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Bridging length scales in polymer melt relaxation for macromolecules with specific local structures

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Abstract

We extend our generalized Langevin equation for cooperative dynamics (CDGLE), a many-chain approach, to investigate liquids composed of macromolecules with different local chemical structure. In particular, the specific role of semiflexibility and local architecture on the overall polymer dynamics is explored. The theory predicts centre-of-mass diffusion in good agreement with simulations for liquids of macromolecules with slightly branched monomeric architectures.

1. Introduction

Dynamical properties that are of experimental relevance in macromolecular liquids span a wide range of length and timescales. From the large-length, long-time properties, such as centre-of-mass (com) diffusion, to local segment disorientation, several orders of magnitude are involved. Global dynamics depends on the local molecular structure so that successful theoretical approaches for polymer liquid dynamics need to bridge in a reliable manner all length and timescales of interest.

We recently presented a theoretical approach that describes the diffusive cooperative dynamics of an *ensemble* of slowly relaxing *semiflexible* polymer chains in the field of fast-moving molecules within a macromolecular liquid [1–3]. The liquid is structurally homogeneous, but dynamically heterogeneous. Dynamical properties predicted by the theory agree quantitatively with data from simulations and experiments for liquids of polyethylene (PE) molecules of increasing degree of polymerization, N . In this paper, we extend our approach to investigate how different monomeric structures and their flexibility affect polymer dynamics. Systems investigated are slightly branched polymers, including polypropylenes in their isotactic (iPP), head-to-head (hhPP), and syndiotactic (sPP) forms. Physical parameters for these systems are reported in table 1.

The conventional approach for the dynamics of unentangled polymeric liquids, i.e. the Rouse theory [4], stands on the assumptions that polymer chains are entirely flexible and that the motion of a single chain is uncorrelated with the dynamics of the surrounding polymer

Table 1. Polyolefin melts ($N = 96$, $T = 453$ K).

Polymer	ρ (sites \AA^{-3})	R_g (\AA)	l_{eff} (\AA)
PE	0.0328	16.78	4.19
sPP	0.0328	13.93	3.48
hhPP	0.0336	13.54	3.38
iPP	0.0328	11.34	2.83

molecules. On a timescale longer than the ballistic regime but shorter than the longest intramolecular relaxation time, where monomer dynamics crosses over to com motion, the theory predicts that the monomer mean-square displacement scales as $\Delta r^2(t) \propto t^\nu$, with $\nu = 0.5$, due to chain connectivity. In the same range of timescales, the theory also predicts that the com mean-square displacement follows a linear scaling with time due to Brownian motion, i.e. $\Delta R^2(t) \propto t^\nu$, with $\nu = 1$. Experiments and simulations of polymeric liquids show, instead, that the monomer mean-square displacement scales as $\Delta r^2(t) \propto t^\nu$, with $\nu > 0.5$, due to the interplay of chain connectivity and *semiflexibility*, the latter of which is related to internal barrier crossing. Moreover, the com mean-square displacement follows $\Delta R^2(t) \propto t^\nu$, with $\nu < 1$, i.e. a subdiffusive regime on a timescale shorter than the longest intramolecular relaxation time where the crossover to diffusion takes place (see, for example, figures 2–4) [5–8]. Analysis of simulation trajectories and experiments relate the inconsistency of the conventional approach to a neglect of the contribution due to correlated motion in both intramolecular and intermolecular dynamics.

The hypothesis that diffusion of a single tagged chain is uncorrelated with the motion of its surrounding molecules stands on the assumption that there is a separation of timescales between the relaxation of solute and solvent [9, 10]. While this conjecture is reasonable for macromolecules in solution, it becomes questionable in polymer melts, since the tagged polymer chain and its surrounding molecules are identical. Simulations of polymer melts show that the dynamics of a single chain is correlated with the motion of its surrounding molecules for a timescale necessary to escape its initial volume. To overcome the limitations of the conventional theory, we derived a generalized Langevin equation (GLE) approach for the dynamics of a group of interacting polymer molecules by projecting the dynamics of the entire liquid onto the coordinates of an ensemble of slowly relaxing chains. The theoretical approach so derived correctly predicts local and global dynamics for PE melts [1–3].

In this paper, we extend our approach to investigate how different local scales, through monomeric structure and flexibility, affect the dynamical properties of a tagged polymer chain in the liquid. One key quantity that enters into our calculations is the intermolecular potential of mean force acting between the com of a pair of interacting polymers. This potential is calculated by solving the Ornstein–Zernike integral equation for monomer and com sites [9, 11]. The solution yields an analytical form of the intermolecular com total pair correlation function [12, 13], which allows for a convenient analytical solution of the dynamical equation through a transformation to normal modes. To test the quality of our procedure, we compare the mesoscopic potential of mean force with united-atom molecular dynamics (UA-MD) simulation data: these are reproduced quite well by the theory with no adjustable parameters. As a second test, we calculate the effective pair interaction potential acting between polymer molecules that are coarse-grained at the com level. This other potential is the input to mesoscopic molecular dynamics (MS-MD) simulations of the macromolecular liquid, where each polymer chain is represented as an interacting, soft colloidal particle. Data from MS-MD yield a coarse-grained liquid structure consistent with data from UA-MD simulations and with our theory, supporting the foundation of the procedure.

Making use of the analytical, Gaussian interpolymer potential of mean force, the generalized Langevin equation for cooperative dynamics (CDGLE) is solved, providing a description of local and global relaxation. Correlations between scaling exponents, friction, number of correlated molecules, and local flexibility are investigated for a series of homopolymer melts where the number of united atoms in each molecule is kept constant ($N = 96$). The effective semiflexibility is measured as the segment length given by $l_{\text{eff}} = (6/N)^{1/2} R_g$, where R_g is the radius of gyration of the molecule. Here, l_{eff} increases with increasing polymer rigidity (see table 1). Single-chain com dynamics, as calculated from the CDGLE, agrees with UA-MD simulations in the whole range of timescales available, which includes subdiffusive and diffusive, long-time regimes.

2. Generalized Langevin equation for cooperative dynamics

In a series of recent papers, we presented a GLE that describes the subdiffusive dynamics of a group of weakly interacting polymer chains in their liquid, which is dynamically heterogeneous but structurally homogeneous [1–3]. If a single polymer chain is assumed to be moving in an uncorrelated way with its surroundings, the resulting equation of motion (eom) is a GLE that, in the limit of completely flexible polymers and upon discarding the memory function, reduces to the Rouse equation. In the Rouse approach, the polymer moves in a structurally and dynamically uniform medium where the polymer com follows Brownian motion for all timescales, in a manner that its mean-square displacement increases with time as $\Delta R^2(t) \propto t$. A second important assumption in traditional approaches to polymer dynamics is that the structure of each polymer chain in a macromolecular liquid is unperturbed, so it follows a Gaussian intramolecular conformational distribution.

Experimental and computational data for polymer melt dynamics show that the mean-square com displacement scales with time as $\Delta R^2(t) \propto t^\nu$, with $\nu < 1$. This subdiffusive regime extends up to a decorrelation time, τ_{decorr} , where the crossover to random Brownian motion takes place. The transition from subdiffusive to diffusive motion, that occurs at τ_{decorr} corresponds to the timescale in which a tagged molecule is able to escape from the volume defined by its own spatial dimension, i.e. R_g . For a homopolymer containing N segments of length l_{eff} , the latter is defined as $R_g = (N/6)^{1/2} l_{\text{eff}}$, consistent with the statistics of an unperturbed chain. By this dynamical mechanism, each polymer chain is able to renew its intermolecular contacts completely, so that if the dynamics is sampled for timescales larger than $\tau_{\text{decorr}} \propto R_g^2/D_{\text{sc}}$, with D_{sc} representing the diffusion coefficient of a single chain, subsequent steps in the motion of a polymer molecule become uncorrelated and it follows Brownian motion. For melts of short (unentangled) chains, $\tau_{\text{decorr}} \propto \tau_{\text{Rouse}}$, i.e. the longest correlation time in the single-chain Rouse approach.

The statistical number of polymeric chains in the volume spanned by the tagged chain, i.e. in the volume defined by its radius of gyration, is given by

$$n(R_g) = \left(4\pi\rho \int_0^{R_g} r^2 [1 + h^{\text{cc}}(r)] dr - 1 \right) \propto N^{1/2} \rho l_{\text{eff}}^3, \quad (1)$$

with $h^{\text{cc}}(r)$ being the com total correlation function, as discussed in the next section. This number should increase with the degree of polymerization, N , increasing chain stiffness, l_{eff} , and increasing total monomer number density, ρ .

For a group of n interacting chains undergoing slow cooperative dynamics in a field of fast-relaxing molecules, a scenario known to hold in undercooled systems and in macromolecular liquids, the eom for a segment a of molecule i positioned at $\mathbf{r}_a^{(i)}(t)$ accounts for forces from three different contributions: the intramolecular potential $-\beta^{-1} \ln\{\Psi[\mathbf{r}^{(i)}(t)]\}$,

the time-dependent intermolecular potential of the mean force $-\beta^{-1} \ln\{g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)]\}$, and the random interactions with the surrounding liquid, given by the projected random force $\mathbf{F}_a^{Q(i)}(t)$. Here, $\beta = (k_B T)^{-1}$ and the eom becomes

$$\zeta \frac{d\mathbf{r}_a^{(i)}(t)}{dt} = \beta^{-1} \frac{\partial}{\partial \mathbf{r}_a^{(i)}(t)} \ln \left[\prod_{j=1}^n \Psi[\mathbf{r}^{(j)}(t)] \prod_{k < j}^n g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)] \right] + \mathbf{F}_a^{Q(i)}(t). \quad (2)$$

When the time-dependent monomer pair distribution function $g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)] \rightarrow 1$, which corresponds to a vanishing potential of mean force $w(r) = -\beta^{-1} \ln g[\mathbf{r}^{(j)}(t), \mathbf{r}^{(k)}(t)] \rightarrow 0$, the eom for a single chain in a uniform bath is recovered. If each polymer reduces to a single unit, equation (2) recovers the eom for two interacting colloidal particles [14].

The key quantities that enter into equation (2) are the *intramolecular* and *intermolecular* potentials of mean force. While in the traditional Rouse approach the intramolecular potential describes a totally flexible chain of effective segments, we extended our development to include finite-size polymers and semiflexibility by adopting Bixon and Zwanzig's formalism [15]. Consistent with the Rouse and semiflexible Rouse theories, in our approach the com motion is decoupled from internal chain dynamics once the eom is translated into the corresponding normal modes description.

While semiflexibility affects all modes of motion, we assume for simplicity that the intermolecular potential affects only the first mode of motion, which corresponds to the com diffusion. This approximation is supported, for example, by a mode analysis of local dynamics of unentangled polymer melts at the crossover to entangled dynamics performed by Richter and co-workers [16], which shows that intermolecular forces mainly affect the lower-index modes of motion. Moreover, analyses from simulation trajectories of local dynamics show that the latter are still Rousian in nature [17], suggesting that intermolecular effects, at least in polymer melts, only slightly perturb local properties. In our study, the calculated monomer dynamics, once the effect of semiflexibility is included in the eom, is found to reproduce well that obtained from simulations [1–3]. This suggests that, at least at the monomer level, intramolecular correlations provide the dominant contribution to monomer dynamics.

At the com level, however, the dynamical correlation in the com motion is entirely due to the effective intermolecular potential of mean force. In fact, semiflexibility does not affect global motion directly, since its effect extends up to the length scale of the persistence length, which is shorter than the overall polymer dimension in real polymeric systems.

Finally, in equation (2), the intermolecular potential contains the simultaneous coupling of n polymers in a global distribution function. We approximate the equation by introducing the product of $n(n-1)$ intermolecular *pair* distribution functions, due to the difficulty of treating many-body potentials. The solution of the approximate equation depends on the calculation of the pair distribution function for the com of polymer molecules.

3. Centre-of-mass potential of mean force for polymer liquids

At the com level, macromolecules can be represented as soft colloids interacting through the potential of mean force, defined as the effective interaction potential acting between the com of a pair of molecules in the field of the surrounding molecules. For chains of sufficiently large degree of polymerization, $N > 30$, the intramolecular distribution for monomer positions follows Gaussian statistics as a consequence of the central limit theorem. Since the com position is obtained by integrating over the intramolecular distribution of monomers, it follows that the *intermolecular* pair distribution largely conserves the Gaussian shape of the intramolecular distribution, as does the potential of mean force derived from the com pair distribution function.

We recently presented an original approach [12, 13, 18], which starts from liquid-state theory and yields an analytical, as well as formally exact, description of liquids of finite-size macromolecules that are coarse-grained at the com level. Our approach was then extended to treat polymer mixtures [18] and diblock copolymer liquids [19].

The function derived in our theory is the total pair correlation function, $h^{cc}(r)$, where c stands for the com site, from which the effective com potential of the mean force is obtained as $\beta w^{cc}(r) = -\ln[1 + h^{cc}(r)]$. This potential is a free energy whose gradient provides the force between two com sites averaged over the equilibrium distribution of all other molecules [9], so it includes many-body effects in an averaged way.

There has been a long-standing interest in deriving effective potentials for coarse-grained macromolecular liquids, leading to the derivation of several empirical formulae for the potential of mean force. Our approach has the advantage over previous studies in providing an *analytical* form for the potential. Since $w^{cc}(r)$ is calculated by integrating over monomer degrees of freedom in the full statistical mechanical system, it is a function of state-dependent parameters such as density, temperature, and degree of polymerization. Therefore, it is useful to provide an analytical form of the potential to avoid the need for performing microscopic simulations for each state point of interest.

The first derivation of an analytical expression for $w^{cc}(r)$ dates back to Flory and Krigbaum [20]. In their approach, however, the intermolecular potential at contact becomes more repulsive with increasing chain length, which disagrees with simulation data, as well as analytical results from scaling and renormalization group theories. Empirical forms of the potential that reproduce numerical results from simulations were derived by Dautenhahn and Hall [21], and later on by Murat and Kremer [22]. We earlier proposed an approximated analytical solution of the pair potential for polymer melts that reproduced numerical data with one fitting parameter [1–3].

For a homopolymer liquid of total monomer number density, ρ , where each molecule is comprised of N monomers, $h^{cc}(r)$ is obtained by solving in reciprocal space the Ornstein–Zernike equation, represented by a matrix form including pair interactions between real (monomer) and auxiliary (com) sites [11–13, 18]. Direct interactions only enter between real sites, leading to a simple analytical expression that formally relates the liquid structure at the com level to the monomer level description as

$$h^{cc}(k) = \left[\frac{\omega^{cm}(k)}{\omega^{mm}(k)} \right]^2 h^{mm}(k), \quad (3)$$

where $h^{mm}(k)$ is the total pair intermolecular monomer/monomer correlation function (cf), $\omega^{cm}(k)$ is the intrachain cf of monomers about the com, and $\omega^{mm}(k)$ is the intramolecular monomer/monomer cf. For long molecular chains, the intramolecular monomer/monomer and com/monomer form factors follow Gaussian statistics [4]. When the simple thread model in the framework of the PRISM approach [23] is adopted for the monomer–monomer total cf, the liquid structure at the com level becomes an analytical function of the microscopic molecular parameters, such as l_{eff} , as well as of the thermodynamic parameters, such as temperature and density.

Using the reduced variables $\tilde{r} \equiv r/R_g$ and $\tilde{\xi}_\rho \equiv \xi_\rho/R_g = [\sqrt{2}(1 + \pi\sqrt{2}\rho_{\text{ch}}^*)]^{-1}$, the equation for the intermolecular total pair correlation function reads

$$h^{cc}(\tilde{r}, \tilde{\xi}_\rho) = \frac{3}{4} \sqrt{\frac{3}{\pi}} \frac{\tilde{\xi}'_\rho}{\tilde{\xi}_\rho} \left(1 - \frac{1}{2\tilde{\xi}_\rho^2} \right) e^{-3\tilde{r}^2/4} - \frac{1}{2} \frac{\tilde{\xi}'_\rho}{\tilde{r}} \left(1 - \frac{1}{2\tilde{\xi}_\rho^2} \right)^2 e^{1/(3\tilde{\xi}_\rho^2)} \\ \times \left[e^{\tilde{r}/\tilde{\xi}_\rho} \text{erfc} \left(\frac{1}{\sqrt{3}\tilde{\xi}_\rho} + \frac{\sqrt{3}\tilde{r}}{2} \right) - e^{-\tilde{r}/\tilde{\xi}_\rho} \text{erfc} \left(\frac{1}{\sqrt{3}\tilde{\xi}_\rho} - \frac{\sqrt{3}\tilde{r}}{2} \right) \right], \quad (4)$$

where ξ_ρ is the length scale of density fluctuations defined as $\xi_\rho^{-1} = \xi_c^{-1} + \xi_\rho'^{-1}$, $\xi_\rho' = R_g/(2\pi\rho_{\text{ch}}^*)$ with $\rho_{\text{ch}}^* \equiv \rho_{\text{ch}}R_g^3$ being the reduced molecular number density while $\rho_{\text{ch}} = \rho/N$ represents the molecular number density, and $\xi_c = R_g/\sqrt{2}$ is the length scale of the correlation hole.

We note that equation (4) is derived under the approximations that the intramolecular monomer distribution obeys Gaussian statistics and that chain end effects are negligible, which corresponds to assuming that all monomer sites along a polymer molecule are equivalent [23]. Both approximations are correct for liquids of long macromolecular chains, representing an essential step in rendering the original site-specific problem into an analytically tractable one. Adopting these approximations is well justified in our theory, since we focus on the liquid structure that is coarse-grained at the com level, where monomeric degrees of freedom are averaged in a mean-field manner.

In the limit of long polymer chains, i.e. $N \rightarrow \infty$, equation (4) simplifies to

$$h^{\text{cc}}(\tilde{r}, \tilde{\xi}_\rho) \approx -\frac{39}{16}\sqrt{\frac{3}{\pi}}\tilde{\xi}_\rho(1 + \sqrt{2}\tilde{\xi}_\rho) \left[1 - \frac{9\tilde{r}^2}{26} + \mathcal{O}(\tilde{\xi}_\rho^2, \tilde{r}^4) \right] e^{-3\tilde{r}^2/4}, \quad (5)$$

where the normalized form $h^{\text{cc}}(\tilde{r}, \tilde{\xi}_\rho)/\tilde{\xi}_\rho$ is a universal function of the reduced distance \tilde{r} when the second-order correction in $\tilde{\xi}_\rho$ is neglected, i.e. for large N . It is to be noted that equation (5) correctly recovers the isothermal compressibility from the Fourier transform of the $k \rightarrow 0$ limit of the mesoscopic static structure factor, $S^{\text{cc}}(0) = 1 + \rho_{\text{ch}}h^{\text{cc}}(0) = (\xi_\rho/\xi_c)^2 = S^{\text{mm}}(0)/N$, where $S^{\text{mm}}(k)$ is the monomer–monomer static structure factor.

The mean force potential obtained from equation (4) has a Gaussian-like repulsive shape, with a slightly attractive contribution. The amplitude of the attractive contribution is one order of magnitude smaller than the value of the potential at contact, which is of the order of a few $k_B T$. Although small in amplitude, the attractive contribution is essential in optimizing the agreement between theoretical and simulated pair distribution functions, as well as in improving the thermodynamic consistency of the coarse-grained model [19]. A simplified analytical form of the mean-force potential at contact reads

$$\beta w^{\text{cc}}(0) = -\ln \left[1 - \frac{3}{8}\sqrt{\frac{3}{\pi}} \left(\frac{1 + \sqrt{2}\tilde{\xi}_\rho}{\tilde{\xi}_\rho} \right) \times \left\{ 1 + \frac{4}{3} \left(1 - \frac{1}{2\tilde{\xi}_\rho^2} \right) \left(1 - \frac{\sqrt{\pi}e^{1/(3\tilde{\xi}_\rho^2)}}{\sqrt{3}\tilde{\xi}_\rho} \text{erfc} \left[\frac{1}{\sqrt{3}\tilde{\xi}_\rho} \right] \right) \right\} \right] \quad (6)$$

$$\approx -\ln \left[1 - \frac{39}{16}\sqrt{\frac{3}{\pi}}\tilde{\xi}_\rho \right]. \quad (7)$$

The last expression corresponds to the $N \rightarrow \infty$ limit, where the second-order contribution of $\tilde{\xi}_\rho$ is neglected. It is important to note that because the intermolecular distribution function in equation (2) contains $n(n-1)/2 \approx N$ pair contributions, increasing the degree of polymerization does not lead to a vanishing *intermolecular* interaction.

In this paper, we present data for liquids of homopolymer chains with slightly different architecture and flexibility. Test systems are polyethylene (PE) and polypropylenes in their isotactic (iPP), head-to-head (hhPP), and syndiotactic (sPP) forms. UA-MD simulations for these polymer melts were performed by Grest, Jaramillo, Heine, Curro, and co-workers [8, 24]. When homopolymers with different monomer architectures are considered, the local polymer flexibility enters into our equations indirectly through the effective polymer size, R_g . A comparable parameter for local flexibility is l_{eff} , which is proportional to (but different in value

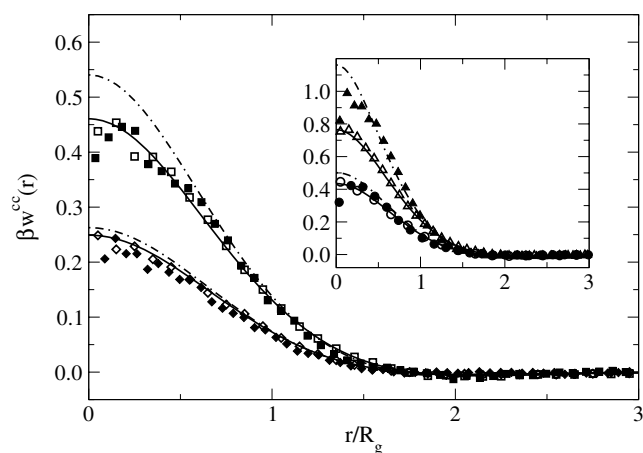


Figure 1. Plot of $\beta w^{\text{cc}}(r)$ comparing theoretical results with simulation data. Shown are data from systems with $N = 96$ united-atom sites for different architectures, PE (diamonds) and hhPP (squares), while in the inset are displayed sPP (circles) and iPP (triangles). Theoretical curves correspond to the full expression, equation (4), (solid line) and the $N \rightarrow \infty$ representation from equation (5) (dashed line). Filled symbols are from united-atom molecular dynamics simulations, while open symbols are from simulations of the coarse-grained liquid.

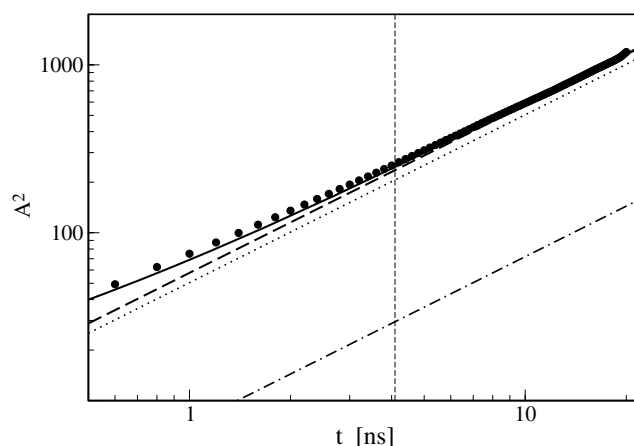


Figure 2. Centre-of-mass mean-square displacement as a function of time for a syndiotactic polypropylene chain. Best fit of the molecular dynamics simulation data (filled circles) with the single-chain Rouse equation (dashed line), and with the many-chain cooperative Langevin equation (2), for polymer melts (solid line). The short-dashed vertical line indicates the longest Rouse correlation time $\approx \tau_{\text{decorr}}$. Also reported are the relative diffusion (dotted line) and collective diffusion (dot-dashed line).

from) the persistence length. In our test systems, the total number of segments in the united-atom representation is constant ($N = 96$). Values of l_{eff} are reported in table 1.

We test our form of the potential against UA-MD simulations. In figure 1, we compare exact and approximate analytical expressions for the potential of mean force with UA-MD simulation data. Exact and approximate expressions coincide within statistical error with data from UA-MD simulations in real and reciprocal (not shown) spaces, while theoretical calculations do not contain any adjustable parameters.

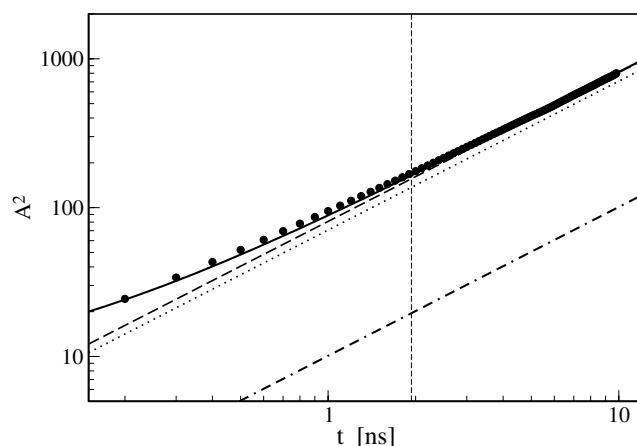


Figure 3. Centre-of-mass mean-square displacement as a function of time for an isotactic polypropylene chain. Symbols and lines as in figure 2.

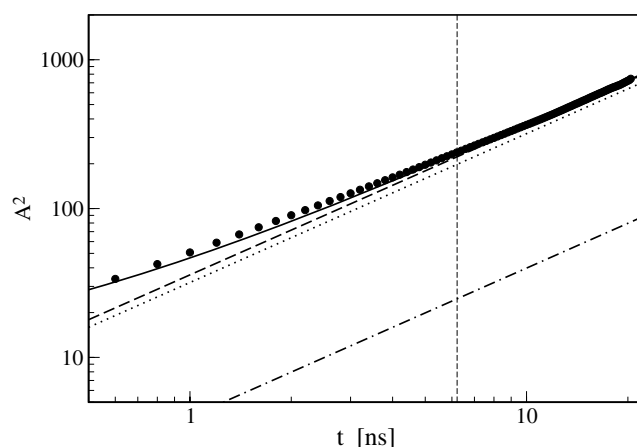


Figure 4. Centre-of-mass mean-square displacement as a function of time for a head-to-head polypropylene chain. Symbols and lines as in figure 2.

As can be gleaned from figure 1, our formalism correctly captures the trend that stiffer polymers can interpenetrate more efficiently, leading to a decrease in the repulsive potential at contact, in line with UA-MD results. This effect is due to the fact that stiff polymers span a larger volume than flexible ones with the same number of united-atom sites.

As a further test of our development, we derive from equation (4) the ‘bare’ pair potential, $v^{cc}(r)$, by enforcing the hypernetted-chain closure. This potential enters into MS-MD simulations, which model a liquid of polymers that is coarse-grained at the com level. In figure 1, it is shown that simulations of the coarse-grained liquid structure are consistent with results from UA-MD simulations and with theoretical predictions.

The agreement between analytical expressions and simulations is slightly less satisfactory for the particular case of the iPP homopolymer. For this system, the disagreement is not surprising because iPP is known to have a highly packed intramolecular structure due to the tacticity of methyl moieties, which suppresses polymer interpenetration. As a

consequence, this system shows a small thermal expansion coefficient and a small isothermal compressibility [12, 25]. In conclusion, our approach provides an accurate analytical procedure for calculating the potentials of mean force *and* effective interactions between the com of a pair of macromolecules.

4. Subdiffusive centre-of-mass dynamics in liquids of homopolymers with different local architectures

Equation (2) represents a set of nN dynamical equations, where the intramolecular potential of mean force couples the internal dynamics of each chain (N monomers), while the intermolecular potential couples the dynamics of n different polymers at the com level. It is convenient to express equation (2) in matrix form and to apply symmetry rules [1–3]. Since all the chains are statistically equivalent, their dynamics can be simply decomposed into a collective contribution, describing the motion of the com of the ensemble of n chains, and a relative contribution, which describes the relative motion of a pair of molecules. Moreover, because of the Gaussian form of the analytical intramolecular and intermolecular potentials, the internal chain dynamics can be decoupled by matrix diagonalization, which translates the dynamical equations from space to normal mode coordinates. At the end of this procedure, any dynamical property of the single chain results from the linear combination of collective and relative contributions, where relative coordinates depend on the effective intermolecular potential of mean force.

For example, as far as the com dynamics is concerned, the time evolution of the relative and collective space coordinates read, respectively, as

$$\begin{aligned}\zeta \frac{d\mathbf{R}_{\text{relative}}(t)}{dt} &= -G(t)\mathbf{R}_{\text{relative}}(t) + \mathbf{F}_{\text{relative}}(t), \\ \zeta \frac{d\mathbf{R}_{\text{collective}}(t)}{dt} &= \mathbf{F}_{\text{collective}}(t),\end{aligned}\quad (8)$$

where the fluctuation–dissipation conditions apply:

$$\langle \mathbf{F}_{\text{relative}}(t) \cdot \mathbf{F}_{\text{relative}}(0) \rangle = \langle \mathbf{F}_{\text{collective}}(t) \cdot \mathbf{F}_{\text{collective}}(0) \rangle = 6\zeta k_B T \delta(t), \quad (9)$$

while $\langle \mathbf{F}_{\text{relative}}(t) \cdot \mathbf{F}_{\text{collective}}(0) \rangle = 0$. The single-chain com mean-square displacement follows as a combination of relative and collective contributions as

$$\Delta R^2(t) = \frac{n-1}{6n} \frac{d\Delta R_{\text{relative}}^2(t)}{dt} + 6D_{\text{collective}}t, \quad (10)$$

where

$$D_{\text{collective}} = D_{\text{sc}}(N^{1/2}\rho l_{\text{eff}})^{-1}, \quad (11)$$

is the cooperative diffusion coefficient representing the dynamics of the com of an ensemble of n interacting molecules, which tends to vanish for systems with a large number of dynamically correlated molecules. At long times, if the polymer intermolecular potential is strong and attractive, the relative diffusion is suppressed and only collective dynamics takes place. On the other hand, if the intermolecular interaction vanishes, the com motion recovers the uncorrelated single chain dynamics. The latter is the case for the intermolecular potential considered in this paper. For the systems under investigation, the relative time-dependent com position is a function of the effective force that a single chain experiences due to the surrounding polymer chains. The latter depends on the potential of mean force derived from equation (5) by introducing a time-dependent intermolecular distance, and it is approximated as

$$G(t)\mathbf{R}_{\text{relative}}(t) \approx nN \frac{171}{32} \sqrt{\frac{3}{\pi}} \frac{\tilde{\xi}_\rho}{R_g^2} (1 + \sqrt{2}\tilde{\xi}_\rho) e^{-75\langle R^2(t) \rangle / (76R_g^2)} \mathbf{R}_{\text{relative}}(t), \quad (12)$$

Table 2. Polyolefin melts: dynamical parameters.

Polymer	D_{sc} ($\text{\AA}^2 \text{ ns}^{-1}$)	Slope	n	τ_{Rouse} (ns)
PE	18.74	0.837	8	3.04
sPP	9.60	0.857	8	4.09
hhPP	5.98	0.859	9	6.22
iPP	13.48	0.869	8	1.93

with $\langle R^2(t) \rangle$ being a relative, many-chain interpolymer distance estimated as

$$\langle R^2(t) \rangle \approx n(\Delta R^2(t) - 6D_{\text{collective}}t). \quad (13)$$

Since the intermolecular force of equation (12) depends on the time-dependent intermolecular distance $\langle R^2(t) \rangle$, the eom is solved self-consistently at a fixed time interval until convergence is obtained: the procedure is then repeated for small increments of time, $\Delta t = 10^{-2}$ ps. The com mean-square displacement exhibits subdiffusive behaviour that crosses over to the diffusive regime when $\langle R^2(t) \rangle > R_g^2$, i.e. when the molecule diffuses beyond the range of the intermolecular potential of mean force. In the long-time limit, the polymer dynamics recovers single-chain diffusion.

As a test of the approach, we compare theoretical predictions with data from UA-MD simulations. The single-chain, long-time diffusion coefficient from UA-MD provides the value of the monomeric friction as $\zeta = k_B T / (N D_{sc})$. Inputs to the theory are the values of ρ , T , N , and l_{eff} from simulations, as reported in table 1.

For all systems investigated, the statistical segment is larger than the chemical bond, $l_{\text{bond}} = 1.54 \text{ \AA}$, because of the intrinsic chain rigidity of the polymer molecules under consideration. In figures 2–4 it is shown that the CDGLE reproduces quantitatively the com dynamics, including the crossover from subdiffusive to diffusive regimes, for polymers with different local semiflexibility. The slope of the subdiffusive regime, as well as the crossover time, is sensitive to the overall polymer spatial dimension, R_g , which depends on the degree of polymerization, N , as well as on the local bond semiflexibility, l_{eff} . The extent of anomalous (i.e. subdiffusive) dynamics observed in the plots increases with increasing degree of polymerization and local chain stiffness, in agreement with our theoretical predictions. The number of molecules undergoing cooperative dynamics, n , obtained by optimizing the agreement between theory and simulation data, is found to be consistent with its estimated value, $n \propto N^{1/2}$, for all systems investigated. These data are summarized in table 2.

5. Summary

In this paper, we have presented a study that considers the effect of local semiflexibility on the cooperative dynamics of a group of weakly interacting macromolecules in a liquid. This study combines the application of two independent theoretical approaches we have recently developed. One approach is a coarse-graining procedure, obtained from the solution of the first-principles Ornstein–Zernike equation, that provides an analytical expression for the effective potential of mean force acting between a pair of polymers in a liquid. This result is then used as input to our cooperative dynamics generalized Langevin equation, obtained from Liouville dynamics by means of Mori–Zwanzig projection operator techniques, that yields an effective equation of motion for the dynamics of a group of polymers undergoing cooperative motion in a structurally uniform but dynamically heterogeneous liquid. Previously, both theories were found to agree quantitatively with data from united-atom molecular dynamics simulation of polyethylene melts, when structural and the dynamical properties were investigated.

As an extension to our previous studies on polyethylene systems, we have considered here the structure and dynamics for polymer melts comprised of slightly branched molecules with different local flexibility. The structure and dynamics of these systems, as predicted by the two approaches, respectively, have been tested against molecular dynamics simulations of polymer liquids described at the united-atom level. Theoretical predictions for the structure and dynamics have been found to be in quantitative agreement with simulation data.

Finally, as a further test of our coarse-graining approach, we calculated for these branched systems the effective 'bare' potential acting between any pair of polymers. This potential is the input to molecular dynamics simulations of the coarse-grained liquid, where each chain is represented as a soft colloidal particle. Structural properties of the coarse-grained liquid, and the related potential of mean force, have been found to be in quantitative agreement with those from united-atom simulations.

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