Experimental study of the fluctuation theorem in a nonequilibrium steady state

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The fluctuation theorem (FT) quantifies the probability of second law violations in small systems over short time scales. While this theorem has been experimentally demonstrated for systems that are perturbed from an initial equilibrium state, there are a number of studies suggesting that the theorem applies asymptotically in the long time limit to systems in a nonequilibrium steady state. The asymptotic application of the FT to such nonequilibrium steady states has been referred to in the literature as the steady-state fluctuation theorem (or SSFT). In this paper, we demonstrate experimentally the application of the FT to nonequilibrium steady states, using a colloidal particle localized in a translating optical trap. Furthermore, we show, for this colloidal system, that the FT holds under nonequilibrium steady states for *all* time, and not just in the long time limit, as in the SSFT.

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I. INTRODUCTION

In many areas of physical chemistry, researchers strive to understand new systems through deterministic equations of motion. They seek to quantify microscopic forces and understand how a system responds to external perturbations, using techniques such as molecular dynamics simulation. At the heart of this endeavor is the notion that if the equations of motion or trajectories of the system are known, then any question about that system may be answered. However, such deterministic equations (such as Newton's equations) are time reversible, so that for every trajectory there exists a time-reversed trajectory or "anti-" trajectory which is also a solution to the equations. The relative probabilities of observing bundles of conjugate trajectories quantifies the "reversibility" of the system: if the probability of observing all trajectories and their respective antitrajectories are equal, the system is said to be perfectly reversible; on the other hand, if the probability of observing antitrajectories is vanishingly small, we say that the system is irreversible. The second law of thermodynamics stipulates that a system evolves irreversibly in one "time-forward" direction, i.e., the probability of all antitrajectories is zero. However, the second law strictly applies to large systems over long time scales and does not describe the reversibility of small systems that are of current scientific interest, such as protein motors and nanomachines. This long-standing question of how irreversible macroscopic equations, as summarized by the second law of thermodynamics, can be derived from reversible microscopic equations of motion was first noted by Loschmidt [1] in 1876.

The fluctuation theorem (FT) of Evans *et al.* [2,3] describes how a system's irreversibility develops in time from a completely time-reversible system at short observation times, to a thermodynamically irreversible one at infinitely long times. That is, it bridges the microscopic and macroscopic descriptions, relating a system's time-reversible equations of motion to the second law. Specifically, the FT relates the relative probabilities of observing trajectories of duration t and their conjugate antitrajectories, each characterized by the dissipation function, Ω_t, taking on arbitrary values A and $-A$, respectively:

$$\frac{P(\Omega_t = -A)}{P(\Omega_t = A)} = \exp(-A). \tag{1}$$

The dissipation function, Ω_t, is, in general, a dimensionless dissipated energy, accumulated along the system's trajectory; expressions for Ω_t differ from system to system. It is an extensive property, i.e., its magnitude scales with system size and observation time, t. Thus, Eq. (1) also shows that as the system size gets larger or the observation time gets longer, antitrajectories become rare and it becomes overwhelmingly likely that the system appears time irreversible, in accord with the second law. In addition, Eq. (1) also shows that the ensemble average of the dissipation function is positive for all t and for any system size; i.e., $\langle \Omega_t \rangle \geqslant 0$ which is referred to as the second law inequality [4]. However, the FT does not prescribe the time or length scales over which such irreversibility evolves. This is gleaned from the specific equations of motion governing the system as well as the distribution of initial states of the system.

In the literature, the reader will find two different labels for the fluctuation theorem, depending upon how the theorem is applied. The transient fluctuation theorem or TFT is simply Eq. (1) applied to transient systems, i.e., systems that evolve from a known initial equilibrium state towards a final equilibrium or nonequilibrium steady state. The steady-state fluctuation theorem or SSFT refers to the steady-state application of the theorem, where the dissipation function is evaluated over trajectory segments of duration t, sampled wholly under nonequilibrium steady-state conditions. When Ω_t is evaluated for steady-state trajectories, the theorem is said to hold only in the long time limit,

$$\lim_{t\to\infty} \frac{P(\Omega_t = -A)}{P(\Omega_t = A)} = \exp(-A), \tag{2}$$

which is precisely the form of the SSFT given in the literature. As we show in this paper, the asymptotic limit in the SSFT is a result of *approximations* made in the argument of the theorem, the dissipation function, Ω_t. When we are able

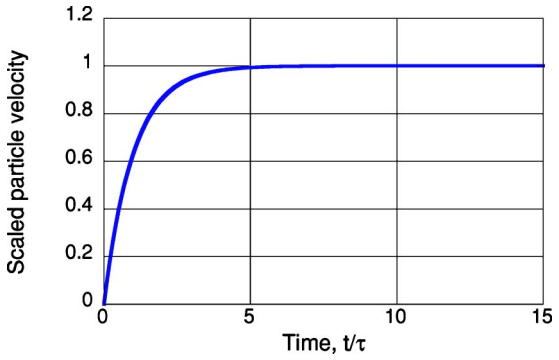

FIG. 1. The transient and steady-state motion of a colloidal particle, shown as relative particle velocity, $\overline{v}(t)/v_{opt}$ versus scaled time t/τ, localized in a stationary optical trap that is translated with constant velocity v_{opt} starting at $t=0$. This average of the particle velocity, measured in the direction of the trap translation, is predicted from a balance of optical force and hydrodynamic drag: $\overline{v}(t)=(1/\tau)[\overline{r}(t)-v_{opt}t]$ where $\overline{v}(t)=d\overline{r}(t)/dt$, τ is the characteristic timescale of relaxation, and the average initial position of the particle is at the center of the optical trap, $\overline{r}(t=0)=0$. A steady-state trajectory of the particle corresponds to trajectory time, $t>5\tau$, where $\overline{v}(t)/v_{opt}$ no longer varies in time and is approximately unity.

to express Ω_t *exactly*, the asymptotic limit is no longer needed and the operative theorem under steady-state conditions is the FT, Eq. (1). Thus, while the literature and its nomenclature might indicate that there are two different theorems [5], the FT is general and applicable to both transient and steady-state conditions. As the detailed proofs of steady-state and transient applications of the FT are different, we will use the labels SSFT and TFT to refer to these different proofs, as well as to the application of the asymptotic limit in Eq. (2).

To demonstrate the use of the FT under steady-state conditions, we chose a system where the dissipation function can be approximated for deterministic dynamics and expressed exactly for stochastic or Langevin dynamics. This system is based upon the drag experiment used by Wang *et al.* [6] where a colloidal particle is weakly held in a stationary optical trap that is translated uniformly with velocity $\mathbf{v}_{opt}$ starting at $t=0$. Initially the particle's position in the harmonic well is distributed according to an equilibrium Boltzmann distribution with an average particle velocity of 0. With trap translation, the particle is displaced from its equilibrium position until, at some later time, the average velocity of the particle is equal to the trap velocity and the average particle position is determined by a balance between the optical force and hydrodynamic drag (Fig. 1). From this point, the system is in a nonequilibrium steady state. In their original experiment, Wang and colleagues evaluated the dissipation function, constructed using deterministic dynamics from an equilibrium initial condition and thereby demonstrated the FT, Eq. (1), under transient conditions. In this paper, we report similar drag experiments using linear and circular translation of a particle-filled optical trap and evaluate the dissipation function under steady-state conditions. Consistent with previous literature on the SSFT, we demonstrate experimentally that the FT holds asymptotically in the long time limit—but only for Ω_t derived approximately. However, when Ω_t is derived exactly, the FT holds for all time, including short times.

The remainder of the paper is organized in the following manner. In the following section, we briefly review the definition of the dissipation function for nonequilibrium processes and its derivation using both deterministic and stochastic dynamics. We show that closed-form expressions used in the literature for deterministically derived steady-state dissipation functions are approximations to an exact, but insoluble expression. Furthermore, we demonstrate that for select systems, it may be possible to construct an exact, closed-form expression for the steady-state dissipation function using stochastic dynamics. In Sec. III we describe the experimental system that generates steady-state trajectories of a colloidal particle localized in a translating optical trap and in Sec. IV we show, using two sets of data, that the FT holds for all time under nonequilibrium steady state whenever the dissipation function is expressed exactly and not approximately.

II. DETERMINISTIC AND STOCHASTIC DISSIPATION FUNCTIONS IN THE STEADY STATE

A. Deterministic derivation of an approximate dissipation function for steady-state trajectories

For a Newtonian, deterministic system, 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, $\mathbf{\Gamma}\equiv\{\mathbf{q},\mathbf{p}\}$. For every trajectory that is initiated at $\mathbf{\Gamma}_0\equiv\{\mathbf{q}_0,\mathbf{p}_0\}$ and terminates at $\mathbf{\Gamma}_t\equiv\{\mathbf{q}_t,\mathbf{p}_t\}$ in a system of reversible dynamics, there is a unique conjugate or antitrajectory that starts at $\mathbf{\Gamma}_0^*\equiv\{\mathbf{q}_t,-\mathbf{p}_t\}$ and ends at $\mathbf{\Gamma}_t^*\equiv\{\mathbf{q}_0,-\mathbf{p}_0\}$. Let $\delta V(\mathbf{\Gamma}_s\equiv\{\mathbf{q}_s,\mathbf{p}_s\})$ represent a volume element of a bundle of trajectories at time s. Then the corresponding bundle of conjugate trajectories or antitrajectories has the volume $\delta V(\mathbf{\Gamma}_s^*\equiv\{\mathbf{q}_{t-s},-\mathbf{p}_{t-s}\})$ at time s. As the dynamics are deterministic, a set of trajectories spanning $\mathbf{\Gamma}_0$ and $\mathbf{\Gamma}_t$ (as well as the corresponding set of antitrajectories) is completely specified by the duration of the trajectories, t, and a set of phase-space points at arbitrary time s, $0\leqslant s\leqslant t$, $\delta V(\mathbf{\Gamma}_s)$.

A measure of reversibility, Ω_t is the ratio of the probabilities of observing sets of trajectories and their time reverse or antitrajectories. The probabilities of the trajectory/antitrajectory can be described by the probabilities of the volume elements at any arbitrary time s along the system's trajectory:

$$\Omega_t(\mathbf{\Gamma})=\ln\left(\frac{P(\delta V(\mathbf{\Gamma}_s))}{P(\delta V(\mathbf{\Gamma}_s^*))}\right), \tag{3}$$

where we have $\mathbf{\Gamma}$ as an argument to the dissipation function, $\Omega_t(\mathbf{\Gamma})$, to signal that the dissipation function is derived using deterministic dynamics. The reader may recognize Eq. (3) as an alternative description of the FT. Equilibrium statistical mechanics provides probability distributions that are simple explicit functions of the phase space, $\mathbf{\Gamma}$. But it is not possible to cast closed-form expressions of distributions of nonequilibrium states in phase-space [7]. However, if we specify that

all trajectories are intiated under equilibrium conditions, then the phase-space probability distributions are known initially, $s=0$. The dissipation function is thus written for deterministic systems as

$$\Omega_t(\mathbf{\Gamma}) = \ln\left(\frac{P(\delta V(\mathbf{\Gamma}_0))}{P(\delta V(\mathbf{\Gamma}_0^*))}\right). \tag{4}$$

Consequently, in order to formulate a closed-form expression for the dissipation function under deterministic dynamics, the trajectories must start from an equilibrium state.

To illustrate Eq. (4) with a specific system, consider Ω_t for an optically trapped particle whose coordinate and momenta are given by $\mathbf{q}_s^1$ and $\mathbf{p}_s^1$ at time s, in a sea of identical particles that are otherwise unaffected by the trap. At $t=0$, the stationary trap is set in motion with constant velocity $\mathbf{v}_{opt}$. This is the molecular analog of Wang's colloidal experiment. Here $P(\delta V(\mathbf{\Gamma}_0)) \sim \exp(-H(\mathbf{\Gamma}_0)/k_BT)$, where the Hamiltonian is $H(\mathbf{\Gamma}_0)=K(\mathbf{p}_0)+\Phi(\mathbf{q}_0)+\Phi_{opt}(\mathbf{q}_0^1)$ with $K(\mathbf{p}_0)$ and $\Phi(\mathbf{q}_0)$ designating the system's kinetic energy and the potential energy arising from interparticle interactions, both being constants of the isothermal system. The trap potential at any time, s, is $\Phi_{opt}(\mathbf{q}_s^1)=\frac{1}{2}k(\mathbf{q}_s^1-\mathbf{v}_{opt}s)^2$, where $\mathbf{v}_{opt}s$ is the position of the trap center, initially located at the origin. Likewise, the distribution of antitrajectories, $P(\delta V(\mathbf{\Gamma}_0^*))$, is determined by the Hamiltonian evaluated at $\mathbf{\Gamma}_0^*$, or equivalently at the phase-space destination point, $\mathbf{\Gamma}_t$ of the forward trajectory, evaluated under initial, equilibrium conditions: $H(\mathbf{\Gamma}_0^*)=K(-\mathbf{p}_t)+\Phi(\mathbf{q}_t)+\Phi_{opt}(\mathbf{q}_t^1)$. Some care is needed in evaluating Φ_{opt}: in order to preserve the time-reversal mapping, the optical trap center is located at $\mathbf{v}_{opt}t$ at the start of an anti-trajectory. Thus

$$\Omega_t(\mathbf{\Gamma}) = \ln\left(\frac{\exp[-H(\mathbf{\Gamma}_0)/k_BT]}{\exp[-H(\mathbf{\Gamma}_0^*)/k_BT]}\right) \tag{5}$$

$$= \frac{1}{k_BT}[H(\mathbf{\Gamma}_0^*) - H(\mathbf{\Gamma}_0)] \tag{6}$$

$$= \frac{1}{k_BT}[H(\mathbf{\Gamma}_t) - H(\mathbf{\Gamma}_0)] \tag{7}$$

$$= \frac{1}{k_BT}\int_0^t ds\left(\frac{dH(\mathbf{\Gamma}_s)}{ds}\right) \tag{8}$$

$$= \frac{1}{k_BT}\int_0^t ds\left(\frac{dK(\mathbf{p})}{ds} + \frac{d\Phi(\mathbf{q})}{ds} + \frac{d\Phi_{opt}(\mathbf{q}^1)}{ds}\right) \tag{9}$$

or

$$\Omega_t(\mathbf{\Gamma}) = \frac{1}{k_BT}\int_0^t ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt}), \tag{10}$$

where we have used

$$-\int_0^t ds\frac{dK(\mathbf{p})}{ds} = \int_0^t ds\, k(\mathbf{q}^1 - \mathbf{v}_{opt}s)\frac{d\mathbf{q}^1}{ds} + \int_0^t ds\frac{d\Phi(\mathbf{q})}{ds},$$

and

$$\int_0^t ds\frac{d\Phi_{opt}(\mathbf{q}^1)}{ds} = \int_0^t ds\, k(\mathbf{q}^1 - \mathbf{v}_{opt}s)\cdot\left(\frac{d\mathbf{q}^1}{ds} - \mathbf{v}_{opt}\right)$$

and where $\mathbf{f}_{opt} \equiv -d\Phi_{opt}/d\mathbf{q}_s^1$ is the optical force acting on the particle. It is important to emphasize again that the system is constrained to be at equilibrium at the lower time integration limit, $t=0$. For a strict derivation that includes thermostatting constraints and phase-space compression factors, the reader can follow the deterministic derivation of $\Omega_t(\mathbf{\Gamma})$ provided by Reid *et al.* for a stationary trap whose strength increases at $t=0$ [8]. For the drag experiment, $\Omega_t(\mathbf{\Gamma})$ corresponds physically to the time integral over the instantaneous rate of work $\Omega(\mathbf{\Gamma}) \equiv (k_BT)^{-1}\mathbf{f}_{opt}\cdot\mathbf{v}_{opt}$ required to translate the trap with constant velocity $\mathbf{v}_{opt}$. If the trap contained no particle, no energy would be dissipated in translating it. In Wang's colloidal experiments, particle trajectories with $\Omega_t(\mathbf{\Gamma})<0$ were observed in a weak, slowly translating trap up to 2–3 s after trap translation. That is, heat fluctuations in the surroundings *provided* useful work for up to a few seconds. For larger systems, this would be a violation of the second law of thermodynamics and, consequently, Wang *et al.* referred to these observable trajectories as "entropy-consuming." It is important to emphasize that the strict derivation of Eq. (10) from Eq. (4) requires that the time integration start under equilibrium conditions so that distributions of initial particle positions are known.

As the deterministic definition of Ω_t requires that the relative probabilities of trajectories be made under initial, equilibrium conditions, it is not possible to construct exact expressions for $\Omega_t(\mathbf{\Gamma})$ for trajectory segments of duration t that are wholly at a nonequilibrium steady state. However, as the dissipation function is extensive, an approximate steady-state dissipation function can be constructed in the following way. We can cast Ω_t in terms of its instantaneous rate of change, $\Omega(s)$ at time s, accumulated from an initial equilibrium state at time $s=0$ to some arbitrary time, t:

$$\Omega_t = \int_0^\tau ds\Omega(s) + \int_\tau^t ds\Omega(s). \tag{11}$$

Here we have introduced τ as an arbitrary "cutoff" time that is sufficiently large that the system can be regarded as being in steady state for $s>\tau$, so that Ω_t is cast as a sum of transient and steady-state contributions. The steady-state contribution is identified with the steady-state dissipation function, Ω_t^{ss}, which we can use to approximate Ω_t with an error of order τ:

$$\Omega_t \approx \Omega_t^{ss} + \mathcal{O}(\tau). \tag{12}$$

It is instructive to express these dissipation functions as time-averages, $\overline{\Omega_t}=\Omega_t/t$, such that

$$\overline{\Omega}_t \approx \overline{\Omega}_t^{ss} + \mathcal{O}\left(\frac{\tau}{t}\right). \tag{13}$$

This shows clearly that the error invoked by approximating $\overline{\Omega}_t$ with $\overline{\Omega}_t^{ss}$ vanishes in the long time limit as τ/t. However, the fluctuations in the measure $\overline{\Omega}_t^{ss}$ along a trajectory also vanish in the longtime limit and, in order that the SSFT be of any importance, it is necessary that these fluctuations vanish more slowly than $\mathcal{O}(\tau/t)$, the error in the $\overline{\Omega}_t^{ss}$ approximation. The measure $\overline{\Omega}_t^{ss}$ along the steady-state portion of a trajectory is

$$\overline{\Omega}_t^{ss} \equiv \frac{1}{t}\int_0^t ds\Omega(s), \tag{14}$$

which can be reexpressed as a sum of measures taken along contiguous trajectory segments of duration Δt:

$$\overline{\Omega}_t^{ss} \equiv \frac{1}{t}\sum_i^{t/\Delta t} \int_{(i-1)\Delta t}^{i\Delta t} ds\Omega(s) \tag{15}$$

$$\equiv \frac{1}{t}\sum_i^{t/\Delta t} \Omega_{\Delta t}. \tag{16}$$

If Δt is larger than the longest correlation time in the system, then the sum $\Sigma\Omega_{\Delta t}$ is of independent measures and the variance in the sum is proportional to the number of measures or $t/\Delta t$. The factor $1/t$ in front of the sum decreases the variance of the sum by a factor t^2. Thus, the standard deviation of the measure $\overline{\Omega}_t^{ss}$ along a steady-state portion of a trajectory diminshes as $\sqrt{t}$, at a rate slower than that of the error in the approximation of $\overline{\Omega}_t$ with $\overline{\Omega}_t^{ss}$. Consequently, we can approximate Ω_t in the FT [see Eq. (1)] with the steady-state dissipation function Ω_t^{ss}, leading to the SSFT:

$$\lim_{t\to\infty} \frac{P(\Omega_t^{ss} = A)}{P(\Omega_t^{ss} = -A)} = \exp(A). \tag{17}$$

In this way, the SSFT is an approximation to the FT that is accurate in the long time limit, i.e., when the transient contribution to the dissipation function becomes negligible, and well before the fluctuations in Ω_t^{ss} vanish along steady-state trajectories. As $\Omega_t(\mathbf{\Gamma})$ cannot be easily expressed for steady-state trajectories, it is approximated specifically for the Wang experiment by

$$\Omega_t^{ss}(\mathbf{\Gamma}) = \frac{1}{k_B T}\int_0^t ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt}), \tag{18}$$

where the time integration *starts* under steady-state conditions. $\Omega_t^{ss}(\mathbf{\Gamma})$ will satisfy the SSFT or, equivalently, will satisfy the FT asymptotically in the long time limit. It is important to note that the asymptotic limit results from our inability to express distributions of states other than equilibrium.

B. Stochastic derivation of the dissipation function for steady-state trajectories

For some systems described using stochastic dynamics, it is possible to construct distributions of trajectories that are wholly in a nonequilibrium steady state. The motion of a system under stochastic dynamics is no longer described by the set of coordinates and momenta of all constituent molecules, but is reduced to coordinates, say in the case of the Wang experiment, of the colloidal particle, $\mathbf{r}(t)=\mathbf{r}_t$. Unlike Newtonian dynamics, the stochastic equations of motion cannot be used to construct conjugate pairs of trajectories through time reversal, as the stochastic force is Markovian. 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 $\mathbf{r}_0$. Letting $P(\mathbf{r}_0,\mathbf{r}_t)$ and $P(\mathbf{r}_t,\mathbf{r}_0)$ represent the normalized probability distribution of a set of forward trajectory and respective backward trajectories, then by analogy with Eq. (3), Reid *et al.* [8] expressed the stochastically determined dissipation function as

$$\Omega_t(\mathbf{r}) = \ln\left(\frac{P(\mathbf{r}_0,\mathbf{r}_t)}{P(\mathbf{r}_t,\mathbf{r}_0)}\right). \tag{19}$$

As above, we incorporate $\mathbf{r}$ as an argument to the dissipation function, $\Omega_t(\mathbf{r})$, to signal that the dissipation function is derived using stochastic dynamics.

To illustrate Eq. (19) with a specific system, consider a stochastic description of the colloidal particle in a harmonic potential that is translated with velocity $\mathbf{v}_{opt}$,

$$\xi\frac{d\mathbf{r}}{dt} = -k(\mathbf{r}-\mathbf{v}_{opt}t) + \mathbf{g}(t), \tag{20}$$

where $\mathbf{r}$ is the coordinate of the colloidal particle, in a fixed coordinate frame whose origin is the trap center at $t=0$, ξ is the friction coefficient, k is the trapping constant, $\mathbf{g}(t)$ is uncorrelated Gaussian noise with zero mean, and $\langle\mathbf{g}(t)\mathbf{g}(t')\rangle = 2\xi k_B T\delta(t-t')$. It is convenient to transform this stochastic equation into a different coordinate system, $\mathbf{x}$, that translates according to $\mathbf{r}=\mathbf{x}+\mathbf{v}_{opt}t-\xi\mathbf{v}_{opt}/k$. The equation of motion in the translating-coordinate frame, $\mathbf{x}$, is then

$$\xi\frac{d\mathbf{x}}{dt} = -k\mathbf{x} + \mathbf{g}(t). \tag{21}$$

This is the equation for a particle in a stationary parabolic potential and it has a well-known and simple Green or propagator function:

$$G(\mathbf{x},\mathbf{x}_0,t) = \frac{k}{2\pi k_B T[1-\exp(-2t/\tau)]} \times\exp\left(-\frac{k[\mathbf{x}-\mathbf{x}_0\exp(-t/\tau)]^2}{2k_B T[1-\exp(-2t/\tau)]}\right), \tag{22}$$

where $\tau\equiv\xi/k$ is the typical time scale of the motion. This expression is the probability distribution associated with the

particle, initially located at $\mathbf{x}_0$, being located at $\mathbf{x}$ some time t later. In the limit of large t, this reduces to the equilibrium Boltzmann distribution

$$P_B(\mathbf{x}) = \frac{k}{2\pi k_B T} \exp\left(-\frac{k\mathbf{x}^2}{2k_B T}\right). \tag{23}$$

Thus, at long times, or in steady state, the distribution of particle positions, $\mathbf{x}$, in a stationary trap is identical to the distribution of particle positions relative to the trap center that translates according to $\mathbf{v}_{opt}t - \xi\mathbf{v}_{opt}/k$; i.e., the distribution of steady-state positions is dragged along by the trap, but always lags a distance $\xi\mathbf{v}_{opt}/k$ behind the trap center. The expressions for distributions of trajectories that initiate and remain at steady state is thus straightforward:

$$P(\mathbf{r}_0, \mathbf{r}_t) = P_B(\mathbf{x}_0 = \mathbf{r}_0 + \xi\mathbf{v}_{opt}/k) \times G(\mathbf{x}_t = \mathbf{r}_t - \mathbf{v}_{opt}t + \xi\mathbf{v}_{opt}/k, \mathbf{x}_0 = \mathbf{r}_0 + \xi\mathbf{v}_{opt}/k, t). \tag{24}$$

Thus, from the defining Eqs. (19) and (24), the dissipation function, expressed for a steady-state trajectory of duration t, is exactly [9]

$$\Omega_t(\mathbf{r}) = \frac{k\mathbf{v}_{opt}t}{k_B T} \cdot \frac{(\mathbf{r}_t - \mathbf{r}_0)}{1 - \exp(-t/\tau)}. \tag{25}$$

As we demonstrate in Sec. IV, this dissipation function will satisfy the FT under nonequilibrium steady-state conditions, including short times. In our experiment we measure and record the trajectories of a colloidal particle, evaluating the approximate and exact dissipation functions, $\Omega_t^{ss}(\mathbf{\Gamma})$ and $\Omega_t(\mathbf{r})$, respectively, from the same sets of steady-state trajectories.

III. EXPERIMENTAL SETUP

The equipment used to generate the particle trajectories is similar to that used in the original drag experiment of Wang *et al.* [6]. It consists of a Nikon DIAPHOT 300 inverted microscope equipped with a 100× (N.A.=1.3) oil-immersion objective lens and a 1 W infrared laser (λ =980 nm) for trapping micron-sized particles, a servo-motor controlled microscope stage with fine piezo-controlled translation in the $x-y$ plane, and a quadrant photodiode sensor for detection of particle position with resolution 15 nm. Laser power, objective focus, and servo-motor controlled motion of the microscope stage are controlled though computer interfaces developed by Cell Robotics Inc., USA. Fine translation of the microscope stage is achieved by feeding the voltage signal from an arbitrary function generator (TGA1242, Thurlby Thander Inst., UK) to the stage-mounted piezocrystals.

Approximately 50 particles (6.3 μm in diameter) were added locally into a stage-mounted, glass-bottomed cell, containing a 3.0 ml aqueous solution of 10 mM Tris-HCl +1 mM EDTA, maintained at a *p*H of 7.5. One particle was optically trapped, isolated from the other particles, and used to calibrate the quadrant photodiode detector and optical trap strength. The optical trapping constant, k, was determined by sampling the particle's position in a stationary trap for 120 s at 200 Hz and applying the equipartition theorem: $k = k_B T/\langle r^2\rangle$. Particle trajectories, i.e. particle position versus time, were then constructed and recorded as the stage was translated in one of two ways: a sequence of linear translations or a continuous circular translation.

An ensemble of particle trajectories was generated by linearly translating the microscope stage in a square velocity profile: the stage was stationary for 5 s, translated at $-\mathbf{v}_{opt}$ =0.29 μm/s for 20 s, stationary for another 5 s, and then translated at $-\mathbf{v}_{opt}$=−0.29 μm/s for an additional 20 s. This sequence was repeated for up to 400 cycles with simultaneous recording of the particle position at millisecond intervals. The time over which the stage is stationary is sufficiently long compared to the relaxation time of the colloidal particle in a stationary harmonic potential, $\tau \equiv \xi/k = 120$ ms (where k=0.48 pN/μm for these linear trajectories), so that the particle position was distributed in the trap according to equilibrium conditions at the start of stage translation. During the first 10 s of translation, the particle position, measured relative to the trap center, follows neither an equilibrium nor steady-state distribution. During this transient period, the measured particle position was used to analyze the dissipation function under transient conditions, as was originally achieved by Wang *et al.* For the remainder of the translating wave, $10 < t < 20$ s, the distribution of particle positions follows a time-independent, steady-state distribution: this portion of the particle trajectory was used to construct the steady-state dissipation functions.

A single long trajectory was generated by continuously translating the microscope stage in a circular path. This was achieved by feeding synchronised sine and cosine voltage waves to two perpendicular piezo crystals attached to the microscope stage. The radius of the circular motion was 7.3 μm and the frequency of the circular motion was 4 mHz. At this low velocity, corresponding to a tangential trap velocity of $-\mathbf{v}_{opt}$=0.18 μm/s, the stage motion can be treated simply as a long linear translation. A laser intensity stabilizer (Model BEOC-LPC, Brockton Electro-Optics Corp., USA) was incorporated in optical path, allowing us to produce and control a weaker trap and increase the relaxation time of the system so that more "entropy-consuming" trajectories could be sampled over longer time. The trapping constant was determined to be k=0.12 pN/μm and the relaxation time of the stationary system was τ=0.48 s. This single long trajectory is advantageous for studying steady-state trajectories as it maximizes the amount of steady-state data; only the first few seconds of the initial, transient trajectory are discarded from the steady-state analysis. The long trajectory was evenly divided into 75 second-long, nonoverlapping time intervals, then each interval was treated as an independent steady-state trajectory from which we constructed the steady-state dissipation functions. This circular drag experiment allowed us to analyze the steady-state dissipation function over longer times, up to 75 s, than in the case of the shorter linear drag experiment which afforded only 10 s of nonequilibrium steady-state data. However, as we collected only one trajectory, the circular drag experiment cannot be used to analyze the dissipation function under transient conditions.

It is important to recognize that two different sets of experimental data were collected: trajectories where the stage is

linearly translated, and another where the stage is circularly translated. Furthermore, for each set of trajectories, we analyze *both* steady-state dissipation functions, i.e., Eq. (10) derived from deterministic dynamics and Eq. (25) derived from stochastic dynamics. To demonstrate experimentally the FT/SSFT, we present our data in terms of the integrated fluctuation theorem (IFT), a form of the theorem that compares total positive to total negative dissipation:

$$\frac{P(\Omega_t<0)}{P(\Omega_t>0)}=\langle\exp(-\Omega_t)\rangle_{\Omega_t>0}, \tag{26}$$

where Ω_t is given by the dissipation function, $\Omega_t(\mathbf{\Gamma})$, the steady-state dissipation function $\Omega_t(\mathbf{r})$, or the transient analog of $\Omega_t(\mathbf{r})$ given in [9]. For the SSFT, we can analogously express an integrated form as

$$\lim_{t\to\infty}\frac{P(\Omega_t^{ss}<0)}{P(\Omega_t^{ss}>0)}=\langle\exp(-\Omega_t^{ss})\rangle_{\Omega_t^{ss}>0}. \tag{27}$$

where, again, Ω_t^{ss}, is an approximate form of the steady-state dissipation function, given by $\Omega_t^{ss}(\mathbf{\Gamma})$, [Eq. (18)].

IV. EXPERIMENTAL RESULTS

Figure 2 shows the integrated form of the FT evaluated from a set of 400 trajectories of a colloidal particle in a linearly translated optical trap. In Fig. 2(a), the FT is analyzed using the deterministically determined dissipation function evaluated from an initial equilibrium state, $\Omega_t(\mathbf{\Gamma})=(k_BT)^{-1}\int_0^t ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt})$. That is, the dissipation function is accumulated for each trajectory, starting from $t=0$, when the particle is equilibrated in the stationary trap and the trap translation is initiated, to some time t after the stage begins to translate. The time dependence of the LHS and RHS of the IFT $\mathbf{(}P(\Omega_t(\mathbf{\Gamma})<0)/P(\Omega_t(\mathbf{\Gamma})>0\mathbf{)}$ and $\langle\exp[-\Omega_t(\mathbf{\Gamma})]\rangle_{\Omega_t(\mathbf{\Gamma})>0}$, respectively**)** are, to within experimental error, identical as predicted by the FT. Data similar to that shown in Fig. 2(a) was first published in Wang *et al.* as an experimental demonstration of the transient application of the fluctuation theorem using a nearly identical experiment.

In Fig. 2(b), the steady-state portions of the same 400 trajectories are used to construct the approximate steady-state dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})$. Here, the first 10 s of each trajectory, corresponding to the transient response of the system to the step change in stage translation, is discarded and the remaining trajectory segments are used to construct the approximate steady-state dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})=(k_BT)^{-1}\int_{10}^{t+10}ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt})$. These truncated trajectory segments are characterized as steady state, as the initial 10 s of discarded data far exceeds the relaxation time of the stationary system, $\tau\equiv\xi/k=120$ ms. As shown in Fig. 2(b), the analogous LHS and RHS of the theorem, $P(\Omega_t^{ss}(\mathbf{\Gamma})<0)/P(\Omega_t^{ss}(\mathbf{\Gamma})>0)$ and $\langle\exp[-\Omega_t^{ss}(\mathbf{\Gamma})]\rangle_{\Omega_t^{ss}(\mathbf{\Gamma})>0}$, agree only at larger time segments ($t>2$s). This is in accord with the approximate form of Ω_t^{ss} for which the FT holds only in the asymptotic time limit, or in accord with the SSFT [Eq. (27)].

As we are comparing functions which approach zero at long times, the equivalence of the LHS and RHS can be

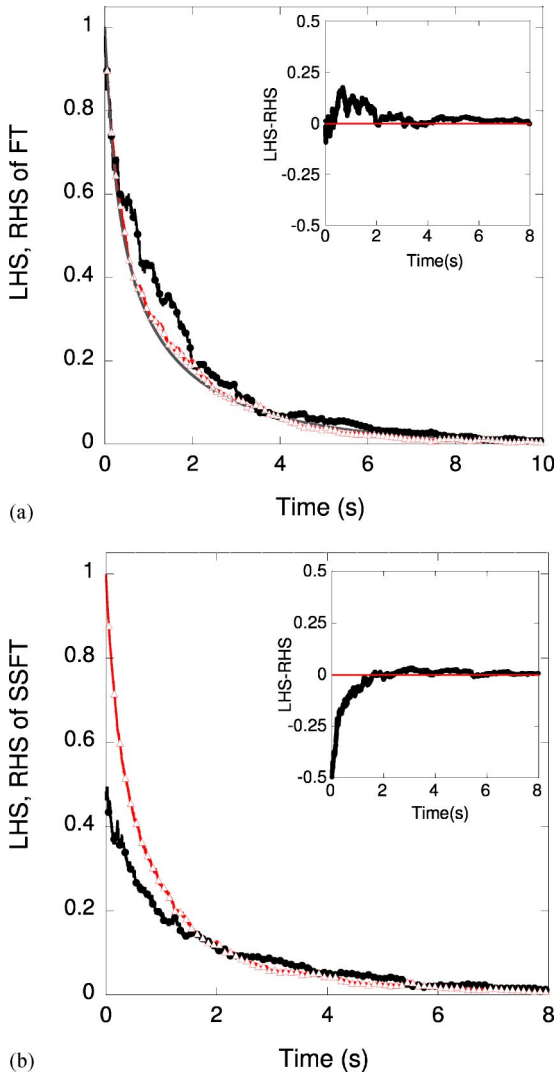

FIG. 2. (Color online) The integrated FT results from a single set of 400 linear drag experiments where the argument of the FT is the determinstically derived dissipation function, $(k_BT)^{-1}\int_a^b ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt})$. The optical trapping constant is $k=0.48$ pN/μm, stage velocity $-\mathbf{v}_{opt}=0.29$ μm/s, and the 6.3 μm colloidal particle's position is sampled at 1 kHz over 20 s trajectories. In (a) the dissipation function is accumulated, starting from an initial resting (equilibrium position) in accord with the exact form of $\Omega_t(\mathbf{\Gamma})$, that is the trajectories analyzed include transient response to the initiation of trap translation from $a=0$ to $b=t$. The LHS of the IFT, $P(\Omega_t(\mathbf{\Gamma})<0)/P(\Omega_t(\mathbf{\Gamma})>0)$ (–●–), and RHS of the IFT, $\langle\exp[-\Omega_t(\mathbf{\Gamma})]\rangle_{\Omega_t(\mathbf{\Gamma})>0}$ (–△–), are plotted against time, t, or the duration of the trajectory. Also shown is a prediction of $P(\Omega_t(\mathbf{\Gamma})<0)/P(\Omega_t(\mathbf{\Gamma})>0)$ versus t (blue line) from stochastic dynamics, Eq. (28). Inset is LHS-RHS versus t for data (–●–) and from the FT prediction of unity (line). In (b) the dissipation function $\Omega_t^{ss}(\mathbf{\Gamma})$ is accumulated from $a=10$ s after the start of stage translation and accumulated for a further t seconds to $b=10+t$. That the system is at a steady state after 10 s of stage translation is justified by the value of $\tau=120$ ms. The LHS of an integrated-form of the SSFT, $P(\Omega_t^{ss}(\mathbf{\Gamma})<0)/P(\Omega_t^{ss}(\mathbf{\Gamma})>0)$ (–●–), and the RHS of the integrated-form of the SSFT, $\langle\exp[-\Omega_t^{ss}(\mathbf{\Gamma})]\rangle_{\Omega_t^{ss}(\mathbf{\Gamma})>0}$ (–△–), are plotted against the segment time, t. Inset shows LHS-RHS versus t against the FT prediction (line).

more easily viewed when the experimental data is replotted as LHS-RHS versus t (inserts of Fig. 2). The FT prediction is shown as a line in both insets. The FT written for the full dissipation function, $\Omega_t(\mathbf{\Gamma})$, is obeyed at all time while the FT cast using the approximate steady-state dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})$, is obeyed only in the long-time limit. Note that the asymptotic limit of the SSFT is met while $\Omega_t^{ss}(\mathbf{\Gamma})$ is appreciably larger than zero. A very similar result to Fig. 2(b) was recently shown by Garnier and Ciliberto who found that the steady-state dissipative power of a resistor/capacitor in parallel, driven out of equilibrium by small current, follows the SSFT [10].

The form of the curves of Fig. 2(a) can be determined from the probability distributions associated with observing trajectories of duration t having dissipation function $\Omega_t(\mathbf{\Gamma})$, $P(\Omega_t(\mathbf{\Gamma}))$. In Appendix A, we derive expressions for $P(\Omega_t(\mathbf{\Gamma}))$ as well as the resulting form of the integrated FT,

$$\frac{P(\Omega_t(\mathbf{\Gamma})<0)}{P(\Omega_t(\mathbf{\Gamma})>0)}=\frac{1-\mathrm{erf}\left(\frac{1}{2}\sqrt{\omega(t)}\right)}{1+\mathrm{erf}\left(\frac{1}{2}\sqrt{\omega(t)}\right)}, \tag{28}$$

where

$$\omega(t)=\mathcal{F}^2\left(\frac{t}{\tau}-(1-e^{-t/\tau})\right)$$

and $\mathcal{F}^2=\xi^2\mathbf{v}_{opt}^2/(kk_BT)$. $\mathcal{F}$ is a dimensionless measure that characterizes the opposing forces acting on a particle localized in the optical trap and is given as the ratio of the lag distance, $\xi|\mathbf{v}_{opt}|/k$, to the typical particle position within the trap, given by equipartition as $\sqrt{k_BT/k}$. For translating trap experiments with different trap velocities and trap strengths, $\mathcal{F}^2$ is a convenient measure of the relaxation time of the translating trap. If the trap is stationary, then $\mathcal{F}^2=0$ and the relaxation time is simply $\tau=\xi/k$; for translating trap systems, the larger $\mathcal{F}^2$, then trajectories with negative dissipation functions persist over longer times. The prediction, Eq. (28), did not compare favorably with the original experimental results of Wang *et al.* [6], presumably because of unaccounted forces in that original experiment. However, as Fig. 2(a) shows, the experimental results presented here compare very favorably to this stochastic prediction.

For steady-state trajectories where the approximate dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})$, is used, the functional form of the asymptotic approach to the FT can also be constructed analytically, using the analytic distribution $P(\Omega_t^{ss}(\mathbf{\Gamma}))$ derived in Appendix B. The distribution of $\Omega_t^{ss}(\mathbf{\Gamma})$ is Gaussian for all t, and, in order for Gaussian distributions to obey the FT, the magnitude of the variance of the distribution must be twice the mean of the distribution. From distribution functions constructed from stochastic dynamics, we show in the Appendix that the ratio of the variance in the distribution, $\sigma^2_{\Omega_t^{ss}(\mathbf{\Gamma})}$, to the mean of the distribution, $\langle\Omega_t^{ss}(\mathbf{\Gamma})\rangle$, approaches 2 according to

$$\frac{\langle\Omega_t^{ss}(\mathbf{\Gamma})\rangle}{\sigma^2_{\Omega_t^{ss}(\mathbf{\Gamma})}}=2\times\left\{1-\frac{\tau}{t}\left[1-\exp\left(-\frac{t}{\tau}\right)\right]\right\}. \tag{29}$$

Because of strong sensitivity of the variance to the size of the system, we cannot easily compare Eq. (29) with the limited number of experimental trajectories. Equations (28) and (29) further emphasize that the FT does not predict the time scales over which $\Omega_t<0$, or in language of Wang *et al.*, over which "entropy-consuming" trajectories are observable. The governing equations of motion and the distributions of initial states determine these time and length scales.

Figure 3 demonstrates the integrated form of the FT using steady-state segments from a single, circular drag trajectory to calculate the approximate steady-state dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})$. As the duration of the single trajectory is considerably longer than that of the linear drag trajectories, we are able to construct $\Omega_t^{ss}(\mathbf{\Gamma})$ for segment times of 75 s, as compared with only 8–10 s in the linear drag case. Consequently, agreement of the LHS and RHS is shown over a significantly longer time scale in the circular drag experiment. Figure 3(b) shows the first 10 s of data and the inset shows the data replotted in the form, LHS-RHS: like the linear drag results, there is a lack of equivalence of the LHS and RHS over short segment times, as anticipated from the SSFT.

In Fig. 4, we have reanalyzed the same experimental data, using the stochastically derived dissipation function, $\Omega_t(\mathbf{r})$ of Eq. (25). This dissipation function is exact; i.e., there are no approximations made in going from its fundamental definition, Eq. (19), to its closed-form expression. The LHS and RHS of the FT are constructed using $\Omega_t(\mathbf{r})$ and plotted versus segment time in Fig. 4(a) for the linear drag data in Fig. 4(b) for the circular drag experiment. Both show that the FT holds over all time, including short times. The decay time of the fluctuations at steady state is longer for the circular trajectories (i.e., "entropy-consuming" trajectories persist over longer time scales), indicative of $\mathcal{F}^2_{circular}/\mathcal{F}^2_{linear}=1.5$. The insets of the figures more clearly show that the FT holds over all segment times, including short segment times, when the steady-state dissipation function is expressed exactly, using stochastic dynamics, $\Omega_t(\mathbf{r})$. This is in contrast to the deterministically derived steady-state dissipation function, $\Omega_t^{ss}(\mathbf{\Gamma})$, for which the theorem does not hold over short time segments.

V. CONCLUSIONS

In this paper, we demonstrate experimentally the application of the FT under nonequilibrium steady states for *all* times, using a colloidal particle localized in a translating optical trap. Starting from the fundamental definition of the dissipation function as a measure of trajectory reversibility, we construct closed-form expressions for the dissipation function, Ω_t, using both deterministic or Newtonian dynamics and stochastic or Langevin dynamics, and evaluate each of the experimental trajectories using these two expressions for Ω_t. Under steady-state conditions, it has not proven possible to construct an exact expression for the dissipation

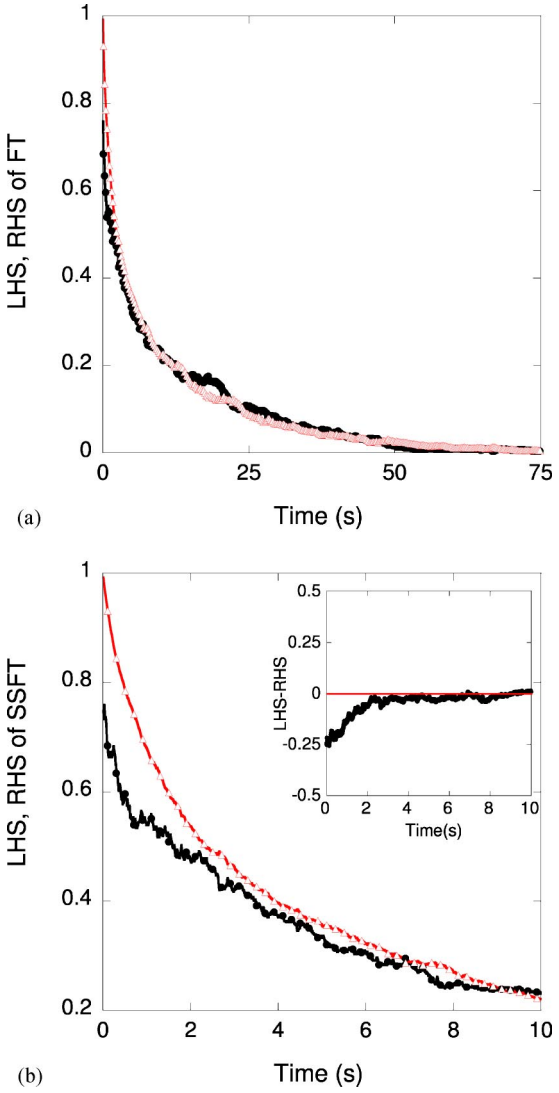

FIG. 3. (Color online) The integrated FT results from a single circular drag trajectory using the approximate, steady-state dissipation function $\Omega_t^{ss}(\mathbf{\Gamma})=(k_BT)^{-1}\int_a^{a+t}ds(\mathbf{f}_{opt}\cdot\mathbf{v}_{opt})$, where a takes on values of multiple values of 75 s, plotted for time ranges (a) $0\leqslant t\leqslant 75$ s and (b) $0\leqslant t\leqslant 10$ s. The optical trapping constant is $k=0.12$ pN/μm, the stage is circularly rotating with a diameter of 14.6 μm at 4 mHz, corresponding to a tangential velocity of 0.18 μm/s, and the 6.3 μm colloidal particle's position is sampled at 1 kHz over the single trajectory. As the ratio of the dimensionless measure $\mathcal{F}^2$ of the circular and linear translating trap experiments is $\mathcal{F}^2_{circular}/\mathcal{F}^2_{linear}=1.5$, "entropy-consuming" trajectories persist over a longer time scale in the circularly translated experiments with $\Omega_t^{ss}(\mathbf{\Gamma})<0$ for t up to 50 s. The LHS of an integrated-form of the SSFT, $P(\Omega_t^{ss}(\mathbf{\Gamma})<0)/P(\Omega_t^{ss}(\mathbf{\Gamma})>0)$ (–●–), and the RHS of the integrated form of the SSFT, $\langle\exp[-\Omega_t^{ss}(\mathbf{\Gamma})]\rangle_{\Omega_t^{ss}(\mathbf{\Gamma})>0}$ (–Δ–), are plotted against the segment time, t. The inset shows LHS-RHS versus t against the FT prediction (line), further demonstrating the lack of equivalence at short times, due to the approximate dissipation function.

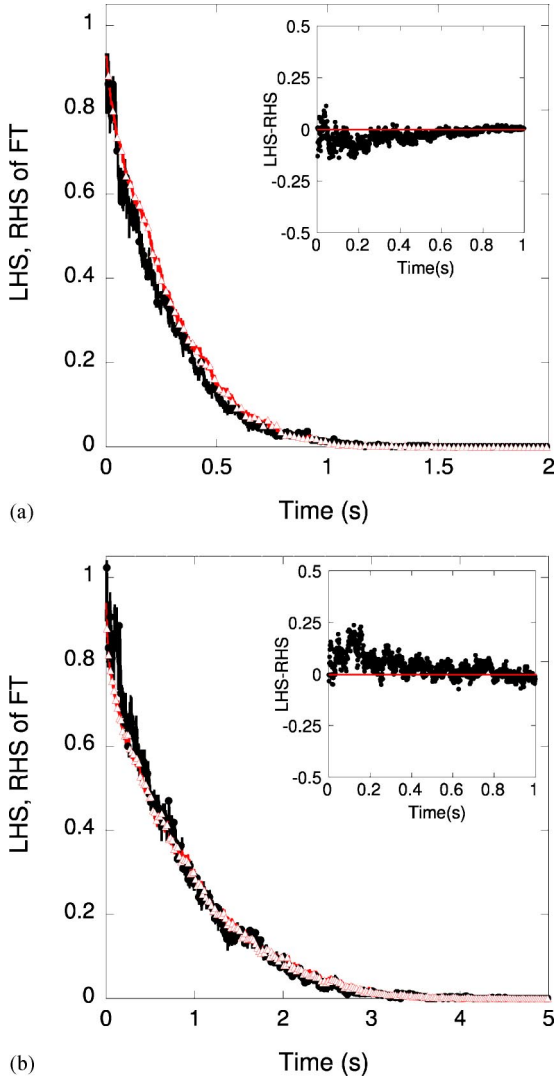

FIG. 4. (Color online) The integrated FT results from (a) 400 linear drag trajectories and (b) a single circular drag trajectory, using an exact expression for the steady-state dissipation function, derived from stochastic dynamics, $\Omega_t(\mathbf{r})$. The experimental details are given in the captions of Figs. 2 and 3. The LHS of an integrated-form of the FT, $P(\Omega_t(\mathbf{r})<0)/P(\Omega_t(\mathbf{r})>0)$ (–●–), and the RHS of the integrated-form of the FT, $\langle\exp[-\Omega_t(\mathbf{r})]\rangle_{\Omega_t(\mathbf{r})>0}$ (–△–), are plotted against the segment time, t. The inset shows LHS-RHS versus t against the FT prediction (line).

function using deterministic dynamics, and it is necessary to approximate the steady-state dissipation function with its form in the asymptotic time limit, $\Omega_t^{ss}(\mathbf{\Gamma})$. Consequently, when $\Omega_t^{ss}(\mathbf{\Gamma})$ is used as an argument in the FT, the FT holds only in the long time limit: indeed the FT written in this asymptotic time limit is referred to in the literature as a separate theorem, the steady-state fluctuation theorem or SSFT. In contrast, when a closed-form expression of the steady-state dissipation function is derived exactly using stochastic, Langevin dynamics, then the FT holds over all time. This suggests that the asymptotic limit in the SSFT is simply due to approximations in the argument of the theorem, and that when the argument of the theorem is derived exactly, the FT is operative over all time. However, it is important to recognize that it may not always be possible to construct exact, closed-form expressions for steady-state dissipation functions using stochastic dynamics, and in such cases approximate dissipation functions are necessary.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF A CLOSED-FORM EXPRESSION FOR $P(\Omega_t<0)/P(\Omega_t>0)$ FOR TRANSIENT TRAJECTORIES OF A PARTICLE IN A TRANSLATING TRAP

We are interested in deriving a closed-form expression for $P(\Omega_t<0)/P(\Omega_t>0)$, where Ω_t is taken to be the deterministically derived dissipation function

$$\Omega_t \equiv \Omega_t(\mathbf{\Gamma}) = \frac{1}{k_B T}\int_0^t ds(f_{opt}\cdot v_{opt}). \tag{A1}$$

[In this appendix, we have shortened notation, dropping the argument of the dissipation function such that $\Omega_t(\mathbf{\Gamma})$ is written as Ω_t. All trajectories are described deterministically.] The form of the LHS or RHS of the FT depends upon the distribution of trajectories with given values of Ω_t. In this appendix we derive an expression for the distribution $P(\Omega_t)$, and hence an expression for $P(\Omega_t<0)/P(\Omega_t>0)$, using stochastic dynamics. It is important to recognize that the dissipation function is derived under deterministic dynamics; however, the functional form of the distribution of trajectories is derived using stochastic dynamics. For simplicity, we cast our derivation in one dimension; an extension to higher dimensions is straightforward.

From the distribution of particle positions, we can construct a distribution of Ω_t at any given time, t. Noting that $f_{opt}+f_{rand}+f_{drag}=0$, i.e., $f_{opt}=\xi dr/dt-g(t)$, and using this in the definition and integrating gives

$$\Omega_t = \frac{-\xi v}{k_B T}\{\delta(t)-[r(t)-r(0)]\}, \tag{A2}$$

where $r(0)$ is the initial position of the particle and $\delta(t)$ is $\delta(t)=\xi^{-1}\int_0^t dsg(s)$. Physically the two terms in Ω_t can be identified as follows: the $\delta(t)$ contribution arises from the random forces alone and the second term, proportional to $r(t)-r(0)$, represents the contribution from the integrated drag force. It is important to note that these two terms are not independent, since the displacement at any time depends upon the history of the random forces. We can reexpress this in terms of the moving coordinate system x using $r=x+vt-\xi v_{opt}/k$ and $r_0=x_0-\xi v_{opt}/k$. The dissipation is then

$$\Omega_t = -\frac{\xi v}{k_B T}[\delta(t)-x(t)-v_{opt}t+x_0]. \tag{A3}$$

We already know the distribution of x_0 (it is an equilibrium, Boltzmann distribution). What we require is the distribution of $w(t)\equiv x(t)-\delta(t)$, since if we know this we can then construct the distribution of Ω_t and hence everything about the problem. We know how to solve the stochastic differential equation for $x(t)$: its solution is

$$x(t) = x_0\exp(-t/\tau)+\xi^{-1}\int_0^t dt'\exp[-(t-t')/\tau]g(t'). \tag{A4}$$

Hence the solution for $w(t)$ [which is just $x(t)$ minus the sum of the random displacements] is

$$w(t) = x_0\exp(-t/\tau)+\xi^{-1}\int_0^t dt'\{\exp[-(t-t')/\tau]-1\}g(t'). \tag{A5}$$

Now we see w is simply the sum of a number of terms, all of which are Gaussian. Hence w itself has a Gaussian distribution:

$$G_w(w,x_0,t) = [2\pi B(t)]^{-1/2}\exp\{-[w-A(t)]^2/[2B(t)]\}. \tag{A6}$$

Here $G_w(w,x_0,t)$ is the probability of finding $w(t)$ given that $x=x_0$ at time $t=0$. To determine the mean $A(t)$ is simple: $A(t)=\langle w(t)\rangle=x_0e^{-t/\tau}$ where the $\langle\ \rangle$ is an ensemble average. $B(t)$ may be determined as follows:

$$\begin{aligned} B(t) &= \langle[w(t)-A(t)]^2\rangle \\ &= \xi^{-2}\int_0^t dt_1\int_0^t dt_2[e^{-(t-t_1)/\tau}-1] \\ &\quad\times[e^{-(t-t_2)/\tau}-1]\langle g(t_1)g(t_2)\rangle. \end{aligned} \tag{A7}$$

Noting that the noise correlation is a delta function allows one to readily integrate this so that

$$B(t) = \frac{k_B T}{\xi}(2t+4\tau e^{-t/\tau}-\tau e^{-2t/\tau}-3\tau). \tag{A8}$$

The initial distribution of x_0 is the Boltzmann distribution and is

$$P_{x_0}(x_0) = \sqrt{\frac{k}{2\pi k_B T}}\exp\left[-\frac{k}{2k_B T}\left(x_0-\frac{\xi v_{opt}}{k}\right)^2\right]. \tag{A9}$$

This gives us directly the probability distribution for the dissipation, since $w=k_BT\Omega_t/\xi v_{opt}+x_0-v_{opt}t$. Integrating over x_0 yields

$$P_{\Omega_t}(\Omega_t) = \frac{k_B T}{\xi v_{opt}}\int_{-\infty}^{\infty} dx_0 G_w\left(\frac{k_B T\Omega_t}{\xi v-opt}+x_0-v_{opt}t,x_0,t\right)P_{x_0}(x_0). \tag{A10}$$

Introducing the function

$$\omega(t) = \mathcal{F}^2\left(\frac{t}{\tau}-(1-e^{-t/\tau})\right) \tag{A11}$$

allows us to write the distribution function for the dissipation as

$$P(\Omega_t) = \frac{1}{2}[\pi\omega(t)]^{-1/2} \exp\left(-\frac{1}{4\omega(t)}[\Omega_t - \omega(t)]^2\right). \tag{A12}$$

From this the FT is easily verified, $P(\Omega_t)/P(-\Omega_t) = \exp(\Omega_t)$. The probabilities of positive and negative dissipation paths are

$$P_{\pm} = \tfrac{1}{2} \pm \tfrac{1}{2}\mathrm{erf}[\tfrac{1}{2}\sqrt{\omega(t)}] \tag{A13}$$

From these the IFT is easily verified.

Note that $P(\Omega_t)$ is Gaussian with a mean (and peak) $\omega(t)$ and width $\sim\sqrt{\omega(t)}$. The peak always moves towards positive Ω_t. At long times it does this linearly in time at a speed $\xi v_{opt}^2/(k_BT)$. This speed is independent of the well strength k, and has a simple physical interpretation—it is just the dissipation production assuming the particles are dragged along at speed v_{opt}. At short times the dissipation peak moves more slowly as $\frac{1}{2}(\xi v_{opt}^2/kk_BT)(t/\tau)^2$ (corresponding to diffusive motion). At long times we have $\omega(t) = (\xi v_{opt}^2/k_BT)t - (\xi^2 v_{opt}^2/kk_BT)$ where the first term arises from the dissipation production in steady state (alluded to above) and the second term is due to the initial transient.

APPENDIX B: DERIVATION OF THE RATIO OF THE MEAN TO VARIANCE OF THE DISTRIBUTION $P(\Omega_t^{ss})$

Our aim is to derive an expression for $P(\Omega_t^{ss})$ where Ω_t^{ss} is the deterministically derived steady-state dissipation function

$$\Omega_t^{ss} \equiv \Omega_t^{ss}(\mathbf{\Gamma}) = \frac{1}{k_BT}\int_0^t ds(f_{opt}\cdot v_{opt}), \tag{B1}$$

where the time integral is taken over steady-state conditions. [In this appendix, we have shortened notation, dropping the argument of the dissipation function such that $\Omega_t^{ss}(\mathbf{\Gamma})$ is written as Ω_t^{ss}. All trajectories are described deterministically.] That is, the optical trap has been moving for some time and the particle is located at its steady-state position for the entire observation time, t. As the transient Ω_t satisfies the FT, Ω_t^{ss} satisfies the FT only in the long time limit.

The derivation of the distribution $P(\Omega_t^{ss})$ is similar to that of $P(\Omega_t)$ given in Appendix A. The only difference is that the distribution of initial positions is no longer the equilibrium distribution of positions in a stationary trap. [Eq. (A9)]. Instead, the initial distribution is that of a particle in equilibrium in the moving coordinate frame,

$$P_{x_0}(x_0) = \sqrt{\frac{k}{2\pi k_BT}}\exp\left(-\frac{kx_0^2}{2k_BT}\right). \tag{B2}$$

Solving Eq. (A10) using the above equation for $P_{x_0}(x_0)$ yields a Gaussian distribution of Ω_t^{ss}:

$$P_{\Omega_t^{ss}}(\Omega_t^{ss}) = \frac{1}{\sqrt{2\pi\sigma^2_{\Omega_t^{ss}}}}\exp\left(-\frac{(\Omega_t^{ss} - \overline{\Omega}_t^{ss})^2}{2\sigma^2_{\Omega_t^{ss}}}\right), \tag{B3}$$

where the mean value of the distribution, $\overline{\Omega}_t^{ss}$, is

$$\overline{\Omega}_t^{ss} = \frac{k}{k_BT}(v_{opt}\tau)^2\left(\frac{t}{\tau}\right) \tag{B4}$$

and the variance in the distribution, $\sigma^2_{\Omega_t^{ss}}$ is

$$\sigma^2_{\Omega_t^{ss}} = \frac{2k}{k_BT}(v_{opt}\tau)^2\left(\frac{t}{\tau} - 1 + \exp(-t/\tau)\right). \tag{B5}$$

For Gaussian distributions to obey the FT, the variance of the distribution must be exactly twice the mean. Here, for the distribution of Ω_t^{ss}, the ratio of the variance to mean is

$$\frac{\Omega^2(t)}{\langle\Omega_t^{ss}\rangle} = 2\times\left(1 - \frac{\tau}{t}[1 - \exp(-t/\tau)]\right), \tag{B6}$$

so that only in the limit of the $t \gg \tau$ will the FT be valid, in accord with what is known about the SSFT.

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evaluated along the trajectory starting from its equilibrium initial condition, can be derived in either the moving or laboratory coordinate frame. In the moving **x** coordinate frame, it is

$$\Omega_t(\mathbf{x}) = -\frac{\xi \mathbf{v}_{opt}}{k_B T} \cdot (\mathbf{x}_t - \mathbf{x}_0),$$

i.e., only the initial, transients contribute to $\Omega_t(\mathbf{x})$. In the **r** stationary laboratory frame, the full dissipation function is

$$\Omega_t(\mathbf{r}) = \left(\frac{k \mathbf{v}_{opt} t}{k_B T[1 - \exp(-t/\tau)]} - \frac{\xi \mathbf{v}_{opt}}{k_B T} \right) \cdot (\mathbf{r}_t - \mathbf{r}_0).$$

The first term on the RHS represents the transient contribution associated with displacing the particle with the bead from the center of the trap to the lag distance. The second term on the RHS is the steady-state contribution and is equivalent to the stochastically derived steady-state dissipation function, Eq. (25), investigated in this paper.

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