Segmental Dynamics in Entangled Linear Polymer Melts

Zuowei Wang,*‡ Alexei E. Likhtman,† and Ronald G. Larson‡

†School of Mathematical and Physical Sciences, University of Reading, Whiteknights, Reading RG6 6AX, United Kingdom
‡Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136, United States

ABSTRACT: We present molecular dynamics (MD) and slip-springs model simulations of the chain segmental dynamics in entangled linear polymer melts. The time-dependent behavior of the segmental orientation autocorrelation functions and mean-square segmental displacements are analyzed for both flexible and semiflexible chains, with particular attention paid to the scaling relations among these dynamic quantities. Effective combination of the two simulation methods at different coarse-graining levels allows us to explore the chain dynamics for chain lengths ranging from \( Z\approx 2 \) to 90 entanglements. For a given chain length of \( Z\approx 15 \), the time scales accessed span for more than 10 decades, covering all of the interesting relaxation regimes. The obtained time dependence of the monomer mean square displacements, \( g_2(t) \), is in good agreement with the tube theory predictions. Results on the first- and second-order segmental orientation autocorrelation functions, \( C_1(t) \) and \( C_2(t) \), demonstrate a clear power law relationship of \( C_m(t) \sim C_m(t)^m \) with \( m = 3, 2, \) and 1 in the initial, free Rouse, and entangled (constrained Rouse) regimes, respectively. The return-to-origin proportionality between the segmental orientation autocorrelation functions and \( g_2(t) \) in the entangled regime, is convincingly verified by the simulation result of \( C_1(t) \propto g_2(t)^{-1/4} \propto t^{-1/4} \) in the constrained Rouse regime, where for well-entangled chains both \( C_1(t) \) and \( g_2(t) \) are rather insensitive to the constraint release effects. However, the second-order correlation function, \( C_2(t) \), shows much stronger sensitivity to the constraint release effects and experiences a protracted crossover from the free Rouse to entangled regime. This crossover region extends for at least one decade in time longer than that of \( C_1(t) \). The predicted time scaling behavior of \( C_2(t) \propto t^{-1/4} \) is observed in slip-springs simulations only at chain length of 90 entanglements, whereas shorter chains show higher scaling exponents. The reported simulation work can be applied to understand the observations of the NMR experiments.

1. INTRODUCTION

Dynamics in entangled polymer melts and concentrated solutions is prominently described by the tube theories.1−5 The original tube theory predicts a number of scaling power laws for the time and molecular weight dependence of the rheological and dynamic behavior that are subject to continuous investigations.1,2 Among them are the famous molecular weight dependence of the zero-shear viscosity, \( \eta_0 \sim M^\lambda \), and the chain self-diffusion coefficient, \( D_{self} \sim M^{-2} \), predicted by the pure reptation model. Deviations from these integer powers, as observed in experiments with polymers of finite lengths, are attributed to additional relaxation mechanisms, such as the contour length fluctuations (CLFs) and constraint release (CR).2,5−7 Development of quantitative theories for entangled polymers demands a clear understanding of these relaxation mechanisms, which can only be achieved from experiments4,5,8−10 and computer simulations11−15 on the microscopic scale. In such microscopic works the most widely studied observables are probably the segmental mean square displacement (MSD), \( g_2(t) \), and the segmental orientation correlation functions, \( C_n(t) \), because for them the tube model predictions are readily available to compare with.

The mean square segment displacement is experimentally accessible via neutron spin echo (NSE) spectroscopy9,16 and NMR diffusometer.17,18 For a highly entangled polymer chain, this quantity is predicted to undergo a series of time-dependent power law changes from \( g_2(t) \sim t^{\lambda/2} \) in the free Rouse regime, to \( \sim t^{1/4} \) in the constrained Rouse regime, \( \sim t^{1/2} \) in the reptation regime, and finally \( \sim t^1 \) in terminal diffusion regime.2 The transition from the \( t^{1/2} \) to \( t^{1/4} \) power, marking the entry to the well-entangled regime, was evidenced by NSE experiments9 and...
molecular dynamics (MD) simulations of monodisperse linear polymer melts.\textsuperscript{11,19}

Many NMR experiments measure the polymer segmental dynamics in terms of an orientation autocorrelation function of the second Legendre polynomial

$$C_2(t) \propto \langle P_2(\cos \Theta(t))P_2(\cos \Theta(0)) \rangle$$

(1)

where $\Theta(t)$ is the angle between the segmental orientation vector and a reference direction typically of the external magnetic field.\textsuperscript{10,20–22} Using the return-to-origin (RTO) argument, Ball et al. proposed an inverse proportionality between this correlation function and the mean square segment displacement, $C_2(t) \propto g_2(t)^{-1}$ for time scales larger than the entanglement time $t_e$, with an additional exponential correction close and beyond the Rouse time $t_R$.\textsuperscript{20} It follows that a power law decay of $C_2(t) \sim t^{-\alpha}$ with $\alpha = 1/4$ would be expected in the constrained Rouse regime ($t_e < t < t_R$), where $g_2(t) \sim t^{1/4}$. This $\sim t^{-1/4}$ scaling, however, has not been convincingly observed in NMR experiments. Measurements of Hermann et al. on linear polybutadiene (PB) melts with chain length up to $Z \approx 9$ entanglements only rendered $\alpha \approx 0.5$ in this regime.\textsuperscript{23} Graf et al. presented a $t^{-1/4}$ power law fitting to the data points obtained from PB melts with much longer chains ($Z \approx 76$),\textsuperscript{21} but the applied NMR method itself may be subject to systematic errors.\textsuperscript{10} The most recent NMR measurements on $C_2(t)$ were reported by Chávez and Saalwächter using linear PB melts with chain length ranging in $12 \leq Z \leq 1100$.\textsuperscript{10,22} Interestingly, their results demonstrated a strong molecular weight dependence of $\alpha$ in the constrained Rouse regime. Even for the longest chain with $Z > 1000$, the asymptotic value of $\alpha$ $\approx 0.29$ is still larger than the expected 1/4 power. The reason was considered to lie in the CR effects, which cause local chain motions less restricted than that predicted by the tube model.\textsuperscript{10,22} This observation seems to be inconsistent with the chain diffusion coefficient data, where the CR effects were shown to diminish as $Z$ increases beyond $\sim 200$ and also the NSE result of $g_2(t) \sim t^{1/4}$ for linear polyethylenes of molecular weight around 100 entanglements.\textsuperscript{7} (Note, however, that the error bars in ref 9 are quite large compared with the NMR experiments.) One of the motivations for the current work is to address the time scaling behavior of $C_2(t)$ as well as its dependence on the CR effects and its correlation with other dynamical observables.

In computer simulations, the chain segmental orientation autocorrelation functions are generally calculated as

$$C_2(t) = \langle P_2(\mathbf{u}(t) \cdot \mathbf{u}(0)) \rangle$$

(2)

where $P_n(x)$ is the Legendre polynomial of order $n$ and $\mathbf{u}(t) = l(t)/|l(t)|$ is the unit segmental vector with $|l(t)|$ being the segment length at time $t$. The triangular brackets here mean time and ensemble average and can also include averaging over different chain segments. For unentangled polymer chains, the Rouse model predicted a power law of $C_2(t) \sim t^{-1/2}$ and a scaling relation of $C_2(t) \propto C_1(t)^2$.\textsuperscript{2,24} The applicability of the Rouse model has been discussed over a wide range of monomer concentration, temperature, and excluded volume interactions.\textsuperscript{25–28} Simulation studies of $C_2(t)$ in the entanglement regime are much less frequent and are mostly on mildly entangled polymer melts.\textsuperscript{12,13,29} Kreer et al. reported Monte Carlo simulation results on $C_2(t)$ and $g_2(t)$ for monodisperse linear polymer melts with various chain lengths.\textsuperscript{12} The 1/4 power law expected in the constrained Rouse regime was not reached in both quantities for the longest chain of $\sim 14$ entanglements. The situation is similar in MD simulations using more realistic polymer chain models.\textsuperscript{13,29} Accordingly, there is also a lack of numerical examination of the scaling relationship between the segmental orientation correlation functions of different orders, namely $C_2(t) \sim C_1(t)^m$ with $m$ a certain constant, of well-entangled polymer systems. The $C_2(t) \propto C_1(t)^2$ relation, which only holds for the free Rouse regime, has been in some cases improperly applied to correlate experimental and simulation data in the entanglement regime.\textsuperscript{23}

In the current work, we present the fine-grained MD\textsuperscript{11} and coarse-grained slip-springs (SS)\textsuperscript{30} simulations of the segmental dynamics of monodisperse entangled linear polymer melts. Particular attention is paid to the time scaling behavior of the segmental diffusion and orientation autocorrelation functions as well as the scaling relationship between them. Both flexible and semiflexible chains are studied in our MD simulations, with the longest chain length in each case above 15 entanglements.\textsuperscript{15,19} The slip-springs model allows us to simulate melt systems with much longer chains up to time scales that are inaccessible to MD simulations.\textsuperscript{30} The SS data presented here are for chain length up to $Z \approx 90$ and time scale reaching the terminal relaxation regime. By effectively mapping the slip-springs simulation results to the MD data, we are able to explore the dynamics of polymer chains with $\sim 15$ entanglements for a total timespan over 10 decades. More importantly, the slip-springs model has the unique advantage of being able to separate out the CR effects by switching such relaxations on and off in simulations,\textsuperscript{31} which is essential for understanding the experimental observations.

This Article is organized as follows: Section 2 gives a brief overview of the theoretical descriptions of the segmental dynamics in entangled polymer melts. We describe the details of the MD and slip-springs simulation methods and the related system parameters in Section 3. The simulation results are presented and discussed in Section 4, and conclusions are summarized in Section 5.

2. THEORETICAL BACKGROUND

2.1. Segment Mean Square Displacement. The translational dynamics of a polymer segment is measured by its mean square displacement, $g_1(t) = \langle (r(t) - r(0))^2 \rangle$, where $r(t)$ is the coordinate of the segmental center of mass. On very short time scales, the segment motion is ballistic

$$g_1(t) = 3k_BTt^2/(Nm), \ t \ll \tau_0$$

(3)

where $N$ is the number of monomers in the segment, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $m$ is the mass of a monomer, respectively.

On larger time scales, the chain connectivity and uncrossability dominate the segmental diffusion behavior of entangled polymers. When neglecting the CR effects, the tube model predicts the following time scaling behavior of the mean
square displacement of the central monomers of a well-entangled polymer chain \(^2,19,32\)

\[
g_t(t) \approx \begin{cases} 
  \frac{b^2}{t^{3/2}}, & \tau_0 < t < \tau_e \\
  ab(t/\tau_0)^{1/4}, & \tau_e < t < \tau_R \\
  \frac{ab}{N^{1/2}}(t/\tau_0)^{1/2}, & \tau_R < t < \tau_d \\
  a^2/N^2(t/\tau_0), & \tau_d < t 
\end{cases}
\]

(4)

where \(a\) is the tube Kuhn step defined from the tube length \(L\) via \(L = Nb^2\), \(b\) is the statistical segment length, and we omit all numerical coefficients. The characteristic time scales are defined by \(\tau_0 = \zeta b^2/(3\pi^2k_BT)\), where \(\zeta\) is the monomeric frictional coefficient, the entanglement time \(\tau_e = N_c^2\tau_0\), Rouse time \(\tau_R = Z^2\tau_e\) and terminal (disengagement) time \(\tau_d = 3Z\tau_R\) respectively. \(Z = N/N_e\) is the number of entanglements per chain and \(N_e = a^2/b^2\) is the number of monomers in each entanglement strand.

### 2.2. Segmental Orientation Autocorrelation Functions

Following eq 2, the segmental orientation autocorrelation functions of orders 1 and 2 can be written explicitly as

\[
C_1(t) = \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle 
\]

(5)

\[
C_2(t) = \frac{1}{2} \langle 3(\mathbf{u}(t) \cdot \mathbf{u}(0))^2 - 1 \rangle 
\]

(6)

\(C_1(t)\) is an analogue of chain end-to-end relaxation measured by dielectric spectroscopy,\(^4\) and \(C_2(t)\) is related to the orientation tensor (measured by optical methods) and to the stress modulus via the stress-optical law.\(^2,33\) The second-order orientation correlation function is directly accessible by NMR experiments, as mentioned in the Introduction. Here we rewrite eq 1 as

\[
C_2(t) = S(P_2(\cos \hat{\theta}(t))P_2(\cos \hat{\theta}(0)))
\]

(7)

where \(\hat{\theta}\) is the angle between the unit segment vector \(\mathbf{u}\) and one of the Cartesian axes, giving \(\cos \hat{\theta}(t) = u_\alpha(t)\) with \(\alpha = x, y, \) or \(z\). The normalization factor 5 in eq 7 results from \(\langle \cos \hat{\theta}(0) \rangle = 1/5\). In practice, the statistics of the \(C_2(t)\) results can be improved by averaging over all three Cartesian components \(u_\alpha\) owing to the isotropic character of the melt system. In Appendix I, we demonstrate that when defined using the unit segment orientation vector, the two second-order segmental orientation autocorrelation functions, \(C_1(t)\) and \(C_2(t)\), are equivalent to each other in equilibrium isotropic systems. Therefore, our following discussions on the second-order orientation correlation functions apply equally to both functions.

**Initial Stage.** On very short time scales, there is a universal relationship between \(C_1(t)\) and \(C_2(t)\). To illustrate this, we note that the angle \(\hat{\theta}(t)\) spanned by a rotating bond vector, defined by \(\cos \hat{\theta}(t) = u(t) \cdot \mathbf{u}(0)\), is small over a small time interval \(t\); therefore, we can Taylor expand

\[
C_1(t) = \langle \cos \hat{\theta}(t) \rangle \approx 1 - \langle \hat{\theta}(t)^2 \rangle/2
\]

(8)

\[
C_2(t) = \frac{1}{2} \langle 3 \cos^2 \hat{\theta}(t) - 1 \rangle \approx 1 - 3\langle \hat{\theta}(t)^2 \rangle/2
\]

(9)

which can be more generally written as

\[
C_n(t) \approx \exp\left(-\frac{n(n + 1)}{4} \langle \hat{\theta}(t)^2 \rangle\right), \quad \theta \ll 1
\]

(10)

This means that for small times these correlation functions must be related by a simple formula

\[
C_{2n}(t) \approx C_1(t)^n
\]

(11)

independent of the dynamics details. For example, it does not matter whether the rotational dynamics is ballistic or diffusive. This argument is more general than the one provided in ref 25.

**Rouse Regime.** On time scales \(\tau_0 < t < \tau_e\), the chain connectivity dominates the rotational dynamics of the segments. The Rouse model predicts (see details in Appendix II)

\[
C_1(t) \approx \frac{\sqrt{\pi}}{2} (t/\tau_0)^{-1/2}, \quad \tau_0 < t < \tau_e
\]

(12)

\[
C_{2n}(t) \approx C_1(t)^n \approx \frac{\pi}{4} (t/\tau_0)^{-n}
\]

(13)

In Appendix II, it should be noted that the normalization factor in \(C_1(t)\), as defined in eq 6 for unit segment orientation vectors, differs from that of the Rouse segment orientation vectors, \(C_0(t)\) (eq A2-2), by a factor of 2 owing to the Gaussian-type fluctuations of the Rouse segment length.

**Entangled Regime.** When \(t > \tau_e\), the topological constraints restrict the motion of the polymer chain to a tube-like region. The segmental displacement along the primitive path of the tube follows the subdiffusive motion of the Rouse model. Because the primitive path itself is a 3D random walk with a Kuhn step size \(a\), the 3D MSD of the chain segment is related to its mean square curvilinear displacement along the tube, \(\langle \Delta s(t)^2 \rangle\), by \(g_t(t) \approx a \langle \Delta s(t)^2 \rangle^{1/2}\). Doi and Edwards indicated that the time correlation function of the segmental orientation vector, essentially defined as \(C_1(t)\) in their book, represents the probability that at time \(t\) the chain segment remains in the original tube segment it occupied at time zero.\(^7\) The same idea was later applied by Ball, Callaghan, and Samulski to describe the correlation function \(C_2(t)\) measured in NMR experiments, where \(C_2(t)\) is proposed to be the probability that \(\Delta s(t)^2 \leq a^2\).\(^20\) It thus follows that all first- and second-order segmental orientation autocorrelation functions are proportional to the coarse-grained Rouse probability\(^20\)

\[
P_{RTO}(t) \sim \frac{1}{\sqrt{2\pi \langle \Delta s(t)^2 \rangle}} \exp(0) \sim g_t(t)^{-1}
\]

(14)

and subsequently

\[
C_1(t) \sim C_{2n}(t) \sim g_t(t)^{-1}, \quad \tau_e < t
\]

(15)

which is qualitatively different from eq 13. The time scaling behavior of these correlation functions in the entangled regime can then be conveniently estimated using the tube model predictions on \(g_t(t)\), as given in eq 4. It is of particular interest in recent NMR experiments and computer simulations to examine the power law scaling in the constrained Rouse regime\(^10,12,22,23\)

\[
C_{1,2n}(t) \sim (t/\tau_e)^{-1/4}, \quad \tau_e < t < \tau_R
\]

(16)
3. SIMULATION DETAILS

3.1. Molecular Dynamics. The linear polymers are represented by the standard Kremer–Grest bead–spring model. All monomers interact via the purely repulsive Lennard-Jones (LJ) potential with the LJ parameter $\epsilon = 1.0k_BT$ and a cutoff radius of $\sigma = 2^{1/6}\sigma$, where $\sigma$ is the bead diameter. The monomers of the same chain are connected to their sequential neighbors by the finite extensible nonlinear elastic (FENE) potential with the spring constant $k = 30\epsilon/\sigma^2$ and the maximum bond length $R_s = 1.5\sigma$. The combination of the LJ and FENE potentials leads to an average bond length $<f^2>_{\text{fl}}^{1/2} = 0.97\sigma$. In addition, the chain stiffness is introduced by using a three-bead bending potential

$$U_{\text{bend}}(\theta) = k_b(1 - \cos \theta) \quad (17)$$

where $\theta$ is the angle in between two adjacent unit bond vectors. The strength of the bending potential is chosen to be $k_b = 0$ and $2\epsilon$ for representing the flexible and semiflexible chains, respectively. The corresponding characteristic ratio and statistical segment length are $C_{\text{ws}} = 1.82$ and $b = 1.31\sigma$ for the flexible chains, and $C_{\text{ws}} = 3.40$ and $b = 1.79\sigma$ for the semiflexible ones, respectively. The primitive path analysis of Everaers et al. yielded the number of monomers per entanglement strand as $N_e = 65$ and 23 for these two types of chains. When discussing the ratio between the mean square displacements of the end and middle monomers in Section 4.1.1, some extra data points, taken from our previous MD simulations using chain stiffness $k_b = 3\epsilon$, are also included.

Trajectories of the monomers are obtained by integrating the following equation of motion using the velocity Verlet algorithm

$$m\ddot{\mathbf{r}}_i = -\nabla U(\mathbf{r}_i) - \Gamma \dot{\mathbf{r}}_i + \mathbf{W}_i(t) \quad (18)$$

where $\mathbf{r}_i$ is the coordinate of the $i$th monomer, $m$ is the monomer mass, and $\Gamma$ is the friction coefficient set to be $\Gamma = 0.5(\text{md}k_BT)^{1/2}/\sigma$. The system is coupled to a Langevin heat bath, and the stochastic force $\mathbf{W}_i$ is a Gaussian white noise related to the friction coefficient $\Gamma$ by $<\mathbf{W}_i(t) \cdot \mathbf{W}_j(t')> = \delta_{ij} \delta(t-t')6k_BT$. The simulations are performed in the NVT ensemble with periodic boundary conditions applied in all three dimensions of the cubic simulation box. The time step $\Delta t = 0.012\tau$ is used in all simulation runs, where $\tau = (m\dot{\mathbf{r}}^2/k_BT)^{1/2}$ is the LJ time unit. The length and time scales in the systems are set by $\sigma$ and $\tau$, respectively. The global number density of the bonds is set to a fixed value of $\rho = 0.85\sigma^{-3}$ for all simulated systems.

The initial configurations of the monodisperse polymer melts are prepared using the equilibration method developed by Auhl et al. as to start the simulations in close proximity to the equilibrium states. Unless specified, simulation results will be presented in the reduced units of $m = \sigma = \epsilon = 1$.

3.2. Slip-Springs Model. The slip-springs model is a recently developed single-chain model for describing the dynamics of entangled polymers. The basic building block of this model is a Rouse chain of $N_e$ beads. The confinement due to entanglements is introduced in a discrete manner using a set of virtual springs of $N_e$ monomers each. One end of each of these springs is fixed in space, and the other end is connected to the Rouse chain by a slip-link. On average, there is a slip-link every $N_e$ monomers. The chain can only slide through these slip-links, and this ensures that the long time dynamics is dominated by reptation. This model contains all mechanisms included in the tube model. Apart from the usual parameters of the Rouse model, there are three adjustable parameters related to entanglements: $N^{\text{ss}}_e$, $N^{\text{ss}}_e$, and $\sigma_{\text{ss}}$, which is the friction of the slip-links when sliding along the chain contour. The values of $N^{\text{ss}}_e$ and $N^{\text{ss}}_e$ can be adjusted to fit the slip-springs model to MD data. For reasons mentioned in ref 14, the $\sigma_{\text{ss}}$ value is fixed at 0.1$\epsilon_{\text{ss}}$, where $\epsilon_{\text{ss}}$ is the bead friction of the Rouse chain.

The stochastic equations of motion for both the beads and the slip-links can be derived from the Hamiltonian of the system. Disentanglement of the chain from a slip-link and re-entanglement with a slip-link are accomplished by the destruction and the creation of slip-links at the chain ends. Constraint release is included by approximating the entanglements as binary events. The total number of entanglements is held constant during the simulations. This is reasonable for a large number of chains at equilibrium; in practice, the large number translates to running the simulations with at least 10 chains that affect each other’s dynamics only through CR. Some of the mechanisms, like reptation, CR, and the sliding movement of the slip-links, can be individually deactivated to isolate their contribution to the relaxation of the chains. This is essential in the current work for separating out the CR effects on the segmental dynamics. The slip-springs equations of motion are solved numerically to the desired accuracy and with no uncontrolled approximations by means of Brownian dynamics simulations. Further details of the model can be found in previous publications.

By construction, the polymer chain in the slip-springs model is Gaussian on all length scales. This avoids the problem of incorrect chain statistics around the scale of the tube step length in the tube model. The polymer chains in the MD simulations are not Gaussian on short length scales. Therefore, to map the slip-springs results onto MD data over all length scales will require the inclusion of repulsive potential between the monomers in the chain. Because we are mainly interested in the slip-springs data on the time and length scales in the entanglement regime, the standard version of this model without repulsive potentials is used in the current work. The system parameters are set to be $N_e = 4$ and $N_e = 0.5$, respectively. It has been shown that to map the slip-springs simulation data obtained with these standard parameters to the tube model requires the usage of $N_e \approx 5.7$ beads per entanglement length. This means that our longest chains with $N_e = 512$ have $\sim 90$ entanglements.

4. RESULTS AND DISCUSSION

4.1. Molecular Dynamics. The monodisperse linear polymer melts studied in our MD simulations are listed in Table 1. In each case, the side length of the cubic simulation box is significantly larger than the end-to-end distance of the polymer chains, so there is no self-entanglement involved. According to the $N_e$ values estimated by primitive path analysis, the chain lengths we simulated correspond to a range of the number of entanglements per chain $Z \approx 2–15$. It is noted that different analysis methods can lead to different estimations of the $N_e$ and consequently $Z$ values. In the current work, these quantities are provided simply to give a guidance of the level of entanglements of the simulated chains. The uncertainties in their values have no qualitative effect on our discussions and conclusions. The MD simulation data are presented for a timespan of about eight decades, starting from one MD time step size $t = 0.012\tau$ to around $10^4\tau$ that is close to the Rouse time of the longest chains. Because the second-order segmental orientation autocorrelation functions, $C_2(t)$
and $C_b(t)$, are equivalent, as demonstrated in Appendix II and verified in our MD simulations, we will only present the simulation results on $C_b(t)$.

4.1.1. Monomer Mean Square Displacement. The monomer MSD has been popularly measured in experiments and computer simulations of entangled polymers.\textsuperscript{11,12,15,19,30,38} Analysis of this quantity was generally done by fitting the $g_1(t)$ curves to different power laws along the time axis and then comparing them with the Doi–Edwards predictions listed in eq 4. For melt systems composed of sufficiently long chains, one would expect that the $g_1(t > \tau)$ curves will display four distinctive relaxation regimes, each described by a well-defined scaling power. The characteristic times, that is, $\tau_e$, $\tau_R$, and $\tau_0$, can then be determined from the intersections between the power law fittings of different regimes. However, the limited chain length and time scale accessible to current molecular simulations using atomistic or fine-grained chain models still make it formidable to achieve such a clear monomer MSD curve containing all four well-defined regimes, especially for the reptation regime of $\tau_e$, the monomer displacement is clearly ballistic, following the scaling of $R(t)$ to the ballistic ($t^{1/2}$), free Rouse motion ($t^{1/4}$), and constrained Rouse ($t^{1/4}$) regimes.

The $g_1(t)$ curve of the longest chains in each case demonstrates a clear transition from the free Rouse to entanglement regime. The expected plateau-like region in $g_1(t)/t^{1/4}$ is approached at both chain stiffness. Power law fitting of $g_1(t) \propto t^\alpha$ to this entangled regime renders $\alpha = 0.25 \pm 0.02$ for the flexible chains and $\alpha = 0.28 \pm 0.02$ for the semi-flexible ones. We can also fit these $g_1(t)$ data in different regimes directly to the scaling laws given in eq 4 and get rough estimates of the tube model parameters. As demonstrated in Figure 1, this gives $\tau_e \approx 2950$ and correspondingly $N_e \approx 50$ for the flexible chains, whereas $\tau_e \approx 2300$ with $N_e \approx 22$ for the semi-flexible ones. We note, however, that these estimates are bound to be very approximate due to numerous assumptions of the tube model, and we list them just as a guidance and will not rely on them in the further discussion.

Another interesting, but less investigated, quantity for identifying entanglement effects is the ratio of the mean square displacements of the end and middle monomers of a chain, $g_{1,\text{end}}/g_{1,\text{mid}}$\textsuperscript{12,44}. For a long ideal Rouse chain, this ratio is 2 on intermediate time scales $\tau_0 < t < \tau_e$ because the effective time-dependent friction on the middle monomer is twice that of the end one. In other words, this is because the chain end has to drag one piece of chain with it, whereas the chain middle has to drag two attached chains. For entangled polymers, the motion of the central chain segment is strongly confined by topological constraints, while the chain ends can still move freely to explore new tube segments. The end monomer diffusion is restricted only by the fact that they are attached to the inner segments, which are still entangled. As a result, the ratio between the MSDs of the two types of monomers increases with enhanced
entanglement effects at intermediate times. The $g_{1,end}(t)/g_{1,mid}(t)$ curve is expected to reach a maximum around the Rouse time $\tau_R$. After that, all monomers start to move coherently, and this ratio starts to decay back to 1. The asymptotic height of the maximum is theoretically predicted to be $4\sqrt{2}$ for the Evans–Edwards model, where a polymer chain diffuses through a lattice of impenetrable obstacles.\textsuperscript{42,43} Our MD simulation data on $g_{1,end}(t)/g_{1,mid}(t)$ are presented in Figure 2. There the MSD data of the middle monomers, $g_{1,mid}(t)$, are taken directly from Figure 1, whereas the $g_{1,end}(t)$ results are calculated by averaging over the 10 outermost monomers of each chain, that is, five end monomers on each side of the chain. Different from Monte Carlo simulations using lattice models where the initial value of $g_{1,end}/g_{1,mid}$ relies on the model details,\textsuperscript{12,42} our MD result starts exactly from $g_{1,end}/g_{1,mid}=1$ in the ballistic regime. It then gradually increases to a maximum and starts to decay afterward. As expected, the height of the maximum is larger than two for all of the chain lengths we studied and increases with the chain length. This height value goes beyond four for the melts with the largest chain lengths. On very long time scales, typically several multiples of the terminal time of the entangled chains, the $g_{1,end}(t)/g_{1,mid}(t)$ ratio reduces to 1, as can be seen in Figure 2 from the results of the chains with few entanglements. The above observations are qualitatively consistent with the theoretical and related Monte Carlo simulation results obtained using the Evan–Edwards model.\textsuperscript{42} The large difference between the diffusion mobilities of the end and middle monomers also elucidates the necessity of excluding the contributions from the fast moving chain ends for the sake of comparing the monomer MSD data with the tube model predictions.

In Figures 3 and 4, we analyze the maximum value of the ratio $g_{1,end}/g_{1,mid}$ and the time $t_{\text{max}}$ at which it occurs. To improve understanding, we also include results on the same quantities obtained from slip-springs simulations with and without CR, tube model simulations without CR, and one extra set of MD simulations with the bending potential strength $k_b = 3\epsilon$. The tube model simulations are described in our previous publications,\textsuperscript{15,44} in which the curvilinear motion of an entangled linear polymer is represented by the diffusion of a 1-D Rouse chain along a 3D random walk with the step size equal to that of the tube Kuhn step $a$. To put all of the models on the same graph, we plot them as a function of $Z^{-1/2}$, where $Z$ is the approximate number of entanglements for the MD, slip-springs, and tube simulation models.

![Figure 2](image-url)  
**Figure 2.** MD results on the ratio of the mean square displacements of the end and middle monomers, $g_{1,end}(t)/g_{1,mid}(t)$, of the flexible (a) and semiflexible (b) chains. The monomer MSD data in Figure 1 are used as $g_{1,mid}(t)$ of the middle monomers. The dotted horizontal line refers to the Rouse model prediction of $g_{1,end}/g_{1,mid} = 2$ in the intermediate time regime.

![Figure 3](image-url)  
**Figure 3.** Maximum of the ratio $g_{1,end}/g_{1,mid}$ as a function of $Z^{-1/2}$ where $Z$ is the approximate number of entanglements for the MD, slip-springs, and tube simulation models.

![Figure 4](image-url)  
**Figure 4.** Time at the maximum of the ratio $g_{1,end}/g_{1,mid}$ normalized by the approximate Rouse time $\tau_R$, as a function of $Z^{-1/2}$ for the MD, slip-springs and tube simulation models.
then asymptotically approaches theoretical prediction $4\sqrt{2}$. This graph illustrates that the convergence is very slow; that is, first-order corrections for finite $Z$ are proportional to $Z^{-1/2}$, typical for the tube model. $^{32}$ Figure 4 shows that the maximum of $g_{L_{\text{end}}/L_{\text{mid}}}$ is achieved around Rouse time $\tau_R$, and the results of tube model simulations, slip-springs with CR and MD of flexible chains, show the similar $Z$ dependence, that is, increasing with $Z$ at small number of entanglements but decreasing at $Z > 10$. We note, however, that MD results for the semiflexible chains with $k_b = 3$ show different $Z$ dependence at small $Z$, which is probably related to the deviations from the random walk statistics on the length scale of entanglement.

4.1.2. Segmental Orientation Autocorrelation Functions. Figures 5 and 6 present the MD simulation results on the orientation autocorrelation functions, $C_1(t)$ and $C_2(t)$, of the unit bond vectors, $\mathbf{u}_i = (r_{i+1} - r_i)/(r_{i+1} - r_i)$, of different melt systems. The results are obtained by averaging over either the whole chain (Figure 5) or only the central part of the chain (Figure 6). The two $C_1(t)$ (or two $C_2(t)$) curves of each system, calculated using these two different averaging methods, start by sitting on top of each other at early times but separate later by showing different decay rates. At a given time $t$, the discrepancy between the two sets of data decreases with the increase in the chain length. As the number of entanglements per chain reaches $Z \approx 15$, this difference becomes negligible below $\tau_c$ (not shown). Therefore, the asymptotic or envelope curves of $C_n(t < \tau_c)$ are well-defined by that of the longest chains at each chain stiffness, independent of the averaging scheme.

The situation is very different on time scales $t > \tau_c$. We can first look at the $C_1(t)$ data of the chains with the highest length in each case. The power law exponent $\alpha$ given by the $C_1(t) \propto t^{\alpha}$ fitting in the entanglement regime, is found to be significantly larger in Figure 5 than that of the same melt system in Figure 6. This is further demonstrated in the inset of Figure 5a for the flexible chains with $N = 1000$. The $\alpha \approx 0.31$ value of these chains obtained by averaging over all bonds is rather close to those reported by NMR measurements$^{10,23}$ and Monte Carlo simulations$^{12}$ using linear polymers of similar number of entanglements per chain. There the whole chain averaging scheme was applied. The expected $\alpha = 1/4$ value was approached in Figure 6 by only considering the central chain segments, consistent with the $g_1(t)$ results in Figure 1. This again reflects the importance of ruling out the chain end contributions when comparing results obtained from limited chain lengths with the tube theory predictions made in the long chain limit. Therefore, all data analyses in the rest of this Article will be focused on the central parts of the linear chains.

Because the MD simulation data obtained from the melt systems with the highest chain lengths construct the envelope curves for all of the dynamic quantities we measured in this work, our following discussions on the segmental relaxation dynamics will be primarily based on these two representative samples. In the flexible chain case with $N = 1000$, the $C_n(t)$ results are averaged over the central 100 bonds, whereas in the
semiflexible case with \( N = 350 \) the averages are taken over the central 50 bonds. In the time window covered by our MD runs, these correlation functions follow exactly the same time-dependent behavior as those obtained by averaging over the central 10 bonds but show smaller statistical errors.

**Unentangled Regimes.** The very short time scales correspond to the ballistic and monomer diffusion regimes. Figure 7 shows that the third power relation of \( C_2(t) = C(t)^3 \) (eq 11) holds up to the time scale of \( t \approx 10 \tau_r \), about two decades in time beyond the ballistic region. After that, the rotation angle \( \theta(t) \) becomes significant. Recent MD simulations of unentangled polymer melts showed qualitatively similar results, although using a different chain model.25

The segmental reorientation dynamics transfers to the Rouse diffusion behavior on larger time scales. The Rouse model predicts a scaling relation of \( C_2(t) \approx C(t)^2 \) (eq 13), which is verified numerically in Figure 7. There the \( C(t)^2 \) data have been multiplied by a numerical coefficient \( b_1 \) for quantitatively matching the \( C_2(t) \) results. The \( b_1 \) values used in Figure 7 are 0.25 for the flexible chains and 0.56 for the semiflexible chains, respectively, both smaller than the 0.85 value predicted for ideal Rouse chains in Appendix II. This is understandable from the fact that at earlier times the second-order orientation correlation function of the segmental vector with unit length, \( C_2(t) \), decays in a third power of the first-order orientation correlation function, \( C(t)^3 \), rather than in a second power of \( C(t)^2 \). As a result, the value of \( C_2(t) \) is always smaller than \( C(t)^2 \) at any given time \( t > 0 \).

Figure 7 also illustrates that the Rouse regime in the segmental reorientation dynamics can be conveniently and reliably determined as the time region where \( C_2(t) \approx C(t)^2 \). This regime is otherwise hard to define using the power law scaling because the ideal Rouse power laws of \( C_2(t) \approx \tau^{-1/2} \) and \( C(t) \approx t^{-1} \) have not been observed in melts of real polymers, mostly attributed to the reduced number of Rouse modes caused by chain local stiffness. Such a deviation from the Rouse predictions is demonstrated in Figures 5 and 6, where we plot the power law fittings of \( C_2(t) \approx \tau^{-\alpha} \) to the Rouse regime defined using the \( C_2(t) \propto C(t)^3 \) relation. The obtained \( \alpha \) values are all smaller than the corresponding Rouse values. The enhanced chain stiffness effect is clearly reflected in the smaller exponent values (\( \alpha \approx 0.31 \) and 0.62, respectively) obtained from the semiflexible chains than those (\( \alpha \approx 0.41 \) and 0.86) from the flexible chains. In the later case, the \( C_2 \) \( \sim t^{-0.86} \) power is very close to the NMR result of \( C_2 \approx t^{-0.85} \) found for linear PB melts, implying that the flexible bead–spring chain model can be used to mimic qualitatively the real polymers typically measured in recent NMR experiments.22,23

**Entangled Regime.** In Figure 6, the first-order orientation autocorrelation function of the unit bond vectors, \( C_1(t) \), shows a clear crossover from the free Rouse to the entanglement regime and subsequently reaches a plateau-like region in the \( C_1(t)^{1/4} \) plot. At each chain stiffness, the onset of the plateau region occurs on roughly the same time scale as that of the corresponding \( g_2(t)/t^{1/4} \) curve in Figure 1. Direct power law fitting of \( C_1(t) \approx \tau^{-\alpha} \) for \( t > 10^3 \tau_r \) yields the exponents of \( \alpha = 0.25 \pm 0.02 \) for the flexible chains and \( \alpha = 0.28 \pm 0.02 \) for the semiflexible ones, both in good agreement with the power laws of \( g_2(t) \) in the same regime.

As discussed above, the second-order orientation autocorrelation function, \( C_2(t) \), decays much faster than its first-order counterpart in the unentangled regime. Consequently, this function possesses much smaller values in the entanglement regime than that of \( C_1(t) \). At the entanglement time \( \tau_e \) estimated from the \( g_1(t) \) data, its value is found to be \( C_2(\tau_e) \approx 4.1 \times 10^{-4} \) for the flexible chains, which is not far from the NMR data measured in various polymer species,22 and 1.26 \( \times 10^{-2} \) for the semiflexible chains, respectively. On time scales \( t > \tau_e \) the \( C_2 \) of the semiflexible chains varies with time rather smoothly due to the relatively strong signals, whereas the data points of the flexible chains become very scattered and can hardly be used for any scaling analysis. Using the former case as an example, Figure 6b shows that the decaying rate of the \( C_2(t) \) function slows down after \( \tau_e \) but the plateau-like region in \( C_2(t)^{1/4} \), as predicted by the RTO argument (eq 16), is not evidently reached even one decade after the onset time of the plateau in \( C_1(t)^{1/4} \). The prolonged crossover of the second-order orientation correlation function from the free Rouse to well-entangled behavior can also be seen in Figure 7b where the \( C_2(t) \) and rescaled \( C_1(t) \) curves begin to match each other on the time scale \( t \sim 10^3 \tau_r \gg \tau_e \). This phenomenon will be addressed in more detail in the following subsections.

The \( C_1(t) \) results presented in Figures 5 and 6 are calculated using the configuration frames recorded at a fixed time interval of 60\( \tau_r \) or every 5000 MD time steps. The poor statistics in the \( C_1(t) \) data of the flexible chains imply that much denser sampling is still needed to get accurate results of these second-order bond vector correlation functions. This situation is similar to measuring the stress relaxation modulus in computer simulations where the stress has to be calculated at every time step to obtain a high signal-to-noise ratio.30 One effective
A way of doing so is to apply the recently developed multiple-tau correlator algorithm to calculate the time correlation functions on the fly.\textsuperscript{40,45,46} We notice that in the entanglement regime the polymer dynamics is dominated by topological constraints, which confine the chain diffusion to a tube-like region with the characteristic tube diameter \(a (\propto N_e^{1/2} b)\). As a consequence, the decay of the orientation autocorrelation functions of all chain segments, whose lengths are much smaller than the entanglement length \(N_e\), should follow the same time-dependent behavior at \(t > \tau_e\). It thus means that we can manage to improve the statistics of the \(C_n(t)\) results by using coarse-grained chain segments to average out the fast fluctuations effectively on small length scales without losing any qualitative conclusions at larger length and time scales. This way we can also make full usage of the recorded trajectories that were generated over a substantial number of computer hours.

**Coarse-Graining.** We apply two different coarse-graining schemes to calculate the segmental orientation autocorrelation functions. In the first scheme, noted as \(UVm\), we calculate \(C_{nm}(t)\) of the vectors linking monomers \(m\) bonds apart, that is, \(u_{nm} = (r_{mm} - r_m)/r_{mm} - r_1\). Obviously, \(m = 1\) corresponds to the unit bond vectors considered in Figure 6. The second scheme is termed as \(CGm\), in which we subdivide the linear chain into \(N/m\) segments or blobs, each containing \(m\) monomers. The center of mass of the \(i\)th blob has the coordinate of

\[
r_{i}^{CG} = \frac{1}{m} \sum_{j=m(i-1)+1}^{mi} r_j
\]

The orientation correlation functions are then calculated for the vectors linking the centers of two adjacent blobs, \(u_{CG} = (r_{CG} - r_i)/r_{CG} - r_{CG}\). In both coarse-graining methods, the lengths of the segmental orientation vectors are normalized to unity. Therefore, the geometric argument on the equivalence of the two second-order orientation autocorrelation functions, \(C_{n}(t) = C_{n}(t)\), as proven in Appendix I, will still apply.

Figure 8 presents the \(C_{n}(t)\) results calculated at different levels of coarse-graining for the two representative melt systems. For each system, the individual calculations are performed using the same central sections of the chains, namely, the middle 100 chemical bonds of the flexible chains of length \(N = 1000\) and the middle 50 bonds of the semiflexible ones with \(N = 350\), same as done in Figure 6. The results are only shown for the free Rouse and entanglement regimes for clarity. Because the coarse-graining process effectively smears out the contributions from the fast bond fluctuations on short time scales, all \(C_n(t)\) data obtained at the coarse-graining level \(m > 1\) demonstrate slower decaying rates in the Rouse regime than those of the unit bond vectors (Figure 6). Taking the melt of flexible chains as an example, when fitting the \(UVm\) data presented in Figure 8a to the power law of \(C_{n}(t) \sim t^{-\alpha}\) in the Rouse regime (fitting not shown), the exponent is found to decrease continuously from \(\alpha \approx 0.41\) at \(m = 1\) to around \(0.39\) at \(m = 3\) and \(0.38\) at \(m = 5\). Correspondingly, the exponent of \(C_{n}(t)\) in the same regime drops from \(\alpha \approx 0.86\) at \(m = 1\) to around \(0.82\) at \(m = 3\) and \(0.80\) at \(m = 5\). The similar trend has been observed in the \(CGm\) results as well as in the melt of semiflexible chains. For the \(CGm\) calculations, we present only the \(CG5\) data in Figure 8 for clarity. Because the \(CG5\) scheme has a relatively higher level of coarse-graining than the \(UV5\) method, the resulted \(C_n(t)\) curves also show somewhat lower scaling powers in the Rouse regime, that is, \(\alpha \approx 0.36\) for \(C_{5}(t)\) and 0.76 for \(C_{5}(t)\), than those given above for \(UV5\).

Comparison of the power laws of the \(C_n(t)\) functions in the Rouse regime also reveals that the Rouse-like scaling relation of \(C_{n}(t) \approx b_1 C_{1}(t)^2\) is well-preserved in the coarse-graining process. The value of \(b_1\) is, however, brought closer to the ideal Rouse chain value. This can be attributed to the averaging out of the early time fast bond fluctuations. Therefore, before entering the Rouse regime, the numerical difference between \(C_{1}(t)\) and \(C_{5}(t)\) of the coarse-grained segmental vectors is much smaller than that of the unit bond vectors. Depending on the levels of coarse-graining, the \(b_1\) value obtained from the melt of flexible chains is found to increase from 0.25 for the unit bond vectors (Figure 7a) to 0.57 for \(UV5\), 0.64 for \(CG5\), and 0.75 for \(CG10\), respectively. Similarly, this value changes from 0.56 for \(UV1\) (Figure 7b) to 0.77 for \(UV5\), 0.81 for \(CG5\), and about 0.85 for \(CG10\) in the melt of semiflexible chains. This is in perfect agreement with the Rouse model prediction of \(b_1 \approx 0.85\), as shown in Appendix II.

On time scales \(t > \tau_e\) all of the \(C_{n}(t)\) curves obtained using different coarse-graining methods become parallel to each other and follow the same power law as that of the unit bond vectors. This is expected for the segmental relaxation dynamics in the entangled regime, as the segmental lengths used in the calculations are considerably smaller than \(N_e\). As shown in Figure 8, the height of the plateau-like region in the \(C_{1}(t)^{1/4}\) curve relies on the decaying history of \(C_{1}(t)\) on previous time scales and thus increases with increasing level of coarse-graining.
The $C_1(t)$ data behave similarly to their first-order counterparts. The stronger signals resulted from coarse-graining make it easier to visualize the significantly extended crossover region in $C_1(t)$ from the free Rouse to well-entangled regimes, especially for the melts of flexible chains. At both chain stiffness values, the level-off of the $C_2(t)^{1/4}$ curves is found to become evident at $t \sim 10^5 \tau$. Power fitting of $C_2(t) \sim t^{-\alpha}$ to data points beyond this time yields the exponent $\alpha = 0.27 \pm 0.03$ for the flexible chains and $\alpha = 0.29 \pm 0.03$ for the semiflexible chains, both approaching the predicted $1/4$ power law. These results also support the relationship of $C_1(t) \sim C_2(t)$ in the entanglement regime, as predicted in eq 16, but on time scales much larger than the entanglement time $r_e$ determined from $g_1(t)$ and $C_1(t)$.

In principle, one can also quantify the crossover behavior of the $C_n(t)$ functions by finding the intersections of their power law fittings in the free Rouse and entanglement regimes, as has been done in Figure 1 for determining the entanglement time $r_e$. The intersection point corresponding to the $C_0(t)$ function will apparently shift to larger time scale in comparison with that of $C_1(t)$. However, because the power laws fitted for these segmental orientation correlation functions do not exactly follow the theoretical predictions in both relaxation regimes (especially in the Rouse regime), the physical interpretation of their intersection points is not straightforward. The problem is further complicated by the change of the power laws in the Rouse regime when using different levels of coarse-graining. We thus leave this quantity for later study.

It is noted that our MD results on the power law exponents ($\alpha = 0.27 \pm 0.03$ for $k_b = 0$ and $0.29 \pm 0.03$ for $k_b = 2$, respectively) of $C_0(t)$ in the entanglement regime are very close to the experimental value of $\alpha \approx 0.29$ obtained in NMR measurements of linear polymer melts with chain length up to $1100$ entanglements, although the chain lengths studied in our simulations are only $\sim 15$ entanglements long. However, as discussed above, our calculations of the segmental dynamic quantities have been focused on the central sections of the polymer chains, which effectively excludes the contributions from the fast moving chain ends. Therefore, our simulation results should yield power laws much closer to those obtained experimentally for very long chains. Moreover, it is also important to identify the right time scale at which the dynamic observable of interest approaches its asymptotic behavior. For $C_1(t)$, this time scale is more than one decade later than that of other observables such as $C_i(t)$ and $g_1(t)$. If the power law fitting of $C_1(t) \sim t^{-\alpha}$ is applied to the same time window (slightly after $r_e$) as that used for fitting the $C_1(t)$ and $g_1(t)$ functions, a much higher $\alpha$ value will be wrongly obtained.

Return to Origin. The most straightforward way of examining the RTO argument is to plot the product of the segmental orientation autocorrelation functions, $C_n(t)$, and the mean square segmental displacement, $g_1(t)$. The tube theory predicts that this quantity should be constant in both entangled regimes, that is, for all times between entanglement time and reptation time

$$C_n(t)g_1(t) = \text{const, } r_e < t < r_d \quad (20)$$

In other words, although $g_1(t)$ changes slope at the Rouse time $r_o$, the product of $C_n(t)g_1(t)$ should not change. In addition, when referring to the Rouse model predictions of $g_1(t) \sim t^{-1/2}$ (eq 4) and $C_1(t) \sim t^{-1/4}$ (eq 12), it also follows that $C_1(t)g_1(t) = \text{const}$ in the free Rouse regime ($r_o < t < r_e$), supposing that the linear polymers behave as ideal Rouse chains. The constant can, however, be different from the constant in entangled regime.

The MD results on $C_n(t)g_1(t)$ are presented in Figure 9. In the Rouse regime, the time scaling of $C_1(t)$ deviates from the ideal Rouse chain behavior, and thus $C_1(t)g_1(t)$ grows with time, rather than being a constant. After the entanglement time $r_e$, all of the $C_n(t)g_1(t)$ curves, regardless of the chain stiffness, become completely flat, which is in strong support of the RTO concept in eq 20. The significance of this result also lies in the fact that even though the power laws of both $g_1(t)$ and $C_1(t)$ of the semiflexible chains somewhat deviate from the ideal $1/4$ value, their product remains constant. The prediction of eq 20 is also supported by the $C_1(t)g_1(t)$ data, where a plateau-like region is also approached, although on much larger time scales. Note that the power law fittings to these plateau regions, as depicted in Figure 9, have relatively large error bars ($\pm 0.03$) due to the limited time window accessed in MD simulations. Extension of the simulation runs to larger time scales is realized in our following slip-springs model simulations.

4.2. Slip-Springs Model. We start by mapping our MD simulations onto the slip-springs model using two adjustable parameters: $N_0$ is the number of MD monomers corresponding to one bead in slip-springs model and $r^\text{MD}_\text{ss}$, which is the ratio of time units in both simulations (i.e., slip-springs time will be multiplied by $r^\text{MD}_\text{ss}$ to get the MD time). We obtain these two parameters from fitting the MD data on the MSDs of the middle monomers of the flexible chains ($k_b = 0$) with the slip-springs model. To this end, we performed a series of 20 slip-springs simulations with $N^\text{ss}$ ranging from 10 to 256 and use RepTate software to interpolate between them. The results depend on course of the parameters of the slip-springs model.
Figure 10 shows the resulting fits in two representations. The left panel shows normal representation with nine orders of magnitude along the vertical axis, which makes it very difficult to see any features. The right panel shows the same data divided by $\sqrt{t^{1/2}}$. This simple transformation reduces the vertical axis scale to 1.5 decades and makes comparison more effective and easy. It is this right panel representation, which we use for fitting.

The right panel in Figure 10 shows slip-springs fits with two levels of coarse graining: $N_{ss}^c = 4$, $N_{ss}^m = 0.5$, which are the standard settings, and two times less coarse-grained parameters with $N_{ss}^c = 8$, $N_{ss}^m = 1$. The fitting parameters are $r_{ss} = 3370$, $N_0 = 9.74$ for the standard settings and $r_{ss} = 840$, $N_0 = 4.87$ for the more fine-grained ones. Notice that the fitting parameters scale perfectly with the level of coarse graining, that is, two times more coarse simulations have four times longer elementary time and two times more MD monomers per one slip-springs bead. (See refs 14 and 31 for detailed discussion.) It is apparent that the more finegrained settings fit MD data better at early times, whereas the coarser simulations agree with them perfectly at later times but are exactly eight times cheaper. Therefore, we used finegrained simulations to get the accurate parameters and the coarser simulations for further discussion. We also notice that for standard settings $r_{ss}^MD = 3700$, $N_0 = 10$ give almost indistinguishable results.

We now simulate much longer chains with slip-springs model (corresponding to up to 5000 MD monomers) to understand different regimes and the role of constraint release on the segmental relaxation. Figure 11 shows slip-springs results averaging over the central bonds of the chain. We see that both $C_1(t)^{1/4}$ and $C_2(t)^{1/4}$ show an extended plateau. In fact, $C_1(t)^{1/4}$ even shows a slightly positive slope of 0.05, corresponding to $C_1 \sim t^{0.22}$. This is surprising feature of the slip-springs model, which probably means that the Rouse model for 1-D motion inside the tube is not completely adequate in this case. The effect is, however, very small. It is also apparent that after the Rouse time the slope of both functions changes to $C_1 \sim t^{-0.5}$ in agreement with the tube theory expectations. However, one needs very long chains to see this second regime clearly (even without CR). The important thing to notice is that $C_2(t)$ attains a plateau later than $C_1(t)$, similarly to MD observations.

To elucidate the role of constraint release, we compare simulations with and without CR in Figure 12. The results are very interesting: the first-order segmental orientation correlation function $C_1$ is almost unaffected by CR, whereas the second-order correlation $C_2$ is affected significantly and shows about two times faster relaxation at the terminal time with CR. The situation is similar to contrasting the end-to-end vector relaxation with the stress (or orientation tensor) relaxations. Therefore, CR makes it more difficult to observe a plateau in the $C_2(t)$ correlation function, which explains NMR findings of refs 10 and 22.

The clearest picture illuminating the role of CR is obtained from the return to origin plot Figure 13. We see that the product of the monomer mean square displacement $g_1(t)$ and $C_1(t)$ shows a perfect plateau in all regimes until the terminal time, and it is not affected by CR. In contrast, the same product with $C_2(t)$ attains a plateau only at late times and only without CR. The constraint release leads to a slope of $C_2(t)g_1(t)$, which persists until the terminal time. This slope seems to approach 0 asymptotically with increasing number of monomers $N^*$ but does not
so very slowly. We note that here we only analyze the middle monomer behavior. If all monomers are averaged over, then the results will be less clear, and we expect a significantly higher slope.

Finally, we attempt a direct comparison between slip-springs and MD simulations for the product of \( C_n(t)g(t) \). To do that we multiply the slip-springs time scale by \( \tau_{\text{ss}} = 3370 \) and the vertical scale by \( N_0b^2 \), where \( N_0 = 9.74 \) is the number of MD monomers in one slip-springs bead and \( b^2 = R_o^2/N = 1.75 \) is the statistical segment in MD simulations of flexible chains. As shown in Figure 14, the amplitude of the results strongly depends on the level of coarse graining. Moreover, the dependence on the level of coarse graining is not universal because the chains on small length scales do not obey perfect random walk statistics. Therefore, our results agree well, but only within a model-dependent vertical shift. Nevertheless, the results for \( C_n(t) \) agree quite well with coarse-graining 10 (CG10, stars), which is close to our level of coarse-graining \( N_o = 9.74 \), and results for \( C_1(t) \) are close to UV10 (triangles) method of coarse graining, which might be more suitable for \( C_1(t) \) correlation function. We note that all coarse-graining results are exactly proportional to each other, and up to a vertical shift our slip-springs data for \( N_o = 128 \) are in a very good agreement with the MD results for times larger than 1000\( \tau \), which is the same time when the mean squared displacement starts to agree (Figure 10).

5. CONCLUSIONS

The combination of MD and slip-springs simulations allows the complete range of polymer dynamics, from ballistic monomer motions all the way to complete relaxation by reptation to be accessed for polymers with up to 90 entanglements. Moreover, by averaging segmental dynamics over only the central part of the chain, scaling laws characteristic of much longer chains (up to around 1000 entanglements) can be effectively accessed. These simulations provide a rather comprehensive picture of relaxation dynamics, including Rouse-like, and reptation regimes, and allow the role of constraint release to be assessed. The simulation results are in agreement with available experimental data and provide a more complete picture than is possible from the experimental data alone.

This work was initiated, in part, because of new NMR experiments, which reported that the segmental orientation correlation function \( C_1(t) \) does not show the tube-model predicted scaling of \( t^{-0.25} \) in the constrained Rouse regime even for the polymers chain length \( Z > 1000 \) entanglements but instead decreases with slightly faster rate \( t^{-0.29} \) In the present Article, we employed MD and slip-springs simulations to effectively separate contributions from different relaxation mechanisms and so revealed that there are three principal reasons for such delayed transition to asymptotic behavior predicted by the tube theory:

- The tube theory scaling predictions focus on the middle monomers, whereas experiments are naturally averaged over all monomers. As illustrated in Figures 5 and 6, this makes a large difference because the end monomers relax faster than the middle ones.
- The second-order segmental orientation correlation function \( C_2(t) \) shows an extended transition regime that goes well beyond the entanglement time \( \tau_e \); therefore, the expected slope \(-1/4\) starts much (by more than one decade) later than that observed in the first-order correlation function \( C_1(t) \).
- Constraint release further decreases the scaling exponent at later times, making it closer to experimentally observed exponent \(-0.29\).

These findings suggest that the asymptotic behavior of \( C_2(t) \) can be expected in experimental measurements using long polymer chains with tailored architectures, where signals can be collected solely from central sections. To provide quantitative descriptions of the segmental relaxation curves obtained in NMR experiments and computer simulations from polymers of finite lengths, tube theories still need to be refined by taking a thorough consideration of the CR and CLF effects.

We have also demonstrated that the return to origin argument is valid for both the first- and second-order segmental orientation correlation functions. However, it holds much better for \( C_1(t) \) than for \( C_2(t) \), which is affected by CR and extended transition zone around \( \tau_e \).

APPENDIX I: EQUIVALENCE OF THE SECOND-ORDER ORIENTATION AUTOCORRELATION FUNCTIONS OF UNIT SEGMENTAL VECTORS

The two second-order segmental orientation correlation functions, \( C_2(t) \) and \( C_1(t) \), as defined in eqs 6 and 7 using the unit segmental orientation vector, can be shown to be equivalent in equilibrium systems due to the spatial symmetry. For a unit segmental vector, \( \mathbf{u} \), the cosine of its orientation angle relative to one of the Cartesian coordinates \( \alpha (x, y, \text{or} \ z) \)
is simply $\cos \theta = u_i$. Equation 7 can then be rewritten as

$$C_2(t) = 5\langle P_2(u_i(t))P_2(u_i(0)) \rangle$$

$$= \frac{45}{4} \langle u_i^2(t)u_i^2(0) \rangle - \frac{5}{4} \tag{A1-1}$$

where $\langle u_i^2(0) \rangle = 1/3$ has been applied based on the equivalence of the three Cartesian axes. Similarly, eq 6 can be expanded as

$$C_2(t) = \frac{3}{2} \langle \langle u(t)u(0) \rangle^2 \rangle - \frac{1}{2} = \frac{9}{2} \langle u_i^2(t)u_i^2(0) \rangle$$

$$+ 2\langle u_i(t)u_i(0)u_i(t)u_i(0) \rangle \rangle_{u \neq \beta} - \frac{1}{2} \tag{A1-2}$$

The ensemble averages in eq A1-2 are invariant under the rotation of the reference coordinate frame. Rotating the Cartesian system $(\alpha, \beta, \gamma)$ around the $\gamma$ axis clockwise by 45° to $(\alpha', \beta', \gamma)$, the components of the unit vector $u$ in the new frame are given as $u_{\alpha'} = (u_\alpha + u_\beta)/\sqrt{2}$ and $u_{\beta'} = (-u_\alpha + u_\beta)/\sqrt{2}$. Using the rotational invariance, the cross term in the second step of eq A1-2 is given by

$$\langle u_i(t)u_i(0)u_i(t)u_i(0) \rangle = \langle u_i(t)u_i(0)u_\beta(t)u_\beta(0) \rangle$$

$$= \frac{1}{2} (\langle u_i^2(t)u_i^2(0) \rangle - \langle u_i^2(t)u_i^2(0) \rangle) \tag{A1-3}$$

Substituting this expression into eq A1-2 and then applying the relations $\langle u_i^2(t)u_i^2(0) \rangle = \langle u_i^2(t)u_i^2(0) \rangle$ and $\langle u_i^2(t)u_i^2(0) \rangle = 1$, one directly gets

$$C_2(t) = \frac{45}{4} \langle u_i^2(t)u_i^2(0) \rangle - \frac{5}{4} = C_2(t) \tag{A1-4}$$

### APPENDIX II: SEGMENTAL ORIENTATION AUTOCORRELATION FUNCTIONS OF A ROUSE CHAIN

We consider a Rouse chain with $N+1$ beads located at positions $\{R_i\}_{i=0}^{N}$; the vector along its $i$th bond is given by $b_i = (R_{i+1} - R_i)$. There are two ways of defining segment orientation functions $C_n(t)$. The definition used in the main text leads to the nonlinear averages and therefore is difficult to calculate analytically. If one normalizes the bond vector by the statistical segment $b = \langle (R_{i+1} - R_i)^2 \rangle^{1/2}$ instead of the instantaneous bond lengths, it becomes straightforward to calculate $C_n(t)$ exactly using the Rouse modes. We shall distinguish correlation functions defined this way by the superscript “$R$”. Below we perform short simulation of the Rouse chains and show that $C_n^R(t)$ normalized by the statistical segment follows exact analytical results, whereas the correlation functions $C_n(t)$ defined in the main text are exactly proportional to the $C_n^R(t)$ after the bond relaxation time.

The first- and second-order correlation functions of the Rouse bond vectors are defined by, respectively

$$C_1^R(t) = \frac{1}{b^2} \langle b(t) \cdot b(0) \rangle \tag{A2-1}$$

$$C_2^R(t) = \frac{1}{4} \left( \frac{3}{b^2} \langle |b(t) - b(0)|^2 \rangle - 1 \right)$$

$$= 9 \langle b_i^R(t)b_i^R(0)b_i^R(0)b_i^R(0) \rangle \tag{A2-2}$$

The normalization factor $1/4$ in eq A2-2 originates from the fact that the fourth moment of the Rouse bond length is $\langle (b_i^R)^2 \rangle = 5b^4/3$ owing to the Gaussian distribution of $b_i^R$.

The first-order bond vector autocorrelation function of the Rouse chain can be found in the Doi and Edwards book. The second order correlation function $C_2^R(t)$ can be rewritten as

$$C_2^R(t) = \frac{1}{b^2} \left( \frac{3}{b^2} \sum_{i<\beta<1} \langle b_i^R(t)b_i^R(0)b_\beta^R(t)b_\beta^R(0) \rangle - 1 \right)$$

$$= \frac{1}{4} \left( \frac{9}{b^2} \langle (b_i^R(t)b_i^R(0))^2 \rangle + \langle b_i^R(0)b_i^R(0) \rangle - 1 \right)$$

$$= \left( \frac{3}{b^2} \right)^2 \langle b_i^R(t)b_i^R(0) \rangle^2$$

$$= C_1^R(t)^2 \tag{A2-6}$$

Figure 15 shows that simulation results for $C_1^R(t)$ (triangles) agree with eq A2-3 apart from the short times, where discreteness of the chain must be taken into account.
where the indexes $\alpha, \beta = 1, 2, 3$ correspond to the three Cartesian coordinates $x, y, z$. The second step in eq A2-6 was obtained by applying the formula

$$
\langle abcd \rangle = \langle ab \rangle \langle cd \rangle + \langle ac \rangle \langle bd \rangle + \langle ad \rangle \langle bc \rangle
$$

(A2-7)

for the Gaussian process with zero mean as well as the statistical independence of the different components of the bond vector $<b^\alpha_R(t_1)b^\beta_R(t_2)> = <b^\alpha_R(t_1)> <b^\beta_R(t_2)>$ for arbitrary times $t_1$ and $t_2$. Finally, the ensemble average value of $<b^\alpha_R(t)b^\beta_R(0)> = b^\alpha b^\beta/3$ is applied in the third step. Figure 15 shows that indeed $C_{\alpha}^2(t) = (C_{\alpha}^0)^2/3$ (squares and red dashed line).

We find from simulations that the functions $C_{\alpha}(t)$ calculated by normalizing bond vectors by their instantaneous values become exactly proportional to the corresponding $C_{\alpha}^0(t)$ functions, as illustrated in Figure 15 with the prefactors given in the legend. In particular, it follows that Rouse model predicts that $C_{\alpha}(t) \approx 0.85C_{\alpha}^0(t)$. Derivation of these prefactors is left as a challenge to an interested reader.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: zuowei.wang@reading.ac.uk*

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Z.W.W. acknowledges the support from the Foundation of Open Projects of Beijing National Laboratory for Molecular Sciences. A.E.L. acknowledges the support from EPSRC grant EP/H016686/1. R.G.L. acknowledges support from NSF under grant DMR 0906587. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation (NSF).

**REFERENCES**