Static and dynamic scaling behavior of a polymer melt model with triple-well bending potential

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We perform molecular-dynamics simulations for polymer melts of a coarse-grained polyvinyl alcohol model that crystallizes upon slow cooling. To establish the properties of its high temperature liquid state as a reference point, we characterize in detail the structural features of equilibrated polymer melts with chain lengths $5 \leq N \leq 1000$ at a temperature slightly above their crystallization temperature. We find that the conformations of sufficiently long polymers with $N > 50$ obey essentially the Flory’s ideality hypothesis. The chain length dependence of the end-to-end distance and the gyration radius follow the scaling predictions of ideal chains and the probability distributions of the end-to-end distance, and form factors are in good agreement with those of ideal chains. The intrachain correlations reveal evidences for incomplete screening of self-interactions. However, the observed deviations are small. Our results rule out any pre-ordering or mesophase structure formation that are proposed as precursors of polymer crystallization in the melt. Moreover, we characterize in detail primitive paths of long entangled polymer melts and we examine scaling predictions of Rouse and the reptation theory for the mean squared displacement of monomers and polymers center of mass.

INTRODUCTION

Polymer melts are dense liquids consisting merely of macromolecular chains. The main characteristic of polymer melts is their high-packing density which leads to overlapping of pervaded volume of their chains [1]. As a result, density fluctuations in a melt are small and similar to a simple fluid every monomer is isotropically surrounded by other monomers that can be part of the same chain or belong to other chains. As a consequence the chains conformations in the molten state are close to random walks. Nevertheless, the crystallization of polymer melts remarkably differs from monomeric liquids due to chain connectivity constraints that must be compatible with lattice spacings of a crystalline structure. Upon cooling of a crystallizable polymer melt, a semicrystalline structure emerges that comprises of regularly packed, extended chain sections surrounded by amorphous strands [2].

Despite intensive research, the mechanism of polymer crystallization is still poorly understood as this process is determined by an intricate interplay of kinetic effects and thermodynamic driving force [3, 4]. From theoretical perspective, attempts have been made to understand thermodynamics of polymer crystallization. These efforts include lattice-based model [5], Landau-de Gennes types of approach [6] and density functional theory [7, 8]. Among these, the density-functional theory is a particularly promising approach as it can predict equilibrium features of inhomogeneous semicrystalline structure from the homogeneous melt structure provided that a suitable free-energy functional is employed and accurate information about chain conformations and structure of polymeric liquids is supplied [9]. Such an input can be obtained from simulations of a crystallizable polymer melt that allow us to compute the intrachain and interchain correlation functions. Here, our aim is to characterize conformations of a crystallizable polymer melt model known as coarse-grained polyvinyl alcohol (CG-PVA) [10]. Owing to its coarse-grained nature, this model allows for simulations of large-scale structure of semicrystalline polymers.

The CG-PVA is a bead-spring polymer model that is obtained by a systematic coarse-graining from atomistic simulations of polyvinyl alcohol [11]. The coarse-graining procedure maps all the atoms of a monomer into one bead and a bending potential is extracted from the bond-angle distribution of atomistic simulations of PVA polymers. The main distinctive feature of the model is its triple-well intrachain bending rigidity that leads to formation of chain-folded crystallites upon slow cooling of the melt [10, 12]. Although the model does not take into account the intermolecular hydrogen bonding interactions, it reproduces the main features of polymer crystallization such as lamella formation. Recently, the CG-PVA model has been employed to study the dependence of polymer crystallization on the chain length [13, 14]. To understand the influence of chain length and entanglements on the melt crystallization [15, 16], the properties of its high-temperature liquid state need to be firmly established as a reference point. Here, we focus on the static and dynamic properties of CG-PVA polymer melts at a temperature which is 1.1 times the crystallization temperature.

The prior studies of structural properties of this system have been limited to static properties of short chains $N \leq 100$ [17] with purely repulsive interactions. Here, we present the results for CG-PVA polymer melts with $5 \leq N \leq 1000$ with attractive interactions. Characterizing the conformational features of longer polymer melts, we
accurately determine the persistence length, the Flory’s characteristic ratio and the entanglement length of CG-PVA polymers. Examining carefully the consequences of the triple-well bending potential on chain conformations, we barely find any evidence of pre-ordering or microstructure formation as precursors of crystallization. Embracing a crossover from short unentangled chains to the entangled ones, we examine the credibility of Flory’s ideality hypothesis and manifestations of incomplete screening of excluded volume and hydrodynamic interactions on the structural and dynamical features of entangled polymer melts with a finite persistence length.

Flory’s ideality hypothesis states that polymer conformations in a melt behave statistically as ideal random-walks on length scales much larger than the monomer’s diameter [18, 19]. This ideality hypothesis is a mean-field result that relies on the negligibility of density fluctuations in polymer melts. Therefore, its validity is not taken for granted. Indeed, the computational studies of fully flexible long polymers for both lattice (bond fluctuation) and continuum (bead-spring) models have revealed noticeable deviations from the ideal chain behavior [20–24]. The theoretical calculations show that these deviations result from the interplay between the chain connectivity and the melt incompressibility which fosters an incomplete screening of excluded volume interactions [21, 23, 25]. However, a recent study of conformational properties of long locally semiflexible polymer melts demonstrates that the deviations diminish as the chains bending stiffness increases and the conformations of sufficiently stiff chains are well described by the theoretical predictions for ideal chains [26].

Investigation of the static scaling behavior of locally semiflexible CG-PVA polymer melts confirms that CG-PVA polymers display globally random-walk like conformations. Notably, for chains with \( N > 50 \), the results of the end-to-end distance, gyration radius, the probability distribution functions and the chain structure factor are in good agreement with the theoretical predictions for ideal chains. However, inspection of intrachain correlations reveals some evidences for deviations from ideality. The mean-square internal distances of long chains \( N > 100 \) are slightly swollen compared to ideal chains due to incomplete screening of excluded volume interactions. Additionally, the second Legendre polynomial of angle between bond vectors exhibits a power law decay for curvilinear distances larger than the persistence length providing another testimony for self-interaction of chains. Nonetheless, we note that these visible deviations are small.

The remainder of the paper is organized as follows. In Sec. II, we briefly review the CG-PVA model and provide the simulation details. We present a detailed analysis of conformational and structural features of polymer melts in Sec. III and we compare simulation results to the theoretical predictions for ideal chains. We investigate conformational properties of the primitive paths of long chains in section IV where we determine the entanglement length of fully equilibrated CG-PVA chains. Sec. V explores the segmental motion of polymers at different characteristic timescales and examines the scaling laws predicted by the Rouse model and the reptation theory [1, 19, 27]. Finally, we summarize our main findings and discuss our future directions in section VI.

**MODEL AND SIMULATION DETAILS**

We equilibrate polymer melt configurations of the coarse-grained polyvinyl alcohol (CG-PVA) model using molecular dynamics simulations. In the following, we first briefly review CG-PVA model and then provide the details of simulations.

**Recap of the CG-PVA model**

In the CG-PVA bead-spring model, each bead of the coarse-grained chain with diameter \( \sigma = 0.52 \text{ nm} \) corresponds to a monomer of the PVA polymer. The fluctuations of the bond length about its average value \( b_0 = 0.5\sigma \) are restricted by a harmonic potential with a bond stiffness constant \( k_{\text{bond}} = 2700 k_B T / \sigma^2 \)

\[
U_{\text{bond}} = \frac{1}{2} k_{\text{bond}} (b - b_0)^2
\]

that leads to bond length fluctuations with a size much smaller than the monomer diameter. Monomers of distinct chains and the same chain that are three bonds or farther apart interact by a soft 6-9 Lennard-Jones potential,

\[
U_{\text{nb}}(r) = \epsilon_0 \left[ \frac{\sigma_0}{r} \right]^9 - \left( \frac{\sigma_0}{r} \right)^6
\]

in which \( \sigma_0 = 0.89\sigma \) and \( \epsilon_0 = 1.511 \ k_B T_0 \). Here, \( T_0 = 550 \text{ K} \) is the reference temperature of the PVA melt [10]. We truncate and shift the Lennard-Jones potential at \( r_C = 1.6\sigma \) in our simulations. Our choice of \( r_C \) is different from initial studies where the non-bonded interactions were truncated at the minimum of the LJ potential \( r_{\text{min}} \approx 1.02\sigma \) and thus were purely repulsive. The purely repulsive model was initially used to study structure formation in the quiescent state [10, 15, 16, 28]. The attractive part is needed for non-equilibrium studies of deformation [12, 13, 29]. Note that the choice of \( r_C = 1.6 \) leads to an increase of density by about 10% with respect to the purely repulsive conditions. However, the structural properties of the melt remain essentially unaffected.

The distinguishing characteristic of the CG-PVA model is its triple-well angle-bending potential [10] as presented in Fig. 1. This bond angle potential is determined directly from atomistic simulations by Boltzmann inversion of the probability distribution of the bond angle \( \theta \) [10, 11]. The minima of \( U_{\text{bend}}(\theta) \) reflect the specific states of two successive torsion angles at the atomistic
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\[
\langle R^2_e \rangle = \frac{1}{n_c} \sum_{i=1}^{n_c} \langle (\mathbf{r}_{i,N} - \mathbf{r}_{i,1})^2 \rangle \tag{3}
\]

STRUCTURAL FEATURES OF CG-PVA POLYMER MELTS

We carry out molecular dynamics simulations of CG-PVA polymers with chains lengths \(5 \leq N \leq 1000\) using LAMMPS [30]. We report the distances in length unit \(\sigma = 0.52\) nm. [10]. The time unit from the conversion relation of units is \(\tau = \sqrt{m \sigma^2 / k_B T}\) with the monomer mass \(m = 1\). The starting melt configurations are prepared by generating an ensemble of \(n_c\) (number of chains) self-avoiding random walks composed of \(N\) monomers with an initial density of \(\rho \sigma^3 = 2.31\). To remove the interchain monomer overlaps, we use a slow push off method in which initially a very weak LJ potential with \(\sigma = 0.5 \sigma_0\) and a very small \(\epsilon_{LJ} = 10^{-3}\) is switched on. Next, the range and strength of Lennard-Jones potential are gradually increased to their final values. We equilibrate disordered melt structures in the NPT ensemble using a Berendsen barostat and a Langevin thermostat with friction constant \(\Gamma = 0.5\). The temperatures and pressures are reported in reduced units \(T = 1.0\) and \(P = 8\), equivalent to \(T_0 = 550\) K and \(P_0 = 1\) bar in atomistic simulations. The time step used through all the simulations is 0.005\(\tau\). The chosen melt temperature is about 10\% higher than the crystallization temperature \(T_c\) of 0.9 of long polymer melts \((N \geq 50)\) obtained at a cooling-rate of \(10^{-6}\) \(\tau^{-1}\) [13].

The polymer configurations for \(N \leq 500\) were equilibrated until the average monomers mean-square displacement \(\langle \Delta r^2(t) \rangle\) is equal or larger than their mean square end-to-end distance \(\langle R^2_e \rangle\). The time for which \(\langle \Delta r^2(t) \rangle = \langle R^2_e \rangle\) is a measure of the relaxation time and it is comparable to the Rouse time for the short chains and the disengagement time for the entangled chains [19] as will be verified in section V. Polymer melts with \(N = 1000\), were equilibrated until \(\langle \Delta r^2(t) \rangle\) is comparable to their mean-square gyration radius \(\langle R^2_g \rangle\). Table 1 provides a summary of configurations of polymers and the simulation time for equilibration after push off stage in units of \(\tau\). Then, the data for characterization of static and dynamic properties are acquired.

In order to analyze the static properties of CG-PVA polymers, we extract from the polymer configurations the normalized probability distribution functions of the internal distances, the gyration radius, the bond length and angle of polymers as well as the bond length and angle of their primitive paths. We acquire the numerical probability distribution of a desired observable \(x\) by accumulating a histogram \(H_N(x)\) of a fixed width \(\Delta x\). Then, we calculate the normalized probability distribution function as

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P_N(x) = \frac{H_N(x)}{\sum_{x'} H_N(x') \Delta x}.
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**Units and simulation aspects**

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\]

**Structural features of CG-PVA polymer melts**

We first present the results on the chain-length dependence of the mean square end-to-end distance and the gyration radius for chain sizes in the range \(5 \leq N \leq 1000\). The mean square end-to-end distance is defined as

\[
\langle R^2_e \rangle = \frac{1}{n_c} \sum_{i=1}^{n_c} \langle (\mathbf{r}_{i,N} - \mathbf{r}_{i,1})^2 \rangle \tag{3}
\]
We begin by characterizing the intrachain correlations for both monomer positions and bond orientations. To quantify the positional intrachain correlations, we calculate the mean-square internal distances (MSID) for various chain lengths defined as

$$\langle R^2(n) \rangle = \frac{1}{n_c N} \left( \sum_{i=1}^{n_c} \sum_{j=1}^{N-n} \frac{1}{N-n} (r_{i,j} - r_{i,j+n})^2 \right)$$

(5)

where $n$ is the curvilinear (chemical) distance between the $j$th monomer and the $(j+n)$th monomer along the same chain. MSID is a measure of internal chain conformation that can be used to evaluate the equilibration degree of long polymers.

In Fig. 3a, we present the rescaled mean square internal distance, $\langle R^2(n) \rangle / n_c^2 b^2$ obtained by averaging over 50 - 200 polymer melt configurations that are $10^3 \tau$ (5 x $10^3 \tau$) apart for short (long) chains. Up to $n \approx 10$, we find a good collapse of all the MSIDs. However, for larger curvilinear distances, the MSIDS of longer chains $N > 100$ are slightly larger but all follow the same master curves suggesting that longer chains are a bit swollen due to chains self-interactions. Note that the deviations of $\langle R^2(n) \rangle / n_c^2 b^2$ of $N = 1000$ chains for curvilinear distances $n > 100$ from other long chains are due to their poor equilibration. These results show that the $N = 1000$ chains are equilibrated at shorter length scales but their large-scale conformation still needs much longer equilibration time $\tau_{eq} \propto 3N^3/N_c \tau \approx 10^8 \tau$ where $N_c \approx 36$ is the entanglement length as will be discussed in the section IV.

From the asymptotic behavior of mean square end-to-end distances of long CG-PVA chains, we can extract their characteristic ratio $C_{\infty}$ and Kuhn length $\ell_K$. The characteristic ratio is defined by the relation $\langle R^2(N) \rangle = C_{\infty} (N-1) \ell_K^2$ where $\ell_K$ is the average bond length. From MSID of longer polymers, $N = 300$ and $N = 500$, we obtain $C_{\infty} = 5.70 \pm 0.04$. The Kuhn length gives us the effective bond length of an equivalent freely jointed chain which has the same mean square end-to-end distance $R_g^2$ and the same maximum end-to-end distance $R_{\text{max}}[1]$. For a freely jointed chain with $N_k$ Kuhn segments with bond length $\ell_K$, we have $R_{\text{max}} = (N_k - 1) \ell_K$ and $\langle R^2(N_k) \rangle = (N_k - 1) \ell_K^2$. For CG-PVA polymers, we find $R_{\text{max}} = (N-1) \ell_b$ and $\langle R^2(N \gg 1) \rangle = 5.70(N-1) \ell_b^2$. Equating $\langle R^2(N) \rangle$ and $R_{\text{max}}$ of the CG-PVA chains with those of the equivalent freely jointed chain, we obtain $\ell_b = 5.70 \ell_b = 2.83 \sigma$.

Next, we compare the mean square internal distance of CG-PVA polymers with $\langle R^2(n) \rangle$ of the generalized freely rotating chain (FRC) model [18, 31] for ideal chains. If the excluded volume interactions between different parts of a certain polymer are screened, one expects the FRC model to provide a good description of CG-PVA polymer melts. $\langle R^2(n) \rangle$ of FRC model only depends on the value of $\langle \cos \theta \rangle$ where $\theta$ is the angle between any two successive
The inset shows a linear-linear plot of diminishing bond-bond orientational correlation function for several chain sizes. The solid line shows the theoretical prediction of the generalized freely rotating chain (FRC) model with $\langle \cos \theta \rangle = 0.699$. (b) Semilog plot of bond-bond orientational correlation function $\langle \cos \theta(n) \rangle$ versus $n$ for various chain sizes. The straight line shows the fit with exponential decay of the form $\exp(-\ell_b/\ell_p n)$ with $\ell_b/\ell_p = 0.35 \pm 0.01$. The inset shows a linear-linear plot of diminishing bond-bond orientational correlation function of $N = 200$, 300 and 500 for $10 < n \leq 40$.

FIG. 3. (a) Rescaled mean square internal distance, $\langle R^2(n) \rangle/n\ell_b^2$ plotted as a function of the curvilinear distance $n$ along the chain backbones for several chain lengths. The solid line shows the theoretical prediction of the generalized freely rotating chain (FRC) model with $\langle \cos \theta \rangle = 0.699$. (b) Semilog plot of bond-bond orientational correlation function $\langle \cos \theta(n) \rangle$ versus $n$ for various chain lengths. The straight line shows the theoretical prediction of the generalized freely rotating chain model with chain backbones for several chain lengths. The solid line shows the theoretical prediction of the generalized freely rotating chain model with chain backbones for several chain lengths. The inset depicts a log-log plot of $\langle \cos \theta(n) \rangle$ at $T = 2$ for which a power law decay at $n > 10$ emerges.

FIG. 4. Bond-bond orientational correlation function $\langle \cos \theta(n) \rangle$ of CG-PVA polymers of chain length $N = 200$ versus $n$ at different temperatures as given in the legend. The samples at $T = 0.9$ and 0.8 are obtained from cooling of melt at $T = 1$ with constant rate of $10^{-6} \tau$. The inset depicts a log-log plot of $\langle \cos \theta(n) \rangle$ at $T = 2$ for which a power law decay at $n > 10$ emerges.

The value of $\langle \cos \theta \rangle$ for the CG-PVA model can be obtained from $P_N(\theta) \propto \exp[-\beta U_{\text{bend}}(\theta)]$ as

$$\langle \cos \theta \rangle = \frac{\int_0^\pi \sin \theta \cos \theta \exp[-\beta U_{\text{bend}}(\theta)]}{\int_0^\pi \sin \theta \exp[-\beta U_{\text{bend}}(\theta)]}.$$  \hspace{1cm} (7)

where $U_{\text{bend}}(\theta)$ is presented in Fig. 1. Doing the integration in Eq. (6) at $T = 1.0$ numerically, we obtain $\langle \cos \theta \rangle = 0.6985$. We can also directly infer $\langle \cos \theta \rangle$ from the MD simulations results as $\langle \cos \theta \rangle = \langle \mathbf{b}_{i,j} \cdot \mathbf{b}_{i,j+1} \rangle$ where $\mathbf{b}_{i,j}$ is the $j$th unit bond vector of the $i$th chain and the averaging is carried out over all the chains and 100-500 equilibrated polymer melt configurations that are $10^3 \tau$ apart. From MD simulations, we deduce the universal value of $\langle \cos \theta \rangle = 0.699 \pm 0.005$ independent of the chain length. This value agrees well with the Boltzmann-averaged mean value.

In Fig. 3a, we have also included the MSID of an equivalent freely rotating chain with $\langle \cos \theta \rangle = 0.699$. We find that MSIDs of short chains $N \leq 100$ fully agree with that of the freely rotating chain model whereas the MSIDs of longer chains present noticeable deviations from the FRC theory for $n > 10$. Hence, FRC model slightly underestimates the MSID of longer chains. Likewise, the characteristic ratio of the FRC model, given by $C_\infty = \frac{1 + \langle \cos \theta \rangle}{\langle \cos \theta \rangle}$, is slightly lower than the $C_\infty = 5.70$ estimated from the simulation results. These very small deviations are most-likely due to the correlation hole effect that stems from incomplete screening of interchain excluded volume interactions and leads to long-range intrachain correlations [27].

The observed swelling of long chains suggests that an evidence of remnant long-range bond-bond correla-
FIG. 5. (a) Non-Gaussian parameter defined as $\alpha(n) = 1/2(5 - 3\langle R^4(n)/\langle R^2(n)\rangle^2\rangle$ plotted as a function of the curvilinear distance $n$ for several chain lengths. The solid line shows the theoretical prediction of the generalized freely rotating chain (FRC) model with $\langle \cos(\theta) \rangle = 0.699$ and $\langle P_2(\cos(\theta)) \rangle = 0.37$. (b) Average of the second Legendre polynomial of cosine of angle between any two bonds with a curvilinear distance $n$. $\langle P_2(\cos(\theta)) \rangle$, decays exponentially versus $n$ for small curvilinear distances $n < 5$, and it exhibits a power law for larger $n$ values. The inset shows that the average of second Legendre polynomial of cosine of angle between two bonds with a separation $r$ oscillates strongly and decays rapidly with distance.
presents the non-Gaussian parameter of CG-PVA polymers of different chain lengths that is compared to that of the FRC model evaluated with \( \langle \cos \theta \rangle = 0.699 \) and \( \langle P_2(\cos \theta) \rangle = 0.37 \) extracted from simulation results. Overall, we find a good agreement between the \( \alpha(n) \) of CG-PVA polymers and that of the FRC model. However, we notice small deviations from the FRC model for long chains and \( n > 50 \).

In Fig. 5b, we have plotted \( \langle P_2(\cos \theta(n)) \rangle \) for different chain lengths. According to the FRC theory, \( \langle P_2(\cos \theta(n)) \rangle \) should also decay exponentially as \( \langle P_2(\cos \theta(n)) \rangle \approx \langle P_2(\cos \theta) \rangle^n \) [33]. We find that the initial decay of \( \langle P_2(\cos \theta(n)) \rangle \) up to \( n = 5 \) is well described by the FRC model predictions. However, for larger \( n \) we observe important deviations from the FRC model and \( \langle P_2(\cos \theta(n)) \rangle \) exhibits a clear power law behavior over more than one decade of \( n \). The observed power law behavior is a manifestation of long-range bond-bond correlations along the chain backbone that result from incomplete screening of excluded volume interactions. As noted by Meyer et. al. in the case of 2D polymer melts, it is related to the return probability after \( n \) bonds and the local nematic ordering of nearby bonds [34].

To understand better the origin of this power law decay, we investigate the intrachain nematic ordering by calculating the \( \langle P_2(\cos \theta(r)) \rangle \) for all bond pairs that belong to the same chain and their midpoints are a distance \( r \) apart. \( \langle P_2(\cos \theta(r)) \rangle \) is almost independent of chain length for \( N > 50 \). In the inset of Fig. 5b, we have presented the \( \langle P_2(\cos \theta(r)) \rangle \) as a function of distance \( r \) for \( N = 500 \). As can be seen, the orientational correlations oscillate and decay rapidly with \( r \). This behavior shows that for a fixed curvilinear distance \( n \) only bonds which are spatially close to each other with separations \( r \approx 1 \) contribute to \( \langle P_2(\cos \theta(n)) \rangle \). Therefore, one expects that \( \langle P_2(\cos \theta(n)) \rangle \) will be directly proportional to the return probability of monomer after \( n \) bonds [34] that we denote by \( p_{\text{ret}}(n) \). More precisely

\[
\langle P_2(\cos \theta(n)) \rangle \propto p_{\text{ret}}(n) \equiv \lim_{R(n) \to 0} \Psi[R(n)] \tag{9}
\]

where \( \Psi[R(n)] \) is the probability distribution function of \( R(n) \) i.e. the end-to-end vector of all the chain segments (subchains) with \( n \) bonds.

For an ideal self-similar chain \( \Psi[R(n)] \) for any subchain of size \( n \) follows a Gaussian distribution of the form

\[
\Psi_{\text{Gauss}}[R(n)] = \left( \frac{3}{2\pi \langle R^2(n) \rangle} \right)^{3/2} \exp \left( -\frac{3R^2(n)}{2\langle R^2(n) \rangle} \right) \tag{10}
\]

where \( \langle R^2(n) \rangle \sim n^{2\nu} \) and \( \int_0^\infty 4\pi R^2 \Psi(R) dR = 1 \) [1, 19]. Hence, the return probability scales as \( p_{\text{ret}}(n) \sim n^{-3\nu} = n^{-3/2} \). For semiflexible CG-PVA polymers with local correlations, we expect that \( \Psi[R(n)] \) follows Eq. 10 for \( n \gg 1 \). The scaling exponent that we obtain from fitting of \( \langle P_2(\cos \theta(n)) \rangle \) with power law is \(-1.4 \pm 0.1\), that is not so far from the prediction for the Gaussian chains. This small discrepancy is most likely due to insufficent statistics for large \( n \) values. To test the validity of Gaussian distribution for the internal distances we examine the behavior of intrachain distributions in the subsequent subsection.

**Intrachain distribution functions**

Having examined the intrachain correlations, we investigate conformational behavior of chains by extracting
the probability distribution of the internal distances, i.e. 
\[ P[R(n)] = 4\pi R^2(n) \Psi[R(n)] \] from the polymer configurations. As before, \( R(n) \) denotes the distance between any pair of monomers \( i \) and \( j \) that are \( n \equiv |i-j| \) bonds apart.

Let us first consider the probability distribution function of bond length \( P_N(b) \) corresponding to \( R(n) = 1 \). In Fig. 6a, we have shown the distribution of bond length that is independent of the chain length \( N \). The normalized distributions of bond length \( b \) can be well described by a Gaussian distribution of the form

\[ P_N(b) = \frac{\exp\left(-\frac{(b-b_{10})^2}{2\sigma_{b0}^2}\right)}{\sqrt{2\pi}\sigma_{b0}}, \tag{11} \]

in which \( \sigma_{b0} \) represents the standard deviation and the peak value \( b_{10} = 0.497 \) agrees with the average bond length.

Next, we examine the probability distributions of bond angles \( P_N(\theta) \) and compare them with the form expected from the Boltzmann distribution \( P_N(\theta) = A_0 \sin \theta \exp[-\beta \mu_{\text{ideal}}(\theta)] \) where \( A_0 \) is a normalization constant such that \( \int_0^{\pi} d\theta P_N(\theta) = 1 \). Fig. 6b presents \( P_N(\theta) \) obtained from accumulating the histograms of bond-angles and the Boltzmann distribution prediction. Overall, we find a good agreement between the two probability distribution functions for all the chain lengths.

Next, we focus on the normalized probability distribution of internal distances \( P[R(n)] \) for \( n > 1 \) and compare them to the theoretical distribution functions. The exact segmental size distribution functions of semiflexible polymers for an arbitrary \( n \) are not known. However, Koyama has proposed approximate expressions for the probability distribution functions of wormlike chain model [35] that are applicable to any semiflexible polymer model for curvilinear distances larger than the persistence segment [36]. The Koyama distribution is constructed in such a way that it reproduces the correct second and forth moments of internal distances, i.e. \( \langle R^2(n) \rangle \) and \( \langle R^4(n) \rangle \) and it interpolates between the rigid-rod and the Gaussian coil limits [36]. It is found to account rather well for the site-dependence of the intrachain structure of short CG-PVA polymers [17].

The Koyama distribution can be expressed in terms of scaled internal distances \( r(n) = R(n)/\sqrt{\langle R^2(n) \rangle} \) as

\[ P_{\text{Koyama}}(r) = \frac{r}{2\sqrt{3\pi n}(1-\eta)} \left[ \frac{3(r^2-\eta^2)}{2(1-\eta)^2} \right] \left[ 1 - \exp\left(-\frac{3r^2}{2(1-\eta)^2}\right) \right] \left[ 1 - \exp\left(-\frac{3r^2}{2(1-\eta)^2}\right) \right] \tag{12} \]

in which \( \eta = \sqrt{\alpha(n)} \) and \( \int_0^\infty P_{\text{Koyama}}(r) dr = 1 \). As one would expect, at sufficiently large \( n \) for which the non-Gaussian parameter \( \alpha(n) \) vanishes, the Koyama distribution becomes identical to the Gaussian distribution valid for fully flexible ideal chains. For ideal chains, the probability distribution function of the \( \mathbf{R}(n) \) is given by Eq. (10). As a result, the corresponding probability distribution function for the reduced internal distances, \( r(n) \), follows from

\[ P_{\text{Gauss}}(r) = 4\pi r^2 \left( \frac{3}{2\pi} \right)^{3/2} \exp(-3r^2/2(r^2)) \tag{13} \]

where \( \int_0^\infty P_{\text{Gauss}}(r) dr = 1 \). Particularly, one expects that the distribution functions of the end-to-end distance of sufficiently long chains should follow this distribution.

Let us first look at the distribution of internal distances for short subchains (segments). We verified the distribution of subchains does not depend on the chain length. Therefore, we focus on subchains of polymers with \( N = 500 \) monomers. Fig. 7a presents \( P[r(n)] \) for subchains comprising of \( n = 2 \) and 5 bonds. As can be seen, for such short segments the features of angular potential are dominant and the Koyama distribution can not provide an accurate description of segmental size distribution although it agrees well with \( P[r(n)] \) in the central region of the distribution and it captures accurately the height of the peaks.

Fig. 7b shows \( P[r(n)] \) for subchains with \( n = 9 \) and 29 bonds that are larger than the persistence segment size. We note that the signature of bending potential is still visible for \( n = 9 \). Thus, the Koyama distribution does not provide a good description. For \( n = 29 \), the Koyama distribution agrees quite well with the \( P[r(n)] \) extracted from simulations whereas the Gaussian distribution exhibits a poorer agreement. Additionally, we have included the distribution of the scaled end-to-end distance of short chains with \( N = 10 \) and \( N = 30 \) monomers in Fig. 7b. They coincide with the distributions of subchains with the same length. These results show that the chain-end effects, if any, are negligible and \( P[r(n)] \) only depends on \( n \). For longer subchains \( n = 50 \) and 100, \( P[r(n)] \) depicted in Fig. 7c displays a perfect agreement with the Koyama distribution. For such long subchains, the distribution functions approach to that of a Gaussian given by Eq. (13), as one would expect.

Finally, we present the normalized probability distributions of the scaled end-to-end distance \( r_e \) for \( N > 50 \) in Fig. 8a. All the data for \( P_N(r_e) \) collapse on a single master curve. We find a very good agreement between the master curves and the theoretical prediction for the \( N \)-independent normalized distribution function given by Eq. (13) as demonstrated in Fig. 8a.

Fig. 8b shows the normalized probability distributions \( P_N(r_g) \) of the scaled gyration radius \( r_g = (R_g^2/(R_g^2))^{1/2} \) for different chain lengths. Similar to \( P_N(r_e) \), the \( P_N(r_g) \) of chains with \( N \geq 50 \) collapse on a single master curve. The exact expression for the probability distribution of the gyration radius is more complicated and does not have a compact form [37]. However, the formula suggested by Lhuillier [38] for polymer chains under good solvent conditions is found to provide a good approximation for ideal chains [24, 26, 39] too. The Lhuillier formula for the scaled gyration radius \( r_g \) in \( d \)-dimensions reduces to

\[ P_N(r_g) = A_g \exp \left(-a_1 r_g^{-od} - a_2 r_g^d\right) \tag{14} \]
FIG. 7. Normalized probability distributions of reduced internal distances $r(n) = (R(n)^2/(R^2(n)))^{1/2}$, $P_N[r(n)]$ for subchains of $n$ bonds for polymers with $N = 500$ monomers. The segment sizes $n$ are given in the legends. Panel (b) also includes $P_N[r(N-1)]$ for $N = 10$ and $N = 30$. The solid lines represent the theoretical predictions for $P_N[r(n)]$ according to the Koyama distribution, Eq. (12), in all the panels and the Gaussian distribution, Eq. (13), in panels (b) and (c).

FIG. 8. a) Normalized probability distribution of reduced end-to-end distance $r_e = (R_e^2/(R^2_e))^{1/2}$, $P_N(r_e)$ shows a very good agreement with the Gaussian distribution (solid line) given in Eq. (13). b) Normalized probability distribution of the reduced gyration radius $r_g = (R_g^2/(R^2_g))^{1/2}$, $P_N(r_g)$. The solid line represents a fit to the theoretical prediction according to Eq. (14) with parameters $\nu = 1/2$, $a_1 = 0.125$, $a_2 = 1.54$ and $A_g = 7.8$.

in which the exponents $\alpha$ and $\delta$ are related to the space dimension $d$ and the Flory exponent $\nu$ by $\alpha = (d\nu - 1)^{-1}$ and $\delta = (1 - \nu)^{-1}$. $a_1$ and $a_2$ are system-dependent nonuniversal constants and $A_g$ is a normalization constant such that $\int_0^\infty P_N(r_g)dr_g = 1$. We find that the data of $P_N(r_g)$ of CG-PVA polymers can be well fitted by the $N$-independent normalized distribution function given by Eq. (14) as plotted in Fig. 8b. Having investigated the conformational properties of CG-PVA polymers, we focus on their structural properties in the Fourier space in the next subsection [17, 34].

**Form factor and structure factor**

A common way to characterize the structural properties of polymer melts is to explore their structure factor that can be measured directly in the scattering experiments. The structure factor encompasses the information about spatial correlations between the monomers via Fourier transform of density-density correlation functions. For spatially homogeneous and isotropic systems such as polymer melts at equilibrium, the static structure factor only depends on the modulus $q$ of the wave vector. The static structure factor $S(q)$ measured in scattering experiments of amorphous melts is often spherically averaged over all the wave vectors $q$ with the same modulus.
interchain contributions to the monomer density and their wave vectors with the same modulus and all the melt configurations. The angular brackets represent averaging over all the monomer pairs. It can be split into intrachain and interchain contributions.

\[ S(q) = S_c(q) + \rho_m h(q) \]  

(16)

where \( \rho_m = Nn_c/V \) (V volume of the simulation box) is the monomer density and \( S_c(q) = \frac{1}{Nn_c} \sum_{i=1}^{n_c} \sum_{m=1}^{N} \langle \exp[-iq \cdot (r_{i,n} - r_{i,m})] \rangle \)  

(17)

includes the contributions from intrachain pair correlations and it is called intrachain or single chain structure factor. Equivalently, \( F(q) = S_c(q)/N \) known as the form factor [1] is used to quantify the intrachain correlations in the Fourier space. The interchain contribution is given by \( h(q) \) that is defined as the Fourier transform of intermolecular pair correlation function [40] as

\[ h(q) = \frac{V}{(Nn_c)^2} \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} \sum_{m=1}^{N} \langle \exp[-iq \cdot (r_{i,n} - r_{j,m})] \rangle \].

(18)

We present the behavior of the form and structure factors for different chain lengths. We first focus on the form factor as depicted in Fig. 9. The form factor of Gaussian chains, known as the Debye function, is described by [1]

\[ F_{Debye}(q) = \frac{2}{Q^2} \left[ \exp(-Q) + Q - 1 \right] \quad \text{with} \quad Q = q^2 \langle R_g^2 \rangle \]  

(19)

In order to compare the behavior of CG-PVA polymers in the melt state with that of ideal Gaussian chains, in Fig. 9a, we have plotted the form factor of CG-PVA chains and the Debye function versus \( qR_g \). For all the chain lengths, we observe deviations from the ideal polymer behavior at high \( q \) values. The onset of deviations shifts progressively to larger wave vectors for longer chains. For the longest chains \( N \geq 300 \), we have also presented the
form factors \( F(q) \) in a Kratky-plot in Fig. 9b. This plot confirms the existence of a Kratky plateau in the scale free regime that extends up to \( qR_\kappa \approx 20 \) for \( N = 1000 \). The deviations at larger \( q \) values reflect the underlying form of the bond angle potential \( U_{\text{bend}}(\theta) \) that dominates the behavior of the form factor at length scales smaller or comparable to the Kuhn length.

Next, we present the structure factor of different chain lengths in Fig. 10. As we notice, the \( S(q) \) of all the polymer melts displays the characteristic features of the liquid-state. We find a very weak dependence on the chain length: for \( N > 50 \), the \( S(q) \) of various chain lengths are identical. We notice several important features in the structure factors. First, the structure factor at low \( q \) is very small. By virtue of compressibility equation that relates the isothermal compressibility \( \kappa_T \) to the structure of the liquid, i.e., \( \lim_{q \to 0} S(q) = \rho_m h_b T \kappa_T \), we conclude that the polymer melts are almost incompressible. Second, the first peak of \( S(q) \) at \( q^* \) characterizes the packing of monomers in the first nearest neighbor shell. The value of \( q^* \) nearly agrees with \( 2\pi/\sigma_0 \) reflecting that the first peak of \( S(q) \) is dominated by interchain contributions.

To gain more insight into the interchain correlations of CG-PVA polymers, we compare \( \rho_m h_b(q) \) with that of simple liquids with no internal structure. For such a simple liquid, we have \( S_c(q) = 1 \), hence \( \rho_m h_b(q) = S(q) - 1 \) [40]. Fig. 11a shows both \( \rho_m h_b(q) \) and \( S(q) - 1 \) for two chain lengths \( N = 50 \) and \( N = 500 \). We find that in the region near the first peak \( \rho_m h_b(q) \) and \( S(q) - 1 \) coincide confirming that the peak at \( q = q^* \) is totally determined by the interchain correlations. In Fig. 11a, we have also included \(-S_c(q)\). We note that for very low wave vectors beyond the peak region, \( \rho_m h_b(q) \) closely agrees with \(-S_c(q)\). This behavior shows that the correlation between monomers of different chains decreases with increasing distance. This decrease is concomitant by the increase of \( S_c(q) \) at low \( q \) values such that the sum of both intrachain and interchain contributions yields a small finite value for \( S(q) \) as \( q \to 0 \).

In the other extreme of \( q \gg q^* \), \( \rho_m h_b(q) \) deviates from \( S(q) - 1 \) as the large \( q \) behavior of structure factor is fully determined by the intrachain correlations due to the correlation hole effect [17, 27]. The correlation hole effect leads to a decreased probability of finding a monomer of another chain in the pervaded volume of a particular chain. To illustrate this point, in Fig. 11b, we have shown \( S_c(q) \) and \( S(q) \) for \( N = 50 \) and \( N = 500 \) in the same plot. We see that the large-\( q \) behavior is entirely dominated by intrachain contributions. These observations are in agreement with the prior investigations for short chain lengths \( 10 \leq N \leq 100 \) [17].

![FIG. 11. Comparison of (a) the interchain structure factor \( \rho_m h_b(q) \) and \( S(q) - 1 \) (b) the intrachain structure factor \( S_c(q) \) and total structure factor of CG-PVA polymer melts with \( N = 50 \) and 500.](image)

![FIG. 12. Normalized probability distributions of bond length of the primitive paths \( P_N(\ell^{(pp)}_b) \) for \( N = 300 \) and 500. The solid lines show fits with the Gaussian distribution given in Eq. (22) with \( \langle \ell^{(pp)}_b \rangle = 0.20 \pm 0.002 \), \( \sigma_{(N=300)} = 0.0287 \pm 0.001 \) and \( \sigma_{(N=500)} = 0.022 \pm 0.001 \).](image)
FIG. 13. (a) The bond-bond orientational correlation function \( \langle \cos \theta(n) \rangle \) versus \( n \). The straight lines show the fits with an exponential functions with the form \( \exp(-\ell_b/\ell_p n) \) with \( \ell_b/\ell_p = 0.35 \pm 0.01 \) and \( \exp(-\langle \ell_b^{pp} \rangle/\ell_p n) \) with \( \langle \ell_b^{pp} \rangle/\ell_p = 0.0544 \pm 0.005 \). (b) Normalized probability distribution of the angle \( \theta \) between any two consecutive bonds for primitive paths and original conformations of CG-PVA polymer melts with \( N = 300 \) and 500.

PRIMITIVE PATH ANALYSIS AND ENTANGLEMENT STATISTICS

Having investigated conformational and structural features of CG-PVA polymer melts, we focus on their topological characteristics, i.e. interchain entanglements. Entanglements stem from topological constraints due to the chain connectivity and uncrossability that restrict the movements of chains at the intermediate time and length scales. As first noted by Edwards [41], the presence of neighboring strands in a dense polymer melt effectively confines a single polymer strand to a tube-like region. The centerline of such a tube is known as the primitive path (PP). A practical and powerful method for characterizing the entanglements is primitive path analysis (PPA). Such an analysis provides us with an operational definition of primitive path and allows to investigate statistics of chain entanglements.

There exists a couple of variants of PPA in the literature [42–44] that are all similar in spirit. Here, we implement the PPA method proposed by Everaers et al. [44] that identifies the primitive path of each polymer chain in a melt based on the concept of Edwards tube model [41]. The primitive path is defined as the shortest path between the chains ends that can be reached from the initial conformations of polymers without crossing other chains. In this analysis, topologies of chains are conserved, and chains are assumed to follow random walks along their primitive paths. Therefore, the primitive path is a random walk with the same mean square end-to-end distance \( \langle R_e^2 \rangle = \langle R_e^{pp} \rangle \) but shorter bond length \( \ell_b^{pp} \) and contour length \( L^{pp} = (N - 1)\ell_b^{pp} \).

In practice, by extracting the average bond length of the primitive paths \( \ell_b^{pp} = 1/(N - 1)\langle \sum_{i=1}^{N-1} |r_{i+1} - r_i| \rangle \), we can determine all the other desired quantities. In particular, the Kuhn length of primitive path \( \ell_K^{pp} \) is obtained as

\[
\ell_K^{pp} = \frac{\langle R_e^2 \rangle}{\langle L^{pp} \rangle} = \frac{\langle R_e^2 \rangle}{(N - 1)\langle \ell_b^{pp} \rangle}. \tag{20}
\]

The so-called entanglement length \( N_e \), defined as the average number of monomers in the Kuhn segment of the primitive path, follows from

\[
N_e = \frac{\ell_K^{pp}}{\langle \ell_b^{pp} \rangle} = \frac{\langle R_e^2 \rangle}{(N - 1)\ell_b^{pp}}. \tag{21}
\]

Operationally, we obtain the primitive paths of polymers in a melt by slowly cooling the system toward \( T = 0 \) while the two chain ends are kept fixed. During this procedure, the intrachain excluded volume interactions and bond angle potential are switched off. The system is then equilibrated using a conjugate gradient algorithm in order to minimize its potential energy and reach a local minimum. We perform primitive path analysis for the two longest chain lengths that are fully equilibrated, i.e. \( N = 300 \) and 500 as it is known that poor equilibration affects the entanglement length [43].

We first examine the probability distributions of the bond lengths of the primitive paths, i.e. \( P_N(\ell_b^{pp}) \) as presented in Fig. 12. The distributions of bond lengths of the primitive paths are chain length dependent but both are centered at \( \ell_b^{pp} = 0.20 \). Furthermore, the primitive path bond length fluctuations are considerably larger than those of their original paths. The normalized distributions of primitive path bond length \( \ell_b^{pp} \) can be
well described by a Gaussian distribution of the form

\[
P_N(\ell_{pp}^b) = \frac{1}{\sqrt{2\pi}\sigma_N^2} \exp\left(-\frac{(\ell_{pp}^b - \langle\ell_{pp}^b\rangle)^2}{2\sigma_N^2}\right).
\]

(22)

where \(\sigma_N = \langle\ell_{pp}^b\rangle^2\) presents the N-dependent standard deviation of \(\ell_{pp}^b\).

Next, we investigate the statistical features of bond angles of the primitive paths. Fig. 13a presents the bond-bond orientational correlation function \(\langle\cos\theta(n)\rangle\) as a function of internal distance \(n\) for the primitive paths of chain lengths \(N = 300\) and 500. For comparison, we have also shown the \(\langle\cos\theta(n)\rangle\) of the original polymer conformations. Similar to the original polymer conformations, the initial decay of \(\langle\cos\theta(n)\rangle\) for \(10 < n < 80\) can be well described by an exponential decay. However, at short scales \(n < 10\), bonds are slightly stretched out because of the constraints of fixed chain ends during minimization of primitive path length. Assuming an exponential function of the form \(\exp(-n(\ell_{pp}^b)/\ell_{pp}^b)\), we can extract the persistence length of the primitive path \(\ell_{pp}^b\).

From the fit values, we find \(\ell_{pp}^b = 19(\ell_{pp}^b) = 3.80\sigma\) that is considerably larger than the persistence length of the original conformations \(\ell_p = 1.42\sigma\).

We also examine the normalized probability distributions of bond angles \(\theta\) of the primitive paths as displayed in Fig. 13b. Unlike the bond angle distributions of the original chain conformations, the bond angles of the primitive paths is unimodal with its peak centered around \(\theta = 4.5^\circ\). Furthermore, the range of angles shrinks from \([0^\circ, 100^\circ]\) for the original paths to \([0^\circ, 20^\circ]\) for the primitive paths reflecting that the primitive paths are mainly in stretched conformations.

To explore the intrachain correlations of the primitive paths, we have plotted the mean square internal distances \(\langle R^2(n)\rangle/n\) for both paths approach the same value with increasing \(n\), since the chains endpoints during the primitive path analysis are held fixed. We find that results of \(\langle R^2(n)\rangle\) for the primitive path can still be relatively well described by the generalized FRC model provided that we use \(\langle\cos\theta\rangle^{pp} = \exp(-\langle\ell_{pp}^b\rangle/\ell_{pp}^b) = 0.947\) extracted from bond-bond orientational correlations. Having confirmed that the mean end-to-end distance of the primitive paths remain identical to those of the original chains, we obtain \(\ell_{pp}^b = 7.1 \pm 0.05\sigma\) for the Kuhn length of the primitive path. We note that \(\ell_{pp}^b\) is larger than the Kuhn length of polymers \(\ell_K = 2.93\sigma\).

Subsequently, we acquire the distribution of entanglement length \(P(N_e)\) as presented in Fig. 15a. We notice that \(P(N_e)\) has a narrow distribution and presents a weak dependence on \(N\) possibly resulting from the finite size of the chains. Our estimated value of the average entanglement length is \(\langle N_e \rangle = 36.2\) for \(N = 300\) and \(\langle N_e \rangle = 36.6\) for \(N = 500\). These results suggest that we are rather close to the asymptotic value of entanglement length \(N_e^\infty\). We have also plotted \(N_e P(N_e)\) in Fig. 15b and we find that the position of the peak of \(N_e P(N_e)\) coincides with our estimated value of \(\langle N_e \rangle \approx 36.5\). This observation is in agreement with the PPA analysis results for the Kremer-Grest (FENE) model [26].
DYNAMIC SCALING OF MONOMER MOTION

To compare the dynamic behavior of polymer melts with the predictions of the Rouse and reptation theories [19], we measure the mean square displacement (MSD) of monomers for short \((N < N_c)\) and long chains \((N > N_c)\). The quantities often used to characterize the segmental motion of polymer chains in a melt are listed below.

i) the mean square displacement of inner monomers

\[
g_1(t) = \frac{1}{n_c(N/2 + 1)} \sum_i n_c \sum_{j=N/4}^{3N/4} \langle [r_{i,j}(t) - r_{i,j}(0)]^2 \rangle
g_2(t) = \frac{1}{n_cN} \sum_i n_c \sum_{j=1}^{N} \langle [(r_{i,j}(t) - r_{i,cm}(t)) - (r_{i,j}(0) - r_{i,cm}(0))]^2 \rangle
\]

where only the monomers in the central region of a chain are considered to suppress the fluctuations caused by the chain ends.

ii) the mean square displacement of inner monomers with respect to the corresponding center of mass (c.m.)

\[
g_3(t) = \frac{1}{n_c} \sum_i n_c \langle [r_{i,cm}(t)]^2 - (r_{i,cm}(0))^2 \rangle
\]

iii) the mean square displacement of the center of mass of chains defined as:

\[
g_3(t) = \frac{1}{n_c} \sum_i n_c \langle [r_{i,cm}(t)]^2 - (r_{i,cm}(0))^2 \rangle
\]

For short chains the topological constraints do not play a dominant role. Hence, all the interchain interactions can be absorbed into a monomeric friction and a coupling to a heat bath. The dynamics of the chain can then be described by a Langevin equation with noise and the constraint that the monomers are connected to form a chain. This description is known as the Rouse random walk model [1, 19]. Beyond the microscopic timescale \(\tau_0\), the Rouse model predicts that both \(g_1(t)\) and \(g_2(t)\) scale as \(\sim t^{1/2}\) for timescales \(\tau_0 < t < \tau_R\) in which \(\tau_R = \tau_0N^2\) is known as the Rouse time. It corresponds to the longest relaxation time of polymers. At longer times corresponding to \(t > \tau_R\), \(g_1(t)\) is expected to follow the Fickian diffusion and scale as \(t\) whereas \(g_2(t)\) is predicted to exhibit a plateau. The mean-square displacement of chain’s center of mass is predicted to be diffusive \(g_3(t) = 6D_cm t\) at all the times \(t > \tau_0\) with the diffusion coefficient scaling as \(D_cm \sim 1/N\).

Fig. 16 presents the results of computed \(g_1(t), g_2(t)\) and \(g_3(t)\) for short non-entangled polymers of chain length \(N = 30\). The microscopic timescale \(\tau_0 \approx 3.1\tau\) is obtained as the time for which \(g_1(t) = \ell_0^2\) where \(\tau\) is the Lennard-Jones (LJ) time unit. The Rouse time is estimated as \(\tau_R = \tau_0N^2 \approx 2.79 \times 10^3\tau\). The dotted vertical lines mark the microscopic and Rouse timescales. As can be seen the Rouse timescale agrees well with the crossover points between two different scaling regimes. The horizontal dotted lines in Fig. 16 depict the values of \(g_1(t)\) and \(g_2(t)\) at \(t = \tau_R\). We find that \(g_1(\tau_R) \approx 3\ell_0^2(N)\) and \(g_2(\tau_R) \approx (2\ell_0^2(N))\). The solid lines show the best fits with power law. For timescales smaller than a Rouse time, \(g_1(t)\) and \(g_2(t)\) exhibit a subdiffusive behavior with exponents 0.64 and 0.6 which are slightly higher than the Rouse random walk model scaling prediction of \(t^{1/2}\).

The observed disagreement most likely originates from the finite persistence length of polymers. Additionally, at this regime \(g_2(t)\) is dominated by the crossover to the plateau. For chains with a persistence length smaller than their contour length, one expects that the monomer mean-square displacement scaling exponents to interpolate between those of the Rouse models for polymers with zero persistence length, i.e. \(t^{1/2}\) [1, 19] and semiflexible worm-like polymers \(t^{3/4}\) [45].

The mean square displacement of center of mass of polymers also deviates from the Rouse theory. At intermediate times \(\tau_0 < t < 200\ \tau\), it displays an apparent power law of the form \(g_3(t) \sim t^{0.83}\) before a crossover to the expected diffusive regime. The observed subdiffusive behavior is predicted by the recent theories [46, 47] that account for the viscoelastic hydrodynamic interactions. These theories attribute the anomalous behavior of \(g_3(t)\) in the transient regime to incomplete screening of hydrodynamic interactions beyond the monomer length combined with the time-dependent viscoelastic relaxation of the melt. This leads to a subdiffusive motion which is not described by a pure power law; an effective exponent should decrease with chain length, but asymptotic behavior is reached extremely slowly [46, 47]. Inspection of Fig. 16 shows that the data of \(g_3\) indeed exhibits a curvature with respect to the fitted power law and the effective

![Fig. 16. Mean square displacement (MSD) of inner monomers \(g_1(t)\), MSD relative to the center of mass of each chain \(g_2(t)\) and the MSD of center of mass \(g_3(t)\) of polymers of length \(N = 30\) as a function of time. The solid lines show the best fits with power law for timescales smaller and larger than the Rouse time \(\tau_R\). shown by solid lines for comparison.](image-url)
exponent of 0.83 is quite close to 1. The asymptotic dynamical scaling exponent for fully flexible chains with the Langevin dynamics is predicted to be 3/4. Considering the finite persistence length and chain size, this value is not surprising.

In long entangled polymer melts, each chain is expected to move back and forth (reptation) inside an imaginary tube with a diameter $d_T \approx N_c^{1/2}a \sim R_e(N_c)$ and a contour length $L^{(pp)}$ around the so-called primitive path. Such a dynamical tube-like confinement affects the segmental motion of entangled polymers. According to the reptation theory, the dynamic scaling behavior of MSD should exhibit a crossover behavior at several timescales, the microscopic timescale $\tau_0$, the entanglement time $\tau_e \sim \tau_0 N_c^2$, the Rouse time $\tau_R \sim \tau_0 N_c^2$, and the disentanglement time $\tau_d \sim \tau_0 N_c^2/\tau_e$ for long chains with $N \gg N_c$. The scaling predictions of reptation theory for various time regimes are given by [19, 48]:

$$g_1(t) \sim \begin{cases} t^{1/2}, & \tau_0 < t < \tau_e \\ t^{1/4}, & \tau_e < t < \tau_R \\ t^{1/2}, & \tau_R < t < \tau_d \\ t, & \tau_d < t, \end{cases}$$

Likewise, $g_2(t)$ is predicted to show the same regimes for $t < \tau_d$ but to go to a plateau with a value of $2(R^2_e)$ for $t > \tau_d$. The reptation theory predicts the following scaling behavior for the polymer center of mass mean square displacement

$$g_2(t) \sim \begin{cases} t, & t < \tau_e \\ t^{1/2}, & \tau_e < t < \tau_R \\ t, & \tau_R < t \end{cases}$$

(27)

To examine these scaling predictions, we compute $g_1(t)$, $g_2(t)$ and $g_3(t)$ for chain lengths $N = 300$ and $N = 500$ up to $t \approx 2 \times 10^7 \tau$. These chain lengths include on the average 8 and 14 entanglement lengths. The results of computed $g_1(t)$, $g_2(t)$ and $g_3(t)$ are presented in Figs. 17 and 18. For each chain lengths, similar to the predictions of reptation theory, we observe crossovers between several scaling regimes. We first estimate the predicted crossover timescales. The microscopic timescale $\tau_0 \approx 3.1 \tau$ is identical to that for short chains. The entanglement time is estimated as the Rouse time of the chain segment between two consecutive entanglements; $\tau_e = \tau_0 N_e^2 \approx 4.13 \times 10^{-7} \tau$. Likewise the Rouse time is obtained as $\tau_R(N) = \tau_0 N^2$ leading to $\tau_R(300) \approx 2.79 \times 10^5 \tau$.
and $\tau_R(500) \approx 3.28 \times 10^6 \tau$. The longest relaxation time determined as $\tau_d(N) = \tau_0 N^3/N_e$ corresponds to $\tau_d(300) \approx 2.29 \times 10^6 \tau$ and $\tau_d(500) \approx 1.08 \times 10^7 \tau$. The vertical lines in Figs. 17 and 18 mark these timescales. As can be noticed these timescales agree well with the crossover points between different scaling regimes for both chain lengths.

The horizontal dotted lines in panels a and b of Figs. 17 and 18 present the values of $g_1(t)$ and $g_2(t)$ at the corresponding timescales according to the reptation theory predictions. At $t = \tau_e$, where a Rouse chain of $N_e$ monomers is relaxed, the monomers displacement should be proportional to the mean squared diameter of the confining tube diameter $d_T$. Assuming that $d_T^2 \approx R_3^2(N_e)$ and the Gaussian picture for the tube, we expect that $g_1(\tau_e) \sim d_T^2/3 \approx 2R_3^2(N_e)$. For $t > \tau_e$, where the entanglement effects set in, monomer motions are restricted to movements along the contour of the confining tube with a contour length $L_T = d_T N/N_e$ until reaching the Rouse timescale $\tau_R(N)$. Since the tube itself is a random walk with a step length $d_T$, the displacement of a monomer at $t = \tau_R$ is $g_1(\tau_R) \sim d_T^2 (N/N_e)^{1/2} \sim (N/N_e)^{1/2} \ell_T$. For $\tau_R < t < \tau_d$, the dynamics of $g_1(t)$ is expected to crossover to a second $t^{1/2}$ regime which corresponds to the diffusion of the whole chain inside the tube-like region. After reaching the disentanglement time (reptation time) a chain has moved a distance comparable to its own size $g_1(\tau_d) \approx g_2(\tau_d) \approx (R_3(N))/2 = 3(R_2(N))$. The initial tube is completely destroyed and a new tube-like regime reappears. We find a good agreement between the measured values of $g_1(t)$ and $g_2(t)$ at various crossover timescales and the predictions of the reptation theory.

Having determined the crossover time and length scales, we obtain the dynamic exponents at various scaling regimes. The best fits of $g_1(t)$ and $g_2(t)$ with power laws are shown by solid lines in Figs. 17 and 18. In the first scaling regime, $\tau_0 < t < \tau_e$, we find that $g_1(t) \approx g_2(t) \propto t^{0.6}$ and the scaling exponent is larger than 1/2. This difference could again be attributed to the finite persistence length of chains as $N_e/\ell_K \approx 6$ is not large enough to fall in the random walk regime. In the second regime $\tau_e < t < \tau_R$, the obtained exponents of $g_1(t)$ and $g_2(t)$ are 0.36 and 0.38 for $N = 300$ and 0.31 and 0.35 for $N = 500$. These values are noticeably larger than the predicted 1/4 exponent. These deviations are probably because chains are not long enough to fully develop this reptation regime. These results suggest that much longer chains with $N/N_e \gg 1$ are needed to observe the predicted exponent in the asymptotic limit [49]. Nevertheless, upon increasing the chain length, the obtained exponents for the second scaling regime slightly improve. In the third regime, $\tau_R < t < \tau_d$, $g_1(t) \propto t^{0.55}$ and the exponents of both chain lengths are slightly larger than 1/2. In this regime, $g_1(t) \propto t^{0.3}$ for $N = 300$ and $g_2(t) \propto t^{0.32}$ for $N = 500$. Unlike the theoretical predictions $g_2(t)$ scaling significantly differs from that of $g_1(t)$. This discrepancy is also most likely because $N/N_e$ is not sufficiently large; the fit region includes the broad crossover to the asymptotic plateau. At the disengagement time, we find that the relation $g_1(\tau_d) \approx g_2(\tau_d)$ roughly holds. For $N = 300$, we can observe the free diffusion regime of $g_1(t)$ beyond $\tau_d$ where $g_1(t) \approx g_2(t)$ and for the $g_2(t > \tau_d)$, we observe the expected plateau value of $2(R_2^2(N))$ for nearly two third of a decade. For $N = 500$, much longer simulation times are required to obtain reliable results for $t > \tau_d$.

Finally, we examine the scaling behavior of the mean square displacement of the center of mass of polymers. In contrast to the predictions of reptation theory, we observe two distinct scaling regimes for $t < \tau_R$. The first one corresponds to $\tau_0 < t < \tau_e$ where $g_3(t)$ exhibits a subdiffusive behavior with $g_3(t) \propto t^{0.76}$ for $N = 300$ and $g_3(t) \propto t^{0.78}$ for $N = 500$. Similar to the short chains, this subdiffusive behavior results from the coupling to time-dependent viscoelastic relaxation of the melt background [46, 47]. At timescales $\tau_e < t < \tau_R$, we observe a second scaling regime where $g_3(t) \propto t^{0.68}$ for $N = 300$ and $g_3(t) \propto t^{0.62}$ for $N = 500$. These exponents again are notably larger than the theoretical predictions due to the finite size of the chains, but as expected, they systematically decrease with chain length.

**CONCLUSIONS**

We have investigated the static and dynamic properties of polymer melts of a locally semiflexible bead-spring model known as the CG-PVA model [10, 28]. The main distinctive feature of this model system is a triple-well bending potential that leads to polymer crystallization upon cooling of the melt. We have equilibrated polymer melts with chain lengths $5 \leq N \leq 500$. The results for the long chains allow us to determine the Kuhn length $\ell_K$, the persistence length $\ell_p$, and the entanglement length $N_e$ of the model polymers accurately as summarized in Table II. We note that the relation $\ell_K \approx 2\ell_p$ holds for the semiflexible CG-PVA polymers.

| $\ell_b/\sigma$ | $\langle \cos \theta \rangle$ | $C_\infty = \ell_K/\ell_b$ | $\ell_p/\ell_b$ | $N_e$ |
|----------------|-------------------------------|-----------------|----------------|------|
| 0.497          | 0.699                         | 5.70            | 2.85           | 36.5 |
| ±0.002         | ±0.005                        | ±0.04           | ±0.01          | ±0.5 |

**TABLE II.** Summary of characteristic features of CG-PVA model where $\ell_b$ is the average bond length, $\theta$ is the angle between two successive bonds, $\ell_p$, $\ell_K$, and $N_e$ are the persistence length, Kuhn length and entanglement length, respectively.

We have also examined the validity of Flory’s ideality hypothesis for this model system. Our detailed examination shows that the conformations of CG-PVA polymers agree with many of the theoretical predictions for ideal chains. Notably, long polymer melts with $N > 50$ follow
the scaling relations \( \langle R_e^2 \rangle / \langle R_g^2 \rangle = 6 \) and \( \langle R_e^2 \rangle \propto N \) valid for ideal chains. The probability distribution functions of the reduced end-to-end distance \( r_e = \langle R_e^2 / \langle R_g^2 \rangle \rangle^{1/2} \) and the reduced gyration radius \( r_g = \langle R_g^2 / \langle R_g^2 \rangle \rangle^{1/2} \) for chain lengths \( N \geq 100 \) also collapse on universal master curves that are well described by the theoretical distributions for the ideal chains.

Investigating the intrachain correlations, we find evidences for deviations from ideality. However, these non-Gaussian corrections are rather small and do not affect most of the large-scale conformational features. The mean square internal distances of short chains show an excellent agreement with the predictions of the generalized freely rotating chain model [18] whereas those of longer chains are slightly larger. The observed swelling of longer chains reflects an incomplete screening of excluded volume interactions and is most likely related to the correlation hole effect [21, 27]. We also compare the non-Gaussian parameter of CG-PVA polymers with that of the freely rotating chain model. The agreement is rather good and we only observe some small deviations for long chains.

Carefully examining the bond-bond correlations of long chains at \( T = 1 \approx 1.1T_c \), we do not observe any long-range bond-bond correlations. Instead, the triple-well angle-bending potential leads to weak anti-correlations for curvilinear distances of about \( n \approx 20 \). The observed anti-correlation is a precursor of chain backfolding in the melt at temperatures slightly above the crystallization temperature. This feature is further enhanced in the semicrystalline state and it is a signature of chain-folded structures [28, 29]. The anti-correlations suppress long-range bond-bond correlations but the long-range intrachain correlations are visible in the second Legendre polynomial of the cosine of angles between the bonds, \( \langle P_2[\cos \theta(n)] \rangle \), that exhibit a power law decay in analogy to the reports for 2D polymer melts [34].

Moreover, we have investigated in detail the intrachain and interchain structure factors of different chain lengths. The interchain structure factor is almost independent of the chain length whereas the intrachain structure factor \( S_c(q) \) depends on \( N \) as expected. We find that \( S_c(q) \) of sufficiently long CG-PVA polymer are well-described by the Debye function for length scales larger than the Kuhn length. The agreement with the Debye function improves upon increase of \( N \). Notably, we observe a plateau in the Kratky plot for the range \( 2 < qR_g < 20 \). Our results are in contrast with the findings for fully flexible chains that exhibit significant deviations from the Debye function at intermediate wave-vectors [21, 23, 24]. But, they agree with the recent findings that increasing the bending stiffness of the chains in a melt, irrespective of details, improves the agreement with the ideal-chain limit [26].

Using the primitive path analysis, we have determined the average entanglement length \( \ell_c \) of long and equilibrated chains and we have compared the original polymer melts with their primitive paths. Probing the bond-bond orientational correlation function and the mean square internal distance of primitive paths, we confirm the assumption that polymers behave nearly as Gaussian chains along their primitive paths. Notably, the Kuhn length of the primitive path \( \ell_K^{(pp)} \) is more than twice the \( \ell_K \) of the original path. The average bond length of primitive paths follows a Gaussian distribution and the peak of the first moment of the entanglement length probability distribution agrees with the average entanglement length.

Investigating the segmental motion of entangled polymer melts, we observe several scaling regimes as predicted by the reptation theory. The crossover time and length scales between distinct scaling regimes agree with the predictions of the reptation theory [19, 48]. However the dynamical exponents of monomer mean square displacements are different from those of the theory most probably due to the finite persistence length and size of polymers. The mean square displacement of center of mass of polymers also exhibits an anomalous diffusion at the timescale where the Rouse and reptation theories predict a Fickian diffusion. However, our results are qualitatively consistent with the more recent theories [46, 47] that attribute the subdiffusive motion of polymers center of mass to viscoelastic hydrodynamic interactions. It still remains an open question, how a finite persistence length of polymers affects quantitatively the dynamic exponents of center of mass particularly in the reptation regime.

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