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From Langevin to generalized Langevin equations for the nonequilibrium Rouse model

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We investigate the nature of the effective dynamics and statistical forces obtained after integrating out nonequilibrium degrees of freedom. To be explicit, we consider the Rouse model for the conformational dynamics of an ideal polymer chain subject to steady driving. We compute the effective dynamics for one of the many monomers by integrating out the rest of the chain. The result is a generalized Langevin dynamics for which we give the memory and noise kernels and the effective force, and we discuss the inherited nonequilibrium aspects.

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I. INTRODUCTION

To relate different levels of physical description belongs to the core business of statistical mechanics. This is accompanied by the emergence of notions as heat and entropy, which are important concepts for bridging the gap between microscopic laws and macroscopic behavior. Moreover, "new" forces can appear, effectively from integrating out certain degrees of freedom. These are commonly called *entropic* or *statistical forces* and they have been discussed since relaxation to equilibrium was first considered. Indeed, for equilibrium dynamics, statistical forces have their origin in the nature of macroscopic systems to evolve towards higher entropy rather than being caused by some specific mechanical force. Though much systematic progress has been made in the study of these entropic forces, there has been less venture into the effects of nonequilibrium driving on statistical forces. Only over the past decade have systematic efforts been made to calculate these nonequilibrium statistical effects. This includes Soret-Casimir forces [1,2] but also general considerations on the law of action and reaction [3].

The first motivation of the present work is to study an explicit example of statistical forcing emerging from integrating out a nonequilibrium environment. Yet the case we treat comes with an extra motivation as it opens some questions regarding the nonequilibrium physics of polymers. In contrast to many ongoing studies of nonequilibrium polymer rheology, transport through polymers, or mechanical folding and stretching of polymers, the present paper considers also steady nonequilibria, i.e., where the driving is constant in time and the condition of detailed balance is broken.

Our working model is the widely studied Rouse model [4], an ideal chain, where monomers are connected through Gaussian springs and excluded volume effects and hydrodynamic interactions are neglected. This model holds a special place, as it is the simplest model that can be exactly solved to describe phenomena like anomalous diffusion of polymers in a bath. Moreover, in the natural context of polymer melts, which are a collection of polymers in a solution, the diffusion of a tagged polymer can be described by Rouse dynamics moving along a one-dimensional tube embedded in a network or mesh of polymers [5,6]. Our general question then addresses the investigation of the effective dynamics of a tagged monomer when the chain is subjected to nonequilibrium driving. We have in mind that the extremal monomers are subject to nonconservative forces, e.g., via a small charged particle or optically driven bead attached to them, and we wish to follow a tagged monomer near the middle of the chain.

Because of the harmonic interaction, the nonequilibrium Rouse model is one of the simplest, still physically interesting, examples to understand the effective dynamics in a driven medium. The equilibrium version of integrating out the Rouse model has been carried out by D. Panja [7]. The dynamics of the tagged monomer is shown to be non-Markovian with memory kernel having a power-law decay $\mu(t) \propto t^{-1/2}$ for short times and exponential decay asymptotically in time,

$$\mu(t) \propto \frac{1}{\sqrt{t}}\, e^{-t/\tau}. \tag{1}$$

The kernel $\mu(t)$ is shown to be the mean relaxation response of the polymers to local strain and its behavior gives good information on the nature of the diffusion, which is anomalous for intermediate times, $\Delta x^2 \propto D\sqrt{t}$.

In the present paper we start with the phantom Rouse dynamics in the inertial regime and we introduce a nonequilibrium driving. The result of integrating out the (other) polymer degrees of freedom is again a generalized Langevin equation (GLE) for the tagged monomer. We show that, in the overdamped limit, the equilibrium results match those of Panja [7]. We discuss the nonequilibrium corrections to the force and memory terms for driving of specific nature to obtain some general information about statistical forces in nonequilibrium.

The more systematic and general approach to integrating out degrees of freedom is commonly referred to as the Mori-Zwanzig approach [8,9] or the approach via adiabatic elimination [10–13]. Generalized Langevin equations have also been derived in nonstationary environments [14] and, similarly in spirit to the present paper, is also the generalization where a coarse-graining is added onto a coarse-grained description [15] or where one Brownian particle is described in a nonequilibrium bath [16]. In the case of nonequilibrium thermostated dynamics, a generalized Langevin equation has also been derived [17]. We do not follow these general schemes here because we work on the more explicit Langevin (not Fokker-Planck) side of the question, and we take no special limits for macroscopic systems or for the speed of motion of nonconserved versus conserved quantities. Moreover, these

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general approaches are less explored for starting with open driven polymer dynamics as we do here. An interesting study of the average square displacement of a tagged monomer in a Rouse polymer chain subjected to random, layered convection flows, both time independent and time dependent, has been made in Refs. [18,19].

In the next section we introduce the model and the various types of nonequilibrium driving. Sections IV, V, and VI summarize the method and the results with a discussion of the effective dynamical behavior. Finally, some more essential elements of the computations are collected in Appendix A.

II. NONEQUILIBRIUM ROUSE DYNAMICS

We consider the positions $\vec{R}_i, i = 1,\dots,N$, of N point particles (also called monomers) in a three-dimensional domain open to thermal exchanges. The particles are harmonically coupled and some are subject to further forces, some of which are nonconservative. The potential energy is quadratic,

$$U(\vec{R}) = \frac{\kappa}{2}(\vec{R}_1 - \vec{R}_2)^2 + \frac{\kappa}{2}(\vec{R}_2 - \vec{R}_3)^2 + \dots + \frac{\kappa}{2}(\vec{R}_{N-1} - \vec{R}_N)^2, \tag{2}$$

and the force on the ith particle is the sum of systematic forces $\vec{K}_i$ and Langevin forces $\vec{L}_i$:

$$\vec{K}_i = -\vec{\nabla}_i U + \vec{F}_i, \quad \vec{L}_i = -m\gamma\dot{\vec{R}}_i + \vec{\xi}_i. \tag{3}$$

There is an independent standard white noise $\vec{\xi}_i$ modeling the action of the thermal environment at temperature T and friction γ, with $\langle\vec{\xi}_{i,\alpha}(t)\vec{\xi}_{j,\beta}(t')\rangle = 2m\gamma k_B T\delta_{i,j}\delta_{\alpha,\beta}\delta(t-t')$, where α and β refer to the various spatial directions. The first term in $\vec{K}_i$ is the conservative part of the force. The force $\vec{F}_i$ need not be conservative or constraining and will be specified below; this is what we refer to as the driver. We then have the equation of motion for the time-dependent coordinates $\vec{R}_i(t)$,

$$m\frac{d^2\vec{R}_i}{dt^2} = \vec{K}_i + \vec{L}_i, \tag{4}$$

with given initial conditions $R_i(0), \dot{\vec{R}}_i(0)$ at time $t = 0$. In many cases of standard polymer physics, the inertial term proportional to the mass in (4) can be fairly ignored. This can be done in the following equations and results but there is, however, no harm in keeping it; in fact, our concern is not with a detailed study of polymer physics. Instead, we use the Rouse polymer model for the simple purpose of illustrating effects of statistical forces in a nonequilibrium environment. To have a workable model, we can exploit the linearity of the Rouse model and the extra forcing $\vec{F}_i$ will also be assumed linear. We will, however, not proceed with a diagonalization, and we will not write the solution in terms of modes. After integrating out all particles but the first one, we obtain explicit information about the final equation of the form

$$m\frac{d^2\vec{R}_1}{dt^2} = -m\int_0^t dt'\mu^{(N)}(t-t')\dot{\vec{R}}_1(t') - m\gamma\dot{\vec{R}}_1(t) + \vec{\eta}^{(N)}(t) + \vec{\xi}_1(t) + \vec{G}^{(N)}(t). \tag{5}$$

Indeed, not surprisingly and as an explicit example of a type of Zwanzig's program [20], we will find the validity of a GLE of the form (5). Our model will enable rather explicit memory and friction kernels. We will discuss the memory kernel $\mu(t)$ (more generally a matrix), the noise $\vec{\eta}(t)$, and the statistical forcing $\vec{G}$ (that all depend on N) in the cases that we introduce next. Obviously, the case of the effective dynamics on another coordinate, e.g., the middle one around $i = N/2$, can be reduced to that case. The effective force $\vec{G}$ can be of convolution type, as in Eq. (24) below, and also contain the memory of the past trajectory of the tagged monomer.

A. Uniform constant driving

The simplest case is to assume that the outer end of the polymer is being driven under a constant external force f. That is a mathematical idealization of a polymer, say, with a charged end, forced under an electric field. As there is no confining force for the polymer, this means the whole system will move in the direction of the field and we discuss that diffusive regime. That is, we take free boundary conditions and $\vec{F}_i = \delta_{N,i}\, f\, \hat{e}_x$ for some constant field f in the x direction. The simplest example corresponds to two linearly coupled degrees of freedom moving in one dimension, with dynamics

$$\begin{aligned} m\frac{d^2R_1}{dt^2} &= -\kappa[R_1 - R_2] - m\gamma\frac{d}{dt}R_1 + \xi_1(t), \\ m\frac{d^2R_2}{dt^2} &= -\kappa[R_2 - R_1] - m\gamma\frac{d}{dt}R_2 + \xi_2(t) + f, \end{aligned} \tag{6}$$

for $R_1, R_2 \in \mathbb{R}$. The constant f induces a drift. We give that dimer case here explicitly also because we have found that for all finite N (size of original polymer) the basic qualitative features of generalized memory and friction are unchanged from $N = 2$, where things are, of course, much simpler.

B. Nonuniform driving

Here we imagine the motion of a polymer in a two-dimensional slab of vertical size L in which the outer end is subject to a forcing in the horizontal direction that is linear in the vertical distance. We can imagine this as the result of a shearing at the outer edge of the polymer, but we do not imagine a surrounding fluid as we wish to stick to the Rouse model (ignoring hydrodynamic interactions as, e.g., in the Zimm model). In terms of a polymer melt we can realize that by attaching a bead or nanoparticle to the end of the polymer chain, which is then driven in one direction but nonuniformly with respect to an orthogonal direction. This provides the well-known case of a nonconservative force.

For explicitness we write out this case again, first, for a polymer of size $N = 2$. One monomer is being acted on by the nonuniform force which depends on its y coordinate. The equation of motion written in Cartesian coordinates is then

$$\begin{aligned} \frac{md^2R_{2x}}{dt^2} &= k[R_{1x} - R_{2x}] - m\gamma\frac{dR_{2x}}{dt} + \xi_{2x}(t) + f\,R_{2y}, \\ \frac{md^2R_{2y}}{dt^2} &= k[R_{1y} - R_{2y}] - m\gamma\frac{dR_{2y}}{dt} + \xi_{2y}(t), \end{aligned}$$

$$\begin{aligned}\frac{md^2R_{1x}}{dt^2} &= -k[R_{1x}-R_{2x}] - m\gamma\frac{dR_{1x}}{dt} + \xi_{1x}(t),\\ \frac{md^2R_{1y}}{dt^2} &= -k[R_{1y}-R_{2y}] - m\gamma\frac{dR_{1y}}{dt} + \xi_{1y}(t),\end{aligned} \tag{7}$$

where f is the nonequilibrium amplitude.

Since the external force now does depend on the position, it is useful here to have a comparison or equilibrium reference, where an external potential U_{ext} is added to the potential energy U to trap the outer monomer. In other words, again, for simplicity of presentation, for the case of a dimer, $F(t) = -f(R_2 - Q)$, which derives from a confining potential around position Q, which holds the outer edge of the polymer,

$$\begin{aligned} m\frac{d^2R_2}{dt^2} &= -\kappa(R_2-R_1) - m\gamma\frac{dR_2}{dt} + \xi_2(t) - f(R_2-Q),\\ m\frac{d^2R_1}{dt^2} &= -\kappa(R_1-R_2) - m\gamma\frac{dR_1}{dt} + \xi_1(t),\end{aligned} \tag{8}$$

which would replace the dynamics of the x components of Eqs. (7).

III. GENERAL METHOD: INDUCTION AND RECURRENCE RELATIONS

In this section we show the methods and intermediate steps involved in reaching our results, which will be summarized in the next three sections. The general method is always to work via iteration and to prove results by induction. More precisely, the tagged particle equation of motion is directly coupled to a second particle, which then is coupled to the other $N-2$ particles. If we now assume that, first, after integrating out these $N-2$ particles, the effective dynamics of the second particle is of the form (5), then we obtain two equations: one is the GLE (5) (with N there replaced by $N-1$) and the other is the original equation of motion of the tagged particle coupled to the second particle. Assuming the structure (5) for $N-1$, specific properties (such as the long time limit) of the memory kernel, noise and force constitute the induction hypothesis. These properties depend on the specific physical constraints. See for example Eq. (A3). The remaining task is then to integrate out that last (second) particle and to prove that the induction hypothesis is indeed reproduced at size N. The crucial step to discover what the correct induction hypothesis is for the case $N = 2$. This is also why the essential first step is to be explicit about the case $N = 2$. We next give more details.

After integrating out $N-2$ particles, we arrive at the following GLE for the $N-1$th monomer, which we label with subscript 2 (second particle). (Note that we skip vector notation, as we can always reduce the problem to more scalar degrees of freedom.)

$$\begin{aligned}\frac{d^2R_2^{(N-1)}}{dt^2}(t) &= -\frac{k}{m}\left(R_2^{(N-1)} - R_1\right) - \gamma\frac{dR_2^{(N-1)}}{dt}(t) + \frac{\xi_2(t)}{m}\\ &\quad + \frac{\eta^{(N-1)}(t)}{m} - \int_0^t dt'\mu^{(N-1)}(t-t')\frac{dR_2^{(N-1)}}{dt}(t')\\ &\quad + \frac{G^{(N-1)}(t)}{m}.\end{aligned} \tag{9}$$

The tagged monomer R_1 is attached to $R_2^{(N-1)}$ by a harmonic spring, the force of which is simply given by

$$\begin{aligned}\Phi^{(N)}(t) = m\frac{d^2R_1}{dt^2}(t) &= -k\left[R_1 - R_2^{(N-1)}\right] - m\gamma\frac{dR_1}{dt}(t)\\ &\quad + \xi_1(t),\end{aligned} \tag{10}$$

where $\xi_1(t)$ and $\xi_2(t)$ are the independent white noise on monomers 1 and 2. These equations represent a system of two monomers, one of which is already a coarse-grained variable, with memory kernel $\mu^{(N-1)}(t)$, external force $G^{(N-1)}(t)$, and noise $\eta^{(N-1)}(t)$.

A second major ingredient in our computation is quite naturally to take the Laplace transform of (9) and (10). After integrating out $R_2^{(N-1)}$, we arrive at the following GLE for R_1:

$$\begin{aligned}\tilde{\Phi}^{(N)}(s) &= -m\kappa\frac{\tilde{\mu}^{(N-1)}(s)+\gamma+s}{ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa}\\ &\quad\times[s\tilde{R}_1(s)-R_1(0)] - m\gamma[s\tilde{R}_1(s)-R_1(0)]\\ &\quad+\frac{\kappa}{ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa}\tilde{G}^{(N-1)}(s)\\ &\quad+m\kappa\frac{\tilde{\mu}^{(N-1)}(s)+\gamma+s}{ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa}\\ &\quad\times\left[R_2^{(N-1)}(0)-R_1(0)\right]\\ &\quad+\frac{m\kappa}{ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa}\dot{R}_2^{(N-1)}(0)\\ &\quad+\kappa\frac{[\tilde{\eta}^{(N-1)}(s)+\tilde{\xi}_2(s)]}{ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa}+\tilde{\xi}_1(s).\end{aligned} \tag{11}$$

This has to be compared with (5) and, in particular, with each of the terms on the right-hand side. In that way we obtain recurrence relations for the memory kernel $\tilde{\mu}^{(N)}(s)$, the noise $\tilde{\eta}^{(N)}(s)$, and the induced force $\tilde{G}^{(N)}(s)$ on the tagged particle when comparing size N polymers with size $N-1$:

$$\tilde{\mu}^{(N)}(s) = \frac{\kappa[\tilde{\mu}^{(N-1)}(s)+\gamma+s]}{[ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa]}, \tag{12}$$

$$\tilde{G}^{(N)}(s) = \frac{\kappa\tilde{G}^{(N-1)}(s)}{[ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa]}, \tag{13}$$

$$\begin{aligned}\tilde{\eta}^{(N)}(s) &= m\tilde{\mu}^{(N)}(s)\left[R_2^{(N-1)}(0)-R_1(0)\right]\\ &\quad+\frac{m\kappa}{[ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+s^2+\kappa]}\dot{R}_2^{(N-1)}(0)\\ &\quad+\frac{\kappa}{[ms\tilde{\mu}^{(N-1)}(s)+ms\gamma+ms^2+\kappa]}\\ &\quad\times[\tilde{\eta}^{(N-1)}(s)+\tilde{\xi}_2(s)].\end{aligned} \tag{14}$$

To these we must add "initial" conditions for the recurrence, i.e., to insert the findings for the case $N = 2$. These will enable the correct induction hypothesis.

Finally, there are the initial conditions to the dynamics; the initial conditions (positions and momenta) of all the other particles (except the tagged particle) contribute to the noise. Their statistical distribution is, in principle, a matter of choice but there are, of course, dynamically more natural choices. We detail them in Appendix A.

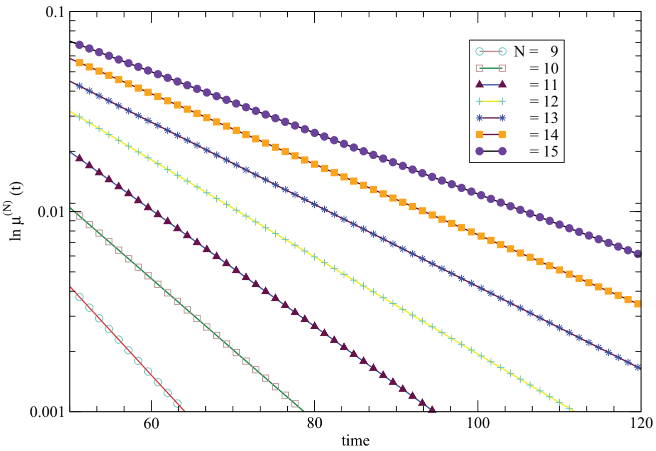

FIG. 1. (Color online) Memory vs time, $\kappa = 3$, $\xi = 1$. The long time limit of memory in a semilog plot.

IV. FREE DIFFUSION UNDER UNIFORM DRIVING

This and the two following sections summarize the main results of the logic explained in the previous section. We always refer to (5) for the notation that we have obtained after integrating out all but one of the particles.

A. In general

Referring to the dynamics (2), (4), and (6), we define the frequency ω as $\omega^2 = \frac{\kappa}{m} - \frac{\gamma^2}{4}$. If ω is real (inertial case), then the friction kernel $\mu^{(N)}$ is oscillating with frequency ω with decreasing amplitude. When, under high friction, ω is imaginary (overdamped case), there is a monotone decay in time.

In the long time limit we find that the friction kernel is always exponentially decaying as $\mu^{(N)}(t) \leqslant e^{-t/\tau_N}$ for large times t, where the decay time τ_N is of the order N^2 for large N; see Fig. 1. In the figure are represented polymers of different sizes. The discrete data points are solutions of numerical evaluation of analytical results. The lines are fits exhibiting the general nature of these solutions. κ is the spring constant and $\chi = m\gamma$. Figure 1 is a semilog plot, which shows the exponential decay of the friction kernel in long time. The slopes of various lines are proportional to the decay exponent τ_N. It is seen in Fig. 1 that τ_N varies as N^{-2}, which is already known to hold in full equilibrium [7]. We show that this remains valid in nonequilibrium. We have also obtained that the time of relaxation is, in general, bounded from below as $\tau_N > 2/\gamma$; see below in Appendix A. This is indeed clear as the time of relaxation grows with the size of the polymer and the tagged particle relaxes fastest when it is connected to just one another monomer, τ_N then being $2/\gamma$.

As is well known and also to be expected under nonequilibrium conditions, for short times $t < \tau_N$, the memory kernel has a power-law decay $\mu(t) \propto \frac{1}{t^{1/2}}$; see also Refs. [5–7]. Indeed, for short times there is no dependence of memory on system size.

Integrating out the other monomers also creates additional colored noise in the system. The noise $\eta^{(N)}(t)$ is Gaussian with a shifted average and breaks the second fluctuation-dissipation relation transiently. However, asymptotically, the stationary covariance satisfies the second fluctuation-dissipation relation,

$$\lim_{t\to\infty} \langle \eta(t+\tau)\eta(t)\rangle = \frac{m}{\beta}\mu(\tau). \tag{15}$$

Finally, the external force f on the outer monomer gives rise to a time-dependent statistical force $G(t)$ on the tagged monomer and reaches a limiting form exponentially fast. The general behavior is exactly similar to what we make explicit in the next subsection; see below in Eq. (19).

B. Two monomer case

To give immediately more explicit formulae, we summarize the results for the dimer case, which is also used to start the recurrence. First, there is the memory kernel ($N = 2$),

$$\mu(t) = \frac{\kappa}{m} e^{-\gamma t/2}\left[\cos\omega t + \frac{\gamma}{2\omega}\sin\omega t\right], \tag{16}$$

where

$$\omega^2 = \frac{\kappa}{m} - \frac{\gamma^2}{4} > 0.$$

For a dimer, a power-law decay for small times is not seen, as can be imagined from the fact that a dimer in one dimension has no conformational degrees of freedom. The mean-squared end-to-end distance $\langle R_{ee}^2\rangle$ is simply equal to the square of the bond length and, thus, shows only simple diffusion.

The colored noise is

$$\begin{aligned}\eta(t) = &-\kappa[R_1(0) - R_2(0)]\left[\cos(\omega t) + \frac{\gamma}{2\omega}\sin(\omega t)\right]e^{-\gamma t/2}\\ &+\kappa \dot{R}_2(0)\frac{\sin(\omega t)}{\omega}e^{-\gamma t/2}\\ &+\frac{\kappa}{m}\int_0^t \frac{\sin[\omega(t-t')]}{\omega}\xi_2(t')e^{-\gamma(t-t')/2}dt'.\end{aligned} \tag{17}$$

It is natural to take the distribution

$$\rho_{\text{st}}(R_2,\dot{R}_2) = \frac{1}{Z}e^{-\beta H}, \tag{18}$$

where $H = \frac{m\dot{R}_2{}^2}{2} + \frac{\kappa}{2}(R_1 - R_2)^2 - fR_2$, which depends on the position R_1 of the tagged particle. When averaged over that initial distribution (18) we get a mean

$$\langle \eta(t)\rangle = f\left[\cos(\omega t) + \frac{\gamma}{2\omega}\sin(\omega t)\right]e^{-\gamma t/2},$$

which is not zero for $f \neq 0$. Indeed, the monomer R_2 is found more on one side than the other due to the force f.

The effective force is found to be

$$G(t) = f\left\{1 - e^{-\gamma t/2}\left[\cos(\omega t) + \frac{\gamma}{2\omega}\sin(\omega t)\right]\right\}, \tag{19}$$

exponentially growing to the applied force f. When the force would be time dependent, $f = f_t$, the effective force gets memory and becomes

$$G(t) = k\int_0^t f_s\, e^{-\gamma(t-s)/2}\,\sin\omega(t-s)\,ds.$$

This appears to be a general feature of nonequilibrium forcing: they create effective forces that themselves depend on the forcing at all earlier times. We still emphasize that the nature of nonequilibrium in this paper and in the present example of constant forcing qualitatively differs from the case of driving forces discussed in some previous works [21], polymer translocation by an external force being one example. Such driving forces are introduced at the macroscopic level or the level of the GLE and, hence, do not have an effect on the nature of the friction kernel or of the noise. On the other hand, the nonequilibrium in our work is introduced microscopically, such that the GLE itself gets modified as a function of the driving.

C. Limiting cases

(1) *The long time limit*. Motion after $t \gg \tau_N$, of the tagged particle appears to be diffusive with a constant drift f.

(2) *Large coupling limit*. A large coupling signifies that the restoring force between any two monomers is very strong and, hence, the monomers undergo high-frequency oscillations given by $\omega \simeq \sqrt{\frac{\kappa}{m}} \to \infty$. Measurements will typically time average over a few periods. The time-averaged behavior of the tagged monomer is, again, of a Brownian particle acted on by a constant force. The effective force goes to the constant force f. The time averaged total noise goes to white noise $\xi_1(t)$ and the time-averaged memory kernel $\mu(t)$ disappears.

(3) *The overdamped limit*. The high friction limit refers to the case when the viscosity of the medium is so high that the acceleration of the monomers is zero, and the only variables which are changing are position. To take the overdamped limit in a meaningful manner, together with taking the friction coefficient γ to infinity, one has to take the mass m of all monomers to zero, preserving the product $\chi = m\gamma$ to be finite. The memory kernel then reduces to

$$\mu(t) = ke^{-kt/\chi}. \tag{20}$$

The memory kernel after taking the continuum limit is

$$\mu(t) = 2\sqrt{\frac{\pi \chi k}{t}} e^{-t/\tau}, \tag{21}$$

where $\tau = N^2\chi/(\pi^2 k)$, as shown before in [7] under equilibrium dynamics.

V. NONUNIFORM DRIVING

We are now in two dimensions with forcing at one end of the polymer in the horizontal direction with an amplitude that is proportional to the vertical distance. This dependence is similar to a shearing force, but we do not insist here on the presence of a fluid (as we treat the Rouse model and not, e.g., the Zimm model). Rather, we have in mind that we can manipulate the outer monomer of a polymer in a melt in a nonuniform way. To a good approximation, that would be the case when nanoparticles are attached to the polymer and undergo nonrigid rotation, where the angular velocity depends on the radial distance (here, the vertical distance).

An interesting result here is that the friction kernel $\mu^{(N)}(t)$ is identical to the case of constant forcing (previous section). To be explicit, and without loss of essential information, we can already state the results for $N = 2$.

The memory kernel in each direction is given by

$$\mu_{1x}(t) = \mu_{1y}(t) = \frac{\kappa}{m} e^{-\gamma t/2} \left[\cos(\omega t) + \frac{\gamma}{2\omega}\sin(\omega t)\right],$$

which is indeed the same as for a dimer in free space under constant forcing. This is due to the fact that the external forcing does not couple to velocity but only to position. The nature of μ in the two mutually perpendicular directions and various limits, hence, remains the same.

The nature of the induced noise, however, gets modified due to the different nature of the external force. The noise in general is dependent on the initial positions and velocities of all the monomers and, hence, picks up additional contributions from the external force, which is coupled to the y component of the position of the first monomer. Here is the explicit noise function:

$$\begin{aligned}\eta_{1x}(t) = {}& -\kappa[R_{1x}(0) - R_{2x}(0)]\left[\cos(\omega t) + \frac{\gamma}{2\omega}\sin(\omega t)\right]e^{-\gamma t/2}\\ &+ \kappa \dot{R}_{2x}(0)e^{-\gamma t/2}\frac{\sin(\omega t)}{\omega}\\ &+ \frac{\kappa}{m}\int_0^t e^{-\gamma(t-t')/2}\frac{\sin[\omega(t-t')]}{\omega}\xi_{2x}(t')dt'\\ &+ \frac{f}{m\omega}\kappa\int_0^t dt' e^{-\gamma(t-t')/2}\sin(\omega(t-t'))\\ &\times \left\{R_{2y}(0)\left[\cos(\omega t') + \frac{\gamma}{2\omega}\sin(\omega t')\right]\right.\\ &\left. + \dot{R}_{2y}(0)\frac{\sin(\omega t')}{\omega}\right\} + \frac{f}{m\omega}\frac{\kappa}{m\omega}\int_0^t\int_0^{t'} dt'dt'' e^{-\gamma(t-t'')/2}\\ &\times \sin[\omega(t-t')]\sin[\omega(t'-t'')]\xi_{2y}(t'').\end{aligned} \tag{22}$$

Putting $f = 0$ in (22) gives us back the noise on a polymer under constant force (17). The external force couples the x component of noise to the dynamics in the y direction. The initial positions in the y direction as well as the component of the white noise $\xi_{2y}(t)$ in the y direction now play a role in the dynamics in the x direction of the second monomer. The y component of the noise remains unaffected by the force, since the external force does not couple to the motion in the y direction,

$$\begin{aligned}\eta_{1y}(t) = {}& -\kappa[R_{1y}(0) - R_{2y}(0)]\left(\cos\omega t + \frac{\gamma}{2\omega}\sin\omega t\right)e^{-\gamma t/2}\\ &+ \kappa\dot{R}_{2y}(0)e^{-\gamma t/2}\frac{\sin(\omega t)}{\omega}\\ &+ \frac{\kappa}{m}\int_0^t e^{-\gamma(t-t')/2}\frac{\sin[\omega(t-t')]}{\omega}\xi_{2y}(t')dt'.\end{aligned} \tag{23}$$

We now come to the induced force. The x component of the effective force is

$$\begin{aligned}G_{1x}(t) = {}& f\frac{\kappa^2}{m^2\omega^2}\int_0^t dt'\int_0^{t'} dt'' e^{-\gamma(t-t'')/2}\sin[\omega(t-t')]\\ &\times \sin[\omega(t'-t'')]R_{1y}(t'').\end{aligned} \tag{24}$$

Again, as a nonequilibrium effect, the effective force has memory. On the other hand, its y component $G_{1y}(t)$ stays zero. Indeed, since the applied force itself is acting in the x direction, there is no reason why the effective dynamics in the y direction of the tagged monomer should become affected by it.

Let us now go to the results for general N. The memory kernels $\tilde{\mu}_x^{(N)}(s)$ and $\tilde{\mu}_y^{(N)}(s)$ look as they did in the case of constant force (12), with the same "initial" conditions. The recurrence relation for the coloured noise picks up changes due to shearing, as discussed under (22) and (23); they arise due to the fact that the nonuniform forcing couples the x and y components of motion.

$$\tilde{\eta}_x^{(N)}(s) = m\tilde{\mu}_x^{(N)}(s)\big[R_x^{(N-1)}(0) - R_x(0)\big] + \frac{m\kappa}{\big[ms\tilde{\mu}_x^{(N-1)}(s) + ms\gamma + s^2 + \kappa\big]}\dot{R}_x^{(N-1)}(0) + \frac{\kappa}{\big[ms\tilde{\mu}_x^{(N-1)}(s) + ms\gamma + ms^2 + \kappa\big]}$$
$$\times\big[\tilde{\eta}_x^{(N-1)}(s) + \tilde{\xi}_x^{(N-1)}(s)\big] + f\kappa^3\frac{\big\{\big[s + \gamma + \tilde{\mu}_y^{(N-1)}(s)\big]R_y^{(N-1)}(0) + \dot{R}_y^{(N-1)}(0) + \tilde{\xi}_y^{(N-1)}(s)/m + \tilde{\eta}_y^{(N-1)}(s)/m\big\}}{\big[ms^2 + m\gamma s + \kappa + ms\tilde{\mu}_x^{(N-1)}\big]\big[ms^2 + m\gamma s + \kappa + ms\tilde{\mu}_y^{(N-1)}\big]\big[ms^2 + m\gamma s + \kappa\big]}. \tag{25}$$

The most interesting aspect of the nonuniform case is the appearance of memory in the induced force. We have already seen this in the case of two monomers (24). This behavior persists in general with

$$\tilde{F}_x^{(N)}(s) = \tilde{G}_x^{(N)}(s)\tilde{R}_y^{(N)}(s), \tag{26}$$

$$\tilde{G}_x^{(N)}(s) = \frac{\kappa^2}{\big[ms^2 + \gamma s + k + ms\tilde{\mu}_x^{(N-1)}(s)\big]\big[ms^2 + \gamma s + k + ms\tilde{\mu}_y^{(N-1)}(s)\big]}\tilde{G}_x^{(N-1)}(s). \tag{27}$$

Starting the recurrence with a single monomer where $\tilde{G}_x^{(1)}(s) = f$, all subsequent forces can be determined using Eqs. (26) and (27). The initial force on a single monomer in the y direction is zero, hence, $\tilde{F}_y^{(N)}(s) = 0$, as also seen in the two-monomer case.

We studied the asymptotic behavior of the force-memory kernel $\tilde{G}_x^{(N)}(s)$ in the same spirit as in Appendix A. It can be shown easily, following the same line of arguments, that $\tilde{G}_x^{(N)}(s)$ decays exponentially in time. In the long time limit, for all N,

$$G_x^{(N)}(t) < e^{-\gamma t/2}.$$

VI. TRAPPED MONOMER

On introducing an external potential U_{ext} such that the force in the x direction on the outer edge depends on the x component of the distance of the monomer from a fixed origin, the resulting force is not nonconservative but simply trapping. This is, thus, an equilibrium reference; the force is conservative in nature. The result is a rescaling of the frequency $\Omega^2 = \frac{k+f}{m} - \frac{\gamma^2}{4}$. The effective force on the tagged monomer due to the action of this external potential is

$$F(t) = -\frac{\kappa f}{\kappa + f}R_1(t) + \frac{\kappa f Q}{\kappa + f}$$
$$\times\left[1 - e^{-\gamma t/2}\left(\cos\Omega t + \frac{\gamma}{2\Omega}\sin\Omega t\right)\right]. \tag{28}$$

We recognize the effective spring replacing two springs connected in series,

$$\frac{1}{\kappa_{\text{eff}}} = \frac{1}{\kappa} + \frac{1}{f}.$$

This is another way to understand the net restoring force on R_1. After all, it looks like a trapping potential around the origin but of strength κ_{eff}.

The colored noise due to unknown initial conditions is

$$\eta_1(t) = \frac{\kappa^2}{\kappa + f}[R_2(0) - R_1(0)]e^{-\gamma t/2}\left(\cos\Omega t + \frac{\gamma}{2\Omega}\sin\Omega t\right)$$
$$+ \frac{\kappa f}{k + f}R_2(0)e^{-\gamma t/2}\left(\cos\Omega t + \frac{\gamma}{2\Omega}\sin\Omega t\right)$$
$$+ \kappa\dot{R}_2(0)e^{-\gamma t/2}\frac{\sin\Omega t}{\Omega}$$
$$+ \frac{\kappa}{m}\int_0^t e^{\gamma(t-t')/2}\xi_2(t')\frac{\sin[\Omega(t - t')]}{\Omega}dt', \tag{29}$$

where $\langle\eta_1(t)\rangle_{\rho_{\text{st}}}^{R_1} = \frac{\kappa f Q}{\kappa+f}e^{-\gamma t/2}[\cos(\Omega t) + \frac{\gamma}{2\Omega}\sin\Omega t]$ for distribution

$$\rho_{\text{st}}(R_2) = \frac{1}{Z}e^{-\beta\frac{(\kappa+f)}{2}(R_2-\frac{(\kappa R_1+fQ)}{\kappa+f})^2}e^{\beta\frac{(\kappa R_1+fQ)^2}{2(\kappa+f)}}e^{-\beta\frac{(\kappa R_1^2+fQ^2)}{2}}.$$

The memory kernel is given as

$$\mu(t) = \frac{k^2}{m(k + f)}e^{-\gamma t/2}\left(\cos\Omega t + \frac{\gamma}{2\Omega}\sin\Omega t\right). \tag{30}$$

Given the conservative nature of the forces, the second fluctuation-dissipation theorem is seen to hold:

$$\langle\eta_1(t_1)\eta_1(t_2)\rangle_\rho = \frac{m}{\beta}\mu(\tau),$$

where $\tau = t_1 - t_2$ and $t_1 + t_2 \longrightarrow \infty$.

VII. CONCLUSIONS AND OUTLOOK

Integrating out degrees of freedom introduces non-Markovian noise, effective forces, and memory in a tagged particle dynamics. This is true in equilibrium as in nonequilibrium, and, when starting from coupled diffusion processes, the result is a generalized Langevin equation. Certain more detailed aspects are also unchanged, like the anomalous nature of the memory kernel for short times which goes into pure diffusion for long times or the N^2 dependence of the relaxation times. Other important aspects fundamentally change when the integration is over nonequilibrium degrees of freedom. Naturally, the remaining and visible degrees of freedom inherit nonequilibrium features and detailed balance gets broken. As a result, the so-called second fluctuation-dissipation theorem or Einstein relation gets violated. For the moment, however, there is no systematic understanding of exactly *how* that Einstein relation is modified. To put it differently, when considering a diffusion model for a particle (e.g., colloids) in a nonequilibrium environment, such as the viscoelastic medium of the cell, we have little idea of how to relate the noise with the friction term, as they have the same physical origin [22]. The outlook is then to find the analog of what has been called the frenetic contribution to the first fluctuation-dissipation theorem [23]. Indeed, we expect a nonentropic and more kinetic contribution in the breaking of the second fluctuation-dissipation theorem, much like that discussed for the modification of the Sutherland-Einstein relation [24]. For the moment, however, we must deal with examples and prototypical examples, such as the Rouse model of the present paper, where exact computations are possible. In that case, say, in the case of nonuniform driving, the second fluctuation-dissipation relation is broken, but for the uniform driving that is only a transient effect as found in (15). A more general theory will, of course, need to conform to the findings of the present paper.

A second set of more general research questions really inverts the calculations of the present paper. The aim is then to be able to reconstruct the nonequilibrium forcing on the hidden degrees of freedom from the effective motion of the probe or tagged or visible degrees of freedom. The standard example from equilibrium statistical mechanics is the free energy of a thermodynamic system which can be measured from the work on some probe that is coupled to the system. For nonequilibrium statistical mechanical systems there are plenty of nonequilibrium entropies and fluctuation functionals [25], but so far, no solid and general operational meaning has been attached to them. We would again like to determine these nonequilibrium fluctuation functionals from the effective forces on probes. In the present paper it would mean reconstructing important nonequilibrium features of the full polymer dynamics from the motion and effective dynamics of the tagged monomer. Clearly, before that program can start, the direct question as in the paper must be sufficiently understood. We conclude that the Rouse dynamics provides an interesting and important playground for questions that in the future must be addressed in the construction of a nonequilibrium statistical mechanics.

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APPENDIX: DETAILS AND COMPUTATIONS

Let us specify the case of constant forcing. The initial conditions for the recurrence are $\tilde{\mu}^{(1)}(s) = 0$, $\tilde{G}^{(1)}(s) = f/s$, and $\tilde{\eta}^{(1)}(s) = 0$. The stationary distribution of $R_2^{(N-1)}(0)$ where $R_1(0)$ is given by

$$\rho_{\rm st} = \frac{1}{Z} e^{-\beta H_{\rm st}},$$

where

$$H_{\rm st} = \frac{\kappa}{2}\big[R_2^{(N-1)}(0) - R_1(0)\big]^2 - G_{\rm st}^{(N-1)} R_2^{(N-1)}(0),$$

where we take it that external force has always been on. Of course, it is also important here to separate transient from stationary behavior. For example, for the force on q_2, we have at stationarity $G_{\rm st}^{(N-1)} = \lim_{t\to\infty} G^{(N-1)}(t)$ and, as an illustration, we will show, using recurrence, that in the case of constant forcing it always equals the originally applied force, $G_{\rm st}^{(N-1)} = f$.

We start from the relation

$$\lim_{t\longrightarrow\infty} G^{(N-1)}(t) = \lim_{s\longrightarrow 0} s\tilde{G}^{(N-1)}(s).$$

The recurrence relation for the force (13) starts from a dimer,

$$\begin{aligned}\tilde{G}^{(2)}(s) &= \frac{\kappa \tilde{G}^{(1)}(s)}{[ms\tilde{\mu}^{(1)}(s) + ms\gamma + ms^2 + \kappa]}\\ &= \frac{\kappa f}{s(ms\gamma + ms^2 + \kappa)}.\end{aligned}$$

By a simple calculation it is seen that

$$\lim_{s\longrightarrow 0} s\tilde{G}^{(2)}(s) = f.$$

Now, for a polymer of size $N-2$ (induction hypothesis),

$$\lim_{s\longrightarrow 0} s\tilde{G}^{(N-2)}(s) = f.$$

We can use the recurrence relation and the property $\lim_{s\longrightarrow 0} s\tilde{\mu}^{(N)}(s) = 0$ shown in Eq. (A4), to see that also

$$\lim_{s\longrightarrow 0} s\tilde{G}^{(N-1)}(s) = f,$$

as wanted. The stationary distribution thus is given by

$$\rho_{\rm st} = \frac{1}{Z} e^{-\beta\{\frac{\kappa}{2}[R_2^{(N-1)}(0) - R_1(0)^2] - fR_2^{(N-1)}(0)\}}. \tag{A1}$$

The mean noise is

$$\big\langle \tilde{\eta}_1^{(N)}(s)\big\rangle_{\rm st} = m\frac{f}{\kappa}\tilde{\mu}_1^{(N)}(s).$$

1. Asymptotic behavior of memory

We show here that the memory kernel $\tilde{\mu}^{(N)}(s)$ decays exponentially in the long time limit, again by recurrence. We take the constant force case as the simplest example.

From (16) we see that, for a dimer,

$$\lim_{t\to\infty} e^{\lambda t}\mu^{(2)}(t) = 0 \text{ for } \lambda < \gamma/2,$$

which translates to

$$\lim_{s\to 0} s\tilde{\mu}^{(2)}(s-\lambda) = 0 \tag{A2}$$

in the Laplace space.

Let us assume that for a polymer of size $N-1$

$$\lim_{s\to 0} s\tilde{\mu}^{(N-1)}(s-\lambda) = 0 \,(\text{induction hypothesis}) \tag{A3}$$

and let us choose $\lambda = \gamma/4$. That would show that, for a polymer of size N,

$$\begin{aligned}\lim_{s\to 0} s\tilde{\mu}^{(N)}(s-\gamma/4) &= \lim_{s\to 0} s\,\frac{\kappa[\tilde{\mu}^{(N-1)}(s-\gamma/4)+\gamma+s-\gamma/4]}{[m(s-\gamma/4)\tilde{\mu}^{(N-1)}(s-\gamma/4)+m(s-\gamma/4)\gamma+m(s-\gamma/4)^2+\kappa]}\\ &= \lim_{s\to 0} 3s\gamma/4 = 0,\end{aligned} \tag{A4}$$

where we have used recurrence relation (12) and hypothesis (A3) and the fact that $\lim_{s\to 0}\tilde{\mu}^{(N)}(s)$ is a constant, as is easy to show. The above result translates to

$$\lim_{t\to\infty} e^{\gamma t/4}\mu^{(N)}(t) = 0.$$

Hence, in the long time limit, for all N,

$$\mu^{(N)}(t) < e^{-\gamma t/2},$$

which also proves the claim made in Sec. IV A that the time of relaxation is bounded from below by $2/\gamma$.

2. Second fluctuation-dissipation relation in Laplace space

The second fluctuation-dissipation relation says that the stationary noise autocorrelation function is proportional to the memory kernel $\mu(t)$ through inverse temperature β,

$$\langle \eta(t)\eta(t+\tau)\rangle = \frac{m}{\beta}\mu(\tau) + O\left(\frac{1}{t},\tau\right), \tag{A5}$$

such that in the long time limit all terms of the order $1/t$ or greater drop out.

We continue by deriving that relation in Laplace space. Let s be the variable in the Laplace space, domain $|\mathrm{Re}\{s\}| < \gamma/2$, such that the Laplace transform is well defined; see Appendix A 1:

$$\langle\tilde{\eta}(s)\tilde{\eta}(s')\rangle = \int_0^\infty\int_0^\infty e^{-st}e^{-s't'}\langle\eta(t)\eta(t')\rangle dt\,dt'$$

Let $t' = t+\tau$

$$\begin{aligned}&= \int_0^\infty e^{-st}dt\int_{-t}^\infty e^{-s't}e^{-s'\tau}\langle\eta(t)\eta(t+\tau)\rangle d\tau\\ &= \int_0^\infty e^{-(s+s')t}dt\int_{-t}^\infty e^{-s'\tau}\langle\eta(t)\eta(t+\tau)\rangle d\tau\end{aligned}$$

Let $(s+s')t = T$

$$\begin{aligned}&= \frac{1}{s+s'}\int_0^\infty e^{-T}dT\int_{-\frac{T}{s+s'}}^\infty e^{-s'\tau}\\ &\quad\times\left\langle\eta\left(\frac{T}{s+s'}\right)\eta\left(\frac{T}{s+s'}+\tau\right)\right\rangle d\tau.\end{aligned} \tag{A6}$$

Rewriting (A5) and plugging in the result in (A6):

$$\left\langle\eta\left(\frac{T}{s+s'}\right)\eta\left(\frac{T}{s+s'}+\tau\right)\right\rangle = \frac{m}{\beta}\mu(\tau) + O(s+s')$$

$$\begin{aligned}\langle\tilde{\eta}(s)\tilde{\eta}(s')\rangle &= \frac{1}{s+s'}\int_0^\infty e^{-T}dT\int_{-\frac{T}{s+s'}}^\infty e^{-s'\tau}\\ &\quad\times\left[\frac{m}{\beta}\mu(\tau)+O(s+s')\right]d\tau.\end{aligned}$$

Hence,

$$\begin{aligned}\lim_{s+s'\to 0}(s+s')\langle\tilde{\eta}(s)\tilde{\eta}(s')\rangle &= \frac{m}{\beta}\int_{-\infty}^\infty e^{-s'\tau}\mu(\tau)d\tau\\ &= \frac{m}{\beta}[\tilde{\mu}(s)+\tilde{\mu}(-s)]\end{aligned} \tag{A7}$$

is the form of the second fluctuation-dissipation relation in Laplace space.

3. Proof by induction

We prove our claim that the second fluctuation-dissipation relation holds in the case of constant force for a polymer of general size N. We give the explicit calculation for the case of a dimer.

Given memory kernel (12) and noise (14), which is distributed as $\rho_{\mathrm{st}}(R_2,\dot{R}_2)$ as given in (A1), one can calculate the correlation function $\langle\tilde{\eta}^{(2)}(s)\tilde{\eta}^{(2)}(s')\rangle_{\mathrm{st}}$. Using the relation

$$\lim_{s+s'\to 0}(s+s')\langle\tilde{\xi}_i(s)\tilde{\xi}_j(s')\rangle = \frac{2m\gamma}{\beta}\delta_{ij}, \tag{A8}$$

it is shown by a simple calculation that

$$\lim_{s+s'\to 0}(s+s')\langle\tilde{\eta}^{(2)}(s)\tilde{\eta}^{(2)}(s')\rangle = \frac{m}{\beta}\{\tilde{\mu}_2(s)+\tilde{\mu}_2(-s)\}, \tag{A9}$$

which proves the result.

To prove it for a general polymer, we use the induction hypothesis that for a polymer of size $N-1$ the second fluctuation-dissipation relation holds:

$$\begin{aligned}&\lim_{s+s'\to 0}(s+s')\langle\tilde{\eta}^{(N-1)}(s)\tilde{\eta}^{(N-1)}(s')\rangle_{\mathrm{st}}\\ &\quad= \frac{m}{\beta}\{\tilde{\mu}^{(N-1)}(s)+\tilde{\mu}^{(N-1)}(-s)\}.\end{aligned}$$

From the recurrence relations (14) and from (A8), one easily shows that

$$\begin{aligned}\lim_{s+s'\to 0}(s+s')\langle\tilde{\eta}^{(N)}(s)\tilde{\eta}^{(N)}(s')\rangle_{\mathrm{st}} &= \frac{\kappa^2[\tilde{\mu}^{(N-1)}(s)+\tilde{\mu}^{(N-1)}(-s)]}{m\beta\left[s\tilde{\mu}^{(N-1)}(s)+s\gamma+s^2+\frac{\kappa}{m}\right]\left[-s\tilde{\mu}^{(N-1)}(-s)-s\gamma+s^2+\frac{\kappa}{m}\right]}\\ &\quad+\frac{2\gamma\kappa^2}{m\beta\left[s\tilde{\mu}^{(N-1)}(s)+s\gamma+s^2+\frac{\kappa}{m}\right]\left[-s\tilde{\mu}^{(N-1)}(-s)-s\gamma+s^2+\frac{\kappa}{m}\right]}.\end{aligned}$$

Using the recurrence relations for memory (12),

$$\tilde{\mu}^{(N)}(s)+\tilde{\mu}^{(N)}(-s)=\frac{\kappa^2[\tilde{\mu}^{(N-1)}(s)+\tilde{\mu}^{(N-1)}(-s)]}{m^2\big[s\tilde{\mu}^{(N-1)}(s)+s\gamma+s^2+\frac{\kappa}{m}\big]\big[-s\tilde{\mu}^{(N-1)}(-s)-s\gamma+s^2+\frac{\kappa}{m}\big]}+\frac{2\kappa^2\gamma}{m^2\big[s\tilde{\mu}^{(N)}(s)+s\gamma+s^2+\frac{\kappa}{m}\big]\big[-s\tilde{\mu}^{(N)}(-s)-s\gamma+s^2+\frac{\kappa}{m}\big]},$$

which proves the claim. Therefore, the second fluctuation-dissipation relation holds for a polymer of arbitrary size under the action of a constant force.

In the case of nonuniform forcing, we are in two dimensions and the computations become more involved, but the basic recurrence relations remain in place.

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