

Comparison of Friction Parametrization from Dynamics and Material Properties for a Coarse-Grained Polymer Melt

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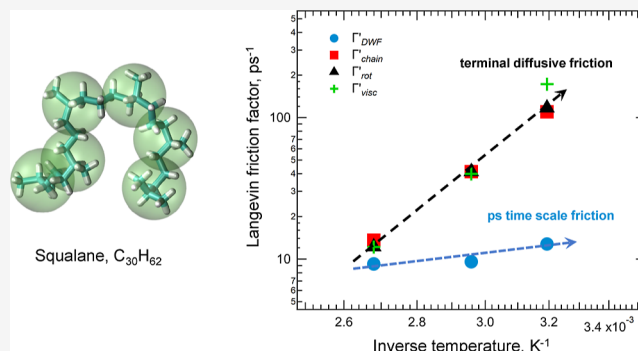


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ABSTRACT: In this work, we extend an approach to coarse-grained (CG) modeling for polymer melts in which the conservative potential is parametrized using the iterative Boltzmann inversion (IBI) method and the accelerated dynamics inherent to IBI are corrected using the dissipative Langevin thermostat with a single tunable friction parameter (*J. Chem. Phys.* **2021**, 154, 084114). Diffusive measures from picoseconds to nanoseconds are used to determine the Langevin friction factor to apply to the CG model to recover all-atom (AA) dynamics; the resulting friction factors are then compared for consistency. Here, we additionally parametrize the CG dynamics using a material property, the zero-shear viscosity, which we measure using the Green–Kubo (GK) method. Two materials are studied, squalane as a function of temperature and the same polystyrene oligomers previously studied as a function of chain length. For squalane, the friction derived from the long-time diffusive measures and the viscosity all strongly increase with decreasing temperature, showing an Arrhenius-like dependence, and remain consistent with each other over the entire temperature range. In contrast, the friction required for the picosecond diffusive measurement, the Debye–Waller factor, is somewhat lower than the friction from long-time measures and relatively insensitive to temperature. A time-dependent friction would be required to exactly reproduce the AA measurements during the caging transition connecting these two extremes over the entire timespan at this level of coarse-graining. For the polystyrene oligomers for which we previously characterized the diffusive friction, the viscosity-parametrized frictions are consistent with the diffusive measures for the smallest chain length. However, for the longer chains, we find different trends based on measurement method with friction derived from rotational diffusion remaining nearly constant, friction derived from translational diffusion showing a modestly increasing trend, and viscosity-derived friction showing a modest decreasing trend. This seems to indicate that there is some sensitivity of the friction measurement method for systems with increased relaxation times and that in particular, the unsteady dynamics of the individual parametrization schemes plays a role in this. Increased difficulty in applying the GK method with increasing relaxation time of the longer chain systems is also discussed. Overall, we find that when the material is in a high-temperature melt state and the viscosity measurement is reliable, the friction parametrization from the diffusive friction measures is consistent and the lower cost diffusive parametrization is a reliable means for modeling viscosity. Our data give insight into the time-dependent friction one might compute using a non-Markovian approach to enable the recovery of AA dynamics over a wider range of time scales than can be computed using a single friction.



1. INTRODUCTION

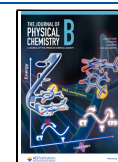
Coarse-graining methods enable computational access to the greater length and time scales inherent to polymers and related soft materials by grouping atoms associated with monomers or other chemical moieties into “coarse-grained” (CG) sites and then describing the physics by means of a potential parametrized for the coarse-grained description of the material. Grouping many atoms into larger units eliminates “fast” degrees of freedom whose length scales are small, thus enabling simulation of larger systems at longer time scales and at a reduced computational effort. While such models are able to preserve certain features, such as chemical specificity or viscoelastic properties, depending on the parametrization method, the penalty for this in a purely Hamiltonian

description of the material is some loss of essential physics due to the reduction in configurational entropy. In the realm of materials, this can result in numerous model defects, such as accelerated dynamics and a softer mechanical response arising from a reduction in frictional forces, loss of fluctuations associated with the fine-grained atomistic details, and loss of

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topological constraints. Repairing such defects entails a need to enhance the Hamiltonian description of the material with either auxiliary potentials or models that recover salient physics in an integrative fashion. Examples include time rescaling to match the CG temporal output to an all-atom (AA) reference system,^{1–8} modification of the pair potential to increase cohesive energy,^{6,9–15} methods in the realm of nonconservative (or dissipative) potentials to directly include friction and noise in coarse-grained molecular dynamics (MD) models,^{16–29} other dissipative models arising from nonequilibrium thermodynamic considerations,^{30–33} and the introduction of entanglements in slip-spring and related models to recover the diffusive dynamics of long polymer chains.^{34–37}

In our recent work,³⁸ we studied a CG method which combined a conservative potential derived from the iterative Boltzmann inversion (IBI) method^{39,40} with nonconservative forces for high-temperature polystyrene oligomer melts. We used Langevin dynamics, which introduces friction and random forces set by a scalar friction parameter, as our dissipative forces. This approach allows us to retain the AA distributions, in particular, the radial distribution function (rdf), while using the friction parameter for dynamic correction. The goal was to test an approach that is chemically specific, thermodynamically consistent,⁴¹ dynamically correct, and at the same time practically applied. We found that the required friction depends on the dynamic quantity being parametrized, with chain center of mass diffusion requiring the lowest friction, monomer diffusion requiring the highest friction, and rotational diffusion falling in between. The values also showed some dependence on chain length, and for the longest chains, they showed about 20% fluctuation about the mean.

Here, we follow-up on that work and study the parametrization of the Langevin friction parameter from material properties, specifically, the zero-shear viscosity, and compare with parametrization from dynamic measures utilized in our previous study.³⁸ The goal is to see how friction parametrization via material property characterization compares to the dynamic measures (which are also characterized) and also to look at the temperature dependence. A fundamental difference between the two is that the measurement of the diffusive properties is more closely related to the integral of the velocity autocorrelation function (VACF), while the viscosity is obtained via the integration of the stress autocorrelation function (SACF). Thus, the methods have different time scales²⁴ and also the friction is relatively more easy to parametrize via diffusive properties. So, exploring the consistency between the two methods is important to understand for theoretical and practical reasons.

The paper is organized as follows. First, we present the theoretical framework of our models, which include a description of our IBI algorithm and background theory on the generalized Langevin equation (GLE) and its relation to Langevin dynamics. In [Methods](#), we give pertinent details related to conducting our numerical simulations. We then present the results for two materials. First, we study squalane, a hydrocarbon for which there is a lot of material data at different temperatures. We characterize the temperature dependence of the monomeric, rotational, and center-of-mass chain friction using the same methods as we employed in our previous paper and additionally characterize the zero-shear viscosity using the Green–Kubo (GK) method. The temperature-dependent results give us key insights into the short- and

long-time diffusive scaling and the weaknesses inherent to a single friction approach. We then study the friction parametrization based on viscosity for the same polystyrene systems as we studied in our previous work and compare the results with the diffusive characterizations obtained there. Finally, we also discuss the time dependence of the friction needed for the CG model to exactly match the AA model. This gives insight into specific modeling regimes and benefits to be expected by the construction of a GLE type model to recover the time-dependent behavior.

2. METHODS

2.1. Theory. We presented our CG approach first in Johnson and Phelan Jr.,³⁸ here, we briefly review the pertinent steps. Inspired by statistical mechanics,¹⁶ we parametrize the conservative and dissipative portions of the CG force-field separately. The conservative part of the force-field is from the familiar IBI method.³⁹ We generate tabular potentials for bond, angle, and pair interactions for the CG model that reproduce target structural distributions, ϕ^{target} , computed from the AA system of interest mapped onto the desired CG sites. The initial guess for the CG potentials are obtained using these target structural distributions by $(U^{\text{cg}})^0 = -k_{\text{B}}T \ln(\phi^{\text{target}})$, where U and ϕ are the potential energy and corresponding structural distribution, k_{B} is the Boltzmann constant, T is the temperature, and the corresponding CG forces are $F^{\text{cg}} = -\nabla U^{\text{cg}}$. This initial force-field $(U^{\text{cg}})^0$ is improved by using this force-field to run a CG simulation, collecting the resulting structural distributions, and comparing the CG structural distributions ϕ^{cg} to ϕ^{target} to correct the CG force-field, by following

$$(U^{\text{cg}})^{n+1} = (U^{\text{cg}})^n - k_{\text{B}}T \ln\left(\frac{(\phi^{\text{cg}})^n}{\phi^{\text{target}}}\right) \quad (1)$$

for each iteration n . Iterative steps that involve first running CG simulations and then updating the force-field with [eq 1](#) continue until ϕ^{cg} adequately recovers ϕ^{target} . We utilize a custom implementation of IBI, the details of which are reported in the Supporting Information of ref 38. The IBI force-field is implemented as a tabular potential to preserve the structural distributions of the AA reference system. To correct for the speed up in dynamics relative to the AA representation that is characteristic of IBI force-fields, we next parametrize the dissipative forces.

Various governing equations have been used to describe CG models depending on the level of resolution and approximations applied.¹⁸ One such governing equation that enables the separation of conservative and dissipative forces is the generalized Langevin equation (GLE)

$$m_i \frac{d^2}{dt^2}(\mathbf{r}_i) = \mathbf{F}_i^{\text{c}} - \int_0^t \mathbf{v}_i(\tau) \zeta(t - \tau) d\tau + \mathbf{F}_i^{\text{B}} \quad (2)$$

which relates the motion of particle i (of mass m_i , position $\mathbf{r}_i$, and velocity $\mathbf{v}_i$) to conservative forces $\mathbf{F}_i^{\text{c}}$, a friction force containing a memory kernel $\zeta(t)$, and a random force $\mathbf{F}_i^{\text{B}}$. Here, $\mathbf{F}_i^{\text{c}} = -\nabla U_i^{\text{c}}$ is the gradient of the conservative potential generated using IBI. The first and second fluctuation–dissipation theorems are obeyed such that $\langle \mathbf{F}_i^{\text{B}}(t) \mathbf{v}_i(0) \rangle = 0$ and $\langle \mathbf{F}_i^{\text{B}}(t) \mathbf{F}_i^{\text{B}}(0) \rangle = 2k_{\text{B}}T \zeta(t) \mathbf{I}$, where $\mathbf{I}$ is the identity tensor. The integral in [eq 2](#) and the strength of the random force describe how the dissipative forces are impacted by the history

of the particle trajectory through a heat bath. The GLE approach is thus non-Markovian.

A simpler description of the dissipative forces can be made in the limit where the Markovian approximation is appropriate. In that case, the GLE simplifies to the Langevin equation where the heat bath responds infinitely quickly and retains no memory of the motion of the CG particle, given by

$$m_i \frac{d^2}{dt^2}(\mathbf{r}_i) = \mathbf{F}_i^c - \Gamma \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i^B(t) \quad (3)$$

where the integral over the memory kernel is replaced with Γ , a constant drag coefficient defined as $\Gamma = \int_0^\infty \zeta(t)dt$. Similarly, the strength of the random force $\mathbf{F}_i^B$ depends on Γ . The first and second fluctuation–dissipation theorems apply, as given by $\langle \mathbf{F}_i^B \rangle = 0$ and $\langle \mathbf{F}_i^B(t) \mathbf{F}_i^B(0) \rangle = 2k_B T \Gamma \delta(t) \mathbf{I}$, where $\delta(t)$ is the Dirac delta function.

Thus, our approach is to implement an IBI force-field as the conservative part of the Langevin equation and parametrize the dissipative forces using the Langevin friction factor Γ tuned to recover dynamic properties of interest of the AA reference system. In our prior work, we studied the consistency of Γ values required to match the target dynamics³⁸ and here we extend our study to the zero-shear viscosity.

2.2. Model System and Simulation Details. Our first model system is squalane in a liquid state at three different temperatures, 100 °C (373.15 K), 65 °C (338.15 K), and 40 °C (313.15 K), at atmospheric pressure. Squalane was selected for the availability of experimental data at a wide range of temperatures^{42–44} and prior simulation studies of dynamics and viscosity with squalane represented via a united atom force-field.^{45–48} Here, squalane allows for a study of the temperature dependence of the friction parametrization method we proposed previously.³⁸ We also revisit the model system we studied in ref 38: a linear, atactic polystyrene (PS) melt at high temperature. Specifically, we study three chain lengths, 11, 21, and 41 monomers per chain (PS11, PS21, and PS41, respectively), at 600 K and atmospheric pressure. PS was selected for its wide use in CG force-field development.^{6,11,12}

Our method for developing and testing the CG approach begins with atomistic reference simulations for two purposes: developing an IBI force-field and generating reference dynamics and viscosity data. We used the Assisted Model Building with Energy Refinement (AMBER) force-field for the AA systems (from Cornell et al.,⁵² see the [Supporting Information](#) of this work for the force-field values) and assigned charges via the Gasteiger algorithm.⁵³ Simulations were carried out utilizing the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code package.⁵⁴ We built, equilibrated, and cooled the systems to the target temperature and pressure according to the steps detailed in the [Supporting Information](#). All systems studied have periodic boundary conditions and are representative of a bulk melt sample. Dynamic properties including viscosity were calculated under isothermal, constant volume (NVT) conditions using a Nosé–Hoover (NH) thermostat with a time constant of 0.1 ps and a time step of 1 fs.

A coarse-grain model corresponding to approximately one CG per monomer was applied to the AA systems, and an IBI force-field is developed with tabular bond, angle, and pair potentials. One CG type was used for each system, with the CG located at the center of mass (COM) of the atoms it replaces. Squalane is represented as 5 carbon atoms per CG (4

backbone carbons and a methyl group in each CG, approximately 15 atoms) such that the squalane AA representation can be divided into six CG sites, [Figure 1a](#).

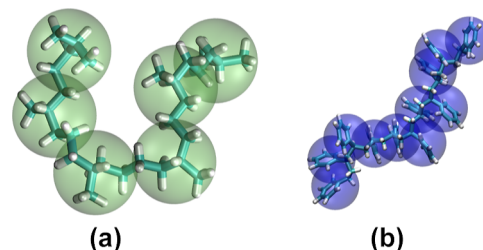


Figure 1. Illustration of a single molecule of each (a) squalane and (b) PS11 shown with the CG representation superimposed over the AA representation. Images were generated using Visual Molecular Dynamics (VMD)^{49,50} and TopoTools.⁵¹ A single CG type, representing roughly one monomer per CG, is utilized for each molecule.

Three separate IBI force-fields (shown in the [Supporting Information](#)) were generated for squalane, one at each temperature studied. PS is represented as one AA monomer per CG (6 ring carbons and 2 backbone carbons, approximately 16 atoms); [Figure 1b](#) shows an example of PS11 where the CG model is a linear chain of 11 CG sites. Three separate IBI force-fields (shown in ref 38) were generated for PS, one for each chain length. Simulations of the CG model were carried out using LAMMPS with a time step of 1 fs. Dynamic properties of the CG systems including viscosity were calculated under NVT conditions using a Langevin thermostat with friction factor, Γ , varied to find the value of Γ which reproduces AA dynamics. Details of the IBI force-field parametrization and dynamics and viscosity calculations are available in the [Supporting Information](#).

3. RESULTS

We test the consistency of the Langevin friction factor for the CG representations via several measures of dynamics and the zero-shear viscosity as a function of temperature for squalane and as a function of chain length for PS. The value of the friction factor, Γ , is presented here normalized on the mass of the CG, m_{cg} , as $\Gamma' = \Gamma/m_{cg}$ so as to study the friction as a time constant. Following the approach of our earlier work,³⁸ we measure the dynamics and, in the present work, the viscosity of the AA representation for each system as a target for the CG dynamics. The CG dynamics are tuned by measuring the CG system at several different values of Γ' and determining the value of Γ' to match the AA measurement.

3.1. Squalane: Temperature-Dependent Friction Parametrization.

3.1.1. Monomer Translational Diffusion. As a measure of the monomer translational diffusion, we compute the mean-square displacement (MSD) of the center of mass (COM) of the monomers $g_i(t)$ as

$$g_i(t) = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle \quad (4)$$

where $\mathbf{r}_i$ is the position of monomer i . The angle brackets represent an ensemble average over all monomers. For the AA system, we track the COM of the monomers equivalent to the atoms assigned to the corresponding CG. For the CG system, $\mathbf{r}_i$ is simply the location of the CG site.

The MSD of the monomer COM for squalane is plotted in [Figure 2](#) as a function of time for (a) 100 °C, (b) 65 °C, and

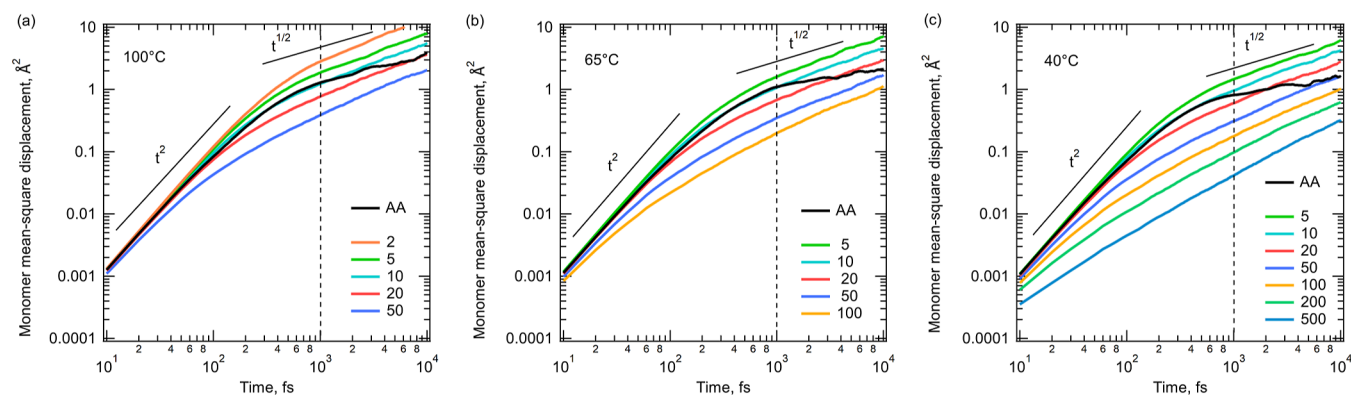


Figure 2. Early time monomer MSD $g_1(t)$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C. The AA reference simulations are shown as solid black curves. The CG systems with varying friction Γ' are shown as a series of curves, as noted in the legend in units of ps^{-1} .

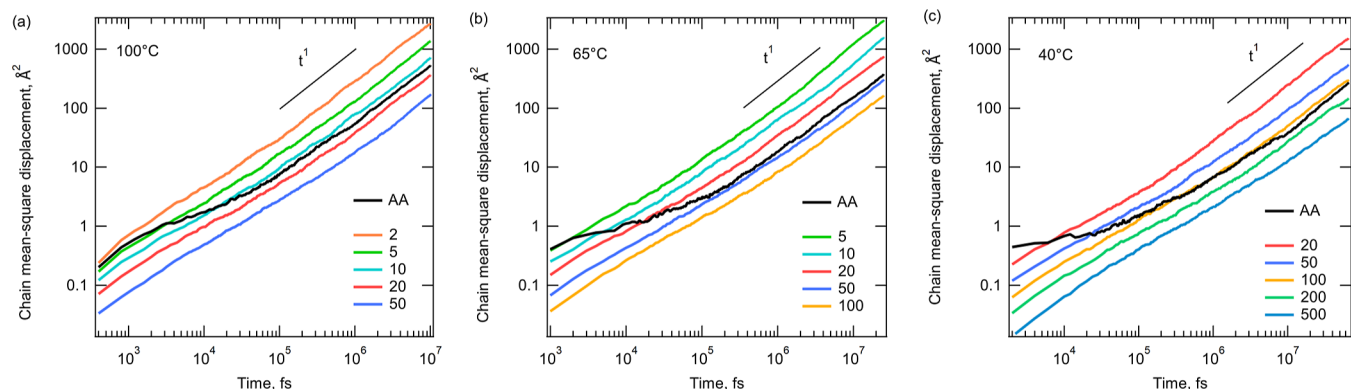


Figure 3. Chain MSD $g_3(t)$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C. The AA reference simulations are shown as solid black curves. The CG systems with varying friction Γ' are shown as a series of curves, as noted in the legend in units of ps^{-1} .

(c) 40 °C. The time scale in the figure covers only the early time behavior from the ballistic through to the beginning of the subdiffusive regime (0 ps to 10 ps); the terminal diffusive regime can be inspected in the [Supporting Information](#). For all temperatures studied, we find that increasing the Langevin friction factor reduces the translational motion of the CG representation of the monomers, which has been reported by others^{18,55} and in our prior work.³⁸ We also note that the friction required to observe the envelope of both faster and slower dynamics compared to the AA reference simulations is highly temperature dependent. For 100 °C, this envelope is reproduced using a similar range of frictions as examined for the PS systems here and in our prior work.³⁸ However, for 65 and 40 °C, a much larger range of friction values are required to obtain CG systems that produce a similar envelope relative to the AA reference systems.

Figure 2 exhibits several temporal regimes. First, we observe a ballistic regime ($g_1(t) \sim t^2$) at the earliest time shown for both the AA and CG systems. For all temperatures, the ballistic regime terminates at about 1 ps for the AA systems, and the CG friction that matches the AA behavior is approximately $\Gamma' \approx 10 \text{ ps}^{-1}$. For CG systems with friction values of $\Gamma' \geq 20 \text{ ps}^{-1}$, the transition from the ballistic regime occurs at increasingly shorter times, which is consistent with overdamped behavior. Next, the AA monomer MSD transitions to a subdiffusive regime that roughly corresponds to the $t^{1/2}$ scaling expected at intermediate times for unentangled systems.⁵⁶ In this region, the AA and CG behaviors become qualitatively different. The AA curves all show more features of a caging transition than

any of the CG curves, and this becomes more pronounced with decreasing temperature. The slopes of the individual CG curves are all steeper than the shallow slope of the AA curves, and thus, the CG friction required to match the atomistic behavior becomes time dependent and rapidly increases until the diffusive region is reached. The range and strength of friction required to capture the AA subdiffusive behavior increases as temperature decreases.

To extract a value from $g_1(t)$ to match the CG to AA dynamics, we select the Debye–Waller factor, which we define as $\text{DWF} \approx g_1(t = 1 \text{ ps})$. DWF provides information about the sampling of local or caging behavior and is reported at a time associated with the time to sample this local environment.^{13,57,58} The friction required to match the AA DWF only weakly increases with decreasing temperature because of the influence of the nearly constant friction required to recover the ballistic regime immediately preceding the transition to subdiffusive behavior. We provide the values of DWF in the [Supporting Information](#).

3.1.2. Chain Translational Diffusion. To measure the chain translational diffusion, we calculated the MSD of the COM of the chains $g_3(t)$ which is computed as

$$g_3(t) = \langle [\mathbf{r}_{\text{com},j}(t) - \mathbf{r}_{\text{com},j}(0)]^2 \rangle \quad (5)$$

where $\mathbf{r}_{\text{com},j}$ is the center of mass of chain j and the angle brackets represent an ensemble average over all chains.

Figure 3 shows the chain COM MSD as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C. We measure $g_3(t)$ over a longer time range for each progressively

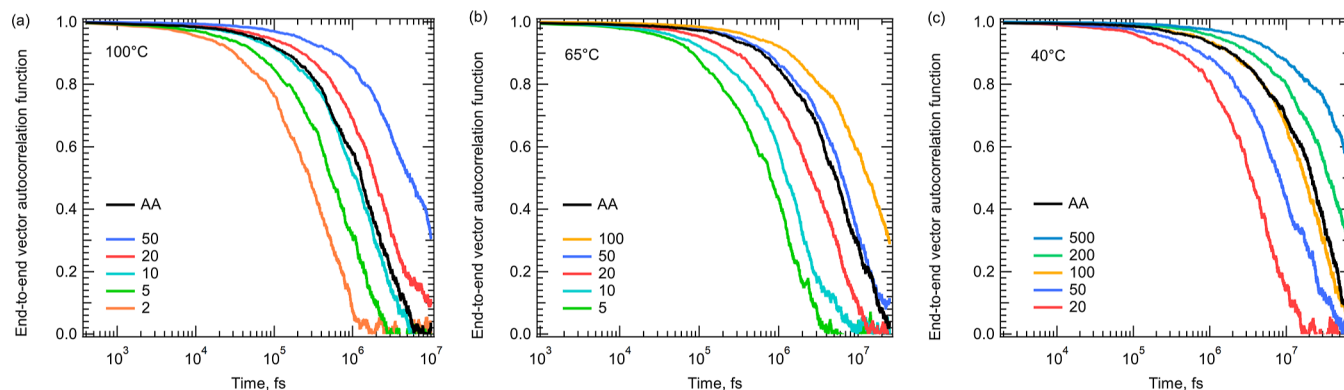


Figure 4. End-to-end vector autocorrelation function $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C. The AA reference simulations are shown as solid black curves. The CG systems with varying friction Γ' are shown as a series of curves, as noted in the legend in units of ps^{-1} .

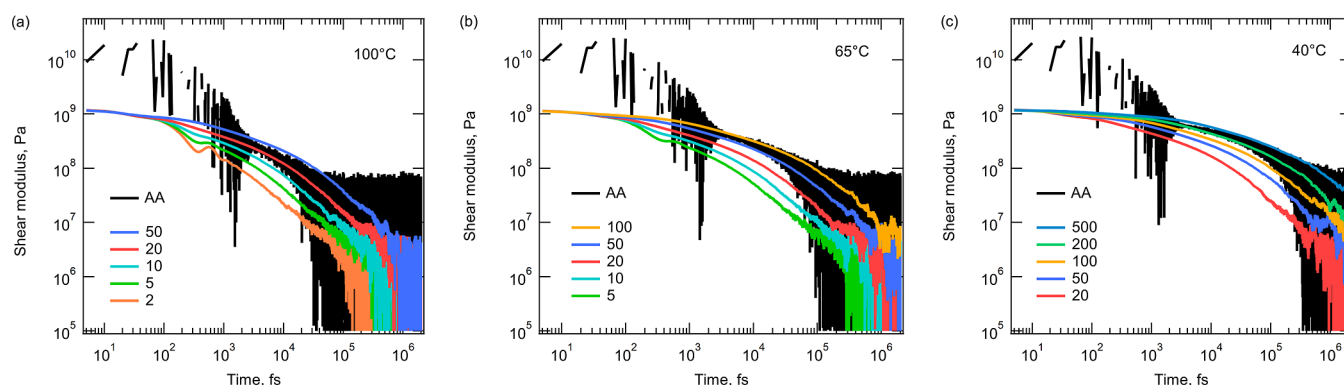


Figure 5. Stress relaxation modulus $G(t)$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C. The AA reference simulations are shown as solid black curves. The CG systems with varying friction Γ' are shown as a series of curves, as noted in the legend in units of ps^{-1} .

cooler system to ensure that the system is sampled at times longer than the relaxation time τ_R (Section 3.1.3). We also note that there are differences in the qualitative scaling at short-times of $g_3(t)$ between the AA and CG representations similar to the qualitative differences seen in $g_1(t)$ in Figure 2 during the subdiffusive regime. This difference in qualitative behavior at short times does not hamper the comparison we can make between the AA and CG systems at long times, where squalane exhibits diffusive scaling [$g_3(t) \sim t^1$] for all temperatures studied. We can see that increasing Γ' suppresses the chain translation of the CG systems as expected. From a visual inspection, the friction factor which most closely matches the long-time behavior of the AA representation increases with decreasing temperature. For the highest temperature studied, 100 °C in Figure 3a, we note that the friction factor that appears to match most closely with $g_3(t)$ at long times is similar to the value that we see for DWF. In contrast, the cooler systems require a higher friction to recover long-time chain translation than the short-time caging behavior captured by DWF, so the high temperature similarity is more of a coincidence than a trend.

To quantify the long-time behavior and define a target value to recover AA motion, we measure the chain diffusivity D_{chain} as $g_3(t) \sim D_{\text{chain}}t$. We report D_{chain} values for the AA and CG systems in the Supporting Information. The diffusivity is measured at times longer than the longest relaxation times in the chain⁵⁹ (Section 3.1.3).

3.1.3. Chain Rotational Diffusion. To measure the rotational chain diffusion, we compute the autocorrelation of

the chain end-to-end vector $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$, where $\hat{\mathbf{u}}$ is the unit vector of the end-to-end vector $\mathbf{R}$, $\hat{\mathbf{u}} = \mathbf{R}/\|\mathbf{R}\|$. The angle brackets represent an ensemble average over all chains. The end-to-end vector in both the AA and CG systems is defined as the vector extending between the COM of the first monomer and the last monomer in the chain.

Figure 4 shows $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C for the AA representation and the CG representation with varying friction factor. Lower friction allows the CG molecules to rotate more rapidly and thus decorrelate from their initial orientation over a shorter time scale, while higher friction impedes the rotational motion and prolongs the decorrelation of molecule orientation. Similar to the chain diffusivity, we note that decreasing the temperature requires an increasing friction factor to recover the AA rotational relaxation. The friction factor that most closely matches the rate of chain orientation relaxation for each temperature is similar to that of the chain diffusivity.

To obtain a target value for the rotational diffusion, we fit $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ to the predicted decay from Rouse theory^{59,60} to extract the Rouse stress relaxation time τ_R . The expression for $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ is given by

$$\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle \propto \sum_{\text{odd } p} \frac{1}{p^2} \exp\left(-\frac{p^2}{2\tau_R}t\right) \quad (6)$$

and represents a summation over odd Rouse mode indices p . Here, we fit eq 6 up to $p = 9$ to the $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$ curves to extract τ_R , reported for each curve in the Supporting

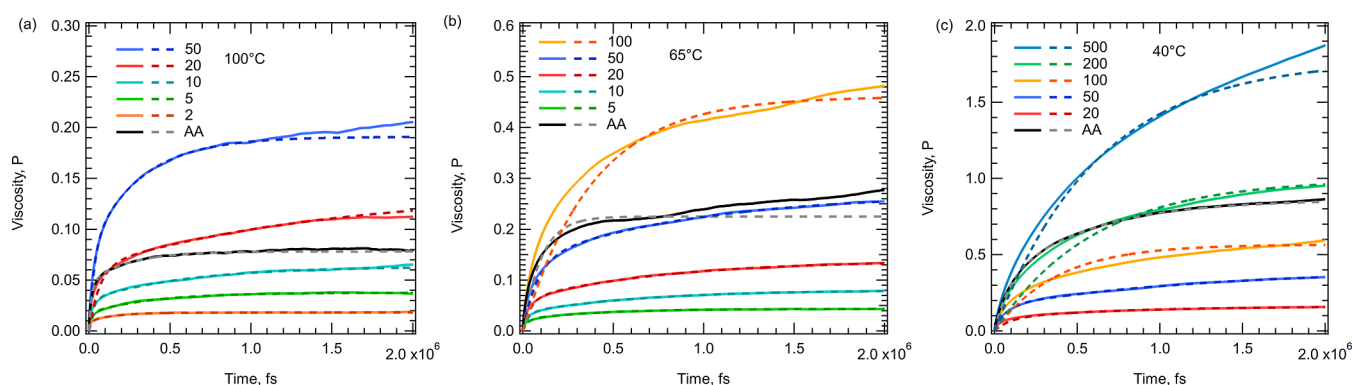


Figure 6. Viscosity $\eta(t)$ as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C, for the AA and CG representations, with applied friction Γ' shown in the legend in units of ps^{-1} . The dashed curves represent the fitting approach described by Zhang et al.⁶¹ which we summarize in the Supporting Information.

Information. This relaxation time is used here to ensure that the long-time regime is sampled in measurements such as D_{chain} . The resulting τ_R can then be used to parametrize the friction required to recover chain rotation. Chain rotation, by the nature of fitting over the entire time scale of the measurement of $\langle \hat{\mathbf{u}}(t) \cdot \hat{\mathbf{u}}(0) \rangle$, imparts a potentially averaged representative time scale. Thus, by using τ_R as the property to target for the recovery of AA dynamics, we inherently seek to match the rotational motion over a range of times.

3.1.4. Zero-Shear Viscosity. To evaluate the ability of the CG system to reproduce material properties in addition to dynamic properties (Sections 3.1.1–3.1.3), we calculate the zero-shear viscosity of the AA and CG squalane systems. We use the Green–Kubo (GK) method to compute the zero-shear viscosity, with fitting and averaging steps following the method of Zhang et al.⁶¹ and summarized in the Supporting Information. First, we compute the SACF, $\langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle$, where $\sigma_{\alpha\beta}$ is the component of the stress tensor with indices α and β with such indices typically defined as the off diagonal stress components. The angle brackets indicate the average over the stress components. Here, we compute the SACF utilizing all six components of the symmetric stress tensor which has been shown to improve the calculation^{62–65} and perform substantial averaging over and within many separate trajectories.⁶¹ The SACF is related to the stress relaxation modulus $G(t)$ as

$$G(t) = \frac{V}{k_B T} \langle \sigma_{\alpha\beta}(t) \sigma_{\alpha\beta}(0) \rangle \quad (7)$$

where V is the volume of the simulation box. In Figure 5, the stress relaxation modulus is plotted as a function of time for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C for the AA representation and the CG representation with varying friction factor.

At times shorter than 1 ps, the AA squalane stress relaxation modulus exhibits fluctuations above and below zero and thus any negative values of $G(t)$ are not shown on the log–log scale in Figure 5; these fluctuations are characteristic of all-atom systems.^{61,66} The magnitude of the initial $G(t)$ for the AA representations is greater than the initial value of the CG representations even when the same range of Γ' is used for each temperature as shown for the dynamics measurements (Sections 3.1.1–3.1.3). The stress relaxation modulus is calculated from the stress and thus includes the effect of collisions and position fluctuations that result in changes to the

conservative force, which necessarily have greater and more rapid fluctuations in the potential energy term for AA representations compared to the CG systems. The influence of Γ' on $G(t)$ is similar to its influence on the dynamics. Increased friction prolongs the decay of $G(t)$ by slowing the rate at which stresses relax in the CG system, while lower friction allows for a more rapid decay. We also note that only in the two higher temperature systems, 100 °C and 65 °C, do we see the oscillations in the CG SACF at picosecond time scales for the lowest friction factors studied; these oscillations do not become negative. In contrast, Kremer–Grest polymer models exhibit fluctuations around zero during this initial decay in $G(t)$ suggesting that perhaps our CG systems are more overdamped in comparison.⁶⁷ Varying friction factor over the range shown, some systems may be more underdamped, corresponding to the picosecond time scale oscillations, and as Γ' increases, the system becomes more overdamped, and thus, $G(t)$ decays more slowly and monotonically.

As $G(t)$ decays toward zero, $G(t)$ fluctuates around zero and the curves become noisy; with the method applied here, this noise is most noticeable when approaching nanosecond time scales. Other approaches involve computing the SACF from the stress per molecule rather than the per atom stress; this method results in a smoother SACF that is equivalent to the SACF of the per atom stress at long times.^{68,69} One study of polymer melts showed improved long-time statistics by using the molecular SACF⁷ but were limited to making comparisons at long times only. Here, we have preferred to calculate the full atomistic or CG stress tensor and relied on the averaging and fitting approach of Zhang et al.⁶¹ to obtain the target dynamic measurement, the zero-shear viscosity.

The next step in computing the zero-shear viscosity is to integrate the stress relaxation modulus

$$\eta(t) = \int_0^t G(t) dt \quad (8)$$

to compute a temporal viscosity $\eta(t)$. This temporal viscosity is plotted as a function of time for the squalane systems in Figure 6 for (a) 100 °C, (b) 65 °C, and (c) 40 °C. Note that the vertical axis is different for each temperature shown in Figure 6, which shows that the combination of decreasing temperature and increasing Γ' from left to right results in a greater value of $\eta(t)$. To extract the zero-shear viscosity, each curve is fitted with a double exponential function that is weighted and

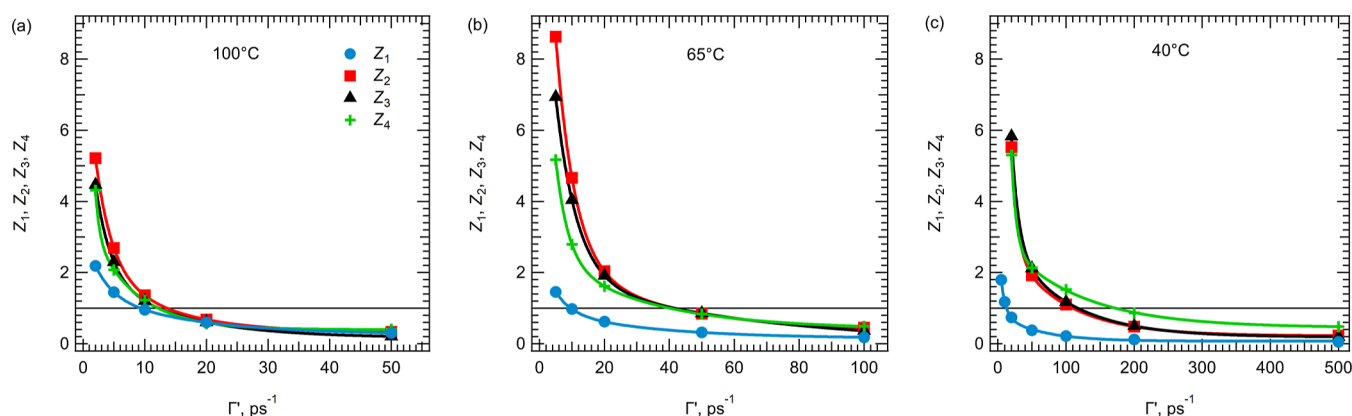


Figure 7. Dimensionless groups Z_1 , Z_2 , Z_3 , and Z_4 represent the relative magnitude of the CG measurement compared to the AA target value plotted as a function of the applied friction, Γ' , for squalane at varying temperatures, (a) 100 °C, (b) 65 °C, and (c) 40 °C. Fittings shown are double exponential.

fit up to a cutoff time following Zhang et al.⁶¹ (see the [Supporting Information](#)); the fittings are shown as dashed lines in [Figure 6](#). The zero-shear viscosity η_0 is thus taken as the value of the long-time plateau of the fitting and is the target parameter to recover in the CG model; a table of η_0 can be found in the [Supporting Information](#). The double exponential fit most closely matches the qualitative features of the data for the AA curves and the CG curves at values of friction falling below the AA curve. The CG curves show a longer time to reach the plateau value with increasing friction, which is consistent with the trend found for τ_R . Similar to the diffusion trends, none of the CG curves exactly match the AA curves at short times and a time-dependent friction would be needed to fully match this behavior. The primary difference between the trend in a time-dependent friction for diffusivity and viscosity is that for the viscosity, the friction values needed to match the short time behavior start off at very large values and then become smaller until a terminal value is reached (see the [Supporting Information](#) to examine [Figure 6](#) over the first 10 ps), while for diffusion, the very opposite is true. We discuss this point in [Section 4](#) and what we will also see shortly is that despite this difference, the terminal values of friction closely match for both cases. We also note that once $G(t)$ is integrated, the CG curves fall above and below the AA curves at long times and thus result in CG η_0 values above and below that of the AA systems, with the value of Γ' that aligns with the long-time plateau increasing with decreasing temperature and appearing to be consistent with chain diffusion and chain rotation. One note is that the GK method is typically used for less viscous systems, $\eta_0 < 0.2P$ (0.02 Pa·s),⁶⁶ for which 100 °C squalane all fall below, but some of the higher Γ' , cooler squalane systems do not, which contributes to uncertainty in this method for the 40 °C system in particular.

3.1.5. Friction Parametrization. In our prior work,³⁸ the first step to parametrize the friction of the CG systems was to define dimensionless parameters of each dynamic measurement to understand the relative difference between the AA target and the friction-dependent CG dynamics measurement. To describe the monomer translational motion, the dimensionless parameter is defined as

$$Z_1 = \frac{(\text{DWF})_{\text{CG}}}{(\text{DWF})_{\text{AA}}} \quad (9)$$

where $(\text{DWF})_{\text{CG}}$ and $(\text{DWF})_{\text{AA}}$ are the Debye–Waller factor of the CG and AA systems, respectively. The chain translational motion is parametrized through the ratio of

$$Z_2 = \frac{D_{\text{chain}}^{\text{CG}}}{D_{\text{chain}}^{\text{AA}}} \quad (10)$$

where $D_{\text{chain}}^{\text{CG}}$ and $D_{\text{chain}}^{\text{AA}}$ are the diffusivity of the chain center of mass for the CG and AA representations, respectively. The rotational motion of the chain is parametrized via the ratio of

$$Z_3 = \frac{\tau_R^{\text{AA}}}{\tau_R^{\text{CG}}} \quad (11)$$

where τ_R^{AA} and τ_R^{CG} are the Rouse stress relaxation time of the AA and CG representations, respectively. We define Z_3 here as the inverse of that which is shown in our prior work.³⁸ The dimensionless target parameter for the viscosity is thus

$$Z_4 = \frac{\eta_0^{\text{AA}}}{\eta_0^{\text{CG}}} \quad (12)$$

where η_0^{AA} is the AA zero-shear viscosity and η_0^{CG} is the CG zero-shear viscosity. We plot each of these ratios as a function of Γ' in [Figure 7](#) for squalane at (a) 100 °C, (b) 65 °C, and (c) 40 °C and fit a double exponential to each ratio to highlight trends as a function of Γ' . The curves of best fit are higher than unity at lower friction factors, and then as friction increases, these ratios decay and cross unity. We find it is useful to emphasize the similarity in the qualitative trends across Z_1 through Z_4 by plotting the inverse of Z_3 as defined in our prior work and by forming Z_4 with the AA viscosity in the numerator. The decay of these normalized comparisons serves to emphasize the qualitatively similar influences of Γ' on each mode of dynamics and allows for some discernment of the strength of the dependence of each measurement on Γ' . As mentioned earlier, the cooler squalane systems require a wider range of friction factors to capture a range of faster and slower dynamics compared with the AA system. Thus, the range of Γ' shown on the horizontal axis in [Figure 7](#) includes progressively larger values of Γ' as temperature decreases.

In [Figure 7](#), each fitted curve can be utilized to interpolate between the data points to find the value of Γ' where each Z ratio is unity, and thus, we assume AA dynamics are equal to CG dynamics. For the highest temperature studied, 100 °C ([Figure 7a](#)), the best fit curves all intersect unity at a similar

value of Γ' . As temperature decreases, the curves that describe properties that consider the motion at nanosecond time scales (Z_2 , Z_3 , and Z_4) cross unity at a similar value of Γ' , while the curve fit to $Z_1(\Gamma')$ crosses unity at a smaller Γ' . Also, the curves that describe Z_2 , Z_3 , and Z_4 almost overlap for the majority of the range of Γ' studied. One issue we note is that for the lowest temperature studied, 40 °C (Figure 7c), the Z_4 curve appears to separate from the curves that describe diffusivity and chain rotation for $\Gamma' > 50 \text{ ps}^{-1}$, potentially due to the issues with calculating the viscosity of squalane at higher CG friction using the GK method (Section 3.1.4).

We extract the interpolated value of Γ' that should recover each AA measurement of interest in Figure 7 and plot these values of Γ' as a function of the inverse temperature in Figure 8. These extracted values of the friction factor are referred to as

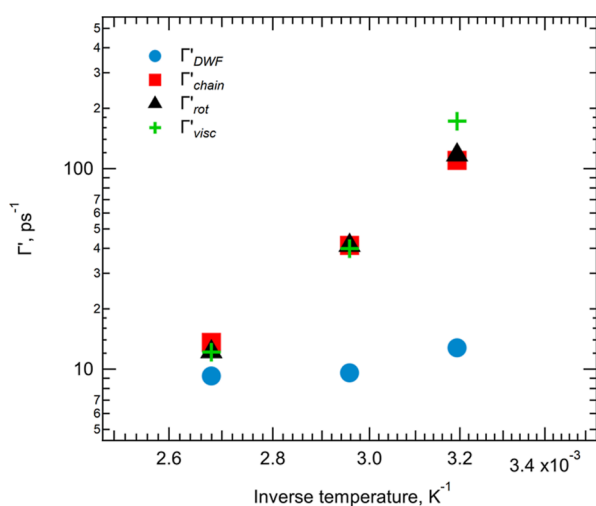


Figure 8. Values of Γ' extracted from curves of best fit, Γ'_{DWF} , Γ'_{chain} , Γ'_{rot} , and Γ'_{visc} , as a function of inverse temperature for squalane.

Γ'_{DWF} , Γ'_{chain} , Γ'_{rot} , and Γ'_{visc} based on the measurement which each friction factor is interpolated from: the Debye–Waller factor, the chain diffusivity, the Rouse stress relaxation time, and the zero-shear viscosity, respectively. Several trends emerge as a function of temperature. First, there is remarkably good agreement between the values of Γ'_{chain} , Γ'_{rot} , and Γ'_{visc} across the entire range of temperatures. The only notable deviation is Γ'_{visc} at 40 °C which we mentioned above may have been affected by numerical error. Second, in terms of temperature dependence, Γ'_{DWF} is relatively insensitive to temperature, while the friction for the long-time diffusive measures and the viscosity all show an Arrhenius-like dependence and strongly increase with decreasing temperature. This shows that matching the long-time dynamics as the temperature decreases requires an increase in friction in addition to just the reduction in motion from decreased thermal energy alone. The lower temperature measurements of the long-time diffusive quantities all reflect a large increase in the required friction to capture the dynamics at times longer than the caging regime. While the temporal evolution of the viscosity friction is distinct, it is ultimately in close agreement with the long-time diffusive frictions.

The weaker influence of the temperature on Γ'_{DWF} is an interesting point to discuss. One would expect that the need for greater friction on the coarse-grains observed for the chain-length scale and long-time properties would come about from a

similar need for increased friction at smaller length scales and shorter time scales. However, the measurement of DWF is distinct in a particular way: all other dynamics and properties which are measured represent the influence of primarily the slowest relaxation, but the DWF is associated with the very fastest. Figure 2 shows that the friction for the fast relaxations in the ballistic regime are relatively insensitive to temperature and that this trend continues through to the 1 ps time typically used as a measure of the DWF.^{57,70,71} This was not clear from our previous study, as we did not include temperature effects there.

We explored this result for Γ'_{DWF} more deeply by calculating the effect of position in the chain on the monomer MSD. Position-dependent motion in linear polymers is particularly obvious for longer chains, as discussed by Kremer and Grest in their study of end effects.⁵⁶ The DWF is extracted from the monomer MSD which is an average of the MSD of each monomer site along the chain, leading to a measurement that is inherently position-averaged. In the literature on the glass transition in polymers, it is well appreciated that there is a position-dependent relaxation behavior in chains. However, we measured the position-dependent monomer MSD and it appears as only a weak influence on the DWF at 40 °C, where we would have expected any position-dependence to be more pronounced than at the other temperatures studied (not shown). Furthermore, the squalane CG representation has only six CG sites, which may not be enough CG sites to distinguish a “middle” region and an “end” region. Thus, we conclude that positional variation was not a factor in our result.

Another interesting point to discuss is the behavior between 1 ps and 10 ps as shown in Figure 2. The AA trends clearly show a caging transition which becomes more pronounced with decreasing temperature in this region. However, the qualitative shape of the CG monomer MSD curves are all quite different from this and have only an almost imperceptible caging feature (Figure 2 in the main text and Figure S5 in the Supporting Information). Thus, a single value of Γ' does not capture the AA monomer MSD behavior, and a time-dependent friction function would be necessary to model this region. We speculate that the level of coarse-graining plays a role in the ability of a single friction model to recover the caging behavior. The results show that a single constant friction slows the dynamics but does not add features that are not already captured by the conservative potential. In that regard, we also cannot ignore the possibility that the AA and CG models used here may differ in their vicinity to the glass transition temperature, T_g , thus suppressing the appearance of a more distinct caging plateau that might appear in the CG conservative potential at lower temperature (regardless of the value of Γ'). However, the results indicate that the single friction models are well suited to recovering nanosecond time scales which are often the focus of measurement studies and for the case of squalane are consistent in both their diffusive and material property (i.e., SACF related) predictions.

3.2. Polystyrene: Chain Length-Dependent Friction Parametrization via Viscosity. 3.2.1. Zero-Shear Viscosity.

We study the zero-shear viscosity of the PS melt systems with three chain lengths whose dynamics we had previously studied in both the AA and CG representations.³⁸ The method used to calculate η_0 is similar to that described in Section 3.1.4 but with a different scheme for the collection of the autocorrelation function. The stress relaxation modulus is plotted as a function of time in Figure 9 for PS11, PS21, and (c) PS41. Rather than

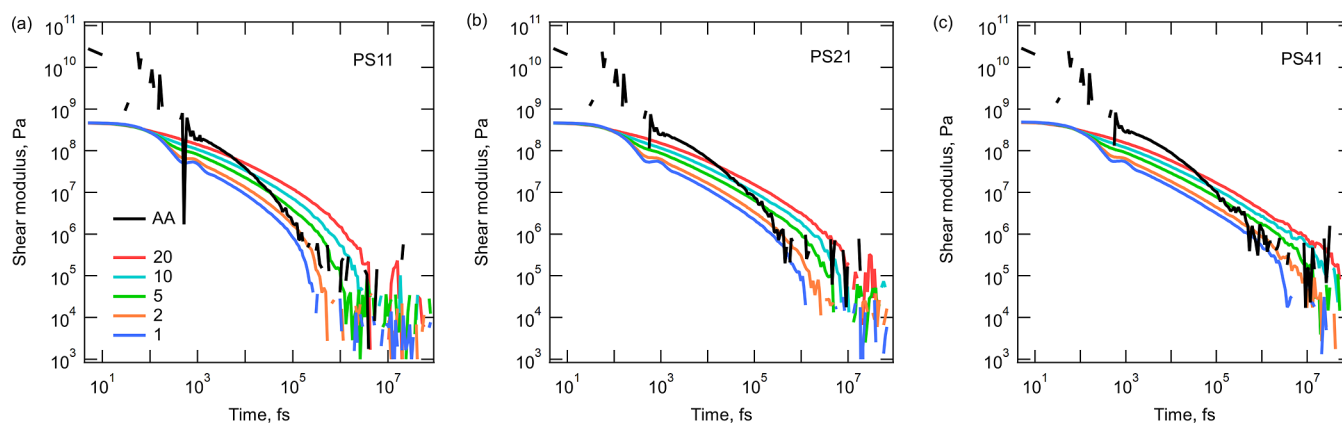


Figure 9. Stress relaxation modulus $G(t)$ as a function of time for (a) PS11, (b) PS21, and (c) PS41. The AA reference simulations are shown as solid black curves. The CG systems with varying friction Γ' are shown as a series of curves, as noted in the legend in units of ps^{-1} .

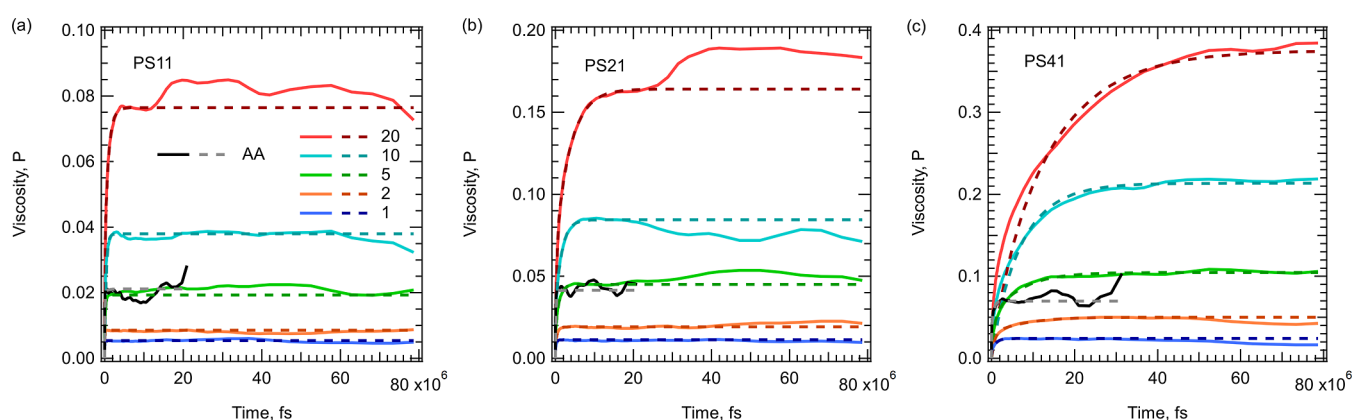


Figure 10. Viscosity $\eta(t)$ as a function of time for (a) PS11, (b) PS21, and (c) PS41 systems for the AA and CG representations with the applied friction Γ' defined in the legend in units of ps^{-1} . The dashed curves represent the fitting approach described by Zhang et al.⁶¹ which we summarize in the Supporting Information.

using many separate trajectories as carried out for the squalane stress relaxation modulus (60 separate trajectories in Figure 5), we use the multiple-tau correlator method from Ramirez et al.⁶⁷ to reduce the noise in the stress relaxation modulus at long times by using 10 separate trajectories that were particularly long (20 ns–30 ns for the AA systems and 300 ns for the CG systems; more details are provided in the Supporting Information). It is difficult to take advantage of the highly parallelized and optimized method of Zhang et al.⁶¹ when the relevant time scale of the decay is O(ns) for the PS systems. Thus, the curves shown in Figure 9 are smoother than those shown in Figure 5 and are shown for a longer range of time. $G(t)$ of PS exhibits several similarities with the squalane data: (1) AA representations exhibit short-time oscillations in $G(t)$ above and below zero; (2) increasing Γ' slows the decay of $G(t)$ for the CG systems; (3) the lowest friction CG curves exhibit oscillations that remain above zero at picosecond time scales, and this behavior is suppressed with increasing friction; and (4) all curves decay toward zero and become noisy at long times. It is also more evident here with the smoother curves that no single friction replicates the intermediate time scale behavior (picoseconds to tens of nanoseconds) of the AA stress relaxation modulus. We observe that stronger frictions better reproduce $G(t)$ at short times, while the decay requires increasingly weak friction; this sheds some light onto fundamental differences between the CG model and the AA model and the features of a Langevin-style CG approach.

Next, we integrate the curves in Figure 9 following eq 8. The result is the viscosity as a function of time, shown as solid curves in Figure 10 for (a) PS11, (b) PS21, and (c) PS41. The zero-shear viscosity is extracted from the long-time plateau value of a double exponential fit following the weighting and fitting procedure of Zhang et al.⁶¹ The fit is shown as the dashed curves in Figure 10 and the values of η_0 are reported in a table in the Supporting Information. For each AA curve, the early time behavior exhibits a steeper rise and then a sharper transition to the plateau value of the viscosity. We also plotted η_0 of the atomistic systems as a function of molecular weight for PS to check for the expected linear relationship for unentangled polymer melts⁵⁹ (see the Supporting Information). We find that drawing a linear relationship between PS11 and PS21 suggests that the zero-shear viscosity of AA PS41 is slightly underpredicted in Figure 10c. For the CG systems, the rise to a plateau takes longer as molecular weight and Γ' increase. When utilizing the method from Zhang et al.⁶¹ to collect the initial $G(t)$ data (short, but many, independent trajectories), the rise to the plateau viscosity is so slow that it exceeds the duration of the measurement, ≈ 3 ns, for longer chains and higher Γ' . This is in contrast to the squalane system, where we were able to observe nearly plateau-like behavior over several nanoseconds for most AA and CG representations across the temperatures studied. We also attempted to optimize the GK viscosity calculation parameters in the method of Zhang et al.⁶¹ for the PS21 and PS41 CG

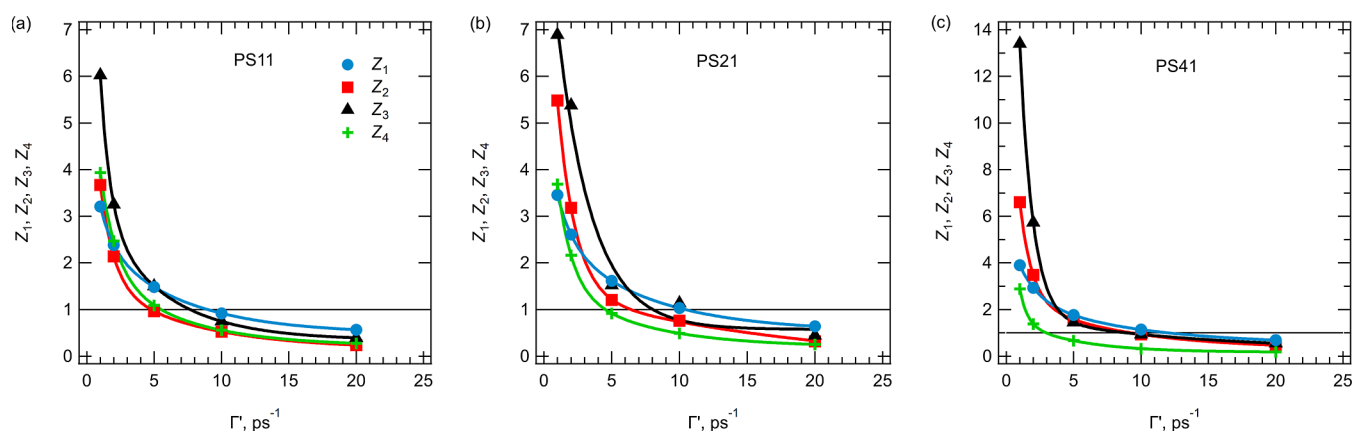


Figure 11. Dimensionless groups Z_1, Z_2, Z_3 , and Z_4 as a function of the applied friction factor Γ' for each chain length for (a) PS11, (b) PS21, and (c) PS41. Fittings shown are double exponential. Z_1, Z_2 , and Z_3 were calculated as a function of Γ' in ref 38 and are replotted here.

systems; the slow growth to a plateau value is characteristic of these longer PS systems and changes to the calculation did not result in evidence of the plateau during the calculated time range (see the Supporting Information for examples). Thus, we used the multiple-tau correlator method to collect statistics over longer times.⁶⁷ In the particular case of the higher molecular weight PS in the CG representation with higher friction, we likely are seeing effects of several things: (1) the distinct early time behavior for the CG representation, (2) higher viscosity with increasing molecular weight and Γ' , and (3) long relaxation times, beyond those which cooler yet simpler liquid systems exhibit. We examine the difficulties in reporting viscosity for the higher friction and higher molecular weight PS cases in the next several sections.

3.2.2. Friction Parametrization. In our prior work,³⁸ we parametrized the friction required for the recovery of three different types of dynamics in polystyrene oligomers of varying chain length. Here, we perform the same steps to determine the friction factor that best reproduces viscosity and compare this friction factor to the prior dynamics-based parametrizations. To investigate the trends of the dimensionless groups, we replot the previously reported Z_1, Z_2 , and Z_3 (redefined following eq 11) alongside the newly measured Z_4 as a function of the applied friction for each PS system in Figure 11. To interpolate between the values of Z at varying Γ' , we fit a double exponential to each data set, shown as solid curves in Figure 11. When the curves are examined as a decaying double exponential form, several features are highlighted. First, small changes in the friction when the friction is relatively weak result in large changes in the resulting normalized dynamics. As the friction factor increases, the dynamics of the system are suppressed, and the curves of the normalized dynamics exhibit a weaker dependence on Γ' .

We extract the target values of the friction factor from Figure 11 and plot them in Figure 12 as a function of chain length, given by the number of monomers, N , using the same method and notation as defined in Section 3.1.5. As we showed in our previous work, for the diffusive dynamics (excluding viscosity) the chain motion requires the lowest friction to recover the AA diffusivity, while the monomer motion requires the highest to recover the picosecond dynamics, with the rotational motion requiring an intermediate friction. All the diffusion-based frictions increase to varying degrees with increasing chain length and the difference between them narrows.³⁸ There is one main difference in Figure 12 between the present work and

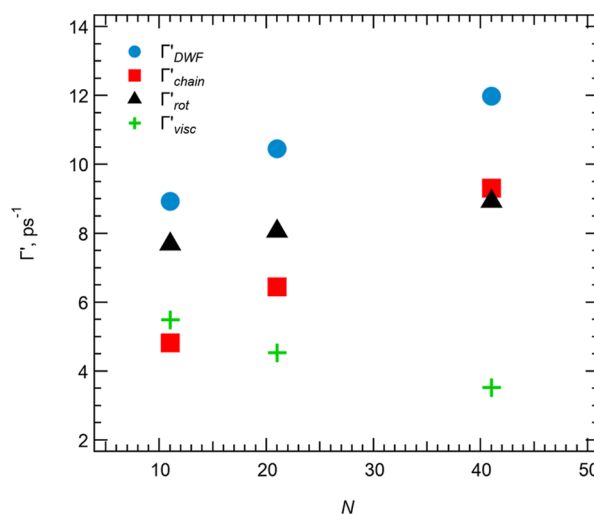


Figure 12. Values of Γ' extracted from curves of best fit, Γ'_{DWF} , Γ'_{chain} , Γ'_{rot} , and Γ'_{visc} , as a function of chain length N for PS. Γ'_{DWF} , Γ'_{chain} , and Γ'_{rot} were derived from data presented in ref 38 and are replotted here.

our prior work with respect to the diffusive data.³⁸ That is, the redefined Z_3 , eq 11, produces a Γ'_{rot} trend that is somewhat flatter, and thus, for the highest chain length, that curve now overlaps with the value of Γ'_{chain} for PS41. We further recognize based on the temperature-dependent squalane data that the difference between the Γ'_{DWF} and Γ'_{chain} is an inherent signature of these measurements, and we look more for congruence between the other measures.

Having explained the updated diffusive data, we now review the new data for Γ'_{visc} with the chain length. A noticeable difference is that the friction required to recover viscosity, $\Gamma'_{visc}(N)$, shows a modest decrease as chain length increases, whereas Γ'_{rot} shows a modest increase and Γ'_{chain} shows a relatively steeper increase over the same range. To unpack this, we first note that for PS11, Γ'_{visc} falls between the values of friction for the rotational diffusion and chain translation. The relatively close agreement among Γ'_{chain} , Γ'_{rot} , and Γ'_{visc} for this chain length suggests that these properties are dominated by a similar averaged or long-time relaxation process.

For the PS21 and PS41 systems, while the calculated values of Γ'_{visc} are still relatively close to the others, the question is whether the divergence in the trend is real or influenced by

some sort of calculation error. The first thing we note is that for all the polystyrene systems, the calculated values of η_0 are less than the $0.2P$ ($0.02 \text{ Pa}\cdot\text{s}$) limit above which the nonequilibrium MD (NEMD) methods are more reasonable.⁶⁶ Furthermore, we parametrized η_0 using both the method of Zhang et al.⁶¹ and the one based on the multiple-tau correlator method,⁶⁷ and found that the Γ_{visc}' trend in Figure 11 was consistent for both methods. Thus, this trend is unlikely to be due to statistical or sampling errors in the calculation of η_0 and there is good support that the calculated trend in Figure 12 is correct for the PS system tested here.

However, it is useful to explore potential sources of a systematic error and how this result might be further tested. One source of systematic error may be from the equilibration step. Lee and Kremer⁷² showed that the stress relaxation modulus of an entangled Kremer–Grest (KG) melt depends on whether the system has been able to reach equilibrium or if motions indicative of long-ranged structural relaxations are captured in the long-time SACF. Thus, we went back and compared our equilibration times at 800 K (see Supporting Information, Section S2.1) with the relaxation times at 600 K (see Table 2 from Johnson and Phelan Jr.³⁸ for PS data and Table S10 in the Supporting Information for squalane data for which squalane is equilibrated at the highest temperature studied, 100 °C). For the systems in which Γ_{visc}' is most congruent with the other frictions, i.e., squalane at 100 °C and PS11 at 600 K, our equilibration times were 5 times or more longer than the relaxation time we later derived for the system at a cooler temperature (or for the same temperature, in the case of squalane). For the PS21 and PS41 systems, the ratios were approximately one and one-third, respectively. It is evident that the highest molecular weight PS is the least congruent with the other friction measures, and they also have the lowest ratio of equilibration time to relaxation time. It is therefore quite possible that the equilibration times we used (which were based on other criteria and not the relaxation times which were computed only after the equilibration), while practical for accurate diffusion calculations, were insufficient for deriving η_0 from the integral of the SACF. This could be tested by further equilibration without any changes to the measurement method. This might be a point to examine in future calculation of GK based viscosity in general to solidly establish best practice criteria for high viscosity or long relaxation time systems. Independent comparison with a nonequilibrium MD approach (which may have advantages for high viscosity systems) is another tack to consider.⁶⁶

4. DISCUSSION

In this work, we further tested a model that augments IBI-derived CG potentials with a single Langevin friction to correct dynamics. Three new ideas were tested: parametrization of a new material (squalane), temperature dependence of friction, and friction parametrization from viscosity in addition to the diffusive measures that were previously used. Here, we evaluate the successes and opportunities that the approach offers to the recovery of consistent dynamics in chemically specific CGs focusing on insight derived from temperature dependence, a clearer picture of different dynamic regimes, the ability to recover the long-time dynamics, and a view toward other means to fully repair the dynamics of CG models.

4.1. Friction Based on Temperature-Dependent Diffusive Dynamics. The temperature-dependent measurements for squalane yield unique insights into the many aspects

of friction parametrization required for the CG model to match the AA diffusive dynamics. In particular, from the translational diffusive data set, a clear picture of the required friction through three distinct dynamic regimes can be recognized. First, in the subpicosecond ballistic regime, the friction has very little temperature dependence (viz., Figure 2) and this trend continues through to the 1 ps time used to measure the DWF.^{57,70,71} We now recognize this not as a discrepancy between the other measures of friction (as we previously speculated) but as being distinct because the short-time friction is based on the very fastest relaxations and a mechanism different from that which drives the long-time behavior. This was not clear from our previous study as we did not include temperature effects there, although it may well have been reasoned based on polymer physics considerations.

Second, in the intermediate caging regime in the range 1 ps–10 ps, the AA trends for both monomer and chain diffusion cut across many constant friction CG curves indicating a large time-dependent increase in the required friction which escalates with decreasing temperature. This comes about because the CG model behavior at constant friction in this region is qualitatively different from the AA model in the sense that the strong caging behavior seen in the AA trends is absent from the CG trends. This behavior was brought out much more clearly in the present study by the lower temperature measurements. The last temporal region is the long-time terminal regime. Here, the AA trend falls in line with a constant friction CG trend at a high friction value. The magnitude of the terminal friction is inversely related to temperature, which is discussed in the next section.

These differences between both the quantitative and qualitative behavior of the AA and CG MSD (Section 3.1.1) elucidate that a time-dependent friction would be required to exactly reproduce the AA measurements over the entire timespan at this level of coarse-graining. Practically, this means that the single friction model studied here can only match the long-time dynamics. A more complex model would be needed to precisely match the short- and intermediate-time behavior if reproduction of those features is required. Some ideas concerning this are discussed in Section 4.4.

4.2. Friction Based on Temperature-Dependent Long-Time Dynamics. Several measurements targeted in this parametrization scheme characterize the dynamics at long times. For example, chain diffusivity is measured in the terminal diffusive regime, chain rotational diffusion is measured via τ_R which is effectively weighted to the longest relaxation times, and zero-shear viscosity is obtained from the long-time behavior of the integral of the SACF. The calculations here for the squalane system (Section 3.1) show that the friction for the long-time diffusive measures and the viscosity are all relatively consistent and strongly increase as the system cools exhibiting an Arrhenius temperature dependence. Thus, the reduction in thermal fluctuations that accompanies a decrease in temperature is not alone enough to recover the dynamics; there must also be a commensurate increase in the Langevin friction. This result is consistent with the temperature dependence of the monomeric friction coefficient which, while not precisely the same as the Langevin friction, is somewhat related.⁵⁶ The monomeric friction is a strong function of temperature and may be modeled with either an Arrhenius model at high temperatures (which we have here) or a VFT type (or similar) model at temperatures closer to the glass transition.^{73–76} The result that friction

changes with temperature is conceptually similar to approaches which modify the pair potential to increase cohesive energy with decreasing temperature, e.g., refs 12 and 15, but differs in that the present approach is based on entropic considerations, while the latter is based on enthalpy. It is clear that understanding the full temperature dependence of the friction provides a pathway toward resolving not only dynamics but also addressing the important issue of temperature transferability in CG models as well.

Our method of applying a Langevin friction factor to the CGs is essentially introducing one new time scale to correct the motion, which is largely sufficient to bring the long-time dynamics in agreement with the AA reference systems. This arises from the similarity of the qualitative behavior of AA and CG representations during long times in contrast to the short-time behavior. The result in this case comes out similar to the time rescaling approach^{1–8} which is a phenomenological means to introduce a time constant which corrects the long-time dynamics. However, the dissipative model approach such as the Langevin equation which is based on statistical mechanics^{16,77} in general retains several advantages besides the theoretical foundation. The Langevin friction, once determined via parametrization, can be applied during the running of the simulation as opposed to after the simulation has been run. Furthermore, the present Langevin method more easily enables modeling of mixtures of different CG types (such as multiple CG types in a single molecule type²² or different molecule types with one or more CG types) where the different CG types have different time scales. For example, a method to model the dynamics of a binary system, combining time rescaling the simulation and a unique Langevin friction factor applied each of the two species, has effectively added two separately tunable time scales for the dynamics of the mixture.⁷⁸ Further work is necessary to develop and prove the utility of a CG-type specific Langevin friction factor for multiple CG types; care would need to be taken to retain the simplicity of the parametrization scheme to make it similarly tractable to a single CG-type system.

4.3. Consistency of Long-Time Friction Measurements. For a molecular model dynamically corrected by friction to be generally useful, it is important that the friction parametrized from different schemes be consistent with the different measures of interest. For squalane, the friction parametrized from the various long-time dynamic measures is quite consistent as a function of temperature. The congruity between Γ_{chain}' and Γ_{rot}' values remains intact across the entire temperature range. The values of Γ_{visc}' are similarly congruent except at the lowest temperature of 40 °C. This difference in the latter may arise from statistical or systematic error in the viscosity calculation, which we mentioned above. Other methods such as NEMD might be better suited to this regime.

For unentangled PS melts, which we studied versus chain length, we compared new friction measurements obtained by viscosity with our previous measurements of friction for the various diffusive measures. Here, we did not find the same congruent behavior of the viscosity-based friction with the diffusive-based friction as observed for squalane. While the diffusive measures of $\Gamma_{\text{rot}}'(N)$ and $\Gamma_{\text{chain}}'(N)$ are relatively consistent and both show an increasing trend, $\Gamma_{\text{visc}}'(N)$ shows the opposite behavior in the form of a modest decreasing trend over the same range. Thus, while the values are not far off, the trends diverge, and it appears that as the number of beads per chain in the CG models increases, the more difficult it is to

match the diffusive and viscous friction measures. We mentioned a number of factors above that could be the cause of this. To add to that, we have to also consider the role that the unsteady dynamics of the individual parametrization schemes plays in this and why that might manifest more with increasing chain length. If one were to determine a Langevin friction factor for each time along any of the translational diffusion measures, the value of the CG friction would start low and increase to a higher friction at longer times. For the viscous measure, the behavior is the opposite. In this case, the matching CG frictions start high and then decrease. For both cases, it appears that the trend in the unsteady friction (whether increasing or decreasing temporally) carries over to the measurement of the long-time friction value, and this effect increases with increasing molecular weight. While the trends found in Figure 12 could be real, it is more likely an artifact or systematic error arising from under equilibration of the longer chain systems that has an inverse effect with respect to the diffusive and viscous parametrization schemes. The inverse relationship between diffusion and viscosity may play a role in this. The rotational diffusion appears to be less sensitive to this. We also note that for the squalane systems where the short chains are expected to be equilibrated more quickly, no effect like this is observed. This would give hope that further, more stringent testing of equilibrium protocols of longer chain systems would eliminate or minimize this problem.

4.4. Time-Dependent Friction Model Considerations.

In Section 4.1, we discussed the idea that the single friction model studied here can only best be used to match the long-time dynamics and that a time-dependent friction model would be needed to recover the full range of short-time regimes important in the molecular modeling of polymers. By “time-dependent friction”, we clarify that we refer to the effective friction that emerges from a more comprehensive model such as the GLE and not to an effective Langevin friction that is a function of time. A goal would be a model which reproduces the ballistic, caging, and diffusive regimes of AA polymer diffusive dynamics. Such a model in principle could yield both information on short-time measures such as the DWF which is important for relating computation to experimental measurements,⁷⁹ as well as long-time measures such as viscosity and modulus which we have shown here are congruent with the diffusive measures.

In terms of approach, Panja,⁸⁰ for example, studied dynamics in various polymeric systems and found that they are non-Markovian and characterized by power-law memory kernels within a GLE framework. So, this would appear to be the appropriate approach for these systems. In that regard, the matter of developing and implementing GLE simulation methodology has been an active area of research in the literature and a number of methods are discussed in Schmid.⁸¹ These methods generally depend on approximating the memory kernel using appropriate auxiliary variables with the goal of recovering the VACF between the AA and CG representations and thus the frequency-dependent behavior found in the fine-grained model. Implementations by Ceriotti et al.,^{82–84} Baczewski and Bond,⁸⁵ Lei et al.,²⁷ and Li et al.⁸⁶ all follow this general methodology, but differ in exact details. Ceriotti et al.⁸⁴ rewrite the memory kernel in an equivalent Markovian form by introducing a set of auxiliary momenta with a colored-noise thermostat. Baczewski and Bond⁸⁵ approximate the memory kernel by a Prony series with colored Gaussian noise. Lei et al.²⁷ compute the memory kernel relying

on a hierarchy of parametrized rational approximations for the kernel function Laplace transform, which can be expanded to arbitrarily high order as necessary. Li et al.⁸⁶ fit the memory kernel by another type of modified Prony series. The models of Ceriotti et al.⁸⁴ and Baczewski and Bond⁸⁵ are available in LAMMPS.

In general, but with some exceptions, these methods have not been widely applied to polymer systems. Li et al.⁸⁶ applied their method to a coarse-grained star-polymer system and were able to reproduce the ballistic, caging, and diffusive regimes of the MSD. Another work, also for a star-polymer system, showed that GLE simulations can capture the relevant correlations in the VACF if not only the slowest evolving variables but also the correlations between fast and slow variables are preserved.⁸⁷ However, the general approach of starting with an AA reference system, applying memory kernel-based coarse-graining techniques, and reproducing the types of dynamics of interest to the polymer community are still work in progress for polymer systems. Thus, investigation of the work required to parametrize each of these models and comparison of run times for more complex polymer systems need to be assessed. These methods are as of yet still computationally expensive and require a more time-consuming (but potentially more transferable) parametrization method than the method tested here. The need for a rapidly parametrizable means of recovering some representation of the lost frictional forces may need to be balanced with whether important physical phenomena will be lost and thus necessitate a more detailed model of the friction, which comes along with simulation efficiency considerations.

5. CONCLUSIONS

In this work, we extended the approach to parametrize a Langevin friction factor for chemically specific CGs³⁸ to a material property, the zero-shear viscosity measured via the GK method. The goals were twofold. First, we wanted to test the consistency of a parametrization of friction from the viscosity with the other dynamic measures. Second, we wanted to test the idea that the friction could be parametrized based on any of the dynamic measures that are more easily calculated and yield a model with a CG viscosity that was consistent with the AA value. We also investigated squalane to see how these methods apply to different materials and looked at the temperature dependence of friction.

In the model system of a squalane melt at varying temperatures, at the highest temperature of 100 °C, all four friction measures are in virtually perfect agreement. Furthermore, the congruity between the friction required for chain diffusivity, Rouse stress relaxation, and zero-shear viscosity remains intact across the entire temperature range (with the exception of the highest viscosity system which was discussed) and shows an Arrhenius temperature dependence. The temperature dependence of the long-time friction provides a very natural new pathway toward resolving the important issue of temperature transferability for CG models. Detailed examination of the temperature-dependent diffusive dynamics also showed the limitations of a single friction model. The picosecond Debye–Waller regime corresponds to a different friction than the long-time value (although the values are close at high temperatures), and the intermediate caging regime corresponds to a transient friction. Precisely matching the short-time dynamics evidently requires the time-dependent friction offered by a non-Markovian model or other model

modifications. From the previously studied model system of polystyrene oligomers at high temperature (600 K), we find that for the shortest 11 monomer chains, the friction to recover viscosity falls into the same range of friction as the dynamics-based measures. However, for the longer chains, the viscous friction somewhat diverges from the diffusive measures, in particular the translational diffusion friction which shows a counter trend. The unsteady dynamics of the individual parametrization schemes seems to play a role in this for the longer chains and will require follow-up work.

Overall, we can conclude on the basis of this work and our previous paper that the use of Langevin friction is a reliable means to repair dynamics for long-time measures where the material is in thermal equilibrium. Furthermore, we showed here that when the viscosity measurement is reliable, the friction parametrization from the diffusive and viscous measures is consistent, and thus, the lower cost diffusive parametrization is a reliable surrogate for modeling the zero-shear viscosity. To enable the most reliable modeling of short-time diffusive dynamics, it is likely necessary to take a GLE approach in which a friction kernel is parametrized rather than a single Langevin friction coefficient. The increase in the ability to represent the entire range of dynamics of interest using a GLE model will likely come along with an increase in complexity to parametrize the friction kernel and some increase in computational expense. It would be of interest to compare the difficulty of parametrization and simulation efficiency between the present Langevin approach and a GLE model and determine criteria for when it is necessary to utilize the GLE approach for polymer melts dynamics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.3c03273>.

Zero-shear viscosity calculation methods, simulation details, lower resolution monomer MSD of squalane, zoom-in of early time viscosity of squalane, dynamics measurements for squalane and zero-shear viscosity for squalane and PS, AA PS zero-shear viscosity versus molecular weight, and Langevin friction factors for each system and parametrization method (PDF)

Tabular squalane IBI force-fields (TXT)

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Notes

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