Path-ensemble averages in systems driven far from equilibrium

Gavin E. Crooks

Department of Chemistry, University of California at Berkeley, Berkeley, California 94720

The Kawasaki nonlinear response relation, the transient fluctuation theorem, and the Jarzynski nonequilibrium work relation are all expressions that describe the behavior of a system that has been driven from equilibrium by an external perturbation. In contrast to linear response theory, these expressions are exact no matter the strength of the perturbation, or how far the system has been driven away from equilibrium. In this paper, I show that these three relations (and several other closely related results) can all be considered special cases of a single theorem. This expression is explicitly derived for discrete time and space Markovian dynamics, with the additional assumptions that the unperturbed dynamics preserve the appropriate equilibrium ensemble, and that the energy of the system remains finite.

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I. INTRODUCTION

If a system is gently driven from equilibrium by a small time-dependent perturbation, then the response of the system to the perturbation can be described by linear response theory. On the other hand, if the system is driven far from equilibrium by a large perturbation then linear response, and other near-equilibrium approximations, are generally not applicable. However, there are a few relations that describe the statistical dynamics of driven systems which are valid even if the system is driven far from equilibrium. These include the Jarzynski nonequilibrium work relation [1–4], which gives equilibrium free energy differences in terms of nonequilibrium measurements of the work required to switch from one ensemble to another; the Kawasaki relation [5–9], which specifies the nonlinear response of a classical system to an arbitrarily large perturbation; and a group of relations that can be collectively called ''entropy production fluctuation theorems'' [10–26]. I will specifically consider the transient fluctuation theorem of Evans and Searles [11,14] which deals with entropy production of driven systems that are initially in equilibrium. The Gallavotti-Cohen [12,13] fluctuation theorem addresses entropy production in nonequilibrium steady states, and will not be considered in this paper.

The relations listed above have been derived for a wide range of deterministic and stochastic dynamics. However, the various expressions and applicable dynamics have several commonalities: the system starts in thermal equilibrium, it is driven from that equilibrium by an external perturbation, the energy of the system is finite, the dynamics are Markovian, and if the system is unperturbed then the dynamics preserve the equilibrium ensemble. In this paper, it will be shown that these conditions are sufficient to derive the far-from-equilibrium expressions mentioned above. Indeed, they can all be considered special cases of a single theorem:

$$\langle \mathcal{F} \rangle_F = \langle \hat{\mathcal{F}} e^{-\beta \mathcal{W}_d} \rangle_R . \tag{1}$$

Here, $\langle \mathcal{F} \rangle_F$ indicates the average of the path function $\mathcal{F}$. Path functions (such as the heat and work) are functionals of the trajectory that the system takes through phase space. An average of a path function is implicitly an average over a suitably defined ensemble of paths. In this paper, the path ensemble is defined by the initial thermal equilibrium and the process by which the system is subsequently perturbed from that equilibrium. The left side of the above relation is simply $\mathcal{F}$ averaged over the ensemble of paths generated by this process. We arbitrarily label this the forward process (subscript ''F'').

For every such process that perturbs the system from equilibrium we can imagine a corresponding reverse perturbation (subscript ''R''). We shall construct this process by insisting that it too starts from equilibrium, and by considering a formal time reversal of the dynamics. The right side of Eq. (1) is $\hat{\mathcal{F}}$, the time reversal of $\mathcal{F}$, averaged over the reverse process, and weighted by the exponential of $\beta \mathcal{W}_d$. Here, $\beta = 1/k_B T$, T is the temperature of the heat bath, k_B is Boltzmann's constant, and $\mathcal{W}_d$ is the dissipative work. The dissipative work is a path function and is defined as $\mathcal{W}_d = \mathcal{W} - W_r$, where $\mathcal{W}$ is the total work done on the system by the external perturbation and W_r is the reversible work, the minimum average amount of work required to perturb the system from its initial to its final ensemble.

In summary, Eq. (1) states that an average taken over an ensemble of paths, which is generated by perturbing a system that is initially in equilibrium, can be equated with the average of another, closely related quantity, averaged over a path ensemble generated by the reverse process. This relation is valid for systems driven arbitrarily far from equilibrium, and several other far from equilibrium relations can be derived from it. It is sufficient that the dynamics are Markovian, preserve the equilibrium ensemble, and that the energy of the system is finite. In the next section, I derive from these conditions that such a system is microscopically reversible, Eq. (13), in a sense that will be made precise. (This derivation is somewhat more general than that given previously [4].) The path ensemble average, Eq. (1), is an almost trivial identity given that the dynamics satisfy this condition. This derivation is given is Sec. III, and various special cases are considered.

II. MICROSCOPIC REVERSIBILITY OF DRIVEN SYSTEMS

Let us consider a classical system that can exchange energy with a constant temperature heat bath, and which has a

finite set of states, $x \in \{1,2,3,...,N\}$. The energies of the states of the system are given by the vector $\mathbf{E}$. If these state energies do not vary with time then the stationary probability distribution, π, is given by the canonical ensemble of equilibrium statistical mechanics;

$$\rho(x|\beta,\mathbf{E}) = \pi_x = \frac{e^{-\beta E_x}}{\sum_x e^{-\beta E_x}} = \exp\{\beta F - \beta E_x\}. \quad (2)$$

In this expression, the sum is over all states of the system and $F(\beta,\mathbf{E}) = -\beta^{-1} \ln \sum_x \exp\{-\beta E_x\}$ is the Helmholtz free energy of the system.

In contrast to an equilibrium ensemble, the probability distribution of a nonequilibrium ensemble is not determined solely by the external constraints, but explicitly depends on the dynamics and history of the system. Let us consider a stochastic dynamics with a discrete time scale, $t \in \{0,1,2,3,...,\tau\}$. The state of the system at time t is $x(t)$, and the path, or trajectory that the system takes through this state space can be represented by the vector $x = [x(0),x(1), x(2),...,x(\tau)]$. We make the assumption that the dynamics are Markovian [27]. This implies that the probability of making a transition between states in a particular time step depends only on the current state of the system, and not on the previous history. The single time step dynamics are determined by the transition matrix $M(t)$ whose elements are the transition probabilities;

$$M(t)_{x(t+1)x(t)} \equiv P[(t) \rightarrow x(xt+1)]. \quad (3)$$

A transition matrix M has the properties that all elements must be nonnegative and that all columns sum to 1 due to the normalization of probabilities:

$$M_{ij} \geq 0, \quad \text{for all } i \text{ and } j,$$

$$\sum_i M_{ij} = 1, \quad \text{for all } j.$$

Let $\rho(t)$ be a (column) vector whose elements are the probability of being in state i at time t. Then the single time step dynamics can be written as

$$\rho(t+1) = M(t)\rho(t), \quad (4)$$

or equivalently as

$$\rho(t+1)_i = \sum_j M(t)_{ij}\rho(t)_j. \quad (5)$$

The state energies $\mathbf{E}(t)$ and the transition matrices $M(t)$ are functions of time due to the external perturbation of the system, and the resulting Markov chain is non-homogeneous in time [28]. The vector of transition matrices $\mathbf{M} = [M(0),M(2),...,M(\tau-1)]$ completely determine the dynamics of the system. We place the following additional constraints on the dynamics; that the state energies are always finite (this avoids the possibility of an infinite amount of energy being transferred from or to the system), and that the single time step transition matrices must preserve the corresponding canonical distribution. This canonical distribution, Eq. (2), is determined by the temperature of the heat bath and

the state energies at that time step. We say that the transition matrix is balanced, or that the equilibrium distribution $\pi(t)$ is an invariant distribution of $M(t)$,

$$\pi(t) = M(t)\pi(t).$$

Essentially this condition says that if the system is already in equilibrium [given $\mathbf{E}(t)$ and β], and the system is unperturbed, then it must remain in equilibrium.

It is often convenient to impose the much more restrictive condition of detailed balance,

$$M(t)_{ij}\pi(t)_j = M(t)_{ji}\pi(t)_i. \quad (6)$$

In particular, many Monte Carlo simulations are detailed balanced. However, it is not a necessity in such simulations [29], and it is not necessary here. It is sufficient that the transition matrices are balanced.

Each time step of this dynamics can be separated into two distinct substeps. At time $t=0$ the system is in state $x(0)$ with energy $E(0)_{x(0)}$. In the first substep, the system makes a stochastic transition to a state $x(1)$, which has energy $E(0)_{x(1)}$. This causes an amount of energy, $E(0)_{x(1)} - E(0)_{x(0)}$, to enter the system in the form of heat. In the second substep, the state energies change from $\mathbf{E}(0)$ to $\mathbf{E}(1)$ due to the external perturbation acting on the system. This requires an amount of work, $E(1)_{x(1)} - E(0)_{x(1)}$. This sequence of substeps repeats for a total of τ time steps. The total heat exchanged with the reservoir, $\mathcal{Q}$, the total work performed on the system $\mathcal{W}$ and the total change in energy ΔE are therefore

$$\mathcal{Q}[x] = \sum_{t=0}^{r-1} [E(t)_{x(t+1)} - E(t)_{x(t)}], \quad (7)$$

$$\mathcal{W}[x] = \sum_{t=0}^{r-1} [E(t+1)_{x(t+1)} - E(t)_{x(t+1)}], \quad (8)$$

$$\Delta E = E(\tau)_{x(r)} - E(0)_{x(0)} = \mathcal{W} + \mathcal{Q}. \quad (9)$$

The reversible work, $W_r = \Delta F = F[\beta,\mathbf{E}(\tau)] - F[\beta,\mathbf{E}(0)]$, is the free energy difference between two equilibrium ensembles. It is the minimum average amount of work required to change one ensemble into another. The dissipative work, $\mathcal{W}_d[x] = \mathcal{W}[x] - W_r$, is defined as the difference between the actual work and the reversible work. Note that the total work, the dissipative work and the heat are all path functions. In this paper, they are written with script letters, square brackets and/or as functions of the path x to emphasize this fact. In contrast ΔE is a state function; it depends only on the initial and final state.

Now, we will consider the effects of a time reversal on this Markov chain. In many contexts a time reversal is implemented by permuting the states of the system. For example, in a Hamiltonian system a time reversal involves inverting the momenta of all the particles. However, it is equivalent, and in the current context much more convenient, to apply the effects of the time reversal to the dynamics rather than the state space. Thus, the time-reversed trajectory, $\hat{x}$, is a simple reordering of the forward trajectory; $\hat{x}(t) = x(\tau-t)$ and $\hat{\mathbf{E}}(t) = \mathbf{E}(\tau-t)$.

We can derive the effect of a time reversal on a transition matrix by considering a time homogeneous Markov chain. Let π be the invariant distribution of the time-independent transition matrix M, given by the equilibrium canonical ensemble. If the system is in an equilibrium ensemble then a time reversal should have no effect on that ensemble, and the probability of observing the transition $i \rightarrow j$ in the forward chain should be the same as the probability of observing the transition $j \rightarrow i$ in the time-reversed chain. Because the equilibrium probability distribution is the same for both chains it follows that

$$\hat{M}_{ji}\pi_i = M_{ij}\pi_j, \quad \text{for all } i,j. \quad (10)$$

In matrix notation this may conveniently be written as

$$\hat{M} = \text{diag}(\pi)M^T \text{diag}(\pi)^{-1}.$$

Here, $\text{diag}(\pi)$ indicates a matrix whose diagonal elements are given by the vector π. $\hat{M}$ is referred to as the reversal of M [27], or as the π dual of M [30]. If the transition matrix obeys detailed balance, Eq. (6), then $\hat{M} = M$.

It is easy to confirm that $\hat{M}$ is a transition matrix; all entries are nonnegative because all equilibrium and transition probabilities are nonnegative, and all rows sum to 1,

$$\sum_j \hat{M}_{ji} = \frac{1}{\pi_i}\sum_j M_{ij}\pi_j = \frac{\pi_i}{\pi_i} = 1, \quad \text{for all } i.$$

Further, we can demonstrate that $\hat{M}$ and M have the same invariant distribution,

$$\sum_i \hat{M}_{ji}\pi_i = \sum_i M_{ij}\pi_j = \pi_j.$$

For the nonhomogeneous chain the time reversal of the vector of transition matrices, $\mathbf{M}$, is defined as

$$\hat{M}(t) = \text{diag}[\pi(\tau-t)]M(\tau-t)^T \text{diag}[\pi(\tau-t)]^{-1}. \quad (11)$$

The time reversal operation is applied to each transition matrix, and their time order is reversed. Note that for the transition matrices of the reverse chain the time index runs from 1 to τ, rather than 0 to $\tau-1$. Therefore, $M(t)$ is the transition matrix from time t to time $t+1$ [see Eq. (4)], but $\hat{M}(t)$ is the transition matrix from time $t-1$ to time t,

$$\hat{\rho}(t) = \hat{M}(t)\hat{\rho}(t-1). \quad (12)$$

This convention is chosen so that the time indexes of the various entities remain consistent. Thus, for the reverse chain at time t the state is $\hat{x}(t)$, the states energies are $\hat{\mathbf{E}}(t)$ and the corresponding equilibrium distribution is $\hat{\pi}(t)$, which is an invariant distribution of $\hat{M}(t)$.

Another consequence of the time reversal is that the work and heat substeps are interchanged in the reverse chain. The heat, total work and dissipative work are all odd under a time reversal: $\mathcal{Q}[x] = -\mathcal{Q}[\hat{x}]$, $\mathcal{W}[x] = -\mathcal{W}[\hat{x}]$, and $\mathcal{W}_d[x] = -\mathcal{W}_d[\hat{x}]$. The total change in energy, and the free energy

change are also odd under a time reversal, but to avoid ambiguity a ''Δ'' always refers to a change measured along the forward process.

We are now in a position to prove an important symmetry for the driven system under consideration. Let $\mathcal{P}[x|x(0),\mathbf{M}]$ be the probability of the trajectory x, given that the system started in state $x(0)$. The probability of the corresponding reversed path is $\hat{\mathcal{P}}[\hat{x}|\hat{x}(0),\hat{\mathbf{M}}]$. The ratio of these path probabilities is a simple function of the heat exchanged with the bath,

$$\mathcal{P}[x|x(0),\mathbf{M}]/\hat{\mathcal{P}}[\hat{x}|\hat{x}(0),\hat{\mathbf{M}}] = \exp\{-\beta\mathcal{Q}[x]\}. \quad (13)$$

At the risk of ambiguity, a system with this property will be described as microscopically reversible [4,22,25].

We proceed by expanding the path probability as a product of single time-step transition probabilities. This follows from the condition that the dynamics are Markovian,

$$\frac{\mathcal{P}[x|x(0),\mathbf{M}]}{\hat{\mathcal{P}}[\hat{x}|\hat{x}(0),\hat{\mathbf{M}}]} = \frac{\displaystyle\prod_{t=0}^{\tau-1} P[x(t)\rightarrow x(t+1)]}{\displaystyle\prod_{t'=0}^{\tau-1} \hat{P}[\hat{x}(t')\rightarrow\hat{x}(t'+1)]}.$$

For every transition in the forward chain there is a transition in the reverse chain related by the time reversal symmetry, Eq. (11). The path probability ratio can therefore be converted into a product of equilibrium probabilities,

$$\frac{\mathcal{P}[x|x(0),\mathbf{M}]}{\hat{\mathcal{P}}[\hat{x}|\hat{x}(0),\hat{\mathbf{M}}]} = \prod_{t=0}^{\tau-1} \frac{\pi(t)_{x(t+1)}}{\pi(t)_{x(t)}} = \prod_{t=0}^{\tau-1} \frac{\rho[x(t+1)|\beta,\mathbf{E}(t)]}{\rho[x(t)|\beta,\mathbf{E}(t)]}$$

$$= \exp\left\{-\beta\sum_{t=0}^{\tau-1}[E(t)_{x(t+1)}-E(t)_{x(t)}]\right\}$$

$$= \exp\{-\beta\mathcal{Q}[x]\}.$$

The second line follows from the definition of the canonical ensemble, Eq. (2), and the final line from the definition of the heat, Eq. (7).

The essential assumptions leading to this condition of microscopic reversibility are that the state energies are always finite, and that the dynamics are Markovian, and if unperturbed preserve the equilibrium distribution. These conditions are valid independently of the strength of the perturbation, or the distance of the ensemble from equilibrium. The extension to continuous time and continuous phase space appears straightforward, although it is technically more difficult to be completely rigorous. However, Jarzynski [26] has recently demonstrated that deterministic Hamiltonian system coupled to many heat baths are also microscopically reversible.

III. PATH ENSEMBLE AVERAGES

We are now in a position to consider the path ensemble average [Eq. (1)] detailed in the introduction. A system that is initially in thermal equilibrium is driven away from that equilibrium by an external perturbation, and the path function $\mathcal{F}[x]$ is averaged over the resulting nonequilibrium ensemble of paths. The probability of a trajectory is determined by the equilibrium probability of the initial state, and by the

vector of transition matrices that determine the dynamics. Therefore, the average of $\mathcal{F}$ over the ensemble of trajectories can be explicitly written as

$$\langle \mathcal{F} \rangle_F = \sum_x \rho[x(0)|\beta,\mathbf{E}(0)]\mathcal{P}[x|x(0),\mathbf{M}]\mathcal{F}[x].$$

The sum is over the set of all paths connecting all possible initial and final states. Given that the system is microscopically reversible it is a simple matter to convert the above expression to an average over the reverse process. We first note that

$$\frac{\rho[x(0)|\beta,\mathbf{E}(0)]\mathcal{P}[x|x(0),\mathbf{M}]}{\rho[\hat{x}(0)|\beta,\hat{\mathbf{E}}(0)]\hat{\mathcal{P}}|\hat{x}(0),\hat{\mathbf{M}}} = e^{+\beta\Delta E - \beta\Delta F - \beta\mathcal{Q}[x]}$$

$$= e^{+\beta\mathcal{W}[x] - \beta\Delta F}$$

$$= e^{+\beta\mathcal{W}_d[x]}. \quad (14)$$

The first line follows from the condition of microscopic reversibility Eq. (13), and the definition of the canonical ensemble, Eq. (2). Recall that ΔF is the reversible work of the forward process, and that $\mathcal{W}_d[x]$ is the dissipative work. The set of reverse trajectories is the same as the set of forward trajectories, and we define $\mathcal{F}[x] = \hat{\mathcal{F}}[\hat{x}]$.

Therefore,

$$\langle \mathcal{F} \rangle_F = \sum_{\hat{x}} \rho[\hat{x}(0)|\beta,\hat{\mathbf{E}}(0)]\hat{\mathcal{P}}[\hat{x}|\hat{M}]\hat{\mathcal{F}}[\hat{x}]e^{-\beta\mathcal{W}_d[\hat{x}]}$$

$$= \langle \hat{\mathcal{F}}e^{-\beta\mathcal{W}_d} \rangle_R.$$

It is frequently convenient to rewrite Eq. (1) as

$$\langle \mathcal{F}e^{-\beta\mathcal{W}_d} \rangle_F = \langle \hat{\mathcal{F}} \rangle_R, \quad (15)$$

where $\mathcal{F}$ has been replaced with $\mathcal{F}e^{-\beta\mathcal{W}_d}$, and $\hat{\mathcal{F}}$ with $\hat{\mathcal{F}}e^{+\beta\mathcal{W}_d}$.

A. Jarzynski nonequilibrium work relations

A variety of previous known relations can be considered special cases or approximations of this nonequilibrium path ensemble average. In the simplest case we start with Eq. (15), and then set $\mathcal{F} = \hat{\mathcal{F}} = 1$ (or any other constant of the dynamics). Then,

$$\langle e^{-\beta\mathcal{W}_d} \rangle_F = \langle 1 \rangle_R = 1. \quad (16)$$

The right side is unity due to normalization of probability distributions. We are now taking an average over a single path ensemble, and the remaining subscript, "F," becomes superfluous. The dissipative work, $\mathcal{W}_d$ can replaced by $\mathcal{W} - \Delta F$, and the change in free energy can be moved outside the average since it is path independent. The result is the Jarzynski nonequilibrium work relation [1–4,22],

$$\langle e^{-\beta\mathcal{W}} \rangle = e^{-\beta\Delta F} \quad (17)$$

This relation states that if we convert one system into another by changing the energies of all the states from an initial set of values to a final set of values over some finite length of time, then the change in the free energies of the corresponding equilibrium ensembles can be calculated by repeating the switching process many times, each time starting from an equilibrium ensemble, and taking the above average of the amount of work required to effect the change. In the limit of instantaneous switching between ensembles, (we change the energies of all the states in a single instantaneous jump) this relation is equivalent to the standard thermodynamic perturbation method that is frequently used to calculate free energy differences by computer simulation [31].

It is possible to extend Eq. (17) to a more general class of relations between the work and the free energy change [32]. Suppose that $\mathcal{F} = f(\mathcal{W})$ where $f(\mathcal{W})$ is any finite function of the work. Then, $\hat{\mathcal{F}} = f(-\mathcal{W})$, because the work is odd under a time reversal. Inserting these definitions into Eq. (1) and rearranging gives

$$e^{-\beta\Delta F} = \frac{\langle f(+\mathcal{W}) \rangle_F}{\langle f(-\mathcal{W})e^{-\beta\mathcal{W}} \rangle_R}. \quad (18)$$

Recall that ΔF is defined in terms of the forward process. Suppose that we have obtained n_F independent measurements of the work required for the forward process, and n_R-independent measurements from the reverse process. An interesting question is what choice of $f(\mathcal{W})$ leads to the highest statistical accuracy for ΔF. For instantaneous switching this question was answered by Bennett [33,31] in his derivation of the acceptance ratio method for calculating free energy differences. For finite time switching Bennett's derivation can be followed almost line for line. We therefore omit the details, and simply record the conclusions in the present notation. The least statistical error will result if we take $\mathcal{F} = (1 + \exp\{+\beta\mathcal{W} + C\})^{-1}$, and $\hat{\mathcal{F}} = (1 + \exp\{-\beta\mathcal{W} + C\})^{-1}$. Then

$$e^{-\beta\Delta F} = \frac{\langle (1 + \exp\{+\beta\mathcal{W} + C\})^{-1} \rangle_F}{\langle (1 + \exp\{+\beta\mathcal{W} - C\})^{-1} \rangle_R} \exp\{+C\}. \quad (19)$$

The optimal choice of the constant C is $-\beta\Delta F + \ln n_F/n_R$. This relation must be solved self-consistently, since ΔF appears on both sides.

B. Transient fluctuation theorem

Another interesting application of the path ensemble average is to replace the finite function of the work used above with a δ function, $\mathcal{F} = \delta(\beta\mathcal{W}_d - \beta\mathcal{W}_d[x])$, $\hat{\mathcal{F}} = \delta(\beta\mathcal{W}_d + \beta\mathcal{W}_d[\hat{x}])$. Plugging these $\mathcal{F}$s into Eq. (1) gives

$$\langle \delta(\beta\mathcal{W}_d - \beta\mathcal{W}_d[x])e^{-\beta\mathcal{W}_d} \rangle_F = \langle \delta(\beta\mathcal{W}_d + \beta\mathcal{W}_d[\hat{x}]) \rangle_R$$

or

$$P_F(+\beta\mathcal{W}_d)e^{-\beta\mathcal{W}_d} = P_R(-\beta\mathcal{W}_d),$$

Here, $P_F(+\beta\mathcal{W}_d)$ is the probability of expending the specified amount of work in the forward process, and $P_R(-\beta\mathcal{W}_d)$ is the probability of expending the negative of that amount of work in the reverse process. If $P_R(-\beta\mathcal{W}_d) \neq 0$ then we can rearrange this expression as

$$\frac{P_F(+\beta\mathcal{W}_d)}{P_R(-\beta\mathcal{W}_d)} = e^{+\beta\mathcal{W}_d}. \quad (20)$$

The system of interest starts in equilibrium and is perturbed for a finite amount of time. If it is allowed to relax back to equilibrium then the change in entropy of the heat bath will be $-\beta\mathcal{Q}$, and the change in entropy of the system will be $\beta\Delta E - \beta\Delta F$. Therefore, the total change in entropy of the universe resulting from the perturbation of the system is $-\beta\mathcal{Q} + \beta\Delta E - \beta\Delta F = \beta\mathcal{W} - \beta\Delta F = \beta\mathcal{W}_d$, the dissipative work. Thus, Eq. (20) can be interpreted as an entropy production fluctuation theorem. It relates the distribution of entropy productions of a driven system that is initially in equilibrium to the entropy production of the same system driven in reverse. As such, it is closely related to the transient fluctuation theorems of Evans and Searles [11,14]. The connection between this fluctuation theorem, the Jarzynski nonequilibrium work relation and microscopic reversibility was originally presented in Ref. [22].

C. Kawasaki response and nonequilibrium distributions

All of the above relations were derived from Eq. (1) by inserting a function of the work. Another group of relations can be derived by instead setting $\mathcal{F}$ to be a function of the state of the system at some time. In particular if we average a function of the final state in the forward process, $\mathcal{F} = f[x(\tau)]$, then we average a function of the initial state in the reverse process, $\hat{\mathcal{F}} = f[\hat{x}(0)]$:

$$\langle f[x(\tau)]e^{-\beta\mathcal{W}_d}\rangle_F = \langle f[\hat{x}(0)]\rangle_R.$$

Therefore, in the reverse process the average is over the initial equilibrium ensemble of the system, and the subsequent dynamics are irrelevant. We can once more drop reference to forward or reverse processes, and instead use labels to indicate equilibrium and nonequilibrium averages:

$$\langle f[x(\tau)]e^{-\beta\mathcal{W}_d}\rangle_{neq} = \langle f[x(\tau)]\rangle_{eq}. \quad (21)$$

This relation (also due to Jarzynski [32]) states that the average of a state function in a nonequilibrium ensemble, weighted by the dissipative work, can be equated with an equilibrium average of the same quantity.

Another interesting relation results if we insert the same state functions into the alternative form of the path ensemble average, Eq. (15) (this is ultimately equivalent to switching $\mathcal{F}$ and $\hat{\mathcal{F}}$):

$$\langle f[x(\tau)]\rangle_F = \langle f[\hat{x}(0)]e^{-\beta\mathcal{W}_d}\rangle_R. \quad (22)$$

This is the Kawasaki nonlinear response relation [5–9], applied to stochastic dynamics, and generalized to arbitrary forcing. This relation can also be written in an explicitly renormalized form [8] by expanding the dissipative work as $-\Delta F + \mathcal{W}$, and rewriting the free energy change as a work average using the Jarzynski relation, Eq. (17).

$$\langle f[x(\tau)]\rangle_F = \langle f[\hat{x}(0)]e^{-\beta\mathcal{W}}\rangle_R / \langle e^{-\beta\mathcal{W}}\rangle_R. \quad (23)$$

Simulation data indicates that averages calculated with the renormalized expression typically have lower statistical errors [8].

The probability distribution of a nonequilibrium ensemble can be derived from the Kawasaki relation, Eq. (23), by setting the state function to be $\mathcal{F} = f[x(\tau)] = \delta[x - x(\tau)]$, a δ function of the state of the system at time τ,

$$\rho_{neq}(x,\tau|\mathbf{M}) = \rho[x|\beta,\mathbf{E}(\tau)]\frac{\langle e^{-\beta\mathcal{W}}\rangle_{R,x}}{\langle e^{-\beta\mathcal{W}}\rangle_R}. \quad (24)$$

Here, $\rho_{neq}(x,\tau|\mathbf{M})$ is the nonequilibrium probability distribution and $\rho[x|\beta,\mathbf{E}(\tau)]$ is the equilibrium probability of the same state. The subscript ''x'' indicates that the average is over all paths that start in state x. In contrast the lower average is over all paths starting from an equilibrium ensemble. The nonequilibrium probability of a state is, to zeroth order, the equilibrium probability, and the correction factor can be related to a nonequilibrium average of the work.

There are several other far-from-equilibrium relations that have been derived from, or are related to the Kawasaki response. The transient time correlation function (TTCF) [34,35] gives another set of relations for the nonlinear response of a system, and are reputable of greater practical utility than the Kawasaki response relation. Unfortunately it appears that TTCF cannot be applied to the systems considered in this paper, since a crucial step linking the two formalisms [7] makes the assumption that the dynamics are deterministic, and therefore that only an average over initial conditions is needed. Similarly, Evans and Morriss have derived several interesting relations for the heat capacity of a nonequilibrium steady state [7], but again these relations are not generally applicable because it is assumed that the probability of a trajectory is independent of the temperature of the heat bath.

IV. CONCLUSIONS

All of the relations derived in this paper are directly applicable to systems driven far from equilibrium. These relations follow if the dynamics are microscopically reversible in the sense of Eq. (13). This relation was shown to hold if the dynamics are Markovian and balanced. Although I have concentrated on stochastic dynamics with discrete time and phase space, this should not be taken as a fundamental limitation. The extension to continuous phase space and time appears straightforward, and deterministic dynamics can be taken as a special case of stochastic dynamics.

ACKNOWLEDGMENTS

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