Quantitative analysis of chain packing in polymer melts using large scale molecular dynamics simulations

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Abstract: We have carried out a quantitative analysis of the chain packing in polymeric melts using molecular dynamics simulations. The analysis involves constructing Voronoi tessellations in the equilibrated configurations of the polymeric melts. In this work, we focus on the effects of temperature and polymer backbone rigidity on the packing. We found that the Voronoi polyhedra near the chain ends are of higher volumes than those constructed around the other sites along the backbone. Furthermore, we demonstrated that the backbone rigidity (tuned by fixing the bond angles) affect the Voronoi cell distribution in a significant manner, especially at lower temperatures. For the melts consisting of chains with fixed bond angles, the Voronoi cell distribution was found to be wider than that for the freely jointed chains without any angular restrictions. As the temperature is increased, the effect of backbone rigidity on the Voronoi cell distributions diminishes and becomes similar to that of the freely jointed chains. Demonstrated dependencies of the distribution of the Voronoi cell volumes on the nature of the polymers are argued to be important for efficiently designing the polymeric materials for various energy applications.

I. INTRODUCTION

Polymers have been proposed\cite{1,2,3} as an alternative materials for providing mechanical flexibility and stability at relatively low cost for myriad energy applications. Such application include lithium batteries\cite{1}, organic photovoltaics\cite{2,3}, and supercapacitors\cite{4}. However, there is considerable scope when it comes to designing and synthesizing efficient polymer materials for energy applications despite a plethora of research both by the experimental and theoretical community.

A fundamental understanding of how polymer chains pack in the melts is of paramount importance for the development of a molecular description of the transport\cite{5,6} of electrolytes through the polymer matrix. Structure-property concepts such as fragility\cite{5} demands a systematic study of the chain packing effects and the free-volume distribution\cite{6,7} in polymeric melts. In general, the chain packing depends on the architecture of the polymers and several other experimental variables affecting crystallinity of the materials. However, in the amorphous state, two key experimental variables are the temperature and the backbone rigidity, which clearly affect the performance of different polymeric materials in devices\cite{1,2,3}.

In this work, we have studied the effects of temperature and backbone rigidity on the packing of chains in amorphous melts using molecular dynamics (MD) simulations. The simulation method is presented in section II followed by the results and conclusions in sections III and IV respectively.

II. SIMULATION METHOD

We have used the Large-scale Atomic/Molecular Massively Parallel Simulator\cite{8} (LAMMPS) for carrying out the Brownian dynamics (BD) simulations for the polymer melts. The polymer

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chains are modeled by a coarse-grained model (known as Kremer-Grest bead-spring model\(^9\)). In particular, the Langevin equation is integrated, given by

\[
m\ddot{r}_i = -\zeta \dot{r}_i - \nabla r_i U (\{r_i\}) + f_i(t),
\]

where \(m, \zeta\) are the mass and the friction coefficient for the beads. \(U (\{r_i\})\) is the pairwise interaction potential and is given by \(U (\{r_i\}) = U_{\text{LJ}}(r_{ij}) + U_{\text{FENE}}(r_{ij})\), where \(U_{\text{LJ}}\) is the truncated and shifted Lennard-Jones potential, which is purely repulsive. Explicitly, it is given by

\[
U_{\text{LJ}} (r_{ij}) = \begin{cases} 
4\varepsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{1}{4} \right], & r_{ij} \leq 2^{1/6}\sigma \\
0, & r_{ij} \geq 2^{1/6}\sigma 
\end{cases}
\]

Furthermore, the finite extensible nonlinear elastic (FENE) potential is used in combination with the Lennard-Jones potential to maintain the topology of the molecules. Explicitly, \(U_{\text{FENE}}\) can be written as

\[
U_{\text{FENE}} (r_{ij}) = \begin{cases} 
-0.5k r_{c}^2 \ln \left[ 1 - \left( \frac{r_{ij}}{r_{c}} \right)^2 \right], & r_{ij} \leq r_c \\
\infty, & r_{ij} \geq r_c 
\end{cases}
\]

so that \(r_c\) is the maximum extent of a bond. Here, we have used the notation \(r_{ij} = |r_{ij}|\). Following Ref.\(^9\), we have chosen \(r_c = 1.5\sigma, k = 30\varepsilon/\sigma^2, \zeta = 0.1/\tau\), where \(\tau = \sigma \sqrt{m/\varepsilon}\) is the parameter used to quantify time steps. Results presented in this paper were obtained by carrying out the simulations in dimensionless units so that \(r^* = r_c/\sigma = 1.5, k^* = k\sigma^2/\varepsilon = 30, \zeta^* = \zeta/\tau = 0.1\) and \(\epsilon^* = 2\epsilon\) (used in \(U_{\text{LJ}}\) replacing \(\epsilon\)) so that explicit values of \(\epsilon, \sigma\) and \(m\) are needed to switch from dimensionless units to the real units.

In this work, we present results for polymer melts corresponding to a number density of monomers \(\rho^* = \rho\sigma^3 = 0.85\), which corresponds to 128,000 particles in a cubic box of edge length \(L^* = L/\sigma = 53.20\). The simulations are performed by using periodic boundary conditions for two sets of chains: freely jointed chains and the chains with fixed angles between adjacent bonds. For the chains with fixed bond angles, we have used the harmonic angular potential to constrain the angle between adjacent bonds. Explicitly, the angular potential used in this work is written as

\[
U_H = \frac{K_\theta}{2} (\theta - \theta_0)^2.
\]

Simulation results presented here were obtained by choosing \(K_\theta = 20\epsilon\) and \(\theta_0 = 2\pi/3\) (in radians), which corresponds to a bond angle of 120 degrees. Polymer chains with 64 beads are studied at five temperatures \(T^* = k_B T/\epsilon = 0.2, 0.4, 0.6, 0.8\) and 1. Furthermore, all the simulations are carried out in the NVT ensemble so that the number density stays the same during the simulation runs. In other words, the effects of thermal expansion and the change in the number density with the change in temperature are not considered here. All the simulations were started from random configurations of the chains followed by a slow push-off set-up run for one million time steps as described in Ref.\(^9\) before moving on to the runs with the interaction potentials described above.

To quantify the chain packing, we have carried out a Voronoi analysis\(^10,11\) for the polymeric melts after fifty million time steps (in units of \(\tau\)). The Voronoi construction is carried out using the C++ library, Voro++. The results presented here are the averages of one thousand configurations spanning 1 million time steps, and we have carefully ensured that the results are independent of subsequent runs. Furthermore, the MD simulations have been carried out by using 2,400 cores on the supercomputer, Jaguar, followed by the Voronoi analysis on the data analysis cluster, Lens.
III. RESULTS

A snapshot of the polymer chains in the simulation box is shown in Fig. 1 along with the Voronoi construction for a single chain in a cubic box. It is clear from Fig. 1(b) that the shape and volume of the Voronoi polyhedra are highly sensitive to the conformations of the chain. In the case of the melts, the conformational degrees of freedom of the chains depends on the intra- and interchain interactions in a complicated manner. The BD simulation procedure described above allows us to study the effect of these interactions on the distribution of the Voronoi polyhedra in the melts and quantify the chain packing.

FIG. 1: Conformations of a couple of chains in the melts (containing 2,000 chains) are shown in Fig. 1(a). The chains are colored differently for demonstration purposes. In Fig. 1(b) a Voronoi construction for a single polymer chain in a cubic box is shown.

In Fig. 2 we present the histograms for the distribution of the Voronoi polyhedra in the melts containing the freely jointed chains and the chains with the fixed bond angles at different temperatures. These results, obtained for a fixed volume of the simulation box, clearly show that the temperature affects the distribution of the Voronoi polyhedra in a significant manner. At higher temperatures corresponding to $T^* = 0.6, 0.8, 1.0$, there are two sets of populations for both the freely jointed chains and the chains with the fixed bond angles. For a number density of $\rho^* = 0.85$, the average volume per particle is $1/0.85 = 1.176$ (in units of $\sigma^3$). Indeed a clear peak at the polyhedra volume of 1.176 is seen at all the temperatures with a finite width. An additional peak at higher volumes is observed and is found to correspond to the chain ends. Higher Voronoi polyhedra volume associated with the chain ends has been reported in the literature.

However, at lower temperatures (e.g., at $T^* = 0.2$) there are significant differences in the distribution of the Voronoi polyhedra, when the case of the freely jointed chains is compared with the chains with fixed bond angle. In the case of the chains with fixed bond angles, which correspond to relatively rigid chains, the distribution is wider in comparison with the freely jointed chains.

IV. CONCLUSIONS

In summary, we have demonstrated that polymer backbone rigidity affects the distribution of the free-volume in the polymeric melts, especially at low temperatures. In contrast to the fully
flexible chains such as in PEO, rigid chains have a wider distribution of the free-volume at lower temperatures. With the assumption that the distribution of the free-volume affects the transport of electrolytes, these results are important for an efficient design of polymeric materials intended for use in energy applications. In the case of organic photovoltaics, conjugated polymers (i.e., polymers with rigid backbones) are already used\(^2\). However, flexible macromolecules such as PEO are used for battery applications and show lower\(^1\) ionic conductivity for room-temperature applications. A wider distribution of the free-volume at lower temperatures is indeed necessary for the materials to conduct. Keeping this in mind, our results show that the polymeric materials with rigid backbone needs to be used for low-temperature applications, in contrast to the widely used approach of PEO-based materials. Also, we point out that this relatively newer idea of using rigid chains for battery applications conforms to some recently published experimental results\(^5\).

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