Supersymmetry and Nonequilibrium Work Relations

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We give a field-theoretic proof of the nonequilibrium work relations for a space-dependent field with stochastic dynamics. The path integral representation and its symmetries allow us to derive Jarzynski’s equality. In addition, we derive a set of exact identities that generalize the fluctuation-dissipation relations to far-from-equilibrium situations. These identities are prone to experimental verification. Furthermore, we show that supersymmetry invariance of the Langevin equation, which is broken when the external potential is time-dependent, is partially restored by adding to the action a term which is precisely Jarzynski’s work. Jarzynski’s equality can also be deduced from this supersymmetry.

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During the last decade a number of exact relations have been derived for non-equilibrium processes. The Jarzynski equality is one of these remarkable results: it shows 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 $\Delta F$ 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 [2] or a discrete Markov equation [3, 4]. Jarzynski’s result has been verified on exactly solvable models [5] and by explicit calculations in kinetic theory of gases [6, 7]. This equality has also been used in various single-molecule pulling experiments [8, 9, 10] to measure folding free energies and has been checked against analytical predictions on mesoscopic mechanical devices such as a torsion pendulum [11]. These experiments 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 (for a review see e.g. [12]).

In the present work, we derive nonequilibrium work relations for a field $\phi(x, t)$ representing a coarse-grained order parameter of a microscopic system. This field evolves according to an effective stochastic equation that depends on the symmetries and conservation laws of the system [13]. We represent the stochastic evolution as a path integral [14, 15, 16] and use the response field formalism [17] to derive the work relations from the invariance of the path integral under certain changes of variables. We obtain correlator identities that generalize the fluctuation-dissipation relations arbitrarily far from equilibrium. These identities can be checked experimentally in single molecule experiments. Furthermore, by introducing auxiliary Grassmannian fields, we interpret this invariance as a manifestation of a hidden supersymmetry. This supersymmetry is known to be the fundamental invariance property that embodies the principle of microscopic reversibility and leads to the fluctuation-dissipation-theorem and the Onsager reciprocity relations for a system at thermal equilibrium [18, 19, 20, 21]. Here, we show that, far from equilibrium, Jarzynski’s theorem, is also a consequence of an underlying supersymmetry. This supersymmetry in turn allows to generalize the fluctuation dissipation-theorem to far from equilibrium situations.

We consider a scalar field $\phi(x, t)$ defined on d-dimensional space with Model A dynamics that describes a system with non-conserved order-parameter [13], (e.g., the Ising model with Glauber dynamics):

\[
\frac{\partial \phi}{\partial t} = -\Gamma_0 \frac{\delta U}{\delta \phi} + \zeta(x, t) = -\Gamma_0 f(\phi) + \zeta(x, t) \tag{1}
\]

$\zeta(x, t)$ is a Gaussian white noise of zero mean value and correlations $\langle \zeta(x, t)\zeta(x', t') \rangle = 2\Gamma_0 kT \delta(t - t')\delta^d(x - x')$, $T$ being the temperature. The dynamics is thus governed by the time-dependent potential

\[
U[\phi(x, t), t] = \mathcal{F}[\phi(x, t)] - \int d^d x \ h(x, t)\phi(x, t) \tag{2}
\]

The potential energy (or Euclidian action) $\mathcal{F}[\phi]$ is, for instance, given by

\[
\mathcal{F}[\phi] = \int d^d x \left\{ \frac{1}{2} r_0 \phi^2 + \frac{1}{2} \nabla \phi^2 + u_0 \phi^4 \right\} \tag{3}
\]

When the external applied field $h(x, t)$ is constant in time, the invariant measure associated with Eq. (1) is the equilibrium Gibbs-Boltzmann distribution:

\[
P_{eq}[\phi] = \frac{e^{-\beta U[\phi]}}{Z[\beta, h]} \quad \text{with} \quad Z[\beta, h] = \int \mathcal{D}\phi \ e^{-\beta U[\phi]} \tag{4}
\]

We now 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, 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 $U$ for $t \leq 0$ and $t \geq t_f$ are denoted by $U_0$ and $U_1$, respectively.

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

$$\mathcal{P}(\phi_1|\phi_0) = \int D\phi \exp \left\{ \int_0^{t_f} dt \left[ \frac{1}{2} \frac{d\phi}{dt} \left( \frac{\delta U}{\delta \phi}(x,t) \right) - \frac{1}{2} \frac{d^2\phi}{dt^2} \right] \right\}$$

(5)

The following identity is now substituted in Eq. (5)

$$1 = \int D\phi \delta \left( \phi(x,t) - \phi_0(x) \right) \left\{ \int D\phi \delta \left( \phi_0(x,0) - \phi_0(x) \right) e^{-\int dt \frac{d^2\phi}{dt^2}} \right\}$$

(6)

where $\tilde{\phi}(x,t)$ is the response field and $\mathcal{M}$ is the operator

$$\mathcal{M} = \frac{\partial}{\partial t} + \Gamma_0 \frac{\partial f(\phi(x,t), t)}{\partial \phi}$$

(7)

Integrating over the noise $\zeta(x,t)$, one finds [21, 22]

$$\mathcal{P}(\phi_1|\phi_0) = \frac{1}{Z_0} \int d\phi \mathcal{D} \tilde{\phi} e^{-\int dt \frac{d^2\phi}{dt^2}}$$

(8)

where the dynamical action $\Sigma$ is given by

$$\Sigma(\phi, \tilde{\phi}, \bar{\phi}) = \Gamma_0 \bar{\phi}(\frac{\delta}{\delta \phi}) - \frac{\delta U}{\delta \phi} \bar{\phi} - \frac{\delta^2 U}{\delta \phi^2}$$

(9)

the last term being the Jacobian of $\mathcal{M}$. We consider now a functional $\mathcal{O}[\phi]$ that depends of 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

$$\langle \mathcal{O} \rangle = \frac{1}{Z_0} \int D\phi_0(x) D\phi_1(x) e^{-\beta U_0[\phi_0]} \mathcal{I} \{ \mathcal{O}, \phi_1, \phi_0 \}$$

(10)

where

$$\mathcal{I} \{ \mathcal{O}, \phi_1, \phi_0 \} = \frac{1}{Z_0} \int_{\phi_0(x,0)=\phi_0(x)}^{\phi(x,t_f)=\phi_1(x)} D\phi D\tilde{\phi} e^{-\int dt \left( \frac{d\phi}{dt} \left( \frac{\delta U}{\delta \phi}(x,t) \right) - \frac{d^2\phi}{dt^2} \right)} \mathcal{O}[\phi]$$

(11)

Under a change of the integration variable $\bar{\phi}$ in Eq. (10),

$$\bar{\phi}(x,t) \rightarrow -\bar{\phi}(x,t) + \beta \frac{\delta U(\phi(x,t), t)}{\delta \phi(x,t)}$$

(12)

the path integral is invariant and $\Sigma$ varies as

$$\Sigma(\phi, \tilde{\phi}, \bar{\phi}) \rightarrow \Sigma(\phi, -\bar{\phi}, \bar{\phi}) + \beta \tilde{\phi} \frac{\delta U(\phi(x,t), t)}{\delta \phi(x,t)}$$

(13)

Writing the second term on the r.h.s. as $(2 H - \frac{2\bar{H}}{\beta})$, gives

$$\int d^2x dt \tilde{\phi} \frac{\delta U(\phi(x,t), t)}{\delta \phi(x,t)} = U_1[\phi_1] - U_0[\phi_0] - \mathcal{W}_J[\phi]$$

(14)

The derivative $\partial U/\partial t$ is related to Jarzynski’s work by

$$\mathcal{W}_J[\phi] = \int_0^{t_f} dt \frac{\partial U}{\partial t} = -\int d^2x dt h(x,t)\phi(x,t)$$

(15)

the last equality being obtained from Eq. (2). The change of sign of the time derivative $\dot{\phi}$ in Eq. (13) is compensated by the change of variables in the path integral

$$\langle \phi(x,t_0), \bar{\phi}(x,t_f) \rangle \rightarrow \langle \phi(x,t_f), \bar{\phi}(x,t_0) \rangle$$

(16)

This time-reversal transformation leaves the functional measure invariant and restores $\Sigma$ 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 [12] and [16] in Eq. (11) and using Eqs. (12) and (14), we find

$$\mathcal{I} \{ \mathcal{O}, \phi_1, \phi_0 \} = e^{\beta(U_0[\phi_0] - U_1[\phi_1])} \mathcal{I} \{ e^{-\beta \mathcal{W}_J} \tilde{\mathcal{O}}, \phi_0, \phi_1 \} R$$

(17)

The subscript $R$ denotes a time-reversed protocol and the time-reversed $\mathcal{O}[\phi]$ is equal to $\mathcal{O}[\phi(x,t_f-t)]$. Inserting this identity in Eqs. (11) and (10), we get

$$\langle \mathcal{O} \rangle = \mathcal{I} \{ e^{-\beta \mathcal{W}_J} \tilde{\mathcal{O}}, \phi_0, \phi_1 \} R$$

(18)

where $\Delta F$ is the free energy difference between the final and the initial states. Finally, we redefine $\mathcal{O}$ as $e^{-\beta \mathcal{W}_J}$. Recalling that the work $\mathcal{W}_J$ is odd under time-reversal, we deduce from the last equation that

$$\langle e^{-\beta \mathcal{W}_J} \rangle = e^{-\beta \Delta F} \langle \tilde{\mathcal{O}} \rangle R$$

(19)

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

$$\langle e^{-\beta \mathcal{W}_J} \rangle = e^{-\beta \Delta F}$$

(20)

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

$$\langle e^{-\lambda \mathcal{W}_J} \rangle = e^{-\beta \Delta F} \langle e^{(\lambda-\beta)\mathcal{W}_J} \rangle R$$

(21)

and a Laplace transform leads to Crooks relation [3, 4]:

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

(22)

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 our 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 (15) for the Jarzynski work appears as a natural outcome of this invariance.

The identity (14), 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. Functional derivatives of Eq. (20) with respect to \( h(x, t) \) at an intermediate time \( t_0 < t < t_f \), and at position \( x \), results in new identities

\[
\langle (\bar{o}(x, t) - \frac{\beta}{\Gamma_0} \dot{o}(x, t)) e^{-\beta W_J} \rangle = 0
\]  

(23)

The \( n \)-th functional derivative of Eq. (20) at intermediate times \( t_1, \ldots t_n \) and positions \( x_1, \ldots x_n \), gives the identity

\[
\langle e^{-\beta W_J} \prod_{i=1}^{n} (\bar{o}(x_i, t_i) - \frac{\beta}{\Gamma_0} \dot{o}(x_i, t_i)) \rangle = 0
\]  

(24)

Similarly, the functional derivative of Eq. (19) leads to

\[
\langle (\bar{o}(x, t) - \frac{\beta}{\Gamma_0} \dot{o}(x, t)) O e^{-\beta W_J} \rangle = e^{-\Delta F} \langle \dot{o}(x, t) O \rangle_R
\]  

(25)

Eq. (28) follows by choosing \( O = \bar{O} = \hat{1} \) since \( \{\phi\} = 0 \). For the special case \( O[\phi] = \phi(x', t') \), we obtain a generalization of the fluctuation-dissipation theorem

\[
\frac{\delta \langle \phi(x', t') e^{-\beta W_J} \rangle_{h_1(x, t)}}{\delta h_1(x, t)} \bigg|_{h_1=0} = -\beta \langle \phi(x, t) \phi(x', t') e^{-\beta W_J} \rangle
\]

\[
e^{-\beta F} \frac{\delta \langle \phi(x', t') \rangle_R}{\delta h_1(x, t)} \bigg|_{h_1=0}
\]

(26)

where \( h_1(x, t) \) is a small perturbation that drives the system out of the protocol \( h(x, t) \). Note that \( h_1 \) does not enter the definition of the Jarzynski work. This new fluctuation-dissipation theorem relates out of equilibrium response functions to derivatives of correlation functions and could be verified experimentally, for example in single molecule pulling experiments (this corresponds to the case where the field \( \phi \) does not depend on space). For a system at thermodynamic equilibrium with constant external field (i.e., \( W_J = \Delta F = 0 \)) and stationary correlations, this equation reduces to the standard fluctuation-dissipation relation (21).

Identities between correlators such as Eqs. (28)-(26) suggest the existence of an underlying continuous symmetry of the system. We first extend the integration range of the path integral in Eq. (10) over the range \(-\infty < t < +\infty\), using the following properties of the probability distribution:

\[
\frac{1}{Z_0} e^{-\beta A_{0}[\phi_0]} = \lim_{T \to -\infty} P(\phi_0|\phi_T)
\]

(27)

\[
1 = \int D\phi(x, T) P(\phi_T|\phi_{t_1}) \text{ for } T > t_1
\]

(28)

The first property assumes ergodicity and the latter is normalization. Inserting into these equations the path integral representation, Eq. (8), of \( P(\phi'|\phi'') \), Eq. (10) is rewritten as

\[
\langle O \rangle = \int D\phi(x, t) D\bar{\phi}(x, t) e^{-\int dt^c x^d \Sigma(\phi, \bar{\phi}, c, \bar{c})} O[\phi]
\]

(29)

where \( \phi(x, t) \) and \( \bar{\phi}(x, t) \) are integrated with \( t \) ranging now from \(-\infty \to \infty\).

To uncover the above mentioned hidden symmetry, in addition to the original field \( \phi(x, t) \) and the response field \( \bar{\phi}(x, t) \), we introduce two auxiliary anti-commuting Grassmannian fields \( c(x, t) \) and \( \bar{c}(x, t) \) that allow us to express the Jacobian of \( M \), defined in Eq. (7), as a functional integral (19, 20). Assuming that \( O \) differs from the identity only for \( 0 \leq t \leq t_f \), the mean value of \( O \) in Eq. (10) can be rewritten as

\[
\langle O \rangle = \int D\phi D\bar{\phi} Dc D\bar{c} e^{-\int dt^c x^d \Sigma(\phi, \bar{\phi}, c, \bar{c})} O[\phi]
\]

(30)

with \( M \) given in Eq. (7).

Consider now the infinitesimal transformation that mixes ordinary fields with Grassmannian fields:

\[
\delta \phi(x, t) = c(x, t) \bar{c} \delta \bar{\phi}(x, t) = -\frac{\beta}{\Gamma_0} \tilde{c}(x, t) \bar{c}
\]

(32)

\[
\delta c(x, t) = 0 \quad \delta \tilde{c}(x, t) = \left( \bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \phi(x, t) \right) \bar{c}
\]

\( \bar{c} \) being a time-independent infinitesimal Grassmannian field. The variation of \( \Sigma(\phi, \bar{\phi}, c, \bar{c}) \) in Eq. (31) under the transformation of Eq. (32) gives

\[
\delta \Sigma(\phi, \bar{\phi}, c, \bar{c}) = \frac{DA}{dt} - \beta \frac{\partial}{\partial \phi} \left( \frac{\delta M}{\delta \phi} \right) c(x, t) \bar{c}
\]

(33)

with the total derivative term

\[
A = \beta \left( \frac{\delta M}{\delta \phi} + \frac{\delta \bar{M}}{\delta \bar{\phi}} - \frac{\beta}{\Gamma_0} \right) \bar{c} \bar{c}
\]

(34)

If the potential \( U \) is independent of time, the variation of \( \Sigma \) under the supersymmetric transformation (32) is a total time derivative that does not modify the action. The supersymmetry in Eq. (32) which is in fact a generalization of supersymmetric quantum mechanics (17, 21), reflects the time reversal invariance of Model A in absence of external field and allows to prove the fluctuation-dissipation theorem (19, 20).

When the potential \( U(\phi, t) \) depends explicitly on time, supersymmetry invariance is broken: the last term in Eq. (33) breaks the invariance. It can be written as

\[
\beta \frac{\partial^2 U}{\partial \phi \partial t} c \bar{c} = \beta \frac{\partial^2 M}{\partial \phi \partial t} \delta \phi = \delta \left( \beta \frac{\partial M}{\partial t} \right)
\]

(35)

and can be interpreted as the variation of a function. Hence, the modified \( \Sigma_J \), defined as
\[ \Sigma_f = \Sigma + \beta \frac{\partial \mathcal{L}}{\partial t} \]

and obtained by adding the Jarzynski work to the initial action, is invariant under the supersymmetric transformation up to a total derivative term: \[ \delta \Sigma = \frac{d}{dt} \mathcal{L} \]. The boundary terms at \( t = \pm \infty \) are, conventionally, assumed to vanish.

We now show that the supersymmetric invariance of \( \Sigma_f \) implies the correlator identities. Introducing a four-component source \( (H, \bar{H}, \bar{L}, L) \), we define the generating function

\[ Z(H, \bar{H}, \bar{L}, L) = \int D\phi D\bar{\phi} Dc D\bar{c} \]

\[ \exp \left( \int d^4x dt \left( -\Sigma_f(\phi, \bar{\phi}, c, \bar{c}) + \bar{H} \phi + H \bar{\phi} + \bar{L} c + L \bar{c} \right) \right) \]

Making the transformation in \( Z(H, \bar{H}, \bar{L}, L) \) and using the supersymmetric invariance of \( \Sigma_f \) in Eq. (36), we deduce as in [20] the Ward-Takahashi identity:

\[ \int \left( - \frac{\beta}{\Gamma_0} \frac{\delta Z}{\delta H} + L \left( \frac{\delta Z}{\delta H} - \frac{\beta}{\Gamma_0} \frac{\delta L}{\delta H} \right) + \bar{H} \frac{\delta Z}{\delta L} \right) = 0 \]

(37)

By applying to the Ward-Takahashi identity the operator \( \frac{d}{dt} \int_{x,t} \prod_{i=1}^n \left( \frac{\delta}{\delta H(x_i,t_i)} - \frac{\beta}{\Gamma_0} \frac{d}{dt} \frac{\delta}{\delta c(x_i,t_i)} \right) \) and setting the source field \( H, \bar{H}, \bar{L}, L \) to zero, we obtain Eqs. [23] and [24]. This lead to Jarzynski’s equality [20]. Replacing \( h(x, t) \) by \( h(x, \alpha t) \) for any \( \alpha > 0 \), we obtain

\[ \frac{d\langle e^{-\beta W_f} \rangle}{d\alpha} = \int d^4x dt \ h(x, \alpha t) \langle \bar{\phi}(x, t) - \frac{\beta}{\Gamma_0} \phi(x, t) \rangle e^{-\beta W_f} \]

Using Eq. [23] that can be obtained from [37], we get \( \frac{d\langle e^{-\beta W_f} \rangle}{d\alpha} = 0 \), which means that the value of \( \langle e^{-\beta W_f} \rangle \) does not depend on \( \alpha \). Hence, this value is the same as that of the quasi-static limit \( \alpha \to 0 \), and is given by \( \exp(-\Delta F) \). Jarzynski’s identity is thus obtained as a consequence of supersymmetry.

The response-field technique in Eqs. [311] that we have used to derive nonequilibrium work theorems for Model A can be extended to multi-component fields and to other stochastic models such as model B. It also can be extended to systems with correlated noise [24] replacing the Gaussian measure in the RHS of Eq. (31) by

\[ \int \mathcal{D} \zeta \ e^{-\frac{1}{2} \int d^4x dt' d^4y dt' \ z(x,t) \Delta^{-1}(x,t,y,t') \ z(y,t')} \]

(38)

where \( \Delta(x, t; y, t') \) is the two point correlation function.

We have obtained correlators identities involving an arbitrary field-operator and a generalization of the fluctuation-dissipation relation that remains valid far from equilibrium. The supersymmetric invariance of the time independent Langevin equation breaks down when the potential varies according to a time-dependent protocol. We have shown that the supersymmetry in Eq. (36) is restored by adding to the action a counter-term which is precisely the Jarzynski work \( \beta W_f \). Furthermore, we proved that the associated supersymmetric Ward identity implies Jarzynski’s theorem. Supersymmetry enforces the exactness of the quasi-static limit even for processes that have a finite duration and that bring the system arbitrarily far from equilibrium. A hidden supersymmetry [23] is also present in classical Hamiltonian systems for which Jarzynski’s equality was initially proved. We finally remark that supersymmetry may also be a useful tool when applied to the fluctuation theorem for stochastic dynamics [24].