

## Cooperative Dynamics in Unentangled Polymer Fluids

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We present a generalized Langevin equation for the dynamics of interacting semiflexible polymer chains undergoing slow cooperative dynamics. The calculated Gaussian intermolecular center-of-mass and monomer potentials are in quantitative agreement with computer-simulation data. The experimentally observed short-time subdiffusive regime of the polymer mean-square displacement emerges from the competition between intra- and intermolecular mean-force potentials.

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The dynamics of low molecular weight unentangled polymer fluids has long been considered a well-understood problem, in spite of its intrinsic complexity. It is commonly accepted that when the degree of polymerization,  $N$ , does not exceed the entanglement value,  $N_e$ , a molecule is free to diffuse in the liquid following Fickian dynamics. In this case the Rouse model successfully describes several key features of the dynamics, such as the  $N$ -dependent scaling of the bulk viscosity and the single-chain diffusion coefficient,  $D_{\text{Rouse}} = k_B T (\zeta N)^{-1}$ . Here  $k_B$  is Boltzmann's constant,  $T$  is the temperature, and  $\zeta$  is the monomer friction coefficient [1].

Nevertheless, there remain important unresolved questions concerning the dynamics of unentangled polymer fluids. In the Rouse theory, local intermolecular interactions are ignored; the single-chain dynamics are driven by intramolecular (entropic) restoring forces and segmental friction, while the dynamics of the surrounding chains provide a heat bath. The polymer center of mass is free to diffuse following Brownian dynamics, and the mean-square displacement scales linearly in time at all time scales. More realistically, a single polymer in a fluid spans a volume  $V \propto R_g^3$ , where  $R_g = \sqrt{N} l / \sqrt{6}$  is the polymer radius of gyration, and  $l$  is the statistical segment length. Inside this volume are, on average,  $n \propto \sqrt{N}$  chains that interact through the potential of mean force [2]. The range of the potential is the same as that of the correlation hole [3] in the pair correlation function  $g(\mathbf{r})$ , a distance of order  $R_g$  in polymer fluids [4]. Intermolecular interactions occurring on length scales shorter than or equal to  $R_g$  lead to the Rouse equation's failure to adequately describe the short-time dynamics.

The disagreement between the Rouse equation and computer-simulation data of short-time unentangled [5,6] and entangled polymer dynamics, both in the melt state and in concentrated solutions [7,8], has been known for many years. In the short-time regime,  $t \leq \tau_{\text{Rouse}} (= 2R_g^2 / [\pi^2 D_{\text{Rouse}}])$ , the single-chain center-of-mass (c.m.) mean-square displacement,  $\Delta R^2(t)$ , of unentangled polymers shows anomalous diffusion. For  $t \leq \tau_{\text{Rouse}}$ ,  $\Delta R^2(t)$  crosses over from short-time ballistic dynamics to long-time Fickian diffusion [ $\Delta R^2(t) \propto t$ ] through an

intermediate regime [ $\Delta R^2(t) \propto t^{0.8-0.9}$ ] [5,6,9]. For  $t \geq \tau_{\text{Rouse}}$  the system obeys Rouse dynamics, and Fickian diffusion is recovered. Similar anomalous behavior is observed for entangled polymer fluids in the short-time regime [7,8]. Short-time anomalous dynamics only appears in melts and in solutions above the polymer overlap concentrations [1,7,8], further supporting the hypothesis that this phenomenon is due to intermolecular interactions.

In a recent paper, we derived a generalized Langevin equation for the cooperative dynamics (CDGLE) of interacting, flexible polymer fluids [10], where intramolecular and intermolecular forces are explicitly included. Here we implement the CDGLE to treat the heterogeneous dynamics of unentangled, semiflexible polymer melts with finite-size chains. The theory is found to be in excellent agreement with computer-simulation data performed by Grest and co-workers [9].

We derive the GLE for a group of  $n$  molecules undergoing slow cooperative dynamics from the first-principles Liouville equation by projecting the dynamics of the entire fluid onto the phase space of the slow variables. The slow variables are taken to be the coordinates of  $n$  molecules statistically comprised inside the volume defined by the range of the mean-force potential. Here  $n = \rho R_g l^2 = O(\sqrt{N})$ , where  $\rho$  is the monomer density. An effective segment  $a$  in molecule  $i$  experiences forces due to three contributions: the stationary *intramolecular* potential,  $-\beta^{-1} \ln \Psi[\mathbf{r}^{(i)}(t)]$ , the time-dependent *intermolecular* potential of mean force,  $-\beta^{-1} \ln g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)]$ , and the random interactions with the surrounding fluid. The projected random force is denoted  $\mathbf{F}_a^{Q(i)}(t)$ . The segment position  $\mathbf{r}_a^{(i)}(t)$  of the vector set  $\mathbf{r}^{(i)}(t) = \{\mathbf{r}_1^{(i)}(t), \mathbf{r}_2^{(i)}(t), \dots, \mathbf{r}_a^{(i)}(t), \dots, \mathbf{r}_N^{(i)}(t)\}$  follows the equation of motion [10]:

$$\zeta_{\text{eff}} \frac{d\mathbf{r}_a^{(i)}(t)}{dt} = \frac{1}{\beta} \frac{\partial}{\partial \mathbf{r}_a^{(i)}(t)} \times \ln \left[ \prod_{j=1}^n \Psi[\mathbf{r}^{(j)}(t)] \prod_{k < j}^n g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)] \right] + \mathbf{F}_a^{Q(i)}(t), \quad (1)$$

with  $\beta = (k_B T)^{-1}$ .

The effective monomer friction coefficient,  $\zeta_{\text{eff}}$ , is given by a linear combination of the bare Rouse friction,  $\zeta_0 = \beta \langle \mathbf{F}_a^i \cdot \mathbf{F}_a^{Q(i)} \rangle / 3$ , the intramolecular ( $i = j$ ), and intermolecular ( $j \neq i$ ) memory functions containing time-space correlation of the random forces:

$$\zeta_{\text{eff}} = \zeta_0 + \frac{\beta}{3} \sum_{b \neq a}^N \int_0^\infty dt \langle \mathbf{F}_a^{(i)}(0) \cdot \mathbf{F}_b^{Q(i)}(t) \rangle + \frac{\beta}{3} \sum_{b=1}^N \sum_{j \neq i}^n \int_0^\infty dt \langle \mathbf{F}_a^{(i)}(0) \cdot \mathbf{F}_b^{Q(j)}(t) \rangle. \quad (2)$$

In Eq. (2), the intermolecular memory term describes the coupling of the random forces acting on different molecules. This contribution is negligible for systems of uncorrelated molecules, for which the pair distribution function  $g(r) \approx 1$ .

To describe the dynamics of finite-size semiflexible polymers, we reformulate Eq. (1) in a matrix formalism, and we introduce semiflexibility following the approach developed by Bixon and Zwanzig [11]. The new equation of motion applies to the overdamped dynamics of a fluid of interacting molecules of any type, including semiflexible polymers of finite length. It recovers the traditional single-molecule equation [1] in the limit  $n = 1$ , and/or with the fluid described as a continuum [ $g(r, t) = 1$ ]. For the case  $n = 2$  and  $N = 1$ , it recovers the diffusion equation for binary interacting particles [12]. Thus our equation correctly reproduces the dynamics of systems characterized by alternatively dominating intramolecular or intermolecular interactions.

Since Eq. (1) is obtained by projecting the fluid dynamics onto the extended set of intra- and intermolecular slow variables, the memory function contributions are minimized and can be neglected in the first approximation [2]. Furthermore, if only the intramolecular polymer coordinates are chosen as slow variables and the memory function is discarded, this procedure recovers the expected Rouse equation. The memory function contribution to the intramolecular equation becomes relevant for melts of high molecular weight polymers, where it describes the crossover from unentangled to entangled polymer dynamics [13].

The GLE is decoupled in center-of-mass diffusion and intramolecular dynamics by a transformation of variables from beads to bond monomer coordinates [14]. The solution of the c.m. diffusion equation requires the derivation of an analytical expression for the c.m. intermolecular potential [15]. We start from the four-point distribution function which relates a pair of monomers belonging to different polymers, and their c.m. positions. The distribution is factorized to the product of two-point distribution functions and integrated over the monomer coordinates,  $g(R) \approx \int d\mathbf{r}_a \Psi(r_a^{(j)}) \int d\mathbf{r}_b \Psi(r_b^{(k)}) g(r_{a,b})$ . In the special case of polymer molecules we adopt the thread-PRISM (polymer reference interaction site model) expression of the monomer pair distribution function [4], and the Gaussian intramolecular distribution [1],

$\Psi(r_a) = (3/2\pi R_g^2)^{3/2} \exp(-3r_a^2/2R_g^2)$ . The effective potential acting between the centers-of-mass of a pair of molecules inside a region of slow cooperative dynamics is approximated by

$$w(R) = -\ln g(R) \approx \frac{27\sqrt{2}}{4\pi\sqrt{\pi}} \frac{1}{\sqrt{N}\rho^*} \times [1 - 108\pi^{-2}(\rho^*)^{-2}(N)^{-1}] e^{-3R^2/4R_g^2}. \quad (3)$$

$w(R)$  is Gaussian and finite for all distances, with a range on the order of the radius of gyration. At full polymer-polymer overlap,  $w(0)$ , decreases with increasing reduced fluid density,  $\rho^* = \rho l^3$ , reflecting the transition towards an incompressible system.  $w(0)$  also decreases with increasing polymer molecular weight due to the increasing interpenetrability of the polymer chains. Figure 1 shows a comparison between Eq. (3) and the potential extracted from the trajectories of molecular dynamics computer simulations for melts of unentangled polyethylene chains [9]. The simulations are performed at constant volume and constant temperature, using the experimental densities at atmospheric pressure. We analyze trajectories from unentangled polyethylene samples with an increasing degree of polymerization, as reported in Table I (the entanglement degree of polymerization  $N_e = 136$ ). The only fitting parameter is the potential at complete polymer overlap,  $w'(0)$ , which is compared in Table I to  $w(0)$ . All the samples are in good agreement with Eq. (3). The value of  $w'(0)$  agrees quantitatively with the simulations for the high  $N$  samples. For the low  $N$  samples, the presence of fine structure, at a short distance due to the local monomer packing, does not allow us to make a quantitative comparison.

The data show a decrease of  $w(0)$  with increasing molecular weight or density, in agreement with Eq. (3) and with a recent study on dilute and semidilute polymer solutions [16]. Equation (3) represents an improvement on the mean-field formula derived by Flory and Krigbaum,

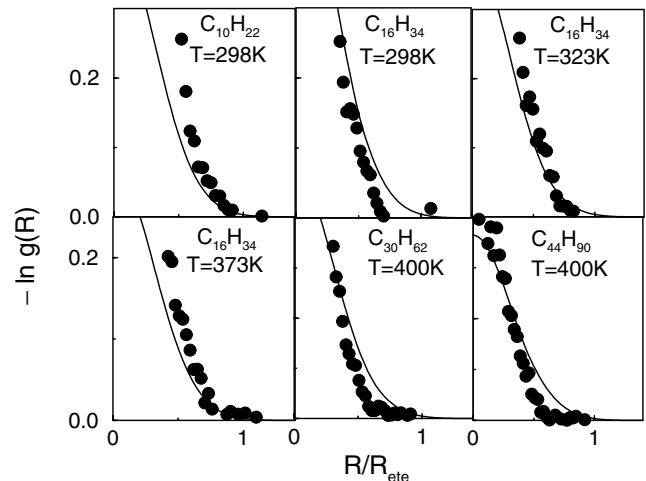


FIG. 1. Comparison between the analytical expression of the soft-core center-of-mass Gaussian potential, Eq. (3), and computer simulations data vs the c.m. interpolymer distance normalized by the polymer end-to-end distance,  $R_{\text{ete}} = \sqrt{N}l$ .

TABLE I. Simulation and fitting parameters.

Polymer	$N$	$T$ [K]	$\rho$ [g/cm <sup>3</sup> ]	$l$ [Å]	$\frac{w(0)}{w'(0)}$	Slope
C <sub>10</sub> H <sub>22</sub>	10	298	0.7250	3.26	2	0.97
C <sub>16</sub> H <sub>34</sub>	16	298	0.7703	3.84	0.4	0.94
C <sub>16</sub> H <sub>34</sub>	16	323	0.7531	3.75	0.6	0.96
C <sub>16</sub> H <sub>34</sub>	16	373	0.7187	3.66	0.8	0.97
C <sub>30</sub> H <sub>62</sub>	30	400	0.7421	4.02	0.3	0.90
C <sub>44</sub> H <sub>90</sub>	44	400	0.7570	4.18	0.3	0.85

which predicts the opposite trend [17]. However, in solution, both simulations and renormalization group calculations show that the  $N \rightarrow \infty$  scaling regime is finite. In our study of polymer melt dynamics we are far from the  $N \rightarrow \infty$  scaling regime, and this feature cannot be investigated.

From Eq. (3) we derive the intermolecular force between the c.m. of two polymers [15]. In Eq. (1), the force is multiplied by the number of polymers interacting with the tagged chain,  $G(t)R(t) = -\sqrt{N}\rho^*dw[R(t)]/dR(t)$ . Here the time evolution of the intermolecular center-of-mass potential follows the time dependence of the interpolymer distance,  $R(t)$ . To obtain an analytical solution of Eq. (1), we approximate  $R^2(t)$  with its statistical average over the polymer configuration space,

$$G(t)R(t) \approx \frac{81\sqrt{2}}{8\pi\sqrt{\pi}} R_g^{-2} [1 - 108\pi^{-2}(\rho^*)^{-2}(N)^{-1}] \times e^{-3\langle R^2(t) \rangle / (4R_g^2)} R(t). \quad (4)$$

When Eq. (4) is introduced in Eq. (1), the latter reduces to a set of coupled Rouse equations with explicit intermolecular contributions

$$\zeta_0 \frac{d\mathbf{R}_{\text{c.m.}}^{(i)}(t)}{dt} = G(t)[\mathbf{R}_{\text{c.m.}}^{(i)}(t) - \mathbf{R}_i(t)] + \mathbf{F}^i(t). \quad (5)$$

Equation (5) obeys the fluctuation-dissipation condition  $\langle \mathbf{F}_\alpha^i(t) \cdot \mathbf{F}_\gamma^j(t') \rangle = 6\zeta_0\beta^{-1}\delta_{\alpha\gamma}\delta_{ij}\delta(t-t')$ , where  $\alpha, \gamma = x, y, z$ , and  $\mathbf{R}_i(t) = n^{-1} \sum_{k=1}^n \mathbf{R}_{\text{c.m.}}^{(k)}(t)$  is the coordinate of the c.m. of the dynamical aggregate.

The advantage of adopting the approximate form of the intermolecular force is that the GLE becomes solvable using the standard techniques of transformation to normal mode coordinates. The set of coupled equations [Eq. (5)] reduces to two GLEs in the relative and cooperative variables, from which the relative many-chain intermolecular distance is  $\langle R^2(t) \rangle \approx n\Delta R^2(t) - 6D_{\text{m.c.}}t$ , where  $\Delta R^2(t)$  is the single-chain mean-square displacement. The many-chain cooperative diffusion coefficient,  $D_{\text{m.c.}} = (\beta\rho^*N\sqrt{N}\zeta_0)^{-1} = D_{\text{Rouse}}/\rho^*\sqrt{N}$ , approaches zero in melts of high molecular weight polymer chains, at low temperature, and/or at high liquid density. Since the intermolecular force depends at each instant on the value of the intermolecular distance  $\langle R^2(t) \rangle$ , we solve Eq. (5) self-consistently for small time increments ( $\Delta t = 10^{-2}$  ps). With this procedure we account for changes in the intermolecular interactions with the time evolution of the system.

Using Eq. (5), we calculate the c.m. mean-square displacement,  $\Delta R^2(t) = \langle [R_{\text{c.m.}}(t) - R_{\text{c.m.}}(0)]^2 \rangle$ . Since the appearance of anomalous c.m. dynamics is related to the amplitude of  $G(t)$  [when  $G(t) \rightarrow 0$  single-chain uncorrelated dynamics is recovered], the anomalies are confined to the time scale  $t \leq \tau_{\text{Rouse}}$ , the time necessary for the system to travel outside the range of the mean-force potential [ $R^2(t) \geq R_g^2$ ].

We test the validity of our approach by comparing the c.m. mean-square displacement calculated from the solution of Eq. (5) with computer-simulation data for the samples previously analyzed. The values of  $\rho$ ,  $T$ ,  $N$ ,  $l$ , and  $\zeta_0$  are the input to the equation together with the effective value of the potential at initial time and zero intermolecular distance,  $w'(0)$ , calculated from fitting the potential. Here the statistical segment is much larger than the chemical bond because of the intrinsic stiffness of the polyethylene molecule. Figures 2 and 3 show that the diffusion equation with the soft-core intermolecular potential quantitatively reproduces the anomalous subdiffusive c.m. dynamics over the complete range of time scales for all of the samples investigated. The slope of the subdiffusive c.m. regime is reported in Table I, and it is found to decrease with an increasing degree of polymerization. The degree of dynamical anomaly increases with increasing  $N$

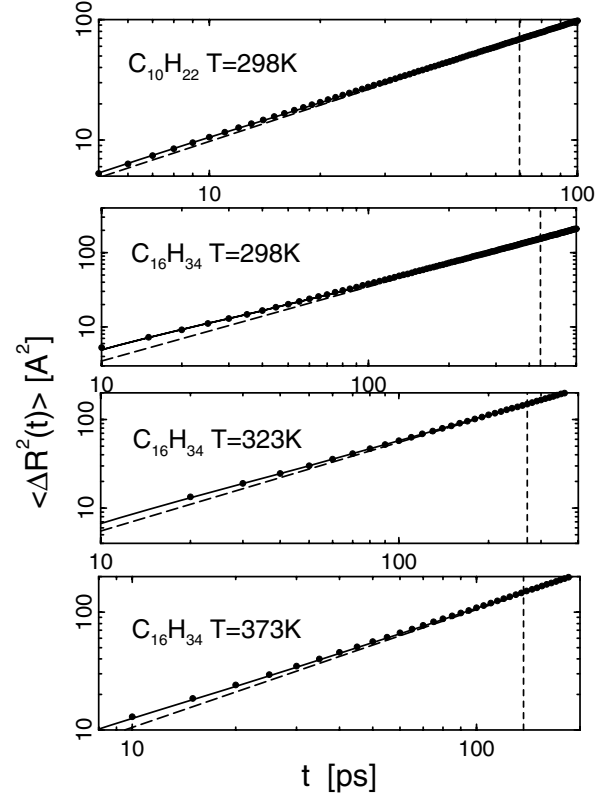


FIG. 2. Center-of-mass mean-square displacement as a function of time. Best fit of the molecular dynamics simulation data (filled circles) with the Rouse equation (dashed lines), and with the intermolecular diffusion equation, Eq. (5), for polymer melts (solid lines). The short-dashed lines indicate the longest Rouse relaxation time,  $\tau_{\text{Rouse}}$ .

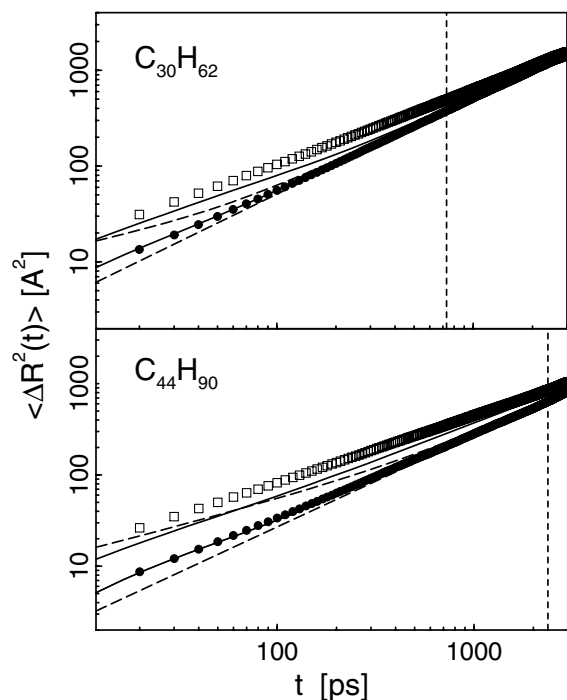


FIG. 3. Monomer and center-of-mass mean-square displacements as a function of time. Best fit of the molecular dynamics simulation data (filled circles for c.m. and open squares for monomer dynamics) with the Rouse equation (dashed lines) and with the diffusion equations for semiflexible polymer melts (solid lines). The short-dashed lines indicate the longest Rouse relaxation time,  $\tau_{Rouse}$ .

and decreasing  $T$ , as the system moves towards its glass transition. For the range of  $N$  investigated in this paper, a scaling regime has yet to be reached.

To describe the polymer flexibility we adopt a freely rotating chain model for segments of length  $l = 1.53 \text{ \AA}$  with an effective stiffness parameter  $g = 0.74$  ( $g = \langle \mathbf{l}_i \cdot \mathbf{l}_{i+1} \rangle / l^2$ ,  $\mathbf{l}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$ ). The value of  $g$  is obtained from the polymer mean-square end-to-end distance calculated from the simulation data, and reproduces the experimental characteristic ratio for a finite polyethylene chain. The introduction of the explicit description of the local stiffness does not affect the dynamics at the c.m. level. This is because both the flexible model with renormalized segments and the explicit semiflexible description are devised to reproduce the global chain properties. In Figs. 2 and 3 the c.m. diffusion is identical if we use a semiflexible or a renormalized flexible model.

The monomer dynamics depends strongly on the local chemical structure and chain stiffness. However, at the monomer level, the intermolecular contributions are negligible. Our mode analysis shows that only the lowest index global modes are affected by the intermolecular potential, in agreement with previous studies [5,7,18]. In analogy with the static picture, we argue that the insensitivity of the local dynamics to the intermolecular forces is due to the presence of similar and compensating monomer-monomer intramolecular and intermolecular excluded-volume interactions [3]. In the  $t \leq \tau_{Rouse}$  regime, the data show

dynamics slightly faster than the Rouse prediction of  $\Delta r^2(t) \propto t^{0.5}$ . This effect is predicted by our diffusion equation which includes local polymer semiflexibility. Figure 3 shows that the monomer mean-square displacement calculated with the semiflexible approach is in better agreement with the simulations than the Rouse function. The inclusion, or exclusion, of the intermolecular contribution does not modify the monomer diffusion.

In conclusion, we show that the center-of-mass intermolecular potential in polymer melts can be described, with a good level of approximation, by an effective Gaussian potential. The introduction of the local intermolecular forces in the GLE strongly improves the description of the global dynamical properties of polymer melts in the short-time domain. The intermolecular forces do not affect the dynamics on the local monomer scale, which is instead strongly dependent on the local polymer semiflexibility.

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