

For a system interacting with a large environment it has been suggested in Ref. [41], using heuristic arguments, that the validity of the nonequilibrium work relation may be insensitive to the particular distribution used and that the canonical ensemble should be viewed primarily as a computational convenience. A more detailed argument supporting this claim has been developed in Ref. [42]. In Ref. [43] the following microcanonical version of the Crooks fluctuation relation was derived:

\[
\frac{P_E(W)}{P_{E+W}(-W)} = \frac{\Sigma_f(E+W)}{\Sigma_i(E)}, \tag{3}
\]

where \( P_E(W) \) stands for the probability density of doing work \( W \) during the forward process and \( P_{E+W}(-W) \) stands for the probability density of doing work \(-W\) during the time reversed process. The subscript indicates the energy of the microcanonical distribution from which the initial conditions are sampled. The right-hand side is the ratio of two densities of states at different energies and associated with initial and final Hamiltonians. (Note that Ref. [43] uses \( \Omega \) to denote the density of states, which we reserve for the system frequency. Thus we opted to use \( \Sigma \) for the density of states instead). It was then argued in Ref. [43] that in the appropriate thermodynamic limit, one recovers Eq. (2). To the best of our knowledge, our paper is the first to explore this issue using a model system for which the work distributions can be computed exactly.

The paper is organized as follows. The model is introduced in Sec. II. Exact expressions for the left-hand side of Eq. (1) are obtained in Sec. IIIA and for the probability distribution of work in Sec. IV A. The validity of nonequilibrium work relation in the limit of an infinite environment is proven in Sec. III B. The validity of microcanonical Crooks relation is shown in Sec. IV B. Ensemble equivalence in its most general form is shown in Sec. V B. Some technical details of the derivation are provided in the Appendix B.

![FIG. 1. A mass on a slope is attached to a spring. The support of the spring is moved according to a time-dependent protocol \( \lambda \). A frictional force acts on a mass on a slope connected to a spring.]()
\[ H_{\text{sys}}(Z; \lambda t) = \frac{P^2}{2M} + \frac{1}{2} M \dot{\Omega}^2 (X - \lambda t)^2 + \alpha X, \]
\[ H_{\text{int}}(Z, z) = - \sum_{n=1}^{N} c_n x_n X, \]
\[ H_{\text{env}}(z) = \sum_{n=1}^{N} \left( \frac{p_n^2}{2m_n} + \frac{1}{2} m_n \omega_n^2 x_n^2 \right). \] (5)

Here \( \lambda t \) is a time-dependent parameter determined by the protocol and \( \alpha \) is a constant. This system Hamiltonian can be realized by the physical system depicted in Fig. 1. A mass on a slope is attached to a spring. The support of the spring is moved according to a time-dependent protocol. To recover the Hamiltonian (5) one identifies \( Mg \cos \theta \) with \( \alpha \). Friction is modelled via linear coupling to \( N \) harmonic oscillators that constitute the environment. Generalization to more than one system oscillator and allowing for interactions among environmental oscillators can be achieved by adopting a matrix notation [44]. However such a general treatment is not necessary for the purpose of this paper.

A. The Solution

It will prove convenient to define
\[ f(\lambda t) \equiv M \dot{\Omega}^2 \lambda t - \alpha, \]
\[ \mathcal{J}(\lambda t) \equiv \frac{1}{2} M \dot{\Omega}^2 \lambda t^2. \] (6)

Then the system Hamiltonian can be written as:
\[ H_{\text{sys}}(Z; \lambda t) = \frac{P^2}{2M} + \frac{1}{2} M \Omega^2 X^2 - f(\lambda t)X + \mathcal{J}(\lambda t). \] (8)

The equation of motion for the system degree of freedom can be obtained by first solving the dynamics of the environmental degrees of freedom in terms of the system variables and substituting that solution into the equation of motion for the system oscillator. The result is an integro-differential equation for the system oscillator [45, 46] and is referred to as a Langevin equation.

\[ M \ddot{X}(t) + 2M \int_0^t ds \gamma(t - s) \dot{X}(s) + M \dot{\Omega}^2 X(t) = f(\lambda t) - 2M \dot{\gamma}(t)X(0) + \xi(t), \] (9)

\[ \gamma(t) \equiv \frac{1}{M} \sum_{n=1}^{N} \frac{c_n^2}{2m_n \omega_n^2} \cos(\omega_n t), \]
\[ \dot{\Omega}^2 \equiv \Omega^2 - 2\gamma(0), \]
\[ \xi(t) \equiv \sum_{n=1}^{N} c_n \left( x_n(0) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) \right). \] (10)

The system-environment coupling is required to satisfy \( \Omega^2 \geq 2\gamma(0) \) for the dynamics to be stable and will make this assumption henceforth.

The solution to Eq. (9) can be written as
\[ X(t) = X(0) h(t) + P(0) g(t) + \int_0^t ds \, g(t - s) [f(\lambda s) - 2M \gamma(s)X(0) + \xi(s)]. \] (13)

Here \( h(t) \) and \( g(t) \) are the homogenous solutions of Eq. (9) with the right hand side set equal to zero and satisfy
\[ h(0) = M \dot{\gamma}(0) = 1; \quad \dot{h}(0) = g(0) = 0. \] (14)

The solutions \( h(t) \) and \( g(t) \) can be calculated using the Laplace transforms:
\[ \hat{h}(s) = \frac{2 \gamma(s) + s}{s^2 + 2s \gamma(s) + \dot{\Omega}^2}, \quad \hat{g}(s) = \frac{1/M}{s^2 + 2s \gamma(s) + \dot{\Omega}^2}, \] (15)

where the hat indicates Laplace transform. The two linearly independent homogenous solutions are related by [47]:
\[ s \hat{h}(s) - M \dot{\Omega}^2 \hat{g}(s), \quad sM \hat{g}(s) = \hat{h}(s) - 2M \dot{\gamma}(s) \hat{g}(s), \] (16)
\[ \dot{h}(t) = -M \dot{\Omega}^2 g(t), \quad M \dot{g}(t) = h(t) - 2M \int_0^t ds \gamma(t - s) g(s). \] (17)

III. NONEQUILIBRIUM WORK RELATION

We assume a protocol \( \lambda t \) in the time interval \([0, \tau]\). This corresponds to a function \( f(\lambda t) \) via Eq. (6). The work associated with the Hamiltonian (8) for the duration of the protocol \( \Delta t = \tau \) is given by
\[ W = \int_0^\tau dt \lambda \frac{\partial H_{\text{tot}}}{\partial \lambda} = -\int_0^\tau dt \frac{\partial f(\lambda t)}{\partial \lambda} X(t) + \Delta \mathcal{J}. \] (18)

The dot over a function indicates time derivative, and \( \Delta \mathcal{J} \equiv \mathcal{J}(\lambda \tau) - \mathcal{J}(\lambda_0) \). This definition of work is motivated by the observation \( dW = d\lambda \frac{\partial \mathcal{W}}{\partial \lambda} = \text{displacement} \times \text{force} \). For a discussion of alternative definitions of work and various fluctuation theorems they lead to see Ref. [48].

For the nonequilibrium work relation Eq. (1) the initial state is sampled from the canonical ensemble at inverse temperature \( \beta \) using the Hamiltonian \( H_{\text{tot}}(Z, z; \lambda_0) \). The free energy difference is defined via \( \Delta F \equiv F(\lambda_\tau) - F(\lambda_0) \). In our model the free energies can be calculated explicitly.
\[ Z_{\beta}(\lambda) = e^{-\beta F(\lambda)} = \int dZ \, dz \, e^{-\beta H_{\text{tot}}(Z, z; \lambda)}. \] (19)
Here $Z_β(λ)$ is the partition function associated with the Hamiltonian $H_{tot}(λ; Z, z)$. The integral over the environmental degrees of freedom gives:

$$\int d\mathbf{z} e^{-β(H_{int}(\mathbf{z})+H_{env}(\mathbf{z}))} \propto e^{βX^2 \sum_n \frac{c_n^2}{2m_n c_n^2}} = e^{βMγ(0)X^2}. \quad (20)$$

Irrelevant constants that will eventually cancel out in the expression for $ΔF$ have been omitted in the above expression. We define the Hamiltonian of mean force as [14, 49]:

$$H^*(Z; λ_t) = H_{sys}(Z; λ_t) - Mγ(0)X^2 = \frac{P^2}{2M} + \frac{1}{2}MΩ^2X^2 - f(λ_t)X + J(λ_t), \quad (21)$$

which amounts to shifting the frequency form $Ω$ to $Ω$ in the original system Hamiltonian. Then Eq. (19) becomes (up to some irrelevant constants):

$$e^{-βF(λ)} \propto \int d\mathbf{z} e^{-βH^*(\mathbf{Z}; λ)} e^{β\frac{(λ^*)^2}{2MΩ^2}} βJ(λ). \quad (22)$$

The free energy difference is given by

$$ΔF = -\frac{f(λ_*)^2 - f(λ_0)^2}{2MΩ^2} + ΔJ = -ΔG + ΔJ, \quad (23)$$

where

$$ΔG \equiv \frac{f(λ_*)^2 - f(λ_0)^2}{2MΩ^2}. \quad (24)$$

Note that an overall shift in $f(λ_0)$ simply changes the equilibrium positions and one is tempted to set $f(λ_0) = 0$ in order to simplify the calculation. However, in the analysis of some fluctuation theorems, where both forward and reverse processes are considered, this would cause a loss of generality. Unless $f(λ_0) = f(λ_*)$, or equivalently $ΔF = 0$, the reverse process is necessarily described with nonzero $f(λ_0)$.

In the next section we will consider the quantity:

$$\langle e^{-βW} \rangle_{mc} = \frac{\int d\mathbf{z} d\mathbf{z} \delta(H_{tot}(\mathbf{z}, \mathbf{z}; λ_0) - E) \exp \left[ β \left( \int_0^T dt \int f(t) X(t; \mathbf{Z}, \mathbf{z}) - ΔJ \right) \right]}{\int d\mathbf{z} d\mathbf{z} \delta(H_{tot}(\mathbf{z}, \mathbf{z}; λ_0) - E)} \quad (25)$$

which represents the average of $e^{-βW}$, over an ensemble of trajectories with microcanonically sampled initial conditions in the full phase space. We will obtain an exact expression for this average, Eq. (27) below, valid for any positive value of the parameter $β$. We will then show that in the thermodynamic limit, $N → ∞$, Eq. 1 emerges when the value of $β$ is set equal to the inverse temperature $β_{mc}$ associated with the microcanonical energy $E$ (see Eq. 36). That is:

$$\lim_{N→∞} \langle e^{-β_{mc}W} \rangle_{mc} = e^{-β_{mc}ΔF}. \quad (26)$$

Although we obtain this result for the case of a single system oscillator, it is easily generalized to any number $N_S$ of system oscillators, provided the limit $N → ∞$ is taken with $N_S$ fixed. Moreover, heuristic arguments [42] suggest that this result holds for more general systems with nonlinear interactions. However nonlinear models are difficult to treat analytically and careful numerical experiments are necessary to test this hypothesis in such models. In this work our aim is to focus on the analytically solvable harmonic oscillator model, for which exact results can be obtained.

### A. Exact Result for finite $N$

The integrals appearing in the denominator and numerator of Eq. (25) have been computed in Appendix A. The trick is to use an integral representation of the delta function in order to transform the integrals over the phase space variables into Gaussian integrals. Once the phase space integrals are performed, it is seen that the integration left over from the representation of the delta function can also be performed exactly. Below we cite the results and refer the reader to Appendix A for the technical details.

Combining Eq. (A15) for the denominator and Eq. (A31) for the numerator of Eq. (25) we obtain for Eq. (25):

$$\langle e^{-βW} \rangle_{mc} = e^{-βΔJ} e^{\tilde{β}g - \tilde{β}^{-1}D} \frac{N!}{(AD)^{N/2}} I_N(\sqrt{4AD}). \quad (27)$$
where

\[ A = E + \frac{f(\lambda_0)^2}{2M\Omega^2} - J(\lambda_0), \]

\[ D = \frac{\beta^2}{M\Omega^2} I_f, \]

\[ I_f = \int_0^\tau \int_0^t ds \, f(\lambda_s) h(t-s) \hat{f}(\lambda_s). \]

Eq. (27) is the exact expression for a system of one harmonic oscillator dragged up a slope in the presence of gravity and coupled to an environment modelled by N harmonic oscillators in a microcanonical ensemble at energy \( E \).

The effect of the environment is implicit in Eq. (27). The microcanonical temperature and \( A \) both depend on the total energy \( E \). Also \( I_f \) depends on \( h(t) \), which is the homogenous solution to the Langevin equation. Finally \( D \) and \( A \) contain factors of \( \Omega \) which is the renormalized frequency.

**B. The thermodynamic limit, \( N \to \infty \)**

In this limit we define energy per particle

\[ \mathcal{E} \equiv \frac{E}{N+1} = \frac{E}{N} + O(N^{-1}), \]

\[ A = N \left( \mathcal{E} + \frac{1}{N} \left( \frac{f(\lambda_0)^2}{2M\Omega^2} - J(\lambda_0) \right) \right) = N\mathcal{E} + O(1). \]

Eq. (27) becomes:

\[ \langle e^{-\beta W} \rangle_{mc} = e^{-\beta \mathcal{E} \mathcal{D}} e^{\beta \mathcal{D} - \beta^{-1} \mathcal{D}} \frac{N!}{(\mathcal{E} \mathcal{D} N)^{N/2}} I_N(\sqrt{4 \mathcal{E} \mathcal{D}}). \]

The asymptotic behaviour of the Bessel function \( I_N(x) \) is usually given for cases where \( x \) goes to zero or infinity while \( N \) is fixed. In Eq. (33) \( x \approx \sqrt{N} \) as \( N \to \infty \). Luckily there is a formula for the limit we are looking for:

\[ \lim_{N \to \infty} I_N(\sqrt{N} x) = \frac{1}{N!} \left( \frac{N x}{4} \right)^{N/2} e^{x/4}. \]

Using this formula with \( x = 4D\mathcal{E} \) in Eq. (33) we obtain

\[ \lim_{N \to \infty} \langle e^{-\beta W} \rangle_{mc} = e^{-\beta (\Delta \mathcal{E} \mathcal{D} - \mathcal{D})} e^{\mathcal{D} - \beta^{-1} \mathcal{D}} = e^{-\beta \Delta \mathcal{F} + (\mathcal{E} - \beta^{-1}) \mathcal{D}}, \]

which, like Eq. (27), is valid for arbitrary \( \beta > 0 \).

Since the quantity \( D \) depends on the protocol used to vary the parameter \( \lambda \) (see Eqs. (29), (30)), the right side of Eq. (27) generally cannot be expressed in terms of a difference between two state functions. However, consider the particular choice

\[ \beta = \beta_{mc} \equiv \mathcal{E}^{-1}, \]

corresponding to the inverse temperature given by the equipartition theorem for a collection of one-dimensional harmonic oscillators. For this choice the protocol dependent term vanishes, and – as advertised (Eq. (26)) – we recover the nonequilibrium work relation.

For more general models there is still going to be a well-defined relationship between energy per particle and temperature, but it will no longer be linear as in Eq. (36). In such models we expect Eq. (35) will be protocol independent only for the particular choice of \( \beta = \beta_{mc} \) which satisfies the corresponding relationship between energy per particle and temperature.

This concludes the derivation of work fluctuation relation for a system plus environment Brownian motion model in the microcanonical ensemble.

**IV. CROOKS’S FLUCTUATION RELATION**

**A. Probability Distribution of Work**

The moment generating function of work is defined as:

\[ G_W(s) = \langle e^{-isW} \rangle_{mc}. \]

It can be obtained from Eq. (27) by analytic continuation via \( \beta \to is \). The probability distribution of work is the Fourier transform of the moment generating function

\[ P_E(W) = \frac{1}{2\pi} \int_C ds e^{isW} G_W(s), \]

where \( P_E(W) \) has been defined earlier in the Introduction.

Assuming \( I_f > 0 \) and after some manipulations we are lead to the following formula:

\[ P_E(W) = \frac{N! 2^N}{2\pi \sqrt{N} 2\sigma_W^2} \int_c ds e^{s \frac{\langle W - \langle W \rangle \rangle}{\sqrt{2\pi \sigma_W}}} J_N(s), \]

where \( \langle W \rangle \equiv \Delta \mathcal{F} + \frac{I_f}{M\Omega^2} \) is the expectation value of work and \( \sigma_W^2 = 2AI_f/NM\Omega^2 \) is related to the variance of work in the canonical ensemble, as we will see later. The integral can be done analytically to give:

\[ P_E(W) = \frac{N!}{\Gamma(N + 1/2) \sqrt{2\pi \sigma_W^2}} \frac{1}{\sqrt{2\pi \sigma_W^2}} \left( W - \langle W \rangle \right)^{N-1/2} \times \left( 1 - \frac{(W - \langle W \rangle)^2}{2\sigma_W^2} \right)^N \times \Theta \left( \sqrt{2N\sigma_W} - |W - \langle W \rangle| \right). \]
This is the exact expression for the probability distribution of work done on a single harmonic oscillator coupled to an environment of \( N \) harmonic oscillators. The step function in Eq. (40) shows that the maximum deviation from the average value of work scales as the square root of \( N \). The fact that the work is bounded is a consequence of the fact that microcanonical ensemble describes a distribution with finite support over the phase space. By applying the method of Lagrange multipliers on the expression of work (18), with the constraint of fixed energy, the extreme values of work can be verified independently. This analysis also yields analytical expressions for the phase space trajectory of each particle for the realizations corresponding to extreme values of work.

The special case of \( I_f = 0 \) is very easy to handle. Using Eq. (A32) with \( \bar{\beta} \rightarrow i\bar{\sigma} \) in Eq. (38) we see that the resulting integral is the representation of the delta function. Hence \( P_{\Sigma}(W) = \delta(W - \Delta F) \) for \( I_f = 0 \).

Next we take the limit of infinite environment. The first factor of Eq. (40) can easily be seen to converge to one as \( N \rightarrow \infty \). For the third factor we use the formula:

\[
e^x = \lim_{N \to \infty} \left[ 1 + \frac{x}{N} \right]^N.
\]

(41)

Thus for the infinite environment limit we recover the Gaussian form:

\[
\lim_{N \to \infty} P_{\Sigma}(W) = \frac{e^{-\frac{(W - \langle W \rangle)^2}{2\sigma_{\Sigma}^2}}}{\sqrt{2\pi\sigma_{\Sigma}^2}},
\]

\[
\lim_{N \to \infty} \sigma_{\Sigma}^2 = 2E \frac{I_f}{M\Omega^2} = \frac{2}{\beta_{mc}} (\langle W \rangle - \Delta F).
\]

(42)

(43)

Eqs. (42) and (43) ensure that the nonequilibrium work and Crooks’s fluctuation relations are satisfied whenever \( \beta \) is identified with \( \beta_{mc} \) in Eqs. (1,2) [50]. The probability distribution (42) is identical to the probability distribution of work for the case where the initial conditions of the system plus environment are sampled from a canonical ensemble, with the temperature of the canonical ensemble related to the total energy of the microcanonical ensemble according to \( \beta = \beta_{mc} \). This can be easily checked, since all the integrations are Gaussian for the system plus environment canonical initial conditions (as opposed to the presence of the delta function in the microcanonical initial conditions).

B. Microcanonical Crooks Relation

Below we will show the validity of Eq. (3) for our specific model. First we note that the initial density of states \( \Sigma_i \) is given by the denominator of Eq. (25), and a similar expression applies to the final density of states \( \Sigma_f \) (only with \( \lambda_0 \) replaced by \( \lambda_f \)). From Eq. (A15) we have:

\[
\frac{\Sigma_f(E + W)}{\Sigma_i(E)} = \left( \frac{\bar{A}}{\bar{A}} \right)^N,
\]

where

\[
\bar{A} \equiv \langle E + W \rangle + \frac{f(\lambda_f)^2}{2M\Omega^2} - \frac{1}{2} M\Omega^2 \lambda_f^2.
\]

(45)

The expressions for \( \Sigma_f(E + W) \) and \( \bar{A} \) for the reverse process have been obtained from Eqs. (A15) and (32) by letting \( \lambda_0 \rightarrow \lambda_f \) and \( E \rightarrow E + W \). The probability distribution of work in the forward and reverse processes are given by:

\[
P_{E}(W) \propto \frac{1}{\sigma_{W \Sigma}^2} \left( \frac{2N\sigma_{W \Sigma}^2 - (W - \langle W \rangle)^2}{2N} \right)^{N-1/2} \times \Theta \left( \sqrt{2N}\sigma_{W} - |\langle W \rangle| \right),
\]

\[
P_{E+\lambda}(W) \propto \frac{1}{\sigma_{W \Sigma}^2} \left( \frac{2N\sigma_{W \Sigma}^2 - (\langle W \rangle-W)^2}{2N} \right)^{N-1/2} \times \Theta \left( \sqrt{2N}\sigma_{W} - |\langle W \rangle| \right),
\]

(46)

(47)

where \( \sigma_{W \Sigma}^2 = 2I_f \bar{A}/NM\Omega^2 \) and the following quantities for the time reversed process have been defined in analogy with the forward process:

\[
\langle \hat{W} \rangle \equiv \Delta F + \frac{I_f}{M\Omega^2} = \langle W \rangle - 2\Delta F = \frac{I_f}{M\Omega^2} - \Delta F,
\]

\[
\Delta \hat{F} \equiv \Delta F = \frac{f(\lambda_f)^2 - f(\lambda_0)^2}{2M\Omega^2} - \frac{M\Omega^2}{2} \left( \lambda_f^2 - \lambda_0^2 \right),
\]

\[
\sigma_{W}^2 = \frac{2I_f}{M\Omega^2 N} \left( E + W + \frac{f(\lambda_f)^2}{2M\Omega^2} - \frac{1}{2} M\Omega^2 \lambda_f^2 \right) = \frac{\bar{A}}{\bar{A}} \sigma_{W \Sigma}^2.
\]

(48)

(49)

(50)

Here we have used the fact that \( I_f \) is the same for the forward and reverse process by the virtue of the symmetry of its defining double integral. Based on these formulas we can write the left-hand side of Eq. (3) purely in terms of \( \lambda \) and \( I_f \), whereas the right-hand side is simply given by Eq. (44). Ignoring the step functions for the moment Eq. (3) can be written as

\[
\frac{P_{E}(W)}{P_{E+\lambda}(W)} = \left( \frac{\sigma_{W}^2}{\sigma_{W \Sigma}^2} \right)^N \left( \frac{2N\sigma_{W \Sigma}^2 - (W - \langle W \rangle)^2}{2N\sigma_{W}^2 - (\langle W \rangle-W)^2} \right) \left( \frac{\bar{A}}{\bar{A}} \right)^N \left( \frac{2N\sigma_{W \Sigma}^2 - (\langle W \rangle-W)^2}{2N\sigma_{W}^2 - (W - \langle W \rangle)^2} \right)
\]

\[
= \left( \frac{\bar{A}}{\bar{A}} \right)^N,
\]

(51)

This implies, again disregarding the step function for the moment,
This equality can be verified by calculating the following relations.

\[
\begin{align*}
\langle W \rangle + \langle \tilde{W} \rangle &= \frac{2I_f}{M\Omega^2}, \\
\langle \tilde{W} \rangle^2 - \langle W \rangle^2 &= -\frac{4I_f}{M\Omega^2} \Delta F, \\
\tilde{\sigma}_W^2 - \sigma_W^2 &= \frac{2I_f}{M\Omega^2N}(W - \Delta F).
\end{align*}
\]

Now we return to the question of whether the step functions appearing in \( P_E(W) \) and \( P_{E+W}(-W) \) are identical, so that they cancel when forming the ratio Eq. (3). To this end consider the conditions for the probabilities \( P_E(W) \) and \( P_{E+W}(-W) \) to vanish:

\[
\begin{align*}
2N\sigma_W^2 &= (W - \langle W \rangle)^2, \\
2N\tilde{\sigma}_W^2 &= (W + \langle \tilde{W} \rangle)^2.
\end{align*}
\]

To see that both conditions are identical observe that the difference of both equations gives Eq. (53) which has been shown to hold. Thus we have demonstrated the validity of the microcanonical Crooks relation in our particular model.

## V. ENSEMBLE EQUIVALENCE

In most textbooks the term ensemble equivalence is used to describe the following property of extensive systems: macroscopic physical quantities assume the same value in any equilibrium ensemble, i.e. microcanonical, canonical or grand canonical. In this section we will deviate from this definition in three ways. The system plus environment model considered in this paper is not extensive. Second, the thermodynamic limit is taken with the system size fixed (in the particular case treated here the system consists of a single oscillator). Thus the quantities we consider do not have to be macroscopic. Third, we will consider multi-time averages taken over nonequilibrium processes.

### A. Initial Phase Space Distribution

In this section we show that as \( N \to \infty \) the phase space probability density of the system oscillator approaches that of a canonical distribution if the probability distribution for the system plus environment closed system is given by the microcanonical distribution.

The derivation is similar to the previous sections.

\[
f_S(Z) = \frac{\int dZ \delta(H_{tot}(\lambda;Z,z) - E)}{\int dZ d\tilde{Z} \delta(H_{tot}(\lambda;Z,\tilde{Z}))}.
\]

For the numerator we again substitute the integral representation of the delta function to obtain:

\[
\int_C dz e^{-izE} \int d\tilde{Z} e^{iz(H_{sys}(Z) + H_{int}(\bar{Z},Z) + H_{ext}(\bar{Z}))} = \int_C dz \frac{e^{-iz(E - H^*(\lambda;Z))}}{z^N}.
\]

Here we used Eq. (A9). This integral can be obtained using the Cauchy theorem. The integrand has a pole of order \( N \) at the origin and the integration contour \( C \) is passing below this pole in the complex plane. For \( E > H^*(\lambda;Z) \) the contour can be closed from above to enclose the pole, and there is a nonzero outcome. For \( E < H^*(\lambda;Z) \) the contour is closed from below where the function is analytic. Hence the outcome of the integral is zero. The final expression for the normalized probability density of system degrees of freedom is given by:

\[
f_S(Z) = \frac{N\Omega}{2\pi} \frac{(E - H^*(0;Z))^{N-1}}{\mathcal{A}^N} \Theta(E - H^*(0;Z)).
\]

where \( \Theta \) denotes the Heaviside step function. The existence of the step function is a manifestation of the fact that the energy of the system oscillator cannot exceed that of the system plus environment.

Next consider the \( N \to \infty \) limit.

\[
\lim_{N \to \infty} f_S(Z) = \frac{\bar{\Omega}}{2\pi \bar{\varepsilon}} \lim_{N \to \infty} \left( 1 - \frac{H^*(Z)/\varepsilon}{N + 1} \right)^{N-1} = \frac{\bar{\Omega}}{2\pi \varepsilon} e^{-\varepsilon^{-1}H^*(Z)},
\]

where we used (41) in the last equality. The limit in Eq. (62) needs to be interpreted as follows: For any finite \( N \) the probability density (61) agrees with the canonical distribution (62) for small energies. However at large enough energies relative differences become significant. These differences would also show up at high order moments of position and momenta. The limit in Eq. (62) means that given an energy interval or equivalently a maximum order for the moments of interest, one can choose a large enough \( N \) such that the microcanonical result will agree with the asymptotic result to the desired degree.

Eq. (62) describes a Boltzmann state with the Hamiltonian of mean force replacing the system Hamiltonian. Note that the same probability distribution is obtained, albeit for any \( N \), if the system plus environment is sampled from a canonical distribution. In fact this is how the Hamiltonian of mean force is usually motivated. Eq. (62) states that for a large environment the phase space density of the system degrees of freedom is the same if the system plus environment is sampled from a canonical or microcanonical distribution.
B. Multi-time Correlations

The most general multi-time correlation function during the nonequilibrium process can be obtained from the generating functional

\[ Z_{\text{ens}}[j(\cdot)] = \langle e^{\int_0^t dt_j(t) X(t)} \rangle_{\text{ens}}, \]

(63)

where \( X(t) \) is the solution to the equations of motion with some initial conditions and the averaging is done over the desired ensemble. Here we will compare the generating functionals for the canonical and microcanonical ensembles. Any multi-time correlation can be obtained from the generating functional by applying differential operators to it, for example:

\[
\frac{\delta}{\delta j(t_1)} Z[j(\cdot)] |_{j=0} = \langle X(t_1) \rangle, \\
M \frac{\partial}{\partial t_1} \frac{\delta}{\delta j(t_1)} Z[j(\cdot)] |_{j=0} = \langle P(t_1) \rangle, \\
M \frac{\partial}{\partial t_1} \frac{\delta}{\delta j(t_1)} \cdots M \frac{\partial}{\partial t_k} \frac{\delta}{\delta j(t_k)} Z[j(\cdot)] |_{j=0} = \langle P(t_1) \cdots P(t_k) X(t_{k+1}) \cdots X(t_1) \rangle.
\]

(64)

(65)

(66)

Note that even the average appearing in nonequilibrium work relation Eq. (25) can be obtained from this generating functional via

\[
\langle e^{-\beta W} \rangle = e^{-\beta \Delta S} \langle e^{\beta \int_0^t dt_j(t) X(t)} \rangle = e^{-\beta \Delta S} Z[\beta \dot{f}(\cdot)].
\]

(67)

The results presented in this section thus include that of Sec. III A as a sub-case.

The calculation of the generating functional in both canonical and microcanonical ensembles is straightforward but tedious. For the canonical ensemble the calculation involves only Gaussian integrals and the use of properties of the solutions of the Langevin equation. The derivation for the microcanonical ensemble mimic closely the treatment presented in Appendix A. Here we only provide the final results.

\[
Z_{\text{can}}[j(\cdot)] = e^{\int_0^t dt_j(t) \left( \frac{\lambda(t)}{\hbar} \dot{X}(t) + \int_0^t dt \sigma_X(t-s) f(\lambda_s) \right)}
\times e^{\int_0^t dt_j(t) \left( \frac{\lambda(t)}{\hbar} \sigma_X(t) \right)}
\times \exp \left( \int_0^t dt_j(t) \langle X(t) \rangle + \int_0^t dt \int_0^t dt' \sigma_X(t, t') \langle j(t) j(t') \rangle \right),
\]

(68)

\[
Z_{\text{mc}}[j(\cdot)] = \exp \left( \int_0^t dt_j(t) \langle X(t) \rangle \right)
\times \left( \frac{N!}{(AD[j(\cdot)])^{N/2}} \right)^N \langle \sqrt{4AD[j(\cdot)]} \rangle.
\]

(69)

(70)

where \( \langle X(t) \rangle \) stands for the average position at time \( t \) and \( \sigma_X(t, t') = \langle X(t) X(t') \rangle - \langle X(t) \rangle \langle X(t') \rangle \) stands for the two time fluctuations of the position. We also defined \( \bar{D}[j(\cdot)] = \int_0^t dt \int_0^t dt' j(t) \ell(t-t') \rangle \) analogus to \( D \) whereby \( j(t) \) replaces \( \beta \dot{f}(\lambda) \).

The equivalence of \( Z_{\text{can}} \) and \( Z_{\text{mc}} \) in the \( N \to \infty \) limit for fixed \( j(\cdot) \) follows directly form the asymptotic formula of the Bessel function given by Eq. (34).

\[
\lim_{N \to \infty} Z_{\text{mc}}[j(\cdot)] = Z_{\text{can}}[\beta f(\cdot)].
\]

(71)

Similar to the discussion at the end of the previous section the meaning of this limit calls for some elaboration. As mentioned before the generating functional can be used to obtain correlation functions. For large but fixed \( N \) and given force protocol and temperature, the low order correlation functions for microcanonical and canonical ensembles will be very close. However one can always go to high enough orders where relative differences will become significant. The limit in Eq. (71) means that given a certain order we can always choose a large enough \( N \) such that the microcanonical correlation functions up to that order agree with the corresponding canonical correlation functions to the desired degree.

VI. DISCUSSION

In this paper we treated the exactly solvable model of a harmonic oscillator driven out of equilibrium by an external force and bilinearly coupled to an environment of \( N \) harmonic oscillators. An exact expression for the probability distribution of work, i.e. Eq. (40), is obtained for any value of \( N \), assuming that the combined system and environment is initially sampled from the microcanonical ensemble. Using this expression the microcanonical Crooks’s relation \( 3 \) is verified. In the limit of an infinite environment, nonequilibrium work relation \( 1 \) and Crooks’s fluctuation relation \( 2 \) are shown to hold. Finally in Sec. VB the equivalence of all multi-time correlations of the system oscillator in the canonical and microcanonical ensembles in the infinite environment limit is obtained.

Our results support the hypothesis that for macroscopically large environments the sampling of the initial conditions from a canonical or microcanonical distribution is equivalent as far as system observables are concerned.

In the model used in this paper the system oscillator is singled out not just by the virtue of the time-dependent force being only applied to it but also by the fact that all the environmental modes are coupled to it but not to each other. This may seem like a limitation of the model. However, the most general system of coupled harmonic oscillators, i.e. allowing for the environmental oscillators to couple among themselves, can be represented by the model used in this paper by first decomposing the environment into its eigenmodes, which in turn leads to a trivial change in the environment frequencies \( \omega_n \) and coupling constants \( c_n \) [51]. Since we allow for arbitrary \( \omega_n \),
and $c_n$ in our derivation, our model is able to represent any set of coupled harmonic oscillators.

**Appendix A: Derivation of the Main Result Eq. (25)**

In this appendix we will compute the integrals appearing in Eq. (25). But first we review the integral representation of the delta function to be used in the derivation.

### a. The Delta Function

The delta functions make the integrals in (25) difficult to evaluate. To get around this difficulty we invoke the following integral representation of the delta function:

$$
\delta(H_{tot}(\mathbf{z}, \lambda) - E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{-i s (H_{tot}(\mathbf{z}, \lambda) - E)} \tag{A1}
$$

The logic behind this is to convert the phase space integral into a simple Gaussian integral. After we perform that integral we will be able to do the $s$ integration as well.

Observe that the integral formula for the delta function can be modified by allowing the integration variable $s$ to have a constant imaginary part. We rename it $\zeta$ to emphasize the complex nature:

$$
\frac{1}{2\pi} \int_{-\infty}^{\infty} i \zeta \exp(-i \zeta (H_{tot}(\mathbf{z}, \lambda) - E)) = \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{-i s (H_{tot}(\mathbf{z}, \lambda) - E)} \tag{A2}
$$

$$
e^{-i \epsilon (H_{tot}(\mathbf{z}, \lambda) - E)} \frac{1}{2\pi} \int_{-\infty}^{\infty} ds e^{-i s (H_{tot}(\mathbf{z}, \lambda) - E)} \tag{A3}
$$

$$
e^{-i \epsilon (H_{tot}(\mathbf{z}, \lambda) - E)} \delta(H_{tot}(\mathbf{z}, \lambda) - E) \tag{A4}
$$

$$\delta(H_{tot}(\mathbf{z}, \lambda) - E) = \frac{1}{2\pi} \int_{C} d\zeta e^{-i \zeta (H_{tot}(\mathbf{z}, \lambda) - E)} \tag{A5}
$$

In the complex plane this contour passes parallel to the real axis, and is shifted down by an amount $\epsilon$. One could reach the same result by noting that the integrand in (A1) is an analytical function everywhere and thus the integration contour can be shifted down without changing the value of the integral. We will denote this contour by $C$ and use

$$\delta(H_{tot}(\mathbf{z}, \lambda) - E) = \frac{1}{2\pi} \int_{C} d\zeta e^{-i \zeta (H_{tot}(\mathbf{z}, \lambda) - E)} \tag{A6}
$$

### b. Denominator of Eq. (25)

The denominator of Eq. (25) gives the density of states associated with the initial Hamiltonian. Using Eq. (A6), we write this density as:

$$
\Sigma_i(E) = \frac{1}{2\pi} \int_{C} d\zeta e^{i \zeta E} \int dZ e^{-i \zeta (H_{tot}(\mathbf{z}, \lambda) - E)} \times \int d\zeta e^{-i \zeta (H_{int}(\mathbf{z}, \lambda) + H_{env}(\mathbf{z}))} \tag{A7}
$$

We begin by evaluating the last factor appearing above:

$$
\int d\zeta e^{-i \zeta (H_{tot}(\mathbf{z}, \lambda) + H_{env}(\mathbf{z}))} = (\frac{2\pi}{i\omega})^N \exp \left(i \zeta X^2 \sum_n \frac{c_n^2}{2m_n \omega_n^2} \right) \tag{A8}
$$

$$
= (\frac{2\pi}{i\omega})^N e^{i \zeta M \gamma(0) X^2} \tag{A9}
$$

where $\omega^N \equiv \omega_1 \cdots \omega_N$. The integrals are convergent due to the negative imaginary part of $\zeta$ as the contour $C$ is shifted below the real axis.

Using the definition of the renormalized frequency (11) we get:

$$
\Sigma_i(E) = \frac{1}{2\pi} (\frac{2\pi}{i\omega})^N \int_{C} d\zeta \frac{e^{i \zeta E}}{\zeta N} \int d\zeta e^{-i \zeta H^r(\mathbf{z}, \lambda)} \tag{A10}
$$

$$
= \frac{1}{i\Omega} (\frac{2\pi}{i\omega})^N \int_{C} d\zeta \frac{e^{i \zeta A}}{\zeta N+1} \tag{A11}
$$

where in the last equality we used the definition of $A$ introduced in Eq. (28). The sign of $A$ will play an important role later in the derivation.

$$
A = E + J(\lambda) - \frac{f(\lambda)^2}{2M\Omega^2} = H_{tot}(\mathbf{z}, \lambda) + J(\lambda) - \frac{f(\lambda)^2}{2M\Omega^2} \tag{A12}
$$

$$
= \frac{P^2}{2M} + \frac{1}{2M\Omega^2} \left( X - \frac{f(\lambda)^2}{M\Omega^2} \right)^2
+ \sum_{n=1}^{N} \left[ \frac{p_n^2}{2m_n} + \frac{1}{2m_n \omega_n^2} \left( x_n - \frac{c_n}{m_n \omega_n} X \right)^2 \right] \geq 0. \tag{A13}
$$

$A = 0$ occurs only for a single point in the phase space. In the rest of this paper we take $A > 0$. The integral in Eq. (A11) can be evaluated by enclosing the residue at the origin:

$$
\int_{C} d\zeta \frac{e^{i \zeta A}}{\zeta N+1} = \frac{2\pi i}{N!} iN \zeta A^N. \tag{A14}
$$

which finally brings us to the expression:

$$
\Sigma_i(E) = \frac{1}{N!} (\frac{2\pi}{i\Omega \omega^N}) A^N. \tag{A15}
$$

### c. Numerator of Eq. (25)

We begin by using Eq. (A6) to express the numerator as follows:
\( e^{-\beta \Delta \gamma} \frac{1}{2\pi} \int_C dz e^{izE} \int dZ e^{-iz(H_{syp}(Z,\lambda_0) + H_{int}(Z,z) + H_{env}(z))} \times e^{\beta \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) [X h(t)+P g(t)+\int_0^t ds \bar{g}(t-s) f(\lambda_0)]} \)

\( = e^{-\beta \Delta \gamma} \frac{1}{2\pi} \int_C dz e^{izE} \int dZ e^{-iz(H_{syp}(Z,\lambda_0) + X [\beta \int_0^t dt \bar{f}(\lambda_0) h(t)-2M \beta \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) g(t-s) + P \beta \int_0^t dt \bar{f}(\lambda_0)]} \times \int dZ e^{-iz(H_{int}(Z,z) + H_{env}(z))} \times \int dZ e^{-i\int_0^t dt \bar{f}(\lambda_0) g(t-s) \sum_n c_n \left( x_n \cos(\omega_n s) + \frac{\beta \int_0^t dt \bar{f}(\lambda_0)}{M \Omega^2} \right)} \).

To simplify the notation we define

\( \phi_n = c_n \bar{\beta} \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) g(t-s) \cos(\omega_n s), \quad (A18) \)

\( \psi_n = c_n \bar{\beta} \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) g(t-s) \sin(\omega_n s), \quad (A19) \)

\( I_h = \int_0^t dt \bar{f}(\lambda_0) h(t), \quad (A20) \)

\( I_g = M \bar{\Omega} \int_0^t dt \bar{f}(\lambda_0) g(t). \quad (A21) \)

After integration by parts the second factor of the first line of Eq. (A17) can be rewritten as

\( e^{\beta \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) g(t-s) f(\lambda_0)} = e^{\beta g - \frac{\beta}{M \Omega^2} I_f - \frac{\beta}{M \Omega^2} \int_0^t dt \bar{f}(\lambda_0) I_h}, \quad (A22) \)

where \( I_f \) has been defined in (30). The last Gaussian integral over \( z \) in Eq. (A17) yields:

\( \left( \frac{2\pi}{i\omega} \right)^N e^{iX^2 \sum_n \phi_n^2 \frac{2}{m_n \omega_n^2} + X \sum_n \frac{\phi_n \psi_n}{m_n \omega_n^2} - \frac{i}{2} \sum_n \phi_n^2 \frac{2}{m_n \omega_n^2}}. \quad (A23) \)

The first term in the exponent above can be added to \(-izH_{syp}(Z,\lambda_0)\) on the second line of Eq. (A17) to give \(-izH^*(Z,\lambda_0)\). The second term in the exponent of Eq. (A23) can be shown to be equal to:

\( X \sum_n \frac{\phi_n \psi_n}{m_n \omega_n^2} = X \bar{\beta} M \int_0^t dt \int_0^t ds \bar{f}(\lambda_0) g(t-s) \gamma(s). \quad (A24) \)

This term cancels the corresponding term on the second line of Eq. (A17).

The third term of the sum in the exponent of Eq. (A23) is independent of \( Z \) and can be pulled out of the \( Z \) integration. Using the definitions of \( \phi_n \) and \( \psi_n \) it can also be written as

\( B = \sum_n \frac{\phi_n^2 + \psi_n^2}{2m_n \omega_n^2} = M \bar{\beta}^2 \int_0^t dt \int_0^t dt' \bar{f}(t) \bar{f}(t') \int_0^t ds ds' g(t-s) \gamma(s-s') g(t'-s'). \quad (A25) \)

In Appendix B it is shown that the expression for \( B \) can be simplified further by using the relations (17) to obtain:

\( 2 \int_0^t dt \int_0^t ds ds' g(t-s) \gamma(s-s') g(t'-s') = \frac{h(t)}{M^2 \Omega^2} - \frac{h(t) h(t')}{M^2 \Omega^2} - g(t) g(t'), \quad (A26) \)

\( B = \frac{\bar{\beta}^2}{2M \Omega^2} \left( 2I_f - I_f^2 - I_g^2 \right). \quad (A27) \)

The factor of two in front of \( I_f \) is due to the fact that both integration limits are from 0 to \( \sigma \) in Eq. (A25) whereas the second integral is from 0 to \( t \) in Eq. (30). Note that \( B \geq 0 \), which can be seen from its definition (A25). Together with (A27) this indicates that \( I_f \geq 0 \). This fact will soon be used in the following derivation.

The \( Z \) integration of Eq. (A17) yields:

\( \int dZ e^{-izH^*(Z,\lambda_0) + X \bar{\beta} I_h} \quad (A28) \)

\( = \frac{2\pi}{i\Omega z} e^{-\frac{i(\bar{\beta} h(t)+iA(t)) z^2}{\beta M^2 \Omega^2}} \quad (A28) \)

Gathering all the terms Eq. (A17) becomes, after a number of cancellations:

\( \left( \frac{2\pi}{iN+1, \Omega^N z} \right)^N e^{-\beta \Delta \gamma} e^{\bar{\beta} \gamma - \frac{\beta}{M \Omega^2} I_f} \int_C dz e^{iZ - \frac{\beta}{M \Omega^2} I_f} \).

In order to proceed further we have to treat two cases separately: \( I_f > 0 \) and \( I_f = 0 \). For the more general case \( I_f > 0 \) we define \( D \) as in (29) and change the integration
variable to \( z \rightarrow z\sqrt{\mathcal{D}/\mathcal{A}} \), where \( \mathcal{D}/\mathcal{A} > 0 \) as explained before. Then the integral becomes
\[
\left( \frac{\mathcal{A}}{\mathcal{D}} \right)^{N/2} \int_C dz \frac{e^{i\sqrt{\mathcal{D}/\mathcal{A}}(z^{-1}/2)}}{z^{N+1}}. \tag{A30}
\]
which is proportional to a Bessel function of second kind:
\[
(2\pi i) J_N(i2\sqrt{\mathcal{D}/\mathcal{A}}) = (2\pi i) i^N I_N(\sqrt{4\mathcal{A}\mathcal{D}}). \tag{A31}
\]
Combining (A15) and (A31) we obtain the final result (27).

In the \( I_f = 0 \) case the integral in (A29) is identical to Eq. (A11), and cancels that term in Eq. (25) to yield:
\[
\langle e^{-\bar{\beta}W} \rangle_{mc} = e^{-\bar{\beta}\Delta F}. \tag{A32}
\]
Note that this is true for any choice of \( \bar{\beta} \) irrespective of the total energy \( E \). As is shown in Sec. IV A, this is a consequence of the fact that \( I_f = 0 \) corresponds to a delta function work distribution at \( W = \Delta F \). One example of this case is given in Ref. [48]. For realistic environments we expect \( I_f > 0 \).²

Finally we note that the result of \( I_f = 0 \) case, i.e. (A32), can be recovered from that of \( I_f > 0 \) case by taking the limit \( I_f \rightarrow 0 \) (or equivalently \( \mathcal{D} \rightarrow 0 \)) in (27) and using the asymptotic formula \( I_N(x) \approx x^N / N! \mathcal{A}^N \) as \( x \rightarrow 0 \). Thus Eq. (27) is valid for the most general case \( I_f \geq 0 \).

Appendix B: Derivation of Eq. (A26)

To derive Eq. (A25) we follow the method described in [47]. First observe that like any even function the damping kernel can be written as:
\[
\gamma(t) = \gamma(t)\theta(t) + \gamma(-t)\theta(-t). \tag{A33}
\]
We substitute this form into Eq. (A25) and then take Laplace transforms with respect to \( t \) and \( t' \) denoted by the operators \( \mathcal{L}_t(z) \) and \( \mathcal{L}_{t'}(z') \) respectively.
\[
\mathcal{L}_{t'}(z')\mathcal{L}_t(z) \times \left\{ 2 \int_0^t ds \int_0^{t'} ds' g(t-s)\gamma(s-s')\theta(s-s')g(t'-s') + 2 \int_0^t ds \int_0^{t'} ds' g(t-s)\gamma(s'-s)\theta(s'-s)g(t'-s') \right\}. \tag{B1}
\]
Let us consider the first term. If we treat \( \gamma(s-s')\theta(s-s') \) as a function of \( s \) only, the Laplace transform with respect to \( t \) has the form of a convolution of this function with \( g(t-s) \). The result is the product of Laplace transforms of each function. Using the formula for the Laplace transform of time-shifted functions:
\[
\mathcal{L}_t(z) \left\{ f(t-a)\theta(t-a) \right\} = e^{-az} f(z), \tag{B2}
\]
we get for the first term of Eq. (B1):
\[
\mathcal{L}_{t'}(z') \left\{ 2 \int_0^t ds' g(t'-s')e^{-z's'}\gamma(z) \right\} = 2 \frac{\hat{g}(z)\hat{g}(z')}{z + z'} \frac{\hat{\gamma}(z)}{z + z'}. \tag{B3}
\]
An identical calculation, except for the change of the order of Laplace transforms, gives \( 2 \frac{\hat{g}(z)\hat{g}(z')}{z + z'} \hat{\gamma}(z') \) for the second term of Eq. (B1). To write the final answer independent of the damping kernel we use Eq. (16) to express \( \hat{\gamma} \) in terms of \( \hat{g} \) and \( \hat{h} \).
\[
\hat{g}(z)\hat{g}(z') \frac{\hat{h}(z)\hat{g}(z') + \hat{h}(z')\hat{g}(z)}{M(z + z')} - \hat{g}(z)\hat{g}(z') = \hat{h}(z)\hat{g}(z') + \hat{g}(z)\hat{h}(z') \frac{1}{M(z + z')} - \hat{g}(z)\hat{g}(z'). \tag{B4}
\]
Then write the first term exclusively in terms of \( \hat{h} \) again using Eq. (16), i.e. \( \hat{g}(z) = \left( 1 - \hat{h}(z) / M\Omega^2 \right) \).
\[
\frac{1}{M^2\Omega^2} \frac{\hat{h}(z) + \hat{h}(z')}{z + z'} - \hat{h}(z)\hat{h}(z') / M^2\Omega^2 - \hat{g}(z)\hat{g}(z'). \tag{B5}
\]
Using \( \mathcal{L}_t(z)\mathcal{L}_{t'}(z') \left\{ \frac{\hat{h}(z)}{z + z'} \right\} = \mathcal{L}_t(z) \left\{ e^{-tz} \hat{h}(z) \right\} = h(t-t')\theta(t-t') \), it is easily verified that the double inverse Laplace transform of Eq. (B5) proves Eq. (A25).

ACKNOWLEDGMENTS

The authors would like to thank Dr. Yury A. Brychkov for the proof of Eq. (34) as outlined in the footnote. C.J. acknowledges support from the National Science Foundation (USA) under grant DMR-1206971. Y.S. is grateful to Perimeter Institute for Theoretical Physics for their hospitality, where part of this work has been done.

² \( I_f \geq 0 \) is a direct consequence of and can be proven directly using the fact that \( \gamma(t) \) is a positive function. Realistic environments will most likely be described by strictly positive dissipation kernels which in turn yield the strict inequality \( I_f > 0 \) via application of Bohner’s theorem [52]. The reason behind this is that for an environment with strictly positive dissipation kernel the average dissipated energy is always positive, whereas for a positive dissipation kernel it is possible that after a while all the dissipated energy, but not more, can flow back into the system. For any finite \( N \) and arbitrarily large \( \tau \) this is certainly the case. But for large environments and realistic \( \tau \) we expect this special case to be very improbable. \( I_f < 0 \) can not occur in our model as mentioned before, which is due to the fact that the harmonic oscillator environment is a passive environment.
[1] C. Bustamante, J. Liphardt, and F. Ritort, Physics Today 58, 43 (2005)
[2] C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997)
[3] C. Jarzynski, Phys. Rev. E 56, 5018 (Nov 1997), http://link.aps.org/doi/10.1103/PhysRevE.56.5018
[4] G. Crooks, Journal of Statistical Physics 90, 1481 (1998), ISSN 0022-4715, http://dx.doi.org/10.1023/A:1001023206217925
[5] G. E. Crooks, Phys. Rev. E 60, 2721 (Sep 1999), http://link.aps.org/doi/10.1103/PhysRevE.60.2721
[6] G. E. Crooks, Phys. Rev. E 61, 2361 (MAR 2000)
[7] C. Jarzynski, Annual Review of Condensed Matter Physics 2, 329 (2011), http://www.annualreviews.org/doi/pdf/10.1146/annurev-conmatphys-062910-140506
[8] J. Liphardt, S. Dumont, S. Smith, I. Tinoco, and C. Bustamante, Science 296, 1832 (2002), http://dx.doi.org/10.1126/science.1071152
[9] F. Douarche, S. Ciliberto, and A. Petrosyan, Journal of Statistical Mechanics: Theory and Experiment 2005, P09011 (2005)
[10] V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger, Phys. Rev. Lett. 96, 070603 (Feb 2006), http://link.aps.org/doi/10.1103/PhysRevLett.96.070603
[11] F. Douarche, S. Ciliberto, A. Petrosyan, and I. Rabbiosi, EPL (Europhysics Letters) 70, 593 (2005)
[12] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Nature 437, 231 (SEP 2005)
[13] N. C. Harris, Y. Song, and C.-H. Kiang, Phys. Rev. Lett. 99, 068101 (Aug 2007), http://link.aps.org/doi/10.1103/PhysRevLett.99.068101
[14] C. Jarzynski, Journal of Statistical Mechanics: Theory and Experiment 2004, P09005 (2004), http://stacks.iop.org/1742-5468/2004/i=09/a=P09005
[15] H. Hasegawa, Phys. Rev. E 84, 011145 (2011)
[16] O. Mazonka and C. Jarzynski, “Exactly solvable model illustrating far-from-equilibrium predictions,” (DEC 1999), arXiv:cond-mat/991212
[17] F. Ritort, C. Bustamante, and I. Tinoco Jr., Proc. Natl. Acad. Sci. USA 99, 13544 (OCT 2002)
[18] F. Ritort, J. Stat. Mech.: Theor. Exp., P10016(OCT 2004)
[19] A. Imparato and L. Peliti, Europhys. Lett. 69, 643 (FEB 2005)
[20] T. Speck and U. Seifert, Eur. Phys. J. B 43, 521 (FEB 2005)
[21] A. Dhar, Phys. Rev. E 71, 036126 (MAR 2005)
[22] R. C. Lua and A. Y. Grosberg, J. Phys. Chem. B 109, 6805 (APR 2005)
[23] I. Bena, C. Van den Broeck, and R. Kawai, Europhys. Lett. 71, 879 (SEP 2005)
[24] S. Pressé and R. Silbey, Phys. Rev. E 74, 061105 (2006)
[25] R. D. Astumian, J. Chem. Phys. 126, 111102 (2007)
[26] G. E. Crooks and C. Jarzynski, Phys. Rev. E 75, 021116 (2007)
[27] A. Jayannavar and M. Sahoo, Phys. Rev. E 75, 032102 (2007)
[28] S. Defner and E. Lutz, Phys. Rev. E 77, 021128 (2008)
[29] J. Sung, Phys. Rev. E 77, 042101 (2008)
[30] P. Talkner, P. S. Burada, and P. H. arXiv(2008)
[31] S. Defner, O. Abah, and E. Lutz, Chem. Phys. 375, 200 (2010)
[32] H. Hijar and J. M. Ortiz de Zarate, Eur. Phys. J. 31, 1097 (2010)
[33] J. I. Jimenez-Aquino, F. J. Uribe, and R. M. Velasco, J. Phys. A: Math. Theor. 43, 255001 (2010)
[34] W. A. M. Morgado and D. O. Soares-Pinto, Phys. Rev. E 82, 021112 (2010)
[35] M. Ohzeki and H. Nishimori, J. Phys. Soc. Jpn 79, 084003 (2010)
[36] T. Speck, J. Phys. A: Math. Theor. 44, 305001 (2011)
[37] A. Ryabov, M. Dierl, P. Chvosta, M. Einax, and P. Maass, J. Phys. A: Math. Theor. 46, 075002 (2013)
[38] R. Balian, From Microphysics to Macrophysics: Methods and Applications of Statistical Physics, Volume I (Theoretical and Mathematical Physics) (Springer, 2006) ISBN 3540454691
[39] J. L. Lebowitz, J. K. Percus, and L. Verlet, Phys. Rev. 153, 250 (Jan 1967)
[40] C. Jarzynski, Phys. Rev. E 73, 046105 (Apr 2006), http://link.aps.org/doi/10.1103/PhysRevE.73.046105
[41] C. Jarzynski, Journal of Statistical Physics 98, 77 (2000), ISSN 0022-4715
[42] S. Park and K. Schulten, The Journal of Chemical Physics 120, 5946 (2004), http://link.aip.org/link/?JCP/120/5946/1
[43] B. Cleuren, C. Van den Broeck, and R. Kawai, Phys. Rev. Lett. 96, 050601 (Feb 2006), http://link.aps.org/doi/10.1103/PhysRevLett.96.050601
[44] Y. Subasi, C. H. Fleming, J. M. Taylor, and B. L. Hu, Phys. Rev. E 86, 061132 (Dec 2012), http://link.aps.org/doi/10.1103/PhysRevE.86.061132
[45] R. Zwanzig, Journal of Statistical Physics 9, 215 (1973), ISSN 0022-4715
[46] G. Ford and M. Kac, Journal of Statistical Physics 46, 803 (1987), ISSN 0022-4715, http://dx.doi.org/10.1007/BF01011142
[47] T. Mai and A. Dhar, Phys. Rev. E 75, 061101 (Jun 2007)
[48] C. Jarzynski, Comptes Rendus Physique 8, 495 (2007), ISSN 1631-0705
[49] J. G. Kirkwood, The Journal of Chemical Physics 3, 300 (1935), http://link.aip.org/link/?JCP/3/300/1
[50] Y. Subasi and B. L. Hu, Phys. Rev. E 85, 011112 (Jan 2012), http://link.aps.org/doi/10.1103/PhysRevE.85.011112
[51] G. W. Ford, J. T. Lewis, and R. F. O’Connell, Phys. Rev. A 37, 4419 (Jun 1988)
[52] R. Bhatia, Positive Definite Matrices (Princeton in Applied Mathematics) (Princeton University Press, 2006) ISBN 0691129185