Work distribution functions in polymer stretching experiments

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(Dated: February 2, 2008)

We compute the distribution of the work done in stretching a Gaussian polymer, made of N monomers, at a finite rate. For a one-dimensional polymer undergoing Rouse dynamics, the work distribution is a Gaussian and we explicitly compute the mean and width. The two cases where the polymer is stretched, either by constraining it's end or by constraining the force on it, are examined. We discuss connections to Jarzynski's equality and the fluctuation theorems.

PACS numbers: 05.40.-a, 05.70.Ln

I. INTRODUCTION.

Classical thermodynamics does not give us all the details about a nonequilibrium process. For example consider a nonequilibrium process during which we perform work W on a system kept in contact with a heat bath at some fixed temperature T. The system starts from an equilibrium state described by the temperature T and some other parameter, say λ (e.g. volume). During the process the parameter changes from its initial value λ_i to a final value λ_f. At the end of the process the system need not be in equilibrium but will eventually relax to an equilibrium state described by T and λ_f. The second law then tells us that

$$W \geq \Delta F \tag{1}$$

where ΔF is the difference of free energy between the two equilibrium states. The equality holds if the process is reversible. For an irreversible process what other information can one extract from a measurement of the work done ? First note that for specified initial and final values of the parameter λ and a fixed path $\lambda(t)$ connecting them, the work done will not have a unique value. Every time we repeat the process we will get a different work done because: (a) the initial microscopic state we start from may be different and (b) for a given initial microscopic state the time evolution is not unique since the system is in contact with a heat bath. Thus we will get a probability distribution for the work done and it is of interest to examine the properties of this distribution. Recently there has been a lot of interest on issues related to properties of such distribution functions. Two very interesting results involving universal properties of these distributions have been proposed.

The first is a very surprising *exact equality* obtained by Jarzynski[1] which states that:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F} \tag{2}$$

where the average is over the work distribution function. This result seems to hold very generally and should be compared with the *inequality* in Eq. 1 that one obtains from usual thermodynamics.

The second set of results are obtained when one looks at the probability distribution of various non-equilibrium quantities (including W) such as, for example, the entropy production. In this case some new fluctuation theorems have been proposed[2,3,4]. These theorems were originally derived for deterministic systems but have also been proved for stochastic systems[5,6,7] These theorems look at the ratio of the probabilities of positive to negative entropy production during a nonequilibrium process and thus give some measure of "second law violations" which can be significant if one is looking either at small systems or at small time intervals. There are two versions of the fluctuation theorem, the steady state fluctuation theorem (SSFT) and the transient fluctuation theorem (TFT). In the former case one looks at a system in a nonequilibrium steady state and the average entropy production rate is examined. In the transient fluctuation theorem a system is initially prepared in thermal equilibrium and one looks at the entropy produced in a finite time τ. An important point to note is that the definition of entropy production in small (non-thermodynamic) systems and in a nonequilibrium situation is somewhat ad-hoc and various definitions have been used. A number of authors[8,9,10,11,12,13]have looked, both theoretically and in experiments, at fluctuations of quantities such as work, power flux, heat absorbed, etc. during a nonequilibrium process. In an interesting work it was shown by Crooks[6] that the Jarzynski equality and the TFT are connected.

Finding universal properties of various nonequilibrium distribution functions is of obvious interest. At the same time the explicit forms of the distributions for different systems is clearly of interest too. Infact for systems such as polymers these are experimentally accessible[14] and it seems plausible that they can give information on the dynamics of the system. There has not been much work in this direction. In a recent paper[15] Speck and Seifert have shown that in the limit of slow driving the work distribution becomes a Gaussian. They consider systems (which could be nonlinear) evolving through Langevin dynamics. Apart from this work, most other explicit calculations of nonequilibrium distribution functions have considered single particle systems.

In this paper we consider the well-known model of a flexible polymer whose motion is governed by Rouse dynamics. We look at the work done when the polymer is stretched at a finite rate. The work distribution func-

tions in different ensembles (constant force and constant extension) are computed explicitly and the dependence of the distributions on switching rates and system sizes is examined. We discuss our results in the context of Jarzynski's equality and the fluctuation theorems (TFT).

II. DISTRIBUTION OF WORK IN THE CONSTANT EXTENSION ENSEMBLE.

We consider a one-dimensional Gaussian polymer whose energy is given by:

$$H = \sum_{l=1,N+1} \frac{k_l}{2}(y_l - y_{l-1})^2 \tag{3}$$

with $y_0 = 0$ and $y_{N+1} = \alpha(t)$ which is a specified function of time. For the moment we take the spring constants k_l to be arbitrary. We assume the following Rouse dynamics for the chain:

$$\dot{y}_l = -\frac{k_l}{\gamma}(y_l - y_{l-1}) + \frac{k_{l+1}}{\gamma}(y_{l+1} - y_l) + \eta_l \quad l = 1, 2...N \tag{4}$$

which can be written in matrix notation as

$$\frac{dy}{dt} = -\frac{1}{\gamma}\mathbf{A}y + \frac{1}{\gamma}h(t) + \eta \tag{5}$$

where $y^T = \{y_1, y_2....y_N\}$, $\eta^T = \{\eta_1, \eta_2, ...\eta_N\}$, $h^T = \{0, 0, ...k_{N+1}\alpha(t)\}$ and the noise satisfies $\langle \eta_l(t)\rangle = 0$ and $\langle \eta_l(t)\eta_m(t')\rangle = 2/(\beta\gamma)\delta_{lm}\delta(t-t')$. The matrix $\mathbf{A}$ is tridiagonal with elements $\mathbf{A}_{l,l} = (k_l + k_{l+1})$, $\mathbf{A}_{l,l+1} = -k_{l+1}$, $\mathbf{A}_{l,l-1} = -k_l$. The general solution of this equation is given by:

$$y(t) = \mathbf{G}(t)y(0) + \int_0^t dt' \mathbf{G}(t-t')\frac{h(t')}{\gamma} + \int_0^t dt' \mathbf{G}(t-t')\eta(t') \tag{6}$$

where $\mathbf{G}(t) = e^{-\mathbf{A}t/\gamma}$. The work done, as defined by Jarzynski, is then given by:

$$\begin{aligned} W_J &= \int_0^\tau \frac{\partial H}{\partial \alpha}\dot{\alpha}dt \\ &= k_{N+1}\int_0^\tau (\alpha - y_N)\dot{\alpha}dt \\ &= \frac{k_{N+1}}{2}(\alpha^2(\tau) - \alpha^2(0)) - \int_0^\tau dt \dot{h}^T y. \end{aligned}$$

This work is equal to the true mechanical work done by the external force which we will call W (thus in this case $W = W_J$). We now plug in the solution for y_N from Eq. 6 to get

$$\begin{aligned} W = \frac{k_{N+1}}{2}(\alpha^2(\tau) - \alpha^2(0)) - \int_0^\tau dt \dot{h}^T[\mathbf{G}(t)y(0) \\ + \int_0^t dt' \mathbf{G}(t-t')\frac{h(t')}{\gamma} + \int_0^t dt' \mathbf{G}(t-t')\eta(t')] \end{aligned} \tag{7}$$

Since W is linear in $y(0)$ and η both of which are Gaussian variables, it follows that the distribution of W will also be Gaussian. We then only need to find the mean and the second moment which we now obtain. We first state a few results on equilibrium properties of the Gaussian chain. The equilibrium free energy of the chain is given by

$$\begin{aligned} Z(\alpha) &= \int dy_1 dy_2 ... dy_N e^{-\beta H} \quad \text{where} \\ H &= \sum_{i=1}^{N+1} \frac{k_i}{2}(y_i - y_{i-1})^2 \\ &= \frac{1}{2}y^T\mathbf{A}y - h^T y + \frac{1}{2}k_{N+1}\alpha^2 \end{aligned} \tag{8}$$

This leads to the following equilibrium free-energy of the polymer (apart from α-independent constants).

$$\begin{aligned} F(\alpha) = \frac{1}{\beta}ln(Z) &= \frac{1}{2}k_{N+1}\alpha^2 - \frac{1}{2}h^T\mathbf{A}^{-1}h \\ &= \frac{1}{2}\bar{k}\alpha^2 \end{aligned} \tag{9}$$

where $1/\bar{k} = 1/k_1 + 1/k_2 + ...1/k_{N+1}$. The mean positions of the particles and their fluctuations can be easily computed at any force and are given by:

$$\langle y\rangle = \mathbf{A}^{-1}h \tag{10}$$

$$\langle\langle (y - \langle y\rangle)(y^T - \langle y^T\rangle)\rangle\rangle = \frac{1}{\beta}\mathbf{A}^{-1} \tag{11}$$

Mean and fluctuations of the work done:
From Eq. 7 we get for the mean work done:

$$\begin{aligned} \langle W\rangle = \frac{k_{N+1}}{2}(\alpha^2(\tau) - \alpha^2(0)) - \int_0^\tau dt \dot{h}^T[\mathbf{G}(t)\langle y(0)\rangle \\ -\frac{1}{\gamma}\int_0^\tau dt \int_0^t dt' \dot{h}^T \mathbf{G}(t-t')h(t') \end{aligned} \tag{12}$$

We do integration by parts so as to express everything in terms of the rates $\dot{h}$. Using the equilibrium results in Eq. (9,10) we finally get:

$$\begin{aligned} \langle W\rangle = \quad & F(\alpha(\tau)) - F(\alpha(0)) \\ & + \int_0^\tau dt \int_0^t dt' \dot{h}^T(t)\mathbf{A}^{-1}\mathbf{G}(t-t')\dot{h}(t') \end{aligned} \tag{13}$$

The fluctuations of the work $\langle (W - \langle W\rangle)^2\rangle = \sigma^2$ is given by:

$$\begin{aligned} \sigma^2 = \int_0^\tau dt \int_0^\tau dt' \dot{h}^T(t)\mathbf{G}(t)\langle [y(0) - \langle y(0)\rangle][y(0) - \langle y(0)\rangle]^T\rangle \\ \times \mathbf{G}(t')\dot{h}(t') + \int_0^\tau dt_1 \int_0^{t_1} dt_1' \int_0^\tau dt_2 \int_0^{t_2} dt_2' \dot{h}^T(t_1)\mathbf{G}(t_1 - t_1') \\ \times \langle \eta(t_1')\eta^T(t_2')\rangle \mathbf{G}(t_2 - t_2')\dot{h}(t_2) \end{aligned}$$

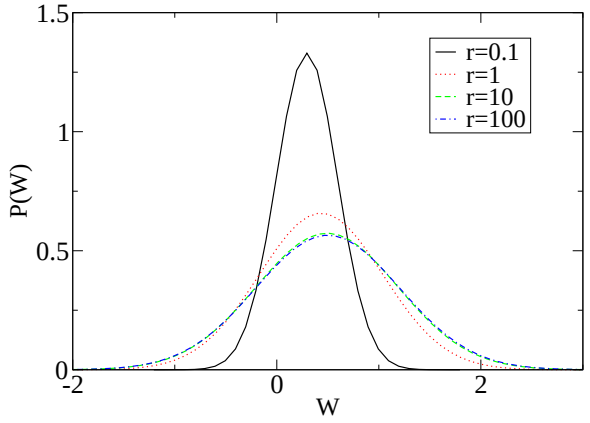

FIG. 1: Distributions of the work done in pulling a short polymer ($N = 1$) at different rates $r = \tau_R/\tau$.

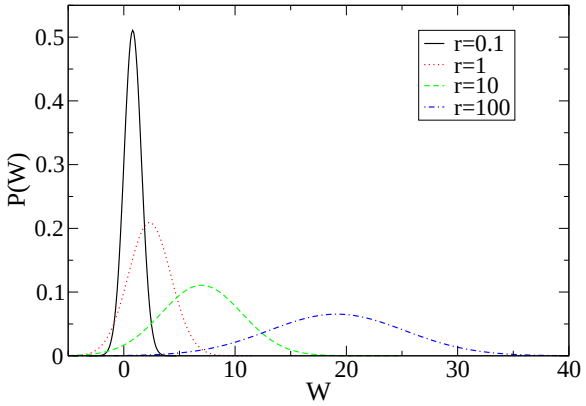

FIG. 2: Distributions of the work done in pulling a long polymer ($N = 100$) at different rates $r = \tau_R/\tau$.

Using Eq. (11) and the relation $\langle \eta(t)\eta^T(t')\rangle = 2/(\beta\gamma)\delta(t-t')\mathbf{I}$ this simplifies to:

$$\sigma^2 = \frac{1}{\beta}\int_0^\tau dt \int_0^\tau dt' \dot{h}^T(t)\mathbf{G}(t)\mathbf{A}^{-1}\mathbf{G}(t')\dot{h}(t') + \frac{4}{\beta\gamma} \times \int_0^\tau dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_2' \dot{h}^T(t_1)\mathbf{G}(t_1-t_2')\mathbf{G}(t_2-t_2')\dot{h}(t_2)$$

Finally using the relation $\int_0^{t_2} dt_2' \mathbf{G}(t_1-t_2')\mathbf{G}(t_2-t_2') = \frac{\gamma\mathbf{A}^{-1}}{2}[\mathbf{G}(t_1-t_2) - \mathbf{G}(t_1)\mathbf{G}(t_2)]$ we get

$$\sigma^2 = \frac{2}{\beta}\int_0^\tau dt \int_0^t dt' \dot{h}^T(t)\mathbf{A}^{-1}\mathbf{G}(t-t')\dot{h}(t') \qquad (14)$$

The distribution of work done is then:

$$P(W) = \frac{1}{(2\pi\sigma^2)^{1/2}} e^{-\frac{(W-\langle W\rangle)^2}{2\sigma^2}} \qquad (15)$$

As expected for a Gaussian process we find that

$$\langle W\rangle - \Delta F = \beta\sigma^2/2. \qquad (16)$$

Note that in the present polymer model both the equilibrium free energy and the average work are independent of temperature while the width of the distribution σ^2 depends linearly on temperature. It is easily verified that the work distribution satisfies the Jarzynski equality $\langle e^{-\beta W}\rangle = e^{-\beta\Delta F}$. On the other hand, with the present definition of work, the fluctuation theorem is not satisfied. However if we define the "dissipated work" $W_{diss} = W - \Delta F$ then the distribution of W_{diss}, $\tilde{P}(W_{diss})$ satisfies the fluctuation theorem:

$$\frac{\tilde{P}(W_{diss})}{\tilde{P}(-W_{diss})} = e^{\beta W_{diss}}.$$

Since W_{diss} gives some measure of deviation from a quasistatic and adiabatic process it seems reasonable to think of it as an entropy production term which is what usually appears in the fluctuation theorems.

Some special cases: Let us consider the case where all spring constants are equal $k_l = k$ and the let us assume that the polymer is pulled at a constant rate so that $\alpha(t) = at/\tau$. The effective spring constant is $k/(N+1)$ and so the free energy of the polymer is $\frac{k\alpha^2}{2(N+1)}$. From Eq. 14 we get the spread in the work done:

$$\sigma^2 = \frac{2a^2\gamma}{\beta\tau}[k^2\mathbf{A}^{-2} + \frac{\gamma}{k\tau}k^3\mathbf{A}^{-3}(e^{-\mathbf{A}\tau/\gamma} - 1)]_{NN} \qquad (17)$$

where $[...]_{NN}$ denotes a matrix element. The average work can be obtained from Eq. 16. In the two limits of very slow ($\tau \to \infty$) and very fast ($\tau \to 0$) processes, we get:

$$\sigma^2 = \frac{2k^2a^2\gamma\mathbf{A}_{NN}^{-2}}{\beta}\frac{1}{\tau} \approx \frac{4a^2\gamma N}{\beta\pi^2\tau} \quad \text{(Slow)} \qquad (18)$$

$$= \frac{ka^2N}{\beta(N+1)} \quad \text{(Fast)} \qquad (19)$$

For an instantaneous pulling process the work done is simply $W = k_{N+1}[(\alpha(\tau) - y_N)^2 - (\alpha(0) - y_N)^2]/2$ and the result in Eq. 19 can be directly obtained.

It is instructive to plot the work distributions for different pulling rates. To see the effect of the polymer length on the distribution we consider two cases: (i) A short polymer with $N = 1,\ k = 1,\ \gamma = 0.1,\ a = 1,\ \beta = 1$ and (ii) a long polymer with $N = 100,\ k = 1,\ \gamma = 0.1,\ a = 10,\ \beta = 1$ (in arbitrary units). In each case the parameter values are chosen so that the change in equilibrium free energy given by $\Delta F = \frac{ka^2}{2(N+1)}$ is of the order of $1/\beta$. The pulling rate has to be compared with the relaxation time of the polymer which is given by $\tau_R = \gamma/\lambda_{sm}$ where $\lambda_{sm} = 4k\sin^2(\frac{\pi}{2(N+1)})$ is the smallest eigenvalue of $\mathbf{A}$. For large N we get $\tau_R = \gamma N^2/(k\pi^2)$. For the cases (i) and (ii) we numerically evaluate Eq. 17 for pulling rates $r = \tau_R/\tau = 0.1,\ 1,\ 10,\ 100$. The resulting distributions are plotted in Fig. 1 and Fig. 2. For the long polymer the probability of negative work realizations is quite small. We can increase their probability by increasing the tem-

perature which broadens the distributions while keeping the mean unchanged.

III. DISTRIBUTION OF WORK IN THE CONSTANT-FORCE ENSEMBLE.

Next we compute the work distribution in the constant-force ensemble. Instead of constraining the end of the polymer we apply a time-dependent force $f(t)$ on it. The time-dependent Hamiltonian of the system is now given by:

$$H = \sum_{l=1,N} \frac{k_l}{2}(y_l - y_{l-1})^2 - f(t)y_N \tag{20}$$

and the equations of motion are again:

$$\frac{dy}{dt} = -\frac{1}{\gamma}\mathbf{A}y + \frac{1}{\gamma}h(t) + \eta$$

with $h^T(t) = [0, 0, ...f(t)]$. In this case we note that the the generalized work W_J, as defined by Jarzynski, is given by $W_J = -\int_0^\tau dt y_N \dot{f}(t)dt$ and is not equal to the true mechanical work done on the system which is $W = \int_0^\tau dt f(t)\dot{y}_N$. In this paper we will compute the distribution of the true mechanical work W. We again find that W has a Gaussian distribution with the following mean and variance:

$$\langle W\rangle = \frac{1}{\gamma}\int_0^\tau dt h^T(t)h(t) - \frac{1}{\gamma^2}\int_0^\tau dt \int_0^t dt' h^T(t) \times \mathbf{G}(t-t')\mathbf{A}h(t') - \frac{1}{g}\int_0^\tau dt h^T(t)\mathbf{G}(t)h(0)$$

$$\sigma^2 = \frac{2}{\beta\gamma}\int_0^\tau dt h^T(t)h(t) - \frac{2}{\beta\gamma^2}\int_0^\tau dt \int_0^t dt' h^T(t) \times \mathbf{G}(t-t')\mathbf{A}h(t')$$

For $f(0) = 0$, we get $\langle W\rangle = \frac{\beta}{2}\sigma^2$ which means that $P(W)$ satisfies the fluctuation theorem. It is then natural to again ask if W is some measure of entropy production. If this was so then W should vanish for an adiabatic process. To check this we first express $\langle W\rangle$ in terms of the rate $\dot{h}(t)$. We get

$$\langle W\rangle = \frac{1}{2}[h^T(\tau)\mathbf{A}^{-1}h(\tau) - h^T(0)\mathbf{A}^{-1}h(0)] - h^T(\tau)\int_0^\tau dt \mathbf{A}^{-1}\mathbf{G}(\tau - t)\dot{h}(t) + \int_0^\tau dt \int_0^t dt' \dot{h}^T(t) \times \mathbf{A}^{-1}\mathbf{G}(t-t')\dot{h}(t')$$

Hence for an adiabatic process we get $\langle W\rangle = -\Delta\mathbf{G}(f)$ where $\mathbf{G}(f) = -h^T\mathbf{A}^{-1}h/2$ is the polymer free energy in the constant force ensemble. Thus in this case $\langle W\rangle$ *is not zero* for an adiabatic process and so it is not an obvious measure of entropy production *even though it does satisfy the fluctuation theorem.*

Interestingly, since $\sigma^2 = 2\langle W\rangle/\beta$, thus even for an adiabatic process, the work-distribution *does not tend* to a δ function as one might naively expect. However in the thermodynamic limit $N \to \infty$ the width approaches zero as $\sigma \sim 1/N^{1/2}$ so in this limit the usual expectation is indeed satisfied.

IV. CONCLUSIONS.

In conclusion, in this paper we have computed explicitly the distribution of work done when a polymer is stretched at a finite rate. We examine different ensembles and look at different definitions of work. As has been noted by earlier authors, for different definitions of the work, the corresponding distributions can have quite different properties. In the constant extension ensemble the generalized work W_J is the same as the true mechanical work W and Jarzynski's identity is satisfied. In this case, the fluctuation theorem is satisfied by a different quantity W_{diss} which does seem like a quantity which gives some measure of entropy production. In the constant force ensemble, W_J is different from the true work W which does not satisfy the Jarzynski identity. On the other hand the distribution of W satisfies a fluctuation-theorem like relation. However in this case we find that it is not possible to identify the work as a measure of entropy production.

As a practical use, the Jarzynski identity has been proposed as an efficient method for computing equilibrium free energy profiles from nonequilibrium measurements, both in simulations and experiments[16,17]. For the specific case of polymers, we expect that a combination of simulations and our exact results on the work distribution, should lead to better estimates on efficiency and of errors[18,19,20] (and how they depend on rates and system sizes) involved while using the nonequilibrium methods in free energy computations.

For non-Gaussian models of polymers such as, for example, semiflexible polymers, the work distribution function is likely to be non-Gaussian. For small pulling rates one again expects a Gaussian distribution. It will be interesting to compute such distributions explicitly and study their dependences on rates, system sizes and other parameters such as the rigidity of the polymer.

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