An optical trap experiment to demonstrate fluctuation theorems in viscoelastic media

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Received 7 January 2007, accepted for publication 12 April 2007
Published 24 July 2007
Online at stacks.iop.org/JOptA/9/S204

Abstract

Conventional 19th century thermodynamics has limited our understanding of statistical physics to systems in the thermodynamic limit, at or near equilibrium. However, in the last decade two new theorems, collectively referred to as fluctuation theorems or FTs, were introduced that quantify the energy distributions of small systems that are driven out of equilibrium, possibly far from equilibrium, by an external field. As such the FTs represent a much needed extension of non-equilibrium thermodynamics that can potentially address systems of interest in the 21st century, including nano/micro-machines and single biomolecular function. Optical trapping has served as an ideal experimental technique for demonstrating these theorems. Measurement of picoNewton scale forces over nanometre-sized displacements of a trapped micron-sized particle allows us to measure the energies to a fraction of thermal energy along the particle’s trajectory—precisely what is needed to demonstrate the predictions of the FTs. Here we review the fluctuation theorems, as cast by Evans and Searles (1994 Phys. Rev. E 50 1645; 2002 Adv. Phys. 51 1529; 2004 Aust. J. Chem. 57 1119) and Crooks (1999 Phys. Rev. E 60 2721), and provide a discussion of their importance and a comparison of their arguments. We further demonstrate an optical trap experiment that confirms the FTs. We have chosen to review an optical trapping experiment that is identical to a previously published experiment (Carberry et al 2004 Phys. Rev. Lett. 92 140601), but where the solvent is viscoelastic rather than purely viscous. This represents the first experimental demonstration where dynamics of the colloidal particle are complex and not known a priori.

Keywords: optical trapping, nonequilibrium statistical mechanics

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Thermodynamics is the study of the flow of heat and the transformation of work into heat. Our understanding of thermodynamics is largely confined to equilibrium states. The field of ‘non-equilibrium thermodynamics’ represents a simple-minded extension of the 19th century concepts of equilibrium thermodynamics to systems that are close to or near equilibrium. Moreover these traditional concepts are limited in application to large systems, referred to as the ‘thermodynamic limit’. However, in the last decade new theorems, referred to collectively as fluctuation theorems (FTs), lift the requirement of the thermodynamic limit, describing small systems that evolve far from equilibrium. In particular, the original FT of Evans et al [1–3] can be thought of as a generalization of the second law of thermodynamics that applies to small systems over short timescales. The FT of Crooks [4] similarly describes the evolution of systems between equilibrium states. It implies that the change in free energy is related to the work done by an external field to drive a system between two states, at arbitrary rates, and not simply quasi-static rates as understood by conventional
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2. The fluctuation theorems

2.1. Evans–Searles fluctuation theorem

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 endeavour 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 anti-trajectories are equal, the system is said to be perfectly reversible; on the other hand, if the probability of observing anti-trajectories is vanishingly small, we say that the system is irreversible. The second law of thermodynamics states that a system evolves irreversibly in one ‘time-forward’ direction, i.e. the probability of all anti-trajectories is zero. However, the second law strictly applies only 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 [11] in 1876 and has been a paradox since the days of Boltzmann. Boltzmann’s successors have simply side-stepped this issue by stating ‘as soon as one looks at bodies of such small dimension that they contain only very few molecules, the validity of this theorem (the second law of thermodynamics) must cease’ [12].

The fluctuation theorem (FT) of Evans and Searles [1, 2] 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, and provides a resolution to the long-standing irreversibility paradox. Specifically, the FT relates the relative probabilities of observing trajectories of duration $t$ characterized by the dissipation function, $\Omega_t$, taking on arbitrary values $a$ and $-a$, respectively:

$$\frac{P(\Omega_t = a)}{P(\Omega_t = -a)} = \exp[a]. \quad (1)$$

The dissipation function, $\Omega_t$, is, in general, a dimensionless dissipated energy, accumulated along the system’s trajectory; expressions for $\Omega_t$ differ from system to system. We express $\Omega_t$ and other energies introduced below, in units of $k_B T$, where $k_B$ is Boltzmann’s constant and $T$ is the temperature of the surroundings with which the system is in contact and is initially at equilibrium. Any trajectory of the system that is characterized by a particular $\Omega_t = a$ has, under time-reversible deterministic mechanics, a conjugate or time-reversed trajectory with $\Omega_t = -a$. In this way, the LHS of
2.2. Crooks' fluctuation theorem

From classical thermodynamics, the work done by an external field to drive a system from one equilibrium state to another equilibrium state is equivalent to the change of free energy, \( \Delta F \), between the states, only in the special case where the path is traversed quasi-statically. That is, the path between the two states must be traversed so slowly that intermediate, as well as the initial and final states of the system, are all in thermodynamic equilibrium.

Crooks' fluctuation theorem [4] states something quite remarkable. In the case of paths that are traversed at arbitrary rate, ranging from quasi-static to ‘far from equilibrium’, the distribution of trajectories, characterized by the work done by the external field over the lifetime of the trajectory, follows

\[
P_f(W = a) = \exp[a - \Delta F].
\]

This expression is similar to the Evans–Searles' FT in that it relates distributions of trajectories, characterized by an energy, specifically the work, \( W \), to the respective equilibrium free energy change, \( \Delta F \). Like the FT, Crooks' FT also quantifies how irreversibility evolves out of reversible equations of motion. A perfectly reversible system is one where the work required to traverse \( B \rightarrow A \) is equal but opposite in sign to the work required in the time-reversed trajectory, \( A \rightarrow B \); under time-reversible mechanics, the RHS of equation (2) is unity for these reversible paths and \( W = \Delta F \), in agreement with classical thermodynamics.

From Crooks' FT and the definition of ensemble averages,

\[
\exp(-\Delta F) = \langle \exp(-W) \rangle_t,
\]

where \( \langle \cdots \rangle_t \) represents the average over a collection of forward trajectories. This expression was first posed by Jarzynski in 1997 [13] and states that the free energy can be determined by measuring the work, \( W \), done by an external field along dynamical paths that connect the two states. These paths may be traversed at arbitrary rates, so that the intervening states may not be in true thermodynamic equilibrium. This is seemingly contrary to 19th century classical thermodynamics. If, instead of averaging the work, you average the exponential of the work, then you can calculate the equilibrium free energy difference from information obtained along non-equilibrium paths. The potential importance of equation (3) has both theoretical and practical aspects. One could theoretically calculate \( \Delta F \) using fictitious paths that ‘morph’ between two states on a computationally convenient (not necessarily realistic) energy surface. (This differs from classical thermodynamics where considerable care must be made to measure the work along a path that is both quasi-static and accurate or realistic.) On the practical side, equation (3) suggests that measuring work on small microscopic processes could yield thermodynamic quantities \( \Delta F \) that are traditionally inferred by calorimetric measurements. The importance here is that, in order to understand molecular-scale processes, it is necessary to probe them using molecular time/length scales.

2.3. Arguments of the FTs

To understand the FTs and their relationship, we need to define the energies dissipated along the trajectories, \( W \) and \( \Omega_t \). In the original derivations of the FTs, these energies were defined over trajectories within deterministic phase space, i.e. where the system's degrees of freedom are given by the vectors of time-dependent positions, \( \mathbf{q} \) and momenta, \( \mathbf{p} \), representing all components of the system. The internal energy, \( \mathcal{U} \), of such a system is the sum of the kinetic energy, \( K(\mathbf{p}) \), the potential interactions amongst constituents, \( \phi(\mathbf{q}) \), and the external potential interacting with the degrees of freedom of the system, \( \phi_{ext}(\mathbf{q}, \lambda) \):

\[
\mathcal{U}(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + \phi(\mathbf{q}) + \phi_{ext}(\mathbf{q}, \lambda).
\]

Here \( \lambda \) parametrizes the value of the external field strength as it changes from an initial value at \( s = 0 \) to a final value at time \( s = t \). The work done by an external field on the degrees of freedom of the system is governed by the first law

\[
W = \int_0^t ds [\dot{\mathcal{U}}(s) - \dot{\mathcal{Q}}(s)],
\]

where \( \dot{\mathcal{Q}}(s) \) is the instantaneous rate of heat exchange with the system’s surroundings. This expression is valid for any system. However, in the original derivation of Crooks' FT and Jarzynski's relation, the authors considered a system governed by a Hamiltonian, \( \mathcal{H}(\mathbf{q}, \mathbf{p}) \), where, by definition, \( \dot{\mathcal{H}} \equiv \mathcal{U} \) and the system is isolated (there is no heat exchange with the surroundings, or \( \dot{\mathcal{Q}}(s) = 0 \)) and obeys Hamilton’s equations,

\[
\dot{\mathbf{q}} = \frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{p}},
\]

\[
\dot{\mathbf{p}} = -\frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{q}}.
\]
For such a Hamiltonian system, the rate of change of the internal energy is
\[ \dot{U}(s) = \dot{\mathcal{H}}(s) = \frac{\partial \mathcal{H}}{\partial \mathbf{p}} \dot{\mathbf{p}} + \frac{\partial \mathcal{H}}{\partial \mathbf{q}} \dot{\mathbf{q}} + \frac{\partial \mathcal{H}}{\partial \lambda} \dot{\lambda}, \quad (8) \]
and the work done by the external field is
\[ W = \int_0^t ds \dot{U} = \int_0^t ds \frac{\partial \mathcal{H}}{\partial \lambda}. \quad (9) \]

Although equation (9) is the original definition used in the derivation of Crooks’ FT and the Jarzynski equality, it is not practical for small systems which are difficult to isolate from the surroundings. Most small systems are difficult to isolate from their surroundings, and even if possible, work performed on a small isolated system, as specified by equation (9), will occur with a simultaneous increase in the temperature of the system. Whilst it can be problematic to attempt any description of the temperature of a small non-equilibrium system, the ΔF would then characterize the free energy change for that non-isothermal system. Indeed, for several decades, computer simulationists have studied necessarily small systems by imposing temperature constraints or thermostats in molecular dynamics simulations. Such temperature constraints are non-holonomic, i.e. we can append a system’s equations of motion with a mathematical constraint to fix the temperature; however, with such constraints it is no longer possible to express the dynamics using the Hamiltonian. For example, it is possible to append Hamilton’s equations of motion with a mathematical constraint to fix the kinetic temperature \[ f(\mathbf{q}, \mathbf{p}): \]
\[ \dot{\mathbf{q}} = \frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{p}} \quad \dot{\mathbf{p}} = -\frac{\partial \mathcal{H}(\mathbf{q}, \mathbf{p})}{\partial \mathbf{q}} - f(\mathbf{q}, \mathbf{p}). \quad (10) \]

Here \( \mathcal{H} \) corresponds to the Hamiltonian without the mathematical constraint, or the internal energy, \( U \), of the system with the constraint. Several different mathematical constraints can be constructed, all of which may be argued to be ‘artificial’, but which must satisfy the conditions that (i) additional thermostating degrees of freedom introduced must be inert to an external field, \( \phi_{\text{ext}} \), (ii) that under a time-invariant \( \phi_{\text{ext}} \), the system relaxes to an equilibrium state, and (iii) that \( \dot{\mathbf{q}}/f(\mathbf{q}, \mathbf{p}) = -\dot{Q}(s) \). That the mathematical constraint is artificial is of no significance, is evident as one substitutes \( \dot{U}(\mathbf{q}, \mathbf{p}) = K(\mathbf{p}) + \phi(\mathbf{q}) + \phi_{\text{ext}}(\mathbf{q}, \lambda) \), the kinetic energy \( K(\mathbf{p}) = \mathbf{p} \cdot \mathbf{p}/(2m) \) and the equations of motion into equation (5) to show that the explicit value of \( \dot{Q}(s) \) vanishes in the expression for \( W \). That is not to say that \( W \) is independent of the heat exchange with the surroundings: the trajectory itself depends sensitively upon the mathematical constraint \( f(\mathbf{q}, \mathbf{p}) \) or \( \dot{Q}(s) = -\dot{\mathbf{q}}/f(\mathbf{q}, \mathbf{p}) \) through the system’s equations of motion, equation (10).

Having properly defined \( W \) for both an isolated Hamiltonian system, and a more general deterministic system which allows heat exchange, we now turn our attention to the argument of the Evans–Searles FT, the dissipation function, \( \Omega \). The dissipation function is cast similarly to \( W \) as
\[ \Omega = \int_0^t ds [\Delta U - \dot{Q}(s)] \quad (11) \]

where \( U_0 \) is the potential energy of the system where the contribution from the time-varying external field is neglected, although the trajectory over which \( U_0 \) is evaluated is determined by the time-varying external field. That is,
\[ U_0 = [\mathcal{U} - \phi_{\text{ext}}(\mathbf{q}, \lambda) + \phi_{\text{ext}}(\mathbf{q}, \lambda = 0)]. \quad (12) \]

For an isolated, Hamiltonian system, \( \dot{Q}(s) = 0 \) and
\[ \dot{U}_0 = \dot{\mathcal{H}}_0 = [\mathcal{H} - \phi_{\text{ext}}(\mathbf{q}, \lambda) + \phi_{\text{ext}}(\mathbf{q}, \lambda = 0) \]

where
\[ \frac{d\mathcal{H}_0}{ds} = \frac{\partial \mathcal{H}_0}{\partial \mathbf{p}} \dot{\mathbf{p}} + \frac{\partial \mathcal{H}_0}{\partial \mathbf{q}} \dot{\mathbf{q}} + \frac{\partial \mathcal{H}_0}{\partial \lambda} \dot{\lambda}, \quad (14) \]

leading to
\[ \dot{\Omega}_0 = \int_0^t ds [\Delta U_0 - \dot{Q}(s)] = \int_0^t ds \mathbf{q} \left[ -\frac{\partial \phi_{\text{ext}}(\lambda = 0)}{\partial \mathbf{q}} - \frac{\partial \phi_{\text{ext}}(\lambda)}{\partial \mathbf{q}} \right]. \quad (17) \]

To develop an expression for \( \dot{\Omega}_0 \) for small systems, it is important to account for heat exchange with the surroundings, or \( \dot{Q}(s) \neq 0 \). By appending Hamilton’s equation with a thermostat constraint, equation (14) becomes
\[ \frac{d\mathcal{H}}{ds} = \dot{Q}(s) + \frac{\partial \mathcal{H}}{\partial \lambda}, \quad (18) \]

which leads to an expression for \( \dot{\Omega}_0 \) that is the same as that of an isolated Hamiltonian system, equation (17). This is not to say that the dissipation function is independent of heat exchange as, like \( W \), exchange of heat will determine the system’s trajectory through the deterministic equations of motion, equation (10).

By analogy, it is now possible to express the dissipation function for any system’s trajectory where the equations of motion and the heat exchange are not necessarily known, but where the external potential, \( \phi_{\text{ext}}(\mathbf{q}, \lambda) \), is known. \( U_0 \) can still be written in terms of the unknown quantity \( \dot{Q}(s) \) as
\[ \dot{U}_0 = \dot{\mathcal{H}} - \phi_{\text{ext}}(\mathbf{q}, \lambda) + \phi_{\text{ext}}(\mathbf{q}, \lambda = 0) \]
\[ = \dot{\mathcal{H}} + \dot{Q}(s) - \phi_{\text{ext}}(\mathbf{q}, \lambda) + \phi_{\text{ext}}(\mathbf{q}, \lambda = 0) \]
\[ = \dot{\mathcal{H}} + \dot{Q}(s) - \phi_{\text{ext}}(\mathbf{q}, \lambda) + \phi_{\text{ext}}(\mathbf{q}, \lambda = 0) \]
\[ = \dot{\mathcal{H}} + \dot{Q}(s) - \phi_{\text{ext}}(\mathbf{q}, \lambda = 0) + \phi_{\text{ext}}(\mathbf{q}, \lambda) \]
so that \( \int_0^t ds [\Delta U_0 - \dot{Q}(s)] \] again yields equation (17). Once again, it is important to note that \( \dot{\Omega}_0 \) is independent of the explicit value of the heat exchanged at any point of the trajectory, although \( \dot{\Omega}_0 \) does depend upon the exchange of heat through the time evolution of the coordinates, \( \mathbf{q}(s) \). If the equations of motion are known, either as deterministic or stochastic, a value of \( \dot{\Omega}_0 \) can either be solved for analytically or numerically; if the equations of motion are intractable, as in the case of an optically trapped particle in a viscoelastic solution,
then $\Omega_t$ can be determined from experimentally measured trajectories, $q(s)$, as $0 \leq s \leq t$.

Finally, it is important to maintain the convention adopted of expressing energies, including $\Omega_t$ and $W$, in units of $k_B T$, where $T$ is the temperature of the surroundings, irrespective of whether the system is adiabatic or exchanges heat with the surroundings. All non-equilibrium trajectories in the FTs must be initiated under equilibrium conditions, by which we mean that the system and surroundings are in equilibrium and at the same temperature. Thus, the surrounding temperature additionally the most convenient reference temperature in FTs, particularly in closed systems where the external field is applied under adiabatic conditions, $\dot{Q} = 0$, and the system’s temperature, if it were possible to define/measure it in small, non-equilibrium systems, would increase as work is done on the system. $T$ is not a scaling factor: normalizing the energy terms $\Omega_t$ and $W$ with any other temperature would render equations (1) and (2) as inequalities.

3. The capture experiment

In the capture experiment, the strength of the stationary optical trap is changed instantaneously, and the time-dependent relaxation of the particle’s position from one equilibrium distribution to another distribution is recorded [5]. For this experiment, a particle is localized in a stationary trap of strength $k_0$ over a sufficiently long time $\tau$ so that its position is described by an equilibrium distribution. At time $s = 0$, the optical trap strength is increased discontinuously from $k_0$ to $k_1$, $k_1 > k_0$, so that we more tightly confine or ‘capture’ the particle. Alternatively we can decrease the trap strength from $k_1$ to $k_0$ to ‘release’ or relax the particle. The particle’s position is recorded as it relaxes to its new equilibrium distribution and we evaluate the functions $W$ and $\Omega_t$ over an ensemble of non-equilibrium trajectories. In the capture experiment, the external field parameter $\lambda(s)$ is the trap strength, $k$, which varies discontinuously:

$$\lambda(s) \equiv k(s) = k_0 + (k_1 - k_0)H(s), \quad (23)$$

where $H(s)$ is the Heaviside function, $\dot{\lambda}(s) = (k_1 - k_0)\delta(s)$, so that

$$\phi_{\text{ext}}(s) = \frac{1}{2}[k_0 + (k_1 - k_0)H(s)]q^2(s). \quad (24)$$

Work, $W$, is simply the change in the internal energy that occurs upon the instantaneous change in the trapping constant. For the capture experiment it is

$$W = \int_0^t ds \dot{\lambda} \frac{\partial \phi_{\text{eff}}}{\partial \lambda} \quad (25)$$

$$= \int_0^t ds (k_1 - k_0)\delta(s) \frac{q^2(s)}{2} \quad (26)$$

$$= \frac{1}{2}(k_1 - k_0)q^2(0). \quad (27)$$

Note that $W$ will always be positive if the trap strength is increased or $k_1 > k_0$ and consequently, distributions for $W$ cannot be Gaussian. As all sampled trajectories initiate under equilibrium conditions, the probability distribution of $q(s = 0, k = k_0)$ is a Boltzmann distribution and the distribution of $W$ is then simply

$$P_{k_0 \to k_1}(W) = \frac{k_0}{\pi(k_1 - k_0)W} \exp \left[\frac{-k_0 W}{k_1 - k_0}\right]. \quad (28)$$

Thus, if we consider the ensemble average, $\langle \exp[-W]\rangle$, then

$$\langle \exp[-W]\rangle = \int_0^\infty dW \ P(W) \exp[-W] = \frac{k_0}{k_1} \quad (29)$$

$$= \exp[-\Delta F] \quad (30)$$

where the change in free energy associated with changing the trapping constant from $k_0$ to $k_1$ is $\Delta F = \ln[\sqrt{k_1/k_0}]$ from classical statistical thermodynamics. Furthermore, if we consider the probability distribution of $W$ for both the forward or capture directions, i.e. $W_{k_0 \to k_1}$ where the trap strength increases from $k_0$ to $k_1$, and the reverse or release direction, i.e. $W_{k_1 \to k_0}$,

$$P_{k_1 \to k_0}(W) = \frac{k_1}{\pi(k_1 - k_0)W} \exp \left[\frac{-k_1 W}{k_0 - k_1}\right]. \quad (32)$$

one can see that these distributions trivially obey Crooks’ FT,

$$P_{k_0 \to k_1}(W = a) \quad (33)$$

$$P_{k_1 \to k_0}(W = -a) = \exp[a - \Delta F].$$

Notice that, in the context of the capture experiment, Crooks’ FT depends only upon the equilibrium distribution of particle positions within the optical trap. This distribution is independent of the viscoelastic response of the surrounding fluid. Consequently, this experimental demonstration of Crooks’ FT depends solely upon the ability to sample an equilibrium or Boltzmann distribution of particle positions within the particle well. An alternative experiment, say where the trapping constant changes linearly over some time period, is different: there $W$ is accumulated over the time period over which $k$ is changing and the distribution of $W$ depends upon the response or microrheology of the fluid.

In contrast, the dissipation function, $\Omega_t$, depends sensitively upon the material properties of the surrounding fluid as this determines the time response of the particle position to an instantaneous change in the trap constant. For any particle trajectory, irrespective of the solvent, we can express the dissipation function $\Omega_t$ as

$$\Omega_t = \int_0^t ds \dot{q} \left[\frac{\partial \phi_{\text{ext}}(\lambda) = 0}{\partial q} - \frac{\partial \phi_{\text{ext}}(\lambda)}{\partial q}\right] \quad (34)$$

$$= \int_0^t ds \left[k_0q \dot{q} - (k_0 + (k_1 - k_0)H(s))q\dot{q}\right] \quad (35)$$

$$= (k_0 - k_1) \int_0^t ds \ q\dot{q} \quad (36)$$

$$= \frac{k_0 - k_1}{2}(q^2(t) - q^2(0)). \quad (37)$$

For a particle embedded in a purely viscous solvent, the motion of the particle can be expressed by the stochastic Langevin equation

$$\frac{dq}{dt} = -k_1q + g(s). \quad (38)$$
where $\xi$ is a friction coefficient and $g(s)$ is uncorrelated Gaussian noise with zero mean and $\langle g(s)g(s') \rangle = 2\xi k_B T b(s-s')$. As demonstrated by Wang et al. [15], it is possible to construct an analytic expression for the probability distributions $P(\Omega_t = A)$ for the capture experiment in purely viscous solvents. From these analytic expressions for $P(\Omega_t)$, one can show that the FT, equation (1), does indeed hold.

However, we are unable to construct such distributions for a particle in a viscoelastic solvent, where $g(s)$ is time-correlated. Under these conditions, it is necessary to construct distribution of $P(\Omega_t)$ from a large ensemble of experimentally recorded particle trajectories and inspect the development of asymmetry in the distributions to determine if the FT does indeed still hold.

Despite our inability to describe generally the non-equilibrium trajectories of a particle in a viscoelastic solution, it is possible to state long time limiting values of $\Omega_t$, where equilibrium distributions of particle positions are expected. First, as any trajectory evolves over infinite time,

$$\lim_{t \to \infty} \Omega_t = -(W_{k_0 \to k_1} + W_{k_1 \to k_0}). \quad (39)$$

That is, the dissipation function over the long time limit is equivalent to the work done by the external field to ‘capture’ a particle equilibrated in a trap of strength $k_0$ and to ‘release’ a particle equilibrated in a trap of strength $k_1$. In addition, the ensemble average of $\Omega_t$ in the long time limit is, by equipartition [19]:

$$\lim_{t \to \infty} \langle \Omega_t \rangle = \frac{(k_0 - k_1)^2}{2k_0k_1} > 0. \quad (40)$$

Note that the long time limit is predicted to be independent of solvent condition and that, as the difference in trapping constants vanish, the trajectory becomes more reversible and $\Omega_t$ approaches 0.

In order to demonstrate the FT in a viscoelastic solution, it is imperative that we demonstrate that the fluid response is viscoelastic over the time and length scales explored in the capture experiment. In accord with the fluctuation–dissipation theorem, the thermal fluctuations of an optically trapped particle can be used to quantify the micro rheological response of the surrounding fluid [16, 17]. Let $q(t)$ represent the temporal displacement of the particle of radius $R$ due to a force, $F(t)$. Then the response function or complex compliance of the single-particle motion, expressed in the frequency domain, $\tilde{G} = \tilde{\alpha} + i\tilde{\omega}'$, relates the Fourier transforms of the displacement and force, $\tilde{q}$ and $\tilde{F}$, respectively:

$$\tilde{q} = \tilde{\alpha} \tilde{F}. \quad (41)$$

The response function is inversely proportional to the complex shear modulus of the fluid, $\tilde{G}$, by a generalized Stokes–Einstein relation (GSER) or

$$\tilde{G} = \frac{1}{6\pi R \tilde{\alpha}}. \quad (42)$$

Here $\tilde{G} = \tilde{G}^\prime + i\tilde{G}''$, where $\tilde{G}^\prime$, the real component, is identified with the elastic or storage modulus and $\tilde{G}''$, the imaginary component, is the loss modulus:

$$\tilde{G}'' = \frac{1}{6\pi R} \frac{-\tilde{\omega}''}{\tilde{\alpha}'' + \tilde{\omega}''^2}. \quad (43)$$

To determine these moduli from the position of the optically trapped particle, we first construct a power spectral density, $S(f)$, of particle fluctuations:

$$S(f) = \lim_{t \to \infty} \frac{2}{f} \tilde{q}_0(f) \tilde{q}_0^*(f) \quad (45)$$

where $\tilde{q}_0(f)$ and $\tilde{q}_0^*(f)$ represent the Fourier transform, $\tilde{q}_0(f) = \int_{-1/2}^{1/2} dq(s) \exp [2\pi i fs]$, and its complex conjugate. The imaginary component of the complex response function $\tilde{G}''$ is then

$$\tilde{\omega}'' = \frac{\pi}{2k_B T} f S(f), \quad (46)$$

and the real component of the complex response function is given by a Kramers–Kronig relation, or

$$\tilde{\alpha}' = \frac{2}{\pi} \int_0^\infty d\omega \frac{f \tilde{\omega}''(\omega)}{\omega^2 - f^2}. \quad (47)$$

For a purely viscous fluid, $\tilde{G}'' = 2\eta f$ and there is no elastic component of the modulus or $\tilde{G}^\prime = 0$. However, confinement of the particle’s motion to the harmonic optical trap gives rise to an elastic contribution to the measured storage modulus, $\tilde{G}''_{\text{measured}}$. So that

$$\tilde{G}''_{\text{measured}} = \tilde{G}'' + \frac{k}{6\pi R}. \quad (48)$$

$\tilde{G}''_{\text{measured}}$ is determined from the experimentally measured power spectral density, $S(f)$ and equations (46) and (47).

For a Brownian particle with uncorrelated Gaussian noise, one can show that the power spectral density is given by [18]

$$S(f) = \frac{k_B T}{\xi \pi^2 (f^2 + f^2)} \quad (49)$$

where $f_c$ is the ‘corner frequency’:

$$f_c = \frac{k}{2\pi \xi}. \quad (50)$$

$\xi = 6\pi R \tilde{\eta}$ is the Stokes drag coefficient and $\tilde{\eta} = \alpha(f = 0)$ is the solution viscosity. For frequencies smaller than the corner frequency, $f \ll f_c$, the power spectral density is nearly constant at a ‘plateau’ value of

$$f \ll f_c \Rightarrow S(f) \approx S_0 = \frac{2k_B T}{\pi k_c} \quad (51)$$

while at high frequencies the power spectral density obeys a power law behaviour,

$$f \gg f_c \Rightarrow S(f) \approx \frac{1}{f^2}. \quad (52)$$

The corner frequency is determined by the intersection of these two regimes. Indeed, the low-frequency plateau value $S_0$ and the corner frequency, $f_c$, provide an alternative method to calibrating the strength, or trapping constant $k$, of the optical trap. This method is particularly advantageous over the equipartition method (where $k$ is determined from the variance in the particle position, or $k \equiv k_B T/\langle q(t)^2 \rangle$) when
the trap strength is large. Note that the variance in the particle displacement, \( q(t)^2 \), is independent of the microrheological properties of the suspending liquid. The integral over the power spectral density corresponds to the variance and depends only upon trap strength and temperature; however, the power spectral density does indeed depend upon the microrheological properties [17]. The corner frequency and shape of \( S(f) \) depend upon these rheological properties of the suspending liquid. Indeed, the power law behaviour of \( S(f) \) at high frequencies is used to qualitatively describe the fluid: \( S(f) \approx f^{-z} \) where \( z = 2 \) for purely viscous solutions and \( z < 2 \) for viscoelastic solutions.

4. Experimental details

The optical trap set-up consists of a Nikon DIAPHOT 300 inverted microscope equipped with a 100× (NA = 1.3) oil-immersion objective lens and a 4 W Nd:YAG laser, \( \lambda = 1064 \) nm (Coherent, USA). The optical trap strength is controlled by adjusting the laser intensity using an LCD power modulator (LPC-NIR, Brockton Electrooptic Corporation, USA). Changes in the laser intensity are recorded using a photodiode (SDP86001, Honeywell, USA) located above the sample cell. The position of a trapped particle is detected by projecting its image onto a quadrant photodiode, which has a resolution of 15 nm (S4349 Hamamatsu, Japan). LabView and a PCI-6014 data acquisition card (National Instruments, USA) are used for automatic data collection.

The sample cell holds approximately 4 ml of liquid to minimize any localized heating from the optical trap. The cell consists of a glass coverslide, a teflon box and is sealed using either mineral oil or a second coverslide. The sample cell is filled with either 8 ml of deionized water or an aqueous solution containing 0.1 wt% of \( 8 \times 10^3 \) MW polyethyleneoxide (PEO). Approximately 1000 polystyrene particles, with a diameter of 6.3 \( \mu \)m, are injected locally into the sample cell. One particle is optically trapped and moved at least 2 mm from the injection site to ensure its isolation from other particles and allowed to equilibrate within the optical trap for at least 1 h before measurements taken for microrheology or FT. The position of the particle is then recorded at 20 kHz.

4.1. Microrheology

First, power spectral densities are constructed from particle positions in optical traps of fixed strength, using water and PEO solutions to demonstrate microrheological differences in the two solutions. Figure 1 shows the power spectral density of a particle in PEO solution, \( S_F(f) \), sampled at 20 kHz and the
We have eliminated from the sum the contribution of $\omega_j = f_i$ for which the integrand has a simple pole. At large frequencies, $f$, the error in $\tilde{\alpha}'(f)$ that is associated with discretization and elimination of this singular term is less than 10% for $\Delta < 0.01$ Hz. In our work, we use a discretization of $\Delta = 1$ Hz, where at large frequencies the error in the moduli is $O(5\%)$. Figure 2(a) shows the storage and loss moduli, $G'_W$ and $G''_W$, calculated for the pure water solution using $S_W(f)$. For water, within the frequency range shown, the storage modulus, $G'_W$, is roughly constant at $G'_W = 4.0 \times 10^{-2}$. This value compares well with the contribution of the optical trap to the measured $G'_W = 3.9 \times 10^{-2}$, indicating that the elastic component of the particle motion is entirely the result of the confining optical trap with no elastic contribution from the solvent at these frequencies [17]. The figure also shows that the loss modulus, $G''_W$, is linear in frequency, $\eta$ is independent of frequency over the sampled frequency range. A least squares fit to $G'_W$ provides a viscosity value of $\eta = 0.96 \times 10^{-3}$ Pa s, agreeing with that obtained from the Lorentzian fitting. Figure 2(b) shows the complex moduli for the viscoelastic PEO solution. It differs considerably from that obtained in pure water: the storage modulus, $G'(W_0)$, is no longer a constant and the loss modulus, $G''(W_0)$ no longer has a simple linear relationship with frequency.

4.2. Fluctuation theorem

To demonstrate the FT, equation (1), in a viscoelastic solvent, we record and analyse the trajectory of a particle in the...
PEO solution as the trap strength is changed discontinuously from $k_0$ to $k_1$. The value of the trap strength is determined by recording the position of the optically trapped particle at 500 Hz for 600 s and applying the equipartition theorem to determine the trapping constant $k$. Due to the possibility of an asymmetric optical trap, the equipartition theorem was calculated along each orthogonal axis within the focal plane separately, resulting in $(k_{0x}, k_{0y}) = (2.24, 2.22) \, \text{pN} \, \text{μm}^{-1}$ and $(k_{1x}, k_{1y}) = (4.54, 4.37) \, \text{pN} \, \text{μm}^{-1}$. These values compare favourably with the fitting parameters of the power spectral density, sampled at 20 kHz for 100 s. We generated several thousand trajectories of an individual particle by cycling the trap strength discontinuously between $k_0$ and $k_1$ with a period of 8 s, i.e. the optical trap strength is $k_0$ for $0 \leq t < 4$ s and $k_1$ for $4 \leq t < 8$ s. The characteristic relaxation times of particle motion in optical traps of strength $k_0$ and $k_1$ is $(2\pi f_c)^{-1} = \xi/k_0 = 0.212$ s and $(2\pi f_c)^{-1} = \xi/k_1 = 0.104$ s; consequently, the particle position obeys a Boltzmann distribution at the instances when the trap constant is discontinuously changed.

Histograms of the dissipation function, i.e. the number of trajectories, $N_\alpha$, having a value of the dissipation function, $\ln[N_\alpha/N_{\alpha-1}]$, versus the dissipation function, $\Omega_\alpha = \alpha + da$, constructed from the histograms of experimental trajectories in figure 3. The points represent the experimental data and the line represents the FT prediction. The closed points represent data where $N_\alpha > 0$ and $N_{\alpha-1} > 0$; that is, 3500 trajectories is sufficient to sample a trajectory with that corresponding value of $\Omega_\alpha = \alpha + da$ at least once. Open points have been placed at $\ln[N_\alpha/N_{\alpha-1}] = 0$ at values of $\Omega_\alpha = \alpha + da$ for which no trajectories were sampled; that is, either $N_\alpha = 0$ or $N_{\alpha-1} = 0$. 3500 trajectories is insufficient to sample these rare trajectories. At these values of $\ln[N_\alpha/N_{\alpha-1}]$, having a value of the dissipation function, $\Omega_\alpha$, at time $t$ within the range $\alpha \pm da$, are constructed from over 3500 particle trajectories and shown in figure 3. Figures 3(a)–(c) show the dissipation function for ‘capture’ where the trapping constant changes from $k_0$ to $k_1$ and the dissipation function per trajectory at time $t$ is evaluated from $\Omega_\alpha = \frac{1}{4}(k_0 - k_1)[q^2(t) - q^2(0)]$. Figures 3(d)–(f) show the dissipation function for ‘release’ where the trapping constant changes from a high value of $k_1$ to a lower value $k_0$ and $\Omega_\alpha = \frac{1}{4}(k_1 - k_0)[q^2(t) - q^2(0)]$ for each trajectory at time $t$. In figures 3(a) and (d), corresponding to data recorded only 2 ms after the change in the optical trap constant, the histogram is approximately symmetric about zero with only a slightly larger number of trajectories having a dissipation function with positive values. The range of values of $\Omega_\alpha$ in figure 3(a) is wider (and more sparsely populated) than that shown in figure 3(d): this reflects that under an initially weaker trap strength, there is a wider distribution of values of $q(0)$ than when the trap strength is initially high and is lowered as in the case of figure 3(d). The number of trajectories with a positive dissipation function increases with time for both $k_0$ to $k_1$ and $k_1$ to $k_0$. Figures 3(b) and (e) show the histograms after 20 ms, i.e. only a fraction of the characteristic.
relaxation time, has elapsed. Here you can see that the number of trajectories with $\Omega > 0$ have increased and that the distribution of $\Omega$ tends to be more asymmetric. Figures 3(c) and (f) show distributions of $\Omega$ evaluated 200 ms after the discontinuous change in $k$, corresponding to trajectories of duration comparable to the characteristic relaxation time of the new trap strength: 200 ms is of the order of the characteristic relaxation time for trajectories in figures 3(c) and twice that for trajectories in figures 3(f). These distributions remain unchanged for $\Omega$ evaluated over trajectories of duration $t > 200$ ms, indicating that the system (particle + trap) has relaxed to a new equilibrium distribution.

The FT plots in figure 4 show $\ln\left(\frac{N_0}{N_a}\right)$ plotted vs $\Omega = a$, where $N_a$ is the number of trajectories where $\Omega = a \pm \Delta a$ and $N_{-a}$ is the number of trajectories, where $\Omega = -a \pm \Delta a$, as calculated from the respective histograms in figure 3. Figures 4(a)–(c) are constructed from figures 3(a)–(c), i.e. from trajectories of a ‘captured’ individual particle in viscoelastic solvent as the trap strength is changed discontinuously from $k_0$ to $k_1$. Figures 4(d)–(f) are constructed from figures 3(d)–(f), i.e. from trajectories of a ‘released’ individual particle in viscoelastic solvent as the trap strength is changed discontinuously from $k_1$ to $k_0$. The line in each of these figures corresponds to the prediction of the fluctuation theorem, equation (1). In all but figure 4(a), the experimental data from 3500 trajectories matches the FT prediction over a significant range of $\Omega$. Note that trajectories that possess a large value of the dissipation function, say $\vert \Omega \vert > 4$, have not been sampled within the 3500 trajectories, i.e. either $N_0 = 0$ or $N_{-a} = 0$, or ‘null’ sampling, for $\Omega = a > 4$. Moreover, the data points associated with the largest value of $\Omega$, for which $N_0 < 0$ and $N_{-a} > 0$ is usually displaced from the FT prediction. These ‘fringe’ points are interspersed amongst ‘null’ samples (open points) and represent dissipation functions $\Omega = a$ that are rarely sampled, or $N_a \sim \mathcal{O}(1)$ as shown in figure 3. Consequently, these fringe points usually have a value of $\ln\left[\frac{N_0}{N_{-a}}\right]$ that is offset from the FT prediction. Increasing the sample size, or number of trajectories sampled, would reduce the statistical error of these ‘fringe’ points, bringing them closer to the FT prediction, but may also populate a point that was ‘null’ in the smaller sample size. For each figures 4(a)–(f)), there is a range of $\Omega$, centred on $\Omega = 0$, over which the FT prediction is demonstrated. These ranges of $\Omega$ are also represented statistically in the histograms of figure 3(a)–(f)) and coincide with the evolution of the histograms in time. Figure 4(a) shows the smallest range of $\Omega$ over which the FT is demonstrated: $-1 < \Omega_1 < 1$, consistent with the description of the corresponding histogram, figure 3(a).

Figure 5 shows $\langle \Omega \rangle$, i.e. the average dissipation function, accumulated to time $t$ after the instantaneous change in trap strength, versus time, $t$, for (a) capture ($k_0 \rightarrow k_1$, $k_1 > k_0$) and (b) release ($k_1 \rightarrow k_0$). The points correspond to averages accumulated over 3500 trajectories of the colloidal particle in the viscoelastic solution and the lines correspond to the predicted values of $\langle \Omega \rangle$ for a purely viscous solution, as determined from the Langevin equation with uncorrelated Gaussian noise and identical trapping constants. As demonstrated previously, the results of the capture experiment accomplished in pure water are nearly identical to the predictions of the Langevin equation. It is clear that the elastic component of the suspending polymer solution has a marked effect upon $\langle \Omega \rangle$ for both capture and release. In the long time limit, $\langle \Omega \rangle$, is independent of solvent (i.e. whether viscoelastic or purely viscous), independent of path (i.e. whether the particle is captured or released) and approaches the average long time limit value of $\lim_{t \rightarrow \infty} \langle \Omega \rangle = 0.26$ predicted by equation (40).

5. Conclusions

In this paper we reviewed the fluctuation theorems of Evans & Searles and Crooks and an optically trapping experiment that demonstrates these theorems. First, we showed that the arguments of the theorems, the dissipation function, $\Omega$ and the work done by the external field, $W$ do not
explicitly depend upon the exchange of heat between system and surroundings. This is not to say that $\Omega$ and $W$ are independent of $\dot{Q}$ as heat exchange will determine the system's trajectory, over which these energies are accumulated. This is a very convenient result and quite necessary for the application of the FTs to small experimental systems where it is difficult to isolate the system from surroundings, control the heat exchange between system and surrounding, or even define and measure the temperature of the small system. Experimentally, it is only necessary to know the temperature of the surroundings with which the system is in initial equilibrium and to record the trajectories of the system in response to the applied external field. Second, we showed that in addition to the similarities in form and arguments of the FTs, the Crooks' & Evans–Searles' FTs can be applied to the same set of non-equilibrium trajectories; specifically, the set of trajectories of a colloidal particle localized in an optical trap whose strength is changed discontinuously. The Crooks’ FT is shown to be trivially satisfied in this experiment. Our previous optical trap experiments used a colloidal particle suspended in a purely viscous solvent, i.e. a system whose dynamics are accurately described by the Langevin equation with uncorrelated Gaussian noise [5, 19]. Recently a derivation of Evans–Searles’ FT from the Langevin equation was given [15], confirming these experimental results. However, the deterministic derivation of the FT shows that the theorem applies more generally, to systems whose dynamics are more complex than the Langevin equation with white noise. Consequently, we presented here an optical trapping experiment using a colloidal particle suspended in a viscoelastic solvent. The dynamics of the particle can be cast in stochastic form but with time-correlated noise and the FT has not been derived from such an equation of motion. Thus the experimental demonstration of the FTs in viscoelastic solvents, presented here, represents the first experimental confirmation with a system involving complex dynamics.

References