

A field-theoretic approach to nonequilibrium work identities

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We study nonequilibrium work relations for a space-dependent field with stochastic dynamics (Model A). Jarzynski's equality is obtained through symmetries of the dynamical action in the path integral representation. We derive a set of exact identities that generalize the fluctuation-dissipation relations to non-stationary and far-from-equilibrium situations. These identities are prone to experimental verification. Furthermore, we show that a well-studied invariance of the Langevin equation under supersymmetry, which is known to be broken when the external potential is time-dependent, can be partially restored by adding to the action a term which is precisely Jarzynski's work. The work identities can then be retrieved as consequences of the associated Ward-Takahashi identities.

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I. INTRODUCTION

During the last decade, many exact relations for non-equilibrium processes have been derived. The Jarzynski equality is one of these remarkable results:

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

This relation implies that the statistical properties of the work performed on a system in contact with a heat reservoir at temperature $kT = \beta^{-1}$ during a *non-equilibrium* process are related to the free energy difference ΔF between two *equilibrium* states of that system. This identity was derived originally using a Hamiltonian formulation [1] and was extended to systems obeying a Langevin equation or a discrete Markov equation [2]. This result was generalized by Crooks [3, 4], who showed that the identity (1) results from a remarkable relation between the probability $P_F(W)$ of performing the quantity of work W in a given (forward) process and the probability $P_R(-W)$ of performing $-W$ in the reversed process, namely

$$\frac{\mathcal{P}_F(W)}{\mathcal{P}_R(-W)} = e^{\beta(W - \Delta F)}. \quad (2)$$

Jarzynski and Crooks' identities are now well established results (a review of the state of the art can be found for example in [5]). These relations have been verified on exactly solvable models [6] and by explicit calculations in kinetic theory of gases [7, 8]. These equalities have also been used in various single-molecule pulling experiments [9–11] to measure folding free energies (for a review of biophysical applications see e.g. [12]), and have been checked against analytical predictions on mesoscopic mechanical devices such as a torsion pendulum [13]. Experimental verifications are delicate to carry out because the mathematical validity of Jarzynski's theorem is insured by rare events that occur with a probability that typically decreases exponentially with the system size [14].

Another type of physical systems where large fluctuations are expected to occur are extended statistical models in the vicinity of a phase transition. Such systems are often modeled by a continuous space-time description with a local coarse-grained order parameter, $\phi(x)$, which minimizes a Ginzburg-Landau type free energy. The equilibrium properties of these models have been thoroughly studied, in particular using renormalization group techniques [15–17]. Besides, in the vicinity of a critical point, the dynamic properties also display anomalous behaviour. If one assumes that universality remains valid [16], it is natural to construct and investigate the simplest dynamical models, with a given static behaviour, which respect some physical constraints such as symmetries and conservation laws. The coarse-grained order parameter of a microscopic system is then represented by a space and time dependent field $\phi(x, t)$ that evolves according to an effective stochastic differential equation. Different possible types of evolution equations have been classified (see e.g. the review paper of Halperin and Hohenberg [18]).

In the present work, we derive nonequilibrium work relations for a field $\phi(x, t)$ that follows the simplest dynamics in Halperin and Hohenberg's scheme: Model A dynamics describes the kinetic Ising model with non-conserved order parameter. We represent the stochastic evolution as a path integral weighted by a dynamical action [17]. Our method is closely related to the one used in [20, 21] to study the case of a Langevin equation for a 0-dimensional scalar coordinate that depends only on time. Adding a spatial dependence allows us to use the powerful response-field formalism that was developed in [19]. The work relations are then derived from elementary invariance properties of the path integral measure under changes of variables that affect simultaneously the original field $\phi(x, t)$ and its conjugate response-field $\bar{\phi}(x, t)$. From the work relations, we derive correlator identities that generalize the equilibrium fluctuation-dissipation relations for situations that can be arbitrarily far from equilibrium.

One advantage of introducing space and time varying fields is to extend the possible symmetries of the system and to consider transformations that can mix space and time. In the present context, this can be achieved by introducing two conjugate auxiliary Grassmann fields, $c(x, t)$ and $\bar{c}(x, t)$. The new dynamical action, which now depends on four fields $\phi, \bar{\phi}, c$ and \bar{c} , exhibits a larger invariance which is a manifestation of a hidden supersymmetric invariance [22, 23]. This property is true at thermodynamic equilibrium and it is known that the equilibrium fluctuation-dissipation theorem as well as the Onsager reciprocity relations can be derived from it [24–26] (see also [17]). In other words, supersymmetry is a fundamental invariance property of the full dynamical action that embodies the principle of microscopic reversibility. For a system out of equilibrium (for example a system subject to a time-dependent external drive), supersymmetric invariance is broken. This leads to a violation of the fluctuation-dissipation theorem or, equivalently, to the occurrence of corrective terms in the formulation of this theorem: this fact was clearly recognized in [27, 28]. Here, we remark that weighing the expectation values by the Jarzynski term $e^{-\beta W}$ amounts to modifying the dynamical action of the model and we show that the modified action exhibits an invariance under a specified supersymmetric transformation. This invariance manifests itself as correlators identities known as the the Ward-Takahashi identities (a field-theoretic counterpart to Noether's theorem). Finally, we prove that the nonequilibrium work relation can be deduced from the Ward-Takahashi identity that encodes the underlying supersymmetry. Therefore, supersymmetric invariance of stochastic evolution equation is a fundamental property that embodies equilibrium relations (Onsager reciprocity, fluctuation-dissipation theorem) as well as nonequilibrium work identities.

The outline of this work is as follows. In Section II, we define the model, use the response-field formalism to derive the work relations for a space-time dependent field, and obtain a fluctuation-dissipation relation, valid far from equilibrium, which can be shown to be mathematically equivalent to the Jarzynski relation. In Section III, we use the formalism of Grassmann fields for the equilibrium case and define precisely the various supersymmetric transformations that leave the dynamical action invariant. We then show that supersymmetry, which is broken when the system is out of equilibrium, is restored by modifying suitably the action and we prove that Jarzynski's equation can be viewed as a consequence of the Ward-Takahashi identity that encodes the restored invariance. Concluding remarks are given in Section IV. Technical details are given in the appendices. In particular, the superfield formalism and the derivation of the Ward-Takahashi identities are recalled in Appendices B and C.

II. STOCHASTIC EVOLUTION OF A SCALAR FIELD

In this section, we derive the field-theoretic version of the non-equilibrium work relations for a system that obeys a time-dependent Ginzburg-Landau equation. The dynamics considered will be purely relaxational and we shall focus on the most elementary case with no conservation laws, described by Model A dynamics. We shall express the Probability Distribution Function of the field at a given time as a path-integral. The Jarzynski and Crooks relations will be obtained via this path integral formalism.

A. Model A dynamics

We consider a scalar field $\phi(x, t)$ that evolves in a d -dimensional space according to Model A dynamics [18], given by the following stochastic equation of motion:

$$\frac{\partial \phi}{\partial t}(x, t) = -\Gamma_0 \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)} + \zeta(x, t), \quad (3)$$

where the dynamics is governed by the time-dependent potential

$$\mathcal{U}[\phi(x, t), t] = \mathcal{F}_{GL}[\phi(x, t)] - \int d^d x h(x, t) \phi(x, t), \quad (4)$$

$h(x, t)$ being an external applied field. The time-independent part of the potential assumes the familiar Ginzburg-Landau form and is given by

$$\mathcal{F}_{GL}[\phi] = \int d^d x \left\{ \frac{1}{2} r_0 \phi^2 + \frac{1}{2} |\nabla \phi|^2 + \frac{u_0}{4} \phi^4 \right\}. \quad (5)$$

The fluctuating driving field $\zeta(x, t)$ is assumed to be a Gaussian white noise of zero mean value and of correlations given by

$$\langle \zeta(x, t) \zeta(x', t') \rangle = 2 \frac{\Gamma_0}{\beta} \delta(t - t') \delta^d(x - x'), \quad (6)$$

where $\beta = (kT)^{-1}$ is the inverse temperature. The fact that the auto-correlation of the noise satisfies Einstein's fluctuation-dissipation relation ensures that the dynamics is microscopically reversible and obeys detailed-balance [30]. The Langevin equation (3) for model A thus reads

$$\frac{\partial \phi}{\partial t}(x, t) = -\Gamma_0 f(\phi(x, t), t) + \zeta(x, t), \quad (7)$$

where, for later convenience, we have defined

$$f(\phi(x, t), t) = \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)} = -\nabla^2 \phi(x, t) + r_0 \phi(x, t) + u_0 \phi^3(x, t) - h(x, t). \quad (8)$$

The dynamics of the order parameter can also be described in terms of the Probability Distribution Function (PDF) $\mathcal{P}(\phi_1 | \phi_0)$ of observing the field $\phi(x, t) = \phi_1(x)$ at time $t = t_f$, knowing that the initial field is $\phi_0(x)$ at time $t = 0$. By definition, this PDF is given by

$$\mathcal{P}(\phi_1 | \phi_0) = \langle \delta(\phi(x, t_f) - \phi_1(x)) \rangle, \quad (9)$$

where the expectation value is taken over all possible realizations of the noise $\zeta(x, t)$ between the initial and the final times (the initial value of the field $\phi_0(x)$ being fixed). Substituting the Gaussian measure for the noise, this expression becomes

$$\mathcal{P}(\phi_1 | \phi_0) = \int \mathcal{D}\zeta(x, t) e^{-\frac{\beta}{4\Gamma_0} \int d^d x dt \zeta^2} \delta(\phi(x, t_f) - \phi_1(x)) \quad \text{with} \quad \phi(x, 0) = \phi_0(x). \quad (10)$$

This expression is nothing but a formal path-integral solution of the functional Fokker-Planck equation associated with the Langevin dynamics (3):

$$\frac{\partial P}{\partial t} = \Gamma_0 \int d^d x \frac{\delta}{\delta \phi} \left(f(\phi, t) P + \frac{1}{\beta} \frac{\delta P}{\delta \phi} \right). \quad (11)$$

When the external field is constant in time $h(x, t) = h(x)$, this Fokker-Planck equation has a stationary solution, which is the equilibrium Gibbs-Boltzmann distribution:

$$P_{eq}[\phi] = \frac{e^{-\beta \mathcal{U}[\phi]}}{Z[\beta, h]} \quad \text{with} \quad Z[\beta, h] = \int \mathcal{D}\phi e^{-\beta \mathcal{U}[\phi]}. \quad (12)$$

Finally, we recall that the equilibrium free-energy $F[\beta, h]$ is defined by

$$F[\beta, h] = -\frac{1}{\beta} \log Z[\beta, h]. \quad (13)$$

B. Dynamic action for the Probability Distribution

The probability $\mathcal{P}(\phi_1 | \phi_0)$ of observing the field $\phi_1(x)$ at time t_f starting from $\phi_0(x)$ at time $t = 0$ is given by equation (10). We now rewrite the path integral in terms of the variable $\phi(x, t)$ using the response-field formalism

of Martin-Siggia-Rose, de Dominicis-Peliti and Janssen [19]. We start with the following identity (that can be found e.g. in [17])

$$\begin{aligned} 1 &= \int \mathcal{D}\phi_1(x) \int_{\phi(x,0)=\phi_0(x)}^{\phi(x,t_f)=\phi_1(x)} \mathcal{D}\phi(x,t) \delta \left(\dot{\phi}(x,t) + \Gamma_0 \frac{\delta \mathcal{U}}{\delta \phi} - \zeta(x,t) \right) |\det \mathbf{M}| \\ &= \int_{\phi(x,0)=\phi_0(x)} \mathcal{D}\phi(x,t) \delta \left(\dot{\phi}(x,t) + \Gamma_0 \frac{\delta \mathcal{U}}{\delta \phi} - \zeta(x,t) \right) |\det \mathbf{M}|. \end{aligned} \quad (14)$$

Note that in the second equality, the configuration $\phi(x, t_f)$ of the field at time t_f , appears as an integration variable (i.e. $0 < t \leq t_f$). The linear operator \mathbf{M} is defined as

$$\mathbf{M} = \frac{\delta \zeta(x,t)}{\delta \phi(x,t)} = \frac{\partial}{\partial t} + \Gamma_0 \frac{\partial f(\phi(x,t), t)}{\partial \phi}. \quad (15)$$

The determinant of this operator can be written as

$$\det \mathbf{M} = \exp\{\text{Tr}(\log \mathbf{M})\} = e^{\frac{\Gamma_0}{2} \int d^d x dt \frac{\delta^2 \mathcal{U}}{\delta \phi^2}}, \quad (16)$$

where the last equation is found by discretizing the operator \mathbf{M} and using the Stratonovich convention [17, 30]. We substitute this expression in the identity (14) and introduce the response field $\bar{\phi}(x, t)$ that allows us to rewrite the functional Dirac distribution $\delta(\cdot)$ as an exponential. Thus, we obtain

$$1 = \int_{\phi(x,0)=\phi_0(x)} \mathcal{D}\phi(x,t) \mathcal{D}\bar{\phi}(x,t) |\det \mathbf{M}| e^{-\int d^d x dt \bar{\phi} \{ \dot{\phi} + \Gamma_0 \frac{\delta \mathcal{U}}{\delta \phi} - \zeta \}} \quad \text{where } 0 < t \leq t_f. \quad (17)$$

We now insert this identity (17) in equation (10), perform the Gaussian integral over the noise variable $\zeta(x, t)$ and substitute the expression (16) for the Jacobian of \mathbf{M} . Finally, the following expression for the PDF is obtained:

$$\mathcal{P}(\phi_1 | \phi_0) = \int_{\phi(x,0)=\phi_0(x)}^{\phi(x,t_f)=\phi_1(x)} \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})}. \quad (18)$$

The PDF is thus expressed as a path-integral over the order parameter $\phi(x, t)$, with an effective dynamical action Σ given by

$$\Sigma(\phi, \dot{\phi}, \bar{\phi}) = \Gamma_0 \bar{\phi} \left(\frac{\dot{\phi}}{\Gamma_0} + \frac{\delta \mathcal{U}}{\delta \phi} - \frac{\bar{\phi}}{\beta} \right) - \frac{\Gamma_0}{2} \frac{\delta^2 \mathcal{U}}{\delta \phi^2}. \quad (19)$$

The non-equilibrium identities will arise from invariance properties of the path-integral with action Σ .

C. Non-Equilibrium Correlations Identities

We consider the case where the applied field varies with time according to a well-defined protocol: for $t \leq 0$, we have $h(x, 0) = h_0(x)$ and the system is in its stationary state; for $t > 0$, the external field varies with time and reaches its final value $h_f(x)$ after a finite time t_f and remains constant for $t \geq t_f$. The values of the potential \mathcal{U} for $t \leq 0$ and $t \geq t_f$ are denoted by \mathcal{U}_0 and \mathcal{U}_1 , respectively.

Let $\mathcal{O}[\phi]$ be a functional that depends on the values of the field $\phi(x, t)$ for $0 \leq t \leq t_f$. The average of $\mathcal{O}[\phi]$ with respect to the stationary initial ensemble and the stochastic evolution between times 0 and t_f is given by the path integral

$$\begin{aligned} \langle \mathcal{O} \rangle &= \frac{1}{Z_0} \int \mathcal{D}\phi_0(x) \mathcal{D}\phi_1(x) e^{-\beta \mathcal{U}_0[\phi_0]} \int_{\phi(x,0)=\phi_0(x)}^{\phi(x,t_f)=\phi_1(x)} \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \mathcal{O}[\phi] \\ &= \int \mathcal{D}\phi_1(x) \int \mathcal{D}\phi_0(x) \frac{e^{-\beta \mathcal{U}_0[\phi_0]}}{Z_0} \langle \phi_1 | \mathcal{O} | \phi_0 \rangle \end{aligned} \quad (20)$$

where we have defined

$$\langle \phi_1 | \mathcal{O} | \phi_0 \rangle = \int_{\phi(x,0)=\phi_0(x)}^{\phi(x,t_f)=\phi_1(x)} \mathcal{D}\phi(x,t) \mathcal{D}\bar{\phi}(x,t) e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \mathcal{O}[\phi]. \quad (21)$$

Under a change of the integration variable $\bar{\phi}$ in equation (20),

$$\bar{\phi}(x, t) \rightarrow -\bar{\phi}(x, t) + \beta \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)}, \quad (22)$$

the path integral measure is invariant but not the action Σ which varies as

$$\Sigma(\phi, \dot{\phi}, \bar{\phi}) \rightarrow \Sigma(\phi, -\dot{\phi}, \bar{\phi}) + \beta \dot{\phi} \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)}. \quad (23)$$

Noticing that

$$\dot{\phi} \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)} = \frac{d\mathcal{U}[\phi(x, t), t]}{dt} - \frac{\partial \mathcal{U}[\phi(x, t), t]}{\partial t}, \quad (24)$$

we obtain

$$\int d^d x \int_0^{t_f} dt \dot{\phi} \frac{\delta \mathcal{U}[\phi(x, t), t]}{\delta \phi(x, t)} = \mathcal{U}_1[\phi_1] - \mathcal{U}_0[\phi_0] - \mathcal{W}_J[\phi]. \quad (25)$$

The last term in this equation represents Jarzynski's work, defined by

$$\mathcal{W}_J[\phi] = \int_0^{t_f} dt \frac{\partial \mathcal{U}}{\partial t} = - \int d^d x dt \dot{h}(x, t) \phi(x, t), \quad (26)$$

the last equality being a consequence of equation (4). The change of sign of the time derivative $\dot{\phi}$ in equation (23) is now compensated by the change of variables in the path integral

$$(\phi(x, t), \bar{\phi}(x, t)) \rightarrow (\phi(x, t_f - t), \bar{\phi}(x, t_f - t)). \quad (27)$$

This time-reversal transformation leaves the functional measure invariant and restores Σ to its original form but with a *time-reversed* protocol for the external applied field $h(x, t) \rightarrow h(x, t_f - t)$. Performing the above change of variables (22) and (27) in equation (21) and using equations (23) and (25), we find, recalling that the work \mathcal{W}_J is odd under time-reversal,

$$\langle \phi_1 | \mathcal{O} | \phi_0 \rangle = e^{\beta(\mathcal{U}_0[\phi_0] - \mathcal{U}_1[\phi_1])} \langle \phi_1 | e^{-\beta \mathcal{W}_J} \hat{\mathcal{O}} | \phi_0 \rangle_R. \quad (28)$$

On the right hand side, the subscript R on the expectation value denotes a time-reversed protocol. The notation with a hat $\hat{\cdot}$ over an operator denotes the time-reversed operator, more precisely:

$$\hat{\mathcal{O}}[\phi] = \mathcal{O}[\phi(x, t_f - t)]. \quad (29)$$

Inserting this identity in equations (20 - 21) allows us to derive the following general relation:

$$\langle \mathcal{O} \rangle = \frac{1}{Z_0} \int \mathcal{D}\phi_0(x) \mathcal{D}\phi_1(x) e^{-\beta \mathcal{U}_1[\phi_1]} \langle \phi_0 | e^{-\beta \mathcal{W}_J} \hat{\mathcal{O}} | \phi_1 \rangle_R = \frac{Z_1}{Z_0} \langle \hat{\mathcal{O}} e^{-\beta \mathcal{W}_J} \rangle_R = e^{-\beta \Delta F} \langle \hat{\mathcal{O}} e^{-\beta \mathcal{W}_J} \rangle_R, \quad (30)$$

where ΔF is the free energy difference between the final and the initial states. Finally, redefining \mathcal{O} as $\mathcal{O} e^{-\beta \mathcal{W}_J}$, we deduce that

$$\langle \mathcal{O} e^{-\beta \mathcal{W}_J} \rangle = e^{-\beta \Delta F} \langle \hat{\mathcal{O}} \rangle_R. \quad (31)$$

When $\mathcal{O} = 1$, we obtain Jarzynski's theorem

$$\langle e^{-\beta \mathcal{W}_J} \rangle = e^{-\beta \Delta F}. \quad (32)$$

Taking $\mathcal{O} = e^{(\beta - \lambda) \mathcal{W}_J}$, where λ is an arbitrary real parameter, we derive the following symmetry property

$$\langle e^{-\lambda \mathcal{W}_J} \rangle = e^{-\beta \Delta F} \langle e^{(\lambda - \beta) \mathcal{W}_J} \rangle_R. \quad (33)$$

The Laplace transform of this equation leads to Crooks relation (2) in its usual form [3, 4]:

$$\frac{\mathcal{P}_F(W)}{\mathcal{P}_R(-W)} = e^{\beta(W - \Delta F)} \quad (34)$$

where \mathcal{P}_F and \mathcal{P}_R represent the probability distribution functions of the work for the forward and the reverse processes, respectively. We emphasize that the proof of Crooks and Jarzynski identities is based on invariance properties of the path integral and does not involve any a priori thermodynamic definition of heat and work. The expression (26) for the Jarzynski work appears here as a natural outcome of this invariance. It is important to notice that time-reversal is crucial to obtain the general identity (31) and Crooks' theorem. However, it is known that Jarzynski's identity can be proved without assuming time-reversal invariance [9].

We emphasize that Jarzynski's identity is valid only under carefully defined boundary conditions: (i) the system is at thermal equilibrium at time $t = 0$; (ii) During the finite time interval $0 \leq t \leq t_f$, the system is subject to an external protocol that drives it away from equilibrium; (iii) After the finite time t_f , all time-dependent parameters are frozen: these fixed parameters define a new state of thermodynamic equilibrium towards which the system relaxes after an infinite amount of time. According to this scheme, all path integrals must range over the finite interval of time $0 \leq t \leq t_f$ and the expectation value of the operator \mathcal{O} , defined in (20), has to be taken with respect to the Boltzmann distribution at $t = 0$ and the uniform distribution at the final time t_f . However, these stringent boundary conditions necessary for Jarzynski's identity to be valid, allow us to embed naturally all the path integrals over the infinite range of time $-\infty < t < +\infty$ by using the following properties of the probability distribution:

$$\frac{1}{Z_0} e^{-\beta \mathcal{U}_0[\phi_0]} = \lim_{\tau \rightarrow -\infty} P(\phi_0 | \phi_\tau), \quad (35)$$

$$1 = \int \mathcal{D}\phi(x, \tau) P(\phi_\tau | \phi_{t_f}) \quad \text{for any } \tau > t_f. \quad (36)$$

The first property assumes ergodicity (i.e. the Gibbs-Boltzmann distribution is reached at time $t = 0$ by starting from any initial condition at $t = -\infty$). The second equality simply results from normalization. In terms of path integrals, the first expression becomes

$$\frac{1}{Z_0} e^{-\beta \mathcal{U}_0[\phi_0]} = \int_{\phi(x, -\infty) = \phi_{-\infty}(x)}^{\phi(x, 0) = \phi_0(x)} \mathcal{D}\phi(x, \tau) \mathcal{D}\bar{\phi}(x, \tau) e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \quad \text{for } -\infty < \tau < 0, \quad (37)$$

where the condition at $t = -\infty$ is taken to be an arbitrary value $\phi_{-\infty}$ (or more generally a distribution of values, normalized to 1). Similarly, equation (36) is rewritten as

$$1 = \int_{\phi(x, t_1) = \phi_1(x)} \mathcal{D}\phi(x, \tau) \mathcal{D}\bar{\phi}(x, \tau) e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \quad \text{where } t_f < \tau < \infty. \quad (38)$$

We now consider an operator $\mathcal{O}[\phi]$ that differs from a constant only for $0 \leq t \leq t_f$ (i.e. the operator $\mathcal{O}[\phi]$ depends on the values taken by ϕ only over the finite range of time $0 \leq t \leq t_f$). Using the relations (37) and (38), the expectation value of $\mathcal{O}[\phi]$, defined in equation (20), can be expressed as

$$\langle \mathcal{O} \rangle = \int \mathcal{D}\phi(x, \tau) \mathcal{D}\bar{\phi}(x, \tau) e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \mathcal{O}[\phi] \quad \text{for } -\infty < \tau < \infty, \quad (39)$$

and where the space-time fields $\phi(x, t)$, $\bar{\phi}(x, t)$ are integrated over an infinite range of time and over the whole space. The only restriction on this path integral is that the initial condition at $t = -\infty$ is fixed (or more generally, the values at $t = -\infty$ are sampled from a normalized distribution). We note that the Jarzynski term $e^{-\beta \mathcal{W}_J}$ is equal to 1 outside the interval $0 \leq t \leq t_f$ and therefore we can also write

$$\langle e^{-\beta \mathcal{W}_J} \rangle = \int \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} e^{-\beta \mathcal{W}_J}. \quad (40)$$

We emphasize that the boundary conditions at finite time, as well as the average over the Boltzmann factor, have been eliminated and all path integrals are now evaluated over the full time line $-\infty < \tau < +\infty$.

D. A Non-Equilibrium Fluctuation-Dissipation Relation

The identity (31), which is at the core of the work fluctuation relations, is valid for any choice of the external field protocol. The free energy variation is a function only of the extremal values of the applied field at $t_0 = 0$ and $t = t_f$ and is independent of the values at intermediate times. Therefore, performing functional derivatives of the Jarzynski

identity (32) with respect to $h(x, t)$ at an intermediate time $t_0 < t < t_f$, and at position x , results in new identities. For example, we have

$$\frac{1}{\Gamma_0} \frac{\delta \langle e^{-\beta W_J} \rangle}{\delta h(x, t)} = \langle (\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t)) e^{-\beta W_J} \rangle = 0. \quad (41)$$

More generally, the n -th functional derivative of equation (32) at intermediate times t_1, \dots, t_n and positions x_1, \dots, x_n , gives the identity

$$\langle e^{-\beta W_J} \prod_{i=1}^n (\bar{\phi}(x_i, t_i) - \frac{\beta}{\Gamma_0} \dot{\phi}(x_i, t_i)) \rangle = 0. \quad (42)$$

Similarly, the functional derivative of equation (31) leads to

$$\langle (\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t)) \mathcal{O} e^{-\beta W_J} \rangle = e^{-\beta \Delta F} \langle \hat{\phi}(x, t) \hat{\mathcal{O}} \rangle_R. \quad (43)$$

In particular, equation (41) follows by choosing $\mathcal{O} = \hat{\mathcal{O}} = \hat{\mathbf{1}}$ and taking into account that $\langle \bar{\phi} \rangle = 0$. [Indeed, if we take the functional derivative of equation (20) with respect to $h(x, t)$ for $\mathcal{O} = \mathbf{1}$, we obtain $\langle \bar{\phi} \rangle = \langle \frac{\dot{\phi}}{\Gamma_0} + \frac{\delta \mathcal{U}}{\delta \phi} \rangle = 0$.]

For the special case $\mathcal{O}[\phi] = \phi(x', t')$, equation (43) leads to:

$$\langle \bar{\phi}(x, t) \phi(x', t') \rangle - \frac{\beta}{\Gamma_0} \langle \dot{\phi}(x, t) \phi(x', t') e^{-\beta W_J} \rangle = e^{-\beta \Delta F} \langle \hat{\phi}(x, t) \hat{\phi}(x', t') \rangle_R, \quad (44)$$

where $\hat{\phi}$ is obtained from $\bar{\phi}$ by time reversal as defined in equation (29). The terms proportional to the response field $\bar{\phi}$ in the correlators can be generated as follows: we consider a small perturbation $h_1(x, t)$ that drives the system out of the fixed protocol $h(x, t)$. However, we keep the definition of the Jarzynski work unchanged so that the perturbing field $h_1(x, t)$ is not included in W_J . The field h_1 couples to $\bar{\phi}$ in the action Σ : therefore performing functional derivatives with respect to h_1 amounts to inserting the field $\bar{\phi}$ inside correlation functions. The previous equation can thus be rewritten as

$$\frac{\beta}{\Gamma_0} \langle \dot{\phi}(x, t) \phi(x', t') e^{-\beta W_J} \rangle = \left. \frac{\delta \langle \phi(x', t') e^{-\beta W_J} \rangle}{\delta h_1(x, t)} \right|_{h_1=0} - e^{-\beta \Delta F} \left. \frac{\delta \langle \hat{\phi}(x', t') \rangle_R}{\delta \hat{h}_1(x, t)} \right|_{h_1=0}. \quad (45)$$

We emphasize that W_J has to be measured for the fixed protocol $h(x, t)$. In this form, equation (45) appears as an exact generalization of the fluctuation-dissipation relation (FDR). The equilibrium FDR [31–33] is retrieved by setting W_J and ΔF to 0. This indeed corresponds to a system prepared in an equilibrium state, which is not subject to any macroscopic protocol (i.e. $h(x, t) = 0$) but which is driven slightly out of equilibrium by the small perturbation $h_1(x, t)$:

$$\frac{\beta}{\Gamma_0} \langle \phi(x', t') \dot{\phi}(x, t) \rangle = \langle \phi(x', t') \bar{\phi}(x, t) \rangle - \langle \bar{\phi}(x', t') \phi(x, t) \rangle = \left. \frac{\delta \langle \phi(x', t') \rangle}{\delta h_1(x, t)} \right|_{h_1=0} - \left. \frac{\delta \langle \hat{\phi}(x', t') \rangle_R}{\delta \hat{h}_1(x, t)} \right|_{h_1=0}. \quad (46)$$

The fact that the equilibrium fluctuation-dissipation relation can be deduced by differentiation from Jarzynski's identity (or equivalently from Crooks' relations) has been understood by various authors (see in particular the works of R. Chetrite et al. [34–37]). This technique can also be used to find analogs of the FDR at higher orders [38]. Generalizations to non-equilibrium stationary states (NESS) have been also proposed [35, 39–41], e.g., starting from the Hatano-Sasa relations which are the counterpart of Jarzynski's identity for a NESS [42]. We emphasize that the identity obtained in equation (45) belongs to a different class. We do not consider a linear perturbation near a state of thermodynamic equilibrium, or near a NESS. Rather, we first apply, as in Jarzynski's scheme, a protocol to a system initially in thermodynamic equilibrium (that can be driven as far from equilibrium as wished) and then, we apply linear perturbations around this fixed protocol: this leads to a new fluctuation-dissipation theorem that relates out of equilibrium and nonstationary response functions to nonequilibrium and nonstationary correlation functions. The insertion of the Jarzynski factor $e^{-\beta W_J}$ inside the correlators leads to formulae which are valid far from equilibrium and look very similar to equilibrium relations. The relation (45) could be verified in single molecule pulling experiments where the protocol corresponds to the pulling force $F(t)$ and ϕ does not depend on space. Then, all the quantities that appear in this relation are susceptible to experimental measurements by adding a small perturbation $\delta F(t)$ to the fixed protocol $F(t)$.

The correlator identity (41) was obtained as a consequence of Jarzynski's equality (32) by taking its first derivative. Conversely, we show in Appendix A that equation (41) implies Jarzynski's equality (32) and is therefore equivalent to it. This converse property will be used in the next section to show that the work relation can be extracted from a hidden supersymmetric invariance of the dynamical action.

III. SUPERSYMMETRY AND NONEQUILIBRIUM WORK RELATIONS

Identities between correlators such as equations (41)-(43) suggest the existence of an underlying continuous symmetry of the system. Indeed, it was recognized in the late seventies that the Langevin equation possesses a hidden invariance under supersymmetric transformations. This property was first discussed in the context of dimensional reduction [22] and then used to derive convenient forms for diagrammatic expansion techniques [23] that were used to study critical dynamics of relaxational models [43–45]. This supersymmetry became an efficient tool to study [46–49] the properties of Fokker-Planck and associated Schrödinger operators (see e.g. [50, 51]). It was also realized that the equilibrium fluctuation-dissipation relation and the Onsager reciprocity relations could be derived from this invariance [24–26, 44]. Conversely, nonequilibrium situations were found to correspond to supersymmetry breaking and corrections to the classic equilibrium relations could formally be calculated [27, 28]. In this section, we extend this investigation further by showing that although supersymmetry is broken under nonequilibrium situations, it is partially recovered by adding to the dynamical action a term, which precisely corresponds to Jarzynski’s work. This restored invariance leads to Ward-Takahashi identities amongst correlation functions. Jarzynski’s relation results from these identities.

A. Supersymmetric Invariance for the time-independent Model A

First, we consider the case where the external field does not depend on time: the Langevin equation (3) has then a well-known supersymmetric invariance. We shall review the formalism that allows to make this invariance explicit, write the Ward-Takahashi and derive the equilibrium fluctuation-dissipation relation following [24].

1. The Supersymmetric Action and its Invariance Properties

To uncover this hidden symmetry, we introduce in addition to the original field $\phi(x, t)$ and the response field $\bar{\phi}(x, t)$, two auxiliary anti-commuting Grassmann fields $c(x, t)$ and $\bar{c}(x, t)$ that allow us to express the Jacobian of \mathbf{M} , defined in equation (15), as a functional integral [17, 24, 25]. These fields $c(x, t)$ and $\bar{c}(x, t)$ can be viewed as hidden classical fermionic fields that ensure the volume conservation constraints: they allow to enforce this conservation property at a dynamical level. Inserting the following identity [17]

$$\det \mathbf{M} = \int \mathcal{D}c \mathcal{D}\bar{c} e^{c \mathbf{M} \bar{c}} = \int \mathcal{D}c \mathcal{D}\bar{c} e^{c \left(\frac{\partial}{\partial \bar{c}} + \Gamma_0 \frac{\delta^2 \mathcal{U}}{\delta \phi^2} \right) \bar{c}}, \quad (47)$$

we observe that the PDF can be rewritten as

$$\mathcal{P}(\phi_1 | \phi_0) = \int_{\phi(x,0)=\phi_0(x)}^{\phi(x,t_1)=\phi_1(x)} \mathcal{D}\phi \mathcal{D}\bar{\phi} \mathcal{D}c \mathcal{D}\bar{c} e^{-\int d^d x dt \Sigma(\phi, \bar{\phi}, c, \bar{c})}, \quad (48)$$

where the effective Lagrangian Σ , which is now a function of the Grassmann variables as well, is given by

$$\Sigma(\phi, \bar{\phi}, c, \bar{c}) = \Gamma_0 \bar{\phi} \left(\frac{\dot{\phi}}{\Gamma_0} + \frac{\delta \mathcal{U}}{\delta \phi} - \frac{\bar{\phi}}{\beta} \right) - c \left(\frac{\partial}{\partial t} + \Gamma_0 \frac{\delta^2 \mathcal{U}}{\delta \phi^2} \right) \bar{c}. \quad (49)$$

The action Σ exhibits two important invariances under infinitesimal transformations that mix ordinary fields with Grassmann fields. We shall now describe them by specifying how each field varies under these transformations. In the Appendix B, we shall use a more elegant presentation in which the four fields $(\phi, \bar{\phi}, c, \bar{c})$ appear to be the components of a unique superfield Φ ; also, in this language, the dynamical action Σ will take a more compact form and the infinitesimal transformations that leave it invariant will have a simple interpretation.

• **Invariance under BRST1 Transformation:** Consider ϵ to be a time-independent infinitesimal Grassmann field. We consider the following transformation (that we call BRST1):

$$\begin{aligned} \delta \phi(x, t) &= -\bar{c}(x, t) \epsilon, & \delta \bar{c}(x, t) &= 0, \\ \delta c(x, t) &= \bar{\phi}(x, t) \epsilon, & \delta \bar{\phi}(x, t) &= 0. \end{aligned} \quad (50)$$

We note that the square of this transformation vanishes. If we calculate the variation of Σ under the transformation (50), we obtain using equation (49):

$$\delta\Sigma = \bar{\phi}(\delta\dot{\phi} + \Gamma_0 \frac{\delta^2\mathcal{U}}{\delta\phi^2} \delta\phi) - \delta c \left(\frac{\partial}{\partial t} + \Gamma_0 \frac{\delta^2\mathcal{U}}{\delta\phi^2} \right) \bar{c} - \Gamma_0 \frac{\delta^3\mathcal{U}}{\delta\phi^3} \delta\phi c \bar{c} = -\bar{\phi}(\dot{c}\epsilon + \Gamma_0 \frac{\delta^2\mathcal{U}}{\delta\phi^2} \bar{c}\epsilon) - \bar{\phi}\epsilon(\dot{c} + \Gamma_0 \frac{\delta^2\mathcal{U}}{\delta\phi^2} \bar{c}) = 0. \quad (51)$$

This expression vanishes identically because of algebraic anti-commutation rules. We note that we do not need to suppose that the potential \mathcal{U} is time-independent.

• **Invariance under BRST2 transformation:** The transformation BRST2 mixes the different fields as follows :

$$\begin{aligned} \delta\phi(x, t) &= c(x, t)\bar{\epsilon}, & \delta c(x, t) &= 0, \\ \delta\bar{\phi}(x, t) &= \frac{\beta}{\Gamma_0} \dot{c}(x, t)\bar{\epsilon}, & \delta\bar{c}(x, t) &= \left(\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t) \right) \bar{\epsilon}, \end{aligned} \quad (52)$$

$\bar{\epsilon}$ being a time-independent infinitesimal Grassmann field. Here again, the square of the transformation (52) vanishes. If we calculate the variation of Σ under the transformation (52), we obtain

$$\delta\Sigma = \frac{d}{dt} \left\{ \left(\frac{\beta}{\Gamma_0} \dot{\phi} - \bar{\phi} \right) c \right\} \bar{\epsilon} + \beta \frac{\delta\mathcal{U}}{\delta\phi} \dot{c}\bar{\epsilon} + \beta \frac{\delta^2\mathcal{U}}{\delta\phi^2} \dot{\phi}c\bar{\epsilon} = \frac{d}{dt} \left\{ \left(\frac{\beta}{\Gamma_0} \dot{\phi} + \beta \frac{\delta\mathcal{U}}{\delta\phi} - \bar{\phi} \right) c \right\} \bar{\epsilon} - \beta \frac{\delta^2\mathcal{U}}{\delta\phi\partial t} c\bar{\epsilon}. \quad (53)$$

If the potential \mathcal{U} is independent of time the last term vanishes and Σ is invariant under the transformation (52) only up to a total time-derivative term that produces boundary contributions to the total action. This does not affect the dynamics if boundary terms vanish or if the time-integral is defined from $-\infty$ to $+\infty$.

The invariance of the dynamical action Σ under both transformations BRST1 (50) and BRST2 (52) is what makes the time-independent dissipative Langevin equation supersymmetric [17]. This supersymmetric property reflects the time reversal invariance of Model A in the absence of an external field and allows to prove the fluctuation-dissipation theorem [24, 25] as will be recalled below.

2. Ward-Takahashi identities and the equilibrium fluctuation-dissipation relation

Introducing a four-component source (H, \bar{H}, \bar{L}, L) , we define the generating function

$$Z(H, \bar{H}, \bar{L}, L) = \int \mathcal{D}\phi \mathcal{D}\bar{\phi} \mathcal{D}c \mathcal{D}\bar{c} \exp \left(\int d^d x dt \left(-\Sigma(\phi, \bar{\phi}, c, \bar{c}) + \bar{H}\phi + H\bar{\phi} + \bar{L}c + L\bar{c} \right) \right). \quad (54)$$

In the Appendix, we rederive the following two Ward identities that result from the invariance of the action under the transformations (50) and (52). The first Ward-Takahashi identity corresponding to invariance under (50) is

$$\int d^d x dt \left(\bar{H} \frac{\delta Z}{\delta L} - \bar{L} \frac{\delta Z}{\delta H} \right) = 0. \quad (55)$$

The second Ward-Takahashi identity corresponding to the transformation (52) is given by

$$\int d^d x dt \left(\frac{\beta}{\Gamma_0} H \frac{d}{dt} \frac{\delta Z}{\delta \bar{L}} + L \left(\frac{\delta Z}{\delta H} - \frac{\beta}{\Gamma_0} \frac{d}{dt} \frac{\delta Z}{\delta \bar{H}} \right) + \bar{H} \frac{\delta Z}{\delta \bar{L}} \right) = 0. \quad (56)$$

We now apply $\delta^2/\delta\bar{L}(x', t')\delta\bar{H}(x, t)$ to the first Ward-Takahashi identity (55) and then put all the sources H, \bar{H}, L , and \bar{L} to 0. This leads to

$$\frac{\delta^2 Z}{\delta\bar{L}(x', t')\delta L(x, t)} - \frac{\delta^2 Z}{\delta H(x', t')\delta\bar{H}(x, t)} = 0. \quad (57)$$

This equation implies, using (C8) and (C9), the following identity between correlation functions:

$$\langle c(x', t')\bar{c}(x, t) \rangle = \langle \bar{\phi}(x', t')\phi(x, t) \rangle. \quad (58)$$

Similarly, applying $\delta^2/\delta\bar{H}(x', t')\delta L(x, t)$ to the second Ward-Takahashi identity (56), and putting all the sources to zero, we obtain

$$\frac{\delta^2 Z}{\delta\bar{H}(x', t')\delta H(x, t)} - \frac{\beta}{\Gamma_0} \frac{\delta}{\delta\bar{H}(x', t')} \left\{ \frac{d}{dt} \frac{\delta Z}{\delta\bar{H}(x, t)} \right\} + \frac{\delta^2 Z}{\delta L(x, t)\delta\bar{L}(x', t')} = 0. \quad (59)$$

This identity implies that

$$\langle \phi(x', t') \bar{\phi}(x, t) \rangle - \frac{\beta}{\Gamma_0} \langle \phi(x', t') \frac{d\phi}{dt}(x, t) \rangle + \langle \bar{c}(x, t) c(x', t') \rangle = 0. \quad (60)$$

In order to eliminate the correlations between the Grassmann variables, we combine equation (57) with equation (59) (or equivalently equation (58) with equation (60)) and use the fact that L and \bar{L} anti-commute (or equivalently that c and \bar{c} anti-commute). This leads us to:

$$\frac{\beta}{\Gamma_0} \langle \phi(x', t') \dot{\phi}(x, t) \rangle = \langle \phi(x', t') \bar{\phi}(x, t) \rangle - \langle \bar{\phi}(x', t') \phi(x, t) \rangle = \frac{\delta}{\delta H(x, t)} \langle \phi(x', t') \rangle - \frac{\delta}{\delta H(x', t')} \langle \phi(x, t) \rangle. \quad (61)$$

Recalling that $\delta\langle\phi\rangle/\delta H$ is a response function, we observe that this equation is nothing but the Fluctuation-Dissipation relation (see (46)). Usually, the FDR is derived by invoking invariance under time-reversal which implies detailed balance. Here, it is the invariance under supersymmetry that plays the role of time-reversal invariance.

B. Model A with a time dependent potential

We now study the case where the potential $\mathcal{U}[\phi(x, t), t]$ that appears in Model A (3) depends explicitly on time, and show how properties related to supersymmetry can still be used in this nonequilibrium situation.

1. Breakdown of the invariance for a time-dependent potential and its restoration by adding the Jarzynski term

When the potential $\mathcal{U}[\phi(x, t), t]$ depends on time (by adding for example a time-dependent external field), the action Σ is no more invariant under supersymmetry. More precisely, we observed that invariance under (50) does remain valid even when \mathcal{U} is a function of time and therefore the first Ward identity (55) is still satisfied. However, invariance under (52) is broken and according to equation (53), we find the variation of $\Sigma(\phi, \bar{\phi}, c, \bar{c})$ to be

$$\delta\Sigma(\phi, \bar{\phi}, c, \bar{c}) = \frac{d\mathcal{A}}{dt} - \beta \frac{\partial}{\partial t} \left(\frac{\delta\mathcal{U}}{\delta\phi} \right) c(x, t) \bar{\epsilon} \quad (62)$$

with the total derivative term

$$\mathcal{A} = \beta \left(\frac{\dot{\phi}}{\Gamma_0} + \frac{\delta\mathcal{U}}{\delta\phi} - \frac{\bar{\phi}}{\beta} \right) c \bar{\epsilon}. \quad (63)$$

Therefore $\delta\Sigma$ is not a total derivative and invariance under (52) is not true anymore for a time-dependent potential. In particular, the second Ward identity (56), which was crucial for the proof of the Fluctuation Dissipation relation, is no more satisfied.

However, we note that the last term in equation (62), which breaks the invariance under (52), can be rewritten as:

$$\beta \frac{\delta^2\mathcal{U}}{\delta\phi\partial t} c \bar{\epsilon} = \beta \frac{\delta^2\mathcal{U}}{\delta\phi\partial t} \delta\phi = \delta \left(\beta \frac{\partial\mathcal{U}}{\partial t} \right) \quad (64)$$

and can be interpreted as the variation of a function. Therefore, the modified action $\Sigma_{\mathbf{J}}$, defined as

$$\Sigma_{\mathbf{J}} = \Sigma + \beta \frac{\partial\mathcal{U}}{\partial t} \quad (65)$$

and obtained by adding the Jarzynski work (26) to the initial action, *is now invariant* under the supersymmetric BRST2-transformation (52) because its variation is given by a total derivative term:

$$\delta\Sigma_{\mathbf{J}} = \frac{d\mathcal{A}}{dt} \quad (66)$$

However, we emphasize that $\Sigma_{\mathbf{J}}$ is no more invariant under BRST1 (50) although Σ was invariant. We have thus restored BRST2-invariance at the expense of BRST1. Therefore, in the time dependent case, neither the original action Σ nor the modified action $\Sigma_{\mathbf{J}}$ are supersymmetric [17]. They only exhibit partial invariances by either BRST1 (in the case of Σ) or BRST2 (in the case of $\Sigma_{\mathbf{J}}$). We shall now see that BRST2-invariance is required to derive nonequilibrium work identities.

For a time-dependent external field $h(x, t)$, the compensating term in equation (64) is given by $-\beta\dot{h}(x, t)\phi$. The boundary terms at $t = \pm\infty$ are, conventionally, assumed to vanish. Therefore, the invariance of the dynamical action under (52) breaks down when the potential is time-dependent but is restored by adding Jarzynski term. This observation allows us to use the Ward-Takahashi identity (56) that results from this invariance. We shall prove that this Ward-Takahashi identity leads to the nonequilibrium work relations.

2. Work relations from supersymmetry

We now show that the invariance of $\Sigma_{\mathbf{J}}$ implies the correlator identities (42). We first remark that in the above proofs of supersymmetric invariance it was noted that the boundary terms (a total time-derivative contribution) are harmless if the integration range of the path integral is from $-\infty$ to $+\infty$.

We consider an operator $\mathcal{O}[\phi]$ that differs from a constant only for $0 \leq t \leq t_f$. Then, as shown in equations (39) and (40), the expectation value $\langle \mathcal{O}e^{-\beta\mathcal{W}_J} \rangle$ can be rewritten over an infinite time range. Using Grassmann variables, we have

$$\langle \mathcal{O}e^{-\beta\mathcal{W}_J} \rangle = \int \mathcal{D}\phi\mathcal{D}\bar{\phi}\mathcal{D}c\mathcal{D}\bar{c} e^{-\int d^d x dt \Sigma(\phi, \bar{\phi}, c, \bar{c})} e^{-\beta\mathcal{W}_J} \mathcal{O}[\phi] = \int \mathcal{D}\phi\mathcal{D}\bar{\phi}\mathcal{D}c\mathcal{D}\bar{c} e^{-\int d^d x dt \Sigma_{\mathbf{J}}(\phi, \bar{\phi}, c, \bar{c})} \mathcal{O}[\phi], \quad (67)$$

where all the space-time fields $\phi(x, t)$, $\bar{\phi}(x, t)$, $c(x, t)$ and $\bar{c}(x, t)$ are integrated over the time interval $-\infty$ to ∞ . In the last equation, we have combined the action Σ with the Jarzynski work \mathcal{W}_J to get the modified action $\Sigma_{\mathbf{J}}$, defined in (65). As shown in (66), the modified action $\Sigma_{\mathbf{J}}$ is invariant under the transformation (52). Therefore, the following generating function $Z_{\mathbf{J}}(H, \bar{H}, \bar{L}, L)$, built from the modified action $\Sigma_{\mathbf{J}}$, satisfies the second Ward-Takahashi identity (56):

$$Z_{\mathbf{J}}(H, \bar{H}, \bar{L}, L) = \int \mathcal{D}\phi\mathcal{D}\bar{\phi}\mathcal{D}c\mathcal{D}\bar{c} \exp\left(\int d^d x dt (-\Sigma_{\mathbf{J}}(\phi, \bar{\phi}, c, \bar{c}) + \bar{H}\phi + H\bar{\phi} + \bar{L}c + L\bar{c})\right). \quad (68)$$

We apply the following operator to the Ward-Takahashi identity (56) satisfied by $Z_{\mathbf{J}}$,

$$\frac{\delta}{\delta L(x, t)} \prod_{i=1}^n \left(\frac{\delta}{\delta H(x_i, t_i)} - \frac{\beta}{\Gamma_0} \frac{d}{dt_i} \frac{\delta}{\delta \bar{H}(x_i, t_i)} \right), \quad (69)$$

and set the source fields H, \bar{H}, \bar{L}, L to zero. For $n = 1$, we find

$$\left\langle \left(\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t) \right) e^{-\beta\mathcal{W}_J} \right\rangle = 0 \quad (70)$$

More generally, for $n \geq 1$, we have

$$\left\langle \left(\bar{\phi}_1 - \frac{\beta}{\Gamma_0} \dot{\phi}_1 \right) \left(\bar{\phi}_2 - \frac{\beta}{\Gamma_0} \dot{\phi}_2 \right) \dots \left(\bar{\phi}_n - \frac{\beta}{\Gamma_0} \dot{\phi}_n \right) e^{-\beta\mathcal{W}_J} \right\rangle = 0, \quad (71)$$

where $\phi_1 = \phi(x_1, t_1)$ etc... These two relations are identical to equations (41) and (42), respectively. In Appendix A, we show that these relations are equivalent to Jarzynski's identity. This concludes the proof that Jarzynski's relation can be obtained as a consequence of a Ward-Takahashi identity that itself results from supersymmetric invariance.

IV. CONCLUSION

We have used field-theoretic methods to derive nonequilibrium work identities for a space-time field driven by a non-linear stochastic equation (Model A). We have obtained a generalization of the fluctuation-dissipation relation that remains valid far from equilibrium and that characterizes the response of a system to infinitesimal perturbations around a given protocol. The introduction of auxiliary fermionic fields has allowed us to explore general symmetries of the dynamical action. In particular, it is well-known that the time independent Langevin equation exhibits a hidden supersymmetric invariance [22, 23] that is known to imply the classic fluctuation-dissipation theorem and Onsager's relations [17, 24, 25]. However, this invariance breaks down when the potential varies according to a time-dependent protocol and drives the system out of equilibrium. In this work, we have shown that the invariance of the effective action under supersymmetric transformation is restored by adding to the action a counter-term which is precisely the Jarzynski work \mathcal{W}_J . Furthermore, we proved that the associated supersymmetric Ward-Takahashi identity implies Jarzynski's theorem. Hence, supersymmetry enforces the exactness of the adiabatic limit even for processes that have a finite duration and that can bring the system arbitrarily far from equilibrium. In other words, weighing all averages with the Jarzynski work (which amounts to modifying the dynamical action by adding to it the Jarzynski work, as in (65)) restores one of the fundamental symmetries valid in equilibrium. Thanks to this invariance, many properties of the system are effectively the same as if it were at equilibrium (although it is neither in equilibrium nor in a stationary state). The idea of considering weighed averages, or equivalently modified path-measure (as

was emphasized by Jarzynski himself in his early works [2]), allows to preserve certain crucial symmetries and has striking consequences in the present context. We believe that a similar arguments should apply in many different fields: in particular, supersymmetry exists in classical Hamiltonian systems [26] for which Jarzynski's equality was initially derived, and can be applied to prove the fluctuation theorem for stochastic dynamics [52]. Besides, the response-field method that we have used here can be extended to multi-component fields, to other stochastic models with conserved order parameter and also to systems with colored noise [53].

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Appendix A: Proof of the equivalence between equation (41) and Jarzynski's relation

In this Appendix, we prove that the correlator identity (41) implies Jarzynski's relation (32) and is therefore equivalent to it. First, we modify the applied external field $h(x, t)$ by considering $h(x, \alpha t)$ for any $\alpha > 0$. We then evaluate the average value $\langle e^{-\beta W_J} \rangle(\alpha)$ using expression (40). From (19) and (26), we observe that the external field $h(x, \alpha t)$ appears only in the following two terms: $\Gamma_0 \bar{\phi}(x, t) h(x, \alpha t) + \beta \alpha \dot{h}(x, \alpha t) \phi(x, t)$ (note that the Jacobian term, $\delta^2 \mathcal{U} / \delta \phi^2$ does not contain h). Thus, we have

$$\frac{d\langle e^{-\beta W_J} \rangle}{d\alpha} = \int \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\beta W_J - \int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \int d^d x dt \left(\Gamma_0 t \bar{\phi}(x, t) \dot{h}(x, \alpha t) + \beta (\dot{h}(x, \alpha t) + t \alpha \ddot{h}(x, \alpha t)) \phi(x, t) \right). \quad (\text{A1})$$

Integrating by parts the last term with respect to time leads to

$$\frac{d\langle e^{-\beta W_J} \rangle}{d\alpha} = \int \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\beta W_J - \int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \int d^d x dt \left(\Gamma_0 t \bar{\phi}(x, t) \dot{h}(x, \alpha t) - \beta t \dot{h}(x, \alpha t) \dot{\phi}(x, t) \right) \quad (\text{A2})$$

$$= \int \mathcal{D}\phi \mathcal{D}\bar{\phi} e^{-\beta W_J - \int d^d x dt \Sigma(\phi, \dot{\phi}, \bar{\phi})} \int d^d x dt t \dot{h}(x, \alpha t) \left(\Gamma_0 \bar{\phi}(x, t) - \beta \dot{\phi}(x, t) \right). \quad (\text{A3})$$

Note that the boundary terms that result from integration by parts vanish because we are integrating for $t \in (-\infty, +\infty)$ and because $\dot{h} = 0$ outside the time interval $0 \leq \alpha t \leq t_f$. The last equality can be rewritten as

$$\frac{d\langle e^{-\beta W_J} \rangle}{d\alpha} = \Gamma_0 \int d^d x dt t \dot{h}(x, \alpha t) \left\langle \left(\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t) \right) e^{-\beta W_J} \right\rangle, \quad (\text{A4})$$

which vanishes because of equation (41). We thus have

$$\frac{d\langle e^{-\beta W_J} \rangle}{d\alpha} = 0. \quad (\text{A5})$$

Hence, the value of $\langle e^{-\beta W_J} \rangle$ does not depend on α and can be evaluated by taking the limit $\alpha \rightarrow 0$ which corresponds to an adiabatic evolution. But then it is well known, from classical thermodynamics, that $W_J = -\Delta F$. This implies $\langle e^{-\beta W_J} \rangle = \exp(-\Delta F)$.

Appendix B: Supersymmetric formalism

In this appendix, we use the superfield formalism, as explained in [17] and [29], to rewrite the dynamical action and to interpret the invariances under the transformations (50) and (52) in more compact and elegant language. In this formalism, the origin of these symmetries will appear more clearly. Besides, the effect of adding the Jarzynski term to make the time-dependent action invariant under (52), will also become more transparent.

We introduce two anti-commuting coordinates θ and $\bar{\theta}$ and define the superfield

$$\Phi(x, t, \theta, \bar{\theta}) = \phi(x, t) + \theta \bar{c}(x, t) + c(x, t) \bar{\theta} + \theta \bar{\theta} \bar{\phi}(x, t). \quad (\text{B1})$$

In terms of this superfield, the action $\Sigma(\phi, \bar{\phi}, c, \bar{c})$, defined in (49), can be written as

$$\Sigma(\phi, \bar{\phi}, c, \bar{c}) = \int d\bar{\theta}d\theta \Sigma(\Phi) \text{ with } \Sigma(\Phi) = \Gamma_0 (\bar{D}\Phi D\Phi + \mathcal{U}(\Phi)), \quad (\text{B2})$$

where the differential operators D and \bar{D} are given by:

$$D = \frac{1}{\beta} \frac{\partial}{\partial \theta}, \quad (\text{B3})$$

$$\bar{D} = \frac{\partial}{\partial \theta} - \frac{\beta}{\Gamma_0} \bar{\theta} \frac{\partial}{\partial t}. \quad (\text{B4})$$

These two operators satisfy the anticommutation relations $D^2 = \bar{D}^2 = 0$ and $\{D, \bar{D}\} = -\frac{1}{\Gamma_0} \frac{\partial}{\partial t}$.

Integration with respect to the Grassmann variables is defined through the following rules [17]:

$$\int d\bar{\theta}d\theta 1 = 0, \quad \int d\bar{\theta}d\theta \theta = 0, \quad \int d\bar{\theta}d\theta \bar{\theta} = 0, \quad \int d\bar{\theta}d\theta \theta \bar{\theta} = 1. \quad (\text{B5})$$

(Integration and derivation are in fact identical).

The action Σ is invariant under the transformations (50) and (52) which act by mixing the four fields $(\phi, \bar{\phi}, c, \bar{c})$. These two symmetries can be viewed as transformations of the superfield Φ that leave the super-action $\Sigma(\Phi)$ invariant.

In the superspace formalism, the transformation (50) corresponds to an infinitesimal translation of the θ coordinate, $\theta \rightarrow \theta + \epsilon$. The generator of this transformation is given by

$$Q = \frac{\partial}{\partial \theta}. \quad (\text{B6})$$

Indeed, one can check that the superfield $\delta\Phi = \epsilon Q\Phi = \delta\phi(x, t) + \theta\delta\bar{c}(x, t) + \delta c(x, t)\bar{\theta} + \theta\bar{\theta}\delta\bar{\phi}(x, t)$ is given by $\delta\Phi = \epsilon\bar{c}(x, t) + \epsilon\bar{\theta}\bar{\phi}(x, t) = -\bar{c}(x, t)\epsilon + \bar{\theta}\bar{\phi}(x, t)\epsilon$. If we identify each of the components we retrieve the transformation (50).

Similarly, the transformation (52) corresponds to $\bar{\theta} \rightarrow \bar{\theta} + \bar{\epsilon}$ and $t \rightarrow t + \frac{\beta}{\Gamma_0} \bar{\epsilon}\theta$. This transformation is generated by the operator

$$\bar{Q} = \frac{\partial}{\partial \bar{\theta}} + \frac{\beta}{\Gamma_0} \theta \frac{\partial}{\partial t}. \quad (\text{B7})$$

The operators Q and \bar{Q} that generate the supersymmetry transformations anticommute with D and \bar{D} . Besides, they satisfy the anticommutation relations $Q^2 = \bar{Q}^2 = 0$ and $\{Q, \bar{Q}\} = \frac{\beta}{\Gamma_0} \frac{\partial}{\partial t}$. When the potential \mathcal{U} does not depend on time, the action $\Sigma(\Phi)$ is symmetric under Q , and is invariant under \bar{Q} upto a total derivative. This fact was checked in equations (51,53) and can be verified again using the supersymmetry formalism. If \mathcal{U} depends explicitly on time the action $\Sigma(\Phi)$ is not invariant anymore under \bar{Q} . However, by adding to it the Jarzynski term (26), we obtain the modified action $\Sigma_{\mathbf{J}}$, defined in equation (65), which is invariant under \bar{Q} . This property is manifest in the supersymmetric formalism in which the modified action is written as

$$\Sigma_{\mathbf{J}} = \Gamma_0 \left(\bar{D}\Phi D\Phi + \mathcal{U}(\Phi, t + \frac{\beta}{\Gamma_0} \theta\bar{\theta}) \right). \quad (\text{B8})$$

Appendix C: Supersymmetric Ward-Takahashi Identities

When the invariances under the transformations generated by the operators (B6) and (B7) are implemented in the generating function $Z(H, \bar{H}, \bar{L}, L)$ defined in (54), the Ward-Takahashi Identities (55) and (56) are obtained. We follow closely the method of [24] to derive these identities. In order to calculate correlation functions it is helpful to rewrite the sources as a superfield \mathbf{J} , defined as:

$$\mathbf{J} = H + \theta\bar{L} + \bar{\theta}L + \theta\bar{\theta}\bar{H} \quad (\text{C1})$$

where $L(x, t)$ and $\bar{L}(x, t)$ are Grassmann fields. We thus have

$$\int d\bar{\theta}d\theta \mathbf{J}(x, t, \theta, \bar{\theta}) \Phi(x, t, \theta, \bar{\theta}) = \bar{H}\phi + H\bar{\phi} + \bar{L}c + L\bar{c}. \quad (\text{C2})$$

We note from this expression that H plays the role of an applied external ‘magnetic’ field. In this formalism, the generating function $Z(H, \bar{H}, \bar{L}, L)$ becomes

$$Z(\mathbf{J}) = \int \mathcal{D}\Phi e^{\int d^d x dt d\bar{\theta} d\theta (-\Sigma(\Phi) + \mathbf{J}\Phi)}. \quad (\text{C3})$$

(In the sequel, the integration element $d^d x dt d\bar{\theta} d\theta$ will be omitted in general.)

In order to derive the first Ward-Takahashi identity, we proceed as follows. In the functional integral (C3), we make the change of variable $\Phi \rightarrow \tilde{\Phi}$ with $\Phi = \tilde{\Phi} + \epsilon Q\tilde{\Phi}$, where Q , defined in (B6) is the infinitesimal generator of the transformation (50) corresponding to θ translations. Taking into account that the Jacobian is 1, we obtain

$$Z(\mathbf{J}) = \int \mathcal{D}\Phi e^{\int -\Sigma(\Phi) + \mathbf{J}\Phi} = \int \mathcal{D}\tilde{\Phi} e^{\int -\Sigma(\tilde{\Phi} + \epsilon Q\tilde{\Phi}) + \mathbf{J}(\tilde{\Phi} + \epsilon Q\tilde{\Phi})} = \int \mathcal{D}\tilde{\Phi} e^{\int -\Sigma(\tilde{\Phi} + \epsilon Q\tilde{\Phi}) + \mathbf{J}(\tilde{\Phi} + \epsilon Q\tilde{\Phi})}. \quad (\text{C4})$$

(The last equality results simply from the fact that $\tilde{\Phi}$ is a dummy variable.) The fact that the action is invariant means precisely that $\int d\bar{\theta} d\theta \Sigma(\Phi) = \int d\bar{\theta} d\theta \Sigma(\Phi + \epsilon Q\Phi)$. Therefore, we deduce that

$$Z(\mathbf{J}) = \int \mathcal{D}\Phi e^{\int -\Sigma + \mathbf{J}\Phi} = \int \mathcal{D}\Phi e^{\int -\Sigma + \mathbf{J}\Phi + \mathbf{J}\epsilon Q\Phi} = \int \mathcal{D}\Phi e^{\int -\Sigma + \mathbf{J}\Phi} (1 + \epsilon \int \mathbf{J}Q\Phi). \quad (\text{C5})$$

This equation being true for any value of ϵ we conclude that

$$\int \mathcal{D}\Phi \left\{ \int d^d x dt d\bar{\theta} d\theta \mathbf{J}Q\Phi \right\} e^{\int -\Sigma + \mathbf{J}\Phi} = 0. \quad (\text{C6})$$

We now calculate explicitly the value of $\mathbf{J}Q\Phi$ and substitute it in equation (C6),

$$\int \mathcal{D}\Phi \left\{ \int d^d x dt \bar{H}(x, t) \bar{c}(x, t) - \bar{L}(x, t) \bar{\phi}(x, t) \right\} e^{\int -\Sigma + \mathbf{J}\Phi} = 0. \quad (\text{C7})$$

By differentiating the generating function $Z(\mathbf{J})$ with respect to \bar{H} , we obtain

$$\frac{\delta Z(\mathbf{J})}{\delta \bar{H}(x_a, t_a)} = \int \mathcal{D}\Phi \phi(x_a, t_a) \exp^{\int -\Sigma + \mathbf{J}\Phi}. \quad (\text{C8})$$

Similarly, we have

$$\frac{\delta Z}{\delta L} \rightarrow \bar{c}, \quad \frac{\delta Z}{\delta \bar{L}} \rightarrow c, \quad \text{and} \quad \frac{\delta Z}{\delta \bar{H}} \rightarrow \bar{\phi}. \quad (\text{C9})$$

Substituting these relations in equation (C7) allows us to derive the first Ward-Takahashi identity (55):

$$\int d^d x dt \left(\bar{H} \frac{\delta Z}{\delta L} - \bar{L} \frac{\delta Z}{\delta H} \right) = 0. \quad (\text{C10})$$

For the second invariance under the BRST2 transformation (52), we use the infinitesimal generator \bar{Q} , defined in (B7). After similar calculations, we find

$$\int \mathcal{D}\Phi \left\{ \int d^d x dt d\bar{\theta} d\theta \mathbf{J}\bar{Q}\Phi \right\} e^{\int -\Sigma + \mathbf{J}\Phi} = 0. \quad (\text{C11})$$

After calculating explicitly $\mathbf{J}\bar{Q}\Phi$, we obtain

$$\int \mathcal{D}\Phi \left\{ \int d^d x dt \frac{\beta}{\Gamma_0} H(x, t) \dot{c}(x, t) + L(x, t) (\bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \dot{\phi}(x, t)) + \bar{H}(x, t) c(x, t) \right\} e^{\int -\Sigma + \mathbf{J}\Phi} = 0. \quad (\text{C12})$$

Expressing the fields in this equation as functional derivatives of the generating function Z , leads us to the second Ward-Takahashi identity (56):

$$\int d^d x dt \left(\frac{\beta}{\Gamma_0} H \frac{d}{dt} \frac{\delta Z}{\delta L} + L \left(\frac{\delta Z}{\delta H} - \frac{\beta}{\Gamma_0} \frac{d}{dt} \frac{\delta Z}{\delta H} \right) + \bar{H} \frac{\delta Z}{\delta L} \right) = 0. \quad (\text{C13})$$

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