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Asymmetry of the work probability distribution

Arnab Saha[1] **and J K Bhattacharjee**[2]

[1] S N Bose National Centre For Basic Sciences, JD-Block, Sector-III, Salt Lake City, Kolkata-700 098, India
[2] Department of Theoretical Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

E-mail: www.arnab.bose.res.in and tpjkb@mahendra.iacs.res.in

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Abstract
We show, both analytically and numerically, that for a nonlinear system making a transition from one equilibrium state to another under the action of an external time dependent force, the work probability distribution is in general asymmetric, even if the evolution dynamics has a symmetry.

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The connection between equilibrium thermodynamic quantities and irreversible trajectories is a matter of continuing interest. A major result in this context has been obtained by Jarzynski. We consider a system in contact with a heat bath, which is driven out of equilibrium by an external time-dependent force. This force drives it from an equilibrium state A to another equilibrium state B. It was shown by Jarzynski [1–3] that the equilibrium free energy difference, ΔF, between these states can be related to the probability distribution of the work done W in taking the system from A to B. In particular,

$$e^{\frac{-\Delta F}{KT}} = \left\langle e^{\frac{-W}{KT}} \right\rangle, \tag{1}$$

where K is the Boltzmann constant and T is the temperature. The angular bracket denotes an average performed over repeated trials. A related equality is that due to Crooks [4, 5] which relates the probabilities for the forward process $(A \to B)$ to the backward process $(B \to A)$. A couple of years ago a simple but effective experiment on a mechanical oscillator was done by Douarche, Ciliberto, Patrosyan and Rabbiosi (DCPR) [6, 7] who showed that for a linear oscillator in the overdamped limit,

$$\Delta F = \langle W \rangle - \frac{\langle (W - \langle W \rangle)^2 \rangle}{2KT}. \tag{2}$$

This is consistent with equation (1) if the distribution of W is Gaussian and has been studied by various authors [8–11]. This relation which is similar to a relation found by Landau and Lifshitz

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[12] in the context of thermodynamic perturbation theory was demonstrated experimentally and also analytically for a particular kind of forcing by DCPR for linear oscillators.

The particularly convenient form of equation (2) made us investigate whether it holds for nonlinear systems. In what follows, we have looked first at the linear system with an arbitrary forcing in the highly viscous limit. The Green function technique used for that proof is then extended to treat the nonlinear system in a perturbative manner. The general dynamics for the system is

$$m\ddot{x} + k\dot{x} = -\frac{\partial V}{\partial x} + M(t) + f(t), \tag{3}$$

where $M(t)$ is an externally applied time-dependent force and $f(t)$ is a random force that allows the system to be in equilibrium in the absence of $M(t)$. The viscous limit corresponds to dropping the inertial term $m\ddot{x}$. The system is supposed to be in equilibrium (state A) at $t = 0$ and then we switch on $M(t)$ for a time τ, after which $M(t)$ takes a constant value $M(\tau)$. The system reaches the state B and equilibrates. In going from state A to state B, the work done is

$$W = -\int_0^{\tau} \dot{M}(t)x(t)\,\mathrm{d}t. \tag{4}$$

We are interested in the moments of W. We will work in the highly damped limit where the inertial term in equation (3) can be dropped. For a quadratic $V(x)$ (linear system), we will prove equation (2) for an arbitrary $M(t)$ and then go on to show that equation (2) needs to be modified for arbitrary $V(x)$. The most significant finding is that, even for a symmetric $V(x)$, the odd moments of $\Delta W = W - \langle W\rangle$ are non-vanishing and hence the distribution of ΔW is asymmetric for all non-quadratic $V(x)$. We will show this analytically, using perturbation theory, suggest a generalization of equation (2) and numerically establish that the probability distribution $P(\Delta W)$ is indeed asymmetric in general. It should be noted that an asymmetric work probability distribution has been obtained by various authors such as Bena *et al* [13], Cleuren *et al* [14], Blickle *et al* [15], Lua-Grosberg [16], etc. In all these cases the potential has been asymmetric. We will specializing the work with a symmetric potential (i.e. $V(x) = V(-x)$) and show that $P(W)$ is still asymmetric.

We begin with the linear harmonic oscillator under the action of a deterministic force $M(t)$ and random force $f(t)$. In the highly viscous limit with unit friction coefficient k, the system evolves according to

$$\dot{x} + \Gamma x = M(t) + f(t), \tag{5}$$

where the random force $f(t)$ has the correlation function

$$\langle f(t)f(t')\rangle = 2KT\delta(t-t'). \tag{6}$$

We calculate the moments of the work done from the above dynamics. The solution for $x(t)$ can be written as

$$x(t) = \int G(t-t')[M(t') + f(t')]\,\mathrm{d}t', \tag{7}$$

where $G(t-t')$ is the causal Green function

$$G(t-t') = \Theta(t-t')\,\mathrm{e}^{-\Gamma(t-t')}. \tag{8}$$

Clearly, the average of the work is

$$\langle W\rangle = -\int^{\tau} \mathrm{d}t_1 \dot{M}(t_1) \int^{t_1} G(t_1-t_2)M(t_2)\,\mathrm{d}t_2, \tag{9}$$

while the deviation from the average is

$$\Delta W = W - \langle W \rangle = -\int^{\tau} \mathrm{d}t_1 \dot{M}(t_1) \int^{t_1} G(t_1 - t_2) f(t_2)\,\mathrm{d}t_2, \tag{10}$$

which has the mean square value of

$$\langle (\Delta W)^2 \rangle = 2KT \int^{\tau} \mathrm{d}t_1 \dot{M}(t_1) \int^{\tau} \mathrm{d}t_2 \dot{M}(t_2) \int^{t_2} \mathrm{d}t'' \int^{t_1} \mathrm{d}t' G(t_1 - t')G(t_2 - t'')\delta(t' - t''), \tag{11}$$

where equation (6) has been used. Noting the identity derived from the time translational invariance

$$\int_0^{t_2} G(t_2 - t'')G(t_1 - t'')\,\mathrm{d}t'' = G(t_1 - t_2)/2\Gamma, \tag{12}$$

we arrive at

$$\frac{\langle (\Delta W)^2 \rangle}{2KT} = \frac{1}{\Gamma} \int^{\tau} \mathrm{d}t_1\, \dot{M}(t_1) \int_1^{t} \mathrm{d}t_2\, \dot{M}(t_2)G(t_1 - t_2). \tag{13}$$

Using the above and equation (9),

$$\langle W \rangle - \frac{\langle (\Delta W)^2 \rangle}{2KT} = -\int^{\tau} \mathrm{d}t_1\, \dot{M}(t_1) \int_1^{t} \mathrm{d}t_2\, G(t_1 - t_2) \left[M(t_2) + \frac{\dot{M}(t_2)}{\Gamma} \right]. \tag{14}$$

Integrating by parts the first term in the integral above and using $G(0) = 0$ due to causality, we find

$$\langle W \rangle - \frac{\langle (\Delta W)^2 \rangle}{2KT} = -\frac{M^2}{2\Gamma}. \tag{15}$$

The free energy change is precisely this amount, and that establishes equation (2) for an arbitrary forcing $M(t)$.

We now consider the inclusion of a nonlinear term in the motion, which becomes

$$\dot{x} + \Gamma x + \lambda x^3 = M(t) + f(t) \tag{16}$$

preserving the $x \to -x$ symmetry of $V(x)$ in equation (3). The question to ask is: whether the equality in equation (2) still holds? To investigate this, we specialize to the case of $M(t) = M_0 t$ as studied by DCPR and carry out a perturbative calculation to $O(\lambda)$.

We write

$$x = x_0 + \lambda x_1 + \lambda^2 x_2 + \cdots \tag{17}$$

and substituting in equation (16) and equating the coefficients of equal powers of λ on either side, we get

$$\dot{x}_0 + \Gamma x_0 = M(t) + f(t) \qquad \dot{x}_1 + \Gamma x_1 = -x_0^3 \tag{18}$$

and so on. We can now expand $W(\tau)$ according to equations (4) and (17),

$$W = W_0 + \lambda W_1 + \cdots, \tag{19}$$

where

$$\begin{aligned} W_0 &= -\int^{\tau} \dot{M}(t) x_0(t)\,\mathrm{d}t \\ W_1 &= -\int^{\tau} \dot{M}(t) x_1(t)\,\mathrm{d}t. \end{aligned} \tag{20}$$

From equation (18), we get

$$x_0 = \int_0^t G(t-t')[M(t') + f(t')]\,dt'$$
$$x_1 = -\int_0^t G(t-t')x_0^3\,dt'. \tag{21}$$

We note that in the way we have set it up, $G(t_1 - t_2)$ is exactly the same G that we had for the linear problem. We have already calculated $\langle W_0\rangle$ (equation (9)) and now we concentrate on $\langle W_1\rangle$. We write

$$\langle W_1\rangle = \int^{\tau} \dot{M}\,dt \int^{t} dt' G(t-t')\left[\int^{t'} dt_1 G(t'-t_1)M(t_1)\right]^3$$
$$+3\int^{\tau} \dot{M}\,dt \int^{t} dt' G(t-t') \int^{t'} dt_1\,dt_2\,dt_3$$
$$\times M(t_1)G(t'-t_1)G(t'-t_2)G(t'-t_3)\langle f(t_2)f(t_3)\rangle. \tag{22}$$

The second term on the rhs vanishes once we use equation (12) and causality. We are left with

$$\langle W_1\rangle = \int^{\tau} \dot{M}\,dt \int^{t} dt' G(t-t')\left[\int^{t'} dt_1 G(t'-t_1)M(t_1)\right]^3. \tag{23}$$

We now use $M(t) = M_0 t$ and carry out the integration to arrive at

$$\langle W_1\rangle = \frac{M_0^4}{\Gamma^3}\left[\frac{\tau^4}{4\Gamma} - \frac{2\tau^3}{\Gamma^2} + \frac{15\tau^2}{2\Gamma^3} - \frac{16\tau}{\Gamma^4}\right], \tag{24}$$

keeping the leading order terms, i.e. terms which increase with τ.

Let us now turn to the calculation of the variance $\langle (W - \langle W\rangle)^2\rangle$. The perturbative calculation generates the following up to $0(\lambda)$:

$$\langle (\Delta W)^2\rangle = \langle (\Delta W_0)^2\rangle + 2\lambda\langle \Delta W_0 \Delta W_1\rangle, \tag{25}$$

where $\Delta W_0 = W_0 - \langle W_0\rangle$ and $\Delta W_1 = W_1 - \langle W_1\rangle$. We have already calculated the first term on the rhs. Now we will concentrate on the second term. In the $O(\lambda)$ correction in the variance, we have found that the disconnected parts (i.e. where the averaging is over ΔW and ΔW_1 separately.) do not contribute. Specializing to the case $M(t) = M_0 t$, calculation leads to the $O(\lambda)$ term of the variance as

$$0(\lambda)\ \ part\ \ of \frac{\langle (\Delta W)^2\rangle}{2KT} = -\frac{M_0^4}{\Gamma^3}\left[\frac{2\tau^3}{\Gamma^2} - \frac{27\tau^2}{2\Gamma^3} + \frac{16\tau}{\Gamma^4}\right], \tag{26}$$

keeping the leading order terms. Thus,

$$\langle W\rangle - \frac{\langle (\Delta W)^2\rangle}{2KT} = \langle W_0\rangle - \frac{\langle (\Delta W_0)^2\rangle}{2KT} + \frac{\lambda M_0^4\tau^4}{4\Gamma^4} - \frac{6\lambda M_0^4\tau^2}{\Gamma^6} + O(\tau). \tag{27}$$

Now, ΔF up to $O(\lambda)$ is $\Delta F_0 + \lambda\frac{M_0^4\tau^4}{4\Gamma^4}$, and hence according to equation (27) the difference $\Delta F - \langle W\rangle + \frac{\langle(\Delta W)^2\rangle}{2KT}$ shows up at $O(\tau^2)$. That $\Delta F \neq \langle W\rangle - \frac{\langle(\Delta W)^2\rangle}{2KT}$ in this case is not surprising since the general result is given by equation (1). What is noteworthy is that in the dynamics with $V(x) = V(-x)$, the work distribution is not symmetric about $\langle W\rangle$. To find a convenient modification of equation (2), we return to equation (1) starting with a work probability distribution $P(W)$ of the form

$$P(W) \propto e^{[-\frac{(W-W_0)^2}{2\sigma^2} - \frac{\mu_1(W-W_0)^3}{\sigma^3} - \frac{\mu_2(W-W_0)^4}{\sigma^4}]}, \tag{28}$$

where μ_1, μ_2 and σ are parameters that arrive at the cumulant expansion

$$\Delta F = \langle W\rangle - \frac{\langle (W-\langle W\rangle)^2\rangle}{2KT} + \frac{\langle (W-\langle W\rangle)^3\rangle}{6(KT)^2} + \frac{1}{24}\left[\frac{3\langle (W-\langle W\rangle)^2\rangle^2 - \langle (W-\langle W\rangle)^4\rangle}{(KT)^3}\right] \tag{29}$$

assuming small departure from Gaussian behaviour. The immediate question is whether the dynamics generates $\langle(\Delta W)^3\rangle$. We note that if it does not, then the symmetric correction to the Gaussian distribution, the flatness factor, proportional to $[\langle(\Delta W)^4\rangle - 3\langle(\Delta W)^2\rangle^2]$ would not be able to satisfy the Jarzynski equality since the dynamics yields for this term a leading behaviour proportional to τ, while the leading discrepancy is at $O(\tau^2)$. This correction can only come from $\langle(\Delta W)^3\rangle$. Within perturbation theory, we note that to the leading order

$$\langle(\Delta W)^3\rangle = 3\lambda\langle(\Delta W_0)^2(\Delta W_1)\rangle \tag{30}$$

and a cursory inspection of the solution of the equation of motion shows that $\langle(\Delta W)^3\rangle$ is nonzero and the leading order term is indeed $O(\tau^2)$.

To test equation (29) numerically, we decided to work first with the quadratic nonlinearity in the equation of motion

$$\dot{x} + \Gamma x + \lambda x^2 = M(t) + f(t). \tag{31}$$

We will restrict ourselves to those values of λ (with $\Gamma = 1$) that the trajectory does not run away. In this case, it is the cubic deviation which is the most significant and that would imply an asymmetric probability distribution for the work W. This is not unexpected since the potential for equation (31) is cubic and hence asymmetric. We have taken

$$\begin{aligned} M(t) &= 0 && xt = 0 \\ &= M_0 t && 0 < t < \tau \\ &= M_0\tau && t \geqslant \tau. \end{aligned} \tag{32}$$

In between the interval τ, we generate the values of x at different points by the following:

$$x(t+\Delta t) = x(t) - (x(t) + \lambda x^2(t))\Delta t + M(t)\Delta t + \sqrt{2KT\Delta t}\,\eta(t), \tag{33}$$

where $\eta(t)$ is a random number between 0 and 1. We calculate all the quantities in the unit of $2KT$. We calculate a trajectory $[x(t)]_\tau$ starting from an initial value and evaluate the work according to equation (4). The ensemble is one of the initial conditions $x(0)$ and we calculate $\langle W\rangle$, $\langle(\Delta W)^2\rangle$, $\langle(\Delta W)^3\rangle$.

λ	$-\langle W\rangle$	$\frac{\langle(\Delta W)^2\rangle}{2K_BT}$	$\frac{\langle(\Delta W)^3\rangle}{6(K_BT)^2}$
0.3	0.357	0.078	− 0.003
1.0	0.304	0.052	− 0.005

We have also found the work distribution function $P(W)$. For $\lambda = 0$ (i.e. the system with quadratic potential) and for $\lambda = 20$ the distributions are shown in figures 1 and 3, respectively. For nonzero λ the distribution is asymmetric, which is expected for an asymmetric potential.

We repeated the numerics with quartic oscillator (i.e. $V(x) = \frac{1}{2}x^2 + \frac{\lambda}{4}x^4$) and found that $\langle(\Delta W)^3\rangle$ is certainly nonzero, indicating an asymmetric distribution. For small values of λ, the asymmetry is striking. For large values of λ due to dominating $\langle(\Delta W)^4\rangle$, the distribution

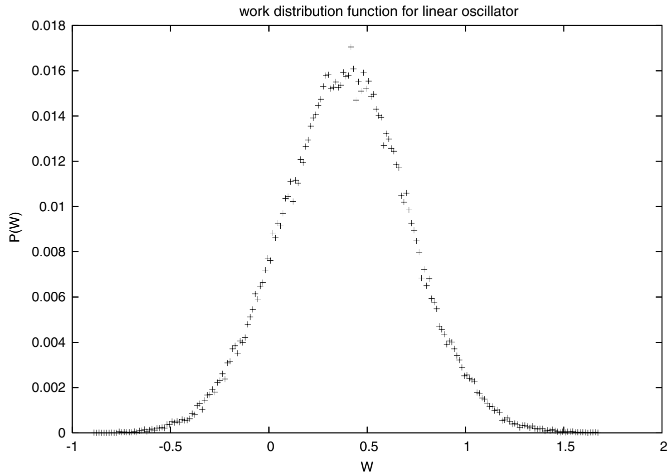

Figure 1. Work probability distribution for $\lambda = 0$. Note the symmetry of the distribution.

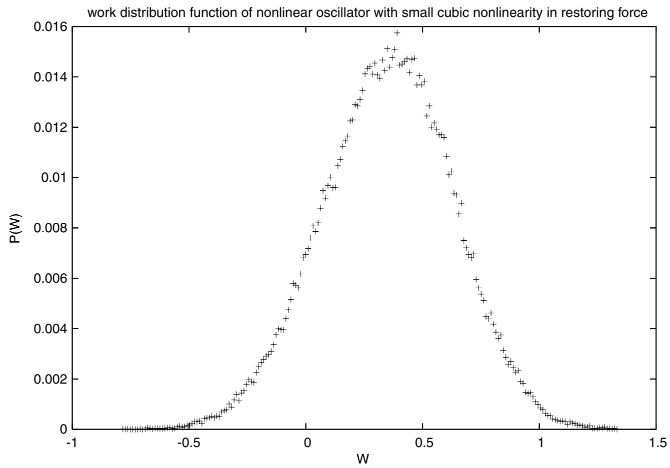

Figure 2. Work probability distribution for $\lambda = 0.1$. The tail on the left-hand side signifies the asymmetrical nature of the distribution here. Here $V(x) = (1/2)x^2 + (0.1/4)x^4$.

becomes sharply peaked, and the asymmetry is difficult to make out, although its existence is guaranteed by the nonzero value of $\langle(\Delta W)^3\rangle$. The distribution for $\lambda = 0.1$ and $\lambda = 20$ is shown in figures 2 and 4, respectively. In figure 5, comparison between the work distribution functions for the cases when $\lambda = 0.1$ and $\lambda = 0$ is shown by plotting together. The asymmetry is clear from it. Recently, Mai and Dhar [18] have found an asymmetric distribution for $V(x) = ax^2 + bx^3 + cx^4$. Our contention is that the asymmetry exists even if $b = 0$. First, we have to calculate F by the following:

$$F = -KT\left[\ln\int \exp\left[-\beta\left(\frac{1}{2}x^2 + \frac{\lambda}{4}x^4 - Mx\right)\right] \mathrm{d}x\right]. \tag{34}$$

We have calculated ΔF using equation (35) at $t = 0$ and $t = \tau$, exactly. Then after calculating required moments from the work probability distribution obtained, and using equation (29), we have calculated ΔF again, which matches well with the previous one. Here we tabulate

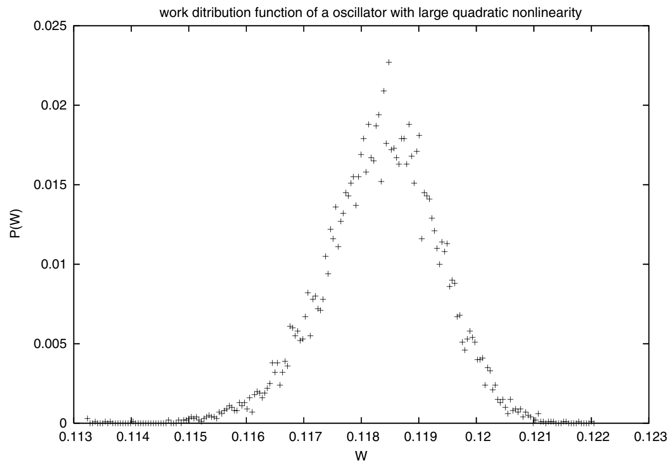

Figure 3. Work probability distribution for $\lambda = 20$. The tail on the left-hand side signifies the asymmetrical nature of the distribution here. Here $V(x) = (1/2)x^2 + (20/3)x^3$.

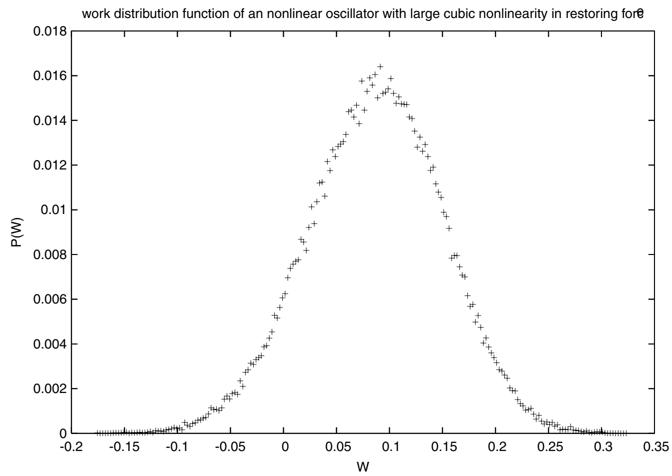

Figure 4. Work probability distribution for $\lambda = 20$. The symmetrical nature is due to dominance of $\langle (W - \langle W \rangle)^4 \rangle$ of the distribution here. Here $V(x) = (1/2)x^2 + (20/4)x^4$.

the numerical results in units of KT for $\lambda = 0.3$, $\lambda = 0.5$, $\lambda = 1$ to show how equation (29) works.

λ	ΔF(from equation (34))	$-\langle W \rangle$	$\frac{\langle (\Delta W)^2 \rangle}{2K_B T}$	$\frac{\langle (\Delta W)^3 \rangle}{6(K_B T)^2}$	$\frac{1}{24}[\frac{3\langle (\Delta W)^2 \rangle^2 - \langle (\Delta W)^4 \rangle}{(KT)^3}]$	ΔF(from equation (29))
0.5	0.4301	0.361	0.077	−0.006	−0.002	0.430
0.3	0.4499	0.373	0.085	−0.007	−0.001	0.450
1.0	0.4010	0.339	0.065	−0.004	−0.006	0.394

Now we will verify Crook's fluctuation theorem. A very important check on the accuracy of our numerical work can be obtained if we try to verify Crooks theorem for our data. Crooks relation gives useful information on the dissipated work and follows from microscopic

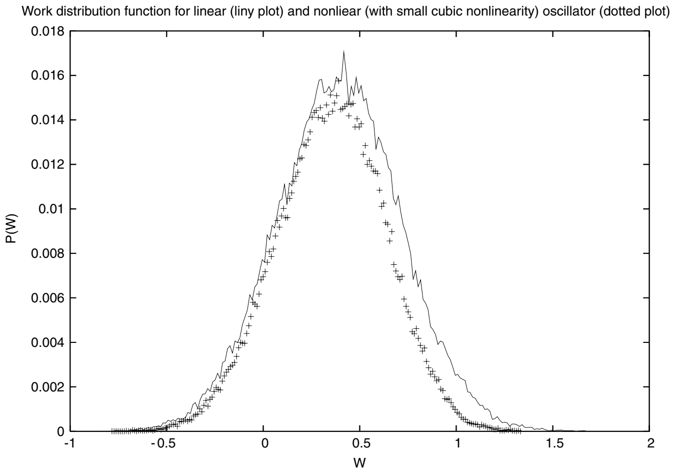

Figure 5. Work probability distributions for $V(x) = (1/2)x^2$ and $V(x) = (1/2)x^2 + (0.1/4)x^4$ are plotted above by the line and dots respectively. The striking asymmetry in the nonlinear case is clear here.

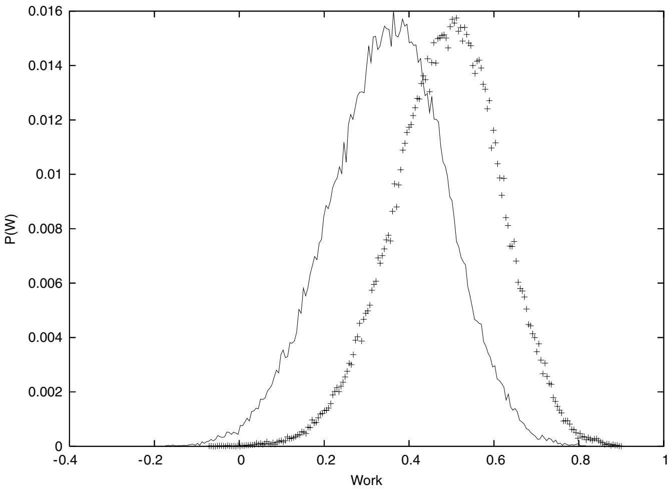

Figure 6. For $\lambda = 0.5$, the line-plot of the work distribution function is for the forward process and other one (dotted plot) is for the backward process. Work corresponding to their crossing point gives the free energy difference precisely.

reversibility and Markovian nature of the dynamics. The result is stated in terms of the forward work, done in driving the system from A to B and the backward work, done in taking it from B to A. If the work probability distribution functions for the forward and backward processes are $P_F(W)$ and $P_R(W)$, then Crooks relation can be written as

$$\frac{P_F(W)}{P_R(W)} = \exp[\beta(W - \Delta F)]. \tag{35}$$

Here we will verify this at $\lambda = 0.5$. To verify the theorem we will use the fact that at the crossing point of the two probability distributions, i.e. the point where $P_F(W) = P_R(W)$, W is precisely ΔF. From figure 6 it is clear that work at the crossing point matches well with the corresponding free energy difference from the table.

We end by pointing out a possible application. We consider a ferromagnet or an Ising magnet near but above its critical point T_c. We can imagine being close to T_c, but sufficiently far away so that the mean field Landau model is valid. If we now switch on a time-dependent magnetic field, then the dynamics of the mean magnetization will be given by an equation of the form shown by equation (16). If we are in the region $T < T_c$, then the dynamics will be governed by equation (16) with an added quadratic nonlinearity—the kind considering [10]. It will be interesting to check the veracity of equation (29) in this case.

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