Work fluctuations in an elastic dumbbell model of polymers in planar elongational flow

Rati Sharma and Binny J. Cherayil*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

(Received 19 December 2010; revised manuscript received 3 February 2011; published 28 April 2011)

We use a path-integral approach to calculate the distribution $P(w,t)$ of the fluctuations in the work w at time t of a polymer molecule (modeled as an elastic dumbbell in a viscous solvent) that is acted on by an elongational flow field having a flow rate $\dot{\gamma}$. We find that $P(w,t)$ is non-Gaussian and that, at long times, the ratio $P(w,t)/P(-w,t)$ is equal to $\exp[w/(k_BT)]$, independent of $\dot{\gamma}$. On the basis of this finding, we suggest that polymers in elongational flows satisfy a fluctuation theorem.

DOI: 10.1103/PhysRevE.83.041805 PACS number(s): 61.41.+e, 05.40.−a, 83.50.Jf

I. INTRODUCTION

Thermodynamics on the scale of single molecules is characterized by a marked sensitivity of its measurable properties to the effects of fluctuations [1]. As a result, and in contrast to the situation in the bulk, measurements of thermodynamic quantities in different samples prepared under nominally identical conditions do not always yield the same value. However, on the basis of very general principles of nonequilibrium statistical mechanics, it is believed that the distributions of these values (for selected stochastic variables) must satisfy certain mathematical constraints that are now referred to as fluctuation theorems [2]. A great deal of current research has been devoted to the experimental study and verification of this idea [1,3–6].

Monitoring the time-dependent work done during many repetitions of the forced unfolding of compact macromolecules (like hairpin RNA) has been one of the many methods by which fluctuation theorems have been tested [4]. The work distributions determined from such experiments are often Gaussian, with the mean and variance so related to each other that a special case of the fluctuation theorem—the so-called Jarzynski relation [7]—is found to be satisfied. The same relation has been shown to hold theoretically in a model system consisting of a Rouse chain acted on by a constant force at one end [8].

Because of their size and conformational flexibility, polymers are particularly attractive objects for the study of fluctuation relations at the single-molecule level. But mechanical pulling (by optical tweezers, for instance [4,9]) is not the only method of stretching them under controlled conditions. Subjecting them to flow fields produces similar (but not necessarily identical) results. Since polymer-flow interactions are also accompanied by the performance of work or the dissipation of heat as the molecule cycles between stretched and relaxed conformations under the action of both the flow field and thermal fluctuations in the medium, the distributions of these quantities can also, in principle, be measured. That does not appear to have been done, however, although numerous other statistical quantities in such systems have been probed [10,11]. It is not yet clear, therefore, whether polymers in flow fields are also governed by the same fluctuation theorems that hold under other conditions. To the best of our knowledge, the question does not appear to have been addressed theoretically either, except somewhat tangentially [12], so any insights that can be provided at this stage are likely to be interesting in their own right and possibly helpful in the interpretation of experimental results, whenever they are obtained.

It is with this in mind that we calculate the work distribution function for a simple but instructive model of a polymer-flow system: an elastic dumbbell in a planar elongational flow field. The elastic dumbbell has been a widely used model of chain conformational behavior [13], and it is expected to serve as a heuristic for calculations based on more realistic but less easily treated models. As we will show, the calculation of the work distribution function for the elastic dumbbell can be carried out exactly using path integrals. Our results indicate that the distribution of work fluctuations for this system satisfies constraints analogous to those associated with mechanical deformations.

The following section sets up the equations for the stochastic evolution in an external flow field of the two harmonically coupled beads that define the dynamics of a dumbbell in a viscous solvent. These equations are separated into independent equations for the position of the center-of-mass $\boldsymbol{\rho}$ and the interbead distance $\mathbf{R}$. The latter, along with the equation for the evolution of the work done during the stretching of the dumbbell by the flow, which can be written entirely in terms of the internal coordinate $\mathbf{R}$, defines our model of chain dynamics. In Sec. III, a path-integral representation of the distribution of this work at time t is derived, and then evaluated in Sec. IV for the special case of an initial distribution corresponding to a collapsed configuration of the dumbbell. The results of the calculation are discussed in Sec. V in the context of a generalized fluctuation theorem. Some details of the evaluation of the path integral are provided in the Appendix.

II. DYNAMICAL EQUATIONS OF DUMBBELL MODEL

The dumbbell is assumed to consist of two point beads of mass m joined by a harmonic spring. The state of the system at time t is defined by the positions of these beads in some laboratory-fixed frame [13]. If these positions are denoted $\mathbf{r}_1$ and $\mathbf{r}_2$, the evolution of the dumbbell in a viscous solvent in a velocity field $\mathbf{v}(\mathbf{r}) \equiv \mathbf{v}_0 + \dot{\gamma}\boldsymbol{\kappa}\cdot\mathbf{r}$ under overdamped conditions and in the absence of hydrodynamic interactions [14] is

*Corresponding author: cherayil@ipc.iisc.ernet.in

given by

$$-\zeta\dot{\mathbf{r}}_i(t)+\zeta[\mathbf{v}_0+\dot{\gamma}\boldsymbol{\kappa}\cdot\mathbf{r}_i(t)]-\frac{\partial U(|\mathbf{r}_i-\mathbf{r}_j|)}{\partial \mathbf{r}_i}+\boldsymbol{\theta}_i(t)=\mathbf{0},\quad i,j=1,2. \tag{1}$$

Here, ζ is the friction coefficient of the bead, $\mathbf{v}_0$ is a constant space-independent background solvent velocity, $\dot{\gamma}$ is the flow rate, $\boldsymbol{\kappa}$ is the velocity gradient tensor (to be specified later), U is the harmonic potential of the spring given by $U=k(\mathbf{r}_1-\mathbf{r}_2)^2/2$ with k being the spring constant, and $\boldsymbol{\theta}_i(t)$ is a random force acting on bead i whose properties are defined by its mean and variance: $\langle\boldsymbol{\theta}_i(t)\rangle=0$ and $\langle\theta_{i\alpha}(t)\theta_{j\beta}(t')\rangle=2\zeta k_BT\delta_{ij}\delta_{\alpha\beta}\delta(t-t')$ with $i,j=1,2$ and $\alpha,\beta=x,y,z$.

The coupled equations for the two beads can be separated into independent equations by introducing coordinates for the center of mass and the interbead separation. These are defined as $\boldsymbol{\rho}=(\mathbf{r}_1+\mathbf{r}_2)/2$ and $\mathbf{R}=\mathbf{r}_2-\mathbf{r}_1$, respectively. The equations of motion for these coordinates are:

$$\dot{\boldsymbol{\rho}}(t)=\mathbf{v}_0+\dot{\gamma}\boldsymbol{\kappa}\cdot\boldsymbol{\rho}(t)+\zeta^{-1}\boldsymbol{\xi}(t), \tag{2a}$$

$$\dot{\mathbf{R}}(t)=\dot{\gamma}\boldsymbol{\kappa}\cdot\mathbf{R}(t)-2\zeta^{-1}\frac{\partial U(|\mathbf{R}|)}{\partial\mathbf{R}}+\zeta^{-1}\boldsymbol{\eta}(t), \tag{2b}$$

where $\boldsymbol{\xi}(t)=[\boldsymbol{\theta}_1(t)+\boldsymbol{\theta}_2(t)]/2$ and $\boldsymbol{\eta}(t)=\boldsymbol{\theta}_2(t)-\boldsymbol{\theta}_1(t)$.

During an interval of time t, a certain amount of work w is done by the beads as they respond to the effects of the flow field of the surrounding solvent. As discussed by Speck [12], the expression that defines w under these conditions is obtained by noting that the work done by a system subject to flow must be the same in both laboratory-fixed (Eulerian) and comoving (Lagrangian) frames of reference. This means, in effect, that the rate $\dot{w}$ of doing work must be given by the material time derivative of the system's internal energy U, which may be regarded (in general) as a function of an external control parameter λ and an internal coordinate $\mathbf{x}$. That is, $\dot{w}=DU/Dt$, where D/Dt is the material time derivative (referred to as the convective derivative in [12]) and is given by $D/Dt=\partial/\partial t+\mathbf{u}(\mathbf{x})\cdot\nabla_{\mathbf{x}}$, where $\mathbf{u}(\mathbf{x})$ is the solvent velocity field at $\mathbf{x}$. Thus, in general, $\dot{w}=\dot{\lambda}\partial U/\partial\lambda+\mathbf{u}(\mathbf{x})\cdot\nabla_{\mathbf{x}}U$. For the elastic dumbbell considered here, therefore, the work rate is given by

$$\dot{w}(t)=\sum_{i=1}^{2}\mathbf{v}(\mathbf{r}_i)\cdot\nabla_{\mathbf{r}_i}U(|\mathbf{r}_2-\mathbf{r}_1|), \tag{3}$$

which, after the substitution of the definitions of the velocity field $\mathbf{v}(\mathbf{r})$ and the internal coordinate $\mathbf{R}$, reduces to

$$\dot{w}(t)=[\dot{\gamma}\boldsymbol{\kappa}\cdot\mathbf{R}(t)]\cdot\frac{\partial U(|\mathbf{R}|)}{\partial\mathbf{R}}. \tag{4}$$

Equations (2b) and (4) are the defining equations of our model.

III. WORK DISTRIBUTION IN PATH-INTEGRAL FORM

The work done by the dumbbell in a time t is a functional of its configuration $\mathbf{R}$, which, in turn, is a functional of the noise $\boldsymbol{\eta}$. Since $\boldsymbol{\eta}$ is a Gaussian stochastic variable [whose mean and variance, as derived from its definition in terms of $\boldsymbol{\theta}$, are given by $\langle\boldsymbol{\eta}(t)\rangle=\mathbf{0}$ and $\langle\eta_\alpha(t)\eta_\beta(t')\rangle=4\zeta k_BT\delta_{\alpha\beta}\delta(t-t')$], the probability $P[\boldsymbol{\eta}]$ that a given realization of the noise is observed in the time t can be written as [15–17]

$$P[\boldsymbol{\eta}]\propto\exp\left[-\frac{1}{8\zeta k_BT}\int_0^t dt'\boldsymbol{\eta}(t')\cdot\boldsymbol{\eta}(t')\right]. \tag{5}$$

The probability $P[\mathbf{R}]$ that the dumbbell is in the configuration $\mathbf{R}$ is therefore given by

$$P[\mathbf{R}]\propto J\exp\bigg[-\frac{1}{8\zeta k_BT}\int_0^t dt'[\zeta\dot{\mathbf{R}}(t')-\mathbf{D}\cdot\mathbf{R}(t')]\cdot[\zeta\dot{\mathbf{R}}(t')-\mathbf{D}\cdot\mathbf{R}(t')]\bigg], \tag{6}$$

where J is the Jacobian of the transformation from $\boldsymbol{\eta}$ to $\mathbf{R}$ variables and $\mathbf{D}$ is the matrix $\mathbf{D}=\zeta\dot{\gamma}\boldsymbol{\kappa}-2k\mathbf{1}$, with $\mathbf{1}$ being the unit tensor. The Jacobian J is defined formally as $|\det(\partial\boldsymbol{\eta}/\partial\mathbf{R})|$ and can be obtained from a discrete representation of the Langevin equation for the evolution of $\mathbf{R}$. Different conventions may be adopted for the discretization procedure; our results are based on the following [15]:

$$\boldsymbol{\eta}(t_i)=\zeta\frac{\mathbf{R}(t_i)-\mathbf{R}(t_{i-1})}{\Delta t}-\mathbf{D}\cdot\frac{\mathbf{R}(t_i)+\mathbf{R}(t_{i-1})}{2},\quad i=1,2,\ldots,N, \tag{7}$$

where Δt is an infinitesimal increment of time and $t_i=i\Delta t$. The continuum limit in this representation corresponds to $\Delta t\to0$, $N\to\infty$, and $N\Delta t\to t$. From Eq. (7), we see that the matrix of derivatives $\partial\boldsymbol{\eta}_i/\partial\mathbf{R}_j$, $i,j=1,N$ is of lower triangular form, so its determinant is easily found to be

$$\begin{aligned}J&=\prod_{i=1}^{N}|\zeta\mathbf{1}/\Delta t-\mathbf{D}\cdot\mathbf{1}/2|=\prod_{i=1}^{N}(\zeta/\Delta t+k)^3\\&=(\zeta/\Delta t)^{3N}\prod_{i=1}^{N}[1+3k\Delta t/\zeta\\&\quad+O(\Delta t^2)]\underset{N\Delta t\to t}{\overset{\Delta t\to0,N\to\infty}{\to}}(\zeta/\Delta t)^{3N}\exp(3kt/\zeta).\end{aligned}$$

If we now consider the special case of planar elongational flow, the velocity gradient tensor is given by

$$\boldsymbol{\kappa}=\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}. \tag{8}$$

For this case, Eq. (6) becomes

$$\begin{aligned}P[\mathbf{R}]\propto\exp(3kt/\zeta)\exp\bigg[-\frac{\zeta}{8k_BT}\int_0^t dt'\bigg\{&\dot{R}_x^2+\dot{R}_y^2+\dot{R}_z^2+\frac{4k}{\zeta}(\dot{R}_xR_x+\dot{R}_yR_y+\dot{R}_zR_z)\\&-2\dot{\gamma}(\dot{R}_xR_y+R_x\dot{R}_y)+\frac{4k^2}{\zeta^2}\bigg[\bigg(1+\frac{\zeta^2\dot{\gamma}^2}{4k^2}\bigg)R_x^2+\bigg(1+\frac{\zeta^2\dot{\gamma}^2}{4k^2}\bigg)R_y^2+R_z^2\bigg]-\frac{8k\dot{\gamma}}{\zeta}R_xR_y\bigg\}\bigg],\end{aligned} \tag{9}$$

where the variables R_x, R_y, etc. are understood to depend on time t' and where the infinite factor of $(\zeta/\Delta t)^{3N}$ has been omitted since it can be absorbed into the definition of a proportionality constant that normalizes the probability distribution.

The probability density $P(w,t)$ that an amount of work w is done at time t can be defined, in general, as

$$P(w,t) = \langle \delta[w - w(t)] \rangle, \tag{10}$$

where $w(t) = k\dot{\gamma} \int_0^t dt' R_x(t') R_y(t')$, and the angular brackets denote an average with respect to the probability density function of Eq. (9). By introducing the Fourier representation of the delta function into Eq. (10), we can express $P(w,t)$ as

$$P(w,t) = e^{3kt/\zeta} \int_{-\infty}^{\infty} d\lambda \int d^3\mathbf{R}_0 \int d^3\mathbf{R}_f \, P(\mathbf{R}_0) \exp\left[-\frac{\beta k}{4}\left(R_{xf}^2 - R_{x0}^2 + R_{yf}^2 - R_{y0}^2 + R_{zf}^2 - R_{z0}^2\right)\right] \times G(\mathbf{R}_f, t|\mathbf{R}_0, 0) \exp(i\lambda w), \tag{11a}$$

where the $P(\mathbf{R}_0)$ is the distribution of initial values of the interbead separation (which will be specified later), and G is the path integral

$$G(\mathbf{R}_f, t|\mathbf{R}_0, 0) = \int_{R_x(0)=R_{x0}}^{R_x(t)=R_{xf}} \mathscr{D}[R_x] \int_{R_y(0)=R_{y0}}^{R_y(t)=R_{yf}} \mathscr{D}[R_y] \int_{R_z(0)=R_{z0}}^{R_z(t)=R_{zf}} \mathscr{D}[R_z] \exp\left[-\int_0^t dt' \mathscr{L}(R_x, R_y, R_z, \dot{R}_x, \dot{R}_y, \dot{R}_z)\right], \tag{12a}$$

where $\mathscr{D}[\mathbf{R}]$ represents the measure on the space of trajectories of $\mathbf{R}$, and

$$\mathscr{L} = a_0\left(\dot{R}_x^2 + \dot{R}_y^2 + \dot{R}_z^2\right) - a_2(\dot{R}_x R_y + R_x \dot{R}_y) - a_3 R_x R_y + a_4\left(R_x^2 + R_y^2\right) + a_5 R_z^2, \tag{12b}$$

with $a_0 = \beta\zeta/8$, $a_2 = \beta\zeta\dot{\gamma}/4$, $a_3 = k\dot{\gamma}(\beta - 2i\lambda)$, $a_4 = \beta k^2[1 + \zeta^2\dot{\gamma}^2/(4k^2)]/(2\zeta)$, and $a_5 = \beta k^2/(2\zeta)$

IV. CHARACTERISTIC FUNCTION OF WORK DISTRIBUTION

Being a quadratic path integral, the propagator $G(\mathbf{R}_f, t|\mathbf{R}_0, 0)$ of Eq. (12a) can be found exactly using Feynman's variational method [17,18]. But the calculations are extremely lengthy (though fairly straightforward), so only an outline of key steps in the derivation is included, which may be found in the Appendix. Once G is determined and a definite choice is made for the distribution function $P(\mathbf{R}_0)$ of initial positions, the next step is to carry out the integrations over the end points of the chain to produce, in effect, the characteristic function of $P(w,t)$ [i.e., the function $\mathscr{C}(\lambda) \equiv \langle \exp[-i\lambda w(t)] \rangle$]. In the present calculations we choose the initial distribution to correspond to a collapsed configuration of the chain. Specifically,

$$P(\mathbf{R}_0) = \delta(R_x)\delta(R_y)\delta(R_z). \tag{13}$$

With this choice, it can be shown that the final expression for $\mathscr{C}$ is

$$\mathscr{C}(\lambda) = 2a_0 \exp(3kt/\zeta) A_1 A_2 A_3 A_4, \tag{14a}$$

where

$$A_1 = \left(\frac{\sqrt{a_0 a_5(\Omega^2 - \varpi^2)}}{\sinh(t\sqrt{a_5/a_0}) \sinh(t\sqrt{\Omega - \varpi}) \sinh(t\sqrt{\Omega + \varpi})}\right)^{1/2}, \tag{14b}$$

$$A_2 = \left(\frac{\beta k}{2} + a_2 + 2a_0\sqrt{\Omega + \varpi} \coth(t\sqrt{\Omega + \varpi})\right)^{-1/2}, \tag{14c}$$

$$A_3 = \left(\frac{\beta k}{2} - a_2 + 2a_0\sqrt{\Omega - \varpi} \coth(t\sqrt{\Omega - \varpi})\right)^{-1/2}, \tag{14d}$$

$$A_4 = \left(\frac{\beta k}{4} + \sqrt{a_0 a_5} \coth(t\sqrt{a_5/a_0})\right)^{-1/2}, \tag{14e}$$

with $\Omega \equiv a_4/a_0$ and $\varpi \equiv a_3/(2a_0)$.

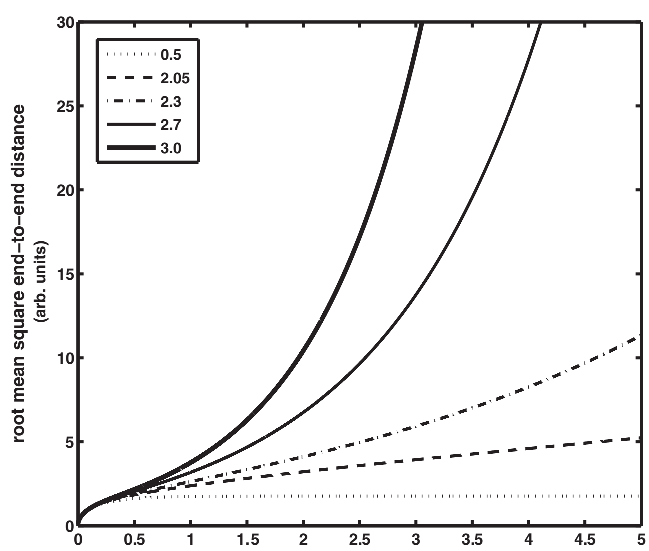

FIG. 1. Time dependence of the mean-square end-to-end distance $\langle \mathbf{R}^2(t) \rangle$, as calculated from Eq. (17), at the following flow rates $\dot{\gamma}$ (in arbitrary units) : 0.5 (dotted line), 2.05 (dashed line), 2.3 (dot-dashed line), 2.7 (thin solid line), and 3.0 (thick solid line). The values of the other phenomenological parameters in Eq. (17) [which are defined after Eq. (12b)] are determined by the values assigned to the thermal energy scale $\beta = (k_B T)^{-1}$, the spring constant k, and the friction coefficient ζ, which have all been set to unity.

The work distribution itself, $P(w,t)$, which is given formally by

$$P(w,t) = \int_{-\infty}^{\infty} d\lambda \exp(i\lambda w)\mathscr{C}(\lambda), \tag{15}$$

cannot be found in closed form from the above expression for $\mathscr{C}(\lambda)$, although it can be evaluated numerically for given values of w, t and the other phenomenological parameters that appear in Eq. (9) and that are defined after Eq. (12b). A discussion of the key features of the numerically evaluated distribution, in particular its connection to a fluctuation theorem, will be presented in the next section. Moments of $P(w,t)$ can, however, be determined analytically from the formulas

$$\langle w(t)\rangle = i\frac{\partial}{\partial\lambda}\langle\exp[-i\lambda w(t)]\rangle\Big|_{\lambda=0}, \tag{16a}$$

$$\langle w^2(t)\rangle = -\frac{\partial^2}{\partial\lambda^2}\langle\exp[-i\lambda w(t)]\rangle\Big|_{\lambda=0}. \tag{16b}$$

The actual expressions for these moments are rather complicated, and are not reproduced here in the interests of brevity.

V. RESULTS AND DISCUSSION

Before turning to the principal result of our calculations—the form of the probability density of the work done by a dumbbell in planar elongational flow—we should first like to note that from the equation we have derived for the propagator $G(\mathbf{R}_f,t|\mathbf{R}_0,0)$ it is a simple matter to calculate the mean square end-to-end distance of the chain, $\langle\mathbf{R}^2(t)\rangle$, using the relation

$$\langle\mathbf{R}^2(t)\rangle = \int d\mathbf{R}_f \int d\mathbf{R}_0 P(\mathbf{R}_0)(\mathbf{R}_f - \mathbf{R}_0)^2 G(\mathbf{R}_f,t|\mathbf{R}_0,0) \times \frac{\exp\left[-\frac{\beta k}{4}\left(R_{xf}^2 + R_{x0}^2 + R_{yf}^2 + R_{y0}^2 + R_{zf}^2 + R_{z0}^2\right)\right]}{\int d\mathbf{R}_f \int d\mathbf{R}_0 P(\mathbf{R}_0) G(\mathbf{R}_f,t|\mathbf{R}_0,0)\exp\left[-\frac{\beta k}{4}\left(R_{xf}^2 + R_{x0}^2 + R_{yf}^2 + R_{y0}^2 + R_{zf}^2 + R_{z0}^2\right)\right]}, \tag{17}$$

with $P(\mathbf{R}_0)$ given by Eq. (13), and the propagator G given by Eq. (12a) with the parameter λ set to 0 in the coefficient a_3. Because the actual expression for this $\langle\mathbf{R}^2(t)\rangle$ is lengthy, it is not reproduced here but is instead shown graphically in Fig. 1 as a function of time t for various flow rates $\dot{\gamma}$. One conclusion that is suggested by these curves is that significant stretching of the chain is possible only after a certain critical value of the flow rate is reached; the same conclusion is suggested by the plot of $\langle\mathbf{R}^2(t)\rangle$ versus $\dot{\gamma}$ at fixed t (Fig. 2). The nature of the curves in Figs. 1 and 2 is broadly consistent with the long-held view (put forward by de Gennes [19]) that compact polymers tend to unravel under a force only after the polymer's entropic elasticity is overcome by a certain threshold force. At this threshold force (or critical strain rate), the polymer undergoes what is generally referred to as a coil-stretch transition [19,20]. Recent single-molecule experiments by Chu *et al.* [10] have,

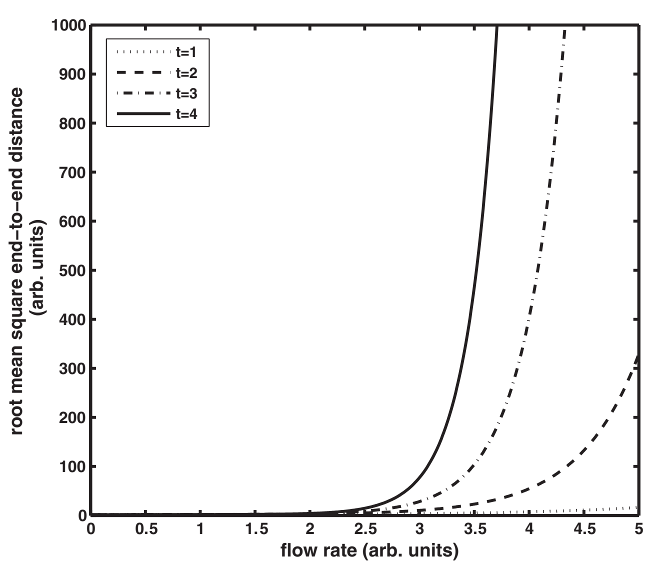

FIG. 2. Flow-rate dependence of the mean-square end-to-end distance $\langle\mathbf{R}^2(t)\rangle$, as calculated from Eq. (17), at the following times t (in arbitrary units): 1.0 (dotted line), 2.0 (dashed line), 3.0 (dot-dashed line), and 4.0 (solid line). The other parameters in the equation are assigned the same values as used in Fig. 1.

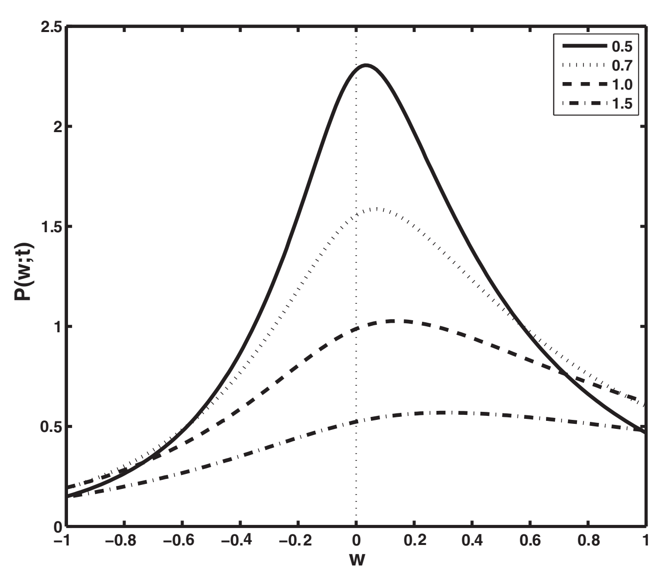

FIG. 3. Work distribution $P(w,t)$ vs. w, as calculated from Eq. (15), at the arbitrary fixed time $t = 1.5$ and at the following flow rates: 0.5 (solid line), 0.7 (dotted line), 1.0 (dashed line), and 1.5 (dot-dashed line). The other parameters in the equation are assigned the same values as used in Fig. 1.

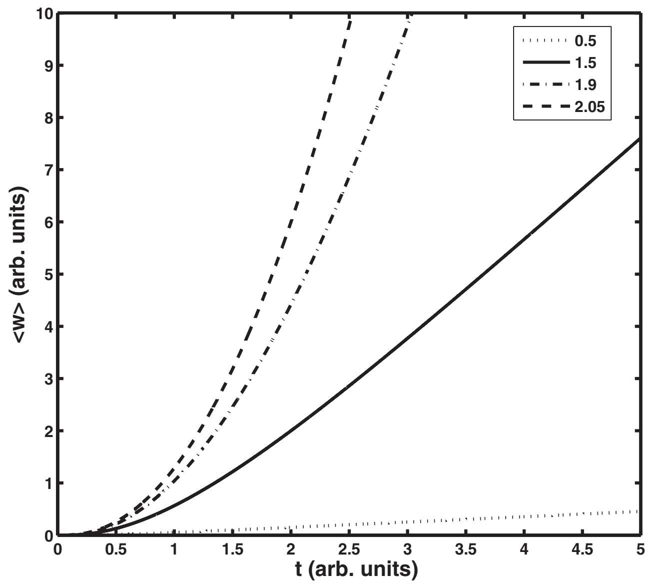

FIG. 4. Time dependence of the mean work $\langle w\rangle$, as calculated from Eq. (16a), at the following flow rates: 0.5 (dotted line), 1.5 (solid line), 1.9 (dot-dashed line), and 2.05 (dashed line). The other parameters in the equation are assigned the same values as used in Fig. 1.

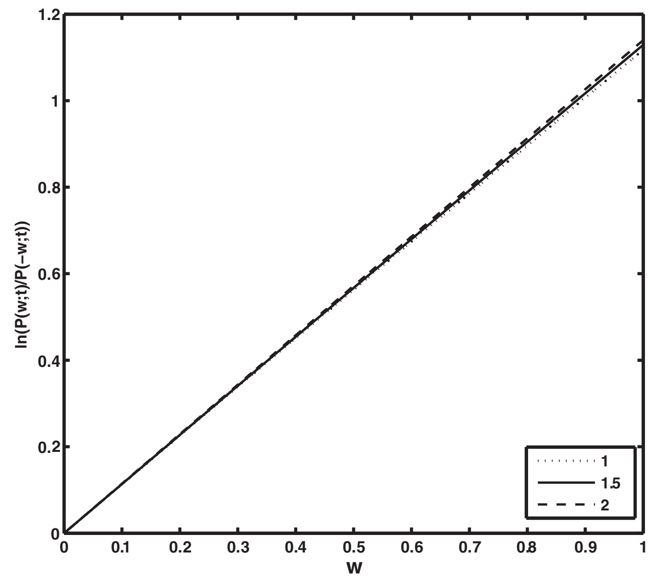

FIG. 6. Dependence of ln $[P(w,t)/P(-w,t)]$ on βw (with β set to 1), as calculated from Eq. (15), at the fixed time $t = 2$ and at the following flow rates: 1.0 (dotted line), 1.5 (full line), and 2.0 (dashed line). The other parameters in the equation are assigned the same values as used in Fig. 1.

in fact, provided direct evidence of such transitions, although they seem to occur less abruptly than the effect predicted by theory. That these general trends are mostly reproduced in our calculations suggests that the underlying dumbbell model is sufficiently realistic to serve as a starting point for the study of work fluctuations in long-chain molecules.

With this in mind, we return to a consideration of the model's work distribution, which is defined formally by Eq. (15), and which is obtained by numerical integration of that equation. A plot of $P(w,t)$ evaluated in this way is shown in Fig. 3 as a function of the work w for different flow rates $\dot{\gamma}$ at the arbitrary fixed time $t = 1.5$. Interestingly, the curves show clear evidence of non-Gaussian behavior at all flow rates, so they are quite distinct from the Gaussian work distributions found by Dhar [8] and Speck and Seifert [21] for the stretching of a model Rouse chain. This is to be expected since the work,

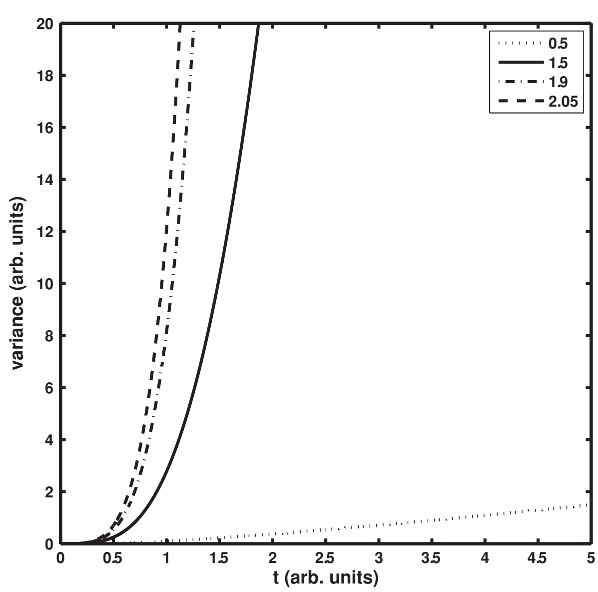

FIG. 5. Time dependence of the variance of the work $\langle w^2\rangle - \langle w\rangle^2$, as calculated from Eq. (16b), at the following flow rates: 0.5 (dotted line), 1.5 (solid line), 1.9 (dot-dashed line), and 2.05 (dashed line). The other parameters in the equation are assigned the same values as used in Fig. 1.

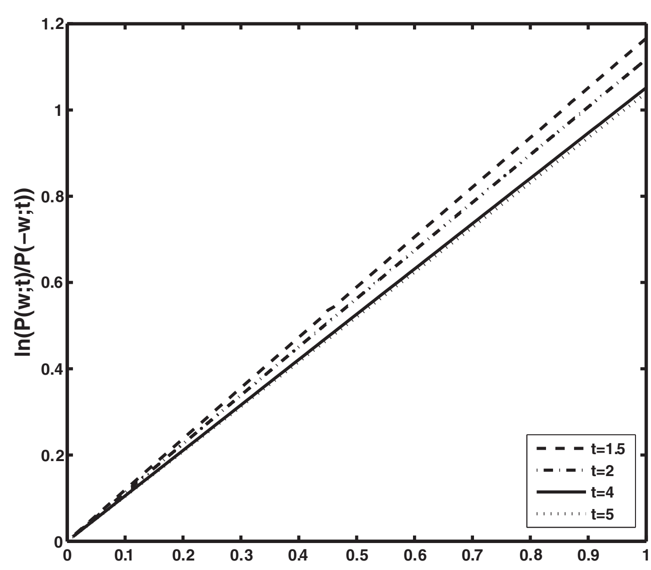

FIG. 7. Dependence of ln$[P(w,t)/P(-w,t)]$ on βw (with β set to 1), as calculated from Eq. (15), at the fixed flow rate $\dot{\gamma} = 1$ and at the following times: 1.5 (dashed line), 2 (dot-dashed line), 4 (full line), and 5 (dotted line). The other parameters in the equation are assigned the same values as used in Fig. 1.

as defined in our calculations [Eq. (4)], is no longer a linear functional of the trajectory of the coordinate **R**.

Both the mean $\langle w\rangle$ and the variance $\sigma \equiv \langle w^2\rangle - \langle w\rangle^2$ of $P(w,t)$ can be calculated analytically from the characteristic function $\mathscr{C}(\lambda)$ [see Eqs. ([14]), (16a), and (16b)]. They are shown, respectively, in Figs. 4 and 5 as a function of time t at fixed flow rate $\dot{\gamma}$. Both variables tend to increase linearly with t at small values of $\dot{\gamma}$, and to increase significantly faster with t at larger values of $\dot{\gamma}$, somewhat in the manner of the mean-square end-to-end distance.

The function $P(w,t)$ itself shows far more interesting behavior when plotted in the form $\ln[P(w,t)/P(-w,t)]$ versus βw (with β set to 1 for convenience) for different $\dot{\gamma}$ at fixed time. The plot is shown in Fig. 6 for $t = 2$ and three different values of $\dot{\gamma}$. The curves all lie essentially on a single straight line (with some slight dispersion at large w) that passes through the origin and has a slope that lies between about 1.1 and 1.2. This suggests, but does not quite establish, that

$$\frac{P(w,t)}{P(-w,t)} = \exp(\beta w), \tag{18}$$

independent of $\dot{\gamma}$. However, if one plots the same function at still larger times, one notices a clear tendency for the slope to decrease towards 1.0 (again independent of $\dot{\gamma}$), though the decrease is quite slow. This trend is shown in Fig. 7, where the variation of $\ln[P(w,t)/P(-w,t)]$ with w is plotted at four successively higher times. Unfortunately, the highest time that appears to be accessible to these calculations before numerical instabilities in the integration routine (MATHEMATICA) lead to nonconvergent results is about 5. Nevertheless, these results strongly suggest that

$$\frac{P(w,t)}{P(-w,t)} = \exp(\beta w), \quad t \gg 1, \tag{19}$$

a relation that also appears to characterize the measured work fluctuations of the harmonic oscillator system of Ref. [6]. Equation (19) is one common mathematical statement of a fluctuation theorem, and it is the key finding of these calculations.

Thus, we believe we have shown that the long-time distribution of the fluctuations in the work done by a Hookean dumbbell placed in a viscous solvent in the presence of a planar elongational flow field and in the absence of hydrodynamic interactions satisfies a fluctuation theorem. Whether real polymers (which behave only approximately as Hookean springs, being finitely extensible, and which are generally not free-draining) likewise satisfy the fluctuation theorem under similar conditions is a question in which we hope our results will spur experimental interest. In addressing this question, the role of hydrodynamic interactions will be especially important to understand. Indeed, recent simulations of the response of collapsed globular polymers to elongational flow [22] indicate that the onset of a coil-stretch transition is strongly influenced by such interactions (modeled in these calculations by the Rotne-Prager tensor). Any effect that influences the transition will therefore also influence the work done, and presumably the distribution of the work done as well, with consequences for the existence of a fluctuation relation that at present are difficult to predict.

APPENDIX: EVALUATION OF THE PROPAGATOR

The basic idea behind Feynman's approach to the evaluation of path integrals [17] is to expand the action $S[\mathbf{R}] \equiv \int_0^t dt' \mathscr{L}[\mathbf{R}(t'),\dot{\mathbf{R}}(t')]$ to second order in the deviation $\mathbf{R} - \bar{\mathbf{R}}$ around the classical action $S[\bar{\mathbf{R}}]$, where the classical path $\bar{\mathbf{R}}$ is determined from the minimization condition $\delta S[\mathbf{R}]/\delta \mathbf{R}|_{\mathbf{R}=\bar{\mathbf{R}}} = 0$. In this way, the path integral is expressed as the product of $\exp(-S[\bar{\mathbf{R}}])$ and a function $\phi(t)$ (the so-called fluctuation integral), which is a function solely of time and which can be evaluated by direct methods [17,18].

In the present problem of a dumbbell in planar elongational flow, the path integral naturally factorizes into a product of two terms: one a contribution from dynamics in the xy plane, and the other a contribution from dynamics along the z direction. The latter path integral (corresponding to a one-dimensional harmonic oscillator) is known [17,18] and will not be discussed further; the former is the subject of this appendix, and for this path integral the fluctuation integral takes the form

$$\phi(t) = \int_0^0 D[\delta R_x] \int_0^0 D[\delta R_y] \exp\left[-\int_0^t dt' \left\{a_0\left(\delta\dot{R}_x^2 + \delta\dot{R}_y^2\right) - a_2(\delta\dot{R}_x\delta R_y + \delta R_x \delta\dot{R}_y) - a_3 \delta R_x \delta R_y + a_4\left(\delta R_x^2 + \delta R_y^2\right)\right\}\right].$$

The first step in the calculation of both $\exp(-S[\bar{\mathbf{R}}])$ and $\phi(t)$ is the determination of the classical path. From the expression for the "Lagrangian" in Eq. (12), the classical equations of motion for the x and y components of the vector $\mathbf{R}$ can be obtained from the relation $(d/dt)\partial\mathscr{L}/\partial\dot{R}_\alpha = \partial\mathscr{L}/\partial R_\alpha$, $\alpha = x,y$. This leads to the equation

$$\ddot{\mathbf{r}}(t) + \varpi \mathbf{J}\mathbf{r}(t) - \Omega \mathbf{1}\mathbf{r}(t) = \mathbf{0}, \tag{A1}$$

where $\mathbf{r}^T = (R_x \quad R_y)$, $\varpi = a_3/(2a_0)$, $\Omega = a_4/a_0$ and $\mathbf{J} = \left(\begin{smallmatrix}0 & 1\\ 1 & 0\end{smallmatrix}\right)$. The corresponding equation for R_z, which is obtained from the relation $(d/dt)\partial\mathscr{L}/\partial\dot{R}_z = \partial\mathscr{L}/\partial R_z$, is $\ddot{R}_z(t) - (a_5/a_0)\,R_z(t) = 0$. It may be verified that the general solution to Eq. (A1) is given by [23]

$$\bar{R}_x(t) = \mathrm{e}^{a_1 t}\,[A\cosh(b_1 t) + B\sinh(b_1 t)] + \mathrm{e}^{-a_1 t}\,[C\cosh(b_1 t) + D\sinh(b_1 t)]\,, \tag{A2a}$$

$$\bar{R}_y(t) = \mathrm{e}^{a_1 t}\,[A\sinh(b_1 t) + B\cosh(b_1 t)] - \mathrm{e}^{-a_1 t}\,[C\sinh(b_1 t) + D\cosh(b_1 t)]\,, \tag{A2b}$$

where $a_1 \equiv (\sqrt{\Omega - \varpi} + \sqrt{\Omega + \varpi})/2$, $b_1 \equiv (\sqrt{\Omega - \varpi} - \sqrt{\Omega + \varpi})/2$ and A, B, C, and D are unknown coefficients to be determined by the conditions $\bar{R}_x(0) = R_{x0}$, $\bar{R}_y(0) = R_{y0}$, $\bar{R}_x(t) = R_{xf}$, and $\bar{R}_y(t) = R_{yf}$. These conditions lead to the results

$$A = \frac{1}{4\text{sh}[(a_1+b_1)t]\,\text{sh}[(a_1-b_1)t]}[-R_{x0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] + e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} + R_{y0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] - e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} + 2R_{xf}\,\text{sh}(a_1t)\,\text{ch}(b_1t) - 2R_{yf}\,\text{sh}(b_1t)\,\text{ch}(a_1t)], \tag{A3a}$$

$$B = \frac{1}{4\text{sh}[(a_1+b_1)t]\,\text{sh}[(a_1-b_1)t]}[R_{x0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] - e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - R_{y0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] + e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - 2R_{xf}\,\text{sh}(b_1t)\,\text{ch}(a_1t) + 2R_{yf}\,\text{sh}(a_1t)\,\text{ch}(b_1t)], \tag{A3b}$$

$$C = \frac{1}{4\text{sh}[(a_1+b_1)t]\,\text{sh}[(a_1-b_1)t]}[R_{x0}\{e^{(a_1-b_1)t}\text{sh}[(a_1+b_1)t] + e^{(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - R_{y0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] - e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - 2R_{xf}\,\text{sh}(a_1t)\,\text{ch}(b_1t) + 2R_{yf}\,\text{sh}(b_1t)\,\text{ch}(a_1t)], \tag{A3c}$$

$$D = \frac{1}{4\text{sh}[(a_1+b_1)t]\text{sh}[(a_1-b_1)t]}[R_{x0}\{e^{-(a_1-b_1)t}\text{sh}[(a_1+b_1)t] - e^{-(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - R_{y0}\{e^{(a_1-b_1)t}\text{sh}[(a_1+b_1)t] + e^{(a_1+b_1)t}\text{sh}[(a_1-b_1)t]\} - 2R_{xf}\text{sh}(b_1t)\text{ch}(a_1t) + 2R_{yf}\text{sh}(a_1t)\text{ch}(b_1t)]. \tag{A3d}$$

The next step in the calculation is the evaluation of the action along the classical path; that is, the evaluation of the integral

$$S_2 \equiv \int_0^t dt'\left[a_0\left(\dot{\bar{R}}_x^2 + \dot{\bar{R}}_y^2\right) - a_2\left(\dot{\bar{R}}_x\bar{R}_y + \bar{R}_x\dot{\bar{R}}_y\right) - a_3\bar{R}_x\bar{R}_y + a_4\left(\bar{R}_x^2 + \bar{R}_y^2\right)\right].$$

This is done using integration by parts in conjunction with the equations of motion [Eq. (A1)]. The result is

$$S_2 = a_0(\dot{\bar{R}}_x(t)R_{xf} - \dot{\bar{R}}_x(0)R_{x0} + \dot{\bar{R}}_y(t)R_{yf} - \dot{\bar{R}}_y(0)R_{y0}) - a_2(R_{xf}R_{yf} - R_{x0}R_{y0}), \tag{A4}$$

which, using the expressions for $\bar{R}_x(t)$ and $\bar{R}_y(t)$ given in Eqs. (A2) and (A3), leads to

$$S_2 = -a_2(R_{xf}R_{yf} - R_{x0}R_{y0}) + a_0\left\{\frac{1}{\sinh[(a_1+b_1)t]\sinh[(a_1-b_1)t]}\left[\left(R_{xf}^2 + R_{yf}^2 + R_{x0}^2 + R_{y0}^2\right) \times[a_1\sinh(a_1t)\cosh(a_1t) - b_1\sinh(b_1t)\cosh(b_1t)] + 2(R_{xf}R_{yf} + R_{x0}R_{y0}) \times[-a_1\sinh(b_1t)\cosh(b_1t) + b_1\sinh(a_1t)\cosh(a_1t)] + 2(R_{x0}R_{yf} + R_{xf}R_{y0}) \times[a_1\sinh(b_1t)\cosh(a_1t) - b_1\sinh(a_1t)\cosh(b_1t)] + 2(R_{xf}R_{x0} + R_{yf}R_{y0}) \times[-a_1\sinh(a_1t)\cosh(b_1t) + b_1\sinh(b_1t)\cosh(a_1t)]\right]\right\} \tag{A5}$$

The so-called fluctuation integral (i.e., the path integral) $\phi(t)$ that appears at second order when expanding around the classical action is obtained from the determinant [17]

$$\phi(t)^2 \propto \begin{vmatrix} \frac{\partial^2 S_2}{\partial R_{xf} R_{x0}} & \frac{\partial^2 S_2}{\partial R_{xf} R_{y0}} \\ \frac{\partial^2 S_2}{\partial R_{yf} R_{x0}} & \frac{\partial^2 S_2}{\partial R_{yf} R_{y0}} \end{vmatrix}. \tag{A6}$$

Thus,

$$\phi(t) \propto 2a_0 \sqrt{\frac{a_1^2 - b_1^2}{\sinh\left[(a_1+b_1)t\right]\sinh\left[(a_1-b_1)t\right]}}. \tag{A7}$$

Thus, the propagator associated with the variables R_x and R_y is given by

$$G(R_{xf}, R_{yf}, t | R_{x0}, R_{y0}, 0) = \phi(t)\exp(-S_2) \tag{A8}$$

The propagator associated with the variable R_z is well known, so we merely report the final result:

$$G(R_{zf}, t | R_{z0}, 0) = \left(\frac{2\sqrt{a_0 a_5}}{\sinh(t\sqrt{a_5/a_0})}\right)^{1/2} \times \exp\left[-\frac{\sqrt{a_0 a_5}}{\sinh(t\sqrt{a_5/a_0})}\left\{\left(R_{zf}^2 + R_{z0}^2\right) \times \cosh(t\sqrt{a_5/a_0}) - 2R_{zf}R_{z0}\right\}\right]. \tag{A9}$$

The expression for the propagator in three dimensions is given by the product of the propagators in Eqs. (A8) and (A9), and this is the expression used in the calculations described in the text.

[1] F. Ritort, C. R. Physique **8**, 528 (2007); Adv. Chem. Phys. **137**, 31 (2008).

[2] E. M. Sevick, R. Prabhakar, S. R. Williams, and D. J. Searles, Annu. Rev. Phys. Chem. **59**, 603 (2008); C. Jarzynski, Eur. Phys. J. B **64**, 331 (2008); M. Esposito and C. Van den Broeck, Phys. Rev. Lett. **104**, 090601 (2010).

[3] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002); D. M. Carberry, J. C. Reid, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, *ibid.* **92**, 140601 (2004); S. Schuler, T. Speck, C. Tietz, J. Wrachtrup, and U. Seifert, *ibid.* **94**, 180602 (2005); G. M. Wang, J. C. Reid, D. M. Carberry, D. R. M. Williams, E. M. Sevick, and D. J. Evans, Phys. Rev. E **71**, 046142 (2005).

[4] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Science **296**, 1832 (2002); D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Nature **437**, 231 (2005).

[5] D. M. Carberry, M. A. B. Baker, G. M. Wang, E. M. Sevick, and D. J. Evans, J. Opt. A: Pure Appl. Opt. **9**, S204 (2007); J. Berg, Phys. Rev. Lett. **100**, 188101 (2008); K. Hayashi, H. Ueno, R. Iino, and H. Noji, *ibid.* **104**, 218103 (2010); L. Y. Chen, D. A. Bastien, and H. E. Espejel, Phys. Chem. Chem. Phys. **12**, 6579 (2010).

[6] S. Joubaud, N. B. Garnier, and S. Ciliberto, J. Stat. Mech.: Thy. Expt. (2007) P09018; S. Ciliberto, S. Joubaud, and A. Petrosyan, *ibid.* (2010) P12003.

[7] C. Jarzynski, Phys. Rev. E **56**, 5018 (1997); Phys. Rev. Lett. **78**, 2690 (1997).

[8] A. Dhar, Phys. Rev. E **71**, 036126 (2005).

[9] J. Liphardt, B. Onoa, S. B. Smith, I. Tinoco Jr., and C. Bustamante, Science **292**, 733 (2001); C. Cecconi, E. A. Shank, C. Bustamante, and S. Marqusee, *ibid.* **309**, 2057 (2005).

[10] T. T. Perkins, D. E. Smith, and S. Chu, Science **276**, 2016 (1997).

[11] D. E. Smith, H. P. Babcock, and S. Chu, Science **283**, 1724 (1999); Y. Liu and V. Steinberg, Eur. Phys. Lett. **90**, 44005 (2010).

[12] T. Speck, Ph. D. thesis, Institut fur Theoretische Physik der Universitat Stuttgart (2007).

[13] R. B. Bird, R.C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids* (Wiley, New York, 1987) Vol. 2, Chpt. 13.

[14] In the presence of hydrodynamic interactions, Eq. (1) is modified to $-\zeta\dot{\mathbf{r}}_i(t) + \zeta(\mathbf{v}_i + \mathbf{v}_i') - \partial U(|\mathbf{r}_i - \mathbf{r}_j|)/\partial\mathbf{r}_i + \boldsymbol{\theta}_i(t) = \mathbf{0}$ where $\mathbf{v}_i = \mathbf{v}_0 + \dot{\gamma}\boldsymbol{\kappa}\cdot\mathbf{r}_i(t)$ as before, and $\mathbf{v}_i'$ is the hydrodynamic interaction (i.e., the perturbation to the flow field at the location of bead i arising from the dynamics of the other bead). The term $\mathbf{v}'_i$ can be expressed in terms of the Oseen tensor $\boldsymbol{\Omega}$, where $\boldsymbol{\Omega} = (8\pi\eta R)^{-1}[\mathbf{1} + \mathbf{RR}/R^2]$ with η being the solvent viscosity. The precise connection between $\mathbf{v}_i'$ and $\boldsymbol{\Omega}$ may be found in Ref. (13). The inclusion of hydrodynamic interactions in the expression for the bead dynamics immediately renders an exact path-integral evaluation of the work distribution function intractable.

[15] M. Bier, I. Derényi, M. Kostur, and R. D. Astumian, Phys. Rev. E **59**, 6422 (1999).

[16] D. D. L. Minh and A. B. Adib, Phys. Rev. E **79**, 021122 (2009).

[17] M. Chaichian and A. Demichev, *Path Integrals in Physics: Stochastic Processes and Quantum Mechanics* (Institute of Physics Publishing, Bristol, 2001), Vol. 1.

[18] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).

[19] P. G. De Gennes, J. Chem. Phys. **60**, 5030 (1974).

[20] R. G. Larson and J. J. Magda, Macromolecules **22**, 3004 (1989).

[21] T. Speck and U. Seifert, Eur. Phys. J. B **43**, 521 (2005).

[22] C. E. Sing and A. Alexander-Katz, Macromolecules **43**, 3532 (2010).

[23] G. J. Papadopoulos, J. Phys. A: Gen. Phys. **4**, 773 (1971); K.-H. Yeon, C.-I. Um, W.-H. Kahng, and T. F. George, Phys. Rev. A, **38**, 6224 (1988); V. Kagalovsky, Phys. Rev. B **53**, 13656 (1996).