

Polymer melt dynamics: Microscopic roots of fractional viscoelasticity

Rati Sharma and Binny J. Cherayil

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

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The rheological properties of polymer melts and other complex macromolecular fluids are often successfully modeled by phenomenological constitutive equations containing fractional differential operators. We suggest a molecular basis for such fractional equations in terms of the generalized Langevin equation (GLE) that underlies the renormalized Rouse model developed by Schweizer [J. Chem. Phys. **91**, 5802 (1989)]. The GLE describes the dynamics of the segments of a tagged chain under the action of random forces originating in the fast fluctuations of the surrounding polymer matrix. By representing these random forces as fractional Gaussian noise, and transforming the GLE into an equivalent diffusion equation for the density of the tagged chain segments, we obtain an analytical expression for the dynamic shear relaxation modulus $G(t)$, which we then show decays as a power law in time. This power-law relaxation is the root of fractional viscoelastic behavior.

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I. INTRODUCTION

The constitutive equations that describe a polymer's rheological properties, and that are the subject of much theoretical research, have, over the years, been variously derived from models of polymer dynamics that range from the microscopically sophisticated [1] to the purely phenomenological [2]. Of the latter class of models, one that increasingly seems to be finding applications in the medical and biological sciences is based on the methods of fractional calculus [3]. Models in this class are typically obtained by replacing ordinary derivatives in the stress-strain relations of existing rheological models (such as those of Thomson [4] or Voigt [5]) by so-called fractional derivatives [6]. The approach, although *ad hoc*, seems to work well in describing the complex relaxation behavior that characterizes most polymeric systems. The goal of this paper is to determine whether a molecular basis can be found for the widespread applicability of fractional operators in the study of viscoelastic phenomena.

This question has already been partly settled by Bagley [7], who showed that the Rouse model of chain dynamics [8] leads to a constitutive equation in which fractional derivatives are a natural outcome of the model's defining properties. But his calculation, although suggestive, only establishes that a *particular* fractional time derivative—one with an exponent having the special value of 1/2—appears in the equation. It does not establish that any other value can appear as well. So what explains the occurrence of those other values?

The calculations presented here will suggest that a possible explanation can be found in a model of polymer melt dynamics introduced by Schweizer [9]. This model is a generalization of the Rouse model and is largely defined by a generalized Langevin equation (GLE) [10] for the time evolution of a tagged chain in a matrix of other polymers. In Schweizer's model, all the effects of the matrix polymers on the tagged chain are contained in an object called the memory function, which in principle can be determined exactly, but which in practice must be approximated. Considerable effort has gone into finding microscopically realistic

and analytically tractable approximations to the memory function [10,11], but the results are often opaque and tend to involve quantities almost as difficult to make physical sense of as the memory function itself. Under the circumstances, it is worth asking how far calculations with the GLE can be pursued using the fewest number of assumptions about the random force. We have found that if the random force is simply treated as a stochastic process whose statistics can be prescribed (rather than as a quantity that must be determined from some complicated many-body potential), it is possible to obtain an analytical expression for the shear relaxation modulus $G(t)$ of a tagged chain by assuming only that the stochastic process is Gaussian. (The structure of the GLE actually demands that the process be Gaussian anyway.) With this assumption, $G(t)$ can be directly related to the memory function (via the autocorrelation of the random force). One can then show that in order for $G(t)$ to decay as a power law in time (and thereby generate fractional derivatives in the chain's constitutive equations) the random force must also decay as a power law (which means that the underlying stochastic process must correspond to fractional Gaussian noise (fGn) [12]).

In the following section, we briefly review the model of polymer melt dynamics developed by Schweizer that will form the starting point of our analysis. We then show, in Sec. III how this model can be converted into a Smoluchowski equation. Using this equation, we proceed in Sec. IV to a calculation of the relaxation modulus, and then establish in Sec. V that for a particular choice of force correlation function it does indeed decay as a power law. We conclude with a discussion of our results and some general observations.

II. RENORMALIZED ROUSE MODEL

Starting from the exact equations that define the dynamics of a collection of n interacting polymers of chain length N , Schweizer [9] showed, using projection operator techniques, that at time t the position $\mathbf{r}(\tau, t)$ of a monomer segment located at the point τ along the chain backbone evolves in time according to the following approximate equation [9,13]:

$$\begin{aligned} & \zeta \int_0^N d\tau' \int_0^t dt' \Gamma(|\tau - \tau'|, t - t') \frac{\partial \mathbf{r}(\tau', t')}{\partial t'} \\ & = \mu \frac{\partial^2 \mathbf{r}(\tau, t)}{\partial \tau^2} + \mathbf{F}(\tau, t). \end{aligned} \quad (1)$$

Here, ζ is the monomer friction coefficient; $\mathbf{F}(\tau, t)$ is a random force acting on the point τ at time t ; μ is effectively a spring constant, defined as $3k_B T/l^2$, with l as a Kuhn length; and $\Gamma(|\tau - \tau'|, t - t')$ is a memory function, which is related to the random force by a fluctuation-dissipation theorem: $\langle F_\alpha(\tau, t) F_\beta(\tau', t') \rangle = \zeta k_B T \delta_{\alpha\beta} \Gamma(|\tau - \tau'|, t - t')$.

As just stated, Eq. (1) is not exact and several approximations have been made in deriving it. These include the neglect of inertia (the equation therefore describes the regime of overdamped dynamics), the use of a harmonic potential of mean force to describe intramolecular near-neighbor interactions (which leads, thereby, to a linear theory that can be analyzed in terms of Rouse normal modes), the neglect of hydrodynamic interactions (which are assumed to be screened out), and the factorization of the memory function into velocity and coordinate contributions (which eliminates the instantaneous configuration dependence of the exact memory function). Despite these approximations, the general approach that leads to Eq. (1) has advantages over several existing models of melt dynamics, especially those—such as reptation [8, 14]—that are purely phenomenological: it is derived from a formally exact set of dynamical equations (the approximations to which are well motivated and largely free of any prior assumptions about the mechanism of chain relaxation), it allows for systematic improvements to these approximations (at least in principle), and it is for the most part analytically tractable. Furthermore, essentially all of the physics that it describes is contained in the structure of the memory function, which is now the only quantity for which a theory must be developed.

Schweizer's analysis of this quantity has chiefly been pursued within the framework of mode-coupling approaches and leads to complicated expressions that are not easily interpreted or reduced to simpler forms [9]. For this reason, his approach, although rigorous, is not ideally suited to a study of the roots of fractional viscoelasticity, a problem that we believe may be better addressed simply by treating the force $\mathbf{F}(\tau, t)$ as a stochastic variable and determining the statistical correlations it must have to produce fractional dynamics in quantities like the relaxation modulus $G(t)$. It turns out that in order to do this it is sufficient that $\mathbf{F}(\tau, t)$ only be a *Gaussian* random variable, a condition that is actually fulfilled by the following two circumstances: one, that the process $\mathbf{r}(\tau, t)$ is itself Gaussian (at least within the harmonic potential of mean force approximation used here) and, two, that $\mathbf{F}(\tau, t)$ is *linearly* related to $\mathbf{r}(\tau, t)$ by Eq. (1). As we will now discuss, the Gaussian character of $\mathbf{F}(\tau, t)$ makes it possible to use Eq. (1) to derive an expression for the relaxation modulus $G(t)$ in terms of the memory function and to determine under what conditions it shows fractional decay.

III. CORRESPONDING SMOLUCHOWSKI EQUATION

To calculate $G(t)$ from Eq. (1), we begin by introducing a set of independent normal modes $\{\mathbf{X}_p\}$, defined as [8]

$$\mathbf{X}_p(t) = \frac{1}{N} \int_0^N d\tau \cos(p\pi\tau/N) \mathbf{r}(\tau, t). \quad (2)$$

The substitution of these variables into Eq. (1) leads (after the neglect of chain end effects) to an equation in which near-neighbor interactions have been decoupled [15],

$$\zeta \int_0^t dt' \Gamma_p(t - t') \frac{\partial \mathbf{X}_p(t')}{\partial t'} + \mu \frac{p^2 \pi^2}{N^2} \mathbf{X}_p(t) = \mathbf{F}_p(t). \quad (3)$$

Here, $\Gamma_p(t - t') = \int_0^N d\tau \cos(p\pi\tau/N) \Gamma(\tau, t - t')$ and $\mathbf{F}_p(t) = N^{-1} \int_0^N d\tau \cos(p\pi\tau/N) \mathbf{F}(\tau, t)$.

The mode-dependent random force $\mathbf{F}_p(t)$ is easily shown to have these following properties (again, after the neglect of chain end effects):

$$\langle \mathbf{F}_p(t) \rangle = 0, \quad (4a)$$

$$\langle F_{p\alpha}(t) F_{q\beta}(t') \rangle = \frac{\zeta k_B T}{2N} \delta_{\alpha\beta} \delta_{pq} \Gamma_p(t - t'), \quad \alpha, \beta = x, y, z. \quad (4b)$$

For many purposes, it proves to be more convenient to work with an evolution equation for the probability density of the normal modes rather than with the evolution equation for the normal modes themselves, so Eq. (1) is now transformed into an equivalent Smoluchowski equation, starting from the definition

$$\begin{aligned} & P(X_{1x}, X_{1y}, X_{1z}, \dots, X_{Nx}, X_{Ny}, X_{Nz}, t) \\ & = \prod_{p=1}^N \prod_{\alpha=x,y,z} \langle \delta(X_{p\alpha}(t) - X_{p\alpha}) \rangle, \end{aligned} \quad (5)$$

where the angular brackets refer to an average over all realizations of the noise [i.e., of the random force $\mathbf{F}_p(t)$]. The evolution of $P(\{\mathbf{X}_p\}, t)$ is obtained by differentiating Eq. (5) with respect to t ; after making use of various properties of the delta function, this leads to

$$\begin{aligned} \frac{\partial P(\{\mathbf{X}_p\}, t)}{\partial t} & = - \sum_{p=1}^N \sum_{\alpha=x,y,z} \frac{\partial}{\partial X_{p\alpha}} \\ & \times \left\langle \prod_{q=1}^N \prod_{\beta=x,y,z} \delta(X_{q\beta}(t) - X_{q\beta}) \dot{X}_{p\alpha}(t) \right\rangle, \end{aligned} \quad (6)$$

where the overdot on \mathbf{X}_p refers to a time derivative. To proceed further, one needs an expression for $\dot{X}_{p\alpha}(t)$, which can be obtained from Eq. (3) using Laplace transform techniques, as discussed in detail in several earlier places [16]. Without going into details, therefore, one can show that

$$\dot{X}_{p\alpha}(t) = -\eta_p(t) X_{p\alpha}(t) + \frac{1}{k_p \zeta} \bar{\theta}_{p\alpha}(t), \quad (7a)$$

where $\eta_p(t) = -\dot{\chi}_p(t)/\chi_p(t)$, and $\chi_p(t)$ is the inverse Laplace transform of the function $\hat{\chi}_p(s)$, which in turn is given by

$$\hat{\chi}_p(s) = \frac{\hat{\Gamma}_p(s)}{s\hat{\Gamma}_p(s) + k_p}, \quad (7b)$$

with $\hat{\Gamma}_p(s)$ as the Laplace transform of $\Gamma_p(t)$. The Laplace transform $\hat{g}(s)$ of a function $g(t)$ is defined as $\hat{g}(s) = \int_0^\infty dt g(t) \exp(-st)$. The parameter k_p in Eqs. (7a) and (7b) is defined as $k_p = \mu p^2 \pi^2 / N^2 \zeta$, while the function $\bar{\theta}(t)$ is the random variable

$$\bar{\theta}_{p\alpha}(t) = \chi_p(t) \frac{d}{dt} \chi_p(t)^{-1} \int_0^t dt' \varphi_p(t-t') F_{p\alpha}(t'), \quad (7c)$$

with $\varphi_p(t)$ being defined as the inverse Laplace transform of the function $\hat{\varphi}_p(s) = 1 - s\hat{\chi}_p(s)$. Equation (7a) is now substituted into Eq. (6), and the functional calculus methods described at length in Ref. [16] are used to transform the latter (after considerable algebra) to the following equivalent Smoluchowski equation:

$$\frac{\partial P(\{\mathbf{X}_p\}, t)}{\partial t} = \sum_{p,\alpha} \eta_p(t) \left[\frac{\partial}{\partial X_{p\alpha}} X_{p\alpha} + \frac{k_B T}{2N\zeta k_p} \frac{\partial^2}{\partial X_{p\alpha}^2} \right] P(\{\mathbf{X}_p\}, t). \quad (8)$$

This transformation is exact and is made possible by the Gaussian character of $\mathbf{F}_p(t)$, which is invoked when applying Novikov's theorem [17] to one of the steps of the calculation. Equation (8) has exactly the structure of the Smoluchowski equation that describes Rouse dynamics (and of the corresponding equation in [16] that describes one-dimensional particle motion on a harmonic potential), but now the diffusion coefficient, $\eta_p(t)$, is time and mode dependent and the equation itself is nonhomogeneous in time, although convolutionless.

IV. RELAXATION MODULUS

To calculate rheological properties from the renormalized Rouse model, it is necessary to incorporate the effects of flow into Eq. (1). This is usually done by the inclusion of the term $\boldsymbol{\kappa}(t) \cdot \mathbf{r}(\tau, t)$, where $\boldsymbol{\kappa}(t)$ is the rate of strain tensor, which specifies the nature of the flow and which may, in general, be time dependent. For simple shear, for example, $\boldsymbol{\kappa}(t)$ is given by

$$\kappa_{\alpha\beta}(t) = \kappa \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (9a)$$

where κ is the strain rate. Unfortunately, if the term $\boldsymbol{\kappa}(t) \cdot \mathbf{r}(\tau, t)$ is directly added to Eq. (1), the Laplace transform techniques that lead from that equation to an equation for $\mathbf{X}_p(t)$ now no longer yield easily invertible results. To get around this difficulty, we instead rewrite $\boldsymbol{\kappa}(t) \cdot \mathbf{r}(\tau, t)$ in terms of normal modes [using the expansion $\mathbf{r}(\tau, t) = 2\sum_{p=1}^N \mathbf{X}_p(t) \cos(p\pi\tau/N)$, with neglect of the center-of-mass coordinate], and then add the result to Eq. (7a) [which is the normal mode representation of Eq. (1)], to produce

$$\dot{X}_{p\alpha}(t) = -\eta_p(t) X_{p\alpha}(t) + \frac{1}{k_p \zeta} \bar{\theta}_{p\alpha}(t) + \sum_{\beta} \kappa_{\alpha\beta}(t) X_{p\beta}(t). \quad (9b)$$

This procedure can really only be justified *a posteriori* by comparing its predictions with known results and checking for self-consistency.

With the inclusion of flow into Eq. (7a), the equivalent Smoluchowski equation can now be shown to be given by

$$\frac{\partial P(\{\mathbf{X}_p\}, t)}{\partial t} = \left[\sum_{p,\alpha} \left\{ \eta_p(t) \frac{\partial}{\partial X_{p\alpha}} X_{p\alpha} + \frac{D_p(t)}{\zeta^2 k_p^2} \frac{\partial^2}{\partial X_{p\alpha}^2} \right\} - \sum_{p,\alpha,\beta} \frac{\partial}{\partial X_{p\alpha}} \kappa_{\alpha\beta}(t) X_{p\beta} \right] P(\{\mathbf{X}_p\}, t), \quad (10)$$

where $D_p(t) \equiv \zeta k_B T \eta_p(t) k_p / 2N$. Knowing the evolution equation for $P(\{\mathbf{X}_p\}, t)$, it is now a simple matter to derive equations for the time correlation functions of the normal modes, which are central to the calculation of $G(t)$. In particular, by multiplying Eq. (10) by $X_{q\mu} X_{qv}$, and integrating the result over all \mathbf{X}_p , we arrive at [18]

$$\begin{aligned} \frac{\partial}{\partial t} \langle X_{q\mu}(t) X_{qv}(t) \rangle &= -2\eta_q(t) \langle X_{q\mu}(t) X_{qv}(t) \rangle + \frac{2D_q(t)}{\zeta^2 k_q^2} \delta_{\mu\nu} \\ &+ \sum_{\beta} \kappa_{\mu\beta}(t) \langle X_{q\beta}(t) X_{qv}(t) \rangle + \sum_{\beta} \kappa_{\nu\beta}(t) \\ &\times \langle X_{q\beta}(t) X_{q\mu}(t) \rangle. \end{aligned} \quad (11)$$

As may be verified by direct substitution, the solution of this equation is

$$\begin{aligned} \langle X_{q\mu}(t) X_{qv}(t) \rangle &= \int_{-\infty}^t dt' \frac{2D_q(t')}{\zeta^2 k_q^2} \sum_{\gamma} E_{\mu\gamma}(t, t') E_{\nu\gamma}(t, t') \\ &\times \exp\left(-2 \int_{t'}^t dt'' \eta_q(t'')\right), \end{aligned} \quad (12a)$$

where

$$\frac{\partial}{\partial t} E_{\mu\nu}(t, t') = \sum_{\gamma} \kappa_{\mu\gamma}(t) E_{\gamma\nu}(t, t'), \quad (12b)$$

$$E_{\mu\nu}(t, t) = \delta_{\mu\nu}. \quad (12c)$$

If the definition of the function $D_q(t)$ is substituted into Eq. (12a), the equation can be rewritten as

$$\begin{aligned} \langle X_{q\mu}(t) X_{qv}(t) \rangle &= \frac{k_B T}{N\zeta k_q} \int_{-\infty}^t dt' \left[\frac{\partial}{\partial t'} \exp\left(-2 \int_{t'}^t dt'' \eta_q(t'')\right) \right] \\ &\times B_{\mu\nu}(\mathbf{E}(t, t')), \end{aligned} \quad (13)$$

where $B_{\mu\nu}(\mathbf{E}(t, t')) = \sum_{\alpha} E_{\mu\alpha}(t, t') E_{\nu\alpha}(t, t')$ is the so-called finger strain tensor [8]. This expression for the correlation function of the normal modes will be needed in the calculation of the stress tensor $\boldsymbol{\sigma}$, which is the quantity that governs rheological behavior. For a chain model that includes only harmonic near-neighbor interactions, the stress tensor as shown, for example, by Doi and Edwards [8] is given by

$$\sigma_{\mu\nu}(t) = \frac{3ck_B T}{Nl^2} \int_0^N d\tau \left\langle \frac{\partial r_\mu(\tau, t)}{\partial \tau} \frac{\partial r_\nu(\tau, t)}{\partial \tau} \right\rangle, \quad \mu, \nu = x, y, z, \quad (14)$$

where c is the polymer concentration. This equation can be re-expressed in terms of normal modes; the result is

$$\sigma_{\mu\nu}(t) = \frac{6\pi^2 ck_B T}{N^2 l^2} \sum_{p=1}^N p^2 \langle X_{p\mu}(t) X_{p\nu}(t) \rangle. \quad (15)$$

If Eq. (13) is now substituted into Eq. (15), a relation is obtained between the stress and the strain (with the strain being contained in the tensor \mathbf{B}), and this relation allows the relaxation modulus to be identified as

$$G(t, t') = \frac{ck_B T}{N} \sum_{p=1}^N \exp \left[-2 \int_{t'}^t dt'' \eta_p(t'') \right], \quad (16a)$$

which, by making use of the definition [16] $\eta_p(t) = -\dot{\chi}_p(t)/\chi_p(t)$, can be further simplified to

$$G(t, t') = \frac{ck_B T}{N} \sum_{p=1}^N \frac{\chi_p^2(t)}{\chi_p^2(t')}. \quad (16b)$$

This is the key result of the present calculations. It expresses the relaxation modulus quite generally in terms of the as yet unspecified memory function $\Gamma(\tau, t)$ through the function $\chi_p(t)$. The relaxation modulus is seen to be explicitly a function of an initial reference time t' , so in this non-Markovian generalization of the Rouse model, the property of time homogeneity is lost (although one can set the reference time t' to zero to ensure dependence on just a single time interval).

V. EFFECTS OF NOISE ON THE RELAXATION MODULUS

In order to understand how $G(t, t')$ is determined by the kinds of correlations that define the statistical properties of the random force $\mathbf{F}(\tau, t)$, we now consider Eq. (16b) in the limit of two illustrative special cases: white noise (which should yield the Rouse model) and fractional Gaussian noise.

A. White noise

For this case, the random forces are delta correlated, so $\Gamma(\tau, t) = \delta(\tau)\delta(t)$ and $\Gamma_p(t) = \delta(t)$ independent of p . $\hat{\Gamma}_p(s)$ then becomes 1, and $\hat{\chi}_p(s) = 1/(s+k_p)$, so that $\chi_p(t) = \exp(-k_p t)$. This produces

$$G(t, t') = \frac{ck_B T}{N} \sum_{p=1}^N \exp[-2p^2(t-t')/\tau_R], \quad (17)$$

where $\tau_R \equiv \zeta N^2 l^2 / 3\pi^2 k_B T$. Equation (17) is the familiar Rouse expression [8] for the relaxation modulus, so the approximation leading to Eq. (9b) does indeed reproduce the expected limiting behavior.

It should be noted that it is only in this Markovian white noise limit that time homogeneity is recovered. In the remainder of this discussion, we will choose the reference time

t' to be zero, so that the relaxation modulus is only a function of the single time t .

B. Fractional Gaussian noise

This kind of noise is a generalization of white noise in the sense that just as white noise leads to Brownian motion, so fGn leads to fractional Brownian motion [19]. The defining characteristic of fGn is that its temporal correlations decay as a power law. Specifically, $\Gamma(\tau, t) \propto 2H(2H-1)t^{2H-2}$, where H , the so-called Hurst index, is a real number lying between 1/2 and 1 that is a measure of the degree of temporal correlation in the noise. In Laplace space, the memory function is given by $\hat{\Gamma}_p(s) = a(p)\Gamma(2H+1)s^{-(2H-1)}$, where $\Gamma(\dots)$ is the gamma function (not to be confused with the memory function itself) and $a(p)$ is a proportionality constant that may depend on the mode p . Schweizer's calculations [9] suggest that the memory function is at most weakly mode dependent; so for convenience we shall simply set $a(p)$ to 1. Our calculations can be extended to consider other (possibly mode-dependent) values of $a(p)$. With this choice of memory function, $\chi_p(t)$ is given by

$$\chi_p(t) = E_{2-2H}(- (t/\tau_p)^{2-2H}), \quad (18)$$

where $E_a(z) \equiv \sum_{n=0}^{\infty} z^n / \Gamma(an+1)$ is the Mittag-Leffler function [20,21] and $\tau_p = [\Gamma(2H+1)/k_p]^{1/(2-2H)}$. The relaxation modulus therefore becomes

$$G(t) = \frac{ck_B T}{N} \sum_{p=1}^N E_{2-2H}^2(- p^2(t/\tau_{RR})^{2-2H}), \quad (19)$$

where $\tau_{RR} \equiv [\zeta N^2 l^2 \Gamma(2H+1) / 3\pi^2 k_B T]^{1/(2-2H)}$. It is easily verified that, when $H=1/2$, the Mittag-Leffler function reduces to an exponential, and $G(t)$ then correctly recovers the Rouse model.

Equation (19) is the link to fractional dynamics, for the nature of its time dependence is what determines whether or not the stress-strain relation can be written in terms of fractional operators. To determine this time dependence, the sum over modes in Eq. (19) must be evaluated. This probably cannot be done exactly, but because N is large, the sum can be approximated by an integral over p from 0 to ∞ (as is done, for instance, by Bagley [7]). $G(t)$ can therefore be written as

$$G(t) \approx \frac{ck_B T}{2N} \int_0^{\infty} dx x^{-1/2} E_b^2(-x\bar{t}^b) \quad (20a)$$

$$\equiv \frac{ck_B T}{2N} J, \quad (20b)$$

where $b=2-2H$ and $\bar{t} \equiv t/\tau_{RR}$. To evaluate the integral J , we first rearrange it to

$$J = \sum_{n=0}^{\infty} \frac{(-1)^n \bar{t}^{na}}{\Gamma(an+1)} \int_0^{\infty} dx x^{n-1/2} E_b(-x\bar{t}^b) \quad (21)$$

using the series expansion definition for one of the Mittag-Leffler functions. The integral over x is a special case of an

integral that has been evaluated in Refs. [20,21]. This integral is

$$\int_0^\infty dt t^{s-1} E_{\beta,\gamma}^\delta(-wt) = \frac{\Gamma(s)\Gamma(\delta-s)}{w^s\Gamma(\delta)\Gamma(\gamma-s\beta)}, \quad (22)$$

where $E_{\beta,\gamma}^\delta(z) \equiv \sum_{n=0}^\infty (\delta)_n z^n / n! \Gamma(\beta n + \gamma)$ is the generalized Mittag-Leffler function, with $(\delta)_n \equiv \Gamma(n+\delta)/\Gamma(\delta)$ as the Pochhammer symbol. The ordinary and generalized Mittag-Leffler functions are related as $E_a(z) = E_{a,1}^1(z)$. Using these results, we find that

$$G(t) \approx \frac{ck_B T}{2N} \left(\frac{t}{\tau_{RR}} \right)^{-(1-H)} \Xi, \quad (23)$$

where

$$\begin{aligned} \Xi &\equiv \sum_{n=0}^\infty \frac{(-1)^n \Gamma(n+1/2) \Gamma(1/2-n)}{\Gamma(bn+1) \Gamma(1-b/2-bn)} \\ &= \sum_{n=0}^\infty \frac{\pi}{\Gamma(bn+1) \Gamma(1-b/2-bn)} \end{aligned}$$

is a positive constant. Thus, $G(t)$ decays as power law, with an exponent that lies between 0 and 1/2. The special case of $H=1/2$, corresponding to Brownian motion of the chain segments, leads to an exponent with the value of 1/2, the result shown earlier by Bagley [7].

VI. DISCUSSION

Having established that the relaxation modulus $G(t)$ can decay as a power law in time, it readily follows (as shown, for instance, by Schiessel *et al.* [3]) that for a step strain, the stress $\sigma(t)$ and the strain $\varepsilon(t)$ are related to each other by a fractional derivative; specifically,

$$\sigma(t) = E \tau_{RR}^{1-H} \frac{d^{1-H}}{dt^{1-H}} \varepsilon(t), \quad (24)$$

where E is the constant $\Gamma(H)ck_B T \Xi / 2N$ and d^{1-H}/dt^{1-H} is a fractional derivative, defined in general by

$$\frac{d^\alpha}{dt^\alpha} f(t) = \frac{1}{\Gamma(1-\alpha)} \frac{d}{dt} \int_0^t dt' (t-t')^{-\alpha} f(t'), \quad 0 < \alpha < 1. \quad (25)$$

Equation (24) can be thought of as interpolating between two limiting cases: the case $H=1$, corresponding to Hooke's law for elastic solids, and the case $H=0$, corresponding to Newton's law for viscous liquids. (Strictly speaking, H lies between 1/2 and 1, so the limits considered above are purely formal. Furthermore, the actual value of H cannot be determined *a priori* from the present model in terms of more fundamental microscopic quantities, such as persistence lengths or interaction strengths, and it must therefore remain a phenomenological parameter of the theory.) Equations with exactly the structure of Eq. (24) (when $1-H$ lies between 0 and 1) have been found to provide a very satisfactory description of the mechanical behavior of several *viscoelastic* fluids, materials whose properties are intermediate between elastic solids and simple viscous liquids. But until now, equations of this kind have generally been regarded as entirely phenomenological. Our calculations suggest that they are in fact a consequence of the kinds of the temporal correlations that exist between the random forces acting on different parts of a tagged chain. If these correlations decay in time as a power law, the stress relaxes in the same way. Thus, the microscopic roots of fractional viscoelasticity can be traced to thermal fluctuations that have the character of fractional Gaussian noise. (If fractional Gaussian noise is indeed the stochastic process that underlies chain dynamics in the melt, it might then be necessary to reexamine the assumptions that form the basis of models like reptation, which are generally formulated in terms of the *simple*—as opposed to fractional—Brownian motion of chain segments in a confining tube.)

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- [15] The eigenvectors of the Rouse matrix are not, in general, eigenvectors of the memory function matrix, so Eq. (3) is actually approximate since the memory function there is not diagonal.
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