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Fock space and field theoretic description of nonequilibrium work relations

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Abstract

We consider classical, interacting particles coupled to a thermal reservoir and subject to a local, time-varying potential while undergoing hops on a lattice. We impose detailed balance on the hopping rates and map the dynamics to the Fock space Doi representation, from which we derive the Jarzynski and Crooks relations. Here the local potential serves to drive the system far from equilibrium and to provide the work. Next, we utilize the coherent state representation to map the system to a Doi–Peliti field theory and take the continuum limit. We demonstrate that time reversal in this field theory takes the form of a gauge-like transformation which leaves the action invariant up to a generated work term. The time-reversal symmetry leads to a fundamental identity, from which we are able to derive the Jarzynski and Crooks relations, as well as a far-from-equilibrium generalization of the fluctuation-dissipation relation.

Keywords: nonequilibrium work relations, Doi Peliti field theory, far from equilibrium

1. Introduction

In the past decades remarkable advances have been made in the field of far from equilibrium statistical physics. The celebrated Jarzynski equation,

$$\langle e^{-W/k_{\mathrm{B}}T} \rangle = e^{-\Delta F/k_{\mathrm{B}}T}, \tag{1}$$

relates via equality the difference in the equilibrium free energy ΔF to a nonequilibrium average of the work W for processes that start in equilibrium at temperature T but are driven arbitrarily far from equilibrium. This holds for Hamiltonian systems [1] as well as

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stochastic systems described by a master equation [2]. This universal constraint on the possible distributions of nonequilibrium work was further developed by Crooks, who showed that the probability $P_F(W)$ of doing work W while following the 'forward' protocol (a specified variation of control parameters) can be related to the probability $P_R(-W)$ of doing negative the work during a reversed protocol via

$$P_F(W) = e^{(W-\Delta F)/k_\mathrm{B}T} P_R(-W), \tag{2}$$

thus elucidating the central role of time reversal [3, 4]. The Jarzynski and Crooks relations are part of an ensemble of fluctuation theorems that describe work fluctuations and entropy production, with by now a large literature that has been summarized in reviews [5–7] and more recently in textbooks [8, 9].

In these studies one typically examines the impact of time reversal on the probability distribution of all possible trajectories, although this probability distribution is generally not available in explicit form. In the present work, we propose to recast the nonequilibrium dynamics into a field theory. While this necessarily represents a loss of trajectory-level information, similar to a master equation treatment, the field theory nevertheless offers advantages. The equivalent of the probability distribution for field, namely the exponential of the action, can be obtained explicitly. The explicit expression for the action enables us to make progress on three fronts: one, as with all field theories, it provides a useful framework for exploring symmetries and near-symmetries, in this case, the behavior under time reversal; two, it enables a variety of possible approximation schemes by perturbation theory; and three, a hierarchy of nonequilibrium identities can be derived by functional differentiation, such as a nonequilibrium generalization of the fluctuation-dissipation relation.

Mallick *et al* examined nonequilibrium work relations via field theory for the critical dynamics of a nonconserved scalar order parameter [10], i.e. Model A in the Heisenberg–Haltering scheme [11]. They were able to derive the Jarzynski and Crooks relations, as well as a nonequilibrium generalization of the fluctuation-dissipation relation, and to elucidate properties of time-reversal symmetry breaking with the field theory. This work was extended by Täuber to the critical dynamics of a conserved scalar order parameter, i.e. Model B [12].

In this work we present a field theoretic description of the Jarzynski and Crooks relations for a system of interacting classical particles coupled to the thermal reservoir and driven by a tun able local potential. We employ Doi–Peliti field theory, i.e. a mapping of the master equation for the classical particle model to a Fock space representation (the Doi representation [13]) and then a subsequent mapping to a field theory via coherent states [14–16]. One of the advantages of this approach is that we are not restricted to near-criticality dynamics.

Our primary results are the following. After defining the model in section 2, we recast the dynamics in the Doi representation in section 3, deriving the general form of a time-evolution operator that is consistent with detailed balance. With this formalism in section 4 we obtain a direct and simple Fock space derivation of the Jarzynski and Crooks relations. Next, in section 5 we obtain the Doi–Peliti field theory for interacting particles coupled to a thermal bath. This field theory contains boundary 'initial' and 'final' terms in the action as well as a bulk action governing the time evolution from $t = 0$ to $t = t_f$. We demonstrate that the bulk action can be transformed by a Cole–Hopf transformation to the Dean–Kawasaki field theory [17–20] obtained by mapping Dean's Langevin equation for interacting particles [21] to a field theory via the Martin–Siggia–Rose–Janssen–de Dominicis procedure [22–24]. This connection was reported previously by Andreanov *et al* [17], but our treatment differs importantly in the boundary terms, which play a role in time reversal. We also demonstrate for noninteracting particles that our field theory reduces to the Fokker–Planck equation for a Brownian particle in a potential.

In section 6 we examine time reversal within the field theory, showing that time-reversal takes the form of a gauge-like transformation, and that the action is invariant under time reversal apart from the introduction of the Jarzynski work term. We note that for interacting particles, it is necessary to introduce a Hubbard–Stratonovich transformation and add a complex field to fully reveal the underlying time reversal symmetry. We obtain a fundamental nonequilibrium identity, equation (65), from which the Jarzynski and Crook's identities follow. Further, in section 7 we employ functional differentiation of equation (65) to derive a far-from-equilibrium generalization of the fluctuation-dissipation relation.

2. Model

2.1. Energy and thermal equilibrium

We begin with a model of N classical particles on a d-dimensional lattice of size L^d; the continuum limit will be taken later. The particles interact with the pair potential V_{ij}, which can be any function of the separation $\mathbf{r}_j - \mathbf{r}_i$ between sites i and j, such as a Lennard–Jones potential, with the only restriction that it is symmetric under interchange of particles, $V_{ij} = V_{ji}$. Additionally, we consider a time-dependent site potential $U_i(t)$, which allows for work to be done on the system. The occupancy of site i is denoted n_i, and the energy of the occupation configuration $\mathbf{n} = (n_1, n_2, \dots)$ is given by

$$E_{\mathbf{n}}(t) = \frac{1}{2}\sum_{i,j}(n_i - \delta_{ij})\,V_{ij}n_j + \sum_i U_i(t)\,n_i, \tag{3}$$

where the Kronecker delta function ensures proper counting of the same-site pairs.

These particles are coupled to a thermal reservoir at temperature T. Because of the time-dependent potential $U_i(t)$, the equilibrium distribution also depends on time t via

$$P^{\mathrm{eq}}_{\mathbf{n}}(t) = \frac{N!}{\mathbf{n}!}\frac{1}{Z(t)}e^{-\beta E_{\mathbf{n}}(t)}. \tag{4}$$

where $\beta^{-1} = k_{\mathrm{B}}T$, $Z(t)$ is the partition function associated with $E_{\mathbf{n}}(t)$, and $\mathbf{n}! \equiv \prod_i n_i!$. The prefactor $N!/\mathbf{n}!$ is the multinomial coefficient that accounts for the multiplicity of microstates for configuration $\mathbf{n}$ under permutation of the particles.

2.2. Dynamics

The particles undergo stochastic hops, and the probability $P(\mathbf{n},t)$ of configuration $\mathbf{n}$ at time t obeys the master equation

$$\frac{\mathrm{d}}{\mathrm{d}t}P_{\mathbf{n}}(t) = \sum_{\mathbf{m}\neq\mathbf{n}}\left[w_{\mathbf{n},\mathbf{m}}(t)\,P_{\mathbf{m}}(t) - w_{\mathbf{m},\mathbf{n}}(t)\,P_{\mathbf{n}}(t)\right]. \tag{5}$$

The particle hopping rates $w_{\mathbf{n},\mathbf{m}}(t)$ for a transition $\mathbf{m}\to\mathbf{n}$ are chosen to obey detailed balance for the instantaneous energy $E_{\mathbf{n}}(t)$,

$$\frac{w_{\mathbf{n},\mathbf{m}}(t)}{w_{\mathbf{m},\mathbf{n}}(t)} = \frac{P^{\mathrm{eq}}_{\mathbf{n}}(t)}{P^{\mathrm{eq}}_{\mathbf{m}}(t)} = \frac{\mathbf{m}!}{\mathbf{n}!}e^{-[\beta E_{\mathbf{n}}(t) - \beta E_{\mathbf{m}}(t)]} \tag{6}$$

and are thus time-dependent.

Work is performed on the system by varying the site potentials $U_i(t)$. For configuration $\mathbf{n}$ at time t, the instantaneous rate of work performed on the system is given by

$$\dot{W} = \sum_i n_i \dot{U}_i(t)\,. \tag{7}$$

This term appears in the nonequilibrium generalization of the first law:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle E\rangle = \sum_{\mathbf{n}} \left[\frac{\mathrm{d}P_{\mathbf{n}}(t)}{\mathrm{d}t} E_{\mathbf{n}}(t) + P_{\mathbf{n}}(t) \sum_i n_i \dot{U}_i(t)\right]. \tag{8}$$

The first term gives the rate of change in $\langle E\rangle$ due to the particle hopping dynamics, reflecting the heat flow between the system and reservoir, while the second term is simply the average rate of work performed, $\langle \dot{W}\rangle$.

For sufficiently slow driving, the system remains in thermal equilibrium and the probabilities are given by equation (4). In contrast, for fast driving, the distribution $P_{\mathbf{n}}(t)$ obtained from equation (5) may be driven far from equilibrium.

3. The Doi representation

These particle dynamics can be mapped to a Fock space representation, i.e. the Doi representation [13], using a standard procedure which we summarize briefly below. Even though these are classical particles, the Fock space representation reflects the permutation symmetry of the particles, and thus provides in this sense the simplest expression of the particle dynamics. We shall see that, indeed, in the Doi representation the Jarzynski relation emerges elegantly.

3.1. States and the Liouvillian

Bosonic creation and annihilation operators $\hat{a}_i^\dagger$ and $\hat{a}_i$ are introduced at each lattice site and, together with the vacuum state $|0\rangle$, used to create a state $|\mathbf{n}\rangle = \prod_i (\hat{a}_i^\dagger)^{n_i}|0\rangle$ corresponding to the configuration $\mathbf{n}$. Note that this state is normalized as $\langle \mathbf{n}|\mathbf{n}\rangle = \mathbf{n}!$. The full probability distribution of the system at time t can then be represented by the state

$$|\psi(t)\rangle = \sum_{\mathbf{n}} P_{\mathbf{n}}(t)\,|\mathbf{n}\rangle, \tag{9}$$

which enables writing the master equation as

$$\frac{\mathrm{d}}{\mathrm{d}t}|\psi(t)\rangle = -\hat{L}(t)\,|\psi(t)\rangle. \tag{10}$$

with Liouvillian operator $\hat{L}$. The utility of the Doi representation is that whenever the particle dynamics respects the permutation symmetry of the particles, the operator $\hat{L}$ can be expressed solely in terms of the $\hat{a}_i$ and $\hat{a}_i^\dagger$ operators, with no dependence on the configuration $\mathbf{n}$. That is, the Liouvillian is determined solely by the processes involved and not dependent on the state of the system. For example, particles undergoing unbiased hops between neighboring lattice sites leads to

$$\hat{L}_{\mathrm{diff}} = \Gamma \sum_{\langle ij\rangle} \left(\hat{a}_i^\dagger - \hat{a}_j^\dagger\right)(\hat{a}_i - \hat{a}_j)\,, \tag{11}$$

where the sum runs over i,j that are nearest neighbor sites.

3.2. The projection state

In the Doi representation, averages and distributions are extracted from the Fock states by means of a projection state, defined as $\langle\mathcal{P}| = \langle 0|e^{\sum_i \hat{a}_i}$, with the property $\langle\mathcal{P}|\hat{a}_i^\dagger = \langle\mathcal{P}|$ for all i. Averages are computed via

$$\langle A\rangle \equiv \sum_{\mathbf{n}} A_{\mathbf{n}} P_{\mathbf{n}}(t) = \langle\mathcal{P}|\hat{A}|\psi(t)\rangle, \tag{12}$$

where $\hat{A} \equiv \sum_{\mathbf{n}} (A_{\mathbf{n}}/\mathbf{n}!)|\mathbf{n}\rangle\langle\mathbf{n}|$ is an operator diagonalized by the occupation states $|\mathbf{n}\rangle$ with eigenvalues $A_{\mathbf{n}}$. Normalization ensures $\langle\mathcal{P}|\psi(t)\rangle = \sum_{\mathbf{n}} P_{\mathbf{n}}(t) = 1$, and probability conservation requires

$$0 = \frac{\mathrm{d}}{\mathrm{d}t}\langle 1\rangle = -\langle\mathcal{P}|\hat{L}(t)|\psi(t)\rangle \tag{13}$$

for all $|\psi(t)\rangle$, thus

$$\langle\mathcal{P}|\hat{L}(t) = 0. \tag{14}$$

This is obeyed, for example, by the diffusion Liouvillian in equation (11).

3.3. The Hamiltonian and detailed balance

Now we consider the class of Liouvillians that correspond to transition rates that satisfy detailed balance, and for clarity we suppress the explicit time dependence in $\hat{L}$ and the rates. Starting from a state $\mathbf{m}$, the probability of being in a state $\mathbf{n}\neq\mathbf{m}$ a short time δt later is, according to the master equation, $P(\mathbf{n},t) = w_{\mathbf{n},\mathbf{m}}\delta t$, while the probability of remaining in $\mathbf{m}$ is $P_{\mathbf{m}}(\delta t) = 1 - \delta t\sum_{\mathbf{n}'\neq\mathbf{m}} w_{\mathbf{n}',\mathbf{m}}$. In the Doi representation, the state at time δt is $|\psi(\delta t)\rangle = (1-\hat{L}\delta t)|\mathbf{m}\rangle$. Using $\langle\mathbf{n}|\psi(t)\rangle = \mathbf{n}!P_{\mathbf{n}}(t)$ we obtain for $\mathbf{n}\neq\mathbf{m}$

$$\langle\mathbf{n}|\hat{L}|\mathbf{m}\rangle = -\mathbf{n}!\,w_{\mathbf{n},\mathbf{m}} \tag{15}$$

while for $\mathbf{n}=\mathbf{m}$

$$\langle\mathbf{n}|\hat{L}|\mathbf{n}\rangle = -\mathbf{n}!\sum_{\mathbf{n}'\neq\mathbf{n}} w_{\mathbf{n}',\mathbf{n}}. \tag{16}$$

For rates that obey the detailed balance condition of equation (6), we obtain

$$\langle\mathbf{n}|\hat{L}|\mathbf{m}\rangle = \langle\mathbf{m}|\hat{L}|\mathbf{n}\rangle e^{-\beta E_{\mathbf{n}}(t)+\beta E_{\mathbf{m}}(t)}. \tag{17}$$

with $E_{\mathbf{n}}$ given by equation (3). Now we introduce the Hermitian Hamiltonian operator

$$\hat{H}(t) = \frac{1}{2}\sum_{i,j} V_{ij}\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_j\hat{a}_i + \sum_i U_i(t)\hat{a}_i^\dagger\hat{a}_i \tag{18}$$

which is diagonalized by the states $|\mathbf{n}\rangle$ with eigenvalues $E_{\mathbf{n}}(t)$. With this energy operator equation (17) becomes $\langle\mathbf{n}|\hat{L}|\mathbf{m}\rangle = \langle\mathbf{m}|e^{\beta\hat{H}}\hat{L}e^{-\beta\hat{H}}|\mathbf{n}\rangle$, which implies

$$\hat{L}^\dagger = e^{\beta\hat{H}}\hat{L}e^{-\beta\hat{H}}. \tag{19}$$

Together equations (14) and (19) imply that necessary and sufficient conditions for detailed balance are that $\hat{L}$ has the form

$$\hat{L} = \hat{Q}e^{\beta\hat{H}} \tag{20}$$

where $\hat{Q}$ is a Hermitian operator that annihilates the projection state: $\hat{Q}|\mathcal{P}\rangle = 0$.

3.4. Constructing the Liouvillian

Finally, we discuss specific choices for the Liouvillian. Consider a particle hop from site i to neighboring site j, which takes the system from configuration $\mathbf{m}$ to $\mathbf{n}$, where $n_k = m_k - \delta_{ik} + \delta_{jk}$. The detailed balance condition (6) for this hop is

$$\frac{w_{\mathbf{n},\mathbf{m}}}{w_{\mathbf{m},\mathbf{n}}} = \frac{m_i}{n_j} e^{-\beta[E_{\mathbf{n}} - E_{\mathbf{m}}]}. \tag{21}$$

We restrict consideration to rates that depend on the energies only via the difference $\Delta E \equiv E_{\mathbf{n}} - E_{\mathbf{m}}$. These have the general form

$$w_{\mathbf{n},\mathbf{m}} = \Gamma m_i f_e(\beta \Delta E) e^{-\beta \Delta E/2}, \tag{22}$$

where $f_e(x)$ is an even function.

To construct the Liouvillian corresponding to (22) it is useful to introduce the Hermitian operator

$$\hat{\epsilon}_k = U_k + \sum_{\ell} V_{k\ell} \hat{a}_\ell^\dagger \hat{a}_\ell \tag{23}$$

with eigenvectors $|\mathbf{m}\rangle$ and eigenvalues $\epsilon_k(\mathbf{m}) = U_k + \sum_\ell V_{k\ell} m_\ell$ equal to the energy required to introduce a particle at site k to configuration $\mathbf{m}$. It is straightforward to show that for the $i \to j$ jump

$$(\hat{\epsilon}_j - \hat{\epsilon}_i)\, \hat{a}_i |\mathbf{m}\rangle = \Delta E \hat{a}_i |\mathbf{m}\rangle, \tag{24}$$

which allows us to write (22) as

$$w_{\mathbf{n},\mathbf{m}} = \frac{1}{\mathbf{n}!} \langle \mathbf{n} | \Gamma \hat{a}_j^\dagger f_e(\hat{\epsilon}_i - \hat{\epsilon}_j)\, e^{\beta(\hat{\epsilon}_i - \hat{\epsilon}_j)/2} \hat{a}_i |\mathbf{m}\rangle. \tag{25}$$

By comparison with (15), we can identify the operator above with the gain term in $\hat{L}$.

For the loss term, we consider the same $i \to j$ hop but starting in $\mathbf{n}$ and going to $\mathbf{n}'$, where $n'_k = n_k - \delta_{ik} + \delta_{jk}$, and $\Delta E = E_{\mathbf{n}'} - E_{\mathbf{n}}$. The appropriate rate is obtained from (16) and (22) to be

$$w_{\mathbf{n} \to \mathbf{n}'} = \frac{1}{\mathbf{n}!} \langle \mathbf{n} | \Gamma \hat{a}_i^\dagger f_e(\hat{\epsilon}_i - \hat{\epsilon}_j)\, e^{\beta(\hat{\epsilon}_i - \hat{\epsilon}_j)/2} \hat{a}_i |\mathbf{n}\rangle. \tag{26}$$

Combining (25) and (26) with the analogous terms for a $j \to i$ hop provides the Liouvillian corresponding to (22),

$$\hat{L} = \Gamma \sum_{\langle ij \rangle} \left(\hat{a}_i^\dagger - \hat{a}_j^\dagger \right) f_e(\hat{\epsilon}_i - \hat{\epsilon}_j) \left(e^{\beta(\hat{\epsilon}_i - \hat{\epsilon}_j)/2} \hat{a}_i - e^{\beta(\hat{\epsilon}_j - \hat{\epsilon}_i)/2} \hat{a}_j \right). \tag{27}$$

As advertised, the Liouvillian is purely an expression of the process and has no dependence on the state of the system, i.e. the occupation numbers. The identity $e^{\beta \hat{\epsilon}_k} \hat{a}_k = e^{-\beta \hat{H}} \hat{a}_k e^{\beta \hat{H}}$, which follows from $[\hat{H}, \hat{a}_k] = -\hat{\epsilon}_k \hat{a}_k$ and the Hadamard lemma, can be used to show this Liouvillian has the necessary form (20).

Later, when taking the continuum limit, the energy difference due to a hop will be of the order of the lattice spacing Δx, which will allow us to linearize (27) in $\hat{\epsilon}_i - \hat{\epsilon}_j$:

$$\hat{L} \simeq \Gamma \sum_{\langle ij \rangle} \left(\hat{a}_i^\dagger - \hat{a}_j^\dagger \right) \left(\hat{a}_i - \hat{a}_j + \beta(\hat{\epsilon}_i - \hat{\epsilon}_j) \frac{\hat{a}_i + \hat{a}_j}{2} \right), \tag{28}$$

where we have set $f_e(0) = 1$ without loss of generality. Note that this linearized Liouvillian is normal ordered.

3.5. Equilibrium state

The Jarzynski and Crooks relations require starting in thermal equilibrium. In the Doi representation the equilibrium state can be written as

$$|\psi_{\rm eq}\rangle = \sum_{\mathbf{n}} P^{\rm eq}_{\mathbf{n}} |\mathbf{n}\rangle = \frac{1}{Z} e^{-\beta\hat{H}} |\bar{n}_0\rangle, \tag{29}$$

where $\bar{n}_0 = N/L^d$ is the average number of particles per site, and $|\bar{n}_0\rangle \equiv e^{\sum_i \bar{n}_0 \hat{a}_i^\dagger}|0\rangle$. This is obtained from (4) by expressing the multiplicity of the occupation state $\mathbf{n}$ in terms of a product of Poisson distributions: $N!/\mathbf{n}! \propto \prod_i \bar{n}_0^{n_i}/n_i!$, with the implied constraint $\sum_i n_i = N$ and the proportionality constant absorbed into Z.

The equilibrium state is necessarily a stationary state of the detailed balance Liouvillian, equation (20). In the Doi representation this can be seen from

$$\hat{L}|\psi_{\rm eq}\rangle = Z^{-1}\hat{Q}|\bar{n}_0\rangle = 0, \tag{30}$$

where the last equation follows from taking $\hat{a} \to \bar{n}_0 \hat{a}$ and $\hat{a}^\dagger \to \bar{n}_0^{-1}\hat{a}^\dagger$, which leaves $\hat{Q}$ invariant and takes $|\bar{n}_0\rangle \to |\mathcal{P}\rangle$.

Finally, we note that all of $\hat{L}$, $\hat{H}$, E, Z, and $|\psi_{\rm eq}\rangle$ are defined in terms of the instantaneous $U_i(t)$, and thus can be time-dependent.

4. Work relations in the Doi representation

We are now equipped to derive the Jarzynski relation for general detailed balance dynamics within the Doi representation. Perhaps unsurprisingly, our methods bear a strong similarity to the operator framework Kurchan used for Langevin dynamics [25]. As usual, the system must begin in thermal equilibrium at time $t = 0$; we denote this state $|\psi_{\rm eq}(0)\rangle$ to emphasize that the time-dependent Hamiltonian is to be evaluated at $t = 0$.

The solution to the master equation (10) can be written as

$$|\psi(t)\rangle = \lim_{\Delta t \to 0} \prod_{n=0}^{t/\Delta t - 1} \left(1 - \hat{L}_{t_n}\Delta t\right) |\psi_{\rm eq}(0)\rangle. \tag{31}$$

where the product of the time-dependent $\hat{L}_t$ operators is time ordered with earlier times on the right, and $t_n = n\Delta t$. Work, as defined in (7), appears in the Doi representation as

$$W = \int_0^{t_f} \mathrm{d}t \sum_i \dot{U}_i(t)\, \hat{a}_i^\dagger \hat{a}_i. \tag{32}$$

The average of the work from time $t = 0$ to t_f is given by

$$\langle e^{-\beta W}\rangle = \langle \mathcal{P}| \prod_{n=0}^{n_f} \left[e^{-\beta \dot{W}_{t_n}\Delta t} \left(1 - \hat{L}_{t_n}\Delta t\right)\right] |\psi_{\rm eq}(0)\rangle \tag{33}$$

where $n_f = t_f/\Delta t - 1$, the product is again time ordered, and the limit $\Delta t \to 0$ is implied. Equation (33) is equivalent to applying a weight $e^{-\beta w(t)}$ to each trajectory, where $w(t)$ is the work done up to time t along that trajectory. This has been demonstrated to provide the desired average [2, 26].

Substituting $e^{-\beta \dot{W}_t \Delta t} = e^{-(\beta \hat{H}_{t+\Delta t} - \beta \hat{H}_t)}$ and regrouping terms gives

$$\langle e^{-\beta W} \rangle = \langle \mathcal{P} | e^{-\beta \hat{H}_{t_f}} \prod_{n=0}^{n_f} \left[e^{\beta \hat{H}_{t_n}} \left(1 - \hat{L}_{t_n} \Delta t \right) e^{-\beta \hat{H}_{t_n}} \right] \times e^{\beta \hat{H}_0} | \psi_{\mathrm{eq}} (0) \rangle. \tag{34}$$

Utilizing the detailed balance condition (19), the square brackets become

$$e^{\beta \hat{H}_t} \left(1 - \hat{L}_t \Delta t \right) e^{-\beta \hat{H}_t} = 1 - \hat{L}_t^\dagger \Delta t, \tag{35}$$

which can be interpreted as simply the time evolution operator acting to the left. This is the essence of how the fluctuation relations appear in the Doi representation: a forward-time average including the work term transforms into the reverse-time average absent the work.

It remains to analyze the initial and final states. We rescale the operators $\hat{a} \to \bar{n}_0 \hat{a}$ and $\hat{a}^\dagger \to \bar{n}_0^{-1} \hat{a}^\dagger$, which leaves $\hat{L}$ and $\hat{H}$ (and therefore the work term) unchanged, but modifies the initial and final terms via

$$e^{\beta \hat{H}_0} | \psi_{\mathrm{eq}} (0) \rangle = Z(0)^{-1} | \bar{n}_0 \rangle \to Z(0)^{-1} | \mathcal{P} \rangle \tag{36}$$

and

$$\langle \mathcal{P} | e^{-\beta H_{t_f}} \to \langle \bar{n}_0 | e^{-\beta H_{t_f}} = Z(t_f)^{-1} \langle \psi_{\mathrm{eq}} (t_f) |. \tag{37}$$

Putting this together, we have

$$\langle e^{-\beta W} \rangle = \frac{Z(t_f)}{Z(0)} \langle \psi_{\mathrm{eq}} (t_f) | \prod_{n=0}^{t_f/\Delta t - 1} \left(1 - \hat{L}_{t_n}^\dagger \Delta t \right) | \mathcal{P} \rangle \tag{38}$$

Conjugating the real expectation value reverses the time ordering, giving

$$\langle e^{-\beta W} \rangle = \frac{Z(t_f)}{Z(0)} \langle \mathcal{P} | \left(1 - \hat{L}_0 \Delta t \right) \ldots \left(1 - \hat{L}_{t_f - \Delta t} \Delta t \right) | \psi_{\mathrm{eq}} (t_f) \rangle_R \tag{39}$$

which can be interpreted as time ordered in the variable $t' = t_f - t$. The expectation value corresponds to $\langle \mathcal{P} | \psi(t' = t_f) \rangle_R = 1$ and we obtain the Jarzynski relation

$$\langle e^{-\beta W} \rangle = \frac{Z(t_f)}{Z(0)} = e^{-\beta [\Delta F(t_f) - F(0)]}. \tag{40}$$

To derive the Crooks relation, consider the characteristic function $\phi_F(q)$ of the forward work distribution function, which is simply the Fourier transform:

$$\phi_F(q) = \int_{-\infty}^{\infty} \mathrm{d}W e^{iqW} P_F(W) = \langle e^{iqW} \rangle_F. \tag{41}$$

This takes the form of equations (33) but with $\beta \to iq$. We now have a repeating pattern of

$$e^{-iq\hat{H}_t} \left(1 - \hat{L}_t \Delta t \right) e^{iq\hat{H}_t} = e^{-(iq+\beta)\hat{H}} \left(1 - \hat{L}_t^\dagger \Delta t \right) e^{(iq+\beta)\hat{H}} \tag{42}$$

which means after time reversal

$$\langle e^{iqW} \rangle_F = \frac{Z(t_f)}{Z(0)} \langle e^{-iqW} e^{-\beta W} \rangle_R \tag{43}$$

or $\phi_F(q) = \phi_R(iW - q)e^{-\beta\Delta F}$. Inverse transforming then gives

$$P_F(W) = \int \frac{\mathrm{d}q}{2\pi} e^{-iqW}\phi_R(iW - q) = e^{\beta W} P_R(-W), \tag{44}$$

which is the Crooks relation.

5. Doi–Peliti field theory

For taking the limit from a lattice to a spatial continuum, it is desirable to convert the Doi representation of the dynamics to a field theory. In this section we use the coherent state representation [15] to derive the Doi–Peliti field theory for the particle model with detailed balance dynamics. The general technique has been presented elsewhere [14, 16, 27], so we provide only a brief sketch here.

5.1. Coherent state representation

Coherent states are introduced at each lattice site,

$$|\boldsymbol{\phi}\rangle = e^{-\frac{1}{2}\sum_i |\phi_i|^2 + \sum_i \phi_i \hat{a}_i^\dagger} |0\rangle \tag{45}$$

with $\boldsymbol{\phi} = (\phi_1, \phi_2, \ldots)$ and complex ϕ_i. These are eigenstates of the annihilation operator, $a_i|\boldsymbol{\phi}\rangle = \phi_i|\boldsymbol{\phi}\rangle$. The identity operator can be expressed with the overcompleteness relation $\mathbf{1} = \int \prod_i \frac{d^2\phi_i}{\pi} |\boldsymbol{\phi}\rangle\langle\boldsymbol{\phi}|$. Time evolution is broken into discrete steps of size Δt, as shown in (31), and the identity operator is inserted at each time slice with a distinct set of coherent states, leading to evaluation of terms of the form

$$\langle \boldsymbol{\phi}_{t+\Delta t}|1 - \hat{L}_t\Delta t|\boldsymbol{\phi}_t\rangle = \langle \boldsymbol{\phi}_{t+\Delta t}|\boldsymbol{\phi}_t\rangle \left[1 - \Delta t \mathcal{L}\left(\boldsymbol{\phi}^*{}_{t+\Delta t}, \boldsymbol{\phi}_t\right)\right]. \tag{46}$$

Using the linearized, normal ordered Liouvillian (28) we obtain

$$\mathcal{L}\left(\boldsymbol{\phi}^*{}_{t+\Delta t}, \boldsymbol{\phi}_t\right) = \Gamma \sum_{\langle ij\rangle} \left(\phi^*_{i,t+\Delta t} - \phi^*_{j,t+\Delta t}\right) \Bigg(\phi_{i,t} - \phi_{j,t} + \frac{\phi_{i,t} + \phi_{j,t}}{2} \left\{\beta\epsilon_i\left(\boldsymbol{\phi}_{t+\Delta t}, \boldsymbol{\phi}_t\right) - \beta\epsilon_j(\boldsymbol{\phi}_{t+\Delta t}, \boldsymbol{\phi}_t)\right\}\Bigg) \tag{47}$$

with the effective potential

$$\epsilon_i\left(\boldsymbol{\phi}_{t+\Delta t}\right) = U_i + \sum_k V_{ik}\phi^*_{k,t+\Delta t}\phi_{k,t}. \tag{48}$$

The coherent state overlap in (46) can be written as

$$\langle \boldsymbol{\phi}_{t+\Delta t}|\boldsymbol{\phi}_t\rangle = e^{\frac{1}{2}|\boldsymbol{\phi}_{t+\Delta t}|^2 - \frac{1}{2}|\boldsymbol{\phi}_t|^2 - \bar{\boldsymbol{\phi}}_{i,t+\Delta t}\cdot(\boldsymbol{\phi}_{t+\Delta t} - \boldsymbol{\phi}_t)} \tag{49}$$

where $|\boldsymbol{\phi}|^2 = \sum_i |\phi_i|^2$ and $\bar{\boldsymbol{\phi}}_1 \cdot \boldsymbol{\phi}_2 = \sum_i \phi^*_{1,i}\phi_{2,i}$. The squared terms cancel between successive time slices.

We take the continuum limit via $\phi_{i,t} \to \phi(\mathbf{x},t)\Delta x^d$ and $\phi^*_{i,t} \to \bar{\phi}(\mathbf{x},t)$, so $\phi(\mathbf{x})$ has dimensions of density while $\bar{\phi}(\mathbf{x})$ is non-dimensional. The result is an action S containing a 'bulk' contribution as well as initial and final contributions at $t = 0$ and t_f, which can be used to compute averages via

$$\langle A\rangle = \int \mathcal{D}\left(\bar{\phi}, \phi\right) A\left(\bar{\phi}, \phi\right) e^{-S[\bar{\phi}, \phi]}. \tag{50}$$

5.2. Doi–Peliti action for interacting particles

From equations (46) and (49) we obtain the bulk action

$$S_{\rm B} = \int_0^{t_f} \mathrm{d}t \int \mathrm{d}\mathbf{x} \left[\bar{\phi}\left(\partial_t - D\nabla^2\right)\phi - \gamma\bar{\phi}\nabla\cdot\left(\phi\nabla U + \phi\nabla\int \mathrm{d}\mathbf{y}\, V(\mathbf{x}-\mathbf{y})\,\bar{\phi}(\mathbf{y})\,\phi(\mathbf{y})\right)\right] \tag{51}$$

with diffusion constant $D = \Gamma\Delta x^2$ and mobility $\gamma = D/k_{\rm B}T$.

Note that for noninteracting particles, with $V = 0$, the action (51) is linear in $\bar{\phi}$, which creates a delta function when integrated over $\bar{\phi}$. The resulting field ϕ then obeys

$$\frac{\partial\phi}{\partial t} = D\nabla^2\phi + \gamma\nabla\cdot(\phi\nabla U) \tag{52}$$

which is the Fokker–Planck equation for particles diffusing in a potential $U(\mathbf{x})$.

The final term, consisting of the projection state and part of the coherent state overlap, contributes a t_f 'boundary' contribution to the action of the form

$$e^{-S_f} = e^{\frac{1}{2}|\boldsymbol{\phi}_{t_f}|^2}\langle\mathcal{P}|\boldsymbol{\phi}\rangle = e^{\sum_i \phi_{i,t_f}} \tag{53}$$

from which we obtain the continuum limit

$$S_f = -\int \mathrm{d}\mathbf{x}\,\phi(\mathbf{x},t_f)\,. \tag{54}$$

Generally this term is eliminated by performing a Doi shift. Instead, we will retain this term, since it plays an essential role in understanding the time-reversal symmetry.

The initial term also provides a $t = 0$ boundary term

$$e^{-S_i} = Z(0)^{-1}\, e^{-\frac{1}{2}|\boldsymbol{\phi}_0|^2}\langle\boldsymbol{\phi}_0|e^{-\beta\hat{H}_0}|\bar{n}_0\rangle. \tag{55}$$

In the case of noninteracting particles, where $\hat{H} = \sum_j U_j\hat{a}_j^\dagger\hat{a}_j$, this becomes

$$e^{-S_i} = Z(0)^{-1}\, e^{-|\boldsymbol{\phi}_0|^2}\exp\left(\sum_j e^{-\beta U_{j,0}}\phi_{j,0}^*\bar{n}_0\right) \tag{56}$$

where we used the coherent state identity $\langle\phi_2|e^{\lambda\hat{a}^\dagger\hat{a}}|\phi_1\rangle = \exp\{(e^\lambda - 1)\phi_2^*\phi_1\}\langle\phi_2|\phi_1\rangle$ [28]. In the continuum limit, we take $\bar{n}_0 \to n_0\Delta x^d$ and obtain

$$S_i = \ln Z(0) - \int \mathrm{d}\mathbf{x}\left[\bar{\phi}(\mathbf{x},0)\, e^{-\beta U(\mathbf{x},0)} n_0 - \bar{\phi}(\mathbf{x},0)\,\phi(\mathbf{x},0)\right]. \tag{57}$$

To derive a simple expression for the initial action with interacting particles, it will be necessary to introduce a Hubbard–Stratonovich transformation, which we will describe below.

Finally, we note that in the field theory the work term (32) becomes

$$W[\bar{\phi},\phi] = \int_0^{t_f}\mathrm{d}t\int \mathrm{d}\mathbf{x}\,\dot{U}(t)\,\bar{\phi}(\mathbf{x},t)\,\phi(\mathbf{x},t)\,. \tag{58}$$

5.3. Cole–Hopf transformation and Dean–Kawasaki field theory

The bulk action (51) can be transformed via the Cole–Hopf transformation $\phi \to e^{-\bar{\rho}}\rho$, $\bar{\phi} \to e^{\bar{\rho}}$ to

$$S_{\rm B} = \int_0^{t_f}\mathrm{d}t\int \mathrm{d}\mathbf{x}\left[\bar{\rho}\left(\partial_t - D\nabla^2\right)\rho - \gamma\bar{\rho}\nabla\cdot(\rho\nabla\epsilon) - \gamma D\rho\left(\nabla\bar{\rho}\right)^2\right] \tag{59}$$

with the effective potential

$$\epsilon(\mathbf{x}) = U(\mathbf{x}) + \int \mathrm{d}\mathbf{y} V(\mathbf{x}-\mathbf{y})\,\rho(\mathbf{y})\,. \tag{60}$$

This matches the Dean–Kawasaki field theory [20] obtained from the Langevin equation for interacting particles derived by Dean [21], then mapped to a field theory using the MSRJD technique [22–24]. However, there appear to be discrepancies with the initial and final terms. In particular, Dean–Kawasaki field theory has no analog of the projection state and final action S_f. Further the Cole–Hopf transformation does not map our initial action to the generally assumed initial conditions for Dean–Kawasaki field theory.

6. Time reversal in Doi–Peliti field theory

We are now equipped to examine the role of time reversal in the field theory. We begin with noninteracting particles, where the symmetry is more directly manifest, and then introduce a Hubbard–Stratonovich transformation to reveal the symmetry for interacting particles.

6.1. Noninteracting particles

When $V = 0$, the bulk action (51) can be written as

$$S_\mathrm{B} = \int_0^{t_f} \mathrm{d}t \int \mathrm{d}\mathbf{x} \left[\bar{\phi}\partial_t\phi + De^{-\beta U}\nabla\bar{\phi}\cdot\nabla\left(\phi e^{\beta U}\right)\right] \tag{61}$$

with S_i and S_f given by equations (57) and (54). The time-reversal symmetry of the action is revealed by the transformation

$$\phi \to n_0 e^{-\beta U}\bar{\psi} \qquad \bar{\phi} \to n_0^{-1} e^{\beta U}\psi \qquad t \to t' = t_f - t. \tag{62}$$

This gauge-like transformation maintains the bilinear product $\bar{\phi}\phi \to \bar{\psi}\psi$ and the action (61) is invariant apart from the time-derivative term. Suppressing the spatial integral, we have

$$\int_0^{t_f} \mathrm{d}t\,\bar{\phi}\partial_t\phi \to \left(\bar{\psi}\psi\right)\Big|_{t=0}^{t=t_f} + \int_0^{t_f} \mathrm{d}t' \left(\bar{\psi}\partial_{t'}\psi + \beta\frac{\partial U}{\partial t'}\bar{\psi}\psi\right) \tag{63}$$

where we have used integration by parts. Note that time reversal generates a work term (58).

The time reversal transformation (62) also maps the initial action (57) into the final action (54) and vice-versa, with the help of the boundary terms in (63). The one exception is the partition function factor, which remains $Z(0)^{-1}$ although the time-reversed averaging would require that we start at $t' = 0$ with $Z(t = t_f)^{-1}$. Adjusting for the partition function and combining the bulk, initial, and final actions, we obtain

$$S\left[\bar{\phi},\phi\right] \to S_R\left[\bar{\psi},\psi\right] + \beta W_R + \beta F(t = t_f) - \beta F(t = 0)\,, \tag{64}$$

where S_R and W_R are the time-reversed action and work term, and $\beta F = -\ln Z$.

As a consequence of this time reversal symmetry we have the identity

$$\begin{aligned}\langle Ae^{-\beta W}\rangle &= \int \mathcal{D}\left(\bar{\phi},\phi\right) A\left[\bar{\phi},\phi\right] e^{-\beta W[\bar{\phi},\phi]} e^{-S[\bar{\phi},\phi]} \\ &\to e^{-\beta\Delta F}\int \mathcal{D}\left(\bar{\psi},\psi\right) A_R\left[\bar{\psi},\psi\right] e^{-S_R[\bar{\psi},\psi]} \\ &= e^{-\beta\Delta F}\langle A_R\rangle_R \end{aligned} \tag{65}$$

for any observable $A[\bar{\phi},\phi]$, with time-reversed $A_R[\bar{\psi},\psi]$. Here we have used that work (58) is odd under time reversal, $W[\bar{\phi},\phi] \to -W_R[\bar{\psi},\psi]$, to move the exponential of negative work to the forward time average. We will show equation (65) holds for interacting particles as well, and provides the basis for deriving multiple nonequilibrium identities.

In particular, setting $A = 1$ produces the Jarzynski relation, while taking $A = e^{(iq+\beta)W}$ reproduces equation (43), which can be inverse Fourier transformed to give the Crooks relation.

6.2. Interacting particles

For interacting particles the bulk action (51) can be written as

$$S_{\mathrm{B}} = \int_0^{t_f} \mathrm{d}t \int \mathrm{d}\mathbf{x} \left[\bar{\phi}\partial_t\phi + De^{-\beta\epsilon}\nabla\bar{\phi}\cdot\nabla\left(\phi e^{\beta\epsilon}\right)\right] \tag{66}$$

where $\epsilon(\mathbf{x},t)$ is the effective potential, given by

$$\epsilon(\mathbf{x},t) = U(\mathbf{x},t) + \int \mathrm{d}\mathbf{y}\, V(\mathbf{x}-\mathbf{y})\,\bar{\phi}(\mathbf{y},t)\,\phi(\mathbf{y},t)\,. \tag{67}$$

To affect time reversal with a local transformation like (62), we need to employ a field Hubbard–Stratonovich transformation:

$$\begin{aligned}
\exp&\left(\beta\int \mathrm{d}\mathbf{y} V(\mathbf{x}-\mathbf{y})\,\bar{\phi}(\mathbf{y})\,\phi(\mathbf{y})\right)\\
&= A\int \mathcal{D}\eta \exp\left\{-\frac{1}{2\beta}\int \mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\,\eta^*(\mathbf{r}_1)\,V^{-1}(\mathbf{r}_{12})\,\eta(\mathbf{r}_2)\right.\\
&\quad\left.+\int \mathrm{d}\mathbf{r}_1\,\eta(\mathbf{r}_1)\,\bar{\phi}(\mathbf{r}_1)\,\phi(\mathbf{r}_1)\right\} e^{-i\eta_2(\mathbf{x})}\\
&\equiv \int \mathcal{D}\eta F\left[\eta,\bar{\phi}\phi\right] e^{-i\eta_2(\mathbf{x})}
\end{aligned} \tag{68}$$

where $\eta(\mathbf{x},t) = \eta_1(\mathbf{x},t) + i\eta_2(\mathbf{x}.t)$ is a complex field, A is a normalization constant, $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and V^{-1} is defined formally via $\int \mathrm{d}\mathbf{y} V(\mathbf{x}-\mathbf{y})V^{-1}(\mathbf{y}-\mathbf{z}) = \delta^{(d)}(\mathbf{x}-\mathbf{z})$. Equation (68) applies for all times t, with $\eta(\mathbf{r},t)$ uncorrelated for different times. With this notation, the bulk action becomes

$$S_{\mathrm{B}} = \int \mathcal{D}\eta F \int \mathrm{d}t\mathrm{d}\mathbf{x}\left[\bar{\phi}\partial_t\phi + De^{-\beta\epsilon}\nabla\bar{\phi}\cdot\nabla\left(\phi e^{\beta U - i\eta_2}\right)\right] \tag{69}$$

where we have suppressed the time integration limits. Now the gauge-like field transformation

$$\phi \to n_0 e^{-\beta U + i\eta_2}\bar{\psi} \qquad \bar{\phi} \to n_0^{-1} e^{\beta U - i\eta_2}\psi \tag{70}$$

with time reversal $t \to t' = t_f - t$ once again leaves the action invariant, i.e.

$$\nabla\bar{\phi}\cdot\nabla\left(\phi e^{\beta U - i\eta_2}\right) \to \nabla\left(\psi e^{\beta U - i\eta_2}\right)\cdot\nabla\bar{\psi} \tag{71}$$

apart from the time derivative term, which again has the form given in equation (63), generating the work term. Importantly, the time derivative on the η field averages to zero because the field is uncorrelated over time.

The Hubbard–Stratonovich transformation also simplifies the initial action. The exponential of the Doi Hamiltonian (18) can be written as

$$e^{-\beta\hat{H}} = A\int\prod_i \mathrm{d}\eta_i e^{-\frac{1}{2\beta}\sum_{jk}\eta_j V_{jk}^{-1}\eta_k + \sum_j(-\beta U_j + i\eta_j)\hat{a}_j^\dagger\hat{a}_j}. \tag{72}$$

Using this in our initial action S_i, as defined in equation (55), we obtain an identical expression to (56) with $e^{-\beta U_{j,0}} \to e^{-\beta U_{j,0}+i\eta_j}$ and the additional integration over the η_j variables. Taking the continuum limit, with $\eta_j \to \eta_2(\mathbf{x},0)$, results in an initial action of the form

$$S_i = \ln Z(0) - \int \mathrm{d}\eta F \int \mathrm{d}\mathbf{x} \left[\bar{\phi}(\mathbf{x},0)\, e^{-\beta U(\mathbf{x},0)+i\eta_2(\mathbf{x},0)} n_0 \right. \\ \left. -\bar{\phi}(\mathbf{x},0)\phi(\mathbf{x},0)\right] \tag{73}$$

while the final action (54) remains unchanged. Thus the field transformation (70) swaps the initial and final actions apart from the partition function, exactly as before with the noninteracting theory. Thus the fundamental identity (65) continues to hold for interacting particles.

7. Nonequilibrium identities

Starting from the fundamental relation (65) we can derive a number of nonequilibrium identities by appropriate choice of the operator $A[\bar{\phi},\phi]$ and functional differentiation. As discussed in the text following (65), choosing $A = 1$ gives the Jarzynski relation, and choosing $A = e^{(iq+\beta)W}$ leads to the Crooks relation.

We can obtain a nonequilibrium generalization of the fluctuation-dissipation relation by differentiating (65) with respect to $U(\mathbf{x},t)$ for some intermediate time $0 < t < t_f$. From the field theoretic average (50) it follows that the derivative of the left hand side is

$$\frac{\delta}{\delta U(\mathbf{x},t)} \langle A e^{-\beta W}\rangle = -\left\langle \left(\beta \frac{\delta W}{\delta U} + \frac{\delta S}{\delta U}\right) A e^{-\beta W}\right\rangle, \tag{74}$$

with

$$\frac{\delta W}{\delta U} = \frac{\delta}{\delta U(\mathbf{x},t)} \int_0^{t_f} \mathrm{d}t' \int \mathrm{d}\mathbf{x}'\, \dot{U}(\mathbf{x}',t')\, \bar{\phi}(\mathbf{x}',t')\, \phi(\mathbf{x}',t') \\ = -\frac{\partial}{\partial t}\left(\bar{\phi}(\mathbf{x},t)\, \phi(\mathbf{x},t)\right) \tag{75}$$

from (58), where we have used integration by parts, and

$$\frac{\delta S}{\delta U} = -\gamma \frac{\delta}{\delta U(\mathbf{x},t)} \int_0^{t_f} \mathrm{d}t' \int \mathrm{d}\mathbf{x}' \bar{\phi} \nabla \cdot (\phi \nabla U) \\ = -\gamma \nabla \cdot \left(\phi(\mathbf{x},t)\, \nabla \bar{\phi}(\mathbf{x},t)\right) \tag{76}$$

from (51), where we have used integration by parts twice. In contrast, the functional derivative of the right hand side of (65) only acts on the action, yielding

$$\frac{\delta}{\delta U} \langle \tilde{A}\rangle_R = \gamma \left\langle \nabla \cdot \left(\phi(\mathbf{x}, t_f - t)\, \nabla \bar{\phi}(\mathbf{x}, t_f - t)\right) \tilde{A} \right\rangle_R. \tag{77}$$

Here we have assumed that A and A_R do not depend on the site potential U. Combining these gives an identity

$$\frac{\partial}{\partial t} \langle \bar{\phi}(\mathbf{x},t)\phi(\mathbf{x},t) A e^{-\beta W}\rangle + D\langle \nabla \cdot (\phi(\mathbf{x},t)\nabla\bar{\phi}(\mathbf{x},t) A e^{-\beta W}\rangle \\ = D e^{-\beta \Delta F} \langle \nabla \cdot (\phi(\mathbf{x}, t_f - t)\nabla\bar{\phi}(\mathbf{x}, t_f - t) A_R\rangle_R, \tag{78}$$

where we have used $\gamma = \beta D$. The significant of this identity is that it holds arbitrarily far from equilibrium, i.e. it is not a linear response relationship. Additional relations could be derived by further differentiation with respect to U.

For the choice $A = \bar{\phi}(\mathbf{x}', t')\phi(\mathbf{x}', t')$ equation (78) becomes a nonequilibrium fluctuation dissipation relation. Let $\rho = \bar{\phi}\phi$ and take $U(\mathbf{x}, t) \to U(\mathbf{x}, t) + U_1(\mathbf{x}, t)$. Then

$$\beta \frac{\partial}{\partial t} \langle \rho(\mathbf{x}, t)\, \rho(\mathbf{x}', t')\, e^{-\beta W} \rangle = \frac{\delta \langle \rho(\mathbf{x}', t')\, e^{-\beta W} \rangle}{\delta U_1(\mathbf{x}, t)} - e^{-\beta \Delta F} \frac{\delta \langle \rho(\mathbf{x}', t_f - t') \rangle_R}{\delta U_1(\mathbf{x}, t_f - t)} \tag{79}$$

with the functional derivatives evaluated at $U_1 = 0$, and with the understanding that W is determined by U and not U_1, as defined in (58). Thus a time derivative of a correlation function, modified to include the Jarzynski work term, is related to a response function. The right hand side has effectively a θ function, with the first term nonzero when $t' > t$ and the second term nonzero with $t' < t$.

We note that taking functional derivatives of the Jarzynski relation to obtain a fluctuation dissipation relation within linear response, as done in [29, 30], differs from this field theoretic result which, like that obtained in [10], applies arbitrarily far from equilibrium.

8. Summary

We have generalized the Doi representation to describe interacting particles coupled to a thermal reservoir, undergoing hops with rates determined by detailed balance. Such a system can be driven far from equilibrium by a rapidly-varying local potential. We demonstrated that the Jarzynski and Crooks relations arise straightforwardly in the Doi representation, with the initial state and the projection state playing a crucial role.

Then, by mapping the Doi representation to a field theory via the coherent state representation, we obtained the Doi–Peliti field theory for these interacting Brownian particles. We demonstrated that time reversal in this field theory has a gauge-like form, and that the time reversal operation results in a fundamental identity (65) from which the Jarzynski and Crooks relations can be derived, along with a nonequilibrium generalization of the fluctuation-dissipation relation.

Future work could include generalizing the formalism to include chemical reactions and allowing for chemical work to be done on the system, and deriving a general framework for entropy production within Doi–Peliti field theory. Note that Doi–Peliti field theory has been employed for entropy production in active particle systems [31]. It could also be fruitful to develop a perturbative expansion in the interaction strength.

Data availability statement

No new data were created or analyzed in this study.

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References

[1] Jarzynski C 1997 *Phys. Rev. Lett.* **78** 2690
[2] Jarzynski C 1997 *Phys. Rev.* E **56** 5018
[3] Crooks G E 1998 *J. Stat. Phys.* **90** 1481
[4] Crooks G E 1999 *Phys. Rev.* E **60** 2721
[5] Jarzynski C 2008 *Eur. Phys. J.* B **64** 331
[6] Jarzynski C 2011 *Annu. Rev. Condens. Matter Phys.* **2** 329
[7] Seifert U 2012 *Rep. Prog. Phys.* **75** 126001
[8] Peliti L and Pigolotti S 2021 *Stochastic Thermodynamics: An Introduction* (Princeton University Press)
[9] Shiraishi N 2023 *An Introduction to Stochastic Dynamics* (Springer)
[10] Mallick K, Moshe M and Orland H 2011 *J. Phys. A: Math. Theor.* **44** 095002
[11] Hohenberg P C and Halperin B I 1977 *Rev. Mod. Phys.* **49** 435
[12] Täuber U C 2014 *Critical Dynamics: A Field Theory Approach to Equilibrium and Non-Equilibrium Scaling Behavior* (Cambridge University Press)
[13] Doi M 1976 *J. Phys. A: Math. Gen.* **9** 1465
[14] Peliti L 1985 *J. Physique* **46** 1469
[15] Schulman L 1996 *Techniques and Applications of Path Integration* (Wiley)
[16] Täuber U C, Howard M and Vollmayr-Lee B P 2005 *J. Phys. A: Math. Gen.* **38** R79
[17] Andreanov A, Biroli G, Bouchaud J-P and Lefèvre A 2006 *Phys. Rev.* E **74** 030101
[18] Andreanov A, Biroli G and Lefèvre A 2006 *J. Stat. Mech.* P07008
[19] Lefèvre A and Biroli G 2007 *J. Stat. Mech.* P07024
[20] Kim B, Kawasaki K, Jacquin H and van Wijland F 2014 *Phys. Rev.* E **89** 012150
[21] Dean D S 1996 *J. Phys. A: Math. Gen.* **29** L613
[22] Martin P C, Siggia E D and Rose H A 1973 *Phys. Rev.* A **8** 423
[23] Janssen H-K 1976 *Z. Phys.* B **23** 377
[24] de Dominicis C 1976 *J. Phys. Colloq.* **37** C1
[25] Kurchan J 2007 *J. Stat. Mech.* P07005
[26] Hummer G and Szabo A 2001 *Proc. Natl Acad. Sci.* **98** 3658
[27] Lee B P 1994 *J. Phys. A: Math. Gen.* **27** 2633
[28] Katriel J 2000 *Phys. Lett.* A **273** 159
[29] Chetrite R and Gawedzki K 2008 *Commun. Math. Phys.* **282** 469
[30] Chetrite R and Gawdzki K 2009 *J. Stat. Phys.* **137** 890
[31] Pruessner G and Garcia-Millan R 2022 Field theories of active particle systems and their entropy production (arXiv:2211.11906)