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ABSTRACT

Recent experiments on the return to equilibrium of solutions of entangled polymers stretched by extensional flows [Zhou and Schroeder, Phys. Rev. Lett. **120**, 267801 (2018)] have highlighted the possible role of the tube model's two-step mechanism in the process of chain relaxation. In this paper, motivated by these findings, we use a generalized Langevin equation (GLE) to study the time evolution, under linear mixed flow, of the linear dimensions of a single finitely extensible Rouse polymer in a solution of other polymers. Approximating the memory function of the GLE, which contains the details of the interactions of the Rouse polymer with its surroundings, by a power law defined by two parameters, we show that the decay of the chain's fractional extension in the steady state can be expressed in terms of a linear combination of Mittag-Leffler and generalized Mittag-Leffler functions. For the special cases of elongational flow and steady shear flow, and after adjustment of the parameters in the memory function, our calculated decay curves provide satisfactory fits to the experimental decay curves from the work of Zhou and Schroeder and earlier work of Teixeira *et al.* [Macromolecules **40**, 2461 (2007)]. The non-exponential character of the Mittag-Leffler functions and the consequent absence of characteristic decay constants suggest that melt relaxation may proceed by a sequence of steps with an essentially continuous, rather than discrete, spectrum of timescales.

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I. INTRODUCTION

Much of the complex dynamics of high molecular weight polymer melts can be traced to the local interactions that prevent individual chains in the melt from crossing one another. These interactions cause the chains to be topologically entangled, effectively allowing them to move only along loci that follow the contours of their own backbones in a type of slithering motion known as reptation.¹ When transiently deformed, therefore—by the application of a step force, for instance—the melt can only return to its equilibrium state via a pathway that is generally some complicated combination of reptation itself and the random segment excursions generated by the intermittent release of topological constraints. Modeling these effects realistically is challenging, but a phenomenological approach to melt relaxation, based on the notion that the entanglements preventing lateral chain displacements create tubes

through which single polymers can slide longitudinally, has proved to be remarkably successful in reproducing many details of the melt's time evolution following the cessation of an applied stress.^{1,2} Despite the success of this “tube model,” several aspects of melt behavior remain either incompletely understood or poorly characterized. For instance, the model predicts that stress relaxation is a two-stage process, beginning with a rapid retraction of individual polymers inside their tubes, followed by slower reptative rearrangements, each taking place on distinct timescales. However, the experimental evidence in support of this mechanism has so far been somewhat equivocal.³ Other discrepancies between the model's predictions and experimental measurements have been reported.⁴

To better understand the dynamics of entangled polymer solutions, Zhou and Schroeder⁵ have recently used fluorescence microscopy to follow the time evolution of a single, 21 μm long YOYO-1 labeled λ -DNA in concentrated solutions of unlabeled

molecules as it relaxed to equilibrium from a stretched state created by an elongational flow field in a microfluidic cross-slot chamber. The polymer concentrations in these solutions ranged from $3.9c^*$ to $15.3c^*$, where c^* is the concentration at which individual polymers in the solution first begin to overlap with each other. In this concentration range, entanglements can be significant and can number between 1 and 12 per chain. A key finding of Zhou and Schroeder's investigations is that at none of these concentrations is it possible to fit the relaxation data to a single exponential (as can be done at concentrations less than c^*), and that the higher the concentration, the greater the departure from single exponential decay. The data are said to point to the existence of two subpopulations in the ensemble of chains: one relaxing via a single-mode exponential decay and the other via a double-mode exponential decay that roughly corresponds to the two-step sequence of fast chain retraction and slow chain reptation predicted by the tube model.

However, the phenomenological character of the tube model (and of even its most sophisticated variants, such as the GLaMM model⁶) as well as the many questions it still leaves unanswered⁷ has over the years motivated the search for alternative descriptions of melt dynamics that make as few prior assumptions as possible about the effects of topological constraints on chain motion. Among the many such descriptions,^{8–18} a formally exact nonlinear generalized Langevin equation (GLE) derived by Schweizer¹⁹ and Schweizer *et al.*²⁰ has proved to be a robust analytical framework for tackling general questions about chain dynamics. In its approximate linearized form, this GLE-based formalism has been used not only to study melt properties (notably the spin lattice relaxation times and segment mobilities explored in the work of Fatkullin *et al.*²¹) but also to understand a variety of many-body phenomena in complex condensed-phase environments, such as non-exponentiality in single-enzyme kinetics,²² fractional viscoelasticity in polymer melts,²³ subdiffusive polymer dynamics,²⁴ chromosome segregation in *E. coli*,²⁵ anomalous diffusion in the Ising model,²⁶ unusual hydration dynamics around motor proteins,²⁷ and target location in the CRISPR-Cas9 system,²⁸ to cite a few representative examples. The generality of the approach,¹⁹ developed from first-principles using the Mori–Zwanzig projection operator technique,²⁹ suggests that it may be a convenient starting point for exploring the flow-induced relaxation effects uncovered in Zhou and Schroeder's recent experiments⁵ as well as in similar experiments carried out earlier by Teixeira *et al.*³⁰

How far the approach can serve in this capacity and what insights it provides into the effects mentioned above are questions we take up in this paper. The goal is not to develop a new theory of melt dynamics or to identify the microscopic mechanisms underlying relaxation in entangled polymeric systems, but to present a tractable yet rigorous description of polymer-flow phenomena that can be used to model experimental data and that, if necessary, can be systematically improved. The paper is organized as follows: In Sec. II, we recall the defining equation of the GLE formalism, generalizing it to account for the effects of an externally imposed hydrodynamic flow field. The equation describes the time evolution, under colored noise, of a Cartesian component of one of the normal modes into which the coordinates of a tagged Rouse polymer in the melt can be decomposed. The added flow field is defined in terms of a velocity gradient tensor, and in the present calculations,

we choose this tensor to correspond to the flow type known as linear mixed flow.^{31,32} In a certain limit, linear mixed flow reduces to elongational flow (the flow type used in Zhou and Schroeder's experiments⁵), and in another, it reduces to steady shear flow (the flow type used in the experiments of Teixeira *et al.*³⁰). In Sec. III, we use the solution of the GLE to construct the time correlation function of the chain's end-to-end distance, which we consider in the steady-state limit, and then compare with experimental data on the fractional extension of a tagged chain in semidilute and concentrated solutions. In Sec. IV, we discuss the results of our calculations, summarize the main points of the paper, and highlight its broad conclusions.

II. A GLE MODEL OF MELT DYNAMICS

The starting point of our calculations is the linearized (or “renormalized Rouse”) form of the equation developed by Schweizer¹⁹ to describe the dynamics of a single Rouse polymer in a melt of other polymers. In the continuum limit, a Rouse polymer at time t is described by the Hamiltonian $H = (\mu/2) \int_0^N d\tau (\partial \mathbf{r}(\tau, t) / \partial \tau)^2$, where $\mathbf{r}(\tau)$ is the spatial location of the chain's τ th monomer, N is the number of monomers, and $\mu = 3k_B T / l^2$, with l being the Kuhn length, k_B being Boltzmann's constant, and T being the temperature. At high concentrations or in the melt, and in the presence of a hydrodynamic flow field characterized by a velocity gradient tensor $\mathbf{A}$, the evolution of this Rouse chain under overdamped conditions is described by the following generalized Langevin equation:¹⁹

$$\zeta \int_0^N d\tau' \int_0^t dt' \Gamma(|\tau - \tau'|, t - t') \frac{\partial \mathbf{r}(\tau', t')}{\partial t'} = \mu \frac{\partial^2 \mathbf{r}(\tau, t)}{\partial \tau^2} + \zeta \dot{\gamma} \mathbf{A} \cdot \mathbf{r}(\tau, t) + \mathbf{F}(\tau, t), \quad (1a)$$

where ζ is the monomer friction coefficient, $\dot{\gamma}$ is a flow rate, $\mathbf{F}(\tau, t)$ is a zero-mean random force that acts on the τ th monomer at time t , and $\Gamma(|\tau - \tau'|, t - t')$ is a memory function, which is connected to the random force by a fluctuation–dissipation relation³³ $\langle F_\alpha(\tau, t) F_\beta(\tau', t') \rangle = \zeta k_B T \delta_{\alpha, \beta} \Gamma(|\tau - \tau'|, t - t')$, where $\alpha, \beta = x, y, z$ and the angular brackets denote an average with respect to the stochastic trajectories of the random force. The memory function contains all the details of the effects of the surrounding matrix on the dynamics of the tagged Rouse polymer. The tensor $\mathbf{A}$, under our assumption (stated in the Introduction) that the flow field acting on the melt is linear mixed flow, has this structure,^{31,32}

$$\mathbf{A} = \begin{pmatrix} 0 & 1 & 0 \\ \alpha & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (1b)$$

where α is a real number called the mixing parameter that spans the range $0 \leq \alpha \leq 1$ with $\alpha = 1$ describing pure elongational flow and $\alpha = 0$ describing steady shear flow.

In using Eq. (1a) as our model of flow-driven chain dynamics, we are explicitly neglecting contributions from excluded volume and hydrodynamic interactions, both of which, as recent experiments and simulations have shown,^{34–36} may, in fact, play a role, at least in solutions with concentrations up to about $3c^*$. Long-range interactions of this kind tend to be screened out at high chain concentrations or in the melt, and their neglect in the present calculations can be justified on those grounds, but it is possible to accommodate them within the GLE formalism, for instance, by adding additional terms to the chain Hamiltonian (to account for excluded volume interactions) and replacing the term $\mu\partial^2\mathbf{r}(\tau, t)/\partial\tau^2$ in Eq. (1a) by $\mu\int_0^N d\tau' \mathbf{H}(\mathbf{r}(\tau, t), \mathbf{r}(\tau', t)) \cdot \partial^2\mathbf{r}(\tau', t)/\partial\tau'^2$ [to account for hydrodynamic interactions, where $\mathbf{H}(\mathbf{r}, \mathbf{r}')$ is an interaction matrix that can be approximated by the Oseen tensor²]. However, the algebra required to treat these extensions to the formalism will, in general, be non-trivial (as earlier work from this group on capillary-confined polymers under steady shear indicates³⁷), so for now, we will not consider them further.

Returning to Eq. (1a), we now introduce the change of variable $\mathbf{X}_p(t) = N^{-1} \int_0^N d\tau \cos(p\pi\tau/N) \mathbf{r}(\tau, t)$; this transforms Eq. (1a) into an equation for $\mathbf{X}_p(t)$, the p th normal mode,²¹

$$\zeta \int_0^t dt' \Gamma_p(t-t') \dot{\mathbf{X}}_p(t') + \lambda_p \mathbf{X}_p(t) = \zeta \dot{\mathbf{y}} \mathbf{A} \cdot \mathbf{X}_p(t) + \mathbf{F}_p(t), \quad (1c)$$

where $\Gamma_p(t-t') = \int_0^N d\tau \cos(p\pi\tau/N) \Gamma(|\tau|, t-t')$, $\mathbf{F}_p(t) = N^{-1} \int_0^N d\tau \cos(p\pi\tau/N) \mathbf{F}(\tau, t)$, $\lambda_p = \mu p^2 \pi^2 / N^2$, and the dot on the normal mode denotes a derivative with respect to the time t . The correlations of the mode-dependent random force are now given by $\langle \mathbf{F}_p(t) \rangle = 0$ and $\langle F_{p\alpha}(t) F_{q\beta}(t') \rangle = (\zeta k_B T / 2N) \delta_{\alpha\beta} \delta_{p,q} \Gamma_p(t-t')$, $\alpha, \beta = x, y, z$.

Equations (1a)–(1c) are the defining equations of our model. We use these equations to construct the time correlation function of the chain's end-to-end distance $\mathbf{R}$, specifically, $\langle \mathbf{R}(t-\tau) \cdot \mathbf{R}(t) \rangle$, which we evaluate in the limit $t \rightarrow \infty$, where the system settles into a steady state at a given value of the flow strength $\dot{\gamma}$. The angular brackets now refer to an average over the distributions of both the random force and the initial chain conformations. The dependence of $\langle \mathbf{R}(t-\tau) \cdot \mathbf{R}(t) \rangle$ on τ under steady-state conditions yields a decay curve, which we compare with experimental data. These data probe the dynamics of chains that have been hydrodynamically stretched at a given flow rate and then allowed to relax to equilibrium in the absence of flow. Hence, the decay curve we derive theoretically does not strictly describe the process in the experimental protocol, but in the regime of linear response, the relaxation dynamics underlying the two processes are expected to be equivalent.³⁸

The calculation of $\langle \mathbf{R}(t-\tau) \cdot \mathbf{R}(t) \rangle$ can be formulated² in terms of normal modes using the relation $\mathbf{R}(t) = -4 \sum_{p: \text{odd}} \mathbf{X}_p(t)$, so by virtue of the independence of normal modes, $\langle \mathbf{R}(t-\tau) \cdot \mathbf{R}(t) \rangle = 16 \sum_p \langle \mathbf{X}_p(t-\tau) \cdot \mathbf{X}_p(t) \rangle$. The function $\mathbf{X}_p(t)$ is obtained from Eq. (1c), which is solved by first applying Laplace transforms to both sides of the equation; this yields

$$\mathbf{P}_p(s) \cdot \hat{\mathbf{X}}_p(s) = \zeta \hat{\Gamma}_p(s) \mathbf{X}_p(0) + \hat{\mathbf{F}}_p(s), \quad (2a)$$

where

$$\mathbf{P}_p(s) = \begin{pmatrix} a_p(s) & -\zeta \dot{\gamma} & 0 \\ -\alpha \zeta \dot{\gamma} & a_p(s) & 0 \\ 0 & 0 & a_p(s) \end{pmatrix} \quad (2b)$$

and $a_p(s) = s \zeta \hat{\Gamma}_p(s) + \lambda_p$. In these expressions, the Laplace transform $\mathcal{L}$ of a function $f(t)$ is defined as $\mathcal{L}f(t) \equiv \hat{f}(s) = \int_0^\infty dt e^{-st} f(t)$ so that formally $f(t) = \mathcal{L}^{-1} \hat{f}(s)$, where the $\mathcal{L}^{-1}$ symbol denotes the operation of taking the inverse Laplace transform with respect to variable s . Equation (2a) is a linear algebraic equation from which $\mathbf{X}_p(t)$ can be obtained as

$$\mathbf{X}_p(t) = \mathcal{L}^{-1} \mathbf{P}_p^{-1}(s) \cdot [\zeta \hat{\Gamma}_p(s) \mathbf{X}_p(0) + \hat{\mathbf{F}}_p(s)]. \quad (3a)$$

Here, $\mathbf{P}_p^{-1}(s)$ is the matrix inverse of $\mathbf{P}_p(s)$ and can be shown to be

$$\mathbf{P}_p^{-1} = \frac{1}{a_p^3(s) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s)} \begin{pmatrix} a_p^2(s) & \zeta \dot{\gamma} a_p(s) & 0 \\ \alpha \zeta \dot{\gamma} a_p(s) & a_p^2(s) & 0 \\ 0 & 0 & a_p^2(s) - \alpha \zeta^2 \dot{\gamma}^2 \end{pmatrix}. \quad (3b)$$

When Eq. (3a) is used to construct the time correlation function $\langle \mathbf{X}_p(t-\tau) \cdot \mathbf{X}_p(t) \rangle$, we arrive at

$$\begin{aligned} \langle \mathbf{X}_p(t-\tau) \cdot \mathbf{X}_p(t) \rangle &= \zeta^2 \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} \hat{\Gamma}_p(s_1) \hat{\Gamma}_p(s_2) \langle (\mathbf{P}_p^{-1}(s_1) \cdot \mathbf{X}_p(0))^T \\ &\quad \cdot (\mathbf{P}_p^{-1}(s_2) \cdot \mathbf{X}_p(0)) \rangle \\ &\quad + \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} \langle (\mathbf{P}_p^{-1}(s_1) \cdot \hat{\mathbf{F}}_p(s_1))^T \\ &\quad \cdot (\mathbf{P}_p^{-1}(s_2) \cdot \hat{\mathbf{F}}_p(s_2)) \rangle \end{aligned} \quad (4a)$$

$$\equiv A_1^{(\alpha)} + A_2^{(\alpha)}, \quad (4b)$$

where $\mathcal{L}_1^{-1}$ and $\mathcal{L}_2^{-1}$ are the inverse Laplace transforms with respect to the variables s_1 and s_2 , which are conjugate, respectively, to the variables $t-\tau$ and t . The superscript α on A_1 and A_2 indicates that these functions depend on the mixing parameter α , and the superscript T on the dot product refers to transpose.

After the matrix multiplications in Eq. (4a) are carried out, the terms on the right-hand side of the equation become

$$\begin{aligned} A_1^{(\alpha)} &= \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} \frac{\zeta \hat{\Gamma}_p(s_1)}{[a_p^3(s_1) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s_1)]} \frac{\zeta \hat{\Gamma}_p(s_2)}{[a_p^3(s_2) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s_2)]} \\ &\quad \times [a_p^2(s_1) a_p^2(s_2) \{ \langle X_{px}^2(0) \rangle + \langle X_{py}^2(0) \rangle \} + \zeta^2 \dot{\gamma}^2 a_p(s_1) a_p(s_2) \\ &\quad \times \{ \alpha^2 \langle X_{px}^2(0) \rangle + \langle X_{py}^2(0) \rangle \} + (a_p^2(s_1) - \alpha \zeta^2 \dot{\gamma}^2) \\ &\quad \times (a_p^2(s_2) - \alpha \zeta^2 \dot{\gamma}^2) \langle X_{pz}^2(0) \rangle] \end{aligned} \quad (5)$$

and

$$A_2^{(\alpha)} = \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} \frac{1}{[a_p^3(s_1) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s_1)][a_p^3(s_2) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s_2)]} \\ \times [a_p^2(s_1) a_p^2(s_2) \{ \langle \hat{F}_{px}(s_1) \hat{F}_{px}(s_2) \rangle + \langle \hat{F}_{py}(s_1) \hat{F}_{py}(s_2) \rangle \} \\ + \zeta^2 \dot{\gamma}^2 a_p(s_1) a_p(s_2) \{ \alpha^2 \langle \hat{F}_{px}(s_1) \hat{F}_{px}(s_2) \rangle + \langle \hat{F}_{py}(s_1) \hat{F}_{py}(s_2) \rangle \} \\ + (a_p^2(s_1) - \alpha \zeta^2 \dot{\gamma}^2)(a_p^2(s_2) - \alpha \zeta^2 \dot{\gamma}^2) \langle \hat{F}_{pz}(s_1) \hat{F}_{pz}(s_2) \rangle]. \quad (6)$$

A definite functional form of the memory function $\Gamma(|\tau|, t)$ must now be specified to proceed further with the calculations. As noted earlier, this function contains all the details of the melt's interactions with the tagged chain, and at present, given the complicated, many-body nature of these interactions, no exact closed-form expression for it is known. However, on timescales much longer than the characteristic timescales of atomic displacements but much shorter than the longest relaxation time of the memory function, the memory function (in normal mode space) can be reasonably well approximated^{14,19,21} by a mode-independent power law in t . (The approximation may also simply be regarded as a testable ansatz.) Memory functions with a power law decay are a natural consequence of the existence of dynamical processes occurring over a range of timescales, such as localized rotations of pendant groups at the fast end to collective motions of chain backbones at the slow end.

In Laplace space, the above approximation to $\Gamma_p(t)$ can be written as

$$\hat{\Gamma}_p(s) = \sigma s^{1-2H}, \quad (7)$$

where H is a real number between $1/2$ and 1 and σ is a constant. The s -dependence of $\hat{\Gamma}_p(s)$ is written in the above form so that the exponent H can be identified with a parameter called the Hurst index, which appears in the theory of fractional Brownian walks,³⁹ where it characterizes the extent to which successive steps in the walk are temporally correlated: A value of $H = 1/2$ indicates no correlation (and describes a walk that corresponds to simple Brownian motion), while larger values of H indicate progressively greater degrees of correlation (and describe walks that are persistent). We regard the constant σ as a phenomenological parameter whose value can be fixed by reference to experiment, though in principle, it can be determined theoretically;^{16,19–21} it is, in general, a function of H and p , but for simplicity, we ignore the p -dependence, which is important chiefly at very short timescales.^{19,21} For the moment, we will confine our attention to the approximation defined by Eq. (7) and see how far it takes us.

Within this approximation, we see that $A_1^{(\alpha)}$ [cf. Eq. (5)] is now determined by the following inverse Laplace transforms:

$$Q_1(t) \equiv \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s) a_p^2(s)}{a_p^3(s) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s)} = \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s) a_p(s)}{a_p^2(s) - \alpha \zeta^2 \dot{\gamma}^2}, \quad (8a)$$

$$Q_2(t) \equiv \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s) a_p(s)}{a_p^3(s) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s)} = \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s)}{a_p^2(s) - \alpha \zeta^2 \dot{\gamma}^2}, \quad (8b)$$

and

$$Q_3(t) \equiv \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s) (a_p^2(s) - \alpha \zeta^2 \dot{\gamma}^2)}{a_p^3(s) - \alpha \zeta^2 \dot{\gamma}^2 a_p(s)} = \mathcal{L}^{-1} \frac{\zeta \hat{\Gamma}_p(s)}{a_p(s)}. \quad (8c)$$

The functions $Q_1(t)$ and $Q_2(t)$ are evaluated by first rewriting them in terms of partial fractions; the resulting expressions as well as $Q_3(t)$ are then inverted using the formula⁴⁰

$$\mathcal{L}^{-1} \frac{k! s^{\alpha-\beta}}{(s^\alpha \pm a)^{k+1}} = t^{\alpha k + \beta - 1} E_{\alpha, \beta}^{(k)}(\mp a t^\alpha), \quad (9)$$

where $E_{\alpha, \beta}(z) \equiv \sum_{n=0}^{\infty} z^n / \Gamma(n\alpha + \beta)$ is the generalized Mittag-Leffler function and the superscript (k) denotes the k th derivative of this function with respect to its argument.

In this way, it can be shown that

$$Q_1(t) = \frac{1}{2} [E_\nu(-A_p^+ t^\nu) + E_\nu(-A_p^- t^\nu)], \quad (10a)$$

$$Q_2(t) = \frac{1}{2\sqrt{\alpha}\zeta\dot{\gamma}} [E_\nu(-A_p^- t^\nu) - E_\nu(-A_p^+ t^\nu)], \quad (10b)$$

and

$$Q_3(t) = E_\nu(-\lambda_p t^\nu / \sigma \zeta), \quad (10c)$$

where $\nu = 2 - 2H$, $A_p^\pm = (\lambda_p \pm \sqrt{\alpha}\zeta\dot{\gamma})/\sigma\zeta$, and $E_\alpha(-xz^\alpha) = E_{\alpha,1}(-xz^\alpha)$. Since $E_\alpha(-xz^\alpha) \rightarrow 0$ as $z \rightarrow \infty$ for $x > 0$, the contribution to the time correlation function from $A_1^{(\alpha)}$ vanishes in the steady-state $t \rightarrow \infty$ limit that we are interested in.

The contribution from $A_2^{(\alpha)}$ in this limit is non-zero, however. Its evaluation requires knowledge of the correlation function $\langle \hat{F}_{p\alpha}(s_1) \hat{F}_{p\alpha}(s_2) \rangle$, which can be found from the corresponding correlation function involving the conjugate variables t_1 and t_2 using the method of double Laplace transforms discussed in detail in Ref. 41; the application of this method leads to the result

$$\langle \hat{F}_{p\alpha}(s_1) \hat{F}_{p\alpha}(s_2) \rangle = \frac{\zeta k_B T}{2N} \frac{(\hat{\Gamma}_p(s_1) + \hat{\Gamma}_p(s_2))}{s_1 + s_2}, \quad \alpha = x, y, z, \quad (11)$$

which is then substituted into Eq. (6), using Eq. (7) for the memory function. The next steps, involving, first, Laplace inversion with respect to the variables s_1 and s_2 and, second, passage to the limit $t \rightarrow \infty$, are fairly complicated, so the details are relegated to Appendix A. Here, we only present the final result

$$\lim_{t \rightarrow \infty} \langle \mathbf{X}_p(t - \tau) \cdot \mathbf{X}_p(t) \rangle \\ = \frac{\zeta k_B T}{4N\sigma\zeta^2} \left[\frac{1}{A_p^+ A_p^-} E_\nu(-A_p^+ \tau^\nu) \left\{ A_p^+ + A_p^- - \left(\frac{1 + \alpha^2}{2\alpha} \right) (A_p^+ - A_p^-) \right\} \right. \\ + \frac{1}{A_p^+ A_p^-} E_\nu(-A_p^- \tau^\nu) \left\{ A_p^+ + A_p^- + \left(\frac{1 + \alpha^2}{2\alpha} \right) (A_p^+ - A_p^-) \right\} \\ + \frac{2\sigma\zeta}{\lambda_p} E_\nu(-\lambda_p \tau^\nu / \sigma \zeta) - \frac{(1 - \alpha)^2}{2\alpha} \\ \left. \times \left\{ I_1 \left(1 - \frac{A_p^+}{A_p^-} \right) + I_2 \left(1 - \frac{A_p^-}{A_p^+} \right) \right\} \right] \equiv C_p(\tau), \quad (12a)$$

where

$$I_1 = \int_{\tau}^{\infty} dx x^{v-1} E_v(-A_p^-(x-\tau)^v) E_{v,v}(-A_p^+ x^v) \quad (12b)$$

and

$$I_2 = \int_{\tau}^{\infty} dx x^{v-1} E_v(-A_p^+(x-\tau)^v) E_{v,v}(-A_p^- x^v). \quad (12c)$$

III. DECAY OF THE END-TO-END DISTANCE

From Eq. (12a), we can express the time-dependence of the steady-state mean square end-to-end distance of the tagged chain as $\langle \mathbf{R}^2(\tau) \rangle = 16 \sum_{p:odd} C_p(\tau)$, but in doing so, we would be ignoring an important detail about Rouse chains, which is that they are infinitely extensible, meaning that in the presence of a tensile force, they can attain configurations that on average exceed their contour lengths. To avoid this unphysical effect, a finite extensibility constraint must be included in the model, and this is typically accomplished by placing restrictions on the maximum permissible length of the bond between adjacent monomers.⁴² We have previously shown⁴³ that the same ends can be achieved, at considerably lower calculational cost, by replacing the original Rouse Hamiltonian H by the Hamiltonian $H_b = b\mu \int_0^N d\tau (\partial \mathbf{r}(\tau)/\partial \tau)^2$, where $b \equiv (1 - \chi)/(1 - z)$ with $\chi \equiv \langle \mathbf{R}^2 \rangle_0 / \langle \mathbf{R}^2 \rangle_m$ and $z \equiv \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_m$. Here, $\langle \mathbf{R}^2 \rangle$, $\langle \mathbf{R}^2 \rangle_0$, and $\langle \mathbf{R}^2 \rangle_m$ are the mean square end-to-end distances of the chain at, respectively, the prevailing flow conditions, zero-flow conditions, and flow conditions leading to maximum chain extension. The parameter b functions as an extensibility constraint in the following way: When $\langle \mathbf{R}^2 \rangle \rightarrow \langle \mathbf{R}^2 \rangle_m$ (at high flows), $b \rightarrow \infty$, so $e^{-H_b} \rightarrow 0$, and the probability that the chain reaches full extension becomes increasingly small, whereas when $\langle \mathbf{R}^2 \rangle \rightarrow \langle \mathbf{R}^2 \rangle_0$ (in the absence of flow), $b \rightarrow 1$, and the chain reverts to its Rouse structure. If $\langle \mathbf{R}^2 \rangle_0$ and $\langle \mathbf{R}^2 \rangle_m$ are known (as is usually the case), b can be determined self-consistently by separately calculating $\langle \mathbf{R}^2 \rangle$ using H_b . Calculations with H_b are carried out exactly as they are with H , and only require the replacement of the eigenvalues λ_p by $b\lambda_p$. Little additional effort is, therefore, needed to treat finite extensibility in this approach, which is the approach we adopt here.

For now, our treatment of flow-driven dynamics will be limited to the special cases of $\alpha = 1$ and $\alpha = 0$, which describe pure elongational and steady shear flow, respectively, and for which there exist experimental data. We discuss these two cases separately below.

A. Elongational flow, $\alpha = 1$

We turn first to the calculation of the steady-state value of $\langle \mathbf{R}^2 \rangle$, which is found from Eq. (12a) by multiplying the expression by 16, substituting $b\lambda_p$ for λ_p , setting α to 1 and τ to 0, and summing over all odd modes. Recalling that $\lambda_p = 3\pi^2 k_B T p^2 / N^2 l^2$ and introducing the definitions $\tau_R = \zeta N^2 l^2 / 3\pi^2 k_B T$ for the longest relaxation time of the Rouse chain² and $Wi = \dot{\gamma} \tau_R$ for the Weissenberg number, we can rearrange the result to

$$\langle \mathbf{R}^2 \rangle = \frac{8Nl^2}{3\pi^2 b} \sum_{p:odd} \left[\frac{1}{p^2} + \frac{2p^2}{p^4 - Wi^2/b^2} \right]. \quad (13)$$

After dividing both sides of this equation by the square of the contour length, L^2 , identifying $\langle \mathbf{R}^2 \rangle / L^2$ with $\langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_m = z$ and Nl^2 / L^2 with $\langle \mathbf{R}^2 \rangle_0 / \langle \mathbf{R}^2 \rangle_m = \chi$, and carrying out the sums in Eq. (13) exactly (using Mathematica⁴⁴), Eq. (13) becomes

$$\frac{z}{\chi} = \frac{1}{3b} \left[1 + \frac{2}{\pi \sqrt{Wi/b}} \left\{ \tan \left(\frac{\pi}{2} \sqrt{\frac{Wi}{b}} \right) + \tanh \left(\frac{\pi}{2} \sqrt{\frac{Wi}{b}} \right) \right\} \right], \quad (14a)$$

which in terms of the unknown parameter b is

$$\frac{3}{\chi} (b + \chi - 1) = 1 + \frac{2}{\pi \sqrt{Wi/b}} \left[\tan \left(\frac{\pi}{2} \sqrt{\frac{Wi}{b}} \right) + \tanh \left(\frac{\pi}{2} \sqrt{\frac{Wi}{b}} \right) \right]. \quad (14b)$$

Equation (14b) is a nonlinear equation in b that can be solved numerically (by a graphical procedure) after assigning definite values to χ and Wi . [Equations (14a) and (14b) reproduce the results derived earlier in Refs. 45 and 46 on the thermodynamics of chain stretching under elongational flow.] In the experiments of Zhou and Schroeder,⁵ $L = 21 \mu\text{m}$, while based on Fig. 1(c) of their paper, we estimate that $\langle \mathbf{R}^2 \rangle_0^{1/2} \approx 2.5 \mu\text{m}$, so $\chi \approx 0.01$. Given this value of χ , we determine b , and from b , the fractional extension $\langle \mathbf{R}^2 \rangle^{1/2} / L$, at a series of arbitrary values of Wi . The resulting “force-extension” curve (which we do not show—it coincides with the results in Refs. 45 and 46) allows us to determine the b and Wi values that correspond to a given $\langle \mathbf{R}^2 \rangle^{1/2} / L$ value.

We turn next to the calculation of $\langle \mathbf{R}^2(\tau) \rangle$, which we obtain from Eq. (12a) as before by multiplying the expression by 16, substituting $b\lambda_p$ for λ_p , setting α to 1 (without setting τ to 0), and summing over all modes. This time, however, to simplify the calculations, we restrict the sum to just the first mode, i.e., to $p = 1$. The error introduced thereby is not expected to be large since the terms beyond the leading order fall off in value fairly quickly. In this way, we find that

$$\frac{\langle \mathbf{R}^2(\tau) \rangle}{L^2} = \frac{8}{3\pi^2 b} \frac{\langle \mathbf{R}^2 \rangle_0}{L^2} \times \left[E_v \left(-\frac{b\tau^v}{\sigma\tau_R} \right) + \frac{E_v \left(-\frac{(b+Wi)\tau^v}{\sigma\tau_R} \right)}{1 + Wi/b} + \frac{E_v \left(-\frac{(b-Wi)\tau^v}{\sigma\tau_R} \right)}{1 - Wi/b} \right], \quad (15)$$

which is the expression we will use in comparisons with the experimental data in Figs. 2(a) and 2(b) of Ref. 5. Figures 2(a) and 2(b) of Ref. 5 show the decay of the fractional chain extension, denoted x/L , as a function of a scaled time at different overlap concentrations $\tilde{c} \equiv c/c^*$. The decay curves start at time 0 from a flow-induced stretched state that an inspection of Fig. 2(a) suggests is given by $x/L \approx 0.35$. In reaching this configurational state, however, the polymer solution—according to the experimental protocol—was first stretched to roughly 60%–70% of its full extension under the action of a strong elongational flow that at some point was abruptly turned off. Hence, at time 0, when the relaxation process is actually first monitored, some “pre-processing” of the chains is likely to have already occurred.

To compare Eq. (15) with the measured x/L data points, therefore, we proceed as follows: First, from the force-extension curves derived from Eq. (14b), we find the b and Wi values that yield $\langle R^2(0) \rangle^{1/2}/L$ equal to 0.35, the value of x/L at time 0; next, we substitute these b and Wi values [equal, respectively, to 1.128 and 1.104] into Eq. (15) along with $\langle R^2 \rangle_0/L^2 = \chi = 0.01$ and $\tau_R = 0.3$ s [the experimentally determined Rouse relaxation time⁵] and plot $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ at different ν values, adjusting ν and σ for best fit to different experimental curves.

As noted, the chains in the experiments of Zhou and Schroeder are apparently 60%–70% fully extended at the time the extensional flow is switched off, so as a way of assessing the impact of the initial chain configurations on the relaxation dynamics, we also construct fits to the experimental data starting from $\langle R^2(0) \rangle^{1/2}/L = 0.65$ (the mid-way point in the 60%–70% range), adjusting the values of ν and σ as before for best fit.

Figure 1 and its inset compare these theoretical curves (colored lines) with experimental data (colored symbols). Figure 1 (main) shows the theoretical curves calculated for the case $\langle R^2(0) \rangle^{1/2}/L = 0.35$, for which the best fit ν and σ values are the following: $\nu = 0.80$, $\sigma = 0.014$ (brown line); $\nu = 0.49$, $\sigma = 0.058$ (red line); and $\nu = 0.45$,

$\sigma = 0.076$ (magenta line). (The parameter ν is dimensionless, but σ has the unit of $s^{-\nu-1}$.) The theoretical curves are overlaid against three experimental curves measured at the overlap concentrations $\tilde{c} = 3.9$ (black circles), $\tilde{c} = 9.8$ (blue circles), and $\tilde{c} = 15.3$ (green circles). The experimental data points were reconstructed from Fig. 2(a) of Ref. 5 using a software program⁴⁷ that reads out their x and y coordinates. The inset shows the theoretical curves calculated for the case $\langle R^2(0) \rangle^{1/2}/L = 0.65$ [which from Eq. (14b) yields the values $b = 1.714$ and $Wi = 1.708$]. The corresponding best fit ν and σ values are $\nu = 0.85$, $\sigma = 0.0015$ (brown line); $\nu = 0.41$, $\sigma = 0.0033$ (red line); and $\nu = 0.39$, $\sigma = 0.0043$ (magenta line). The experimental data points to which these curves are fit are the same as those in the main figure.

Figure 2 and its inset compare three other experimental curves, corresponding to the overlap concentrations $\tilde{c} = 5$ (cyan circles), $\tilde{c} = 7.5$ (brown circles), and $\tilde{c} = 13$ (purple circles) to the theoretical curves for the case $\langle R^2(0) \rangle^{1/2}/L = 0.35$ (main figure) and the case $\langle R^2(0) \rangle^{1/2}/L = 0.65$ (inset). The best fit ν and σ values in the main figure are $\nu = 0.57$, $\sigma = 0.041$ (magenta line); $\nu = 0.49$, $\sigma = 0.050$ (red line); and $\nu = 0.48$, $\sigma = 0.064$ (green line). The corresponding ν and σ values in the inset are $\nu = 0.45$, $\sigma = 0.0024$ (magenta curve); $\nu = 0.42$, $\sigma = 0.0030$ (red curve); and $\nu = 0.40$, $\sigma = 0.0035$ (green

FIG. 1. (Main) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (15) at fixed values of χ (0.01), b (1.128), Wi (1.104), and τ_R (0.3 s), and at the following values of the adjustable parameters ν and σ : $\nu = 0.80$, $\sigma = 0.014$ (brown line); $\nu = 0.49$, $\sigma = 0.058$ (red line); and $\nu = 0.45$, $\sigma = 0.076$ (magenta line). (The unit of σ is $s^{-\nu-1}$.) The symbols are experimental data points reconstructed from Fig. 2(a) of Ref. 5 and correspond to the following polymer concentrations: $3.9c^*$ (black circles), $9.8c^*$ (blue circles), and $15.3c^*$ (green circles), where c^* is the overlap concentration. The chosen values of b and Wi are those that yield $\langle R^2(0) \rangle^{1/2}/L = 0.35$ from the force-extension curve described by Eq. (14b). Additional details may be found in the text. (Inset) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (15) at fixed values of χ (0.01), b (1.714), Wi (1.708), and τ_R (0.3 s), and at the following values of the adjustable parameters ν and σ : $\nu = 0.85$, $\sigma = 0.0015$ (brown line); $\nu = 0.41$, $\sigma = 0.0033$ (red line); and $\nu = 0.39$, $\sigma = 0.0043$ (magenta line). (The unit of σ is $s^{-\nu-1}$.) The symbols represent the same experimental data points as those in the main figure. The chosen values of b and Wi are those that yield $\langle R^2(0) \rangle^{1/2}/L = 0.65$ from the force-extension curve described by Eq. (14b).

FIG. 2. (Main) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (15) at fixed values of χ (0.01), b (1.128), Wi (1.104), and τ_R (0.3 s), and at the following values of the adjustable parameters ν and σ : $\nu = 0.57$, $\sigma = 0.041$ (magenta line); $\nu = 0.49$, $\sigma = 0.050$ (red line); and $\nu = 0.48$, $\sigma = 0.064$ (green line). (The unit of σ is $s^{-\nu-1}$.) The symbols are experimental data points reconstructed from Fig. 2(a) of Ref. 5 and correspond to the following polymer concentrations: $5.0c^*$ (cyan circles), $7.5c^*$ (brown circles), and $13.0c^*$ (purple circles), where c^* is the overlap concentration. The chosen values of b and Wi are those that yield $\langle R^2(0) \rangle^{1/2}/L = 0.35$ from the force-extension curve described by Eq. (14b). Additional details may be found in the text. (Inset) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (15) at fixed values of χ (0.01), b (1.714), Wi (1.708), and τ_R (0.3 s), and at the following values of the adjustable parameters ν and σ : $\nu = 0.45$, $\sigma = 0.0024$ (magenta line); $\nu = 0.42$, $\sigma = 0.0030$ (red line); and $\nu = 0.40$, $\sigma = 0.0035$ (green line). (The unit of σ is $s^{-\nu-1}$.) The symbols represent the same experimental data points as those in the main figure. The chosen values of b and Wi are those that yield $\langle R^2(0) \rangle^{1/2}/L = 0.65$ from the force-extension curve described by Eq. (14b).

TABLE I. Parameters used in the construction of Figs. 1 and 2.

Figure	Concn. (c/c^*)	$\langle R^2(0) \rangle^{1/2}/L$	b	Wi	ν	σ
1 main	3.9	0.35	1.128	1.104	0.80	0.014
	9.8	0.35	1.128	1.104	0.49	0.058
	15.3	0.35	1.128	1.104	0.45	0.076
1 inset	3.9	0.65	1.714	1.708	0.85	0.0015
	9.8	0.65	1.714	1.708	0.41	0.0033
	15.3	0.65	1.714	1.708	0.39	0.0043
2 main	5	0.35	1.128	1.104	0.57	0.041
	7.5	0.35	1.128	1.104	0.49	0.050
	13	0.35	1.128	1.104	0.48	0.064
2 inset	5	0.65	1.714	1.708	0.45	0.0024
	7.5	0.65	1.714	1.708	0.42	0.0030
	13	0.65	1.714	1.708	0.40	0.0035

curve). The experimental data points are the same as those in the main figure.

The various parameters used in the construction of Figs. 1 and 2 are summarized in Table I.

B. Steady shear flow

For this case, $\alpha = 0$, and the time correlation function $C_p(\tau)$ for this value can be obtained from Eq. (12a) by taking the limit $\alpha \rightarrow 0$ in that equation, but this requires care, and it is simpler to start from Eq. (4) and directly set α to 0 there. When this is done, and the limit $t \rightarrow \infty$ taken, the result is

$$C_p(\tau) = A_2^{(\alpha=0)},$$

which, applying the methods introduced to treat the $\alpha \neq 0$ case, can be shown to reduce to

$$C_p(\tau) = \frac{k_B T}{2N} \left[\frac{3}{\sigma \zeta} K_1 + \frac{\dot{\gamma}^2}{\sigma^3 \zeta} K_2 \right], \quad (16a)$$

where

$$K_1 = \int_{\tau}^{\infty} dx \left\{ (x - \tau)^{\nu-1} E_{\nu, \nu}(-\Lambda_p(x - \tau)^{\nu}) E_{\nu}(-\Lambda_p x^{\nu}) + x^{\nu-1} E_{\nu, \nu}(-\Lambda_p x^{\nu}) E_{\nu}(-\Lambda_p(x - \tau)^{\nu}) \right\} \quad (16b)$$

and

$$K_2 = \int_{\tau}^{\infty} dx \left\{ x^{\nu} (x - \tau)^{2\nu-1} E_{\nu}^{(1)}(-\Lambda_p x^{\nu}) E_{\nu, \nu}^{(1)}(-\Lambda_p(x - \tau)^{\nu}) + x^{2\nu-1} (x - \tau)^{\nu} E_{\nu}^{(1)}(-\Lambda_p(x - \tau)^{\nu}) E_{\nu, \nu}^{(1)}(-\Lambda_p x^{\nu}) \right\}, \quad (16c)$$

where $\Lambda_p \equiv \lambda_p / \sigma \zeta$ and the superscript on the Mittag-Leffler function denotes differentiation with respect to its argument, as before. The integral K_1 can be further simplified to

$$K_1 = \frac{1}{\Lambda_p} E_{\nu}(-\Lambda_p \tau^{\nu}), \quad (17a)$$

using integration by parts and the identities in Eqs. (A4a) and (A4b) for the derivatives of Mittag-Leffler functions. The integral K_2 does not appear to admit of a similar closed form expression, but as outlined in Appendix B, it can be rewritten in the following more compact form:

$$K_2 = \frac{1}{\nu \Lambda_p} \int_{\tau}^{\infty} dx x^{\nu-1} (x - \tau)^{\nu-1} (2x - \tau) \times E_{\nu, \nu}(-\Lambda_p x^{\nu}) E_{\nu, \nu}(-\Lambda_p(x - \tau)^{\nu}). \quad (17b)$$

Recalling that $\langle R^2(\tau) \rangle = 16 \sum_{p: \text{odd}} C_p(\tau)$ in the steady state at time τ , we can show that

$$\frac{\langle R^2(\tau) \rangle}{L^2} = \frac{8}{\pi^2 b} \frac{\langle R^2 \rangle_0}{L^2} \left[E_{\nu} \left(-\frac{b \tau^{\nu}}{\sigma \tau_R} \right) + \frac{Wi^2}{3 \nu \sigma^2 \tau_R^2} \times \int_{\tau}^{\infty} dx x^{\nu-1} (x - \tau)^{\nu-1} (2x - \tau) \times E_{\nu, \nu} \left(-\frac{b x^{\nu}}{\sigma \tau_R} \right) E_{\nu, \nu} \left(-\frac{b(x - \tau)^{\nu}}{\sigma \tau_R} \right) \right] \quad (18)$$

after limiting the sum to the lowest $p = 1$ mode for mathematical convenience, substituting $b \lambda_p$ for λ_p to account for the finite extensibility of the chain, and introducing the definitions $\tau_R = \zeta N^2 l^2 / 3 \pi^2 k_B T$ for the Rouse relaxation time and $Wi = \dot{\gamma} \tau_R$ for the Weissenberg number.

To find an expression for the steady-state mean square end-to-end distance, we set τ to 0 in Eq. (16a) and sum the result over all odd p 's, but restrict the sum over K_2 to the lowest $p = 1$ mode. In this way, following the introduction of the parameters b , Wi , and τ_R , we arrive at

$$\frac{\langle R^2 \rangle}{L^2} = \frac{\langle R^2 \rangle_0}{b L^2} \left[1 + \frac{16 Wi^2}{3 \pi^2 \nu \sigma^2 \tau_R^2} \int_0^{\infty} dx x^{2\nu-1} E_{\nu, \nu}^2 \left(-\frac{b x^{\nu}}{\sigma \tau_R} \right) \right], \quad (19)$$

which, from the definition $b = (1 - \chi)/(1 - z)$, can be rearranged to

$$b = 1 + \frac{16 \chi Wi^2}{3 \pi^2 \nu \sigma^2 \tau_R^2} \int_0^{\infty} dx x^{2\nu-1} E_{\nu, \nu}^2 \left(-\frac{b x^{\nu}}{\sigma \tau_R} \right). \quad (20)$$

Hence, to track the decay of $\langle R^2(\tau) \rangle$ with τ , we proceed as follows: First, we set χ in Eq. (20) to a definite numerical value, which we find by writing χ as $\langle R^2 \rangle_0 / L^2 \div \langle R^2 \rangle_m / L^2$, estimating $\langle R^2 \rangle_0^{1/2} / L$ from the long-time limit of the decay curves in Figs. 7(A), 7(B), or 7(C) of Ref. 30 (which correspond, respectively, to the concentrations $16c^*$, $23c^*$, and $35c^*$), and assigning $\langle R^2 \rangle_m^{1/2} / L$ the value

0.5 that we estimated for it in Ref. 43. We take $\langle \mathbf{R}^2 \rangle_0^{1/2}/L$ to be 0.1 in Figs. 7(A) and 7(B) and 0.12 in Fig. 7(C), and with these numbers, we find that $\chi = 0.04$ for $\bar{c} = 16$ and 23 and $\chi = 0.057$ for $\bar{c} = 35$. Next, we assign values of our choice to ν , σ , τ_R , and Wi and obtain b from Eq. (20) by solving it numerically. [The right-hand side of Eq. (20) turns out to be independent of $\sigma\tau_R$, so it proves convenient to simply set $\sigma\tau_R$ to 1.0 in the calculation.] Having found b at given values of ν , χ , and Wi , we then determine the corresponding value of z from the relation $b = (1 - \chi)/(1 - z)$. It will be recalled that $z = \langle \mathbf{R}^2 \rangle / \langle \mathbf{R}^2 \rangle_m$, where $\langle \mathbf{R}^2 \rangle_m$ is the mean square maximum extension. Now, in the case of elongational flow, $\langle \mathbf{R}^2 \rangle_m$ could be taken to be L^2 without serious error, but in the case of shear flow, earlier experiments⁴⁸ have shown that even in the limit $Wi \rightarrow \infty$, flexible polymers (such as molecules like λ -DNA) are never stretched to their contour length and usually only reach about 40%–50% of full extension. If z is, therefore, multiplied and divided by L^2 , the fractional extension of the chain, $\langle \mathbf{R}^2 \rangle^{1/2}/L$, can be written as $\sqrt{zz_m}$, where $z_m \equiv \langle \mathbf{R}^2 \rangle_m/L^2 = 0.5^2 = 0.25$. We now determine the locus of $\langle \mathbf{R}^2 \rangle^{1/2}/L$ values at different Wi and a given ν , thereby generating a force-extension curve. From this curve, which varies very little with ν and is essentially coincident with the curve derived in Ref. 43, it is possible to find that value of Wi (and the corresponding value of b) that produces the fractional extension to which chains in the experiments are stretched before the flow is turned off and relaxation to equilibrium is allowed to proceed. Finally, we use these b and Wi values in Eq. (18) to calculate the time evolution of $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$. [The $\tau = 0$ limit of Eq. (18) does not reduce identically to Eq. (19) but differs from it by the factor $\chi(8/\pi^2 - 1)/b$, which is negligibly small for all χ and b values used here.]

Before turning to the results of these calculations, we note that in the experiments of Teixeira *et al.*,³⁰ as in those of Zhou and Schroeder,⁵ some pre-processing of the chains will also have taken place prior to the time 0 at which relaxation is recorded. However, it is unclear from the information provided just how much, on average, the chains are stretched by the imposed flow before the flow is turned off. What is known is that the flow rate applied to the system, $\dot{\gamma}$, is greater than 1000 s^{-1} and that the system's Rouse relaxation time, τ_R , is 0.19 s, so the Weissenberg number Wi associated with this initial period of extension is at least on the order of 190. At these Weissenberg numbers, the chains will likely be up to 25% more extended than they are shown to be at time 0 in Figs. 7(A)–7(C) of Ref. 30. Hence, to explore the effect on chain relaxation of a larger average initial chain configuration, we also calculate $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ vs τ for the case of a starting configuration generated by a flow corresponding to $Wi = 200$.

Figures 3–5 and their insets show the time-dependence (in units of seconds) of $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ (colored lines), as calculated from Eq. (18) and fitted to the three experimental decay curves of x/L , as reconstructed from the data in Figs. 7(A)–7(C) of Ref. 30 (colored circles). From these data, we estimate that the fractional extensions at time 0 are 0.23, 0.245, and 0.23, respectively, and we set $\langle \mathbf{R}^2(0) \rangle^{1/2}/L$ to these values to construct the theoretical curves shown in the main figures, after determining the associated b and Wi values to be (1.211, 9.1), (1.263, 10.5), and (1.206, 7.5), respectively. Fits of these theoretical curves to the experimental data were achieved by adjustment of ν and $\sigma\tau_R$. For $\bar{c} = 16$, the best fit values of these parameters are $\nu = 0.33$ and $\sigma\tau_R = 0.52$; for $\bar{c} = 23$, they

FIG. 3. (Main) $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.04), b (1.211), Wi (9.1), $\sigma\tau_R$ (0.52), and $\nu = 0.33$. The symbols are experimental data points reconstructed from Fig. 7(A) of Ref. 30 and correspond to a polymer concentration of $16c^*$. The chosen values of b , Wi , and ν are those that yield $\langle \mathbf{R}^2(0) \rangle^{1/2}/L = 0.23$ from the force-extension curve described by Eq. (20). Additional details may be found in the text. (Inset) $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.04), b (5.66), $\sigma\tau_R$ (0.50), and $\nu = 0.33$. The given values of b and ν are those obtained from the value $Wi = 200$ that is used to set $\langle \mathbf{R}^2(0) \rangle^{1/2}/L$ to 0.45 in the force-extension curve described by Eq. (20).

FIG. 4. (Main) $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.04), b (1.263), Wi (10.5), $\sigma\tau_R$ (0.90), and $\nu = 0.41$. The symbols are experimental data points reconstructed from Fig. 7(B) of Ref. 30 and correspond to a polymer concentration of $23c^*$. The chosen values of b , Wi , and ν are those that yield $\langle \mathbf{R}^2(0) \rangle^{1/2}/L = 0.245$ from the force-extension curve described by Eq. (20). Additional details may be found in the text. (Inset) $\langle \mathbf{R}^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.04), b (5.7), $\sigma\tau_R$ (0.90), and $\nu = 0.40$. The given values of b and ν are those obtained from the value $Wi = 200$ that is used to set $\langle \mathbf{R}^2(0) \rangle^{1/2}/L$ to 0.45 in the force-extension curve described by Eq. (20).

FIG. 5. (Main) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.057), b (1.206), Wi (7.5), $\sigma\tau_R$ (0.80), and $\nu = 0.30$. The symbols are experimental data points reconstructed from Fig. 7(C) of Ref. 30 and correspond to a polymer concentration of 35c*. The chosen values of b , Wi , and ν are those that yield $\langle R^2(0) \rangle^{1/2}/L = 0.23$ from the force-extension curve described by Eq. (20). Additional details may be found in the text. (Inset) $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ as calculated from Eq. (18) at fixed values of χ (0.057), b (6.32), $\sigma\tau_R$ (0.80), and $\nu = 0.30$. The given values of b and ν are those obtained from the value $Wi = 200$ that is used to set $\langle R^2(0) \rangle^{1/2}/L$ to 0.46 in the force-extension curve described by Eq. (20).

are $\nu = 0.41$ and $\sigma\tau_R = 0.90$; and for $\tilde{c} = 35$, they are $\nu = 0.30$ and $\sigma\tau_R = 0.80$.

The insets to Figs. 3–5 show fits of $\langle R^2(\tau) \rangle^{1/2}/L$ vs τ (colored lines) to the same experimental curves shown in the main figures. The theoretical curves were calculated from Eq. (18) using $\langle R^2(0) \rangle^{1/2}/L \approx 0.45$, the value of the initial chain extension generated by $Wi = 200$ [for which the corresponding b values are 5.66 ($\tilde{c} = 16$, Fig. 3), 5.7 ($\tilde{c} = 23$, Fig. 4), and 6.32 ($\tilde{c} = 35$, Fig. 5)]. Fits of the theoretical curves to the data were obtained by adjusting ν and $\sigma\tau_R$ to the following values: $\nu = 0.33$ and $\sigma\tau_R = 0.50$ ($\tilde{c} = 16$, Fig. 3), $\nu = 0.40$ and $\sigma\tau_R = 0.90$ ($\tilde{c} = 23$, Fig. 4), and $\nu = 0.30$ and $\sigma\tau_R = 0.80$ ($\tilde{c} = 35$, Fig. 5).

TABLE II. Parameters used in the construction of Figs. 3–5.

Figure	Concn. (c/c^*)	$\langle R^2(0) \rangle^{1/2}/L$	b	Wi	ν	$\sigma\tau_R$
3 main	16	0.23	1.211	9.1	0.33	0.52
3 inset	16	0.45	5.66	200	0.33	0.50
4 main	23	0.245	1.263	10.5	0.41	0.90
4 inset	23	0.45	5.7	200	0.40	0.90
5 main	35	0.23	1.206	7.5	0.30	0.80
5 inset	35	0.46	6.32	200	0.30	0.80

The various parameters used in the construction of Figs. 3–5 are summarized in Table II.

IV. DISCUSSION

What we have attempted to do in this paper is ascertain how well a model based on the non-Markovian dynamics of a single flow-driven finitely extensible Rouse chain describes the relaxation to equilibrium of an entangled solution of long-chain polymers. Our results suggest that the model, which is formulated in terms of a generalized Langevin equation (GLE), is successful in reproducing, qualitatively, trends in two sets of experiments, one on melt relaxation under elongational flow (cf. Figs. 1 and 2) and the other on melt relaxation under shear flow (cf. Figs. 3–5), though it is largely silent on questions about the mechanism of melt relaxation. The answers to such questions chiefly reside in the details of the GLE's memory function, which at present is an essentially unknown quantity. In the present calculations, the memory function is taken to have the simplified form—a mode-independent power law in time—that it reduces to under certain conditions. This form is defined by just two parameters, ν and σ [cf. Eq. (7)], and while it obviously does not characterize the structure and dynamics of the melt in granular detail, it is a sufficiently non-trivial extension of its Markovian limit (a delta function) that it is expected to capture at least some of the melt's basic physics. We regard the two parameters that define the power law as phenomenological constants that can be adjusted for best fit to experimental or numerical data, as in some semiempirical treatments of melt dynamics.¹⁴ (That the number of adjustable parameters in the model falls below von Neumann's threshold for fitting an elephant is gratifying.)

As discussed in Sec. III A, Fig. 1 (main) compares the dependence on time (in viscosity-scaled units⁵) of three graphs of $\langle R^2(\tau) \rangle^{1/2}/L$ (full lines), as calculated from Eq. (15) (which applies to elongational flows) at different values of ν and σ , and three graphs of the experimental x/L (filled circles), at different chain overlap concentrations $\tilde{c}$, as reconstructed from data in the work of Zhou and Schroeder.⁵ Each of the theoretical curves was drawn at the same fixed values of τ_R , χ , b , and Wi , starting from the $\langle R^2(0) \rangle^{1/2}/L$ value of 0.35 that the experimental x/L is estimated to equal at $t = 0$. The $\tilde{c}$ values in Fig. 1 (main) increase from bottom to top and, therefore, represent greater and greater departures from Rouse (unentangled) dynamics. In the corresponding theoretical curves, the exponent ν decreases from bottom to top, while the parameter σ increases. Since the limit $\nu = 1$ (where $H = 1/2$) describes Rouse dynamics, a decrease in ν represents an increase in non-Rouse behavior, so the trends in the theoretical curves exactly track those of the experimental curves. The increase in σ , however, is less easily interpreted since σ encompasses in a single number various complicated structural details of the melt that are difficult to directly relate to physical quantities. There is fairly close agreement between the theoretical and experimental curves at all three concentrations, and the fact that it is achieved using a highly nonexponential function, with no clear demarcation between regimes of fast and slow decay, suggests that the two-step process of melt relaxation mentioned in the Introduction could be open to question. According to the present theory, the process may follow a smoother trajectory, characterized by

continuous small changes spanning a broad spectrum of time and length scales.

These broad conclusions remain unaltered even if the theoretical curves are constructed from an initial stretched configuration $\langle R^2(0) \rangle^{1/2}/L$ that is set to the value of 0.65 that the actual experimental chains are assumed to attain just before the strong flows inducing extension are switched off [cf. Fig. 1 (inset)]. There are differences in the fitted values of the parameters ν and σ under this new initial condition, but their trends mirror those in Fig. 1 (main).

Figure 2 (main) shows fits of the decay curves obtained from Eq. (15) (full lines) to the curves reconstructed from the remaining three sets of data shown in Fig. 2(a) of Ref. 5 (filled circles). (Figures 1 and 2 were drawn separately to avoid clutter.) The theoretical curves were drawn at the same fixed values of τ_R , χ , b , Wi , and $\langle R^2(0) \rangle^{1/2}/L$ that were used in Fig. 1 (main) with ν and σ being adjusted for best fit. The overlap concentrations $\bar{c}$ of the experimental curves increase from bottom to top, while the ν and σ values decrease and increase respectively, in the same direction, as in Fig. 1 (main). Given the apparently larger fluctuations in the experimental data points at these concentrations, the degree of agreement between theory and experiment can still be adjudged to be quite close, and the same broad conclusions about melt relaxation can be suggested. These conclusions are further supported by the curves in Fig. 2 (inset), which are based on the initial condition $\langle R^2(0) \rangle^{1/2}/L = 0.65$. Again, there are differences in the fitted ν and σ values under this new initial condition, but these values follow the corresponding trends in Fig. 2 (main).

As discussed in Sec. III B, Figs. 3–5 (main) compare the time-dependence (in units of seconds) of the fits of the theoretical fractional extensions (full lines) calculated from Eq. (18) (which applies to shear flows) to three experimental decay curves, reconstructed from the data in Figs. 7(A)–7(C) of Ref. 30 (filled circles). Starting from the $\langle R^2(0) \rangle^{1/2}/L$ value of approximately 0.23 that the experimental x/L curves are estimated to be equal to $t = 0$, each of the theoretical curves was drawn at fixed, but differing, values of χ , b , and Wi and then fit to the numerical data for a given concentration by adjustment of ν and $\sigma\tau_R$. The overlap concentrations $\bar{c}$ in the experimental curves are 16 (Fig. 3), 23 (Fig. 4), and 35 (Fig. 5), and the associated best fit values of ν in the corresponding theoretical curves are 0.33, 0.41, and 0.30, respectively, so in contrast to the elongational flow case, there is no simple correlation between higher chain concentrations and greater deviations from Rouse dynamics, though this may have something to do with differences in the initial conditions in the experimental systems. However, the overall trends in the experimental data are matched fairly closely by the theoretical curves, so while the data are broadly consistent with a two-step mechanism of chain relaxation (since they can be well-fit to biexponentials, at least at the two highest concentrations), they do not rule out an interpretation based on a continuum of dynamical events spanning multiple timescales. Exactly the same trends are seen in the fits shown in the insets of Figs. 3–5, which are based on the initial condition $\langle R^2(0) \rangle^{1/2}/L \approx 0.45$ that is associated with the $Wi = 200$ value assumed to describe the lower bound on the flow strengths used to stretch the chains experimentally before the flows are switched off.

In summary, then, our results suggest that a generalized Langevin equation with a power law memory function can indeed

serve as a useful starting point for considering problems related to the flow-driven dynamics of polymers in semidilute to concentrated solutions.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this work.

DEDICATION

This paper is dedicated to Parbati Biswas, Arti Dua, Pallavi Debnath, Srabanti Chaudhury, Debarati Chatterjee, Rati Sharma, Aishani Ghosal, Neha Tyagi, and Asawari Pagare, who as past and present students of the Cherayil group have been instrumental in advancing our understanding of complex molecular phenomena using statistical mechanical principles.

APPENDIX A: EVALUATION OF $A_2^{(\alpha)}$

The final expression for the function $A_2^{(\alpha)}$ [cf. Eq. (6)] is obtained by first evaluating the following terms:

$$G_1(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} U(s_1) \hat{f}_p(s_1) \frac{1}{s_1 + s_2} U(s_2), \quad (A1a)$$

$$G_2(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} U(s_1) \frac{1}{s_1 + s_2} \hat{f}_p(s_2) U(s_2), \quad (A1b)$$

$$G_3(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} V(s_1) \hat{f}_p(s_1) \frac{1}{s_1 + s_2} V(s_2), \quad (A1c)$$

$$G_4(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} V(s_1) \frac{1}{s_1 + s_2} \hat{f}_p(s_2) V(s_2), \quad (A1d)$$

$$G_5(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} W(s_1) \hat{f}_p(s_1) \frac{1}{s_1 + s_2} W(s_2), \quad (A1e)$$

and

$$G_6(t, \tau) \equiv \mathcal{L}_1^{-1} \mathcal{L}_2^{-1} W(s_1) \frac{1}{s_1 + s_2} \hat{f}_p(s_2) W(s_2), \quad (A1f)$$

where $U(s) = a_p(s)/[a_p^2(s) - \alpha\zeta^2\dot{\gamma}^2]$, $V(s) = 1/[a_p^2(s) - \alpha\zeta^2\dot{\gamma}^2]$, and $W(s) = 1/a_p(s)$. The Laplace convolution theorem and the result $\mathcal{L}^{-1}e^{-sa} = \delta(t - a)$ are now used with the relations $\mathcal{L}^{-1}U(s)\hat{f}_p(s) = Q_1(t)/\zeta$, $\mathcal{L}^{-1}V(s)\hat{f}_p(s) = Q_2(t)/\zeta$, and $\mathcal{L}^{-1}W(s)\hat{f}_p(s) = Q_3(t)/\zeta$ [where $Q_1(t)$, $Q_2(t)$, and $Q_3(t)$ are defined in Eqs. (10a)–(10c)], and the relations

$$\mathcal{L}^{-1}U(s) = \frac{t^{\nu-1}}{2\sigma\zeta} [E_{\nu,\nu}(-A_p^+ t^\nu) + E_{\nu,\nu}(-A_p^- t^\nu)], \quad (A2a)$$

$$\mathcal{L}^{-1}V(s) = \frac{t^{\nu-1}}{2\sqrt{\alpha\sigma\zeta^2\dot{\gamma}}} [E_{\nu,\nu}(-A_p^- t^\nu) - E_{\nu,\nu}(-A_p^+ t^\nu)], \quad (A2b)$$

and

$$\mathcal{L}^{-1}W(s) = \frac{t^{\nu-1}}{\sigma\zeta} E_{\nu,\nu}(-\lambda_p t^\nu / \sigma\zeta) \quad (\text{A2c})$$

to reduce $G_1(t, \tau)$, $\dots$, $G_6(t, \tau)$, after simple changes of variable, to the following integrals:

$$\begin{aligned} G_1(t, \tau) = & \frac{1}{4\sigma\zeta^2} \int_{\tau}^t dx (x-\tau)^{\nu-1} [E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu) \\ & + E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu) \\ & + E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu) \\ & + E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu)], \end{aligned} \quad (\text{A3a})$$

$$\begin{aligned} G_2(t, \tau) = & \frac{1}{4\sigma\zeta^2} \int_{\tau}^t dx x^{\nu-1} [E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu) \\ & + E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu) \\ & + E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu) \\ & + E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu)], \end{aligned} \quad (\text{A3b})$$

$$\begin{aligned} G_3(t, \tau) = & \frac{1}{4\sigma\zeta^4 \dot{\gamma}^2} \int_{\tau}^t dx (x-\tau)^{\nu-1} [E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu) \\ & - E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu) \\ & - E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu) \\ & + E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu)], \end{aligned} \quad (\text{A3c})$$

$$\begin{aligned} G_4(t, \tau) = & \frac{1}{4\sigma\zeta^4 \dot{\gamma}^2} \int_{\tau}^t dx x^{\nu-1} [E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu) \\ & - E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu) \\ & - E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu) \\ & + E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu)], \end{aligned} \quad (\text{A3d})$$

$$G_5(t, \tau) = \frac{1}{\sigma\zeta^2} \int_{\tau}^t dx (x-\tau)^{\nu-1} E_{\nu}(-\lambda_p x^\nu / \sigma\zeta) E_{\nu,\nu}(-\lambda_p (x-\tau)^\nu / \sigma\zeta), \quad (\text{A3e})$$

and

$$G_6(t, \tau) = \frac{1}{\sigma\zeta^2} \int_{\tau}^t dx x^{\nu-1} E_{\nu}(-\lambda_p (x-\tau)^\nu / \sigma\zeta) E_{\nu,\nu}(-\lambda_p x^\nu / \sigma\zeta). \quad (\text{A3f})$$

The above expressions are then simplified using the following identities:

$$\frac{\partial}{\partial x} E_a(-bx^a) = -bx^{a-1} E_{a,a}(-bx^a), \quad (\text{A4a})$$

$$\frac{\partial}{\partial x} E_a(-b(x-y)^a) = -b(x-y)^{a-1} E_{a,a}(-b(x-y)^a). \quad (\text{A4b})$$

Using these results, along with integration by parts, it can be shown that in the limit $t \rightarrow \infty$,

$$\begin{aligned} & \int_{\tau}^{\infty} dx [(x-\tau)^{\nu-1} E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu) \\ & + x^{\nu-1} E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu)] \\ & = \frac{1}{A_p^+} E_{\nu}(-A_p^+ \tau^\nu). \end{aligned} \quad (\text{A5a})$$

Similarly,

$$\begin{aligned} & \int_{\tau}^{\infty} dx [(x-\tau)^{\nu-1} E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu) \\ & + x^{\nu-1} E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu)] \\ & = \frac{1}{A_p^-} E_{\nu}(-A_p^- \tau^\nu) \end{aligned} \quad (\text{A5b})$$

and

$$\begin{aligned} & \int_{\tau}^{\infty} dx [(x-\tau)^{\nu-1} E_{\nu}(-\lambda_p x^\nu / \sigma\zeta) E_{\nu,\nu}(-\lambda_p (x-\tau)^\nu / \sigma\zeta) \\ & + x^{\nu-1} E_{\nu}(-\lambda_p (x-\tau)^\nu / \sigma\zeta) E_{\nu,\nu}(-\lambda_p x^\nu / \sigma\zeta)] \\ & = \frac{\sigma\zeta}{\lambda_p} E_{\nu}(-\lambda_p \tau^\nu / \sigma\zeta). \end{aligned} \quad (\text{A5c})$$

The other integrals in Eq. (A3) can be reduced to the following form:

$$\begin{aligned} & \int_{\tau}^{\infty} dx [(x-\tau)^{\nu-1} E_{\nu}(-A_p^+ x^\nu) E_{\nu,\nu}(-A_p^-(x-\tau)^\nu) \\ & + x^{\nu-1} E_{\nu}(-A_p^-(x-\tau)^\nu) E_{\nu,\nu}(-A_p^+ x^\nu)] \\ & = \frac{1}{A_p^-} E_{\nu}(-A_p^+ \tau^\nu) + \left(1 - \frac{A_p^+}{A_p^-}\right) I_1, \end{aligned} \quad (\text{A5d})$$

where I_1 is defined in Eq. (12b). In the same way,

$$\begin{aligned} & \int_{\tau}^{\infty} dx [(x-\tau)^{\nu-1} E_{\nu}(-A_p^- x^\nu) E_{\nu,\nu}(-A_p^+(x-\tau)^\nu) \\ & + x^{\nu-1} E_{\nu}(-A_p^+(x-\tau)^\nu) E_{\nu,\nu}(-A_p^- x^\nu)] \\ & = \frac{1}{A_p^+} E_{\nu}(-A_p^- \tau^\nu) + \left(1 - \frac{A_p^-}{A_p^+}\right) I_2, \end{aligned} \quad (\text{A5e})$$

where I_2 is defined in Eq. (12c). The substitution of Eqs. (A3a)–(A3f) and Eqs. (A5a)–(A5e) into Eq. (6) finally yields Eq. (12a).

APPENDIX B: DERIVATION OF EQ. (17b)

The function K_2 is defined in Eq. (16c), and it can be written as $K_2 = K_{21} + K_{22}$, where

$$K_{21} = \int_{\tau}^{\infty} dx x^v (x - \tau)^{2v-1} E_v^{(1)}(-\Lambda_p x^v) E_{v,v}^{(1)}(-\Lambda_p (x - \tau)^v) \quad (B1a)$$

and

$$K_{22} = \int_{\tau}^{\infty} dx x^{2v-1} (x - \tau)^v E_v^{(1)}(-\Lambda_p (x - \tau)^v) E_{v,v}^{(1)}(-\Lambda_p x^v), \quad (B1b)$$

where the superscripts on the Mittag-Leffler functions denote differentiation with respect to their respective arguments. This means that

$$\begin{aligned} K_{21} &= \int_{\tau}^{\infty} dx x^v (x - \tau)^{2v-1} \left(\frac{\partial}{\partial y} E_v(-\Lambda_p x^v) \right) \frac{1}{(-\Lambda_p v x^{v-1})} \\ &\quad \times \left(\frac{\partial}{\partial y} E_{v,v}(-\Lambda_p (x - \tau)^v) \right) \frac{1}{(-\Lambda_p v (x - \tau)^{v-1})} \\ &= \frac{1}{\Lambda_p^2 v^2} \int_{\tau}^{\infty} dx x (x - \tau)^v (-\Lambda_p x^{v-1}) \\ &\quad \times E_{v,v}(-\Lambda_p x^v) \frac{\partial}{\partial x} E_{v,v}(-\Lambda_p (x - \tau)^v). \end{aligned} \quad (B2)$$

Integration by parts then produces

$$\begin{aligned} K_{21} &= \frac{1}{\Lambda_p v^2} \int_{\tau}^{\infty} dx E_{v,v}(-\Lambda_p (x - \tau)^v) \\ &\quad \times \left\{ v x^{v-1} (x - \tau)^v E_{v,v}(-\Lambda_p x^v) + v x^v (x - \tau)^{v-1} \right. \\ &\quad \times E_{v,v}(-\Lambda_p x^v) + x^v (x - \tau)^v \frac{\partial}{\partial x} E_{v,v}(-\Lambda_p x^v) \left. \right\}. \end{aligned} \quad (B3)$$

After substitution of the following identities into Eq. (B3), viz.,

$$\begin{aligned} \frac{\partial}{\partial x} E_{v,v}(-\Lambda_p x^v) &= \frac{\partial}{\partial (-\Lambda_p x^v)} E_{v,v}(-\Lambda_p x^v) (-\Lambda_p v x^{v-1}) \\ &= -\Lambda_p v x^{v-1} E_{v,v}^{(1)}(-\Lambda_p x^v) \end{aligned} \quad (B4a)$$

and

$$\begin{aligned} E_{v,v}(-\Lambda_p (x - \tau)^v) &= -\frac{1}{\Lambda_p} (x - \tau)^{1-v} \frac{\partial}{\partial x} E_v(-\Lambda_p (x - \tau)^v) \\ &= v E_v^{(1)}(-\Lambda_p (x - \tau)^v), \end{aligned} \quad (B4b)$$

the result is

$$\begin{aligned} K_{21} &= \frac{1}{\Lambda_p} \int_{\tau}^{\infty} dx E_v^{(1)}(-\Lambda_p (x - \tau)^v) E_{v,v}(-\Lambda_p x^v) \\ &\quad \times [x^{v-1} (x - \tau)^v + x^v (x - \tau)^{v-1}] \\ &\quad - \int_{\tau}^{\infty} dx x^{2v-1} (x - \tau)^v E_v^{(1)}(-\Lambda_p (x - \tau)^v) E_{v,v}^{(1)}(-\Lambda_p x^v). \end{aligned} \quad (B5)$$

The substitution of Eq. (B5) into the definition of K_2 then yields

$$\begin{aligned} K_2 &= \frac{1}{\Lambda_p} \int_{\tau}^{\infty} dx E_v^{(1)}(-\Lambda_p (x - \tau)^v) E_{v,v}(-\Lambda_p x^v) \\ &\quad \times [x^{v-1} (x - \tau)^v + x^v (x - \tau)^{v-1}] \\ &= \frac{1}{\Lambda_p v} \int_{\tau}^{\infty} dx E_{v,v}(-\Lambda_p (x - \tau)^v) E_{v,v}(-\Lambda_p x^v) \\ &\quad \times [x^{v-1} (x - \tau)^v + x^v (x - \tau)^{v-1}], \end{aligned} \quad (B6)$$

which is the expression shown in Eq. (17b).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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