

Diffusion and Relaxation Dynamics of Supercooled Polymer Melts

Deng Pan^{a,b} and Zhao-Yan Sun^{a,c*}^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China^b University of Chinese Academy of Sciences, Beijing 100049, China^c Xinjiang Laboratory of Phase Transitions and Microstructures in Condensed Matters, College of Physical Science and Technology, Yili Normal University, Yining 835000, China

Electronic Supplementary Information

Abstract The dynamic properties of polymer melts are investigated in the range of normal liquid regime to the supercooled liquid regime. The polymer is modeled as a coarse-grained bead-spring model with chain length ranging from 5 to 160. The mean squared displacement and non-Gaussian parameter are used to describe the self diffusion of polymer beads. We find slow dynamics with decreasing temperature and increasing chain length. The time evolution of non-Gaussian parameters shows two peaks (or one peak one shoulder) in the α -relaxation time, τ_α , regime and sub-diffusion time regime, respectively, where the first primary peak indicates the dynamic heterogeneity stemmed from the motion of beads, and the secondary peak is the result of correlated motion along a polymer chain. Moreover, the relaxation of polymer beads shows clear two-step decay in supercooled melts and the dynamics shows growing heterogeneity with decreasing temperature. As chain length is increased, a peak of the dynamic susceptibility occurs, and the peak height, χ_4^* , increases and then reaches a plateau. The curves of the height of the first peak of α_2 , α_2^* , versus τ_α and the curves of χ_4^* versus τ_α follow two master curves for different chain lengths. Our results indicate the similarity of dynamic heterogeneity dominated by the motion of single bead even the chain length is different. It is interesting to find that the Stokes-Einstein (SE) relation between τ_α and diffusion coefficient D , $D \sim \tau_\alpha^{-1}$, is highly length-scale dependent. The SE relation breaks down in both normal melts regime and supercooled regime at large magnitude of wave vectors, attributed to the non-Brownian motion arising from the chain connectivity and growing heterogeneity due to supercooling. However, the SE relation is reconstructed when the probing length scale is large (at small magnitude of wave vectors). Our results show a hierarchical physical picture of the supercooled polymeric dynamics.

Keywords Supercooled polymer melt; Molecular dynamics simulation; Diffusion; Relaxation

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INTRODUCTION

Polymers have long chain lengths and complex chain architectures, thus they normally exhibit multi-scale structures and dynamics^[1]. The Rouse^[2] and reptation^[3, 4] models are widely accepted as dynamic theories in describing the unentangled and entangled polymer melts, respectively. In both models, the dynamics of polymer melts can be characterized by the scaling of mean squared displacement of beads (MSD, $g_1(t)$) versus time, *i.e.*, $g_1(t) \sim t^x$. For unentangled polymer melt, the power law exponent x is 1/2 for free Rouse regime and 1 for free diffusion regime, while for highly entangled polymer melt, the exponent x is 1/2 for free Rouse regime, 1/4 for constrained Rouse regime, 1/2 for reptation regime and 1 for free diffusion regime^[5].

When decreasing the temperature of polymer melts with a fast speed, the melts will undergo the glass transition and

turn into a glass. As the glass transition point is approached in a supercooled polymer melt, the structure shows negligible change but the dynamics dramatically slows down and heterogeneity rapidly grows up^[6–11]. However, the origin of this dynamic slowing down is still far from being understood. To uncover this problem, Götze *et al.*^[12] developed Mode-Coupling Theory (MCT), and predicted some remarkable scaling properties in α and β relaxation regimes. Chong and Fuchs presented first-principles theory for unentangled polymer chains^[13, 14] based on the MCT of glasses. Recently, some predictions of MCT were proposed for different model polymers with short chain length, such as flexible polymer model^[15–18], polymer model with stiffness^[19] and all-atom polymer model^[20, 21]. Extensive experiment and simulation studies suggest that the structural arresting mechanism in polymer systems is quite different from simple liquids^[20–25]. The recent theory^[26] and simulation^[27] investigations reveal that the chain structures also play an important role in the colloidal polymer system. Not only packing structures but also intrachain structures contribute to the structural arresting dynamics^[1, 28].

* Corresponding author: E-mail zysun@ciac.ac.cn

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The dynamics of glass-forming liquids can be described by transport coefficients (viscosity η and translational diffusion coefficient D) and the structural relaxation time τ . Normally the relation between relaxation and diffusion for a simple liquid with Brownian motion follows the Stokes-Einstein relation, *i.e.*, $D \sim \tau^{-1}$, which is the variant of $D \sim T/\eta$ ^[29–32]. However, this relationship breaks down and is often replaced by $D \sim \tau^{-\nu}$ with $\nu < 1$ for glass-forming liquids upon cooling^[33–35]. It is widely believed that the decoupling of diffusivity and viscosity in supercooled liquids, violation of SE relation, is due to the development of dynamic heterogeneity^[30, 36–40]. Since the typical lifetime and length scale of the heterogeneities increase as the temperature is lowered toward the glass transition point^[41], the length-scale-dependent decoupling between relaxation and diffusion is expected. However, up to now, the relation between relaxation and diffusion for supercooled polymer melt has not been well understood.

In order to uncover the relationship between relaxation and diffusion, in this work, we study the multi-scale dynamics in the supercooled polymer melts with different chain lengths by using molecular dynamics simulation. We find that the breakdown of SE relation occurs in both the normal melt regime and the supercooled regime at large magnitude of wave vectors (*i.e.*, the probing length scale is around the bead size), attributed to the non-Brownian motion arising from the chain connectivity and growing heterogeneity due to supercooling. However, the violation of SE relation disappears when the probing length scale is larger than the characteristic size, illustrating a hierarchical physical picture of the supercooled polymeric dynamics.

MODEL AND SIMULATION DETAILS

Coarse-grained bead-spring model is used to describe the polymer chain^[42], which is often used to study the glassy dynamics of polymeric systems^[43, 44]. Beads interact with each other *via* the truncated and shifted Lennard-Jones (LJ) potential, $U_{\text{LJ}}(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] + C$. The LJ potential is truncated at $2\frac{1}{6}\sigma$ and $2 \times 2\frac{1}{6}\sigma$, for bonded and non-bonded pairs, respectively, and C guarantees $U_{\text{LJ}}(2\frac{1}{6}\sigma) = 0$ or $U_{\text{LJ}}(2 \times 2\frac{1}{6}\sigma) = 0$. The finitely extensible nonlinear elastic potential, $U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln(1 - (\frac{r}{R_0})^2)$ with $R_0 = 1.5\sigma$, $k = 30\epsilon/\sigma^2$, is used to embody the connection between neighboring monomers of a chain. Here r is the distance between two beads, σ defines the length scale, and ϵ governs the strength of the interaction. For simplicity, we use reduced units in the simulation, where σ , ϵ , and the mass of each bead m are set to be unity. The LJ time scale $\tau_{\text{LJ}} = \sqrt{m\sigma^2/\epsilon}$.

The number of beads N in each chain (chain length) is 5, 10, 20, 40, 80, and 160 (slightly entangled^[42, 45]), respectively. The total number of beads N_b in the simulation box is 10240. Larger simulation boxes are also used for some state points and the results indicate that the finite size effects for the dynamics are small, and therefore we only show the result of systems with $N_b = 10240$ in the present work. The typical simulation procedure consists of three steps. (I) The

random walk like initial configuration of polymer chain was generated and randomly placed in the simulation box under periodic boundary conditions, and then relaxed for $4.0 \times 10^4 \tau_{\text{LJ}}$ with a soft potential where chain crossing is permitted. Then the polymers were relaxed in the canonical ensemble for $4.0 \times 10^5 \tau_{\text{LJ}}$ with LJ potential at temperature 1.50 to obtain an equilibrium configuration. (II) The volume was allowed to fluctuate in each simulation at a given temperature and pressure ($P = 1.0$) to determine the equilibrium density at this thermodynamic state point. In this procedure, the equilibrium density was obtained by averaging the densities for last $2.0 \times 10^5 \tau_{\text{LJ}}$ equilibrated run and ten independent samples. (III) With the resulting density the subsequent runs were performed for another $2.4 \times 10^4 \tau_{\text{LJ}}$ in the canonical ensemble to make sure that the polymers were fully equilibrated. Then the productive run was performed and all the dynamic properties were calculated from these productive canonical simulations. For the state points at other temperatures, the last configuration of productive run at higher temperature was used as the initial configuration instead of generating random walk initial configuration in order to save the simulation time. The temperature of this configuration was continuously decreased to the new target temperature (the cooling procedure is performed for $2.0 \times 10^4 \tau_{\text{LJ}}$, and the cooling rate varies from 2.5×10^{-5} to 1.0×10^{-6} according to different temperatures), in which the volume was allowed to fluctuate at pressure 1.0. Then the properties of this new state point can be collected after proceeding with step (II) and step (III).

In our molecular dynamics simulations, Newton's equations of motion were integrated with the velocity form of the Verlet algorithm and the temperature T was maintained by the Generalized Gaussian moment thermostat ($M = 2$), which is equivalent to the standard Nosé-Hoover thermostat when $M = 1$ ^[46]. The temperatures used in the simulation were 1.50, 1.00, 0.80, 0.70, 0.60, 0.55, 0.52, 0.50, 0.48, 0.46, respectively. In this work, the system at $T = 0.60$ started to show some typical properties of supercooled liquid, *i.e.*, slow dynamics and two-step relaxation, thus this temperature can be considered as the onset temperature. The pressure was maintained by the Anderson barostat. The time step was 0.002 for $T > 0.50$ and 0.004 for $T \leq 0.50$. Ten independent samples were used to improve the statistics. All the simulations were performed with the aid of NVIDIA GPU hardware.

RESULTS AND DISCUSSION

In this section, we first investigate the self-diffusion dynamics and relaxation of supercooled polymer melts with different chain lengths at various temperatures, and then we focus on the dynamic heterogeneity by calculating the non-Gaussian parameter and dynamic four-point susceptibility. We find slow dynamics and the growing dynamic heterogeneity induced by decreasing temperature and increasing chain length. Finally we study the relation between relaxation and diffusion in the polymer melts. We find decoupling of relaxation and diffusion in both normal

melt regime and supercooled regime at large vectors.

Self-diffusion

Typical rescaled MSD, $g_1(t)/b^2$, curves for chain length $N = 20$ (unentangled chain) as a function of rescaled time t/τ_{msd} at various temperatures are shown in Fig. 1(a). The $g_1(t)$ is defined as

$$g_1(t) = \langle r^2(t) \rangle = \frac{1}{N_b} \left\langle \sum_{j=1}^{N_b} (\mathbf{r}_j(t) - \mathbf{r}_j(0))^2 \right\rangle \quad (1)$$

where the $\mathbf{r}_j(t)$ is the position vector of particle j at time t , $\langle \dots \rangle$ indicates the time and ensemble average. The characteristic time τ_{msd} is defined as the time when $g_1(t)$ reaches b^2 , where b^2 is the effective squared bead size, calculated with $b^2 = \frac{\langle R^2 \rangle}{N-1}$, where $\langle R^2 \rangle$ is the mean squared end-to-end distance. The polymer chain remains Gaussian in the temperature range we studied, while the size of the chain shrinks a little upon cooling due to the attractive tail of LJ potential^[47]. Therefore the values of b^2 increase a little as chain length increasing ($b^2 = 1.54$ at $T = 1.50$, and $b^2 = 1.47$

at $T = 0.46$ for $N = 20$). After the ballistic regime, a plateau regime gradually develops with decreasing temperature, corresponding to the particles temporarily trapped in the cage formed by their neighbors. The duration of cage regime increases with decreasing temperature. After the plateau region, the $g_1(t)$ for different temperatures tends to follow a master curve, which is in accordance with the prediction of time-temperature superposition principle. Note that the power law exponent x in $g_1(t) \sim t^x$ is ~ 0.60 in the Rouse regime for $N = 20$, which is slightly larger than the theoretical prediction 0.50 for unentangled chains, attributed to the contribution of motion of free ends. For longer chain lengths (Fig. 1b), the Rouse motion is greatly suppressed and the reptation motion dominates in entangled melts (especially when $N = 160$). The fitted power law exponent x (the insert of Fig. 1b) in free Rouse regime decreases from ~ 0.7 to ~ 0.5 with increasing chain length, due to the negligible contribution of chain ends for longer chains. The rescaled MSD curves for different chain lengths at $T = 0.50$ are shown in Fig. 1(c). The height of the plateau is almost identical for all chain lengths, while the duration of this plateau increases with increasing chain length. In the region where $g_1(t) \geq b^2$, the values of $g_1(t)/b^2$ of longer chains decrease, indicating slower dynamics for longer polymer chains.

The non-Gaussian parameter

$$\alpha_2(t) = \frac{3\langle r^4(t) \rangle}{5\langle r^2(t) \rangle^2} - 1 \quad (2)$$

quantifies the deviation of the displacement distribution from the Gaussian behavior expected in simple diffusion, which is also used to measure the dynamical heterogeneity. For normal liquids, the motions driven by thermal fluctuations are usually time independent and their sum naturally converges to a Gaussian distribution due to the central limit theorem (CLT). For supercooled liquids, a peak will emerge upon cooling, indicating the growing dynamical heterogeneity of particles. However, for polymeric systems, the dynamics of polymer beads in a polymer chain is correlated within a time scale (especially in the range of Rouse relaxation time) due to the chain connectivity, and therefore the values of α_2 will exhibit another peak in the Rouse regime. The profiles of $\alpha_2(t)$ for $N = 80$ are shown in Fig. 2(a). It is clearly seen that $\alpha_2(t)$ of supercooled polymer melts shows two peaks^[48]. With decreasing temperature, the position and the height of the first peak increase, indicating growing heterogeneity and increasing relaxation time when approaching glass transition temperature. The second peak roughly begins at τ_{msd} and ends at the time when the free diffusion emerges. In this time regime, the motion of beads is greatly influenced by their adjacent beads due to chain connectivity. It is interesting to see that the temperature dependence of the peak height and the position of the second peak is very weak, indicating that the second peak is dominated by the chain connectivity but not temperature. It should be mentioned that the non-Gaussian statistics of dynamics in Rouse regime (roughly the second peak of α_2) might emerge in all polymeric systems, attributed to the correlated motion of polymer beads. When the dynamics of polymer beads enters into diffusive regime, the values of α_2

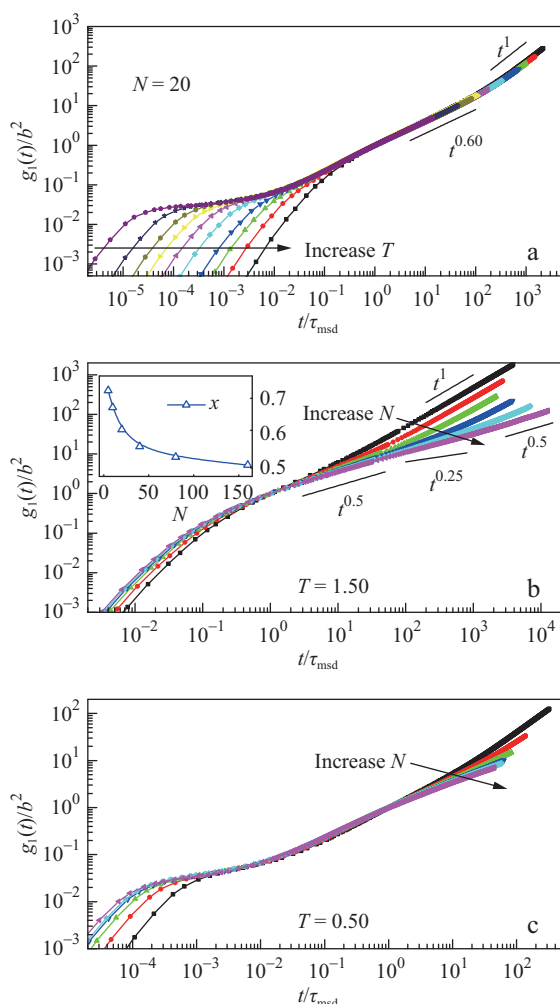


Fig. 1 The rescaled mean squared displacement versus rescaled time t/τ_{msd} for (a) $N = 20$ at different temperatures and for different chain lengths at (b) $T = 1.50$ and (c) $T = 0.50$. The inset is the chain length dependence of exponent x in free Rouse regime for $T = 1.50$.

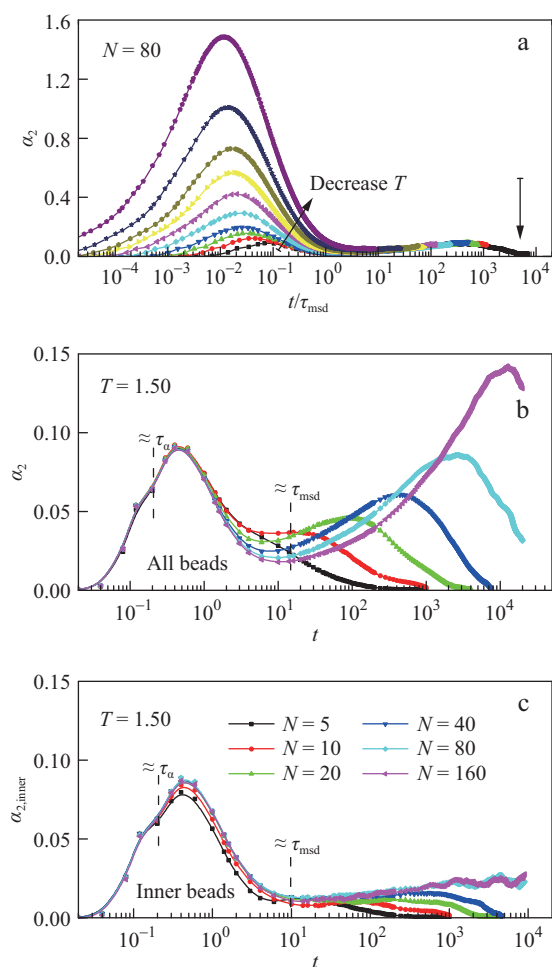


Fig. 2 (a) The non-Gaussian parameter for $N = 20$ at different temperatures. The vertical arrow points at the time when free diffusion emerges. The non-Gaussian parameter for (b) all beads and (c) inner beads at $T = 1.50$ for different chain lengths. The vertical dashed lines indicate the time scale of τ_α and τ_{msd} .

will converge to zero due to independent motions of each particle.

The profiles of $\alpha_2(t)$ for different N at $T = 1.50$ are shown in Fig. 2(b). Interestingly, the height and position of the first peak are almost the same for different chain lengths at $T = 1.50$, indicating the similarity of dynamic heterogeneity dominated by the motion of single bead even the chain length is different. However, the second peak is very sensitive to the chain length, corresponding to the regime dominated by chain connectivity. The deviation from Gaussian distribution in this regime is also related to higher mobility of the chain ends due to less constraint on the chain ends^[49]. In order to elucidate the effect of chain ends on the dynamic heterogeneity, we plot non-Gaussian parameters of inner beads, $\alpha_{2,inner}(t)$, as a function of time, as shown in Fig. 2(c). It is seen that the values of $\alpha_{2,inner}(t)$ in the chain connectivity dominating regime are much smaller than those in Fig. 2(b). These results imply that the second peak is the result of correlated motion of segments in a polymer chain.

Relaxation

The self-intermediate scattering function (SISF) is employed

to describe the relaxation dynamics, which is defined as

$$F_s(t, q) = \frac{1}{N_b} \left\langle \sum_{j=1}^{N_b} \exp(i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))) \right\rangle \quad (3)$$

where the magnitude of the wave vector $q = |\mathbf{q}|$. SISF at different q measures the self correlations in different length scales, and therefore SISF is highly length-scale dependent. Decreasing q implies increasing the probing length scale. To probe the multi-scale dynamics of polymer melts, the SISF at different wave vectors is investigated. The relaxation time τ_q is defined as the time when SISF decays to a threshold, such as e^{-1} or a smaller value^[1, 17, 42, 50]. Since the relaxation of particles in supercooled liquids usually obeys the time-temperature superposition principle at long-time scale, the choice of threshold of relaxation time does not change the qualitative properties of supercooled system as long as the time scale is long enough. So in our analysis, the relaxation time τ_q is defined as the time when SISF decays to 0.3^[47, 51, 52] at different wave vectors, where the time for $q^* = 7.1$ (approximately the first peak of the static structure factor) is defined as α -relaxation time, τ_α , and the corresponding static structure factors are given in Fig. S1 (in electronic supplementary information, ESI)^[1, 47].

The rescaled SISF plot at $q = 7.1$ (approximately q^*) is shown in Fig. 3. After the initially ballistic regime, the SISF exhibits quick one-step decay at higher temperatures. With decreasing temperature, a second decay develops, which follows a master curve for different temperatures ($T \leq 0.60$), as predicted by MCT^[15, 47, 53]. The master curve of the second decay can be well fitted by Kohlrausch-Williams-Watts (KWW) equation^[41], $\phi_x(t) = f_x \exp(-(t/\tau_{kww})^\beta)$, where β is the non-exponential parameter measuring the dynamic heterogeneity, τ_{kww} is the KWW relaxation time, and f_x is the non-ergodicity parameter. The fitted non-exponential parameter β is shown in the insert of Fig. 3. The values of β slightly decrease with increasing N , as an evidence for

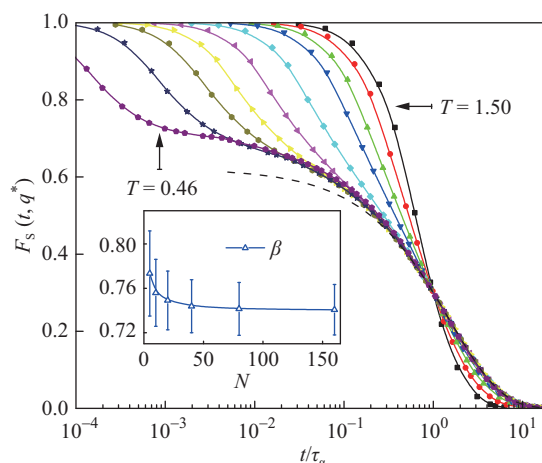


Fig. 3 Rescaled SISF plot at $q = 7.1$ for $N = 20$. The temperature T is 1.50, 1.00, 0.80, 0.70, 0.60, 0.55, 0.52, 0.50, 0.48, 0.46. The dashed line is the KWW fitting (for the data when $T \leq 0.60$) of the master curve for the second step decay. The chain length dependence of fitted non-exponential parameter β is shown in the inset.

growing dynamic heterogeneity for supercooled polymer systems with long chain lengths.

The dynamic susceptibility $\chi_4(t)$ is used to measure the scope to which the dynamics in space are correlated within a time interval, which is defined as $\chi_4(t) = N_b(\langle F^2(t) \rangle - \langle F(t) \rangle^2)$, and $F(t) = \frac{1}{N_b} \sum_{j=1}^{N_b} \cos(\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0)))$, where the

wave vector $\mathbf{q}$ normally takes q^* [54, 55]. The peak height χ_4^* approximately measures the volume over which the dynamic processes relevant to structural relaxation are correlated[8]. The curves of $\chi_4(t)$ for $N = 20$ are shown in Fig. 4(a). A peak occurs with time evolution and the peak height increases rapidly with decreasing temperature, indicating more cooperative dynamic processes for supercooled systems. Moreover, with increasing chain length, the peak height increases and then reaches a plateau (Fig. 4b), implying growing dynamic heterogeneity with increasing chain lengths for short chains and weak chain length dependence for longer chains.

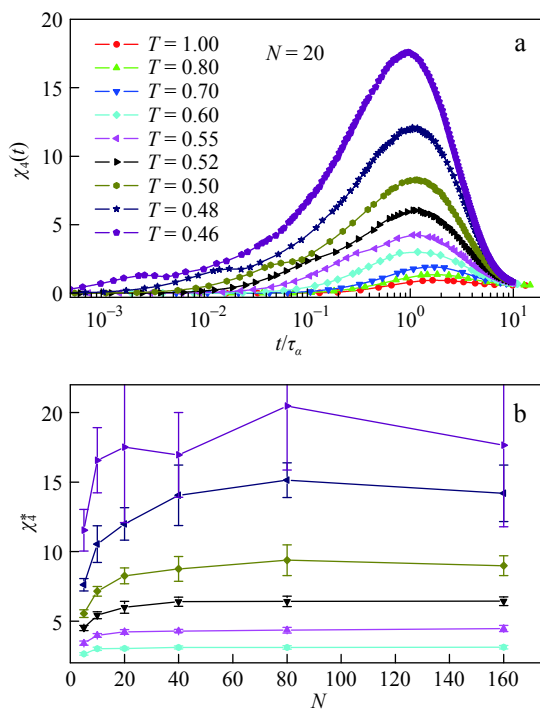


Fig. 4 (a) The time dependence of the dynamic susceptibility $\chi_4(t)$ for $N = 20$. (b) The chain length dependence of the peak value χ_4^* at selected temperatures 0.60, 0.55, 0.52, 0.50, 0.48, 0.46, from bottom to top.

Based on the data of $g_1(t)$, α_2 , $F_s(t, q = 7.1)$, and χ_4 , four characteristic times are obtained, which are τ_{msd} , τ_{α_2} , τ_α , and τ_{χ_4} , respectively. τ_{α_2} and τ_{χ_4} are defined as the peak time of non-Gaussian parameter α_2 (the first primary peak) and dynamic susceptibility χ_4 , respectively, which are related to the dynamic heterogeneity. Four characteristic times at different temperatures for $N = 20$ are shown in Fig. 5(a). With decreasing temperature, these four characteristic times increase rapidly, and τ_{msd} is much longer than τ_α , τ_{α_2} , and τ_{χ_4} .

Nevertheless, these four times can be well fitted by Vogel-Fulcher-Tamman (VFT) equation in the supercooled regime

(the solid lines in Fig. 5a), $\tau(T) = \tau_0 \exp(\frac{KT_0}{T - T_0})$, where T_0 is

the VFT glass transition temperature, and K is the fragility parameter. More interestingly, the fitting temperatures indicating the VFT glass transition points calculated with different relaxation times are surprisingly coincide with each other, as summarized in Table 1, implying the equivalence of these relaxation times when characterizing the dynamical slowing down of glass formers.

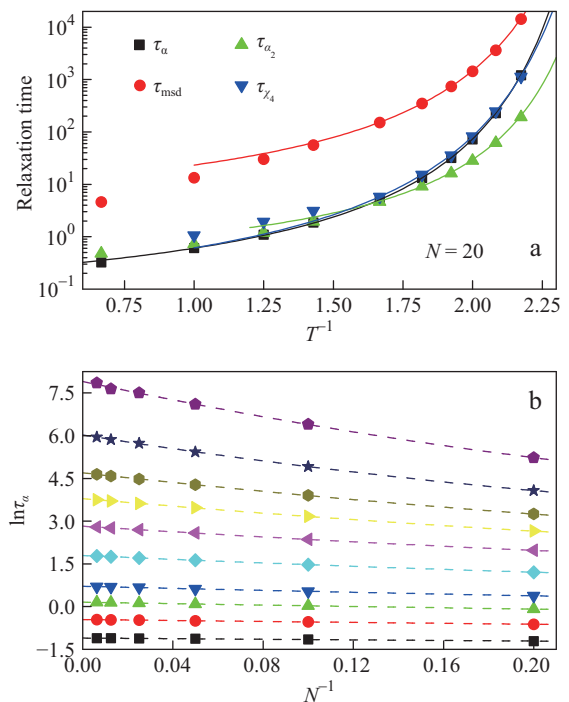


Fig. 5 (a) The temperature dependence of characteristic time τ_α , τ_{msd} , τ_{α_2} and τ_{χ_4} for $N = 20$. The solid lines are fitted with VFT equation. (b) The chain length dependence of τ_α at different temperatures. The dashed lines are fitted with $\ln \tau_{\alpha,T}(N) = \ln A + \frac{Bv_0}{v_{f,T}(\infty) + k_T N^{-1}}$. The temperatures decrease from the bottom to the top.

Table 1 VFT fittings for τ_{msd} , τ_{α_2} , τ_α , and τ_{χ_4} at different temperatures for $N = 20$

	τ_0	K	T_0
τ_α	0.18	2.00	0.375
τ_{msd}	7.88	1.86	0.369
τ_{α_2}	0.49	1.27	0.375
τ_{χ_4}	0.16	2.28	0.366

The chain length dependence of τ_α is shown in Fig. 5(b). The relaxation time increases with increasing chain length, which can be understood with the free volume picture. In the framework of free-volume picture, the specific volume of polymers should obey the classical Fox-Flory empirical equation, $v_T(N) = v_{\infty,T} + k_T N^{-1}$, where $k_T > 0$ [56]. Assuming that the close-packed volume of a given polymer is constant,

as a consequence, the free volume, v_f , should also obey this empirical equation. On the other hand, the relation between relaxation time and free volume has been given by the Doolittle equation in the free-volume model, $\ln \tau_\alpha = \ln A + B \frac{v_0}{v_f}$, where v_0 is the occupancy volume and $B > 0$ [57].

Coupling Fox-Flory relation and Doolittle equation, the relation between relaxation time and chain length can be

obtained as $\ln \tau_{\alpha,T}(N) = \ln A + \frac{Bv_0}{v_{f,T}(\infty) + k_T N^{-1}}$. As shown in

Fig. 5(b), $\ln \tau_\alpha(N)$ can be perfectly fitted with the above equation (the dashed lines), being an evidence of the validity of the free volume theory in describing the glass transition of polymer systems. Other three characteristic times also increase with increasing chain length, which can also be fitted with the above equation, as shown in Fig. S2 (in ESI). This might be another evidence of the equivalence of these relaxation times when characterizing the dynamical slowing down of glass formers.

Relationship between Relaxation and Diffusion

As we have already known, for the simple liquid with Brownian motion, the relaxation and diffusion should satisfy $D \sim \tau^{-1}$. However, this relationship often breaks down for glass-forming liquids upon cooling. Moreover, the relation between relaxation and self-diffusion of monomers for supercooled polymer system has not been well understood. In this work, we calculate the diffusion coefficient through the Einstein relation from the long time data of the MSD of beads, $D = \lim_{t \rightarrow \infty} \frac{g_1(t)}{6t}$ and we use τ_q to describe the relaxation time. Since decreasing q implies increasing the probing length scale, the relation between D and τ_q should be highly vector (length) dependent.

As is shown in Fig. 6, at large q (small length scale), clear decoupling between diffusion and relaxation is found in both normal melt regime ($T \geq \sim 0.7$) and supercooled regime ($T \leq \sim 0.6$) for polymer melt with $N = 10$. Different from normal liquid, the exponent ν for polymer system is 1.55 instead of 1.0 even in the normal melt regime. For polymer melt, the motion of beads is strongly influenced by the bonded neighbour beads, which limits the Brownian motion characteristics of polymer beads, leading to the breakdown of SE relation even in the normal melt regime. Moreover, the SISF at large q already decays, whereas the MSD is not yet diffusive. This might be another reason why SE relation breaks down even in the normal melt regime. In the supercooled regime, the exponent ν is ~ 0.83 , lower than 1.0, which is quite similar to the supercooled colloidal system. With decreasing temperature, the cage breaking process occurs cooperatively and heterogeneously, leading to the breakdown of SE relation in supercooled regime. With decreasing q (increasing length scale), the exponent ν approaches to 1.0 (the insert in Fig. 6), similar to the prediction of SE relation. It is widely accepted that the breakdown of SE relation is related to the dynamic heterogeneity. Since decreasing q implies increasing the probing length scale, and when the probing length scale is larger than the characteristic size (*i.e.*, cage size or

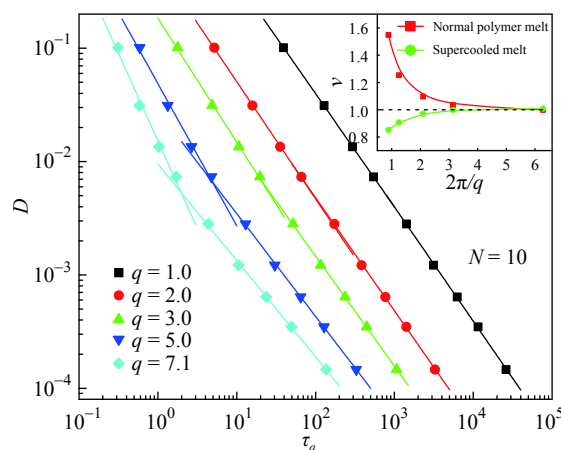


Fig. 6 lg-lg plot of D versus τ_q at several magnitudes of wave vector q for $N = 10$. The solid lines are the fitting curves by the power law $D \sim \tau_q^{-\nu}$ in normal melts ($T \leq \sim 0.7$) and supercooled melts ($T \leq \sim 0.6$), respectively. The fitted exponents ν are shown in the inset and the horizontal dashed line is the line of $\nu = 1.0$.

correlation size), the dynamics will be homogeneous. Therefore the SE relation is obeyed at smaller q region. These results imply that the SISF at various q can capture the dynamic slowing down in different length scales. Moreover, the length-scale dependence of the relation between relaxation and diffusion uncovers the hidden truth that the glassy dynamics at bead-size scale is significant for polymer melts.

To further investigate the relationship between the decoupling and the dynamic heterogeneity, in Fig. 7, we plot χ_4^* and the first primary peak value of non-Gaussian parameter α_2^* for different temperatures against the α relaxation time τ_α . Both values of χ_4^* (Fig. 7 left axis, closed symbol) and α_2^* (Fig. 7 right axis, open symbol) increase in going from high temperature to low temperature for different chain lengths. However, the increasing tendency for χ_4^* and α_2^* is different. χ_4^* has two power law relations with τ_α in the fast relaxation time with the exponent ~ 0.60 and in the middle relaxation time region with the exponent ~ 0.37 , respectively, which is consistent with the prediction of

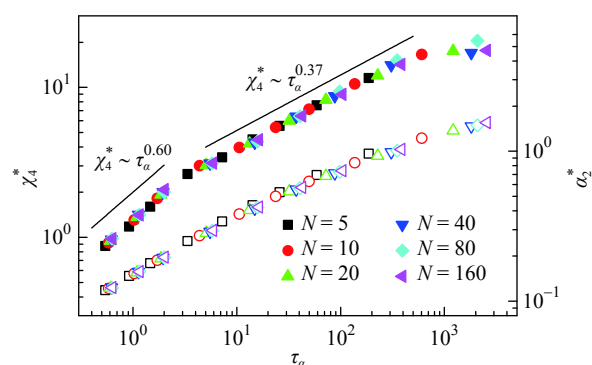


Fig. 7 τ_α dependence of χ_4^* (left axis, closed symbol) and α_2^* (right axis, open symbol) at different temperatures and chain lengths. The solid lines are the power law relations between χ_4^* and τ_α with exponents ~ 0.60 and ~ 0.37 in normal and supercooled melts, respectively.

MCT^[8, 54], while there is no apparent power law relation that can be fitted for α_2^* . This may provide some hints of the decoupling between the relaxation and diffusion. Our results also indicate that the dynamic heterogeneity grows in different ways in normal and supercooled melts. Nevertheless, both the relation between χ_4^* and τ_α and the relation between α_2^* and τ_α for different chain lengths follow master curves. This means that the chain length dependence of χ_4^* and α_2^* is very weak. It is believed that χ_4^* characterizes the dynamic heterogeneity described by the relaxation of beads, and α_2^* describes the dynamic heterogeneity related to the diffusion of beads. Both these two quantities are in the length scale of bead size, and therefore the chain length dependence of dynamic heterogeneity characterized by χ_4^* and α_2^* is invisible.

CONCLUSIONS

In this work, we investigate the diffusion and relaxation dynamics of polymer melt by molecular dynamics simulations. We find slow dynamics and growing heterogeneity with increasing chain length and decreasing temperature. For supercooled polymeric melts, there are two peaks (or one peak one shoulder) of non-Gaussian parameters, corresponding to the dynamic heterogeneity stemmed from the motion of beads and the correlated motion along a polymer chain. Moreover, the relaxation of polymer beads shows clear two-step decay in supercooled melts and the dynamics shows growing heterogeneity with decreasing temperature. Interestingly, for different chain lengths, both the curves of α_2^* versus τ_α and the curves of χ_4^* versus τ_α follow master curves, imply that the dynamic heterogeneity dominated by the motion of single bead is similar although the chain length is different. In order to understand the relation between diffusion and relaxation of supercooled polymeric system, we further discuss the applicability of Stokes-Einstein (SE) relation for polymer systems. We find that the relation between τ_q and diffusion coefficient D , $D \sim \tau_q^{-1}$, is highly length-scale dependent. At small length scales, the SE relation breaks down in both normal melts regime and supercooled regime. This may be attributed to the non-Brownian motion arising from the chain connectivity and growing heterogeneity due to supercooling. At large length scales, the SE relation is reconstructed due to the probing length scale larger than the characteristic size (bead size). This shows a hierarchical physical picture of the supercooled polymeric dynamics. The present work also supports the multi-scale physical picture that the dynamics of supercooled liquid can be coarse-grained into normal liquids over a relevant length scale^[58] (*i.e.*, cage size or correlation size). Our work may shed some light on uncovering the mystery of the relation between the structure and dynamics of polymeric glass-formers.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2132-9>.

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