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Dissipated work in driven harmonic diffusive systems: General solution and application to stretching Rouse polymers

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Abstract. We study n-dimensional diffusive motion in an externally driven harmonic potential. For these systems the probability distribution of the applied work is a Gaussian. We give explicit expressions for its mean and variance, which are determined by a non-local integral kernel relating the time-derivatives of the applied forces. As illustrations, we specialize our results to dragging a colloidal particle through a viscous fluid and to stretching a Rouse polymer with different protocols.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 05.70.Ln Nonequilibrium and irreversible thermodynamics

1 Introduction

Notions of classical thermodynamics like applied work and exchanged heat have recently been extended to processes on mesoscopic systems [1,2]. Typical examples are colloidal particles [3–6] and biopolymers like DNA or proteins (for reviews, see [7–12]) driven out of equilibrium by laser tweezers or atomic force microscopes. On these length scales, the ever present thermal fluctuations imply that quantities like the work W spent to induce configurational changes in a polymer fluctuate according to a characteristic distribution function $p(W)$, which, in general, depends on the specific non-equilibrium protocol of the process. In a seminal paper, Jarzynski has shown that this distribution function obeys a general constraint [2]

$$\int_{-\infty}^{+\infty} \mathrm{d}W\, p(W) e^{-\beta W} = e^{-\beta \Delta F}. \tag{1}$$

The right-hand-side involves the equilibrium free energy difference ΔF between the two states connected by the non-equilibrium process in a thermal environment of inverse temperature $\beta \equiv 1/k_{\mathrm{B}}T$, where k_{B} is Boltzmann's constant. The left-hand-side is the non-equilibrium average over many realizations of this process. Hence, as an important application, the Jarzynski relation allows the reconstruction of free energy profiles from non-equilibrium work data extracted from experiments [13] or simulations [14–18].

An interesting class of systems are those for which the work distribution $p(W)$ is Gaussian. In this case, Jarzynski's relation implies that the mean $\overline{W}$ and the variance σ^2 are related by [2]

$$\overline{W} = \Delta F + (\beta/2)\sigma^2. \tag{2}$$

There are basically two scenarios for obtaining a Gaussian distribution. For slow driving, one may expect that the distribution is always Gaussian. For general diffusive systems [19], this has indeed been shown with a constructive proof which yields explicit expressions for mean and variance [20].

This paper deals with the second general class of systems for which one expects a Gaussian distribution even at fast driving. This is the case if the basic dynamics is linear. We show that for general n-dimensional diffusive motion in a harmonic potential under arbitrary time-dependent forces the work distribution is Gaussian and derive its mean and variance. As illustrations of our general result, we consider the paradigmatic colloidal particle dragged through a viscous fluid and, as a new result, a Rouse polymer stretched by an external force.

2 General theory

2.1 Equations of motion

We consider a finite classical system coupled to a heat reservoir at constant inverse temperature β. Let

$$\boldsymbol{z} \equiv (z_1, \ldots, z_n)^{\mathrm{T}} \tag{3}$$

denote the state of a system with n degrees of freedom. The potential energy is a quadratic form

$$V_0(\boldsymbol{z}) \equiv \frac{1}{2}\boldsymbol{z}^{\mathrm{T}}\mathsf{T}\boldsymbol{z}, \tag{4}$$

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where $\mathsf{T} \equiv (T_{ij})$ is a symmetric, time-independent coupling tensor with inverse T^{-1}.

The stochastic dynamics of the system is governed by the Langevin equations [21]

$$\dot{z}_i = \mu_{ij}\left[-\frac{\partial V_0}{\partial z_j} + f_j(t)\right] + \eta_i(t), \tag{5}$$

which describe a diffusive evolution of the state $\boldsymbol{z}$ in an overdamped environment with constant, symmetric mobility coefficients $\mu \equiv (\mu_{ij})$. Summations are carried out over same indices. We drive the system by applying time-dependent external forces $\boldsymbol{f}(t)$. The Gaussian white noise $\boldsymbol{\eta}(t)$ represents the interaction between system and heat reservoir. It has the properties

$$\langle \eta_i(t)\rangle = 0 \quad \text{and} \quad \langle \eta_i(t)\eta_j(t')\rangle = \frac{2}{\beta}\mu_{ij}\delta(t-t'), \tag{6}$$

where the brackets $\langle\cdots\rangle$ denote an ensemble average.

The calculation of the work spent to drive the system requires a time-dependent total energy including the driving forces,

$$V(\boldsymbol{z},t) \equiv \frac{1}{2}[\boldsymbol{z}-\boldsymbol{h}(t)]^{\mathrm{T}}\mathsf{T}[\boldsymbol{z}-\boldsymbol{h}(t)] + \mathcal{V}(t), \tag{7}$$

with $\boldsymbol{h}(t) \equiv \mathsf{T}^{-1}\boldsymbol{f}(t)$. For quasi-statically driven systems, $\langle \boldsymbol{z}(t)\rangle = \boldsymbol{h}(t)$ corresponds to the adiabatic trajectory. Because we restricted the external forces to be independent of the state $\boldsymbol{z}$, this total energy is quadratic, too. The additional energy $\mathcal{V}(t)$ is a yet undetermined function independent of the state $\boldsymbol{z}$. The equations of motion (5) now read

$$\dot{z}_i = -\mu_{ij}\frac{\partial V}{\partial z_j} + \eta_i(t). \tag{8}$$

In order to solve these equations, we introduce the tensor $\mathsf{L} \equiv \mu\mathsf{T}$. It is positive definite $\mathsf{L} \geqslant 0$ and symmetric. In the following, we mark the components of tensors in the basis where L becomes diagonal by a tilde. With the set of ordered eigenvalues $\{\varepsilon_i : \varepsilon_1 < \varepsilon_2 < \ldots\}$ of L, the equations of motion (8) decouple into normal modes

$$\dot{\tilde{z}}_i + \varepsilon_i\tilde{z}_i = \varepsilon_i\tilde{h}_i(t) + \tilde{\eta}_i(t), \tag{9}$$

which are solved as

$$\tilde{z}_i(t) = \int_0^t \mathrm{d}t'\; e^{-\varepsilon_i(t-t')}\left[\varepsilon_i\tilde{h}_i(t') + \tilde{\eta}_i(t')\right] + \tilde{z}_i(0)e^{-\varepsilon_i t}. \tag{10}$$

Here, we identify $\tau_i \equiv 1/\varepsilon_i$ as the relaxation time of the ith mode. The mode relaxing on the slowest time scale τ_1 is called the fundamental mode.

2.2 Work

We drive the system by a time-dependent force during the time interval $0 \leqslant t \leqslant t_\mathrm{s}$. The total work performed along one particular stochastic trajectory $\boldsymbol{z}(t)$ is the functional [1,2]

$$W[\boldsymbol{z}(t)] \equiv \int_0^{t_\mathrm{s}} \mathrm{d}t\; \frac{\partial V}{\partial t}(\boldsymbol{z}(t),t), \tag{11}$$

depending on the entire trajectory $\boldsymbol{z}(t)$.

The calculation of the work (11) using the total energy (7) is straightforward. We first write the change in free energy for the entire process as

$$\Delta F \equiv \frac{1}{\beta}\ln\frac{\int \mathrm{d}\boldsymbol{z}\;\exp\{-\beta V(\boldsymbol{z},0)\}}{\int \mathrm{d}\boldsymbol{z}\;\exp\{-\beta V(\boldsymbol{z},t_\mathrm{s})\}} = \mathcal{V}(t_\mathrm{s}) - \mathcal{V}(0). \tag{12}$$

Gaussian integration in the numerator and denominator gives identical contributions which cancel out, determining the additional energy $\mathcal{V}(t)$ as the free energy up to an irrelevant constant.

Next, we calculate the work (11) as

$$W = \left[\frac{1}{2}\boldsymbol{h}^{\mathrm{T}}(t)\mathsf{T}\boldsymbol{h}(t) + \mathcal{V}(t)\right]_0^{t_\mathrm{s}} - \int_0^{t_\mathrm{s}} \mathrm{d}t\; \dot{\boldsymbol{h}}^{\mathrm{T}}(t)\mathsf{T}\boldsymbol{z}(t). \tag{13}$$

Inserting the trajectory (10) leads to

$$\begin{aligned} W = {} & \Delta F + \left[\frac{1}{2}\boldsymbol{h}^{\mathrm{T}}(t)\mathsf{T}\boldsymbol{h}(t)\right]_0^{t_\mathrm{s}} \\ & - \tilde{T}_{ij}\int_0^{t_\mathrm{s}} \mathrm{d}t\; \dot{\tilde{h}}_j(t)\int_0^t \mathrm{d}t'\; e^{-\varepsilon_i(t-t')}\left[\varepsilon_i\tilde{h}_i(t') + \tilde{\eta}_i(t')\right] \\ & - \tilde{T}_{ij}\tilde{z}_i(0)\int_0^{t_\mathrm{s}} \mathrm{d}t\; \dot{\tilde{h}}_j(t)e^{-\varepsilon_i t}. \end{aligned} \tag{14}$$

To bring the work in a form more suitable for obtaining its distribution, we interchange $t \leftrightarrow t'$ in the double-integral and adjust the limits to keep the integration area the same. By doing this, we can pull the expression in the square brackets into the outer integral and perform an integration by parts. After introducing the vector $\boldsymbol{a}(t)$ with components

$$\tilde{a}_i(t) \equiv \int_t^{t_\mathrm{s}} \mathrm{d}t'\; \dot{\tilde{f}}_i(t')e^{-\varepsilon_i(t'-t)} \tag{15}$$

we finally obtain

$$\begin{aligned} W = {} & \Delta F + \int_0^{t_\mathrm{s}} \mathrm{d}t\; \tilde{a}_i(t)\dot{\tilde{h}}_i(t) \\ & - \tilde{a}_i(0)\left[\tilde{z}_i(0) - \tilde{h}_i(0)\right] - \int_0^{t_\mathrm{s}} \mathrm{d}t\; \tilde{a}_i(t)\tilde{\eta}_i(t) \\ \equiv {} & \overline{W} + W_0(\boldsymbol{z}_0) + W_1[\boldsymbol{\eta}(t)]. \end{aligned} \tag{16}$$

Hence, the total work (16) is the sum of three contributions

$$\overline{W} \equiv \Delta F + \int_0^{t_\mathrm{s}} \mathrm{d}t\; \boldsymbol{a}^{\mathrm{T}}(t)\dot{\boldsymbol{h}}(t), \tag{17}$$

$$W_0(\boldsymbol{z}_0) \equiv -\boldsymbol{a}^{\mathrm{T}}(0)[\boldsymbol{z}_0 - \boldsymbol{h}(0)], \tag{18}$$

$$W_1[\boldsymbol{\eta}(t)] \equiv -\int_0^{t_\mathrm{s}} \mathrm{d}t\; \boldsymbol{a}^{\mathrm{T}}(t)\boldsymbol{\eta}(t). \tag{19}$$

The first contribution is independent of the trajectory. The second contribution is the work depending on the initial state $\boldsymbol{z}_0 \equiv \boldsymbol{z}(0)$ whereas the third contribution originates from coupling to the heat reservoir.

2.3 Probability distribution of work

We now consider an ensemble of systems, each initially in thermal equilibrium with the heat reservoir and evolving according to the stochastic equations of motion (5). The expectation value of a functional $\mathcal{G}$ resulting from such a process, e.g. the work, is defined by [2]

$$\langle \mathcal{G} \rangle \equiv \int \mathrm{d}\boldsymbol{z}_0 \; \rho_0(\boldsymbol{z}_0) \int \mathrm{d}[\boldsymbol{\eta}(t)] \; P[\boldsymbol{\eta}(t)] \mathcal{G}[\boldsymbol{\eta}(t), \boldsymbol{z}_0]. \quad (20)$$

The average $\langle \cdots \rangle$ thus involves both the average over the initial state $\boldsymbol{z}_0$ according to the canonical distribution

$$\rho_0(\boldsymbol{z}_0) = e^{-\beta V(\boldsymbol{z}_0,0)} \Big/ \int \mathrm{d}\boldsymbol{z} \; e^{-\beta V(\boldsymbol{z},0)} \quad (21)$$

and the path integral average over the noise $\boldsymbol{\eta}(t)$. The statistical weight of a particular path is

$$P[\boldsymbol{\eta}(t)] \sim \exp\left\{ -\frac{1}{2} \int_0^{t_\mathrm{s}} \mathrm{d}t \; \int_0^{t_\mathrm{s}} \mathrm{d}t' \; \boldsymbol{\eta}^\mathrm{T}(t') \mathsf{K}^{-1}(t,t') \boldsymbol{\eta}(t) \right\}, \quad (22)$$

where $\mathsf{K}(t,t') \equiv \left\langle \boldsymbol{\eta}(t) \boldsymbol{\eta}^\mathrm{T}(t') \right\rangle$ is the correlation matrix of the Gaussian stochastic variables. Inserting the equations (16)-(19) into equation (20) leads to $\langle W_0 \rangle = 0$, $\langle W_1 \rangle = 0$, and $\langle W \rangle = \overline{W}$.

We now determine the distributions $p_0(W_0)$ and $p_1(W_1)$ of the two stochastic contributions W_0 and W_1 to the total work (16). In order to obtain $p_0(W_0)$, we rather calculate the characteristic function $C_0(\chi) \equiv \left\langle e^{i\chi W_0} \right\rangle$, which is given by

$$C_0(\chi) = \int \mathrm{d}\boldsymbol{z}_0 \; \rho_0(\boldsymbol{z}_0) e^{i\chi W_0(\boldsymbol{z}_0)} = \exp\left\{ -\frac{1}{2} \chi^2 \sigma_0^2 \right\}. \quad (23)$$

Hence, the distribution $p_0(W_0)$ is a Gaussian with zero mean and variance

$$\sigma_0^2 = \frac{1}{\beta} \boldsymbol{a}^\mathrm{T}(0) \mathsf{T}^{-1} \boldsymbol{a}(0). \quad (24)$$

This part corresponds to a system which is initially in thermal equilibrium with the heat reservoir, and then evolves further isolated from the reservoir.

Next, we obtain $p_1(W_1)$ by investigating its characteristic function $C_1(\chi) \equiv \left\langle e^{i\chi W_1} \right\rangle$. In this case the system stays coupled to the reservoir. Since the path integral

$$C_1(\chi) = \int \mathrm{d}[\boldsymbol{\eta}(t)] \; P[\boldsymbol{\eta}(t)] \exp\{ i\chi W_1[\boldsymbol{\eta}(t)] \} \quad (25)$$

is a simple multi-dimensional Gaussian integral, we can solve it analytically and obtain

$$C_1(\chi) = \exp\left\{ -\frac{1}{2} \chi^2 \sigma_1^2 \right\}. \quad (26)$$

The distribution $p_1(W_1)$ is again a Gaussian with zero mean and variance

$$\sigma_1^2 = \frac{2}{\beta} \int_0^{t_\mathrm{s}} \mathrm{d}t \; \boldsymbol{a}^\mathrm{T}(t) \mu \boldsymbol{a}(t), \quad (27)$$

which after integration by parts using equation (15) takes the form

$$\sigma_1^2 = \frac{2}{\beta} \int_0^{t_\mathrm{s}} \mathrm{d}t \; \boldsymbol{a}^\mathrm{T}(t) \dot{\boldsymbol{h}}(t) - \sigma_0^2. \quad (28)$$

The resulting probability distribution $p(W)$ for the total work as the sum of two uncorrelated Gaussian stochastic variables W_0 and W_1 is a Gaussian

$$p(W) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{ -\frac{(W - \overline{W})^2}{2\sigma^2} \right\}. \quad (29)$$

We already know its mean from equation (17) whereas the variance is the sum

$$\sigma^2 = \sigma_0^2 + \sigma_1^2 = \frac{2}{\beta} \int_0^{t_\mathrm{s}} \mathrm{d}t \; \boldsymbol{a}^\mathrm{T}(t) \dot{\boldsymbol{h}}(t). \quad (30)$$

By comparing this with equation (17), we recover the relation (2) between mean and variance as expected.

This explicit expression for the mean or variance is the central result of our paper. For any given potential energy $V_0(\boldsymbol{z})$ and any given time-dependent forces $\boldsymbol{f}(t)$, these relations yield the resulting distribution of work. Since $\dot{\boldsymbol{h}}(t)$ is linear in $\dot{\boldsymbol{f}}(t)$ and $\boldsymbol{a}(t)$ is linear but non-local in $\dot{\boldsymbol{f}}(t)$, the variance (30) can formally be expressed as

$$\sigma^2 = \frac{2}{\beta} \int_0^{t_\mathrm{s}} \mathrm{d}t \; \int_0^{t_\mathrm{s}} \mathrm{d}t' \; \dot{\boldsymbol{f}}^\mathrm{T}(t') \mathsf{M}(t'-t) \dot{\boldsymbol{f}}(t) \quad (31)$$

with the non-local integral kernel

$$\mathsf{M}(t'-t) \equiv \Theta(t'-t) \exp\{ -\mathsf{L}(t'-t) \} \mathsf{T}^{-1}, \quad (32)$$

relating the time-derivatives of the external forces. The function $\Theta(t'-t)$ is the Heaviside step function.

The distribution of the dissipated work $W_\mathrm{d} \equiv W - \Delta F$ is the same Gaussian $p(W_\mathrm{d})$ shifted by ΔF. Its mean and variance become

$$\overline{W}_\mathrm{d} = \frac{\beta}{2} \sigma^2 = \int_0^{t_\mathrm{s}} \mathrm{d}t \; \int_0^{t_\mathrm{s}} \mathrm{d}t' \; \dot{\boldsymbol{f}}^\mathrm{T}(t') \mathsf{M}(t'-t) \dot{\boldsymbol{f}}(t). \quad (33)$$

2.4 Slow driving regime

In the limiting case of slow but finite driving, the distribution of the dissipated work for arbitrary diffusive systems has been derived previously [20]. For non-linear equations of motion this distribution is also a Gaussian as long as $\tau_1 \ll t_\mathrm{s}$ holds. While in the present paper we consider the fluctuation of the state $\boldsymbol{z} - \boldsymbol{h}(t)$ around its mean adiabatic trajectory $\boldsymbol{h}(t)$ using a path integral approach, in the case of a general potential $V(\boldsymbol{z},t)$ another route was pursued. There we investigated the fluctuation of the energy

$$S(\boldsymbol{z},t) \equiv \frac{\partial V}{\partial t}(\boldsymbol{z},t) - \int \mathrm{d}\boldsymbol{z}' \; \rho(\boldsymbol{z}',t) \frac{\partial V}{\partial t}(\boldsymbol{z}',t) \quad (34)$$

along the trajectory using a Fokker-Planck equation approach. Here

$$\rho(\boldsymbol{z},t) \equiv e^{-\beta V(\boldsymbol{z},t)} \Big/ \int \mathrm{d}\boldsymbol{z}'\; e^{-\beta V(\boldsymbol{z}',t)} \tag{35}$$

is the time-dependent, accompanying canonical distribution, which can be defined irrespectively of whether the system is in or out of thermal equilibrium with the heat reservoir. With this definition, the integral in equation (34) corresponds to the adiabatic expectation value of $\partial V/\partial t$.

The variance of the slow driving Gaussian for the nonlinear equations of motion in a notation similar to equation (31) is [20]

$$\sigma^2 = \frac{2}{\beta}\int_0^{t_\mathrm{s}} \mathrm{d}t \int \mathrm{d}\boldsymbol{z}\; S(\boldsymbol{z},t)\hat{M}(t)S(\boldsymbol{z},t). \tag{36}$$

In contrast to equation (32), the integral kernel is now an operator

$$\hat{M}(t) \equiv -\beta \hat{L}^{-1}(t)\rho(\boldsymbol{z},t) \tag{37}$$

local in time. Here, $\hat{L}^{-1}(t)$ is the inverse of the time-dependent Fokker-Planck operator $\hat{L}(t)$ and both $\hat{L}(t)$ and $\hat{M}(t)$ are non-hermitian operators acting to the left. The minus sign in equation (37) arises from the fact that the eigenvalues $\{\varepsilon_i\}$ of $\hat{L}$ are defined through $\hat{L}\psi_i = -\varepsilon_i\psi_i$ with eigenfunctions $\{\psi_i\}$.

We now prove that equation (36) yields the same variance as equation (31) does in the limiting case of slowly driven harmonic systems. For linear systems, the Fokker-Planck operator becomes [21]

$$\hat{L}(t) \equiv \frac{\partial}{\partial z_i}\left[L_{ij}[z_j - h_j(t)] + \frac{\mu_{ij}}{\beta}\frac{\partial}{\partial z_j}\right]. \tag{38}$$

The eigenvalues of operator $\hat{L}$ are the same as of tensor L, both defining the relaxation time scales of the system. It is straightforward to calculate the variance (36) inserting the energy (7) into equation (34). Skipping the algebra, we just present the result as

$$\sigma^2 = \frac{2}{\beta}\int_0^{t_\mathrm{s}} \mathrm{d}t\; \dot{\boldsymbol{f}}^{\mathrm{T}}(t)(\mathsf{TL})^{-1}\dot{\boldsymbol{f}}(t). \tag{39}$$

We can get the same expression from equation (31) by replacing the exponential time dependence in equation (32) by a short-ranged interaction $\Theta(t'-t)\exp\{\mathsf{L}(t'-t)\} \to \mathsf{L}^{-1}\delta(t'-t)$. Then

$$\mathsf{M}(t'-t) = (\mathsf{TL})^{-1}\delta(t'-t) \tag{40}$$

leads to the same variance as equation (39).

3 Trapped particle

As a first illustration, we consider a colloidal particle in a viscous fluid with friction coefficient γ trapped by an optical or magnetic tweezer. This system has been analyzed before both theoretically [3–5] and experimentally [6].

The position of the focus of the trap is $\boldsymbol{u}(t)$, whereas the position of the particle is denoted by $\boldsymbol{r}$. Near the focal point we assume a linear force acting on the particle

$$\boldsymbol{F}(\boldsymbol{r},t) = -k[\boldsymbol{r} - \boldsymbol{u}(t)], \tag{41}$$

with effective strength k.

As the initial and final state we choose two positions of the trap at distance L. We investigate the transient non-equilibrium state, i.e., we first trap the particle and let it equilibrate. After equilibration, we move the trap at constant speed $v = L/t_\mathrm{s}$ and drag the trapped particle through the viscous fluid. For this one-dimensional movement, the total work

$$W = \int_0^{t_\mathrm{s}} \mathrm{d}t\; \dot{\boldsymbol{u}}^{\mathrm{T}}(t)\boldsymbol{F}(\boldsymbol{r}(t),t) \tag{42}$$

can be written in the form of equation (11). (for an comprehensive discussion of this quantity, see [4,5]) The total energy in this case becomes

$$V(z,t) = \frac{k}{2}[z - h(t)]^2, \tag{43}$$

where z is now the coordinate of the particle and $h(t)$ is the position of the focal point in one dimension. Since the free energy in this case is independent of the position $h(t)$ of the optical tweezer, $\Delta F = 0$ follows.

The relaxation time is $\tau = \gamma/k$. We calculate the mean dissipated work (33) under an external force $f(t) = kh(t)$ and $\dot{h}(t) = v$ as [3,20]

$$\overline{W}_\mathrm{d} = L^2 k\left[\frac{\tau}{t_\mathrm{s}} - \left(\frac{\tau}{t_\mathrm{s}}\right)^2\left(1 - e^{-t_\mathrm{s}/\tau}\right)\right]. \tag{44}$$

With the solution for the mean path

$$\bar{z}(t) = L - v\tau\left(1 - e^{-t/\tau}\right), \tag{45}$$

we can rearrange equation (44) and obtain $\overline{W}_\mathrm{d} = \gamma v\bar{z}(t_\mathrm{s})$. The average dissipated work is, not surprisingly, given by a friction force γv times the mean distance $\bar{z}(t_\mathrm{s})$ the particle is dragged.

4 Stretching a Rouse polymer

As a non-trivial example of our general result, we consider stretching a Rouse polymer. A Rouse polymer is modeled as a linear chain of $N+1$ monomers at $\boldsymbol{r}_i$ connected by N harmonic springs with strength k [22]. The polymer is in solution in a viscous fluid with friction coefficient γ and isotropic mobility $\mu_{ij} \equiv \delta_{ij}/\gamma$.

To stretch the polymer, we hold the first monomer fixed ($\boldsymbol{r}_0 \equiv 0$) and manipulate the last one, e.g. by attaching it to the cantilever of an AFM [23]. Another possibility is the use of an optical tweezer, where the end of the polymer could be attached to a polystyrene bead which follows the focus of the trap [13,24]. However, for the sake of brevity, here we assume an ideally stiff connection so that we directly manipulate the Nth monomer.

4.1 The system

The total energy of the polymer is

$$V(\{\boldsymbol{r}_i\}) \equiv \frac{k}{2}\sum_{i=1}^{N}(\boldsymbol{r}_i - \boldsymbol{r}_{i-1})^2. \tag{46}$$

We move $\boldsymbol{r}_N \equiv \boldsymbol{u}(t)$ according to a protocol $\boldsymbol{u}(t)$. For one-dimensional pulling, the equations of motion decouple. Motion perpendicular to the pulling direction remains at equilibrium. We only have to consider one-dimensional motion governed by

$$\dot{z}_i = \gamma^{-1}[-T_{ij}z_j + f_i(t)] + \eta_i(t), \tag{47}$$

where the index runs $i = 1, \ldots, N-1$. Hence, the system has $n = N-1$ degrees of freedom which equals the number of free monomers. Inserting the energy (46), we get the tridiagonal coupling matrix

$$\mathsf{T} = k\begin{pmatrix} 2 & -1 & 0 & 0 & \\ -1 & 2 & -1 & 0 & \\ 0 & -1 & 2 & -1 & \\ 0 & 0 & -1 & 2 & \\ & & & & \ddots \end{pmatrix}_{n\times n} \tag{48}$$

and the external forces as $\boldsymbol{f}(t) = (0, \ldots, 0, ku(t))^{\mathrm{T}}$.

By comparing the energy of the polymer (46) with the general form (7), we obtain $\mathcal{V}(t) = (\bar{k}/2)u^2(t)$, where $\bar{k} \equiv k/N$. Because of relation (12), the free energy difference is

$$\Delta F = \mathcal{V}(t_\mathrm{s}) - \mathcal{V}(0) = (\bar{k}/2)[u^2(t_\mathrm{s}) - u^2(0)]. \tag{49}$$

Hence, the whole polymer behaves like a single spring with an effective spring constant $\bar{k}$.

4.2 Dissipated work

To calculate the dissipated work (33) of a Rouse polymer, we need the eigenvalues of $\mathsf{L} = \mu\mathsf{T}$, which are given by

$$\varepsilon_i = 2\frac{k}{\gamma}\left(1 - \cos\frac{i\pi}{N}\right). \tag{50}$$

The relaxation times are $\{\tau_i = 1/\varepsilon_i\}$ whereas the eigenvalues of the coupling tensor T are $\{\gamma\varepsilon_i\}$. The components of the integral kernel (32) become

$$\tilde{M}_{ij}(t'-t) = \Theta(t'-t)\frac{\tau_i}{\gamma}e^{-(t'-t)/\tau_i}\delta_{ij}. \tag{51}$$

Furthermore, we need the transformation matrix U, for which the three tensors L, T, and $\mathsf{M}(t'-t)$ become diagonal. Its components

$$U_{ij} = \sqrt{\frac{2}{N}}\sin\frac{i\pi j}{N} \tag{52}$$

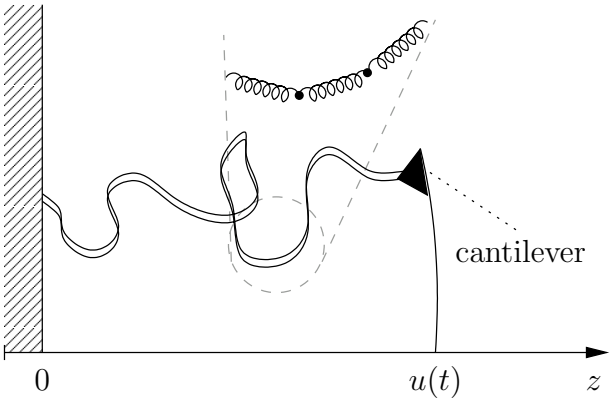

Fig. 1. Typical setup for a single-molecule experiment. A polymer in solution is attached to the tip of the cantilever of an AFM. It is then stretched by moving the AFM. Recording both the force exert on the cantilever and the speed $\dot{u}(t)$, we can calculate the work spent to stretch the polymer. The polymer is modeled as a linear chain of harmonic springs.

are given by the eigenvectors of matrix (48). The transformed external forces now read

$$\tilde{f}_i(t) = U_{ij}f_j(t) = \sqrt{\frac{2}{N}}\sin\frac{i\pi n}{N}ku(t) \tag{53}$$

and for one-dimensional pulling we, therefore, get a scalar integral kernel

$$M(t'-t) = \Theta(t'-t)\frac{2}{N}\sum_{i=1}^{N-1}\frac{\tau_i}{\gamma}\left(\sin\frac{i\pi}{N}\right)^2 e^{-(t'-t)/\tau_i} \tag{54}$$

resulting in the dissipated work (33)

$$\overline{W}_\mathrm{d} = k^2\int_0^{t_\mathrm{s}}\mathrm{d}t\int_0^{t_\mathrm{s}}\mathrm{d}t'\,\dot{u}(t')M(t'-t)\dot{u}(t) \tag{55}$$

for arbitrary driving protocols $u(t)$. This is the exact expression for a finite Rouse polymer, which must be evaluated numerically for arbitrary N. However, it is instructive to discuss limiting cases analytically.

4.3 Slow driving and continuous limit

In the limiting case of slow driving (see Sect. 2.4), the integral kernel $M(t'-t)$ reduces to a δ-function and equation (54) becomes

$$M(t'-t) = \gamma^{-1}\frac{2}{N}\sum_{i=1}^{N-1}\left(\tau_i\sin\frac{i\pi}{N}\right)^2\delta(t'-t). \tag{56}$$

It is now feasible to evaluate the sum

$$\frac{2}{N}\sum_{i=1}^{N-1}\left(\tau_i\sin\frac{i\pi}{N}\right)^2 = \frac{1}{2N}\frac{\gamma^2}{k^2}\sum_{i=1}^{N-1}\left(\cot\frac{i\pi}{2N}\right)^2 \approx \frac{N}{3}\frac{\gamma^2}{k^2} \tag{57}$$

by expanding $\cot x \approx 1/x$ and using $\sum_i 1/i^2 \to \pi^2/6$. Comparison of the exact result with the approximation shows a reasonable error $\simeq 5\%$ even for small polymer sizes $N \simeq 30$, which vanishes for large N. Inserting the approximated integral kernel into equation (55), the average dissipated work takes the particularly simple form

$$\overline{W}_{\rm d} = \frac{N\gamma}{3}\int_0^{t_{\rm s}} {\rm d}t\ \dot{u}^2(t) \tag{58}$$

for slow driving.

In the Rouse model the index i is regarded as a continuous variable [22]. In this continuous limit the relaxation times are $\tau_i = \tau_1/i^2$ with the fundamental time scale $\tau_1 = \gamma N^2/k\pi^2$. Often the polymer size N cannot be controlled exactly but is assumed to be large. Note in passing that then we cannot distinguish a slow regime $\tau_1 \ll t_{\rm s}$ anymore as $\tau_1 \propto N^2$. We calculate the integral kernel by replacing the summation in (54) by an integration with the upper limit extended to infinity leading to

$$M(t'-t) = \Theta(t'-t)\frac{1+\exp\{-\tau_\infty/(t'-t)\}}{k\sqrt{\pi(t'-t)/\tau_\infty}}. \tag{59}$$

The kernel is now independent of N and determined by the fastest time scale in the system $\tau_\infty \equiv \gamma/4k$ alone. Equation (59) agrees well with the exact solution (54) except for small $(t'-t)/\tau_\infty < 1$ (see Fig. 2). It diverges because of the integration there is no cut-off of the fast modes. This in turn would lead to a wrong behavior of the mean dissipated work (55). It is therefore convenient to use a regulated integral kernel

$$M(t'-t) = \Theta(t'-t)k^{-1}[1+(\pi/4)(t'-t)/\tau_\infty]^{-1/2}, \tag{60}$$

which does not diverge. The quality of these approximations is compared to the exact result in Figure 2.

4.4 Linear and symmetric protocol

We specialize to a specific protocol and drive the Rouse polymer by

$$u(t) \equiv vt, \tag{61}$$

i.e., we pull at constant speed v and stretch the polymer to a length $L = vt_{\rm s}$. The expectation value of the dissipated work (55) is

$$\overline{W}_{\rm d} = \frac{L^2k^2}{\gamma}\frac{2}{N}\sum_{i=1}^{N-1}\tau_i\left(\sin\frac{i\pi}{N}\right)^2 \times\left[\frac{\tau_i}{t_{\rm s}} - \left(\frac{\tau_i}{t_{\rm s}}\right)^2\left(1-e^{-t_{\rm s}/\tau_i}\right)\right], \tag{62}$$

whereas in the the slow driving regime it simply becomes

$$\overline{W}_{\rm d} = \frac{N\gamma}{3}vL = \frac{\pi^2}{3N}L^2k\frac{\tau_1}{t_{\rm s}} \tag{63}$$

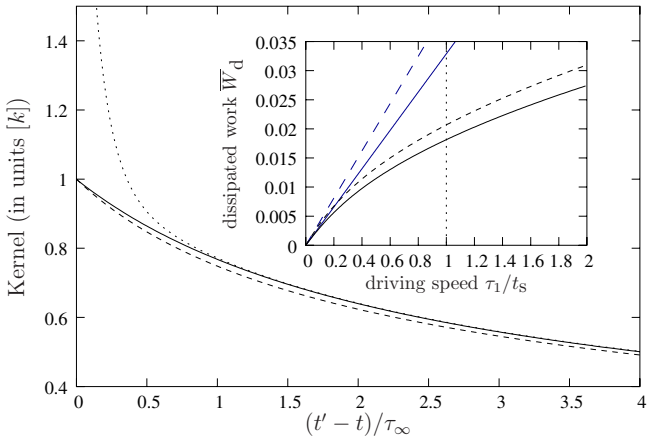

Fig. 2. Comparison between the exact integral kernel $M(t'-t)$ for $N = 1000$ from equation (54) (solid line) and the two continuous limit approximations (59) (dotted line) and (60) (dashed line). The inset plot shows the mean dissipated work as a function of the driving speed $\tau_1/t_{\rm s}$ for two protocols applied to finite size polymers ($N = 100$). The solid curves mark the linear driving protocol where the straight line is the slow driving approximation (63). Respectively, the dashed curves show the symmetric protocol (66) with $\omega = \pi/2t_{\rm s}$. (Numerical parameters are $L = \gamma = k = 1$, the mean dissipated work is given in units of $k_{\rm B}T$)

following equation (58). This can be interpreted as a friction force $N\gamma v/3$ times the length L the polymer is extended. For a Gaussian chain with bond length b and the end-to-end distance $l = \sqrt{N}b$, we set $k \equiv 3/\beta b^2$ [22]. Then the mean dissipated work in the slow regime

$$\overline{W}_{\rm d} = \frac{\pi^2}{\beta}\left(\frac{L}{l}\right)^2\frac{\tau_1}{t_{\rm s}} \tag{64}$$

becomes proportional to the square of the stretching factor L/l.

Another protocol, which was proposed in the context of probing free energy landscapes, is the symmetric protocol [18]

$$u(t) = L\sin\omega t. \tag{65}$$

From equation (58), we easily obtain for the slow driving regime

$$\overline{W}_{\rm d} = \frac{N\gamma}{3}\frac{L^2\omega}{4}\left[2\omega t_{\rm s} + \sin 2\omega t_{\rm s}\right]. \tag{66}$$

To compare it with the linear protocol we set $\omega = \pi/2t_{\rm s}$. As we see in Figure 2, the non-linear driving results in larger dissipation for the same final state.

4.5 Experimental requirements

We are not aware of any experiments yet which fit precisely the conditions we used to derive the explicit results given in Section 4.4 for two paradigmatic experimental protocols. First, single molecule experiments often involve hydrodynamical effects, which are better described within

the framework of the Zimm model. The equations of motion become non-linear which is beyond the scope of the present paper. However, for a single-stranded DNA embedded on a supported lipid membrane stretched by an electric field, highly viscous but free draining Rouse dynamics has successfully been applied previously [25]. On the other hand, using such a semi-flexible polymer as a Gaussian chain one is limited in the range of extensions available. If the overall size approaches the contour length, semi-flexible elasticity becomes relevant.

In a quantitative comparison with experiments recording the work is also an important issue. Usually, this is achieved by measuring the force $F(t)$ applied by the cantilever from which one obtains, for a given protocol $u(t)$, the work as

$$W = \int_0^{t_s} \mathrm{d}t\, \dot{u}(t) F(t). \tag{67}$$

In our set-up, where we control the position of the last bead directly, this requires measuring the extension of the last spring to get $F(t)$. In practice, it will be better to include the cantilever as a $N+1$-th spring with a, in general, different spring constant k'. If k' is equal to k, the explicit expressions (55) with (54) are directly applicable. If k' deviates significantly from k, one has to diagonalize the corresponding T matrix. For any specific choice of parameters, the explicit calculation of mean and variance would then follow the route outlined in Section 4.2 for the general model straightforwardly.

5 Summarizing perspective

For a n-dimensional diffusive system with harmonic internal energy driven by arbitrary time-dependent forces, we have determined mean and variance of the resulting Gaussian distribution for the work spent in a non-equilibrium process. We have specialized the general result to the previously studied case of one degree of freedom in a harmonic potential which corresponds to dragging a colloidal particle through a viscous fluid. For stretching a Rouse polymer we have discussed the dissipated work in detail and derived simple expressions for two experimental protocols.

It will be interesting to investigate other systems with a harmonic internal energy like semi-flexible polymers or polymers with internal degrees of freedom. A generalization to time-dependent coupling $\mathsf{T} = \mathsf{T}(t)$ should be feasible as well, since the equations of motion remain linear.

A challenging extension of our result would be to include hydrodynamic effects like in the Zimm model for polymer dynamics [22]. Since in this case the mobility coefficients become dependent on the state $\boldsymbol{z}$, the resulting equations of motion are non-linear and the distribution of work, a priori, no longer Gaussian [26]. Whether variational approaches or perturbative techniques in the corresponding path integral are more promising to derive the work distribution remains to be seen.

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