Stationary and Transient Work-Fluctuation Theorems for a Dragged Brownian Particle

R. van Zon and E.G.D. Cohen

The Rockefeller University, 1230 York Avenue, New York, New York 10021
(Dated: December 12, 2002)

Abstract

Recently Wang et al. carried out a laboratory experiment, where a Brownian particle was dragged through a fluid by a harmonic force with constant velocity of its center. This experiment confirmed a theoretically predicted work related integrated (I) Transient Fluctuation Theorem (ITFT), which gives an expression for the ratio for the probability to find positive or negative values for the fluctuations of the total work done on the system in a given time in a transient state. The corresponding integrated stationary state fluctuation theorem (ISSFT) was not observed. Using an overdamped Langevin equation and an arbitrary motion for the center of the harmonic force, all quantities of interest for these theorems and the corresponding non-integrated ones (TFT and SSFT, resp.) are theoretically explicitly obtained in this paper. While the (I)TFT is satisfied for all times, the (I)SSFT only holds asymptotically in time. Suggestions for further experiments with arbitrary velocity of the harmonic force and in which also the ISSFT could be observed, are given. In addition, a non-trivial long-time relation between the ITFT and the ISSFT was discovered, which could be observed experimentally, especially in the case of a resonant circular motion of the center of the harmonic force.
I. INTRODUCTION

Fluctuations of physical properties of statistical mechanical systems were first considered, in the modern context of dynamical Hamiltonian or dissipative systems theory, by Evans, Cohen and Morriss [1]. It concerned here the statistics of phase space contraction or entropy production fluctuations over a certain time interval. In particular, the probabilities for equal positive or negative entropy production fluctuations of a certain magnitude were considered. Two different physical situations have been treated. First, in Ref. [1], for a non-equilibrium stationary state, possibly far from equilibrium, the fluctuations of the dissipative (viscous) part of the pressure tensor of a fluid were studied. Next, Evans and Searles [2] studied the fluctuations of entropy production in an ensemble of phase space trajectories emanating from an initial equilibrium state in the course of time. While the first case concerned a study of stationary state fluctuations in trajectory segments of a given duration along a single trajectory in a non-equilibrium stationary state and will be called the Stationary State Fluctuation Theorem (SSFT), the second case involved a study of an ensemble of many transient phase space trajectories each over a time $\tau$, all emanating from an equilibrium ensemble at time $t = 0$, which will be called a Transient Fluctuation Theorem (TFT).

Mathematical proofs have been given of both theorems [2, 3, 4, 5] and many computer simulations have confirmed both theorems (e.g. [1, 2, 5]). While the original proofs of both FT’s were based on the deterministic dynamics of many particles, later proofs for systems with stochastic dynamics were given by Kurchan [6] and Lebowitz and Spohn [7]. Only one laboratory experiment had been carried out for the SSFT [8] and none for the TFT, until recently by Wang et al. [9].

All deterministic theories were concerned with systems in phase space consisting of many particles. The experiment of Wang et al. was carried out for a single Brownian particle which was dragged by means of a uniformly moving harmonic potential generated by a laser through a many particle molecular solvent. This system differs in an important aspect from the many particle systems in the phase space considerations. This is due to the fact that the (mesoscopic) Brownian particle is much heavier than the surrounding fluid particles, which makes it tractable in a different, much simpler though approximate, way from the full dynamical systems treatment in phase space mentioned above. In fact, the treatment generally applied to such systems is via a Langevin equation for the stochastic motion of the Brownian particle in a medium in real space, which is characterized only by its friction with the particle and its temperature. As a consequence the very complicated many particle problem can be treated by a single particle Langevin equation, if it is near equilibrium and on the level of Irreversible Thermodynamics [10].

However, for the investigation of the Fluctuation Theorems, an additional difficulty is that the experiment considered here, uses a time dependent force on the particle, since the Langevin equation contains a laser-induced harmonic force on the particle, where the position of the minimum of the harmonic potential changes in time. As a consequence, the treatments in Refs. [3] and [4] do not directly apply to this experiment.

Furthermore, the phase space treatments of dynamical systems have always been such that (at least if the total energy of the system is kept constant) the total phase space contraction can be directly related to the total entropy production of the system. This has led to the TFT [2, 5] and the SSFT [1, 3, 4] for the entropy production. To be sure, this connection between phase space contraction and entropy production can only be made if the total work done on the system is purely dissipative. However, in the Wang et al.
experiment, this is not so.

To see this, it is useful to consider the total (tot) work \( W_{\tau}^{tot} \) done on the system during a time \( \tau \):

\[
W_{\tau}^{tot} = \int_0^\tau dt \, v_t^* \cdot F(x_t, x_t^*),
\]

where

\[
F(x_t, x_t^*) = -k(x_t - x_t^*). \tag{2}
\]

is the harmonic force exerted on the particle, with \( x_t \) the position of the particle and \( x_t^* \) the position of the minimum of the harmonic potential, and \( k \) the force constant of this potential. Furthermore, in Eq. (1) \( v_t^* \equiv \dot{x}_t^* \).

At \( t \leq 0 \), in the Wang experiment, the center of the harmonic potential is at rest at \( x_0^* = 0 \). At \( t = 0 \), the harmonic potential is set in motion relative to the fluid with a constant velocity \( v^* \), so that \( x_t^* = v^* t \) for \( t \geq 0 \).

The crucial question is now what is the dissipative part of \( W_{\tau}^{tot} \) which is responsible for the heat or entropy produced in the system as a result of the friction of the particle with the surrounding fluid. The dissipative part should not include any purely mechanical work. To see how \( W_{\tau}^{tot} \) is related to the dissipated work over a time \( \tau \), we rewrite the total work done, \( W_{\tau}^{tot} \) in Eq. (1), as follows

\[
W_{\tau}^{tot} = \int_0^\tau dt \, v_t^* \cdot F(x_t, x_t^*)
\]

\[
= -\int_0^\tau dt \, (v_t - v_t^*) \cdot F(x_t, x_t^*) + \int_0^\tau dt \, v_t \cdot F(x_t, x_t^*)
\]

\[
= k \int_0^\tau dt \, (x_t - x_t^*) \cdot (x_t - x_t^*) + \int_0^\tau dt \, v_t \cdot F(x_t, x_t^*)
\]

\[
= \Delta U + W_{\tau}^{Br}, \tag{3}
\]

defining \( \Delta U \equiv \frac{k}{2} [||\Delta x_t||^2 - ||\Delta x_0||^2] \) with \( \Delta x_t = x_t - x_t^* \), and

\[
W_{\tau}^{Br} \equiv \int_0^\tau dt \, v_t \cdot F(x_t, x_t^*). \tag{4}
\]

Here, \( W_{\tau}^{Br} \) is the work done on the Brownian (Br) particle by the harmonic force. As (at least ideally) the Brownian particle has no internal energy, all this work is converted into heat, which is the source of the entropy production. Hence, \( W_{\tau}^{Br} \) is the dissipated work. On the other hand, the term \( \Delta U \) in Eq. (3) represents the purely mechanical (“center of mass”) work done on the particle in the external harmonic potential.

Therefore, Wang et al.’s entropy production during time \( \tau \), denoted by \( \Sigma_\tau \) in Ref. [9], is really the total dimensionless work done on the system, and we will denoted it by

\[
W_\tau = \beta W_{\tau}^{tot} = \beta \int_0^\tau dt \, v_t^* \cdot F(x_t, x_t^*), \tag{5}
\]

where \( \beta \equiv 1/(k_B T) \), with \( k_B \) Boltzmann’s constant and \( T \) the temperature of the surrounding fluid. By following the position of many, independent Brownian particles and using Eqs. (2) and (3), Wang et al. measured this dimensionless work \( W_\tau \) — or what they called the entropy production \( \Sigma_\tau \) — over time intervals \( \tau \) and constructed from that the probability distribution function \( P(W_\tau) \), which they found satisfies

\[
\frac{P(W_\tau)}{P(-W_\tau)} = e^{W_\tau}. \tag{6}
\]
So they established experimentally the validity of a TFT for the total work done on the system ($\beta W^\text{tot}_\tau$), rather than for the entropy production of the system. Strictly speaking, Wang et al. measured an integrated variant (an ITFT) of the TFT in Eq. (3), explained in Sec. III. A direct transformation of the TFT (3) for $W_\tau$ to a TFT for the dimensionless entropy production, which would be $\beta W^{Br}_\tau$, is not obvious, since $\Delta U$ in Eq. (3) fluctuates also.

We remark that Mazonka and Jarzynski[12] studied the same system as used in the experiment of Wang et al. theoretically — before the experiment — and derived the TFT and the SSFT for the total work done on the system, but not for the entropy production[13].

Unaware of Mazonka and Jarzynski’s work, but in view of the experiment of Wang et al., we studied this experiment independently[14]. For, Wang et al.’s experiment is clearly important for practical purposes, since it involves a general property of the work done on a system. We discuss the observability of the work related TFT as well as SSFT for an arbitrary rather than a uniform motion of the harmonic potential. So, for the purpose of treating the experiment and its generalizations, in this paper we too will treat the TFT and SSFT for the dimensionless work, with a focus on the feasibility to do a convincing SSFT experiment. To the best of our knowledge, no Fluctuation Theorem for entropy production, either an (I)TFT or an (I)SSFT, has been derived for a Wang-type system, neither from a phase space perspective nor in real space (via a Langevin equation).

The outline of the paper is as follows. In Sec. II we present our Langevin model and we develop the general theory for the verification and the experimental observability of the work related fluctuation theorems, and discuss a new relation between the fluctuations in the transient and in the stationary state. In Sec. III we specialize the general theory to the case of a linear and a circular motion of the minimum of the harmonic potential, investigating in detail the observability of the ITFT and the ISSFT. In Sec. IV we end with a discussion.

II. THEORY

A. Definition of the Model

Like in the experiment of Wang, the model we consider has a spherical Brownian particle in three dimensions with a radius $R$ and mass $m$ in a fluid with viscosity $\eta$ and temperature $T$ and the Brownian particle is subject to an external harmonic potential with a time dependent position $x^*_t$ of its minimum. For $t \leq 0$ the minimum of the harmonic potential is at the origin, $x^*_t = 0$, whereas for $t > 0$ it moves with a velocity $v^*_t$, which can be, in principle, an arbitrary function of time. The equations of motion for the particle are then of the Langevin-type:

$$\dot{x}_t = v_t \quad (7a)$$
$$m\dot{v}_t = -\alpha v_t - k(x_t - x^*_t) + \zeta_t, \quad (7b)$$

where $x_t$ and $v_t$ are the position and velocity of the Brownian particle, respectively. In this equation, the Brownian particle feels three forces. The first force is the drag force $-\alpha v_t$, with according to Stokes’ law

$$\alpha = 6\pi\eta R. \quad (8)$$
The second force is due to the harmonic potential [see Eq. (2)]. The third and last force is a random force \( \zeta_t \), which is taken to be Gaussian and delta-correlated in time:

\[
\langle \zeta_t \rangle = 0; \quad \langle \zeta_t \zeta_s \rangle = 2k_B T \alpha \delta(t - s),
\]

The strength of the random force in Eq. (9) is such that the equilibrium distribution function \( p_{eq} \) for \( x \) and \( v \)

\[
f_{eq}(x, v) = \left( \frac{\beta \sqrt{k m}}{2\pi} \right)^3 e^{-\beta \left( \frac{1}{2} m v^2 + \frac{1}{2} k |x|^2 \right)},
\]

is stationary under the equations of motion Eqs. (7a-b). The system will only be considered in the strongly overdamped case

\[
m k \ll \alpha^2.
\]

Effectively therefore, the mass can be seen as a small parameter and will be set equal to zero. From Eqs. (7a-b), we find then a simplified Langevin equation for the position of the particle only

\[
\dot{x}_t = -\tau_r^{-1}(x_t - x^*_t) + \alpha^{-1} \zeta_t,
\]

with a relaxation time

\[
\tau_r = \frac{\alpha}{k}.
\]

When we only use \( x_t \), the equilibrium distribution in Eq. (10) reduces to

\[
p_{eq}(x) = \int d v f_{eq}(x, v) = (k/\beta/2\pi)^{3/2} e^{-\beta k |x|^2}.
\]

It is convenient to separate the average motion of the Brownian particle (which results from the deterministic forces alone), from the stochastic motion. The average motion is given by the solution \( y^*_t \) of the deterministic part of the Langevin equation (12), i.e., by

\[
\dot{y}^*_t = -\tau_r^{-1}(y^*_t - x^*_t).
\]

with initial condition \( y^*_0 = 0 \). We can then look at the deviations from this average motion by introducing the transformation

\[
X_t = x_t - y^*_t.
\]

This turns the Langevin equation (12) into the simple form

\[
\dot{X}_t = -\tau_r^{-1} X_t + \alpha^{-1} \zeta_t.
\]

\( y^*_t \) follows from the general solution of Eq. (15):

\[
y^*_t = e^{-t/\tau_r} y^*_0 + \tau_r^{-1} \int_0^t dt' e^{-(t - t')/\tau_r} X_{t'}.
\]
so that with \(y_0^* = 0\), and a partial integration, one obtains

\[
y_t^* = x_t^* - \int_0^t dt' e^{-(t-t')/\tau_r} v_t^*.
\]  

(19)

The transformation (16) with Eq. (19) can be interpreted as going to a co-moving frame, but it is not co-moving with the minimum of the harmonic potential, but with \(y_t^*\) which is what the motion of a particle starting at \(x_0^* = 0\) would be if there would be no noise term in the Langevin equation (12).

Eq. (17) shows that in the co-moving frame, one has the standard Ornstein-Uhlenbeck process[15, 16]. Its solutions are well-known. The Green’s function of the Ornstein-Uhlenbeck process, which gives the probability for the particle to be at \(X_1\) at time \(t_1\), given that it was at \(X_0\) at time \(t_0\), is Gaussian in both \(X_0\) and \(X_1\). Its stationary solution is of the form \(p_{eq}(X)\), with \(p_{eq}\) given in Eq. (14). Initially the particle is distributed according to Eq. (14), but because \(X_0 = x_0 (y_0^* = 0)\), one sees that the initial distribution is already the stationary one, and in this special, co-moving coordinate frame, the distribution of the Brownian particle has an equilibrium distribution for all time:

\[
P(X, t) = (\beta k/2\pi)^{3/2} e^{-\beta k |X|^2/2}.
\]  

(20)

We end this section by writing \(W_\tau\) in Eq. (5) in terms of \(X_t\),

\[
W_\tau = -k\beta \int_0^\tau dt \left[ v_t^* \cdot X_t + v_t^* \cdot (y_t^* - x_t^*) \right].
\]  

(21)

**B. Transient Fluctuation Theorem for the Total Work**

In Eq. (21), \(W_\tau\) is a linear function of \(X_t\). Combined with the Gaussian nature both of the Green’s function of the Ornstein-Uhlenbeck process [Eq. (17)] and of the initial distribution[Eq. (20)], this means that the distribution \(P_T\) of \(W_\tau\) is Gaussian

\[
P_T(W_\tau) = \frac{e^{-\frac{(W_\tau - M_T(\tau))^2}{2V_T(\tau)}}}{\sqrt{2\pi V_T(\tau)}},
\]  

(22)

where the subscript \(T\) denotes that the transient case is considered. The mean \(M_T\) of \(W_\tau\) is, from Eq. (21),

\[
M_T(\tau) = -k\beta \int_0^\tau dt v_t^* \cdot (y_t^* - x_t^*),
\]  

(23)

since \(\langle X_t \rangle = 0\) [Eq. (20)]. Using the expression for \(y_t^*\) in Eq. (19), this can be also written as

\[
M_T(\tau) = k\beta \int_0^\tau dt_2 \int_0^{t_2} dt'_1 e^{-(t_2 - t'_1)/\tau_r} v_{t_2}^* \cdot v_{t_1}^*.
\]  

(24)

The variance \(V_T\) of \(W_\tau\) is only affected by the first term in Eq. (21), so that

\[
V_T(\tau) = \langle (W_\tau - \langle W_\tau \rangle)^2 \rangle = 2k^2 \beta^2 \int_0^\tau dt_2 \int_0^{t_2} dt'_1 v_{t_2}^* \cdot \langle X_{t_2} X_{t'_1} \rangle \cdot v_{t'_1}^*,
\]  

(25)
where we used the symmetry of the time-correlation function \( \langle X_{t_1} X_{t_2} \rangle \) under interchange of \( t_1 \) and \( t_2 \). To calculate this function, notice that \( X_t \) has a stationary distribution so it can be written as \( \langle X_{t - t'} X_0 \rangle \). Using the formal solution of the Langevin equation in the co-moving frame [Eq. (17)] for \( t > 0 \),

\[
X_t = e^{-t/\tau} X_0 + \alpha^{-1} \int_0^t dt' e^{-(t-t')/\tau} \zeta_t,
\]

one obtains with \( \langle \zeta_t \rangle = 0 \), \( \langle X_0 \rangle = 0 \), \( \langle \zeta_t X_0 \rangle = 0 \) and \( \langle X_0 X_0 \rangle = [k\beta]^{-1} \mathbb{1} \),

\[
\langle X_t X_0 \rangle = [\beta k]^{-1} e^{-t/\tau} \mathbb{1}.
\]

(27)

The variance in Eq. (25) then becomes

\[
VT(\tau) = 2k\beta \int_0^\tau dt_2 \int_0^{t_2} dt_1 e^{-(t_2-t_1)/\tau} v_{t_2}^* \cdot v_{t_1}^*.
\]

(28)

Comparing with the mean in Eq. (24), we see

\[
VT(\tau) = 2MT(\tau).
\]

(29)

This relation leads straightforwardly to the TFT: Given the distribution function of \( W_\tau \) in Eq. (22), one easily shows that

\[
\frac{PT(W_\tau)}{PT(-W_\tau)} = e^{\frac{2MT(\tau)W_\tau}{VT(\tau)}},
\]

(30)

which, by Eq. (29), becomes

\[
\frac{PT(W_\tau)}{PT(-W_\tau)} = e^{W_\tau},
\]

(31)

which is identical to the TFT in Eq. (1).

C. Stationary State Fluctuation Theorem for the Total Work

To move on to the SSFT, it is necessary to clarify what the stationary state means, since in the \( X \) coordinate system, the distribution is stationary, which would suggest that the TFT is also the SSFT. This is not the case. If one defines a stationary state as that state in which (on average) the physical (macroscopic) parameters do not change, then the time-independence of the distribution of \( X \) is not enough because \( X \) involves, through its definition Eq. (16), a time-dependent transformation from the laboratory frame, in which the physical parameters are measured, so that they would still depend on time. Only when these parameters have become stationary can one say that the system is stationary.

The SSFT was originally formulated for the average entropy production fluctuations on trajectory segments of length \( \tau \) along a single trajectory in the stationary state. Here we consider the statistics of the total work done on the system over time \( \tau \), divided by \( k_B T \),

\[
W_\tau = \beta \int_{t_1}^{t_1+\tau} dt v_t^* \cdot F(x_t, x_t^*),
\]

(32)
for a sequence of initial times \( t_i \) of segments, all of length \( \tau \), along a single stationary state trajectory \((i = 1, 2, 3, \ldots)\). To get the distribution of \( W_\tau \) of the segments along a trajectory, we use the following reasoning. According to the Eqs. (4) (for the force) and (11) (the definition of \( X \)), the expression in Eq. (32) is linear in \( W_\tau \) (just as in the transient case) and \( \text{as } X_t \) obeys the Langevin equation (17) we still have a Gaussian Green’s function and a Gaussian stationary state, so that the distribution of \( W_\tau \) for each \( t_i \) is again Gaussian:

\[
P_{t_i}(W_\tau) = \frac{e^{-\frac{|W_\tau - M_{t_i}(\tau)|^2}{2V_{t_i}(\tau)}}}{\sqrt{2\pi V_{t_i}(\tau)}},
\]

with the mean and the variance given by, respectively:

\[
M_{t_i}(\tau) = -k\beta \int_{t_i}^{t_i+\tau} dt \mathbf{v}_i^* \cdot (\mathbf{y}_i^* - \mathbf{x}_i^*),
\]

\[
V_{t_i}(\tau) = 2k\beta \int_{t_i}^{t_i+\tau} dt \int_{t_i}^{t_i+\tau} dt' \mathbf{v}_i^* \cdot \mathbf{v}_i^* e^{-|t_i - t'|/\tau}. \tag{34}
\]

We assume that for sufficiently large \( t_i \), \( M_{t_i} \) and \( V_{t_i} \) will reach steady state values (see Sec. III for examples), and become independent of \( i \). If in addition, the correlation between different segments \([t_i, t_i + \tau] \) and \([t_j, t_j + \tau] \), say) decays sufficiently fast (when \(|t_i - t_j| \) gets larger), then the distribution of \( W_\tau \) along a trajectory in the stationary state is given by:

\[
P_S(W_\tau) = \frac{e^{-\frac{|W_\tau - M_S(\tau)|^2}{2V_S(\tau)}}}{\sqrt{2\pi V_S(\tau)}}, \tag{36}
\]

Here the subscript \( S \) denotes that this distribution refers to the distribution of \( W_\tau \) over segments along the stationary state trajectory. The mean \( M_S \) is, from Eq. (34) and using Eq. (19), given by:

\[
M_S(\tau) = \lim_{t \to \infty} k\beta \int_{t}^{t+\tau} dt' \int_{t}^{t+\tau} dt' e^{-|t_i - t'|/\tau} \mathbf{v}_{i_2}^* \cdot \mathbf{v}_{i_1}^*, \tag{35}
\]

while the variance \( V_S \) is, from Eq. (35), given by

\[
V_S(\tau) = \lim_{t \to \infty} 2k\beta \int_{t}^{t+\tau} dt' \int_{t}^{t+\tau} dt' e^{-|t_i - t'|/\tau} \mathbf{v}_{i_2}^* \cdot \mathbf{v}_{i_1}^*. \tag{37}
\]

Note that in the inner most integral in the expression for the mean in Eq. (37), the lower bound extends to time zero, whereas in the expression for the variance in Eq. (38), it extends to \( t \). This is the origin of the fact that \( V_S \) and \( 2M_S \) are not identical [while \( V_T = 2M_T \), Eq. (29)]. The deviation can be characterized by

\[
\varepsilon(\tau) \equiv \frac{2M_S(\tau) - V_S(\tau)}{2M_S(\tau)} \tag{39}
\]

Using this definition and Eq. (36), one sees that

\[
\frac{P_S(W_\tau)}{P_S(-W_\tau)} = \exp \left\{ \frac{W_\tau}{1 - \varepsilon(\tau)} \right\}. \tag{40}
\]
This means that provided that

$$\varepsilon(\tau) \to 0 \text{ as } \tau \to \infty,$$

we have

$$V_S(\tau) \to 2M_S(\tau) \text{ as } \tau \to \infty,$$

and the SSFT holds

$$\frac{P_S(W_\tau)}{P_S(-W_\tau)} \to e^{W_\tau} \text{ as } \tau \to \infty.$$  

Of course, for any given \(v_*^t\), Eq. (41) can be tested, but how general can we expect it to be satisfied? We write thereto Eq. (39) with Eqs. (37) and (38) as:

$$\varepsilon(\tau) = \lim_{t \to \infty} k\beta \int_t^{t+\tau} dt' \int_0^t dt' \cdot v_*^t e^{-(t'_2-\cdot t'_1)/\tau}$$

$$= \lim_{t \to \infty} k\beta (x_*^t - y_*^t) \int_0^\tau dt' e^{-t'_2/\tau} v_*^t,$$

where Eq. (19) has been used. Here, the denominator is the total work done of the system in the stationary state in time \(\tau\). If we are not in equilibrium, this is positive and grows with \(\tau\). In the numerator, the exponential in the integral will make the integral bounded for large \(\tau\), provided that \(v_*^t\) does not grow exponentially in time with an exponent bigger than \(\tau^{-1}\). Then \(\varepsilon\) will become zero \(\propto 1/\tau\) as \(\tau\) approaches infinity, and the SSFT in Eq. (43) holds.

**D. Integrated Fluctuation Theorems**

In experiments such as done by Wang et al. [9], it is easier to check an integrated fluctuation theorem [17], because it is easier to obtain then good statistics for the required quantities. The Integrated Transient Fluctuation Theorem (ITFT) reads

$$\frac{P_T(W_\tau < 0)}{P_T(W_\tau > 0)} = \langle e^{-W_\tau} \rangle_+^T,$$

where the left hand side is the quotient of the probabilities to see a negative resp. a positive total work \(W_\tau\) after a time \(\tau\):

$$P_T(W_\tau < 0) = \int_{-\infty}^0 dW_\tau P_T(W_\tau)$$

$$P_T(W_\tau > 0) = 1 - P_T(W_\tau < 0)$$

and the right hand side of Eq. (45a) is the average of \(\exp(-W_\tau)\) over positive \(W_\tau\), i.e.,

$$\langle e^{-W_\tau} \rangle_+^T = \frac{\int_0^\infty dW_\tau P_T(W_\tau) e^{-W_\tau}}{\int_0^\infty dW_\tau P_T(W_\tau)}.$$
The ITFT of Eq. (45a) can be derived from the TFT in Eq. (31) by first rewriting $P_T(W_τ < 0) = \int_{-\infty}^{0} dW_τ P_T(W_τ)$ as
\[
\int_{-\infty}^{0} dW_τ P_T(W_τ) = \int_{-\infty}^{0} dW_τ P_T(-W_τ)e^{W_τ} = \int_{0}^{\infty} dW_τ P_T(W_τ)e^{-W_τ},
\]
and then dividing by $P_T(W_τ > 0)$.

An Integrated Stationary State Fluctuation Theorem (ISSFT) can also be derived, but it is a little more subtle. Thereto, one has to consider whether
\[
\frac{P_S(W_τ < 0)}{P_S(W_τ > 0)} \xrightarrow{τ \to \infty} \langle e^{-W_τ} \rangle^+_S
\]
holds, where
\[
P_S(W_τ < 0) \equiv \int_{-\infty}^{0} dW_τ P_S(W_τ) \tag{47b}
\]
\[
P_S(W_τ > 0) \equiv 1 - P_S(W_τ < 0), \tag{47c}
\]
and
\[
\langle e^{-W_τ} \rangle^+_S \equiv \frac{\int_{0}^{\infty} dW_τ P_S(W_τ)e^{-W_τ}}{\int_{0}^{\infty} dW_τ P_S(W_τ)}. \tag{47d}
\]
To start the derivation of the ISSFT of Eq. (47a), the numerator of Eq. (47d) is rewritten, using Eq. (40), as
\[
\int_{0}^{\infty} dW_τ P_S(W_τ)e^{-W_τ}
= \int_{0}^{\infty} dW_τ P_S(-W_τ)e^{W_τ} \exp \left\{ \frac{\varepsilon(τ) W_τ}{1 - \varepsilon(τ)} \right\} 
= \int_{-\infty}^{0} dW_τ P_S(W_τ) \exp \left\{ -\frac{\varepsilon(τ) W_τ}{1 - \varepsilon(τ)} \right\} 
= \int_{-\infty}^{0} \exp \left\{ -\frac{[W_τ - M_S(τ)]^2}{2V_S(τ)} - \frac{\varepsilon(τ) W_τ}{1 - \varepsilon(τ)} \right\} \sqrt{\frac{2\pi V_S(τ)}{2V_S(τ)}} \tag{48}
\]
where Eq. (30) was used. We saw that the SSFT holds if $\varepsilon \to 0$ for large $τ$. Consider the exponent in Eq. (48). Writing out the square, this has a term linear in $W_τ$ of the form:
\[
\left[ \frac{M_S(τ)}{V_S(τ)} - \frac{\varepsilon(τ)}{1 - \varepsilon(τ)} \right] W_τ = \frac{M_S(τ)}{V_S(τ)}[1 - 2\varepsilon(τ)]W_τ. \tag{49}
\]
As $τ \to \infty$, we can neglect $\varepsilon$ compared to 1. Since this is the only place where $\varepsilon$ occurs, we can set $\varepsilon$ equal to zero on the right hand side of Eq. (48), which then becomes $P(W_τ < 0)$. Dividing by $P(W_τ > 0)$ on both sides in Eq. (48) now yields the ISSFT in Eq. (47a).
For the purpose of the investigation of the observability of the fluctuation theorems, discussed in Sec. III, we end this section by giving the explicit forms of the left and right hand sides of the integrated fluctuation theorems Eq. (45a) and Eq. (47a). Defining

\[ L_T(\tau) \equiv \frac{P_T(W_\tau < 0)}{P_T(W_\tau > 0)}; \quad R_T(\tau) \equiv \langle e^{-W_\tau} \rangle_T^+; \quad (50a) \]

\[ L_S(\tau) \equiv \frac{P_S(W_\tau < 0)}{P_S(W_\tau > 0)}; \quad R_S(\tau) \equiv \langle e^{-W_\tau} \rangle_S^+; \quad (50b) \]

the TFT states that \( L_T = R_T \), and the SSFT that \( L_S = R_S \) (the latter for large \( \tau \) only). Using Eqs. (22), (36) and (45a), we get the following explicit expressions:

\[ L_T(\tau) = R_T(\tau) \quad (51a) \]

\[ R_T(\tau) = \frac{1 - \text{erf} \left( \frac{M_T(\tau)}{\sqrt{2V_T(\tau)}} \right)}{1 + \text{erf} \left( \frac{M_T(\tau)}{\sqrt{2V_T(\tau)}} \right)} \quad (51b) \]

\[ L_S(\tau) = \frac{1 - \text{erf} \left( \frac{M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)}{1 + \text{erf} \left( \frac{M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)} \quad (51c) \]

\[ R_S(\tau) = e^{\frac{V_S(\tau) - M_S(\tau)}{2}} \frac{1 - \text{erf} \left( \frac{V_S(\tau) - M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)}{1 + \text{erf} \left( \frac{M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)} \quad (51d) \]

We can simplify the expressions for \( L_T \) and \( R_T \) using the relation between \( M_T \) and \( V_T \) in Eq. (29):

\[ L_T(\tau) = \frac{1 - \text{erf} \left( \frac{1}{2} \sqrt{M_T(\tau)} \right)}{1 + \text{erf} \left( \frac{1}{2} \sqrt{M_T(\tau)} \right)} \quad (52) \]

In order to demonstrate the difference between \( L_S \) and \( R_S \), we rewrite Eq. (51d), using Eq. (39), in terms of \( \varepsilon \) as

\[ R_S(\tau) = e^{-\varepsilon(\tau)M_S(\tau)} \frac{1 - \text{erf} \left( \frac{|1 - 2\varepsilon(\tau)|M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)}{1 + \text{erf} \left( \frac{M_S(\tau)}{\sqrt{2V_S(\tau)}} \right)} \quad (53) \]

which shows that only for \( \tau \to \infty \), \( L_S = R_S \), i.e., that the work related ISSFT holds.

E. Transient Fluctuations versus Stationary Fluctuations

An interesting relation can be derived for the ratio of the probability of a negative total work and that of a positive one, for the transient case (\( L_T \)) and the stationary case (\( L_S \)).
Using Eqs.(51a-c) and the asymptotic expansion of the error function,

\[ \text{erf}(x) = 1 - e^{-x^2/\sqrt{\pi}} [x^{-1} + O(x^{-2})], \]

one obtains

\[ \frac{L_T}{L_S} \to \sqrt{\frac{V_T}{V_S}} \frac{M_S}{M_T} e^{-\frac{M_T^2}{2V_T(\tau)} + \frac{M_S^2}{2V_S(\tau)}}. \]

Here the \( O(x^{-2}) \) in Eq. (54) could be neglected. This, because when \( \tau \to \infty \), \( M_T \) and \( M_S \) [Eqs. (24) and (37) respectively] will both grow linearly in time, \( M_T \sim M_S \sim \mathcal{O}(\tau) \) and similarly \( V_T \sim V_S \sim \mathcal{O}(\tau) \) [by Eqs. (29) and (42)], so that the arguments of the error functions in Eqs.(51b) and (51c) become large (\( \sim \sqrt{\tau} \)) for large \( \tau \). In fact, \( M_S \) and \( M_T \) will grow with the same coefficient, as the rate of work done on the system will become stationary, but they will in general have a bounded difference, i.e., \( M_S - M_T \sim \mathcal{O}(1) \), as will \( V_S \) and \( V_T \), i.e., \( V_S - V_T \sim \mathcal{O}(1) \). One therefore has, using Eq. (29) and Eq. (42), an asymptotic behavior

\[
\begin{align*}
M_T(\tau) &\to w\tau + a_1; & V_T(\tau) &\to 2w\tau + 2a_1 \\
M_S(\tau) &\to w\tau + a_2; & V_S(\tau) &\to 2w\tau + a_3
\end{align*}
\]

for \( \tau \to \infty \), where the \( a_i \) are independent of \( \tau \). \( w \) is in fact the asymptotic rate at which work is supplied to the system, i.e., the consumed power. By expanding in terms of \( 1/\tau \), we obtain for the exponent in Eq. (55):

\[
-\frac{M_T^2}{2V_T(\tau)} + \frac{M_S^2}{2V_S(\tau)} = -\frac{1}{4}a_1 + \frac{1}{2}a_2 - \frac{1}{8}a_3,
\]

i.e., it approaches a non-zero constant. The prefactor in Eq. (55) can similarly be shown to go to one as \( \tau \to \infty \), so that we have for large \( \tau \),

\[
\frac{L_T(\tau)}{L_S(\tau)} \sim e^{\frac{1}{4}a_1 + \frac{1}{2}a_2 - \frac{1}{8}a_3}
\]

where Eq. (56) has been used to re-express this ratio in terms of the means and variances of the transient, resp. stationary state. Because the right hand side of Eq. (57) is not equal to 1 in general, this shows that the ISSFT is not just the limit of the ITFT for large \( \tau \).

III. APPLICATIONS

In this section, two kinds of motion are considered for the harmonic potential. In both cases parameters will be varied to see under what conditions an experiment would be able to demonstrate the integrated work fluctuation theorems (both transient and stationary) most convincingly. The motion that will be considered first, corresponds to the situation in the experiment of Wang et al., i.e., it is a uniform linear motion. The other is a circular motion and might be implemented in a future experiment. Both approach a stationary state.

A. Linear Motion of the Harmonic Potential

The particular case considered here is a linearly moving harmonic potential, i.e., \( x_t^* = v_{opt}t\hat{x} \) for \( t \geq 0 \). The quantities with which to test the work fluctuation theorems, are given
in Eqs. (51a–d). The only unknowns are the means and variances of the transient and stationary distributions and these are given by Eqs. (24), (29), (37) and (38). If we insert $v^*_t$, which is a constant $v_{opt}$ here, into these equations, we obtain straightforwardly

$$M_T(\tau) = w \{\tau - \tau_r[1 - e^{-\tau/\tau_r}]\}$$  \hspace{1cm} (58a)$$
$$V_T(\tau) = 2M_T(\tau)$$  \hspace{1cm} (58b)$$
$$M_S(\tau) = w\tau$$  \hspace{1cm} (58c)$$
$$V_S(\tau) = V_T(\tau) = 2w \{\tau - \tau_r[1 - e^{-\tau/\tau_r}]\}$$  \hspace{1cm} (58d)

where

$$w = \alpha \beta v_{opt}^2$$  \hspace{1cm} (58e)

which can be interpreted according to Eq. (58c) as the rate of work delivered to the system per unit time. The equality between $V_S$ and $V_T$ in (58d) follows because the velocity of the center of the harmonic potential $v^*_t$ is constant, so that the integrands in Eqs. (28) and (38) only depend on the difference $t'_2 - t'_1$, and the shift over $t$ in the definition of $V_S$ is irrelevant.

By the theory presented in the Sec.II, the TFT holds for any motion of the harmonic potential, hence also in this case $L_T = R_T$. The SSFT holds if $\varepsilon$ [Eq. (39)] vanishes as $\tau \to \infty$, and this is so here, since

$$\varepsilon(\tau) = \frac{\tau_r[1 - e^{-\tau/\tau_r}]}{\tau}$$  \hspace{1cm} (59)

We now discuss the observability of the work related ITFT and the ISSFT for this model. There are only two relevant parameters for the fluctuation theorems here, the relaxation time $\tau_r$ [Eq. (13)] and the rate of dimensionless work done $w$ [Eq. (58e)]. To obtain realistic values for these parameters, orders of magnitude of various quantities can be taken from Ref. [9]. With the radius $R$ of the order of three microns, and the viscosity of water $\eta$ of the order of $10^{-3}$ kg m$^{-1}$s$^{-1}$, according to Eq. (8), $\alpha$ is of the order of $5 \times 10^{-8}$ kg/s. With $k$ of the order of $10^{-7}$ kg s$^{-2}$, $\tau_r$ becomes of the order of 0.5 s [Eq. (13)]. Furthermore, taking the temperature to be 300 K, gives $\beta$ of the order of $2.4 \times 10^{20}$ kg m$^2$ s$^{-2}$, and with $v_{opt}$ of the order of 1 $\mu$m/s, we find from Eq. (58e) that $w$ is of the order of 12 s$^{-1}$.

For the case that $w = 12$ s$^{-1}$ and $\tau_r = 0.5$ s, the expressions in Eqs. (51a–d) using Eqs. (58a–d), are plotted together in Fig. 1a. It is striking that even though we know that the ISSFT holds for sufficiently large $\tau$, this is not at all observed in the figure: the curves of $L_S$ and $R_S$ are completely different; in fact, the curve for $L_S$ is indistinguishable from the $\tau$ axis. Furthermore, both of these curves are different from $L_T$, which, given the result in Eq. (57) of Sec. [11], is less of a surprise. Clearly, the range of $\tau$ for which the ISSFT is valid lies beyond the point where both $L_S$ and $R_S$ have relaxed to zero in Fig 1a. This means that for the parameters typical of the Wang experiment, the ISSFT cannot be observed, in contrast to the ITFT, as the curve of $L_T$ can be seen clearly, and $L_T$ equals $R_T$, so that the ITFT could be observed.

The reason that there is such a big difference in the signal for the transient and the stationary case, i.e., that the negative work fluctuations are more suppressed in $L_S$ than in $L_T$, is the following. Since $M_T(0) = 0$ [Eq. (23)] in the argument of the error functions in Eq. (22), $L_T(\tau = 0) = 1$. As the function $L_T$ decays with increasing $\tau$, the question of whether it can be observed depends on whether it does not decay too quickly. On the other
FIG. 1: Integrated Fluctuation Theorems for the work for the linearly moving harmonic potential: $L_T = R_T$ [cf. Eq. (51a)], $R_S$ and $L_S$ versus $\tau$ (varying ranges) with (a) $\tau_r = 0.5$ s and $w = 12$ s$^{-1}$, (b) $\tau_r = 0.2$ s and $w = 4.8$ s$^{-1}$, (c) $\tau_r = 0.08$ s and $w = 1.92$ s$^{-1}$, and (d) $\tau_r = 0.032$ s and $w = 0.768$ s$^{-1}$ (in the last case the curves of $L_T = R_T$ and $R_S$ are indistinguishable).

hand, the argument of the error function in Eq. (51c), $M_S/\sqrt{2V_S}$ does not have a limit of zero for $\tau \to 0$. In fact, using Eqs. (58c) and (58d) and expanding in $\tau$, one finds

$$\lim_{\tau \to 0} \frac{M_S(\tau)}{\sqrt{2V_S(\tau)}} = \sqrt{\frac{w\tau_r}{2}},$$

which can be large. So with Eq. (51c), one has for $\tau \to 0$:

$$L_S(0) = \frac{1 - \text{erf}(\sqrt{\frac{w\tau_r}{2}})}{1 + \text{erf}(\sqrt{\frac{w\tau_r}{2}})}.$$  

For the case plotted in Fig. 1(a), $\sqrt{w\tau_r/2} = \sqrt{3}$, so that $L_S(0) = 7 \times 10^{-3}$. No wonder we cannot see it in Fig. 1(a). $L_S$ is exponentially suppressed for large values of $w\tau_r$, which is the average work done in the stationary state during a relaxation time $\tau_r$. As $W_{\tau} = 0$ for $\tau = 0$ for all trajectories, it follows from definition (50b) that $R_S(0) = 1$. Comparing this
FIG. 2: Illustration of the relation between transient and stationary work fluctuations [Eq. (57)], for the linearly moving harmonic potential. $L_T$ and $L_S$ are plotted logarithmically as a function of $\tau$, with $\tau_r = 0.2\text{ s}$ and $w = 4.8\text{ s}^{-1}$ [cf. Fig. (1b)]. The constant ratio in Eq. (57) becomes a constant distance between the curves in this logarithmic plot.

value with the value of $L_S(0)$ [Eq. (61)], we see that there is no chance to observe the SSFT if the work done during $\tau_r$ is too large.

Thus in order to observe the SSFT we have to reduce the work done in the time $\tau_r$. One direct way to do this is to change the particle’s radius. From Eqs. (8) and (13), we see that $\tau_r \propto R$, whereas from Eq. (58c), $w \propto R$ as well, so $w\tau_r \propto R^2$. Another way would be to reduce the velocity of the harmonic potential, which does not affect $\tau_r$, but changes $w \propto v_{opt}^2$. Choosing to work with the radius as the control parameter (partly because smaller particles than used in the Wang experiment are commercially available), we plotted in Fig. (1b–d), what happens when we make the particle 2.5 times smaller consecutively, thus reducing the work done per relaxation time each time by a factor 6.25. In first instance [Figs. (1b and 1c)] the curve of $L_S$ gets closer to the curve $R_T$, and $L_S$ starts to get visible. But only in the last graph, Fig. (1d), where the particle’s diameter is about 15 times smaller than in Fig. (1a) (which would mean $R \approx 200\text{ nm}$ in the Wang experiment), do we clearly see that $L_S$ approaches $R_S$. In this case, $w\tau_r \approx 0.02$, confirming that the work done in $\tau_r$ needs to be small to see a convincing signal of the SSFT.

Finally, we look at Eq. (57), which says that in the long $\tau$ limit, the ratio of $L_T$ and $L_S$ becomes a constant. Using Eqs. (58a–d) in this case, Eq. (57) reads

$$\frac{L_T(\tau)}{L_S(\tau)} = e^{w\tau_r/2}. \quad (62)$$

Taking $\tau_r = 0.2\text{ s}$ and $w = 4.8\text{ s}^{-1}$, we plotted $L_T$ and $L_S$ logarithmically to illustrate Eq. (62). Eq. (62) shows once more that negative fluctuations of the work are more suppressed in the stationary state than in the transient period.
B. Circular Motion of the Harmonic Potential

In the case of a circular motion of the harmonic potential, we write

\[ x_t^* = r \{ \sin(\Omega t) \hat{x} + [1 - \cos(\Omega t)] \hat{y} \}, \]  

(63)

for \( t \geq 0 \). We use the same procedure as in the previous case, i.e., we determine \( v_t^* \)

\[ v_t^* = r \Omega \{ \cos(\Omega t) \hat{x} + \sin(\Omega t) \hat{y} \}, \]  

(64)

for \( t \geq 0 \), insert this into Eqs. (24), (37) and (38), and obtain straightforwardly

\[ M_T(\tau) = w \left\{ \tau - \tau_r \frac{2\Omega \tau_r \sin(\Omega \tau) e^{-\tau/\tau_r}}{1 + \Omega^2 \tau_r^2} \right\} \]  

(65a)

\[ V_T(\tau) = 2M_T(\tau) \]  

(65b)

\[ M_S(\tau) = w \tau \]  

(65c)

\[ V_S(\tau) = V_T(\tau) = 2M_T(\tau), \]  

(65d)

where now

\[ w = \frac{\alpha \beta r^2 \Omega^2}{1 + \Omega^2 \tau_r^2}. \]  

(65e)

The expression for \( \varepsilon \) follows using its definition Eq. (39),

\[ \varepsilon(\tau) = \frac{\tau_r}{(1 + \Omega^2 \tau_r^2)\tau} \left\{ 2\Omega \tau_r \sin(\Omega \tau) e^{-\tau/\tau_r} \right\} \]  

(66)

which again vanishes like \( 1/\tau \) when \( \tau \to \infty \), so that the ISSFT holds, i.e., \( L_S = R_S \) for large \( \tau \).

Note that the Eqs. (65a-e) and (66) reproduce the Eqs. (58a-e) and (59) in the limit for \( \Omega \to 0 \), keeping \( v_{opt} = r \Omega \) constant. But these equations are not just an extension of the linear case. Under the resonance condition \( \Omega \tau_r = 1 \), \( \varepsilon \) in Eq. (56) becomes

\[ \varepsilon(\tau) = \frac{\tau_r \sin(\tau/\tau_r)}{\tau} e^{-\tau/\tau_r}, \]  

(67)

i.e., it decays exponentially, rather than \( \propto 1/\tau \) (which it does for all other choices of \( \Omega \)). In addition, in the resonance case \( \varepsilon \) is zero at times \( n \pi \tau_r \) for \( n = 1, 2, 3, \ldots \), and exponentially small (\( \sim e^{-n \pi} \)) in between; consequently, at those times, \( L_S \) and \( R_S \) are equal [Eqs. (51c) and (53)], whereas they are exponentially close in between. This means that the ISSFT holds and can be visible at much shorter time scales than in the linear case.

In Fig. 3, \( L_T = R_T \), \( L_S \) and \( R_S \) from Eqs.(51a-d) are shown for two cases, which for \( \Omega = 0 \) become identical to the cases (b) and (c) in Fig. 1. For these cases we show what
FIG. 3: Integrated Fluctuation Theorems for the work for the circular motion $L_T = R_T$ [cf. Eq. (51a)], $L_S$ and $R_S$ versus $\tau$ with (b') $\tau_r = 0.2 \text{s}$, $w = 4.8 \text{s}^{-1}$ (cf. Fig. 1b) at resonance $\Omega = 1/\tau_r$, (b'') same $\tau_r$ and $w$ but $\Omega = 5/\tau_r$, (c') $\tau_r = 0.08 \text{s}$, $w = 1.92 \text{s}^{-1}$ (cf. Fig. 1c), $R_S$ is indistinguishable from $L_T = R_T$ at resonance $\Omega = 1/\tau_r$, and (c'') same $\tau_r$ and $w$ but $\Omega = 5/\tau_r$. Note that in (b') and (c'), beyond a time $\pi \tau_r$, all curves become indistinguishable.

happens at their respective resonance points $\Omega = 1/\tau_r$ and what happens when $\Omega$ is larger, $5/\tau_r$. In varying the frequency, we keep $w$ fixed, which physically means we would have to adjust $r$ according to Eq. (65e).

From Fig. 3b', we see that at the resonant point $\Omega = 1/\tau_r$, while $L_S$ could not be seen in the $\Omega \approx 0$ case (cf. Fig. 1b), it can now be seen, but is still too small compared to $R_S$ to check the SSFT. If at $\Omega = 0$ the value of $L_S$ could be seen (Fig. 1c), then going to the resonance, improves the situation: in Fig. 3c', $L_S$ and $R_S$ approach each other after a far shorter time than in Fig. 1c, and become indistinguishable after $\tau = \pi \tau_r$, because of the exponentially small difference between them as discussed above. We remark that when the agreement is already good in the $\Omega = 0$ case (like in Fig. 1d), going to the resonance changes little. Furthermore, we see from Fig. 3 that going beyond the resonance ($\Omega = 5/\tau_r$) will cause the curves to deviate from each other again. We also note that above resonance, the work fluctuations in the stationary state are larger than those in the transient case, which
is the opposite as for the linear motion. In fact, the form Eq. (57) takes here is [using Eqs. (65a), (65c) and (65d)]

\[
\frac{L_T(\tau)}{L_S(\tau)} \xrightarrow{\tau \to \infty} \exp \left\{ \left(1 - \Omega^2 \tau_r^2 \right) \frac{w^2 \tau_r}{2} \right\},
\]

for \( \tau \to \infty \). The exponent changes sign going from \( \Omega \tau_r < 1 \) to \( \Omega \tau_r > 1 \). What is happening physically is that the system is driven so fast that it cannot relax within one cycle. This increases the fluctuations \( W_\tau \). On the basis of the foregoing, we see that in order to demonstrate the ISSFT, it helps to go to a resonant circular motion.

IV. DISCUSSION

1. Inspired by the experiment of Wang et al. [9] which showed that the work related ITFT holds when a small latex bead is dragged linearly through a fluid by means of a laser-induced harmonic force, a model of a Brownian particle in a harmonic potential with an arbitrarily moving minimum was used to study both the work related ITFT and ISSFT, under more general conditions. From the Langevin equation that describes the motion of the Brownian particle in this simple model, everything can be explicitly calculated. As expected, the work related TFT holds for all time, as does its integrated variant (ITFT). The work related SSFT and its integrated version (ISSFT) hold for sufficiently large times provided a stationary state exists.

We also found a new relation between work related ISSFT and ITFT. If one looks at the ratios for the probability to find in a time \( \tau \) a negative vs. a positive work done on the system, in the transient state \( (L_T) \) and in the stationary state \( (L_S) \), then \( L_T/L_S \) approaches a constant (which is not 1) as \( \tau \to \infty \), given by Eq. (57).

2. We have not found many choices for the motion of the harmonic potential \( (x^*_t) \) for which a stationary state exists [in the sense that the limits of Eqs. (37) and (38) exist]. There is the linear motion corresponding to the Wang et al. experiment, which has been worked out in Sec. III A and there is the possibility of a circular motion treated in Sec. III B, as well as a spiral motion, which is a trivial superposition of the previous two. However, any motion which in the course of time approaches one of these cases, will also reach a stationary state, corresponding to that case. In contrast to the simple motion of the harmonic potential considered in Sec. II, allowing for an arbitrary motion of the harmonic potential, may give rise to (arbitrarily) different fluctuations in the transient and the stationary cases.

3. We note that on the basis of our explicit calculations, we are able to explore under what conditions the work related ITFT and ISSFT might be observable, which is relevant for the devise of future experiments.

For the ITFT, which holds for all time, observability is purely a matter of how fast the quantity \( L_T \) decays: if it decays too fast, the ITFT will not be measurable. We showed that if one inserts values taken from the Wang experiment into the explicit expression of \( L_T \), the ITFT shows a clear signal which decays on the order of a second, consistent with the fact that the ITFT could be observed in that experiment. The relaxation time, i.e. \( \tau_r \), however is off; the relaxation time found in the experiment is of the order of 1 to 2 seconds, whereas the value of the harmonic force constant and the application of Stokes’ Law give a relaxation time of 0.5 seconds. This could be due to boundary effects, local heating due to the laser, deviations from the harmonic nature of the laser-induced force.
The fact that the ITFT can be observed does not imply that the ISSFT can be observed. In fact, problems with observability arise when we insert values taken from the Wang experiment \[9\] into the quantities for the ISSFT: the signal of \(L_S\) is then too small because the work done on the system in a relaxation time is too large. There are a few ways to improve this situation, i.e., to make the ISSFT observable in an experiment: first, one can take a smaller particle, or second, make the velocity with which it moves through the fluid smaller. Both methods reduce the work done in a relaxation time \(\tau_r\). If the diameter of the particle is reduced to about 16 times smaller than the original one (which means about 400 nm across), we see that the ISSFT can indeed be observed.

The circular motion that we investigated offers a third possibility to improve the observability of the ISSFT: Under resonance conditions \((\Omega \tau_r = 1)\), the deviations from the ISSFT become exponentially small after a time \(\pi \tau_r\).

4. We end by giving some issues which are open for future investigation. Some possible extensions of the theory could be the following. The theory developed here is for the overdamped case only. One might wonder if there is ever any practical need to consider the situation where the damping is not so large. That would mean the theory would start with a Langevin equation of motion for \(x\) and \(v\), or a Kramers equation. We have carried out such calculations for the case of a linear motion of the harmonic potential and found the same results as reported here. In the case of the circular motion, this would also allow a more precise discussion of the role of the centrifugal force (due to \(\Omega\)), which a rough estimate limits to \(\Omega \ll \alpha/m\) (this is of the order of \(10^5\) Hz for parameters taken from the Wang et al. experiment). One could also consider the case of anharmonic rather than harmonic potentials. On a practical level, is seems plausible that the theory could be applied to other systems, such as linear electrical circuits and could be particularly relevant to nano-technology.

On a more fundamental level, one could ask what the precise relation is of the work fluctuation theorem (for \(\beta W^\text{tot}_\tau\)) discussed here and the usual entropy production theorems (for \(\beta W^\text{Br}_\tau\)) for dynamical and stochastic systems\[1, 2, 3, 4, 5\]. While the work fluctuation theorems hold for all classes of systems considered so far, this appears not to be the case for the entropy production theorems. In a future publication, we intend to discuss this question in detail, since the theory needed for this deviates too much from the present one to be included it in this paper. We can state, however, that for the models considered here, such a theory indicates that while an SSFT for the entropy production, i.e., for \(\beta W^\text{Br}_\tau\), appears to hold for long times only as usual, the TFT for the entropy production seems to hold for long times only as well\[13\], and not as an identity for all times, as would be expected\[13\].

This work has been supported by the U.S. Department of Energy, under grant No. DE-FG-02-88-ER13847.

---

[1] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. 71, 2401 (1993).
[2] D. J. Evans and D. J. Searles, Phys. Rev. E 50, 1645 (1994).
[3] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. 74, 2694 (1995).
[4] G. Gallavotti and E. G. D. Cohen, J. Stat. Phys. 80, 931 (1995).
[5] D. J. Searles and D. J. Evans, J. Chem. Phys. 113, 3503 (2000).
[6] J. Kurchan, J. Phys. A, Math. Gen. 31, 3719 (1998).
[7] J. L. Lebowitz and H. Spohn, J. Stat. Phys. 95, 333 (1999).
[8] S. Ciliberto and C. Laroche, J. Phys. IV, France 8, 215 (1998).
[9] G. M. Wang et al., Phys. Rev. Lett. 89, 050601 (2002).
[10] E. M. Sevick, D. R. M. Williams, D. J. Searles and D. J. Evans also developed a Langevin based theory of the TFT experiment [9] (private communication).
[11] Physically, it is not immediately clear that Eq. (1) expresses any kind of work, since the force \( F \) is exerted on the particle at position \( x_t \), while \( \mathbf{v}_t^* \) refers to the motion of the center of the harmonic potential. However, the force \( F \) on the particle implies a reaction force \(-F\) on the harmonic potential (laser), which must be overcome by an external force \( F \) exerted on the laser. Therefore, the force in Eq. (1) is also the external force exerted on the laser and \( W_{\tau}^{\text{tot}} \) is indeed the work performed on the system, e.g. by the experimentalist.
[12] O. Mazonka and C. Jarzynski, Exactly solvable model illustrating far-from-equilibrium predictions, 1999, arXiv:cond-mat/9912121.
[13] Mazonka and Jarzynski [12] were aware of the difference between the entropy production and the total work done, although they used a different wording.
[14] R. van Zon and E. G. D. Cohen, Theory of the Transient and Stationary Fluctuation Theorems for a Dragged Brownian Particle in a Fluid, 2002, arXiv:cond-mat/0210505.
[15] G. E. Uhlenbeck and L. S. Ornstein, Phys. Rev. 36, 823 (1930).
[16] N. G. van Kampen, Stochastic Processes in Physics and Chemistry, revised and enlarged ed. (North Holland, Amsterdam, 1992).
[17] G. Ayton, D. J. Evans, and D. J. Searles, J. Chem. Phys. 115, 2033 (2001).
[18] R. van Zon and E. G. D. Cohen, (unpublished).
[19] E. G. D. Cohen and G. Gallavotti, J. Stat. Phys. 96, 1343 (1999).