Reversibility in nonequilibrium trajectories of an optically trapped particle

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The fluctuation theorem (FT) describes how a system's thermodynamic irreversibility develops in time from a completely thermodynamically reversible system at short observation times, to a thermodynamically irreversible one at infinitely long times. In this paper, we present a general definition of the dissipation function Ω_t, the quantitative argument in the fluctuation theorem (FT), that is a measure of a system's irreversibility. Originally cast for deterministic systems, we demonstrate, through the example of two recent experiments, that the dissipation function can be defined for stochastic systems. While the ensemble average of Ω_t is positive definite irrespective of the system for which it is constructed, different expressions for Ω_t can arise in stochastic and deterministic systems. Moreover, within the stochastic framework, Ω_t is not unique. Nevertheless, each of these expressions for Ω_t satisfies the FT.

I. INTRODUCTION

As Loschmidt pointed out in 1876, the equations of motion are time reversible, so that for every trajectory that satisfies Newton's equations, there is a time-reversed trajectory, or "antitrajectory," that is also a solution to the equations of motion [1]. If a system evolves from state A to state B along a given path, then the system's antitrajectory is described by the time-reversed path from an initial state B to a final state A. But while a particular trajectory and its conjugate antitrajectory are both solutions of the equations of motion, the probability of observing an antitrajectory can be exceptionally small compared with that of its respective trajectory. That is, the evolution of a system proceeds preferentially in one direction. The second law of thermodynamics stipulates that a macroscopic system evolves overwhelmingly in one, time-forward direction, and is "irreversible." However, the second law is strictly applicable only to large systems over long time scales and does not describe small nanosystems which may not be completely irreversible over small time and length scales. A *quantitative* description of irreversibility for systems of arbitrary size is given by the fluctuation theorem (FT) of Evans and colleagues [2,3]. The theorem bridges the gap between the mathematical description of reversible dynamics and the second law expectation of irreversible processes. In fact the FT predicts that small systems are reversible over short time scales, and this has been verified in computer simulation and experiment.

The principle argument of the FT is the dissipation function, which is a measure of a system's irreversibility and is defined as the ratio of probability densities of observing a trajectory of duration t to that of its antitrajectory. The FT describes the asymmetry in the distribution of a dissipation function with observation time. In other words, the FT describes the transition from a fully reversible system, at vanishingly short observation times, to an irreversible one, at infinitely long observation times. However, the FT does not prescribe the time or length scales over which reversibility can be observed. These time and length scales have been

demonstrated from deterministic [2,3], and stochastic equations of motion [4–10], and recently measured in experiment [11]. In each of these cases, the dissipation function was derived from deterministic Newtonian equations of motion or "detailed balance." However, in some of these studies [9–11], the time and lengths scales of interest are too large to be easily simulated using molecular dynamics simulations. Lebowitz and Spohn [12], on the other hand, derive a dissipation function using local detailed balance together with stochastic dynamics. In this paper, we provide a definition for a fully stochastically derived dissipation function which can be applied to systems whose time and length scales are consistent with Langevin dynamics. Two recent experiments demonstrated that trajectories of an isolated colloidal particle in an optical trap obey the FT [11,13]. An optical trap is formed when a transparent, micron-sized particle, whose index of refraction is greater than that of the surrounding medium, is located within a focused laser beam. The refracted rays differ in intensity over the volume of the sphere and exert a subpico-Newton force ($\mathrm{pN}=10^{-12}\mathrm{N}$) on the particle, drawing it towards the region of highest light intensity, i.e., the focal point or trap center. The optical trap is harmonic: a particle located $\mathbf{r}$ from the center of the trap has an optical force, $\mathbf{F}_{opt}=-k\mathbf{r}$, acting to restore its position to the trap center. k is the trapping constant which can be tuned by adjusting the laser power. The first experiment by Wang *et al.* [11], which we refer to as the "drag" experiment, recorded particle trajectories in a translating trap and showed that the dissipation function follows an integrated form of the FT. The second and more recent experiment by Carberry *et al.* [13], named the "capture" experiment, recorded particle trajectories in a trap whose strength was increased discontinuously in time. This showed that the dissipation function directly satisfies the FT [14].

In this paper, we investigate the measure of irreversibility, referred to as the dissipation function, that serves as the quantitative argument in the FT. In the next section, we review the derivation of the dissipation function using both Newtonian and Langevin dynamics and show how, by con-

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struction, the dissipation function obeys the FT. In Sec. III, we analyze the dissipation function for the capture experiment and in Sec. IV, we analyze the dissipation functions that apply to the drag experiment. For these experiments, we derive dissipation functions directly from Langevin dynamics and show that the dissipation function can have different forms which nevertheless satisfy the FT.

II. IRREVERSIBILITY MEASURE

A. Newtonian derivation of the dissipation function

Under Newtonian dynamics, a system's state is described in terms of the coordinates $\mathbf{q}$ and momenta $\mathbf{p}$ of all constituent molecules, including solvent molecules, and is represented by a point in phase space, $\Gamma \equiv \{\mathbf{q}, \mathbf{p}\}$. Trajectories in phase space are deterministic; that is, each point in phase space corresponds to a unique trajectory and a trajectory can be identified by its point in phase space at any arbitrary time s, Γ_s. Consider a trajectory initiated at $\Gamma_0 \equiv \{\mathbf{q}_0, \mathbf{p}_0\}$, at $t=0$, that terminates after time t at $\Gamma_t \equiv \{\mathbf{q}_t, \mathbf{p}_t\}$. Let $\delta V_\Gamma(\Gamma_t)$, represent an infinitesimal volume of states about the point Γ_t:

$$\delta V_\Gamma(\Gamma_t) \equiv \lim_{\delta\mathbf{q},\delta\mathbf{p}\to 0} \delta\mathbf{q}\,\delta\mathbf{p}. \qquad (1)$$

For every initial state within volume element $\delta V_\Gamma(\Gamma_0)$ there exists a unique destination point within volume element $\delta V_\Gamma(\Gamma_t)$. Thus $\delta V_\Gamma(\Gamma_s)$, where s can take on any value between 0 and t, represents a unique "bundle" of trajectories, identified by their state points at time s. Since the same exclusive set of trajectories are described by both $\delta V_\Gamma(\Gamma_0)$ and $\delta V_\Gamma(\Gamma_t)$, the probabilities of observing the bundle of trajectories at $t=0$ and again at any other time s must be identical, $P(\delta V_\Gamma(\Gamma_0),0) = P(\delta V_\Gamma(\Gamma_s),s)$. This probability can be expressed as

$$P(\delta V_\Gamma(\Gamma_s),s) = f(\Gamma_s,s)\delta V_\Gamma(\Gamma_s), \qquad (2)$$

where $f(\Gamma_s,s)$ is the phase space probability density, or distribution function, at Γ_s at time s. From the Lagrangian form of the Liouville equation [15], the time evolution of the probability density from the density at its initial state, $f(\Gamma_0,0)$, is

$$f(\Gamma_t,t) = f(\Gamma_0,0)\exp\left(-\int_0^t ds\Lambda(\Gamma_s)\right), \qquad (3)$$

where Λ is the phase space compression factor [15]. Thus the size of the volume element varies in time along the bundle of trajectories, according to

$$\frac{\delta V_\Gamma(\Gamma_t)}{\delta V_\Gamma(\Gamma_0)} = \exp\left(\int_0^t ds\Lambda(\Gamma_s)\right), \qquad (4)$$

where the right-hand side quantifies the phase space contraction along the trajectory from Γ_0 to Γ_t. Such contraction of phase space occurs for thermostated dissipative systems, and the average degree of contraction is related to the spontaneous entropy production in the system.
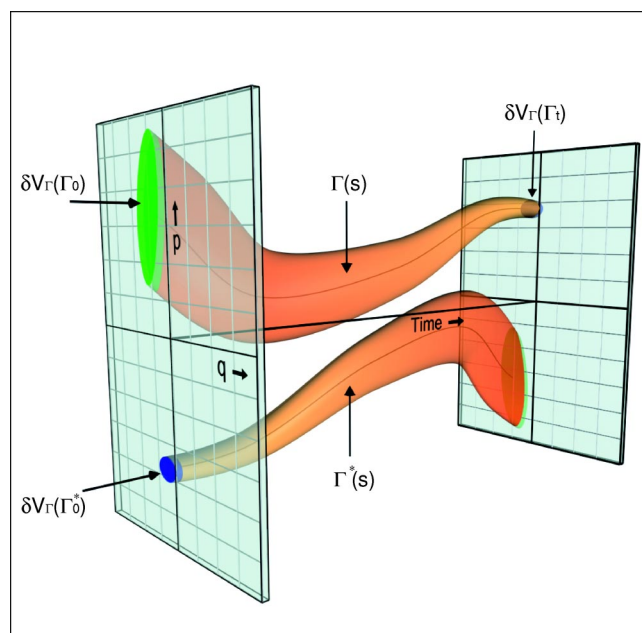

FIG. 1. (Color online) An illustration of a set of neighboring Newtonian trajectories initiated in a volume element $\delta V_\Gamma(\Gamma_0)$ (top tube) and the corresponding set of time reverse or antitrajectories initiated in $\delta V_\Gamma(\Gamma_0^*)$ (lower tube) in coordinate, momentum ($\Gamma \equiv \mathbf{q}, \mathbf{p}$) and time t space. For every trajectory that starts at $\Gamma_0 \equiv (\mathbf{q}_0, \mathbf{p}_0)$ in volume element $\delta V_\Gamma(\Gamma_0)$ and ends at $\Gamma_t \equiv (\mathbf{q}_t, \mathbf{p}_t)$ in volume element $\delta V_\Gamma(\Gamma_t)$ at some time t later, there exists its time reversed or antitrajectory that starts at $\Gamma_0^* \equiv (\mathbf{q}_t, -\mathbf{p}_t)$ in element $\delta V_\Gamma(\Gamma_0^*)$ and ends at $\Gamma_t^* \equiv (\mathbf{q}_0, -\mathbf{p}_0)$ in $\delta V_\Gamma(\Gamma_t^*)$. The size of the volume elements $\delta V_\Gamma(\Gamma_t)$ and $\delta V_\Gamma(\Gamma_0^*)$ are equivalent by time reversal of the equations of motion. For thermostated, dissipative systems, there is a contraction of phase-space volume in time [i.e., $\delta V_\Gamma(\Gamma_t) < \delta V_\Gamma(\Gamma_0)$], represented in the figure by the tube cross section shrinking in time, and quantified by a thermodynamic entropy loss.

For every trajectory that is initiated at $\Gamma_0 \equiv \{\mathbf{q}_0, \mathbf{p}_0\}$ and terminates at $\Gamma_t \equiv \{\mathbf{q}_t, \mathbf{p}_t\}$ in a system with reversible dynamics, there is a unique conjugate or antitrajectory that starts at $\Gamma_0^* \equiv \{\mathbf{q}_t, -\mathbf{p}_t\}$ and ends at $\Gamma_t^* \equiv \{\mathbf{q}_0, -\mathbf{p}_0\}$. Like its forward component, a bundle of time-reversed, conjugate trajectories is represented at time s by the volume element $\delta V_\Gamma(\Gamma_s^*)$ centered about the point $\Gamma_s^* \equiv \{\mathbf{q}_{t-s}, -\mathbf{p}_{t-s}\}$. For every initial state within volume element $\delta V_\Gamma(\Gamma_0^*)$ there exists a unique, destination point within volume element $\delta V_\Gamma(\Gamma_t^*)$. Since Γ^* is the time-reverse mapping of Γ, and the Jacobian of the map is unity, the size of the volume element $\delta V_\Gamma(\Gamma_0^*)$ is equal to $\delta V_\Gamma(\Gamma_t)$, but centered around a different point in phase space. Moreover, if there is a volume contraction from $\delta V_\Gamma(\Gamma_0)$ to $\delta V_\Gamma(\Gamma_t)$, as shown in Fig. 1, then there is an equivalent volume expansion associated with the conjugate antitrajectories.

A measure of reversibility is the ratio of the probabilities of observing sets of trajectories and their time reverse or antitrajectories. This probability ratio is expressed for initial state points of forward trajectories initiated in the $\delta V_\Gamma(\Gamma_0)$ and antitrajectories in the conjugate volume element $\delta V_\Gamma(\Gamma_0^*)$, and its logarithm is the dissipation function Ω_t [16]:

$$\Omega_t(\mathbf{\Gamma}_0) = \ln\left(\frac{P(\delta V_\Gamma(\mathbf{\Gamma}_0),0)}{P(\delta V_\Gamma(\mathbf{\Gamma}_0^*),0)}\right). \tag{5}$$

The magnitude of $\Omega_t(\mathbf{\Gamma}_0)$ indicates the degree of irreversibility over time t for trajectories that originate within $\delta V_\Gamma(\mathbf{\Gamma}_0)$: $\Omega_t = 0$ corresponds to a perfectly reversible bundle of trajectories of duration t, while a large value of Ω_t characterizes trajectories whose time-reversed conjugate is less likely to be observed.

B. Langevin derivation of the dissipation function

For colloidal systems, such as those investigated in Wang *et al.* and Carberry *et al.* [11,13], a stochastic approach is used to characterize the trajectories of the colloidal particle, namely the inertialess Langevin equation [17]:

$$\xi\frac{d\mathbf{r}}{dt} = \mathbf{f}_{ext} + \mathbf{g}(t). \tag{6}$$

This is a first-order stochastic differential equation describing the balance of drag and external forces acting on the colloidal particle where the force of inertia is negligible. This equation is cast in terms of the particle's coordinates $\mathbf{r}$, where the many degrees of freedom associated with the solvent molecules are recast into the macroscopic material property of viscosity η, and the buffeting action of the solvent molecules on the particle is represented by a fluctuating random force $\mathbf{g}(t)$ which is uncorrelated Gaussian noise with zero mean and $\langle\mathbf{g}(t)\mathbf{g}(t')\rangle = 2\xi k_B T\delta(t-t')$, and $\mathbf{f}_{ext}$ is the external force exerted on the particle. The drag coefficient for the particle of radius a is $\xi = 6\pi\eta a$. The state of the colloidal system is no longer described by the set of coordinates and momenta of all constituent molecules, but is reduced to only the coordinates of the colloidal particle, $\mathbf{r}(t) = \mathbf{r}_t$. Unlike Newtonian dynamics, this stochastic equation cannot be used to construct conjugate pairs of trajectories through time reversal, as the random force is Markovian and $\xi > 0$. Moreover, as the particle position is not unique to any given trajectory, there exist infinitely many trajectories that originate at $\mathbf{r}_0$ and a subset of these arrive at a given destination $\mathbf{r}_t$ at time t. Let $\{\mathbf{r}_0, \mathbf{r}_t\}$ represent those stochastic trajectories that evolve from $\mathbf{r}_0$ to $\mathbf{r}_t$, and let $\{\mathbf{r}_t, \mathbf{r}_0\}$ represent a conjugate set of "backward" trajectories evolving from $\mathbf{r}_t$ to $\mathbf{r}_0$. For each set of forward trajectories $\{\mathbf{r}_0, \mathbf{r}_t\}$ there exists a corresponding backward set of trajectories $\{\mathbf{r}_t, \mathbf{r}_0\}$, Fig. 2. In analogy to Eq. (1), let $\delta V_{r,r}(\{\mathbf{r}_0, \mathbf{r}_t\})$ represent an infinitesimal volume of sets of trajectories about the set of trajectories that initiate at $\mathbf{r}_0$ and terminate at $\mathbf{r}_t$, or $\{\mathbf{r}_0, \mathbf{r}_t\}$:

$$\delta V_{r,r}(\{\mathbf{r}_0, \mathbf{r}_t\}) \equiv \lim_{\delta \mathbf{r}_0, \delta \mathbf{r}_t \to 0} \delta \mathbf{r}_0 \delta \mathbf{r}_t. \tag{7}$$

The probability of observing a stochastic trajectory with the colloid particle located at an initial position between $\mathbf{r}_0$ and $\mathbf{r}_0 + \delta\mathbf{r}_0$ and a final position between $\mathbf{r}_t$ and $\mathbf{r}_t + \delta\mathbf{r}_t$ is then

$$P[\delta V_{\mathbf{r},\mathbf{r}}(\{\mathbf{r}_0, \mathbf{r}_t\})] = p(\mathbf{r}_0, \mathbf{r}_t)\delta\mathbf{r}_0\delta\mathbf{r}_t, \tag{8}$$

where the normalized distribution $p(\mathbf{r}_0, \mathbf{r}_t)$ can be expressed using well-known probability distributions, and where the
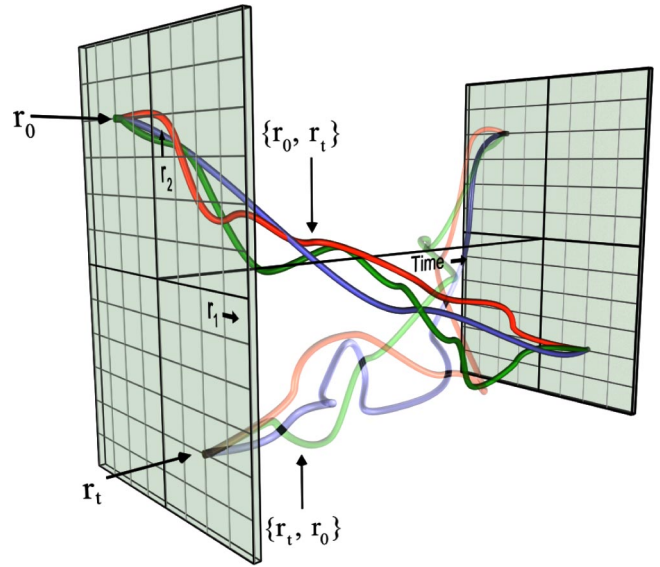

FIG. 2. (Color online) An illustration of a subset of the stochastic trajectories that initiate at $\mathbf{r}_0$ and terminate at $\mathbf{r}_t$, denoted by $\{\mathbf{r}_0, \mathbf{r}_t\}$, and the corresponding subset of backwards trajectories $\{\mathbf{r}_t, \mathbf{r}_0\}$. Such stochastic trajectories are represented by the position of the Brownian particle(s) at time s, $\mathbf{r}_s$ from $0 < s < t$; i.e., the degrees of freedom of the solvent molecules are reduced to a material parameter, viscosity, and a random fluctuating force. The stochastic Langevin equation of motion is not time reversible and consequently, it is not possible to construct an antitrajectory that is conjugate to any particular trajectory as is possible using Newtonian dynamics. Moreover, as position is not unique to any given stochastic trajectory, a bundle of trajectories is determined by both initial and terminating positions, $\mathbf{r}_0$ and $\mathbf{r}_t$, unlike deterministic trajectories where each trajectory is fully defined by only one state point $\mathbf{\Gamma}_s$ at any time s along its trajectory. While it is artificial to construct conjugate pairs of stochastic trajectories, it is possible to numerically construct a set of forward trajectories $\{\mathbf{r}_0, \mathbf{r}_t\}$ and a set of backwards trajectories $\{\mathbf{r}_t, \mathbf{r}_0\}$ whose probability distribution can be expressed analytically or constructed numerically from simulation.

volume elements integrated over are of the same size; $|\delta\mathbf{r}_0| = |\delta\mathbf{r}_t|$.

The reversibility of a system subjected to a change at $t = 0$ does not depend on whether we use Newtonian mechanics or Langevin stochastics to model it. We can therefore express the dissipation function for stochastic dynamics by analogy to Eq. (5),

$$\Omega_t(\mathbf{r}_0, \mathbf{r}_t) = \ln\left(\frac{P(\delta V_{\mathbf{r},\mathbf{r}}(\{\mathbf{r}_0, \mathbf{r}_t\}))}{P(\delta V_{\mathbf{r},\mathbf{r}}(\{\mathbf{r}_t, \mathbf{r}_0\}))}\right) = \ln\left(\frac{p(\mathbf{r}_0, \mathbf{r}_t)}{p(\mathbf{r}_t, \mathbf{r}_0)}\right). \tag{9}$$

Equation (9) applies not only to single, colloidal particles, but also to a many-colloidal particle system. In that case $\mathbf{r}$ is a Nd vector where N is the number of colloidal particles embedded in d-dimensional space. However, the probability distributions of Eq. (9) cannot be described analytically for dense many-particle systems.

Despite the apparent simplicity of this approach, it has not been used for stochastic systems. Most papers have simply applied the dissipation function derived using deterministic

dynamics to stochastic systems [9,10]. Our derivation is solely based upon Langevin dynamics. Within the Langevin approach we find that the expression for the dissipation functions is not unique, but that each function nevertheless satisfies the FT.

C. Fluctuation theorem

We now show that the dissipation function given in Eq. (9) obeys the FT. The probability density associated with observing a set of trajectories of duration t for which $\Omega_t = A$ is simply

$$P(\Omega_t = A) = \int d\mathbf{r}_0 d\mathbf{r}_t \delta(\Omega_t(\mathbf{r}_0, \mathbf{r}_t) - A) p(\mathbf{r}_0, \mathbf{r}_t). \quad (10)$$

Likewise, the density associated with a trajectory with $\Omega_t = -A$ is

$$P(\Omega_t = -A) = \int d\mathbf{r}_0 d\mathbf{r}_t \delta[\Omega_t(\mathbf{r}_0, \mathbf{r}_t) + A] p(\mathbf{r}_0, \mathbf{r}_t)$$

$$= \int d\mathbf{r}_0 d\mathbf{r}_t \delta[\Omega_t(\mathbf{r}_t, \mathbf{r}_0) - A] p(\mathbf{r}_0, \mathbf{r}_t), \quad (11)$$

where we have used $\Omega_t(\mathbf{r}_0, \mathbf{r}_t) = -\Omega_t(\mathbf{r}_t, \mathbf{r}_0)$. Using the definition of Ω_t from Eq. (9), we can rewrite $P(\Omega_t = -A)$ as

$$P(\Omega_t = -A) = \int d\mathbf{r}_0 d\mathbf{r}_t \delta[\Omega_t(\mathbf{r}_t, \mathbf{r}_0) - A]$$

$$\times \exp[-\Omega_t(\mathbf{r}_t, \mathbf{r}_0)] p(\mathbf{r}_t, \mathbf{r}_0). \quad (12)$$

Thus

$$\frac{P(\Omega_t = A)}{P(\Omega_t = -A)}$$

$$= \frac{\int d\mathbf{r}_0 d\mathbf{r}_t \delta(\Omega_t(\mathbf{r}_0, \mathbf{r}_t) - A) p(\mathbf{r}_0, \mathbf{r}_t)}{\int d\mathbf{r}_0 d\mathbf{r}_t \delta[\Omega_t(\mathbf{r}_t, \mathbf{r}_0) - A] \exp[-\Omega_t(\mathbf{r}_t, \mathbf{r}_0)] p(\mathbf{r}_t, \mathbf{r}_0)}$$

$$(13)$$

and recognizing that the integration variables $\mathbf{r}_0$ and $\mathbf{r}_t$ can be written arbitrarily, we see that the result is the FT [2]:

$$\frac{P(\Omega_t = -A)}{P(\Omega_t = A)} = \exp(-A). \quad (14)$$

This approach can also be used to derive the FT using the analogous deterministic quantities, Eqs. (1)–(5). From this, you see that the FT does not describe the distribution $P(\Omega_t)$, but rather specifies that distribution's asymmetry and how it evolves in time. To get better statistics, the FT is sometimes expressed as the integrated fluctuation theorem (IFT) [15]:

$$\frac{P(\Omega_t < 0)}{P(\Omega_t > 0)} = \langle \exp(-\Omega_t) \rangle_{\Omega_t > 0}. \quad (15)$$

When Eqs. (14) and (15) are applied to systems that are being driven from their initial state, they are referred to as

the transient fluctuation theorem, or TFT, and the integrated transient fluctuation theorem, or ITFT.

For systems that are well described by Newtonian and Langevin dynamics, we can construct expressions for Ω_t. For some simple systems, we can explicitly calculate the distribution of Ω_t. In the following two sections, we construct the dissipation function for a colloidal particle in an optical trap whose strength is changed, and for a particle in an optical trap that is translated.

III. IRREVERSIBILITY IN THE CAPTURE EXPERIMENT

In the capture experiment [13], an isolated colloidal particle is localized in a trap of strength k_0 over a sufficiently long time that the particle position $\mathbf{r}$ is distributed according to the equilibrium Boltzmann distribution. At time $t=0$, the trap strength is increased discontinuously from k_0 to k_1, so that the particle is held or "captured" more tightly and the particle's trajectory is recorded as it relaxes into its new equilibrium distribution. Here, we use Langevin dynamics to construct an expression for Ω_t.

An ensemble of trajectories can be constructed using the Langevin equation,

$$\xi \frac{d\mathbf{r}}{dt} = -k_1 \mathbf{r} + \mathbf{g}(t), \quad (16)$$

where the initial position $\mathbf{r}_0$ of the particle in a two-dimensional trap is distributed according to the Boltzmann distribution

$$P_B(\mathbf{r}_0, k_0) = \left(\frac{k_0}{2\pi k_B T} \right) \exp\left(-\frac{k_0 \mathbf{r}_0^2}{2k_B T} \right). \quad (17)$$

For a particle in a harmonic well, we can construct distributions $p(\mathbf{r}_0, \mathbf{r}_t)$ of Eq. (9) from well-known formulas for the time-dependent distribution for the particle positions [17]. The Green's function provides the probability of observing a particle at $\mathbf{r}_t$ in a trap of strength k_1, given its position $\mathbf{r}_0$ at time t earlier,

$$G(\mathbf{r}_t; \mathbf{r}_0, k_1, t) = \left(\frac{k_1}{2\pi k_B T[1 - \exp(-2t/\tau)]} \right)$$

$$\times \exp\left(-\frac{k_1[\mathbf{r}_t - \mathbf{r}_0 \exp(-t/\tau)]^2}{2k_B T[1 - \exp(-2t/\tau)]} \right), \quad (18)$$

where $\tau = \xi/k_1$ is the characteristic relaxation time of the particle residing in a harmonic potential of strength k_1. In the limit of long time, $t \to \infty$, the Green's function reduces to the time-independent Boltzmann distribution for a particle in a well of strength k_1. Thus the probability density of forward trajectories, $p(\mathbf{r}_0, \mathbf{r}_t)$, is the product of the probability that an equilibrated particle resides at $\mathbf{r}_0$ at $t=0$ in a trap of strength k_0, i.e., $P_B(\mathbf{r}_0, k_0)$, and the probability of observing the particle at $\mathbf{r}_t$ some time t after the trap strength was changed to k_1, given the initial position $\mathbf{r}_0$, or $G(\mathbf{r}_t; \mathbf{r}_0, k_1, t)$. That is, $p(\mathbf{r}_0, \mathbf{r}_t) \equiv P_B(\mathbf{r}_0, k_0) G(\mathbf{r}_t; \mathbf{r}_0, k_1, t)$. Likewise, the probability density of the corresponding antitrajectories is $p(\mathbf{r}_t, \mathbf{r}_0) \equiv P_B(\mathbf{r}_t, k_0) G(\mathbf{r}_0; \mathbf{r}_t, k_1, t)$, and the dissipation function, Eq. (9) simplifies to
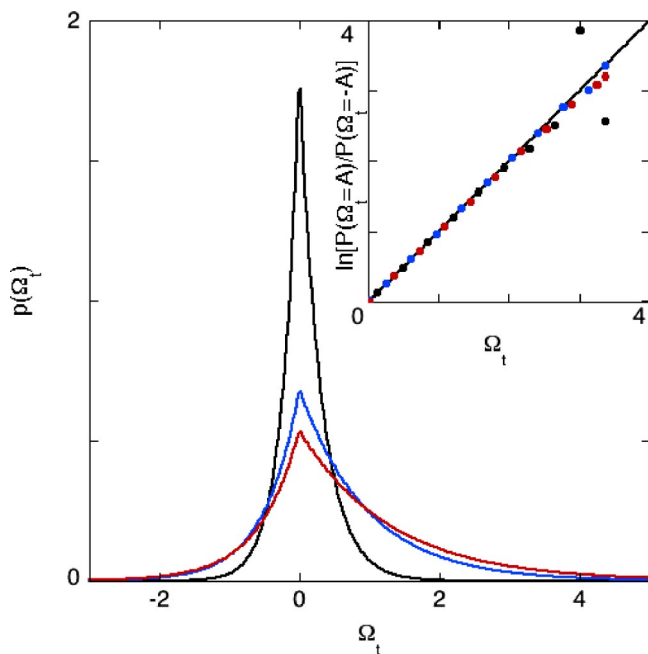
FIG. 3. (Color online) Distributions of $P(\Omega_t)$ at $t = (\bullet)$ 2 ms, $(\bullet)$ 20 ms (blue online), $(\bullet)$ 200 ms (red online) constructed from Langevin simulation of a particle in a two-dimensional harmonic well whose strength increases from k_0 to k_1 at $t=0$. The values of the characteristic time, $\tau \equiv \xi/k_1$, and trapping constants have been chosen to mimic the experiment of Carberry *et al.* [13]: $\xi = 1.05 \times 10^{-7}$Ns/m, $k_0 = 1.22$ pN/μm, and the orthogonally resolved trapping constants of $k_1^x = 2.9$ and $k_1^y = 2.7$ pN/μm. The simulated distributions are strikingly similar to the distributions sampled in the capture experiment [13], and within 1% of an analytic formula $P(\Omega_t = A) = \exp\left[A/2 - \sqrt{a_t^{-1} + (1/4)|A|}\right]/\sqrt{a_t^2 + 4a_t}$ where $a_t = [1 - \exp(-2t/\tau)](k_0 - k_1)^2/(k_0 k_1)$. The inset plots $\ln[P(\Omega_t = A)/P(\Omega_t = -A)]$ against Ω_t for these three distributions, and compares them with the prediction of the TFT (line).

$$\Omega_t = \frac{1}{2k_B T}(k_0 - k_1)(\mathbf{r}_t^2 - \mathbf{r}_0^2). \qquad (19)$$

This expression is identical to that derived from Eq. (5) using Newton's (deterministic) equations of motion for a comparable system: a single solute molecule under the influence of a harmonic potential, in a sea of thermostated solvent molecules that are unaffected by the trap. Equation (19) is also the expression used by Carberry *et al.* in their demonstration of the TFT [13].

The distribution of the dissipation function, $P(\Omega_t)$, from Langevin dynamics is found from $P(\Omega_t = A) \equiv \int d\mathbf{r}_0 d\mathbf{r}_t \delta(\Omega_t - A)p(\mathbf{r}_t, \mathbf{r}_0)$ and Eq. (19). A numerical solution of $P(\Omega_t)$ in two dimensions using values matching the experimental parameters in Carberry *et al.* is clearly non-Gaussian, Fig. 3. The distribution is highly peaked at $\Omega_t \sim 0$ and becomes highly asymmetric, tending towards positive values of Ω_t as the duration of the trajectory increases. The functional form of the dissipation function results from the difference between the squares of two Gaussian variables, $\mathbf{r}_0$ and $\mathbf{r}_t$.

While the ensemble average of the dissipation function for this system cannot be identified with the entropy produc-

tion, as it can be in the drag experiment [11], $\langle \Omega_t \rangle$ does have several entropy productionlike properties. The ensemble average of the dissipation function is

$$\langle \Omega_t \rangle = \frac{\int d\mathbf{r}_0 d\mathbf{r}_t \Omega(\mathbf{r}_0, \mathbf{r}_t) p(\mathbf{r}_0, \mathbf{r}_t)}{\int d\mathbf{r}_0 d\mathbf{r}_t p(\mathbf{r}_0, \mathbf{r}_t)}. \qquad (20)$$

In the long time limit, the average square particle position is given by the equipartition theorem, $\langle \mathbf{r}^2 \rangle = k_B T/k$, and the average accumulated work done is then

$$\langle \Omega_{t \to \infty} \rangle = \tfrac{1}{2}(k_0 - k_1)[1/k_1 - 1/k_0], \qquad (21)$$

or

$$\langle \Omega_{t \to \infty} \rangle = \cosh\left(\frac{2\Delta F(k_0, k_1)}{k_B T}\right) - 1, \qquad (22)$$

where $\Delta F(k_0, k_1) \equiv F(k_1) - F(k_0) = 1/2 k_B T \ln(k_1/k_0)$ is the difference in the Helmholtz free energy for systems with different trapping strengths. Note that $\langle \Omega_{t \to \infty} \rangle$ is positive definite: its sign is unchanged by the direction of strength of the trap, i.e., whether the trap is strengthened or weakened at $t=0$. Moreover, from Eq. (20), the dissipation function at any time t after the change in the optical trap strength can be written as

$$\langle \Omega_t \rangle = \langle \Omega_{t \to \infty} \rangle [1 - \exp(-2t/\tau)]. \qquad (23)$$

Figure 4 demonstrates the Langevin prediction and experimentally determined values of $\langle \Omega_t \rangle$ as a function of t. The average of the dissipation function, evaluated over all trajectories of any duration t, $\langle \Omega_t \rangle$, is positive for all time, irre-
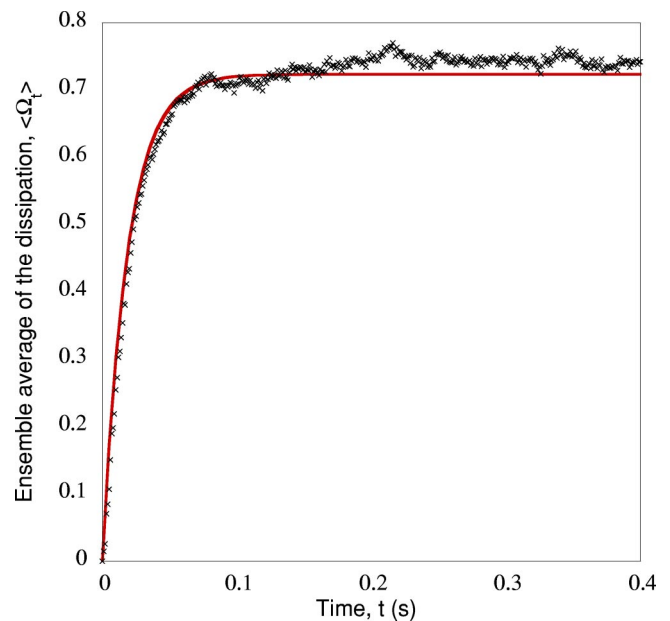

FIG. 4. (Color online) The ensemble average of the dissipation function $\langle \Omega_t \rangle$ versus trajectory time t from Carberry's capture experiment (points) and predicted from Langevin dynamics, Eqs. (21) and (23).
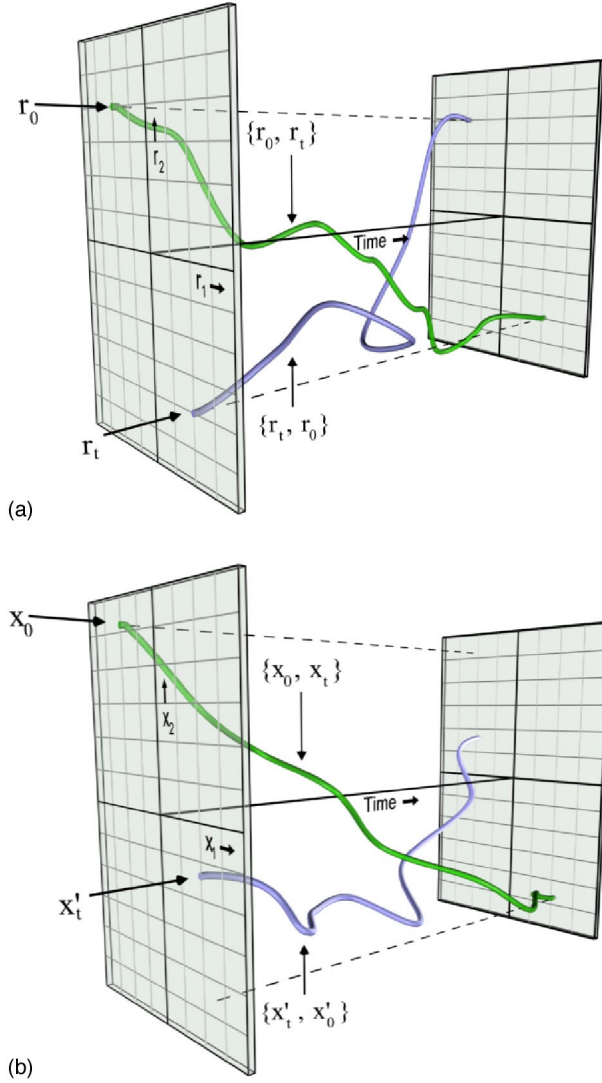
(a)

(b)

FIG. 5. (Color online) Two example trajectories generated for the drag experiment using Langevin dynamics, one from a set of forward trajectories $\{\mathbf{r}_0, \mathbf{r}_t\}$ and another from a set of backward trajectories $\{\mathbf{r}_t, \mathbf{r}_0\}$. These trajectories are from *conjugate* trajectory sets in the $\mathbf{r}$-coordinate frame as the initial position in the forward trajectory is identical to the destination position in the backward trajectory [see dashed lines in (a)]. In (b), these same trajectories are transformed into the moving $\mathbf{x}$-coordinate frame where they are no longer members of conjugate trajectory sets. The forward trajectory initiates at $\mathbf{x}_0$ and terminates at $\mathbf{x}_t$, while the backward trajectory starts at $\mathbf{x}_t'$ (where $\mathbf{x}_t' \neq \mathbf{x}_t$) and ends at $\mathbf{x}_0'(\mathbf{x}_0' \neq \mathbf{x}_0)$.

spective of whether the trap is strengthened or weakened.

IV. IRREVERSIBILITY IN THE DRAG EXPERIMENT

In the drag experiment [11], a colloidal bead is located in a stationary optical trap of strength k and for $t \geq 0$, the trap is translated with constant velocity $\mathbf{v}_{opt}$ relative to the solvent. The inertialess Langevin equation governing the particle motion is
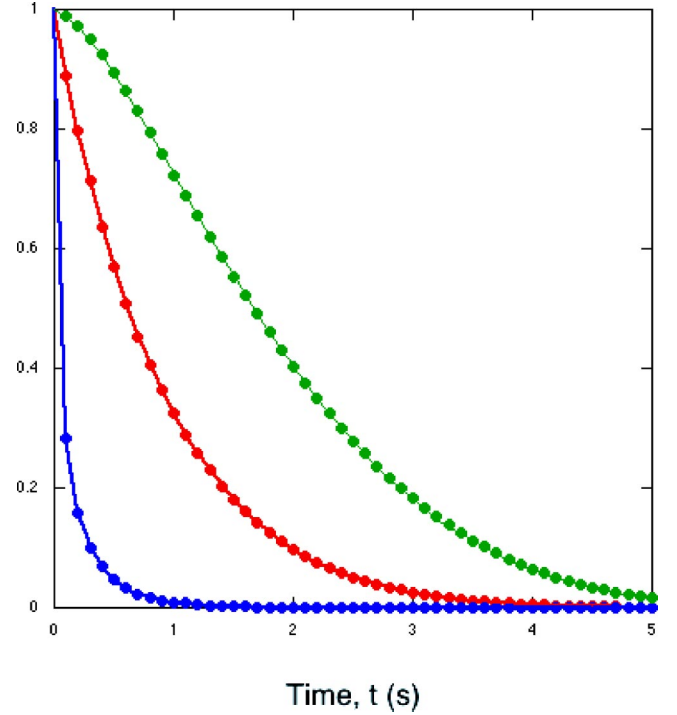

FIG. 6. (Color online) Langevin simulations of the drag experiment for three different dissipation functions; $\Omega_t^N(\bullet)$ (red online), $\Omega_t^{L,x}(\bullet)$ (blue online), $\Omega_t^{L,r}(\bullet)$ (green online). The dots represent the probability ratio, $P(\Omega_t < 0)/P(\Omega_t > 0)$, and the lines represent the average of the exponential, $\exp(-\Omega_t)$, Eq. (15). The parameters for this simulation are; $k=0.5$, $\mathbf{v}=2$, $\xi=3$, where energy is in units of $k_B T$, length is in micrometers, and time is in seconds. All three dissipation functions obey the ITFT, but have different values at different times.

$$\xi \frac{d\mathbf{r}}{dt} = -k(\mathbf{r} - \mathbf{v}_{opt}t) + \mathbf{g}(t). \quad (24)$$

We can transform this equation of motion into a different coordinate system $\mathbf{x}$ that translates with constant velocity $\mathbf{v}_{opt}$ with its origin displaced by $\xi \mathbf{v}_{opt}/k$, using $\mathbf{r} = \mathbf{x} + \mathbf{v}_{opt}t - \xi \mathbf{v}_{opt}/k$. The equation of motion in the moving and displaced-coordinate frame $\mathbf{x}$ is then

$$\xi \frac{d\mathbf{x}}{dt} = -k\mathbf{x} + \mathbf{g}(t). \quad (25)$$

This is the equation of motion of a particle in a stationary trap, for which we already have time-dependent distributions of the particle position, Eqs. (17) and (18). Consequently, in the limit of large time (or in the steady state) the distribution of particle position in a stationary trap is identical to the distribution of particle positions relative to the center of a trap which translates according to $\mathbf{v}_{opt}t - \xi \mathbf{v}_{opt}/k$; i.e., the distribution is dragged along by the trap, but always lags a distance $\xi \mathbf{v}_{opt}/k$ behind the center of the trap. At early times $t \ll \tau$, this is not the case as there are some initial transients.

As in the capture experiment, we can construct expressions for the distributions of forward and backward trajectories, and we can express the dissipation function as the ratio of these distributions. But unlike the capture experiment,

there are two obvious coordinate frames, the fixed **r**-coordinate and the moving **x**-coordinate frame, in which we can cast the trajectories. We can express a set of forward trajectories using either coordinate frame ($\{\mathbf{r}_0,\mathbf{r}_t\}\equiv\{\mathbf{x}_0,\mathbf{x}_t\}$); however, because the displacement of the **x**-coordinate frame from the **r**-coordinate frame depends upon time, the corresponding sets of backwards trajectories are not identical ($\{\mathbf{r}_t,\mathbf{r}_0\}\neq\{\mathbf{x}_t,\mathbf{x}_0\}$). That is, trajectories that are conjugate in the **x** coordinate cannot be conjugate in **r**, unless $\mathbf{v}_{opt}=0$, Fig. 5. Consequently, the dissipation function constructed from Eq. (9) depends upon the coordinate frame used to describe forward and backward trajectories.

First, let us consider the dissipation function generated by trajectories that are conjugate in the **x**-coordinate frame. This is a convenient coordinate frame as we can express the propagator distributions in the **x**-coordinate frame as simple Green's functions, as a consequence of Eq. (25). Thus we consider a pair of conjugate sets of trajectories: the forward trajectories go from $\mathbf{x}_0$ to $\mathbf{x}_t$ and the conjugate or backward trajectories proceeds from $\mathbf{x}_t$ to $\mathbf{x}_0$. The probability density associated with the forward set, given that it starts at $\mathbf{x}_0$ is $G(\mathbf{x}_t;\mathbf{x}_0,k,t)$. The probability density of the backward set of trajectories, given that it starts at $\mathbf{x}_t$ is $G(\mathbf{x}_0;\mathbf{x}_t,k,t)$. The probability densities of the trajectory set are obtained by multiplying through by the probability of observing the initial position, $\mathbf{x}_0\equiv\mathbf{r}_0-\xi\mathbf{v}_{opt}/k$ and $\mathbf{x}_t\equiv\mathbf{r}_t-\xi\mathbf{v}_{opt}/k$:

$$p(\mathbf{x}_0,\mathbf{x}_t) = P_B\left(\mathbf{x}_0 \equiv \mathbf{r}_0 - \frac{\xi\mathbf{v}_{opt}}{k},k\right)G(\mathbf{x}_t;\mathbf{x}_0,k,t), \quad (26)$$

and

$$p(\mathbf{x}_t,\mathbf{x}_0) = P_B\left(\mathbf{x}_t \equiv \mathbf{r}_t - \frac{\xi\mathbf{v}_{opt}}{k},k\right)G(\mathbf{x}_0;\mathbf{x}_t,k,t). \quad (27)$$

From Eq. (9), the dissipation function is

$$\Omega_t^{L,x} = -\frac{\xi\mathbf{v}_{opt}}{k_BT}(\mathbf{x}_t - \mathbf{x}_0), \quad (28)$$

where the superscript L,x indicates that the function was derived using Langevin trajectories that are conjugate in **x**. Similarly, $\Omega_t^{L,r}$, the dissipation function constructed from trajectories that are conjugate in **r**, is

$$\Omega_t^{L,r} = \left(\frac{k\mathbf{v}_{opt}t}{k_BT[1 - \exp(-t/\tau)]} - \frac{\xi\mathbf{v}_{opt}}{k_BT}\right)(\mathbf{r}_t - \mathbf{r}_0). \quad (29)$$

As for the capture experiment, the ensemble average for both of these dissipations will be greater or equal to zero, $\langle\Omega_t\rangle > 0$.

Unlike the stochastically derived dissipation functions, there can be only one dissipation function derived from deterministic Newtonian dynamics, Eq. (5). This is because an initial point in phase space, $\boldsymbol{\Gamma}_0$, fully specifies a trajectory of duration t, and its conjugate antitrajectory. Thus any trajectory of duration t and its antitrajectory are fully determined by a single point in phase space, irrespective of the coordinate frame in which the point is described, then the dissipation function also has a unique and coordinate-frame independent expression. This is in contrast to the stochastic-generated trajectories where particle position is not unique to any given trajectory such that both the initial position $\mathbf{r}_0$ *and* position at time t, $\mathbf{r}_t$, are required to construct sets of forwards and backwards trajectories. The Newtonian dissipation function, denoted by Ω_t^N and first used in the experimental analysis [9,11], is

$$\Omega_t^N = \frac{1}{k_BT}\int_0^t ds(\mathbf{F}_{opt} \cdot \mathbf{v}_{opt}). \quad (30)$$

This expression was originally evaluated from Eq. (5) [11].

Consequently, for this one experiment, there are three apparently "different" dissipation functions, each associated with how the equations of motion are cast (deterministic or stochastic), and, if stochastic, the coordinate frame used to describe the stochastic trajectories. Wang *et al.* demonstrated that Ω_t^N obeys the ITFT [11], and van Zon and Cohen demonstrated that Ω_t^N obeyed the transient form of the FT using Langevin dynamics [9,10]. Furthermore, both $\Omega_t^{L,x}$ and $\Omega_t^{L,r}$ obey the FT by construction [see Eqs. (9)–(14)]. To demonstrate this, we have evaluated the different dissipation functions Ω_t^N, $\Omega_t^{L,x}$, and $\Omega_t^{L,r}$ from 500 000 stochastic trajectories and plotted the left-hand side and right-hand side of the ITFT as a function of trajectory time t in Fig. 6. This figure shows that the dissipation functions derivable from Eqs. (5) and (9) obey the FT.

It is easy to see that we can describe other related functions that obey the FT. The dissipation functions Ω_t^N and $\Omega_t^{L,x}$ are related via a force or energy balance of the optical, drag, and random forces derived from Eq. (6);

$$\mathbf{F}_{opt} + \mathbf{F}_{drag} + \mathbf{F}_{rand} = 0, \quad (31)$$

which we can re-express in terms of the particle positions,

$$\int_0^t ds\mathbf{F}_{opt}(s) - \xi\int_0^t ds\frac{d\mathbf{r}_s}{ds} + \int_0^t ds\,\mathbf{g}(s) = 0, \quad (32)$$

$$\int_0^t ds\mathbf{F}_{opt}(s) - \xi(\mathbf{x}_t - \mathbf{x}_0) - \xi\mathbf{v}_{opt}t + \int_0^t ds\,\mathbf{g}(s) = 0. \quad (33)$$

We can express the last force balance as a sum of work terms by projecting the forces into $\mathbf{v}_{opt}/k_BT$:

$$\Omega_t^N = -\Omega_t^{L,x} + \frac{\xi\mathbf{v}_{opt}^2t}{k_BT} + \frac{-\mathbf{v}_{opt}}{k_BT}\int_0^t ds\,\mathbf{g}(s). \quad (34)$$

The left-hand side is the work associated with translating the optical trap as it was originally referred to in Wang *et al.* [11]. This is simply the work needed to overcome the hydrodynamic drag accumulated over the observation time: if no particle were present in the trap, no work would be expended in translating the trap. The first term on the right-hand side is the work associated with dragging the particle relative to the center of the trap. The second term is the work done to drag the trap containing a particle that is stationary relative to the trap center. The final term represents the energy expended in displacing the particle against the random force acting on the

particle. A Gaussian distribution satisfies the FT if its variance is numerically equal to twice its mean [9]. The distributions $P(\Omega_t^N)$ and $P(\Omega_t^{L,x})$ have Gaussian distributions that satisfy the FT. As the mean of the time-integrated random force is zero and its variance is $2\xi k_B T t$, the distribution of the sum of the final two terms in Eq. (34) also obeys the FT. A similar exercise can be applied to Ω_t^N and $\Omega_t^{L,\mathbf{r}}$.

V. CONCLUSION

We present a general derivation of the dissipation function using stochastic dynamics. This description is based upon Evans and Searles' original derivation of the FT using time-reversible mechanics; however, we demonstrate that it can be applied equally to systems described by stochastic, Langevin dynamics. This is important as several stochastic studies of the FT simply assume a functional form of Ω_t, or derive Ω_t from Newtonian mechanics or "using detailed balance," rather than construct Ω_t consistently using its stochastic definition. We have shown, through analysis of two recent experiments, that the stochastically derived Ω_t can have a different functional form from the deterministically derived dissipation function. Moreover, while the dissipation function is uniquely defined for deterministic systems, it is not unique for stochastic systems. Despite these differences, stochastic dissipation functions obey the FT, and as a consequence, the ensemble averages of Ω_t are positive definite, reminiscent of entropy production.

Finally, from thermodynamics we know that a system evolves reversibly along any quasistatic path, and consequently any measure of a system's irreversibility must equal zero for this infinitely slow process. To demonstrate this, consider the capture experiment where the trap strength is changed quasistatically. That is, the value of the trapping constant changes slowly from k_0 to k_1 so that the system is always at equilibrium. We can model such a quasistatic change in the trap strength by a series of n small step changes in k separated by infinitely long time intervals. Let $\langle \Omega^i \rangle$ represent the average dissipation function associated with the ith step change from k'_{i-1} to k'_i, in the long time limit. Here $k'_i = k_0 + i\Delta k$ where $k'_n = k_1$ and $\Delta k = (k_1 - k_0)/n$ is the step change in the trapping constants. The dissipation function for the entire quasistatic process is $\langle \Omega \rangle \equiv \lim_{n \to \infty} \Sigma_{i=1}^n \langle \Omega^i \rangle$. From Eq. (22), $\langle \Omega^i \rangle = (\Delta k)^2/2k'_i k'_{i-1}$, and therefore

$$\langle \Omega \rangle \equiv \lim_{n \to \infty} \sum_{i=1}^n \langle \Omega^i \rangle = \lim_{n \to \infty} \sum_{i=1}^n \frac{(\Delta k)^2}{2k'_i k'_{i-1}}. \quad (35)$$

In the quasistatic limit $(n \to \infty)$, $\Delta k \to 0$ as $O(1/n)$. Furthermore, all k'_i are bounded between k_0 and k_1, so in this limit, $\langle \Omega^i \rangle \to 0$ as $O(1/n^2)$. Hence

$$\langle \Omega \rangle = \lim_{n \to \infty} \sum_{i=1}^n \langle \Omega^i \rangle = \lim_{n \to \infty} n O\left(\frac{1}{n^2}\right) = 0. \quad (36)$$

This shows that in the quasistatic limit $\langle \Omega \rangle = 0$, and the system is always at equilibrium so no energy is dissipated. This confirms that the dissipation function is a measure of the irreversibility of the system.

APPENDIX: NEWTONIAN DERIVATION OF THE DISSIPATION FUNCTION FOR THE CAPTURE EXPERIMENT

In this paper we present a derivation of the dissipation function for the capture experiment using stochastic dynamics. For completeness, we present a Newtonian derivation for the same system. In the capture experiment, a particle is held in a harmonic trap that changes strength discontinuously at the start of measurement. In Newtonian dynamics, we represent this as a system of N particles, and identify each particle with an index i. The dynamics of the system is tracked in terms of the position $\mathbf{q}_i$ and momentum $\mathbf{p}_i$ of each particle. Each particle's motion is influenced by the interparticle force $\mathbf{F}_{ij}$. In addition, we identify one particle, $i=1$, as being subject to the harmonic trap which contributes the potential energy

$$\Phi_{trap}(k(t),\mathbf{q}_1(t)) = \tfrac{1}{2}\mathbf{q}_1^2(t)k(t).$$

The trap constant is defined such that $k(0) = k_0$ and $k(t > 0) = k_1$.

Since the experiment is in thermal contact with its surroundings, we introduce a thermostat. We use a Nose-Hoover thermostat to control the temperature of these particles through a switch S_i, where $S_i = 1$ for each of the N_W thermostated particles, and $S_i = 0$ for unthermostatted particles, including the optically trapped particle. This thermostat introduces another dynamic variable ζ, and the equations of motion for each particle is defined as

$$\dot{\mathbf{q}}_i(t) = \frac{\mathbf{p}_i(t)}{m_i},$$

$$\dot{\mathbf{p}}_i(t) = \sum_j [\mathbf{F}_{ij}] - \delta_{i1}k_1\mathbf{q}_i(t) - S_i\zeta(t)\mathbf{p}_i(t),$$

$$\dot{\zeta} = \frac{1}{Q}\left[\sum_{i=1}^N \left(\frac{S_i\mathbf{p}_i^2(t)}{m_i}\right) - dN_w\beta^{-1}\right].$$

Note that d is the number of Cartesian dimensions for the system, $\beta^{-1} = k_B T$ where k_B is the Boltzmann constant and T the thermostat temperature, m_i is the mass of the particle, and Q the effective mass of the thermal reservoir.

Now that we have defined our system in terms of its deterministic equations of motion, we can define the distribution function for our $t=0$ starting system:

$$f(\mathbf{\Gamma},0) \approx \exp\left[-\beta\big(K(\mathbf{p}) + \Phi(\mathbf{q}) + \Phi_{trap}(\Gamma,k(0)) + \tfrac{1}{2}Q\zeta^2\big)\right],$$

where $K(\mathbf{p})$ is the kinetic energy, and $\Phi(\mathbf{q})$ is the potential energy due to interparticle interactions. Re-expressing the

dissipation function in terms of the distribution function using Eqs. (2), (4), and (5) yields

$$\Omega_t(\mathbf{\Gamma}_0) = \ln\left(\frac{P(\delta V_\Gamma(\mathbf{\Gamma}_0),0)}{P(\delta V_\Gamma(\mathbf{\Gamma}_0^*),0)}\right) = \ln\left(\frac{f(\mathbf{\Gamma}(0),0)}{f(\mathbf{\Gamma}(t),0)}\right) - \int_0^t ds \Lambda[\mathbf{\Gamma}(s)], \tag{A1}$$

where the variable Λ corresponds to the phase space contraction of a trajectory bundle in time (see Fig. 1). This contraction or expansion is due to the action of the thermostat upon the system. The first term on the right-hand side equation, written with the expressions for the distribution functions inserted, gives

$$\ln\frac{f(\mathbf{\Gamma}(0),0)}{f(\mathbf{\Gamma}(t),0)} = \ln\left(\frac{\exp\left[-\beta\left\{K[\mathbf{p}(0)] + \Phi[\mathbf{q}(0)] + \Phi_{trap}(\mathbf{\Gamma}(0),k(0)) + \frac{1}{2}Q\zeta^2(0)\right\}\right]}{\exp\left[-\beta\left\{K[\mathbf{p}(t)] + \Phi[\mathbf{q}(t)] + \Phi_{trap}(\mathbf{\Gamma}(t),k(0)) + \frac{1}{2}Q\zeta^2(t)\right\}\right]}\right)$$

$$= \beta\int_0^t ds\{\dot{K}[\mathbf{p}(s)] + \dot{\Phi}[\mathbf{q}(s)] + \dot{\Phi}_{trap}(\mathbf{\Gamma}(s),k_0) + Q\zeta\dot{\zeta}\}$$

$$= \beta\int_0^t ds[(k_0 - k_1)\mathbf{q}_1(s) \cdot \dot{\mathbf{q}}_1(s) - dN_W k_B T\zeta(s)]. \tag{A2}$$

As $\int_0^t ds\, dN_W\zeta(s)$ is equal and opposite to the phase space compression integral, $\int_0^t ds\Lambda[\mathbf{\Gamma}(s)]$, Eqs. (A1) and (A2) yield

$$\Omega_t = \tfrac{1}{2}\beta(k_0 - k_1)[\mathbf{q}^2(t) - \mathbf{q}^2(0)].$$

This corresponds with the dissipation function derived using stochastic dynamics.

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