Work-probability distribution in systems driven out of equilibrium

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We derive the differential equation describing the time evolution of the work probability distribution function of a stochastic system which is driven out of equilibrium by the manipulation of a parameter. We consider both systems described by their microscopic state or by a collective variable which identifies a quasiequilibrium state. We show that the work probability distribution can be represented by a path integral, which is dominated by "classical" paths in the large system size limit. We compare these results with simulated manipulation of mean-field systems. We discuss the range of applicability of the Jarzynski equality for evaluating the system free energy using these out-of-equilibrium manipulations. Large fluctuations in the work and the shape of the work distribution tails are also discussed.

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I. INTRODUCTION

Recent improvements in micromanipulation techniques have made it possible to observe experimentally work fluctuations and to measure the probability distribution of the work exerted on a system subject to external manipulation. In particular, the probability distribution of the work has been measured in RNA pulling experiments [1,2] and for micrometer-sized colloidal particles dragged through a fluid [3]. Usually, because of technical limitations, this class of experiments is characterized by time scales much faster than the typical system relaxation time. This hinders the possibility to perform the experiments in quasistatic conditions and thus to obtain direct measurements of the system thermodynamic state variables. The importance of the knowledge of work distributions in such experiments resides in the fact that one can evaluate the free energy difference between the final and the initial state of the system by exploiting the Jarzynski equality (JE) [4–6]

$$\langle e^{-\beta W}\rangle = e^{-\beta \Delta F}. \tag{1}$$

According to previous work [2], a precise knowledge of the tails in the distributions provides information on how many experiments are needed in order to evaluate correctly the free energy difference of a system using nonequilibrium experiments. Thus *a priori* estimates of $P(W)$ are in principle needed to evaluate the actual usefulness of this approach.

In two recent works [7,8], we introduced and discussed a differential equation describing the time evolution of the probability distribution of the work done on a system by manipulating an external field (force) μ, according to a given protocol $\mu(t)$. In particular, in Ref. [7], we considered the case of a system characterized by a discrete phase space, while in Ref. [8] we considered a mean field system characterized by a generic equilibrium free energy $\mathcal{F}_\mu(M)$.

The aim of this paper is to extend those works by exploiting an approach due to Felix Ritort [9]. In particular, we first derive explicitly the differential equations governing the time evolution of $P(W,t)$. We then derive an expression of the work probability distribution of a system described by a collective variable, on the hypothesis that, during the manipulation, the system finds itself in a quasiequilibrium state constrained by the value of that coordinate. We solve the resulting equation by path integrals and show that, in the limit of large system size, the path integral is dominated by the classical path which satisfies canonical equations of motion, and suitable boundary conditions. The expression for the probability distribution function follows straightforwardly. We highlight the analogy between the path functionals obtained in this way and classical thermodynamics. We apply the obtained results to some simple systems and we explore in particular the possibility of the existence of exponential tails in the work probability distribution: such tails are related, via the thermodynamic analogy, to phase transitions in the path distribution. We show that, contrary to what was conjectured in Ref. [9] on the basis of numerical evidence, such tails are not present in a paramagnet, or in a ferromagnet above the critical temperature, but are present in a mean-field ferromagnet below the critical temperature, provided the manipulating protocol is fast enough. The implications of our results are further discussed.

II. PROBABILITY DISTRIBUTION OF THE WORK FOR THE MICROSCOPIC COORDINATES

In this section, we see how the probability distribution function of the work W exerted on a system can be evaluated by considering the joint probability distribution of W and the microscopic state of the system. This equation was derived in Refs. [7,10] (see also [6]). Let us first consider a system whose microscopic state i can take on a finite number of values. To each such state is assigned an energy value $H_i(\mu)$, where μ is a parameter which is manipulated according to some protocol $\mu(t)$, starting at $t=0$. We assume that the evolution of the system is described by a Markovian stochastic process: given, for all pairs (i,j), the transition rate $k_{ij}(t)$

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from state j to state i at time t, the system satisfies the set of differential equations

$$\frac{\partial p_i}{\partial t} = \sum_{j(\neq i)} [k_{ij}(t)p_j(t) - k_{ji}(t)p_i(t)], \tag{2}$$

where $p_i(t)$ is the probability that the system is found at state i at time t. Let $p_i^{\mathrm{eq}}(\mu)$ represent the equilibrium distribution corresponding to a given value of μ. We have

$$p_i^{\mathrm{eq}}(\mu) = \frac{e^{-\beta H_i(\mu)}}{Z_\mu}, \tag{3}$$

where $Z_\mu = \Sigma_i e^{-\beta H_i(\mu)} = e^{-\beta F_\mu}$ is the partition function corresponding to the value μ of the parameter, and F_μ the corresponding free energy. We require that the transition rates $k_{ij}(t)$ are compatible with the equilibrium distribution $p_i^{\mathrm{eq}}(\mu)$, i.e., that, for any i,

$$\sum_{j(\neq i)} [k_{ij}(t)p_j^{\mathrm{eq}}(\mu(t)) - k_{ji}(t)p_i^{\mathrm{eq}}(\mu(t))] = 0. \tag{4}$$

We assume that the system is at equilibrium at $t=0$, and therefore that $p_i(t)$ satisfies the initial condition

$$p_i(t=0) = p_i^{\mathrm{eq}}(\mu(0)). \tag{5}$$

As pointed out in Ref. [7], the function $p_i(t)$ does not provide sufficient information on the work performed on the system during the manipulation process. We can, however, consider the joint probability distribution $\Phi_i(W,t)$ that the system is found in state i, having received a work W, at time t. If the system is in the state i at time t, the infinitesimal work δW_i done on it in the interval δt reads

$$\delta W_i = \dot{\mu}\frac{\partial H_i(\mu(t))}{\partial \mu}\delta t. \tag{6}$$

We have thus

$$\begin{aligned}\Phi_i(W,t+\delta t) &\simeq \Phi_i(W-\delta W_i,t) + \delta t \sum_{j(\neq i)} [k_{ij}(t)\Phi_j(W-\delta W_j,t) \\ &\quad - k_{ji}(t)\Phi_i(W-\delta W_i,t)] \\ &= \Phi_i(W,t) - \delta t \dot{\mu} H_i'(\mu(t))\partial_W \Phi_i(W,t) \\ &\quad + \delta t \sum_{j(\neq i)} [k_{ij}(t)\Phi_j(W,t) - k_{ji}(t)\Phi_i(W,t)].\end{aligned} \tag{7}$$

The last equality is obtained by substituting the expression for δW_i given in Eq. (6) and by taking the first order expansion in δt of the right-hand side (rhs). We are now able to write the set of differential equations which describe the distribution functions $\Phi_i(W,t)$

$$\frac{\partial \Phi_i}{\partial t} = \sum_{j(\neq i)} [k_{ij}(t)\Phi_j(W,t) - k_{ji}(t)\Phi_i(W,t)] - \dot{\mu} H_i'(\mu(t))\frac{\partial \Phi_i}{\partial W}. \tag{8}$$

The joint probability distribution $\Phi_i(W,t)$ satisfies the initial condition

$$\Phi_i(W,0) = \delta(W)p_i^{\mathrm{eq}}(\mu(0)). \tag{9}$$

We are interested in the state-independent work probability distribution $P(W,t)$ defined by

$$P(W,t) = \sum_i \Phi_i(W,t). \tag{10}$$

It is convenient to introduce the generating function of Φ_i with respect to the work distribution, defined by

$$\Psi_i(\lambda,t) = \int dW e^{\lambda W}\Phi_i(W,t). \tag{11}$$

(Notice that we adopt here, for later convenience, the opposite sign convention with respect to that adopted in Ref. [8].) We assume that $\Phi_i(W,t)$ vanishes fast enough, as $|W| \to \infty$, for $\Psi_i(\lambda,t)$ to exist for any λ. The function Ψ_i satisfies the initial condition

$$\Psi_i(\lambda,t_0) = \frac{\exp[-\beta H_i(\mu(0))]}{Z_{\mu(0)}}, \tag{12}$$

and evolves according to the differential equation

$$\begin{aligned}\partial_t \Psi_i(\lambda,t) &= \int dW e^{\lambda W}\partial_t \Phi_i(W,t) = \int dW e^{-\lambda W}\left\{\sum_{j(\neq i)} [k_{ij}\Phi_j \right. \\ &\quad \left. - k_{ji}\Phi_i] - \dot{\mu}\frac{\partial}{\partial \mu}\frac{\partial \Phi_i}{\partial W}\right\} = \sum_{j(\neq i)} [k_{ij}\Psi_j - k_{ji}\Psi_i] \\ &\quad + \lambda \dot{\mu}\frac{\partial H_i(\mu(t))}{\partial \mu}\Psi_i(\lambda,t).\end{aligned} \tag{13}$$

Exploiting Eq. (4), it is easy to verify that if $\lambda = -\beta$, for any i at any time t, the solution of Eq. (13), with the initial condition (12), reads

$$\Psi_i(-\beta,t) = \frac{e^{-\beta H_i(\mu(t))}}{Z_{\mu(0)}} = \frac{Z_{\mu(t)}}{Z_{\mu(0)}}p_i^{\mathrm{eq}}(\mu(t)). \tag{14}$$

We can thus straightforwardly verify the Jarzynski equality:

$$\begin{aligned}\langle e^{-\beta W}\rangle &= \int dW e^{-\beta W}P(W,t) = \sum_i \int dW e^{-\beta W}\Phi_i(W,t) \\ &= \sum_i \Psi_i(-\beta,t) = \frac{Z_{\mu(t)}}{Z_{\mu(0)}}\sum_i p_i^{\mathrm{eq}}(\mu(t)) = \frac{Z_{\mu(t)}}{Z_{\mu(0)}} \\ &= e^{-\beta(F(\mu(t))-F(\mu(0)))}.\end{aligned} \tag{15}$$

It is thus possible, in principle, to evaluate the probability distribution function of the work W by solving the equations (8) or (13) for all the microscopic states i. This approach has been implemented in Ref. [7] for a simple model of a biopolymer.

III. COLLECTIVE VARIABLES

The approach discussed in the previous section becomes quickly unwieldy as the complexity of the system increases: the dimension of the system (8) is equal to the number of microscopic states of the system. Clearly the system phase space must be sufficiently small for this protocol to be car-

ried out, as in the case discussed in [7]. In all the other cases, where the system considered is characterized by a large number of degrees of freedom, one usually introduces some collective variables, and an effective free energy, in order to reduce the complexity of the problem. The assumption underlying this approach is that the system reaches on a comparatively short time scale a quasiequilibrium state constrained by the instantaneous value of the collective coordinate. Thus on the time scale of the experiment, the state of the system can be well summarized by the collective coordinate, with the corresponding free energy playing the role of the Hamiltonian.

Thus we consider in the following a system characterized by a generic equilibrium free energy function $\mathcal{F}_\mu(M)$, where μ is again the parameter which is manipulated, and M is some collective (mean-field) variable. (We shall consider in the following the case in which M is a scalar, but the analysis holds also if M is a collection of real variables.) We assume that the system dynamics is stochastic and Markovian: let $P(M,t)$ denote the probability distribution function of the variable M at time t, then its time evolution will be described by the differential equation

$$\frac{\partial P}{\partial t} = \hat{\mathcal{H}} P, \tag{16}$$

where $\hat{\mathcal{H}}$ is a differential operator which depends on the parameter μ. We require that the operator $\hat{\mathcal{H}}$ is compatible with the equilibrium distribution function of the system, i.e., that the relation

$$\hat{\mathcal{H}} e^{-\beta \mathcal{F}_\mu(M)} = 0 \tag{17}$$

holds for any value of μ.

The developments which follow were first obtained in Ref. [9] for a collection of noninteracting spins.

We will consider a general mean-field system, described by a collective variable M and a generic free energy function $\mathcal{F}_\mu(M)$. (The derivation can be easily generalized to the case in which M has more than one component.) The work done on a system during the manipulation, along a given stochastic trajectory $M(t)$, is given by

$$W = \int_0^t dt' \dot{\mu}(t') \frac{\partial \mathcal{F}_\mu(M(t'))}{\partial \mu}. \tag{18}$$

Using the same arguments as for the discrete case, one finds that the time evolution of the joint probability distribution $\Phi(M,W,t)$ of M and W is described by the differential equation

$$\frac{\partial \Phi}{\partial t} = \hat{\mathcal{H}} \Phi - \dot{\mu} \frac{\partial \mathcal{F}_\mu}{\partial \mu} \frac{\partial \Phi}{\partial W}. \tag{19}$$

It can be easily shown that the solution of Eq. (19) satisfies the Jarzynski equality (1) identically [8].

Equation (19) becomes much easier to treat if one introduces the generating function $\Psi(M,\lambda,t)$ for the work distribution:

$$\Psi(M,\lambda,t) = \int dW e^{\lambda W} \Phi(M,W,t). \tag{20}$$

Equation (19) becomes thus

$$\frac{\partial \Psi}{\partial t} = \hat{\mathcal{H}} \Psi + \lambda \dot{\mu} \frac{\partial \mathcal{F}_\mu}{\partial \mu} \Psi, \tag{21}$$

with the initial condition

$$\Psi(M,\lambda,0) = \frac{e^{-\beta \mathcal{F}_{\mu(0)}(M)}}{Z_{\mu(0)}}. \tag{22}$$

These equations are exact for a collection of free spins, or for a mean-field Ising model. The partial differential equation (21) replaces the 2^N ordinary differential equations (13), with $i \in \{-1,+1\}^N$, that one would obtain without the use of the collective coordinate M.

We now derive a path integral representation of the solution of Eq. (21), taking for the differential operator $\hat{\mathcal{H}}$ the expression

$$\hat{\mathcal{H}} \cdot = \sum_{k=0}^{\infty} \frac{\partial^k}{\partial M^k} \{ g_k(M) \cdot \}. \tag{23}$$

[The coefficients $g_k(M)$ also depend on μ, but this dependence is understood to lighten the notation.] Let us introduce the generating function of $\Psi(M,\lambda,t)$:

$$\Omega(\gamma,\lambda,t) = \int dM e^{-\gamma M} \Psi(M,\lambda,t). \tag{24}$$

Multiplying both sides of Eq. (21) by $\exp(-\gamma M)$, and integrating over M, we obtain

$$\begin{aligned} \partial_t \Omega(\gamma,\lambda,t) &= \int dM e^{-\gamma M} (\hat{\mathcal{H}} + \lambda \dot{\mu} \partial_\mu \mathcal{F}_\mu) \Psi \\ &= \int dM e^{-\gamma M} \left[\sum_k \frac{\partial^k}{\partial M^k} (g_k \Psi) + \lambda \dot{\mu} \partial_\mu \mathcal{F}_\mu \Psi \right] \\ &= \int dM e^{-\gamma M} \left[\sum_k \gamma^k g_k + \lambda \dot{\mu} \partial_\mu \mathcal{F}_\mu \right] \Psi. \end{aligned} \tag{25}$$

Then the function $\Omega(\gamma,\lambda,t)$ satisfies

$$\Omega(\gamma,\lambda,t+\delta t) = \int dM e^{-\gamma M} \{ 1 + \delta t [\mathcal{H}(\gamma,M) + \lambda \dot{\mu} \partial_\mu \mathcal{F}_\mu] \} \Psi, \tag{26}$$

where the function $\mathcal{H}(\gamma,M)$ is defined as

$$\mathcal{H}(\gamma,M) = \sum_k \gamma^k g_k(M). \tag{27}$$

Given $\Omega(\gamma,\lambda,t)$, we can evaluate $\Psi(M,\lambda,t)$ from the expression

$$\Psi(M,\lambda,t) = \int_{-i\infty}^{+i\infty} \frac{d\gamma}{2\pi i} e^{\gamma M} \Omega(\gamma,\lambda,t). \tag{28}$$

(In the following, we shall understand the integration limits on γ.) We obtain therefore

$$\Psi(M,\lambda,t+\delta t) = \int \frac{d\gamma}{2\pi i} \int dM' e^{\gamma(M-M')}\{1+\delta t[\mathcal{H}(\gamma,M') + \lambda\dot{\mu}\partial_\mu \mathcal{F}_\mu]\}\Psi(M',\lambda,t)$$
$$\simeq \int \frac{d\gamma}{2\pi i} \int dM' e^{\gamma(M-M')+\delta t[\mathcal{H}(\gamma,M')+\lambda\dot{\mu}\partial_\mu\mathcal{F}_\mu]} \times \Psi(M',\lambda,t). \quad (29)$$

Iterating, we obtain

$$\Psi(M,\lambda,t+N_t\delta t) = \int dM_0 \int \prod_{i=0}^{N_t} \frac{d\gamma_i dM_i}{2\pi i} \delta(M-M_t) \times \exp\{\mathcal{S}[\gamma,M]\}\Psi(M_0,\lambda,0), \quad (30)$$

where the "action" $\mathcal{S}[\gamma,M]$ is given by

$$\mathcal{S}[\gamma,M] = \sum_{i=1}^{N_t} \{\gamma_i(M_i - M_{i-1}) + \delta t[\mathcal{H}(\gamma_i,M_i) + \lambda\dot{\mu}\partial_\mu \mathcal{F}_{\mu(t_i)}(M_i)]\}. \quad (31)$$

In the continuum limit, Eq. (30) becomes

$$\Psi(M,\lambda,t_f) = \int dM_0 \int_{M(0)=M_0}^{M(t_f)=M} \mathcal{D}\gamma\mathcal{D}M \times \exp\{\mathcal{S}[\gamma,M]\}\Psi(M_0,\lambda,0), \quad (32)$$

where

$$\mathcal{S}[\gamma,M] = \int_0^{t_f} dt\mathcal{L}(t). \quad (33)$$

The "Lagrangian" $\mathcal{L}$ is given by

$$\mathcal{L}(t) = \left(\gamma\dot{M} + \mathcal{H}(\gamma,M) + \lambda\dot{\mu}\frac{\partial\mathcal{F}_\mu}{\partial\mu}\right)\Bigg|_{\gamma(t),M(t),\mu(t)}. \quad (34)$$

Let N indicate the size of the system, and let us define the "intensive quantity" $m=M/N$. We can thus define, in the thermodynamic limit $N\to\infty$, $m=$const, the densities

$$f_\mu(m) = \lim_{N\to\infty} \frac{\mathcal{F}_\mu(Nm)}{N}, \quad (35)$$

$$H(\gamma,m) = \lim_{N\to\infty} \frac{\mathcal{H}(\gamma,Nm)}{N}. \quad (36)$$

The Lagrangian density "per spin" then reads

$$\ell(t) = \lim_{N\to\infty} \frac{\mathcal{L}(t)}{N} = \gamma\dot{m} + H(\gamma,m) + \lambda\dot{\mu}\frac{\partial f_\mu}{\partial\mu}. \quad (37)$$

In this way, the path integral appearing in Eq. (32) assumes a form suitable for a saddle-point approximation for large system sizes N, as pointed out in [8,9]. The parameter N plays a role akin to the inverse of Planck's constant $\hbar$ in the quasi-classical approximation of Feynman's path integral for quantum amplitudes [11]. The result is the leading term in an asymptotic expansion in powers of N^{-1}, which corresponds to the mean-field solution of a statistical model. In Ref. [9] it was shown that the approximation works well for free spins. In Ref. [8] it was shown that for a mean-field spin system above the phase transition the approximation works rather well for system sizes N of the order of 10 and larger, but deteriorates as the transition is approached. It would be interesting to investigate in full the behavior of a finite-size system, in a situation when the corresponding infinite-sized system exhibits a phase transition. For a sufficiently fast manipulation protocol, in a large but finite system, the probability that a fluctuation overcoming the free energy barrier spontaneously arises should be very small. We expect therefore that the results of the infinite-size limit should hold better for faster protocols than for slower ones. These issues will be dealt with in future work.

In the leading approximation, the path integral in Eq. (32) is dominated by the classical path $[\gamma_c(t),m_c(t)]$ solution of the differential equations

$$\frac{\delta\mathcal{S}}{\delta\gamma(t)} = 0 \Rightarrow \dot{m} = -\frac{\partial H}{\partial\gamma}; \quad (38)$$

$$\frac{\delta\mathcal{S}}{\delta m(t)} = 0 \Rightarrow \dot{\gamma} = \frac{\partial H}{\partial m} + \lambda\dot{\mu}\frac{\partial^2 f_\mu}{\partial m\partial\mu}. \quad (39)$$

We shall now see that the requirement that the system is in equilibrium before the manipulation starts imposes an initial condition on these equations. In order to evaluate the integral over M_0 in Eq. (32) with the saddle-point method, we note that $\Psi(M,\lambda,0)$ appearing on its rhs, is given by Eq. (22). Furthermore, from the definition of $\ell(t)$, Eq. (37), it follows that

$$\int_0^{t_f} dt\ell(t) = m_{t_f}\gamma_{t_f} - m_0\gamma_0 + \int_0^{t_f} dt[-\dot{\gamma}m + H + \lambda\dot{\mu}\partial_\mu f_\mu]. \quad (40)$$

Thus substituting Eq. (40) into Eq. (32), and taking the derivative with respect to $m_0=M_0/N$, we obtain the saddle-point condition

$$\gamma(t=0) = -\beta \left.\frac{\partial f_\mu}{\partial m}\right|_{t=0}. \quad (41)$$

In this way one can devise a strategy to evaluate $\Psi(M,\lambda,t_f)$ for a given manipulation protocol $\mu(t)$ when the system size N is large enough. One has to solve the classical evolution equations (38) and (39) with a two-point boundary condition: namely, Eq. (41) should be imposed at $t=0$, and the condition $Nm(t_f)=M$ should be imposed at the final time t_f. Once the relevant classical path $[\gamma_c(t),m_c(t)]$ has been evaluated, one can obtain the action density $s[\gamma_c,m_c] = \lim_{N\to\infty}\mathcal{S}[\gamma_c,Nm_c]/N$ from the expression

$$s[\gamma_c,m_c] = \int_0^{t_f} dt\ell(t). \quad (42)$$

Then, taking into account the initial condition (22), we obtain the following asymptotic expression for $\Psi(Nm,\lambda,t_f)$:

$$\Psi(Nm,\lambda,t_f) \propto \exp\{N[s[\gamma_c,m_c] - \beta f_{\mu(0)}(m_c(t=0))]\}. \tag{43}$$

However, we are essentially interested in the state-independent work probability distribution

$$P(W,t_f) = \int d\lambda e^{-\lambda W}\Gamma(\lambda,t_f), \tag{44}$$

where we have defined

$$\Gamma(\lambda,t_f) = \int dM\Psi(M,\lambda,t_f). \tag{45}$$

We shall now see that evaluating $\Gamma(\lambda,t_f)$ identifies a well-defined boundary condition on $\gamma_c(t_f)$. We have indeed

$$\Gamma(\lambda,t_f) = \int dMdM_0 \int_{M(0)=M_0}^{M(t_f)=M} \mathcal{D}\gamma\mathcal{D}M \times \exp\left[N\int dt\ell(t)\right]\Psi(M_0,\lambda,0). \tag{46}$$

In order to evaluate the integral over M with the saddle-point method, we notice that, upon derivation of the rhs of Eq. (40) with respect to m_{t_f}, we obtain the condition

$$\gamma_f \equiv \gamma(t_f) = 0. \tag{47}$$

Thus, the equation of motions (38) and (39) have to be solved with the initial and the final conditions (41) and (47): let $[\gamma_c^*(t),m_c^*(t)]$ denote the solution of Eqs. (38) and (39) satisfying these conditions. For each value of λ, taking into account the initial value condition (22), the following saddle-point estimation for $\Gamma(\lambda,t_f)$ is obtained by Eq. (46):

$$\Gamma(\lambda,t_f) \propto \frac{\exp\{-Ng(\lambda)\}}{Z_0}, \tag{48}$$

where

$$g(\lambda) = \beta f_{\mu_0}(m_0^*) - \int_0^{t_f} dt\ell_c^*(t). \tag{49}$$

In this equation, $\ell_c^*(t)$ is $\ell(t)$ evaluated along the classical path $[\gamma_c^*(t),m_c^*(t)]$. In order to evaluate the integral on the rhs of Eq. (44), we use the saddle-point method again, and obtain

$$P(Nw,t_f) = \mathcal{N}\exp\{-N[\lambda^*(w)w + g(\lambda^*(w))]\}, \tag{50}$$

where $\lambda^*(w)$ is the solution of

$$g'(\lambda^*) = -w, \tag{51}$$

and $\mathcal{N}$ is a normalization constant. Notice that the saddle-point estimate for $P(W,t_f)$ obtained in this way implies that the distribution becomes more and more sharply peaked around its maximum value as $N\to\infty$. This is compatible with the expectation that the work fluctuations become relatively smaller as the size of the system increases, and in the limit $N\to\infty$, which can be thought of as the limit of a macroscopic system, no work fluctuations are observed, and the work done on the system during the manipulation takes one single value, corresponding to the most probable value of $P(W,t_f)$.

In Ref. [8] we showed that the JE is identically satisfied at the level of classical paths. For completeness, this derivation is reproduced in the Appendix.

IV. A MEAN-FIELD SYSTEM WITH LANGEVIN DYNAMICS

We wish to discuss a few properties of the work distribution obtained by the present method by considering a definite example. The case of free Ising spins has been considered (within a slightly different formalism) in Ref. [9]. We shall return to it in Sec. VI. We thus take an Ising-like system with mean-field interaction, with free energy

$$\mathcal{F}(M) = -\frac{J}{2N}M^2 - hM - TS(M), \tag{52}$$

where $S(M)$ is the usual entropy for an Ising paramagnet,

$$S(M) = -k_B\left[\left(\frac{N+M}{2}\right)\log\left(\frac{N+M}{2}\right) + \left(\frac{N-M}{2}\right)\log\left(\frac{N-M}{2}\right)\right], \tag{53}$$

expressed as a function of the continuous variable M. We assume that the system evolves according to Langevin dynamics. The corresponding Fokker-Planck differential operator reads

$$\hat{\mathcal{H}}\cdot = \omega_0 N\frac{\partial}{\partial M}\left[\left(\frac{\partial\mathcal{F}}{\partial M}\right)\cdot + \beta^{-1}\frac{\partial}{\partial M}\cdot\right], \tag{54}$$

leading to the Hamiltonian

$$H(\gamma,m) = \omega_0\left[\gamma\left(\frac{\partial f}{\partial m}\right) + \beta^{-1}\gamma^2\right], \tag{55}$$

where the free energy density $f(m)$ is given by

$$f(m) = -\frac{J}{2}m^2 - hm + \beta^{-1}\left[\left(\frac{1+m}{2}\right)\log\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\log\left(\frac{1-m}{2}\right)\right]. \tag{56}$$

The stochastic process described by this operator can be simulated by integrating the corresponding Langevin equation, using the Heun algorithm [12]: for each realization of the process, the work W done on the system can be evaluated. The resulting histogram of w represents an estimate of the work probability distribution. This estimated distribution can be then compared with the expected distribution (valid asymptotically for $N\to\infty$) obtained by the classical paths.

We consider the case where the system is subject to the external manipulation of the magnetic field $h(t)$, according to the simple protocol

$$h(t) = h_0 + (h_1 - h_0)\frac{t}{t_f}; \quad 0 \leq t \leq t_f. \tag{57}$$

The equations of motion (38) and (39) become

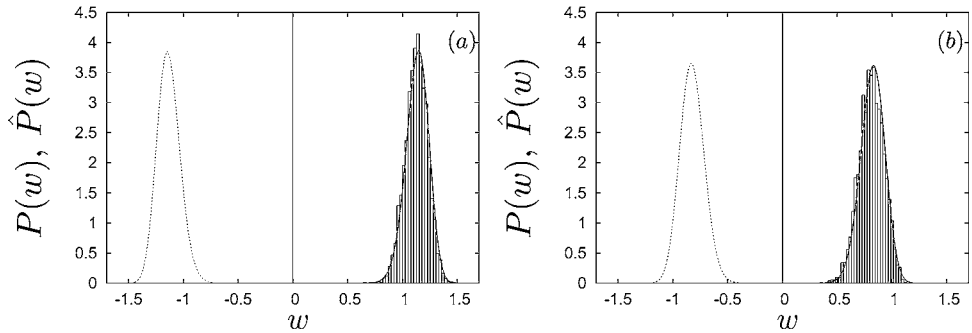

FIG. 1. Results for the system described by the differential operator (54) with equilibrium free energy (52), manipulated according to the protocol (57), with $J=0.5$, $h_0=-h_1=-1$, and (a) $t_f=2$, (b) $t_f=4$. Continuous line: probability density $P(w)$ of the work "per spin" $w=W/N$, with $N=100$. The histogram of the work is obtained by 10 000 simulations of the process, see text. Dotted line: $\hat{P}(w)$ as given by Eq. (60), whose integral verifies the Jarzynski equality. Vertical line: thermodynamic value of the work $w_{\mathrm{rev}}=\Delta F/N$.

$$\dot{m} = -\frac{\partial H}{\partial \gamma} = -\omega_0 \frac{\partial f}{\partial m} - 2k_B T \omega_0 \gamma, \tag{58}$$

$$\dot{\gamma} = \frac{\partial H}{\partial m} + \lambda \dot{\mu} \frac{\partial^2 f}{\partial m \partial \mu} = \omega_0 \frac{\partial^2 f}{\partial m^2} \gamma - \lambda \dot{h}. \tag{59}$$

In the following we will take $\beta=1$. In Fig. 1, we consider the case where the system is above the critical temperature, i.e., $\beta J<1$. In this case, as expected, the peak of the distribution moves towards the value of the work done on the system along a reversible trajectory $w_{\mathrm{rev}}=\delta f=0$, as the transformation becomes slower. But the most important indication emerging from such a figure is that the JE cannot be applied to obtain an independent estimation of the free energy difference between the final and initial states of the transformation if N is too large. In fact, we plot in the same figure the quantity $\hat{P}(w)$ defined as

$$\hat{P}(w) = \exp[-\beta N w] P(w), \tag{60}$$

on the one hand we find $\int dw \hat{P}(w) = \exp[-\beta \Delta F] = 1$ as predicted by the JE, while on the other hand the histogram obtained by the simulations exhibits no point (no realization of the process) with $w<0=w_{\mathrm{rev}}$. Thus the work distribution obtained by the simulation of the process cannot reliably be used for estimating ΔF. This is a typical example of how the lack of knowledge of the tails of the work distributions in micromanipulations experiments hinders the possibility of using Eq. (1) to evaluate free energy differences.

We now consider a system below the transition temperature, i.e., for $\beta J>1$. In Fig. 2 the work probability distribution obtained by the theory here discussed is plotted for $J=1.1$, $h_0=-h_1=-1$, and for two values of the final time t_f. In the same figure, the probability distribution obtained by simulations is also plotted. As for the case $\beta J<1$ (Fig. 1), the JE is satisfied, i.e., $\langle \exp(-\beta W) \rangle = 1$, there is a good agreement between the theory and the histograms obtained by simulations. But also in this case, such simulations cannot be used for estimating ΔF, since the histograms exhibit no point with $w<w_{\mathrm{rev}}$.

Since the amplitude of work fluctuations is expected to be relatively large in a small system, we calculate now the work probability distribution for smaller systems and compare them with the results of simulations. First, we consider the case $N=10$, Fig. 3: it can be seen that the histogram of the work obtained by simulations is closer to the thermodynamic value of the work $w_{\mathrm{rev}}=0$ than the distribution function obtained by the theory discussed in the present paper. Indeed, since $P(Nw,t)$, as given by Eq. (50), is exact only in the limit $N\to\infty$, that expression fails to describe the actual work distribution for small N. Furthermore, even for $N=10$, there are

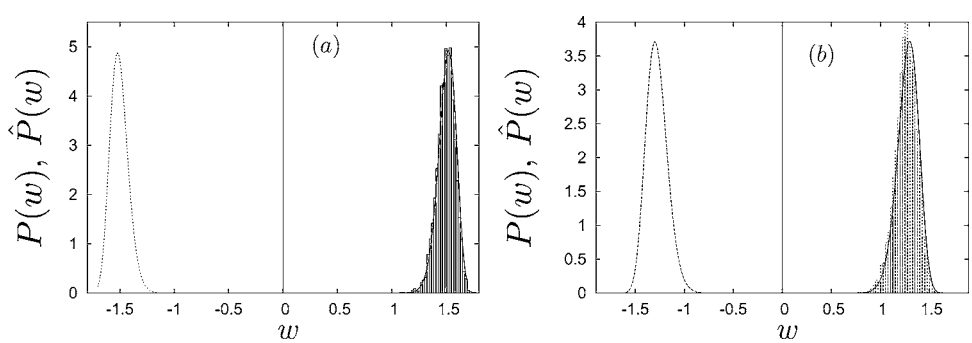

FIG. 2. Results for the system described by the differential operator (54) with equilibrium free energy (52), manipulated according to the protocol (57), with $J_0=J_1=1.1$, $h_0=-h_1=-1$, and (a) $t_f=2$, (b) $t_f=4$. Continuous line: probability density $P(w)$ of the work "per spin" $w=W/N$, with $N=100$. The histogram of the work is obtained by 10 000 simulations of the process, see text. Dotted line: $\hat{P}(w)$ as given by Eq. (60), whose integral verifies the Jarzynski equality. Vertical line: thermodynamic value of the work $w_{\mathrm{rev}}=\Delta F/N$.

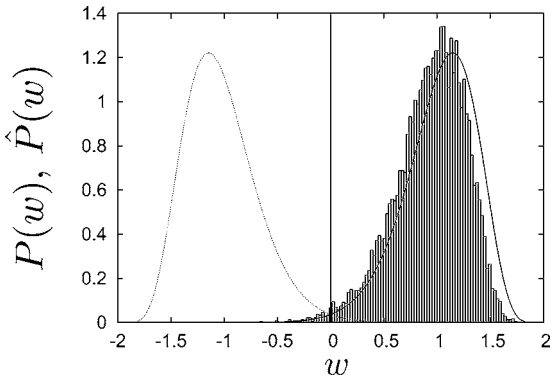

FIG. 3. Results for the system described by the differential operator (54) with equilibrium free energy (52), manipulated according to the protocol (57), with $J_0=J_1=0.5$, $h_0=-h_1=-1$, and $t_f=2$. Continuous line: probability density $P(w)$ of the work "per spin" $w=W/N$, with $N=10$. The histogram of the work is obtained by 10 000 simulations of the process, see text. Dotted line: $\hat{P}(w)$ as given by Eq. (60), whose integral verifies the Jarzynski equality. Vertical line: thermodynamic value of the work $w_{\rm rev}=\Delta F/N$.

few points in the histogram with $w<w_{\rm rev}$, and thus no reliable estimate of ΔF can be obtained from the simulations.

We further decrease the value of N and take $N=2$, see Fig. 4. In this case the agreement of the histogram with the theoretical curve is worse than the case $N=10$, as expected. But the small size of the system entails a broader work distribution, and thus enables a sufficient sampling of trajectories with $w<w_{\rm rev}$. In the same figure, the histogram of the distribution $\exp[-\beta Nw]P(w)$ is plotted: from this histogram we obtain the estimate for the free energy difference $\Delta f_{\rm exp}=-N^{-1}k_BT\ln[\exp(-\beta Nw)P(Nw)]_{\rm exp}$, where $[\cdots]_{\rm exp}$ is the mean over all realizations of the process. We obtain $\Delta f_{\rm exp}\simeq 0.015$, against a theoretical value of $w_{\rm rev}=\Delta f=0$, and a most probable value of the work $w_{\rm mp}\simeq 0.6$.

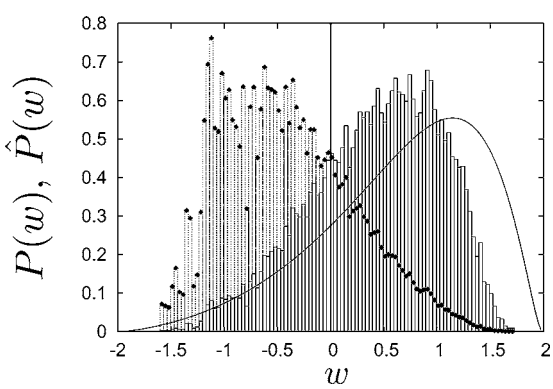

FIG. 4. Results for the system described by the differential operator (54) with equilibrium free energy (52), manipulated according to the protocol (57), with $J_0=J_1=0.5$, $h_0=-h_1=-1$, and $t_f=2$. Continuous line: probability density $P(w)$ of the work "per spin" $w=W/N$, with $N=2$. The histogram of the work is obtained by 10 000 simulations of the process, see text, and is plotted with a full line. Dotted line with black diamonds: histogram of $\hat{P}(w)=\exp(-\beta Nw)P(w)$. Vertical line: thermodynamic value of the work $w_{\rm rev}=\Delta F/N$.

V. PATH THERMODYNAMICS

The work distribution can be interpreted in terms of path thermodynamics, as first suggested in Ref. [9]. Indeed, $g(\lambda)=-\lim_{N\to\infty}\log\Gamma(\lambda,t_f)/N$ plays the role of a path Gibbs free energy. Thus

$$\phi(w)=-\lim_{N\to\infty}\frac{1}{N}\log P(Nw,t_f) \tag{61}$$

plays the role of the corresponding Helmholtz free energy. The two functions are related by a Legendre transformation:

$$\phi(w)=\inf_{\lambda}(g(\lambda)+\lambda w)=g(\lambda^*(w))+\lambda^*(w)w, \tag{62}$$

where $\lambda^*(w)$ is the solution of Eq. (51). Thus λ and w appear like thermodynamically conjugate variables. Notice that if $[\lambda,w^*(\lambda)]$ are a pair of mutually conjugate variables, then $w^*(\lambda)$ is a monotonically *increasing* function of λ. Indeed the relation between $\phi(w)$ and λ reads

$$\phi'(w^*(\lambda))=\lambda. \tag{63}$$

It is clear that the most probable value of the work $w_{\rm mp}$ corresponds to the value $\lambda=0$.

In Ref. [9], w is taken to play the role of the internal energy, and thus $-\phi(w)$ that of the entropy. Therefore $\lambda=\phi'(w)$ can be considered as an inverse temperature. We have preferred to draw the analogy with more familiar functions.

Indeed, one can generalize this point of view by going back to the joint probability distribution function $\Phi(M,W,t)$. If we define

$$\phi(m,w)=-\lim_{N\to\infty}\log\Phi(Nm,Nw,t_f), \tag{64}$$

we obtain straightforwardly

$$\phi(m,w)=\inf_{\gamma,\lambda}(\omega(\gamma,\lambda)+\gamma m+\lambda w), \tag{65}$$

where $\omega(\gamma,\lambda)$ is defined in terms of $\Omega(\lambda,\gamma,t)$, which we have defined in Eq. (24) by

$$\omega(\gamma,\lambda)=-\lim_{N\to\infty}\frac{1}{N}\log\Omega(\gamma,\lambda,t_f). \tag{66}$$

One may notice that the γ appearing in this equation may be identified with $\gamma_f=\gamma(t_f)$.

VI. LARGE FLUCTUATIONS AND EXPONENTIAL TAILS

It was suggested in Ref. [9], on the basis of numerical evidence, that, for slow protocols, the work distribution exhibits exponential tails. Here we discuss this intriguing question. From Eq. (61) we see that if $P(Nw,t_f)\propto\exp(-N\lambda_0 w)$ in some interval $w_-\leqslant w\leqslant w_+$, one has

$$\phi(w)=\lambda_0 w+\text{const}, \tag{67}$$

in the same interval. A linear behavior in the Helmholtz free energy is the signature of a first-order phase transition. In the corresponding Gibbs free energy one has an angular point, i.e., a point λ_0 in which

$$\lim_{\lambda\to\lambda_0^-} g'(\lambda) = w_-; \quad \lim_{\lambda\to\lambda_0^+} g'(\lambda) = w_+. \tag{68}$$

Thus a horizontal plateau in a plot of λ^* vs w corresponds to an exponential tail in $P(Nw,t_f)$.

We shall now follow Ref. [9], by considering a system of N noninteracting spins $\sigma_i = \pm 1$, evolving according to the Glauber dynamics. The collective coordinate M is the total magnetization $M = \Sigma_i \sigma_i$, (a discrete variable) and the role of μ is played by the magnetic field h. The system evolves according to the master equation

$$\frac{\partial P}{\partial t} = \left\{ p^{\downarrow}\left[\left(\frac{N+M+2}{2}\right)P(M+2,t) - \left(\frac{N+M}{2}\right)P(M,t)\right] + p^{\uparrow}\left[\left(\frac{N-M+2}{2}\right)P(M-2,t) - \left(\frac{N-M}{2}\right)P(M,t)\right]\right\}, \tag{69}$$

where the spin flip rates $p^{\uparrow,\downarrow}$ are given by

$$p^{\downarrow} = \omega_0(h)e^{-\beta h}, \quad p^{\uparrow} = \omega_0(h)e^{\beta h}, \tag{70}$$

in which $\omega_0(h)$ is a microscopic "attempt frequency" for spin flip. In this case, the free energy $\mathcal{F}_h(M)$ reads

$$\mathcal{F}_h(M) = -hM - TS(M), \tag{71}$$

where $S(M)$ is given by Eq. (54) as a function of M.

We can make the connection with our formalism by momentarily considering M as a continuous variable, and by expressing the shift operator

$$T_{\pm} f(M) = f(M \pm 2) \tag{72}$$

in the following way:

$$T_{\pm} = e^{\pm 2(\partial/\partial M)}. \tag{73}$$

The master equation (69) then assumes the form

$$\frac{\partial P}{\partial t} = \hat{\mathcal{H}} P,$$

where the differential operator $\hat{\mathcal{H}}$ is given by

$$\hat{\mathcal{H}}\cdot = \left[(e^{2(\partial/\partial M)} - 1)\left(\frac{N+M}{2}\right)p^{\downarrow}\cdot + (e^{-2(\partial/\partial M)} - 1) \times \left(\frac{N-M}{2}\right)p^{\uparrow}\cdot\right], \tag{74}$$

where it is understood that the derivative on M acts on all instances of M it finds on its right. Then the Hamiltonian H, as given by Eqs. (27) and (36), has the form

$$H = \left[(e^{2\gamma} - 1)\frac{1+m}{2}p^{\downarrow} + (e^{-2\gamma} - 1)\frac{1-m}{2}p^{\uparrow}\right]. \tag{75}$$

Equations (38) and (39) yield the equations of motion for the classical path:

$$\dot{m} = e^{-2\gamma}p^{\uparrow}(1-m) - e^{2\gamma}p^{\downarrow}(1+m), \tag{76}$$

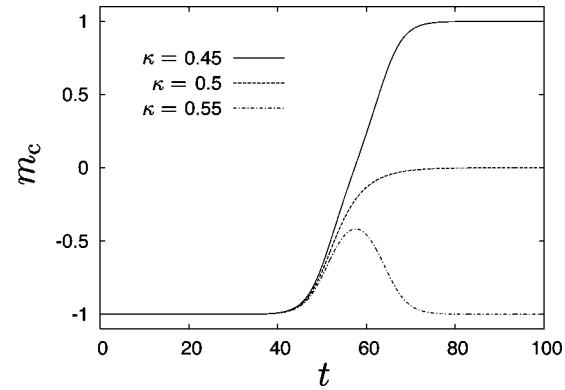

FIG. 5. Plot of $m_c(t,\kappa)$ as a function of t, as given by Eq. (82), for three values of the parameter κ. The external field is manipulated according to Eq. (57), with $t_f = 100$. The function is monotonic for $\kappa \leqslant \kappa_c$.

$$\dot{\gamma} = \frac{1}{2}[(e^{2\gamma} - 1)p^{\downarrow} - (e^{-2\gamma} - 1)p^{\uparrow}] - \lambda\dot{h}. \tag{77}$$

A different and more complicated approach, used in Ref. [9], leads to the same results.

We shall suppose that the applied magnetic field h is manipulated according to the simple protocol (57)

$$h(t) = h_0 + (h_1 - h_0)\frac{t}{t_f}, \quad 0 \leqslant t \leqslant t_f.$$

We also suppose that $\omega_0(h) = \omega_0/(e^{\beta h} + e^{-\beta h})$ so that the functions $p^{\uparrow}$, $p^{\downarrow}$ are explicitly given by

$$p^{\uparrow}(t) = \omega_0 \frac{e^{\beta h(t)}}{e^{\beta h(t)} + e^{-\beta h(t)}}, \tag{78}$$

$$p^{\downarrow}(t) = \omega_0 \frac{e^{-\beta h(t)}}{e^{\beta h(t)} + e^{-\beta h(t)}}, \tag{79}$$

where ω_0 is a constant.

Let us now consider the quasistatic limit $\dot{h} \to 0$, with $\lambda\dot{h} \to \kappa = \text{const}$. It is then possible to neglect the left-hand side (lhs) of Eqs. (76) and (77), yielding

$$m = \tanh(\beta h - 2\gamma), \tag{80}$$

$$2\kappa = p^{\downarrow}(e^{2\gamma} - 1) - p^{\uparrow}(e^{-2\gamma} - 1). \tag{81}$$

Combining these equations, one obtains an expression for m as a function of h:

$$m_c = \frac{\sinh(\beta h) - 2\kappa\cosh(\beta h)}{\sqrt{1 + [\sinh(\beta h) - 2\kappa\cosh(\beta h)]^2}}. \tag{82}$$

Thus m_c depends on t via h, in terms of this equation. It also depends on the parameter κ. One can check that $m_c(t,\kappa)$ exhibits an extremum as a function of t in the interval $[0,t_f]$, if $|\kappa| > \kappa_c = 1/2$, otherwise it is strictly monotonic. In order to discuss an explicit example, we set $\beta = 1$, $h_1 = -h_0 = 10$. In Fig. 5, the function $m_c(t,\kappa)$, as given by Eq. (82), is plotted for three different values of the parameter κ: the function clearly exhibits a different behavior for $\kappa < \kappa_c$ and $\kappa > \kappa_c$.

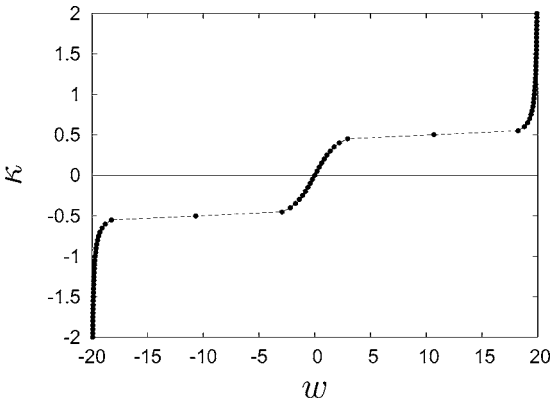

FIG. 6. Plot of κ as a function of w in the quasistatic limit, as given by Eq. (83). The line is a guide to the eye.

Thus as κ becomes greater than its critical value κ_c, we expect a singular behavior of the curve $[\kappa, w(\kappa)]$, where

$$w(\kappa) = -\int_0^{t_f} dt\dot{h}(t)m_c(t,\kappa), \tag{83}$$

and $m_c(t,\kappa)$ is given by Eq. (82). Evaluating $w(\kappa)$ we obtain the curve plotted in Fig. 6: one can see that it exhibits, for $|\kappa| = \kappa_c$, a pronounced minimum in $d\kappa/dw$ rather than a horizontal plateau.

The simplicity of the system allows us to check this prediction by directly solving the equations (13) for the generating function $\Psi_\sigma(\lambda,t)$, $\sigma = \pm 1$, for the transition rates given by Eqs. (78) and (79). One thus obtains the function $\Gamma_1(\lambda,t_f)$ for the single spin, from the expression

$$\Gamma_1(\lambda,t_f) = \sum_{\sigma=\pm 1} \Psi_\sigma(\lambda,t_f). \tag{84}$$

Since $g(\lambda) = -\log[\Gamma_1(\lambda,t_f)]$, we can obtain the curve $[w,\lambda^*(w)]$ from Eq. (51) and compare it with the predicted curve for the quasistatic limit, as given by Eq. (83). Such a comparison is shown in Fig. 7: as the value of $\dot{h} = (h_1 - h_0)/t_f$ decreases the agreement between the theory and the curve predicted by Eq. (83) improves.

We checked that this behavior depends on the details of the dynamics by considering the same paramagnetic system, but evolving by a Langevin rather than a Glauber dynamics, with the method reported in Sec. IV. As shown in Fig. 8, the corresponding (w,κ) curve exhibits no plateau, and therefore there are no exponential tails in the work distribution. These results are confirmed by a detailed analysis of the quasistatic limit.

Let us now turn again to the ferromagnetic mean-field system with Langevin dynamics. In the left panel of Fig. 9, we plot m_c^* as a function of t for different values of λ, obtained by numerical solution of Eqs. (58) and (59), for $J = 0.5$ and $t_f = 2$. It can be seen that the shape of $m_c^*(t)$ varies continuously as λ is varied. Accordingly there is no horizontal plateau in the λ^* vs w plot, implicitly defined by Eq. (51), as shown in the right panel of Fig. 9. The same behavior is obtained by varying t_f and implementing a slower or a faster protocol (data not shown). According to the above discussion, the work distribution exhibits no exponential tails for the case $\beta J < 1$.

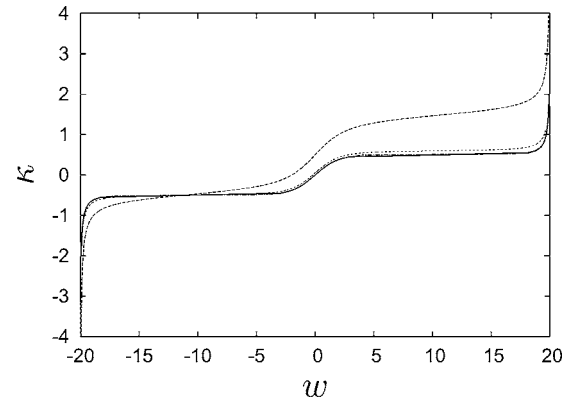

FIG. 7. Plot of $\kappa = \lambda\dot{h}$ as a function of w, for different values of $\dot{h} = (h1 - h0)/t_f$. Thick full line: $\kappa(w)$ in the quasistatic limit, as obtained by Eq. (83). The other curves are obtained from the evolution equations (13). Dashed line $t_f = 20$ $(\dot{h} = 1)$, dotted line $t_f = 200$ $(\dot{h} = 0.1)$, the curve with $t_f = 2000$ $(\dot{h} = 0.01)$ is practically indistinguishable from the quasistatic limit.

We now investigate whether a different behavior can appear when the system is manipulated across the symmetry-breaking transition it exhibits at $\beta J = 1$. Let us look at the behavior of the classical path $m_c^*(t,\lambda)$ corresponding to the $\gamma_f = 0$ boundary condition, both above $(\beta J < 1)$ and below $(\beta J > 1)$ the transition.

In the left panel of Fig. 10, we plot m_c^* as a function of t for different values of λ, obtained by numerical solution of Eqs. (58) and (59), for $J = 1.1$ and $t_f = 2$: we observe no discontinuity in $m_c^*(t,\lambda)$ as λ is varied, and thus w is a continuous function of λ, see Fig. 10 (right panel).

We now consider a faster protocol, $t_f = 0.2$, with the same value of J and h_0: the results are plotted in Fig. 11. One can clearly see that $m_c^*(t,\lambda)$ exhibits a discontinuity for $\lambda = 0.5$, jumping from negative to positive values. Accordingly, $w(\lambda^*)$ exhibits a discontinuity at $\lambda^* = 0.5$, as shown in the right panel of Fig. 11.

If we now evaluate the path Helmholtz free energy $\phi(w)$ from Eq. (62), we obtain the results shown in Fig. 12. As

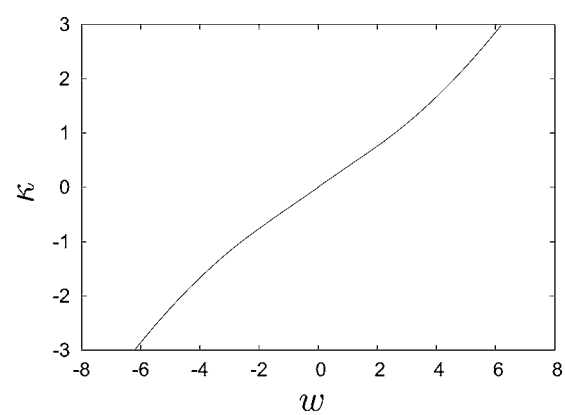

FIG. 8. Plot of κ as a function of w for the paramagnet evolving according to a Langevin dynamics. Manipulation protocol (57), with $h_0 = -h_1 = -5$, $t_f = 1000$.

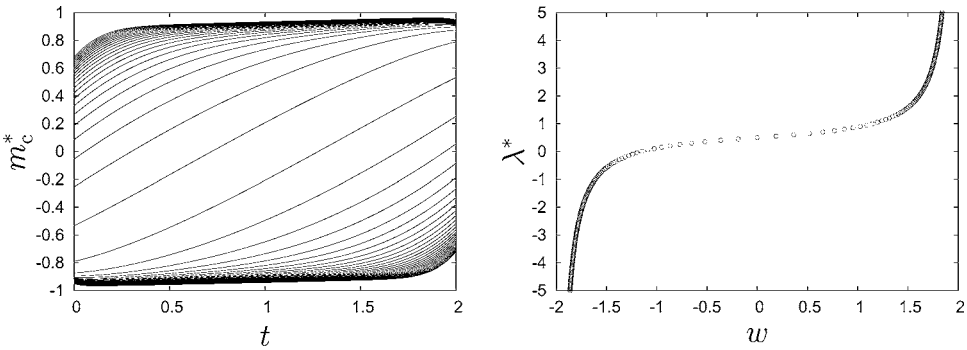

FIG. 9. Left: plot of m_c^* as a function of t for different values of λ, with $J=0.5$, $h_0=-h_1=-1$, and $t_f=2$. The values of λ vary between $\lambda=-5$ (bottom curve) and $\lambda=5$ (top curve), with a step $\Delta\lambda=0.2$. Right: plot of λ^* as a function of w, as defined by Eq. (51).

discussed in Sec. V, $\phi(w)$ should be obtained by a linear interpolation between $[w_+,\phi(w_+)]$ and $[w_-,\phi(w_-)]$, where $w_\pm$ are the values of w either side of the discontinuity. This corresponds to an exponential tail in the distribution of the work. In this case, the existence of an equilibrium phase transition shows up as a path phase transition, i.e., an exponential tail, provided that the manipulation protocol is fast enough. The same behavior is obtained for $h_0=-h_1=-0.1$, $t_f=0.2$ (no discontinuity) and $t_f=0.02$ (discontinuity, data not shown). This last result suggests thus that the presence of exponential tails in the work probability distribution is due to a path "phase separation," which is induced by a sufficiently fast manipulation protocol: inspection of Fig. 11 indicates that the trajectories $m_c^*(t,\lambda)$ form two groups, as λ is varied, and none of the trajectories belonging to each of the two groups crosses the line $m=0$, differently from what happens for a slower protocol, see Fig. 10. We checked that the resulting distribution $\phi(w)$ satisfies the following relation, which is a consequence of Crooks' identity [5] and of the symmetry $h(t_f-t)=-h(t)$ satisfied by our protocol:

$$\phi(w)-\phi(-w)=-\beta w. \tag{85}$$

It would be interesting to see if such a "path phase transition" takes place in more realistic models.

VII. DISCUSSION

In this work, we have examined the distribution of the work W exerted on a system which is manipulated out of equilibrium. We have first obtained its expression by considering the joint distribution of the microscopic state of the system and of the work. The expression one obtains is in principle exact, but is amenable to a numerical solution only for very simple systems. We have then considered a system whose quasiequilibrium state can be described by one (or more) collective variables, to which an effective free energy function is associated. The resulting equation for the joint distribution of the collective variables and work is a partial differential equation which can in principle be numerically solved. However, we found that it is possible to explore a different direction. Indeed, following Ref. [9], one sees that one can express the solution to this equation as a path integral. In the limit of system size N going to infinity, the path integral is dominated by the classical paths, which satisfy a "canonical" system of ordinary differential equations, with suitable boundary conditions. Building on this information, it is possible to estimate the work probability distribution function for large system size, in the form

$$P(W)\propto\exp[-N\phi(w)],$$

where $w=W/N$, and $\phi(w)$ plays the role of a work free energy density, or of a function of large deviations. This quantity is obtained as a Legendre transform of $g(\lambda)$ as given by Eq. (49). It is natural to interpret the relations between these quantities as corresponding to those between the Helmholtz and the Gibbs free energy densities in thermodynamics. Within this picture, the parameter λ can be viewed as the intensive field conjugated with the extensive variable w, which acts as an order parameter for the single path. Thus horizontal plateau in the λ^* vs w plot indicates a first-order phase transition in the paths. In this case the work distribution exhibits an exponential tail in a given range of w, depending on the manipulation details. Our results suggest that the system exhibits such path "phase separation" for sufficiently fast manipulation protocols, and below the mean-field equilibrium transition temperature, whereas above it one can

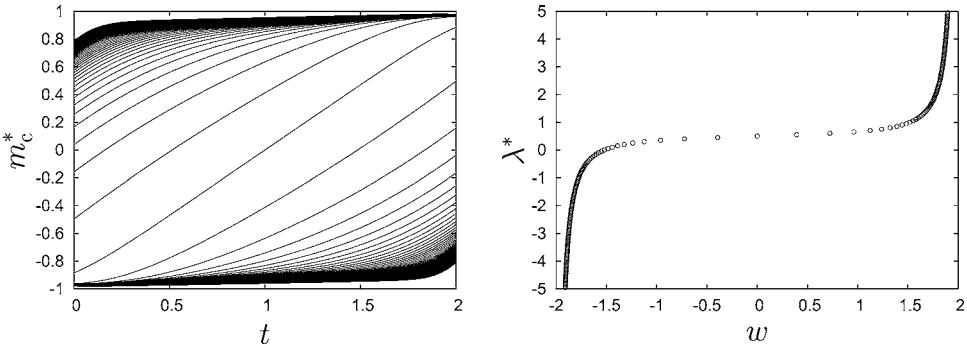

FIG. 10. Left: plot of m_c^* as a function of t for different values of λ, with $J=1.1$, $h_0=-h_1=-1$, and $t_f=2$. The values of λ vary between $\lambda=-5$ (bottom curve) and $\lambda=5$ (top curve), with a step $\Delta\lambda=0.2$. Right: plot of λ^* as a function of w, as defined by Eq. (51).

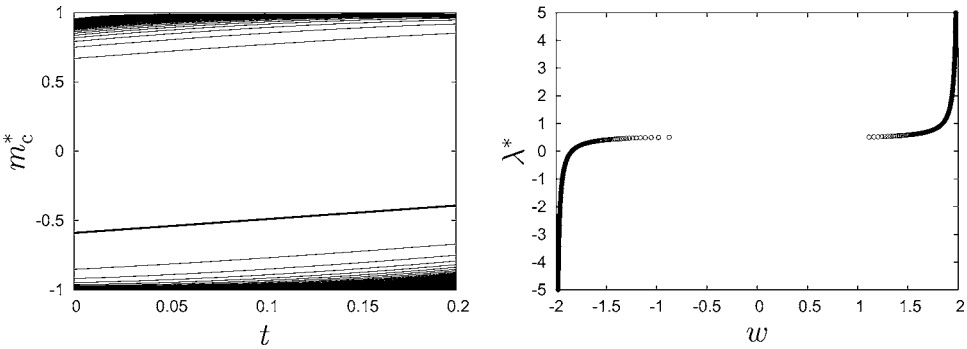

FIG. 11. Left: plot of m_c^* as a function of t for different values of λ, with $J=1.1$, $h_0=-h_1=-1$, and $t_f=0.2$. The values of λ vary between $\lambda=-5$ (bottom curve) and $\lambda=5$ (top curve), with a step $\Delta\lambda=0.2$. Thick line: $\lambda=0.5$. Right: plot of λ^* as a function of w, as defined by Eq. (51).

find only a marked inflection point in the λ^* vs w plot, but not a horizontal plateau.

The results we obtain are interesting in their own right, since they exhibit a number of nontrivial properties of the classical paths. However, their usefulness for assessing the feasibility of the use of the Jarzynski equality for the reconstruction of the equilibrium free energy landscape can be *a priori* doubted. Indeed, the $P(W)$ one obtains in this way is only asymptotically valid for large N, and in this case, the probability of observing, in an actual experiment, a sufficient number of large fluctuations to evaluate the Jarzynski average (1) with some confidence, is extremely small. We found, however, that the estimated distribution is not too far from the actual distribution for system sizes as small as 2, at least when the manipulation protocol is not too fast and does not cross an equilibrium phase transition line [8]. In this case the JE can be successfully applied to the work distribution obtained by simulations: the estimate of the free energy difference differs little from the expected value.

It is reasonable to expect, for our mean-field-like systems, that the existence of a first-order transition could cause some problems. Formally, in the limit $N\to\infty$ and for a manipulation protocol with a finite speed, the system would remain close to the free energy minimum it finds itself in until it reaches the spinodal line. In a finite system, if the protocol is slow enough, the system can cross the free energy barrier and reach the real minimum in a finite time. We found that the classical paths are able to interpolate between the minima for slow enough protocols, whereas they tend to split in different phases for fast ones. Thus this effect takes place even for mean-field systems.

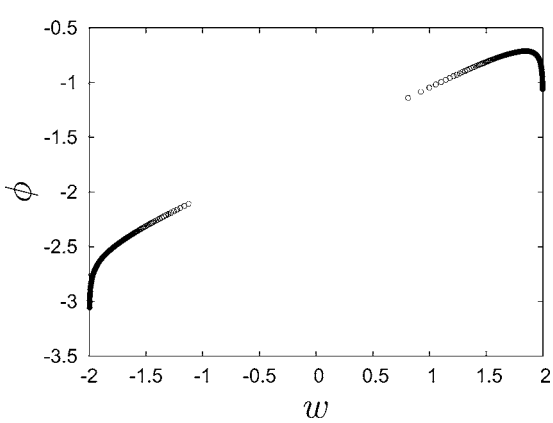

FIG. 12. Path Helmholtz free energy for the system described by the differential operator (54), manipulated according to the protocol (57), with $J=1.1$, $h_0=-h_1=-1$, and $t_f=0.2$.

It is possible to extend this work to more realistic systems, provided that the basic assumption of the existence of relevant collective variables holds. One should also consider what information can be gathered by exploiting other manipulation protocols.

ACKNOWLEDGMENTS

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APPENDIX: DERIVATION OF THE JARZYNSKI EQUALITY FOR THE CLASSICAL PATHS

We report here, for completeness, the derivation of the Jarzynski equality at the level of classical paths, obtained in Ref. [8]. We first show that, for $\lambda=-\beta$, the solution of the classical equations of motion (38) and (39) satisfies an equation analogous to Eq. (41) at all times, namely

$$Q \equiv -\gamma - \beta\frac{\partial f_\mu}{\partial m} = 0. \tag{A1}$$

By multiplying both sides of Eq. (17) by $e^{-\gamma M}$ and integrating by parts over M one obtains

$$\int dM\mathcal{H}(\gamma,M)e^{-\beta\mathcal{F}_\mu(M)-\gamma M} = 0, \tag{A2}$$

where $\mathcal{H}(\gamma,M)$ is given by Eq. (36). Evaluating this integral by the saddle-point method in the large N limit, we obtain

$$H(\gamma,m^*) = 0, \tag{A3}$$

if γ and m^* are related by Eq. (A1). By differentiating Eq. (A3) with respect to γ at fixed μ we obtain

$$\frac{\partial H}{\partial \gamma} + \frac{\partial H}{\partial m}\bigg|_{m^*}\frac{\partial m^*}{\partial \gamma}\bigg)_\mu = 0. \tag{A4}$$

Let us now take the derivative of Eq. (A1) with respect to γ at fixed μ. We obtain

$$\beta\frac{\partial^2 f_\mu}{\partial m^2}\frac{\partial m}{\partial \gamma}\bigg)_\mu = -1. \tag{A5}$$

By multiplying both sides of Eq. (A4) by $\partial^2 f_\mu/\partial m^2$ and substituting Eq. (A5), we obtain the following relation:

$$\beta\frac{\partial^2 f_\mu}{\partial m^2}\frac{\partial H}{\partial \gamma} - \frac{\partial H}{\partial m} = 0, \tag{A6}$$

which holds when γ and m are related by Eq. (A1). We can now evaluate the time derivative of the lhs of Eq. (A1), when γ and m satisfy Eqs. (38) and (39). We have

$$\begin{aligned}\dot{Q} &= -\dot{\gamma} - \beta\frac{\partial^2 f_\mu}{\partial m^2}\dot{m} - \beta\frac{\partial^2 f_\mu}{\partial m \partial \mu}\dot{\mu} \\ &= -\left(\frac{\partial H}{\partial m} - \beta\frac{\partial^2 f_\mu}{\partial m \partial \mu}\dot{\mu}\right) + \beta\frac{\partial^2 f_\mu}{\partial m^2}\frac{\partial H}{\partial \gamma} - \beta\frac{\partial^2 f_\mu}{\partial m \partial \mu}\dot{\mu}.\end{aligned} \tag{A7}$$

The second and the last terms cancel out. Substituting Eq. (A6), we see that also the first and the third terms cancel out. Thus if γ and m satisfy Eqs. (38) and (39) at all times, and satisfy Eq. (A1) at a given time, they satisfy this last equation at any time.

Thus, for $\lambda = -\beta$, the Lagrangian, evaluated along the classical path, is given by

$$\mathcal{L}_c = N\left[\gamma\dot{m} - \beta\dot{\mu}\frac{\partial f_\mu}{\partial \mu}\right] = N\left[-\beta\frac{\partial f_\mu}{\partial m}\dot{m} - \beta\frac{\partial f_\mu}{\partial \mu}\dot{\mu}\right] = -\beta N\frac{df_\mu}{dt}, \tag{A8}$$

where we have exploited Eq. (A1). Substituting this expression in Eq. (32) one recovers Eq. (14) and the Jarzynski equality.

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