PRAMANA
— journal of
physics

Vol. 72, No. 4
April 2009
pp. 665–677

Transient state work fluctuation theorem for a classical harmonic oscillator linearly coupled to a harmonic bath

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MS received 3 October 2008; accepted 20 January 2009

Abstract. Based on a Hamiltonian description we present a rigorous derivation of the transient state work fluctuation theorem and the Jarzynski equality for a classical harmonic oscillator linearly coupled to a harmonic heat bath, which is dragged by an external agent. Coupling with the bath makes the dynamics dissipative. Since we do not assume anything about the spectral nature of the harmonic bath the derivation is not restricted only to the Ohmic bath, rather it is more general, for a non-Ohmic bath. We also derive expressions of the average work done and the variance of the work done in terms of the two-time correlation function of the fluctuations of the position of the harmonic oscillator. In the case of an Ohmic bath, we use these relations to evaluate the average work done and the variance of the work done analytically and verify the transient state work fluctuation theorem quantitatively. Actually these relations have far-reaching consequences. They can be used to numerically evaluate the average work done and the variance of the work done in the case of a non-Ohmic bath when analytical evaluation is not possible.

Keywords. Fluctuation theorems; classical dissipative system; system plus bath coupling.

PACS Nos 05.40.Jc; 05.40.Ca; 05.40.-a

1. Introduction

Although the fields of equilibrium thermodynamics and equilibrium statistical mechanics are well-explored, there existed almost no theory for systems arbitrarily far from equilibrium until the advent of fluctuation theorems (FTs) [1–7] in the mid-90's. In general, these theorems have provided a general prescription on energy exchanges that take place between a system and its surroundings under general nonequilibrium conditions and explain how macroscopic irreversibility appears naturally in systems that obey time reversible microscopic dynamics. Fluctuation theorems have been proposed for various nonequilibrium quantities like heat, work, entropy production etc. and for systems obeying Hamiltonian [8] as well as stochastic dynamics [9,10]. Quantum versions of FTs are also known [11,12].

Apart from fluctuation theorems, Jarzynski [13,14] had also provided a remarkable relation between the work done on a system and the equilibrium free energy difference. To illustrate the relation, consider a classical system in contact with a classical heat bath at temperature T. Initially the system is in equilibrium with the bath and is then subjected to a thermodynamic process by varying some work parameter of the system, f (generalized force). In doing so the system is driven out of the equilibrium unless the process is carried out very slowly. Now the free energy F for the system can be calculated by computing the partition function Z_f when the generalized force is fixed at the value f, since $F_f = -\beta^{-1}\ln Z_f$, where $\beta = \frac{1}{k_{\rm B}T}$, $k_{\rm B}$ is the Boltzman constant. Let the system starts in equilibrium at time $t = 0$ specified by $f = A$ and then driven off to a later time $t = \tau$. As expected, if this process is done quasi-statically, then the system remains in equilibrium at each stage of the process and also at $t = \tau$ specified by $f = B$. Then the work done W on the system equals the free energy difference, $\Delta F = F_B - F_A$. On the other hand, if the process is carried out with a finite rate (i.e. in nonequilibrium conditions), W will on average exceed ΔF.

$$\langle W\rangle \geq \Delta F. \tag{1}$$

The external agent f is always varied in precisely the same manner from A to B. After each realization the work W performed on the system is calculated and $P(W)$, the distribution function for W, is constructed. Jarzynski derived the following mathematical equality popularly known as the Jarzynski equality (JE) or Jarzynski relation where the angular bracket indicates the average taken over the distribution function $P(W)$:

$$\langle\exp(-\beta W)\rangle = \exp(-\beta\Delta F). \tag{2}$$

Essentially there are two classes of fluctuation theorems, the steady state [5,7] and the transient state fluctuation theorems (TFT) [6]. Since the paper deals with the transient state fluctuation theorem for work, here we do not discuss anything further on steady state fluctuation theorem. The transient state work fluctuation theorem gives the ratio of probabilities for the production of positive work to the production of negative work as follows:

$$\frac{P(+W)}{P(-W)} = \exp(\beta W), \tag{3}$$

where W is the work done on the system by an external agent for an arbitrary time period τ. The theorem holds for any value of τ, provided one starts with the system in equilibrium.

In this paper we demonstrate the derivation of the transient state work fluctuation theorem for a classical harmonic oscillator coupled linearly to a harmonic bath. Because of the coupling to the bath, the system becomes dissipative. We start from a Hamiltonian description for the system plus the harmonic heat bath and then the system is driven by an external agent for a time period of τ for a series of measurements. We analytically calculate the distribution function for work and show that it obeys the transient state fluctuation theorem. For our particular choice of the external agent the free energy change for the process is zero and hence the transient fluctuation theorem and the Crooks fluctuation theorem are the same.

In the recent past, experiments [15,16] were carried out to verify the FTS. In the experiment by Wang *et al* a colloidal particle was trapped using laser and then dragged through a solvent and subsequently the fluctuation theorem was verified. Our Hamiltonian efficiently models such a situation since the harmonic oscillator in our model could be viewed as the colloidal particle in the harmonic trap caused by lasers and the harmonic bath as the solvent through which the colloidal particle is dragged. People have already verified FTs [9,17,18] in the context of the above-mentioned experiment. This modelling was based on a Langevin description which was Markovian. Only very recently, Mai and Dhar [19], Speck and Seifert [20] and Ohkuma and Ohta [21] have reported derivations based on generalized Langevin equation (GLE) taking care of the non-Markovian nature of the dynamics. But here we do not start with a Langevin description, rather we start with a Hamiltonian description. Since we couple our system with a set of bath oscillators effectively it produces a noise acting on the system which depends on bath variable and thus the dynamics becomes stochastic. Also, our derivation does not assume anything about the spectral nature of the bath and the particle coupling. Hence the results are of very general validity. The paper is arranged as follows: In the next section we define work done on the system. In §3 we introduce our model. Section 4 contains the detailed derivation of the fluctuation theorem, §5 highlights the important results of the paper and quantitatively verifies the TFT for the Ohmic bath and in the last section we conclude our results.

2. Definition of heat

According to Jarzynski [14] the work done on the system (described by the Hamiltonian $H_{\rm S}$) by an external agent f acting on the system from $t = 0$ to $t = \tau$ is defined as

$$W = \int_0^\tau \dot{f} \frac{\partial H_{\rm S}}{\partial f} {\rm d}t. \tag{4}$$

We shall use this definition.

3. Our model

We consider a classical particle of unit mass described by the positional coordinate x which is linearly coupled to a set of harmonic oscillators, each unit mass described by a positional coordinate $q_i (i = 1, 2, ..., N)$ forming a harmonic heat bath, a model for the environment. In the experiment by Wang *et al* the colloidal particle was dragged through the solvent using a laser trap. The particle experiences a harmonic trap whose minimum moves in time. To model such a situation we assume that the particle x is in a harmonic well whose minimum is time-dependent. We thus introduce the Hamiltonian [23–25]

$$H = H_{\rm S} + H_{\rm B} + h_{\rm int}, \tag{5}$$

where

$$H_{\rm S} = \frac{p_x^2}{2} + \frac{k}{2}(x - \alpha(t))^2$$

and

$$H_{\rm B} + h_{\rm int} = \sum_{i=1}^{N} \left(\frac{p_i^2}{2} + \frac{\omega_i^2}{2} \left(q_i - \frac{c_i}{\omega_i^2} x \right)^2 \right).$$

$H_{\rm S}$ is the Hamiltonian for the system, $H_{\rm B}$ is that for the harmonic bath and $h_{\rm int}$ represents the coupling of the system with the bath. Here p_x and p_i are the momenta for the particle and the ith bath harmonic oscillator, respectively and ω_i^2 is the force constant for the ith bath coordinate, k is the force constant of the optical trap and $\alpha(t)$ is the time-dependent mean position of the harmonic trap. It is easy to see that here the generalized force, $f = k\alpha(t)$.

4. Derivation of TFT for work and JE

The time evolution of the system plus bath is governed by the Hamiltonian H. The equations of motion for the system and the bath oscillators are

$$\dot{p}_x = -\frac{\partial H}{\partial x} = -k(x - \alpha(t)) - \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2} x + \sum_{i=1}^{N} c_i q_i \tag{6}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} = -\omega_i^2 q_i + c_i x \tag{7}$$

$$\dot{x} = \frac{\partial H}{\partial p_x} = p_x \tag{8}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} = p_i. \tag{9}$$

In our case the external agent f is $\alpha(t)$ and hence the work done on the system is

$$W = \int_0^\tau \dot{\alpha}(t) \frac{\partial H_{\rm S}}{\partial \alpha} {\rm d}t = \int_0^\tau -k\dot{\alpha}(t)(x(t) - \alpha(t)){\rm d}t. \tag{10}$$

Thus within the harmonic Hamiltonian description the work done on the system W is linear in x. As we start with the corresponding equilibrium distribution, we would have a Gaussian distribution for W [19] with a mean $\langle W\rangle$ and the variance $\sigma_W^2 = \langle W^2\rangle - \langle W\rangle^2$. So the distribution function for W is

$$P(W) = \frac{1}{\sqrt{2\pi\sigma_W^2}} \mathrm{e}^{-(W-\langle W\rangle)^2/2\sigma_W^2} \tag{11}$$

with

$$\langle W\rangle = \int_0^\tau -k\dot{\alpha}(t)(\langle x(t)\rangle - \alpha(t))\mathrm{d}t \tag{12}$$

and

$$\sigma_W^2 = k^2 \int_0^\tau \mathrm{d}t_1 \int_0^\tau \mathrm{d}t_2 \dot{\alpha}(t_1)\dot{\alpha}(t_2) C(t_1,t_2) \tag{13}$$

with $\Delta x(t_1) = x(t_1) - \langle x(t_1)\rangle$ and $C(t_1,t_2) = \langle \Delta x(t_1)\Delta x(t_2)\rangle$.

With the above Gaussian distribution function for work it is easy to see that $(P(W)/P(-W)) = \mathrm{e}^{2W\langle W\rangle/\sigma_W^2}$. So in order to satisfy the TFT for work it is enough to show that $\sigma_W^2 = 2\langle W\rangle/\beta$.

Now it is obvious that to calculate the work done, its mean and the variance, one has to know x as a function of time t. To find x as a function of time t we proceed as follows. We take a Laplace transform of eqs (6) and (7) to get

$$\tilde{x}(s) = \frac{(k\tilde{\alpha}(s) + \dot{x}(0) + \sum_{i=1}^N c_i \tilde{q}_i(s) + s x(0))}{\left(s^2 + k + \sum_{i=1}^N \frac{c_i^2}{\omega_i^2}\right)} \tag{14}$$

and

$$\tilde{q}_i(s) = \frac{(p_i(0) + s q_i(0) + c_i \tilde{x}(s))}{(s^2 + \omega_i^2)}. \tag{15}$$

Now we substitute $\tilde{q}_i(s)$ in eq. (14) by eq. (15) and get $\tilde{x}(s)$ in terms of the initial momenta and position of the bath coordinates in time and that of the system itself.

$$\tilde{x}(s) = k\tilde{\alpha}(s) + (p_x(0) + x(0)s + \tilde{g}(s))\tilde{b}(s), \tag{16}$$

where

$$\tilde{b}(s) = \frac{1}{\left(k + s^2 + \sum_{i=1}^N \frac{c_i^2}{\omega_i^2} - \sum_{i=1}^N \frac{c_i^2}{(s^2+\omega_i^2)}\right)} \tag{17}$$

and

$$\tilde{g}(s) = \sum_{i=1}^N c_i \frac{(p_i(0) + s q_i(0))}{(s^2 + \omega_i^2)}. \tag{18}$$

Taking the inverse Laplace transform of eq. (16) one gets $x(t)$ as

$$x(t) = x(0)y(t) + v(0)b(t) + \int_0^t \mathrm{d}t' b(t-t')\left(k\alpha(t') + \xi(t')\right) \tag{19}$$

with

$$\xi(t) = g(t) - \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2} \cos(\omega_i t) x(0)$$

and

$$y(t) = \int_0^t \mathrm{d}t' \left(\dot{b}(t')\delta(t-t') + \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2} \cos(\omega_i t') b(t-t') \right).$$

Now eq. (19) should be consistent with the initial conditions. This readily gives

$$y(0) = 1 \tag{20}$$

$$b(0) = 0 \tag{21}$$

$$\dot{b}(0) = 1 \tag{22}$$

$$\dot{y}(0) = 0. \tag{23}$$

One can substitute $x(t)$ from eq. (19) to eq. (10) to calculate W. Next task is to calculate $\langle W \rangle$ which is obtained from eq. (10) by replacing $x(t)$ with its thermal average

$$\langle x(t) \rangle = \langle x(0) \rangle y(t) + \langle v(0) \rangle b(t) + \int_0^t \mathrm{d}t' b(t-t') \left(k\alpha(t') + \langle \xi(t') \rangle\right). \tag{24}$$

Here the angular bracket indicates a thermal average taken in the initial state of the harmonic bath (at $t = 0$) with the shifted canonical equilibrium distribution (since we start from an initial equilibrium distribution) given by $\rho \sim \mathrm{e}^{-\beta H^{(0)}}$. Thus $\langle p_x(0) \rangle = 0$, $\langle x(0) \rangle = \alpha(0)$. Now to calculate $\langle g(t) \rangle$ we proceed as follows: First we take the inverse Laplace transform of eq. (18) to get

$$g(t) = \sum_{i=1}^{N} c_i \left\{ p_i(0) \frac{\sin(\omega_i t)}{\omega_i} + q_i(0) \cos(\omega_i t) \right\}. \tag{25}$$

Next we take the thermal average with respect to the initial distribution $\rho \sim \mathrm{e}^{-\beta H^{(0)}}$ to get

$$\langle g(t) \rangle = \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2} x(0) \cos(\omega_i t) \tag{26}$$

as $\langle p_i(0)\rangle = 0$, $\langle q_i(0)\rangle = \frac{c_i}{\omega_i^2}x(0)$. Thus $\langle \xi(t)\rangle = \langle g(t)\rangle - \sum_{i=1}^N \frac{c_i^2}{\omega_i^2}\cos(\omega_i t)x(0) = 0$. The quantity $\xi(t)$ is a Gaussian random force from the bath with the statistical properties, $\langle \xi(t)\rangle = 0$, $\langle \xi(t)\xi(t')\rangle = \beta^{-1}\Gamma(t-t')$, where $\Gamma(t) = \sum_{i=1}^N \frac{c_i^2}{\omega_i^2}\cos(\omega_i t)$.

Finally we get

$$\langle x(t)\rangle = \alpha(0)y(t) + \int_0^t \mathrm{d}t' k\alpha(t')b(t-t'). \tag{27}$$

Next we derive a set of equations in the Laplace and the time domain. These are used to get the TFT for work.

In a few steps one can show $s\tilde{y}(s) = 1 - k\tilde{b}(s)$, where $y(s) = s\tilde{b}(s) + \tilde{\Gamma}(s)\tilde{b}(s)$, $\tilde{\Gamma}(s) = \sum_{i=1}^N \frac{sc_i^2}{\omega_i^2(s^2+\omega_i^2)}$. Inverse Laplace transform of $s\tilde{y}(s) = 1 - k\tilde{b}(s)$ gives $\dot{y}(t) = -kb(t)$. Also $s\tilde{b}(s) = \tilde{y}(s) - \tilde{\Gamma}(s)\tilde{b}(s)$ whose inverse Laplace gives $\dot{b}(t) = y(t) - \int_0^t \mathrm{d}t'\Gamma(t')b(t-t')$. So we have the following set of important relations in the Laplace and the time domain:

$$\begin{aligned}
&s\tilde{y}(s) = 1 - k\tilde{b}(s)\\
&s\tilde{b}(s) = \tilde{y}(s) - \tilde{\Gamma}(s)\tilde{b}(s)\\
&\dot{y}(t) = -kb(t)\\
&\dot{b}(t) = y(t) - \int_0^t \mathrm{d}t'\Gamma(t')b(t-t').
\end{aligned} \tag{28}$$

Using the above set of equations one can show that the average work done on the system (which is given by eq. (12)) is [22]

$$\langle W\rangle = \left(\frac{1}{k}\right)\int_0^\tau \mathrm{d}t \int_0^t \mathrm{d}t' k\dot{\alpha}(t)y(t-t')k\dot{\alpha}(t'). \tag{29}$$

To derive it we proceed as follows: First we replace $\langle x(t)\rangle$ in eq. (12) by eq. (27) to get

$$\begin{aligned}
\langle W\rangle = {}& \frac{k}{2}\left(\frac{\alpha^2(\tau)}{2} - \frac{\alpha^2(0)}{2}\right)\\
&- \int_0^\tau \mathrm{d}t k\alpha(0)\dot{\alpha}(t)y(t) - \int_0^\tau \mathrm{d}t \int_0^t \mathrm{d}t' k\dot{\alpha}(t)b(t-t')k\alpha(t')
\end{aligned}$$

and then using eq. (28) followed by integration by parts and using eq. (20) one ultimately gets

$$\langle W\rangle = \left(\frac{1}{k}\right)\int_0^\tau \mathrm{d}t \int_0^t \mathrm{d}t' k\dot{\alpha}(t)y(t-t')k\dot{\alpha}(t')$$

which is eq. (29).

In order to evaluate the variance we first have to calculate the correlation function, $C(t_1,t_2) = \langle \Delta x(t_1)\Delta x(t_2)\rangle$. Now using eq. (19) one can show

$$C(t_1,t_2) = (k\beta)^{-1}\, y(t_1)y(t_2) + (\beta)^{-1}\, b(t_1)b(t_2) + \beta^{-1}\int_0^{t_1} \mathrm{d}t_1' \int_0^{t_2} \mathrm{d}t_2' b(t_1-t_1')b(t_2-t_2')\Gamma(t_1'-t_2'), \qquad (30)$$

where we have used $\langle \xi(t)\xi(t')\rangle = \beta^{-1}\Gamma(t-t')$, $\langle (x(0)-\alpha(0))^2\rangle = (k\beta)^{-1}$, $\langle v^2(0)\rangle = (\beta)^{-1}$.

The above expression for $C(t_1,t_2)$ is then put back in eq. (13) to get

$$\sigma_W^2 = \left(\frac{1}{\beta k}\right)\left(\int_0^\tau \mathrm{d}t k\dot{\alpha}(t)y(t)\right)^2 + \left(\frac{1}{\beta}\right)\left(\int_0^\tau \mathrm{d}t k\dot{\alpha}(t)b(t)\right)^2 + \frac{1}{\beta}\int_0^\tau \mathrm{d}t_1 \int_0^\tau \mathrm{d}t_2 \int_0^{t_1} \mathrm{d}t_1' \times \int_0^{t_2} \mathrm{d}t_2' \Gamma(t_1'-t_2')k\dot{\alpha}(t_1)b(t_1-t_1')b(t_2-t_2')k\dot{\alpha}(t_2). \qquad (31)$$

Let us define

$$J(t_1,t_2) = \int_0^{t_1} \mathrm{d}t_1' \int_0^{t_2} \mathrm{d}t_2' \Gamma(t_1'-t_2')b(t_1-t_1')b(t_2-t_2').$$

With the help of Laplace and Fourier transforms one can show (see Appendix for the evaluation of the integral)

$$J(t_1,t_2) = \left(\frac{1}{k}\right) y(t_1-t_2) - \left(\frac{1}{k}\right) y(t_1)y(t_2) - b(t_1)b(t_2). \qquad (32)$$

When the above expression for $J(t_1,t_2)$ is plugged into eq. (31) one gets

$$\sigma_W^2 = \left(\frac{1}{k\beta}\right)\int_0^\tau \mathrm{d}t_1 \int_0^\tau \mathrm{d}t_2 k\dot{\alpha}(t_1)y(t_1-t_2)k\dot{\alpha}(t_2). \qquad (33)$$

In eq. (29), t and t' being dummy variables one can change these into t_1 and t_2 respectively and rewrite eq. (29).

$$\langle W\rangle = \left(\frac{1}{k}\right)\int_0^\tau \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 k\dot{\alpha}(t_1)y(t_1-t_2)k\dot{\alpha}(t_2). \qquad (34)$$

Now we interchange t_1 and t_2.

$$\langle W\rangle = \left(\frac{1}{k}\right)\int_0^\tau \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_1 k\dot{\alpha}(t_2)y(t_2-t_1)k\dot{\alpha}(t_1). \qquad (35)$$

Add eqs (34) and (35). Since $y(t)$ is an even function of t one gets

$$2\langle W\rangle = \left(\frac{1}{k}\right)\int_0^\tau \mathrm{d}t_1 \int_0^\tau \mathrm{d}t_2 k\dot{\alpha}(t_1)y(t_1-t_2)k\dot{\alpha}(t_2) = \beta\sigma_W^2.$$

This shows that the TFT for work is satisfied and reads as

$$\frac{P(+W)}{P(-W)} = \exp(\beta W). \tag{36}$$

JE is obtained easily by integrating the above equation

$$\begin{aligned}\langle\exp(-\beta W)\rangle &= \int_{-\infty}^{\infty} \mathrm{d}W P(+W)\exp(-\beta W) \\ &= \int_{-\infty}^{\infty} \mathrm{d}W P(-W) = 1.\end{aligned}$$

5. Important results and verification of the TFT for Ohmic bath

In this section we focus on the most important results of the paper and also demonstrates the verification TFT when the noise–noise correlation is a delta function. From eqs (19) and (24) on can write

$$(x(t) - \langle x(t)\rangle) = \Delta x(t) = \Delta x(0)y(t) + v(0)b(t) + \int_0^t \mathrm{d}t' b(t-t')\xi(t'). \tag{37}$$

Then multiplying the above equation with $\Delta x(0)$ and taking an average over noise one gets the following

$$C(t,0) = \langle\Delta x(t)\Delta x(0)\rangle = \left\langle\Delta x(0)^2\right\rangle y(t) = \frac{y(t)}{\beta k}, \tag{38}$$

where in the last step we have used the equipartition theorem. Now using the time translational invariance property one can write in general

$$C(t_1,t_2) = \frac{y\left(|t_1-t_2|\right)}{\beta k}. \tag{39}$$

This is one of the most important results of the paper along with eqs (28), (29) and (33). Since this basically says that if one can calculate $y(|t_1-t_2|)$ then one gets $C(t_1,t_2)$ or vice versa. Subsequently, one can compute the average work done and the variance of the work done and quantitatively check whether the transient state work fluctuation theorem holds for different choices of noise–noise correlations.

Here we consider the case when the particle is dragged with a constant velocity v_0, i.e. $\alpha(t) = v_0 t$ and the noise coming from the bath has a delta function correlation or in other words the noise is white noise. For this, everything can be done analytically.

Let us calculate $\langle W\rangle$ and σ_W^2 when the dynamics is overdamped (we dropped the inertia term in the Hamilton's equation of motion and proceed). Here $\tilde{\Gamma}(s) = \Gamma$, a constant and $\tilde{b}(s) = \frac{1}{k+s\Gamma}$, $\tilde{y}(s) = \frac{\Gamma}{k+s\Gamma}$. Then $y(t)$ is

$$y(t) = \mathrm{e}^{-kt/\Gamma} \tag{40}$$

and

$$\langle W \rangle_{\text{over}} = \Gamma v_0^2 \tau \left\{ 1 + \frac{\Gamma}{k\tau} \left(\mathrm{e}^{-k\tau/\Gamma} - 1 \right) \right\}. \tag{41}$$

Then using the relation given by eq. (39) and putting it in eq. (33) one verifies the TFT for this case too by showing that

$$\left(\sigma_W^2\right)_{\text{over}} = \frac{2\,\langle W \rangle_{\text{over}}}{\beta}. \tag{42}$$

When $v_0 = 0$ the average work done is zero. This is obvious since $v_0 = 0$ means the trap is not moving and hence no work is done.

6. Conclusions

Firstly, we have proved the TFT for work and verified the JE for a classical dissipative system which is dragged through by an external agent. We start from a Hamiltonian description of our system which is linearly coupled to a bath. The coupling makes the dynamics stochastic and non-Markovian in general. A non-Markovian bath is more realistic because of the existence of finite correlation time of the noise acting on the particle. As far as our knowledge goes this is the first detailed derivation of the TFT for work for such a classical dissipative system starting from a Hamiltonian description rather than from a Langevin equation. To keep our derivation analytic we had to restrict ourselves to a harmonic system and a harmonic bath.

Secondly, we derive expressions of the average work done and also the variance of the work done in terms of the two-time correlation function of the fluctuations of the position of the harmonic oscillator. In the case of an Ohmic bath, we use these relations to evaluate the average work done and the variance of the work done analytically and verify the transient state work fluctuation theorem quantitatively. Actually, these relations have far-reaching consequences. They can be used to numerically evaluate the average work done and the variance of the work done in the case of a non-Ohmic bath when analytical evaluation may not be possible.

Appendix

The integral $J(t_1, t_2)$ is evaluated as follows: First let us consider the integral

$$\begin{aligned} &\int_0^\infty \mathrm{d}t_2 \mathrm{e}^{-s_2 t_2} \int_0^{t_2} \mathrm{d}t_2' b(t_2 - t_2') \mathrm{e}^{-i\omega t_2'} \\ &= b(s_2) \int_0^\infty \mathrm{d}t_2 \mathrm{e}^{-s_2 t_2} \mathrm{e}^{-i\omega t_2} = b(s_2) \frac{\mathrm{e}^{-(s_2 + i\omega)t_2}}{(s_2 + i\omega)} \bigg|_0^\infty = \frac{b(s_2)}{(s_2 + i\omega)}. \end{aligned} \tag{A1}$$

Similarly

$$\int_0^\infty \mathrm{d}t_1 \mathrm{e}^{-s_1 t_1} \int_0^{t_1} \mathrm{d}t_1' b(t_1 - t_1') \mathrm{e}^{i\omega t_1'} = \frac{b(s_1)}{(s_1 - i\omega)} \tag{A2}$$

Then with the help of eqs (A1) and (A2) double Laplace transform of $J(t_1, t_2)$ can be written as

$$\tilde{J}(s_1, s_2) = \int_0^\infty \mathrm{d}t_1 \mathrm{e}^{-s_1 t_1} \int_0^\infty \mathrm{d}t_2 \mathrm{e}^{-s_2 t_2} \int_0^{t_1} \mathrm{d}t_1' \times \int_0^{t_2} \mathrm{d}t_2' \Gamma(t_1' - t_2') b(t_1 - t_1') b(t_2 - t_2'). \tag{A3}$$

We also define

$$\Gamma(t_1' - t_2') = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \tilde{\Gamma}(\omega) \mathrm{e}^{i\omega(t_1' - t_2')}$$

and

$$\tilde{\Gamma}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}t \Gamma(t) \mathrm{e}^{-i\omega t}.$$

Then after some algebraic manipulations eq. (A3) becomes

$$\begin{aligned}
\tilde{J}(s_1, s_2) &= \int_0^\infty \mathrm{d}t_1 \mathrm{e}^{-s_1 t_1} \int_0^\infty \mathrm{d}t_2 \mathrm{e}^{-s_2 t_2} \int_0^{t_1} \mathrm{d}t_1' \\
&\quad \times \int_0^{t_2} \mathrm{d}t_2' b(t_1 - t_1') b(t_2 - t_2') \left(\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \tilde{\Gamma}(\omega) \mathrm{e}^{i\omega(t_1' - t_2')} \right) \\
&= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\tilde{b}(s_1) \tilde{b}(s_2) \tilde{\Gamma}(\omega)}{(s_1 - i\omega)(s_2 + i\omega)} \\
&= \frac{\tilde{b}(s_1) \tilde{b}(s_2)}{(s_1 + s_2)\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \left(\frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} + \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} \right).
\end{aligned} \tag{A4}$$

$$\tilde{J}(s_1, s_2) = \frac{\tilde{b}(s_1) \tilde{b}(s_2)}{(s_1 + s_2)\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \left(\frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} + \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} \right). \tag{A5}$$

Next consider the integral $\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega}$ which can be evaluated as follows:

$$\begin{aligned}
\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\tilde{\Gamma}(\omega)}{s_1 - i\omega} &= \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{(s_1 - i\omega)} \int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-i\omega t} \Gamma(t) \\
&= \int_{-\infty}^{\infty} \mathrm{d}t \Gamma(t) \left(\frac{1}{-2\pi i} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{(\omega + i s_1)} \mathrm{e}^{-i\omega t} \right) \\
&= \int_{-\infty}^{\infty} \mathrm{d}t \Gamma(t) \Theta(t) \mathrm{e}^{-s_1 t} = \int_0^\infty \mathrm{d}t \Gamma(t) \mathrm{e}^{-s_1 t} = \tilde{\Gamma}(s_1).
\end{aligned} \tag{A6}$$

Similarly

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{\tilde{\Gamma}(\omega)}{s_2 + i\omega} = \tilde{\Gamma}(s_2). \tag{A7}$$

Now we use eqs (A6) and (A7) to get

$$\tilde{J}(s_1, s_2) = \frac{\tilde{b}(s_1) + \tilde{b}(s_2)}{(s_1 + s_2)}(\tilde{\Gamma}(s_1) + \tilde{\Gamma}(s_2)). \tag{A8}$$

The above equation is then simplified with the help of eq. (28) to get

$$\tilde{J}(s_1, s_2) = \frac{\tilde{y}(s_1) + \tilde{y}(s_2)}{k(s_1 + s_2)} - \frac{\tilde{y}(s_1)\tilde{y}(s_2)}{k} - \tilde{b}(s_1)\tilde{b}(s_2). \tag{A9}$$

Taking the double Laplace transformation of the above equation we get

$$J(t_1, t_2) = \left(\frac{1}{k}\right) y(t_1 - t_2) - \left(\frac{1}{k}\right) y(t_1)y(t_2) - b(t_1)b(t_2)$$

which is eq. (32).

Acknowledgements

The author is grateful to Prof. K L Sebastian for suggesting this particular approach to the problem. The author acknowledges Council of Scientific and Industrial Research (CSIR), India for financial support. The author is also thankful to Prof. Abhishek Dhar for arranging the workshop on fluctuation theorems.

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