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Probing Intermittent Motion of Polymer Chains in Weakly Attractive Nanocomposites

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Electronic Supplementary Information

Abstract In this study, we investigate the motion of polymer segments in polymer/nanoparticle composites by varying nanoparticle (NP) volume fractions. By studying the probability distribution of segment displacement, segment trajectory, and the square displacement of segment, we find the intermittent motion of segments, accompanied with the coexistence of slow and fast segments in polymer nanocomposites (PNCs). The displacement distribution of segments exhibits an exponential tail, rather than a Gaussian form. The intermittent dynamics of chain segments is comprised of a long-range jump motion and a short-range localized motion, which is mediated by the weakly attractive interaction between NP and chain segment and the strong confinement induced by NPs. Meanwhile, the intermittent motion of chain segments can be described by the adsorption-desorption transition at low particle loading and confinement effect at high particle loading. These findings may provide important information for understanding the anomalous motion of polymer chains in the presence of NPs.

Keywords Nanocomposites; Intermittent dynamics; The probability distribution of displacement; Confinement; Adsorption-desorption mechanism

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INTRODUCTION

Polymer nanocomposites (PNCs), formed by the mixture of nanoparticles (NPs) and polymer chains, have drawn intense attention over the last several decades. This is due to their unique characteristics associated with the properties of polymer and NPs, such as thermal stability, chemical resistance, and optical properties, all of which are of crucial importance in many practical applications.^[1–4] It is widely believed that these characteristics are related to many factors at the molecular scale, such as the interaction between NP and polymer chain,^[5–11] the chain rigidity,^[11–13] and the molecular weight.^[14–16] For example, modifying the polymer/NP interactions can tune viscoelastic properties of PNCs relevant to materials' processing and applications, and PNCs containing grafted NPs exhibit higher storage and loss module than those containing bare NPs.^[17] However, despite the significant progresses in PNCs on its role in the macroscopic properties of PNCs, a more detailed understanding of how the microscopic parameters affect macroscopic PNCs' properties remains requisite, just as a tip of the iceberg, due to the complexity of NPs and polymers, especially for the dynamics of polymer chains.

In a simple liquid, due to thermal fluctuations, particle motion follows Brownian motion originally derived by Einstein.^[18] The mean square displacement of particle becomes a linear function of time at long times. However, when particles move in a variety of complex environments,^[19–23] the motion of particles exhibits a nonlinear relation with time, *i.e.*, $\langle \Delta r^2(t) \rangle \sim t^\beta$, where $\beta < 1$. Such sub-diffusive behavior is usually accompanied with non-Gaussian distribution of particle's displacement, which can be characterized by the distribution of displacement probability, termed as self-part of the van Hove correlation function, $G_s(\mathbf{r}, t)$, which describes the probability of finding a particle at position $\mathbf{r}$ at a time t , given that it was located at the origin when $t = 0$. This distribution typically follows a Gaussian behavior in a simple liquid when the mean square displacement is linearly dependent on time. However, in some complex environments, this distribution generally shows multiple peaks together with an exponential tail at larger distance, which seems to be a universal dynamic feature of slow dynamics,^[24] as has been observed in recent simulations^[22,25,26] and experiments.^[27,28] More interestingly, the distribution of particle displacement could be non-Gaussian although the mean square displacement of particles follows a linear relation with time, which is firstly observed by Granick's group.^[20,28] This unexpected phenomenon then has been repeatedly shown in a diverse range of systems,^[21,23,26,27,29] attributed to the slowly changing, hetero-

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geneous fluctuations of the environment at comparable or slower timescale than that before the onset of Fickian diffusion.^[28]

In the past few decades, much attention has been paid to understanding the motion of polymer chains in different environments, where anomalous chain diffusion occurs due to topological constraints of polymer chains or external environmental factors.^[30–38] In PNCs^[15,16] or at polymer/solid interfaces,^[23,32,36] the confinement and/or adsorption/desorption occur due to the presence of NPs or substrates. These behaviors result in more seriously anomalous chain diffusion, and bring more interesting phenomenon including the immobilization of partial chains or hopping events. For instance, the jamming of NPs renders the dynamics of polymer chains more heterogeneous and leads to substantial enhancement in elasticity at high NP volume fraction than that of pure melt.^[39] Similarly, an anomalous chain diffusion occurs over the full range of time and the non-Gaussian motion is observed due to strong confinement at high NP volume fractions, which is confirmed by the simulation with the Asakura-Oosawa model.^[40] In addition, jump motion of polymer chain is observed on the surface of the substrate with strong attractive interaction due to the presence of hydrogen bonding, which can be explained by an adsorption-desorption mechanism.^[21]

According to the above studies, at polymer/solid interfaces, the origin of anomalous chain diffusion has been considered to be related to strong attractive interaction, which has greatly enhanced our understanding of the motion of polymer chains near the solid substrate. In PNCs, while various effects lead to anomalous chain diffusion and the occurrence of non-Gaussian behavior, the origin of the non-Gaussian behavior of polymer is not fully understood. Moreover, one difference between the substrate and spherical nanoparticle is that the surface curvature of NPs plays an important role in the motion of polymer chains. This means that the origin of non-Gaussian behavior of polymer may differ from that onto the substrate.^[21,23,41] Therefore, it is necessary to explore the motion of polymer chains and the origin of non-Gaussian behavior of polymer in PNCs.

Here, through employing a coarse-grained molecular dynamic simulations of PNCs with well-dispersed NPs,^[42] we provide new insights into the motion of chains by analyzing the probability distribution of displacement, particle trajectory, and the square displacement of particle. Our calculation shows that, with increasing NP volume fractions, a significant slowdown in the motion of polymer chains occurs due to the strong confinement induced by NPs, and the distribution of segment displacement gradually deviates from the Gaussian behavior. We demonstrate that the non-Gaussian behavior of polymer chains results from intermittent motion of segments. Then we explore the link of intermittent motion of segments with local environments that they stay by the ratio of slow segments, fast segments, and interfacial segments among all the segments. We find that, at low volume fractions, intermittent motion greatly depends on the interaction between NP and segment, while at high volume fractions, the confinement caused by NPs dominates the intermittent motion of

polymer segments.

The rest of this paper is constructed as follows. We first describe the model and simulation methods of PNCs in detail, including the equilibration procedure of systems. Then the motion of polymer chains is presented and analyzed, and the intermittent motion of polymer segments is discussed. Finally, the results are summarized.

MODEL AND SIMULATION DETAILS

Model Construction

In this paper, we employ a coarse-grained model of a system consisting of M_c flexible linear polymers with the chain length $N = 25$ and a number M_{NP} of spherical NPs with the radius $R = 2.0\sigma$. A pure polymer melt without NP is also investigated as a reference. We use the standard Kremer-Grest bead-spring model to describe the polymer chain.^[43] All non-bonded monomers interact with each other through the Weeks-Chandler-Anderson (WCA) potential, which is a purely repulsive Lennard-Jones (LJ) potential:

$$U_{ij}^{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & r_{ij} \leq 2^{\frac{1}{6}}\sigma \\ 0 & \text{others} \end{cases} \quad (1)$$

In addition to the WCA potential, the bonded monomers interact via a finitely extensible nonlinear elastic (FENE) potential:

$$U_{FENE}(r) = -\frac{1}{2}kR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right] \quad (2)$$

where $k = 30(\epsilon/\sigma^2)$ and $R_0 = 1.5\sigma$, from which the bond-crossing can be avoided. The average bond length r_b is about 0.97σ .

In this paper, ϵ , σ , and m represent the units of energy, length, and the bead mass, respectively. The time is given in the unit of $\sigma\sqrt{m/\epsilon}$. r_{ij} is the distance between bead i and bead j . By setting ϵ , σ , and m to be unity, all the quantities including the following results are given in LJ reduced units.

Each NP is modeled as a hollow sphere with N_b beads (the diameter of each bead and the mass is σ and m , respectively) stacked uniformly on the NP's surface. These beads are fixed by the rotations in the icosahedral group of order 60.^[44] A snapshot of a PNC is shown in Fig. 1. The number density of the surface beads is ~ 3.0 and the number of surface beads (depending on NP's size) is enough to prevent the chain from penetrating into the NP, and all beads belonging to one NP

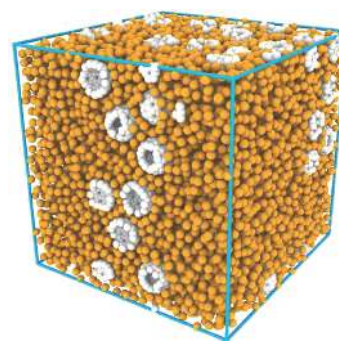


Fig. 1 Typical snapshot of PNCs with the radius of NP equal to 2.0σ . The volume fraction of NP is 0.18.

are grouped into a rigid body as a single entity. For the interaction involving NPs, the NP-NP interaction is given by the same WCA potential as Eq. (1), and the polymer-NP interaction is described by LJ potential including the attractive part with a cutoff distance $r_{\text{cut}} = 2.5$ in order to avoid the aggregation of NPs:

$$U_{ij}^{\text{LJ}}(r) = \begin{cases} 4\epsilon_{\text{NP}} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + C & r_{ij} \leq r_{\text{cut}} \\ 0 & \text{others} \end{cases} \quad (3)$$

where the constant C assures that the LJ potential vanishes if $r_{\text{cut}} \geq 2.5$, and $\epsilon_{\text{NP}} = \epsilon$. For comparison, the above detailed parameters of pure polymer and PNC melt (such as NP volume fraction, the simulation box size, and the number of NPs) are listed in Table 1.

Table 1 Simulated parameters containing volume fractions of NP (ϕ), the radius of NPs (R), the number of polymer chains (M_c), the number of NPs (M_{NP}), as well as the simulated box size (L). We define the NP volume fraction as $\phi = 4\pi R^3 M_{\text{NP}} / 3L^3$, and set the number density of polymer monomer to be $\rho = 0.85$.

R	ϕ	M_{NP}	M_c	L
—	0.00	0	1600	36.10
2.0	0.05	22	478	24.52
2.0	0.10	47	478	25.00
2.0	0.18	100	512	26.40
2.0	0.25	150	512	27.18
2.0	0.36	250	512	28.62
2.0	0.44	350	512	29.92
2.0	0.50	450	512	31.12

Simulation Details

In our simulations, the simulation box is cubic and the temperature is fixed $T = 1.0$, and periodic boundary conditions are applied in all directions to minimize the finite size effects. Meanwhile, the velocity-Verlet algorithm with a time step $\Delta t = 0.004$ is used to integrate the equations of motion. The initial pre-equilibrated configurations are generated by randomly placing polymer chains and NPs in a large box. Subsequently, NPT ensemble is used to compress the system with low density until the desired state with the monomer number density $\rho = 0.85$ is reached. After that, the NVT ensemble with a No -Hoover thermostat is switched on to equilibrate all configurations until each chain has moved several (at least 5) times radius of gyration on average. Finally, these equilibrated structures are provided as the starting configurations for the following collections. The length of the collections is 2×10^8 . All the simulations are carried out with the in-house software GALAMOST package.^[45]

RESULTS AND DISCUSSION

In this section, we investigate the motion of polymer chains in PNCs in terms of the distribution of probability displacement, the particle trajectory, and the displacement of particles. We will focus on these properties especially when the dynamics of polymer chain is more heterogeneous. Moreover, the motion of chain segments in distinct environments is investigated to help understand the physical insight of non-Gaussian behavior in PNCs.

The Distribution of Segment Displacement (DSD) in PNCs

As observed in earlier studies,^[40,46] the motion of polymer chains starts to be hindered and the deviation of displacement distribution from Gaussian behavior occurs with increasing rigid NP loadings. Here, we explore the effect of NPs on the motion of polymer segments by listing some symbolic times (segmental relaxation time τ_s , Rouse relaxation time τ_R , and structural relaxation time τ_α). τ_s and τ_R are defined as the time when the chain segment moves a distance of its statistical segment length b ($b^2 = \langle R_{\text{ee}}^2 \rangle / (N - 1)$) and the end-to-end distance R_{ee} , respectively. It is interesting to see that the effect of NPs on the segmental relaxation time is more obvious than on the Rouse relaxation time, implying a decoupling relationship between both. This decoupling is also accompanied with the non-monotonous change of dynamical heterogeneity of polymer segments.^[42] Moreover, decreasing the size of NPs to some extent and increasing segment-NP interactions will increase the segmental relaxation time since the segmental dynamics near the NP surface is slowed down due to the increasing interfacial area and the strong attraction between segments and NPs.^[42]

In order to explore the distribution of segment displacement in PNCs, we analyze the self-part of van Hove correlation function, $G_s(\mathbf{r}, t)$, which characterizes the probability of a segment moving a distance r during time t , defined by

$$G_s(\mathbf{r}, t) = \langle \delta[\mathbf{r} - \{\mathbf{r}_i(t) - \mathbf{r}_i(0)\}] \rangle \quad (4)$$

where $\mathbf{r}(t)$ denotes the position vector of segment at time t . For an ideal polymer chain, the van Hove correlation function $G_s(r, t)$ associated with the displacement of polymer segments should follow Gaussian form according to its definition,^[47] which can be rewritten as:

$$G_s^G(r, t) = \left(\frac{3}{2\pi \langle r^2(t) \rangle} \right)^{\frac{3}{2}} \exp \left(-\frac{3r^2}{2 \langle r^2(t) \rangle} \right) \quad (5)$$

where $\langle r^2(t) \rangle$ represents the mean-square displacement of segments. For a real polymer melt, it is well-known that chain motion at intermediate time (Rouse regime) can often be considered as a part of anomalous chain diffusion due to chain connectivity, following $t^{0.56}$, unlike the normal diffusion. However, to some extent, chain motion still follows Gaussian behavior over the entire range of time in pure polymer melt even though anomalous chain diffusion appears.^[48] The $G_s(r, t)$ function and the corresponding Gaussian fit at some typical time scales for pure polymer melt are shown in Fig. 2, where $t = 0.08$ belongs to ballistic regime, $t = 10000$ corresponds to free diffusion regime, and other times are within Rouse regime. It is clearly seen that the probability distribution of the simulated displacement can be well fitted with the ideal Gaussian form for all three regions.

As listed in Table 2, the relaxation time increases greatly with increasing particle loading, suggesting that adding NPs has great impact on the segment motion. In the following, we will discuss the distribution of segment displacement in PNCs with different particle loadings. Since chain motion at Rouse regime is anomalous but the displacement still follows Gaussian form for polymer melt, we will focus on the segment dynamics at Rouse region and compare DSD in PNCs with those Gaussian distribution. DSD and the corresponding Gaussian

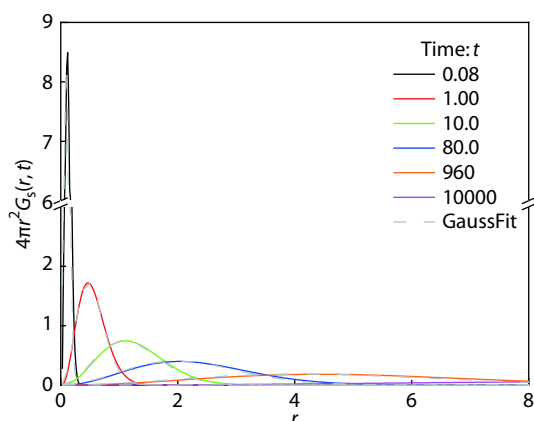


Fig. 2 Plots of the van Hove correlation function $4\pi r^2 G_s(r, t)$ versus the segmental distance r in pure polymer melt for different times (from left to right). Grey dashed lines are Gaussian fits to the van Hove correlation function.

Table 2 Symbolic relaxation times containing segmental relaxation time τ_s , Rouse relaxation time τ_R , and structural relaxation time τ_α . The mean squared end-to-end distance R_{ee}^2 is also listed. Notably, at $\phi = 0.50$, chain motion does not reach its own size in the range of our simulation time.

ϕ	τ_s	τ_α	τ_R	R_{ee}^2
0.00	8.28	0.41	1600	37.79
0.10	13.6	0.44	2848	38.38
0.18	23.8	0.53	5400	39.12
0.25	44.8	0.70	9600	40.32
0.36	170.4	1.36	42400	42.64
0.44	640	4.32	164800	44.67
0.50	2800	29.6	—	46.96

fits for $\phi = 0.10$ and $\phi = 0.50$ are shown in Fig. 3. At $\phi = 0.10$, there are only some slight deviations from the Gaussian form for all three curves. However, when the volume fraction is up to 0.50, multiple peaks evolve with time evolution, implying that the dynamics is heterogeneous and the degree of deviation from Gaussian behavior increases with the addition of NPs to the polymer matrix. The small displacement peak indicates that the polymer chain starts to experience a spatially heterogeneous environment at short time, *i.e.*, some segments are confined in a cage constructed by neighbor segments while others still move freely. The multiple peaks showing up at $t = 960.0$ indicate that there are different subsets of chain segments that travel for different distances, and these peaks are separated by a distance about 0.8. Indeed, in a two dimensional colloidal system,^[49–51] the phenomenon of multiple peaks and the behavior of equidistant distribution have been found in hexatic phases, which is also an evidence of intermittent particle motion. It should be noted that $G_s(r, t)$ displays a long-range exponential tail at large r , which can be well fitted by the exponential formula $e^{-r/\lambda}$,^[24] as depicted in the inset of Fig. 3(b). The exponential tail at a large distance is commonly observed in other systems including glasses,^[52] gels,^[53,54] as well as colloidal suspensions.^[21] The length scale λ obtained by fitting the exponential formula is considered as a “jump length”, which has a close relation with an activated

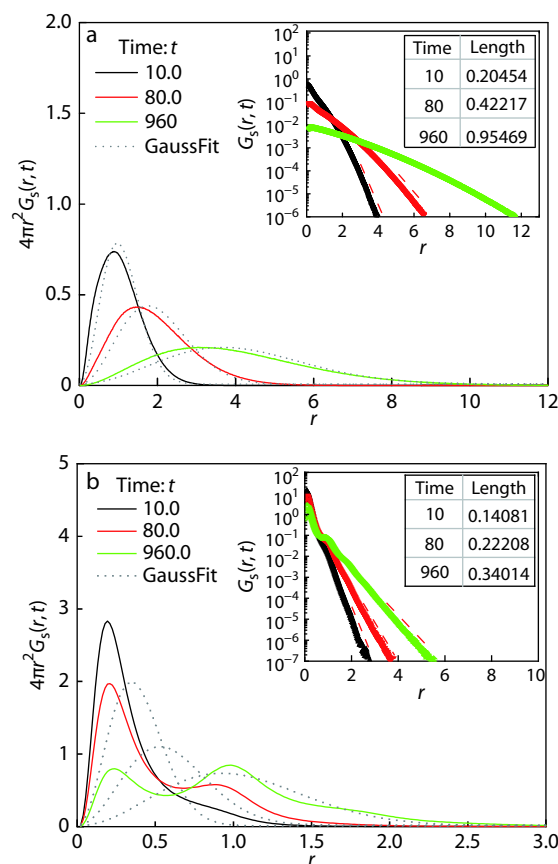


Fig. 3 Plots of the van Hove correlation function $4\pi r^2 G_s(r, t)$ versus the segmental distance r for PNCs with different particle loadings: (a) $\phi = 0.10$, (b) $\phi = 0.50$. Different colored curves in each panel represent increasing simulation time from left to right. The grey dashed lines are Gaussian formula fits to the DSD data. In the inset, red dashed lines are used to show the exponential relation of the tails with the distance, and the fitted values of length scale λ are listed.

hopping motion.^[24] The occurrence of multiple peaks over time and length scale λ suggests that there may exist a similar mechanism in our PNC systems leading to strongly heterogeneous displacements of chain segments. Therefore, in the following parts, we will focus on the occurrence of jump-like motion of polymer segments, which might be the key factor of heterogeneous dynamics in PNCs.

To shed insight into the origin of non-Gaussian behavior of segment motion, we examine the trajectories of some typical segments within Rouse region for PNCs with different particle loadings, as shown in Fig. 4. At small particle loading ($\phi = 0.10$), most of the segments move randomly in the time range of $t = 0-80$, and only few segments exhibit an intermittent motion consisting of short-time localized motion and long-time jump motion connecting two or more localized areas, as depicted in the enlarged trajectory of Fig. 4(a). However, upon increasing the NP volume fraction to 0.50, most of the segments move in a localized manner, and only few segments exhibit a jump-like motion, as shown in the enlarged trajectory of Fig. 4(b). More interestingly, enlarged trajectory in Fig. 4(b) displays multiple localized regions containing

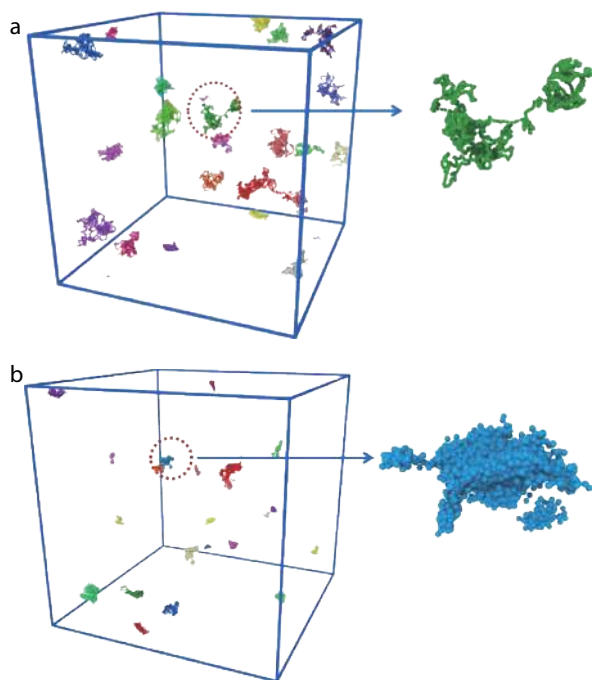


Fig. 4 Representative trajectories of some segments in PNCs: (a) $\phi = 0.10$; $t = 80$, and the length of box is 25; (b) $\phi = 0.50$, $t = 80$, and the length of box is 31.12. In each panel, different colored lines represent the trajectories of different segments. The arrows in both panels play the role as a megascopelike, pointing out the discontinuity and locality of the segment motion.

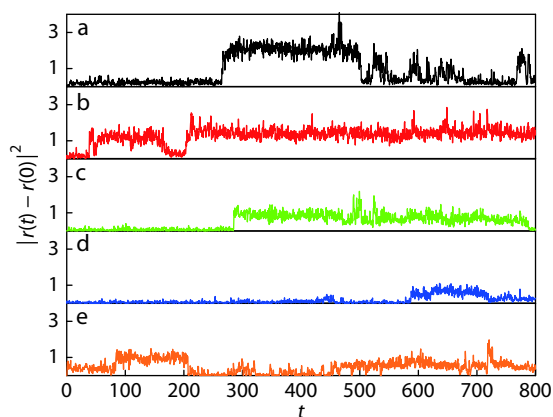


Fig. 5 Square-displacements of randomly selected segments with jump-like motion in PNCs for $\phi = 0.50$. (a–e) Represent the displacement of different segments.

both small and large regions in the time range of $t = 0$ –80, which may arise from the narrow slit-like aisle between two nearest NPs and wide pore among three or more neighboring NPs.

Typical jump-like motion can be clearly seen from the square displacements of chain segments, as shown in Fig. 5 ($\phi = 0.50$). These selected segments clearly exhibit discontinuous motions, accompanied with the localized motion and the jump-like motion. There are different types of segment motions at $\phi = 0.50$. For example, some of segments leave their initial positions at short times, and then return to their initial

positions again (b and e). Some segments leave their initial positions and stay for a quite long time and then go back to their initial positions (a and c). Some segments stay in their initial positions within a certain time, and then leave their initial positions (d). These discontinuous motions might occur as a consequence of weak attraction between NP and chain segment, and strong confinement arising from the increasing particle loadings. Similar intermittent dynamics has also been reported in a variety of systems including glassy state, crowded and confined media, as well as the substrate surface.^[19,23,41,55,56] For polymer chains diffusing onto a surface, a relevant study has shown that the intermittent motion of chains depends on the number of attractive sites between chain segment and the surface of substrate.^[36] If the chains are weakly adsorbed, they may be quickly desorbed after a relatively short waiting time, as indicated by a jump event. After being desorbed, they may be re-adsorbed or gradually diffuse away from their initial positions. Therefore, the adsorption-desorption mechanism can well explain the intermittent behavior of segment motion in PNCs. Combining the results of DSD data, we may conclude that the intermittent behavior of chain segments will lead to the non-Gaussian behavior of polymer chain, and the jump-like event results in the long-range exponential decay of the probability distribution of segment displacement.

The Distributions of Fast, Slow, and Interfacial Segments

In the previous section, we propose that the adsorption-desorption mechanism could be used to explain the intermittent behavior of segment motion in PNCs, and the jump-like motion might result from the absorption-desorption process of polymer segments near the surface of NPs. To verify this, we investigate the relation between the segment motion (fast or slow) and its local environment (near or far away from the surface of NPs).

Similar to the definition of slow or fast particles in supercooled liquids,^[57,58] in the present system, slow segments are defined when their displacements are smaller than those expected from Gaussian behavior, and fast segments are defined for the displacements larger than those expected from Gaussian fit in the time interval $t = 0$ –80. In addition, the interfacial segments are designated when the distance between the mass center of the segment and the surface of NP is smaller than 1.0 at $t = 0$. It should be noted that the definition of interfacial segments is indulgent since some “interfacial” segments may leave their initial surface region and turn into bulk segments in the time range $t = 0$ –80. However, we still call these segments as the interfacial segments. In this case, all the segments initially located at the surface region are designated as the interfacial segments. We have also checked a more rigorous definition, *i.e.*, only those segments staying at the surface of NPs within the time scale $t = 0$ –80 are designated as the interfacial segments. Actually, similar results are qualitatively found, as shown in Figs. S1 and S2 in the electronic supplementary information (ESI). Some typical displacements of fast, slow, and interfacial segments are shown in Fig. 6. It is clearly seen that the fast segments always move farther than slow segments and interfacial seg-

ments in the studied time range. Meanwhile, we notice that the fast segments follow random diffusion at low volume fraction, yet experience intermittent dynamics consisting of localized motion and long-range jump at high volume fraction, although the localized region is much larger than that for slow segments and interfacial segments. On the other hand, at $\phi = 0.50$, it is clearly seen that the desorption and ab-

sorption behavior (sample I1 in Fig. 6b) is accomplished with the emergence of hopping motion at $t \sim 50$. Moreover, the waiting time of some interfacial segments is so long that the desorption cannot be observed within a certain time range $t \sim 400$ (samples I2 and I3 in Fig. 6b). Thus, the jumping behavior of segments is clearly reflected in Fig. 6. More interestingly, it seems that the displacements of slow segments are

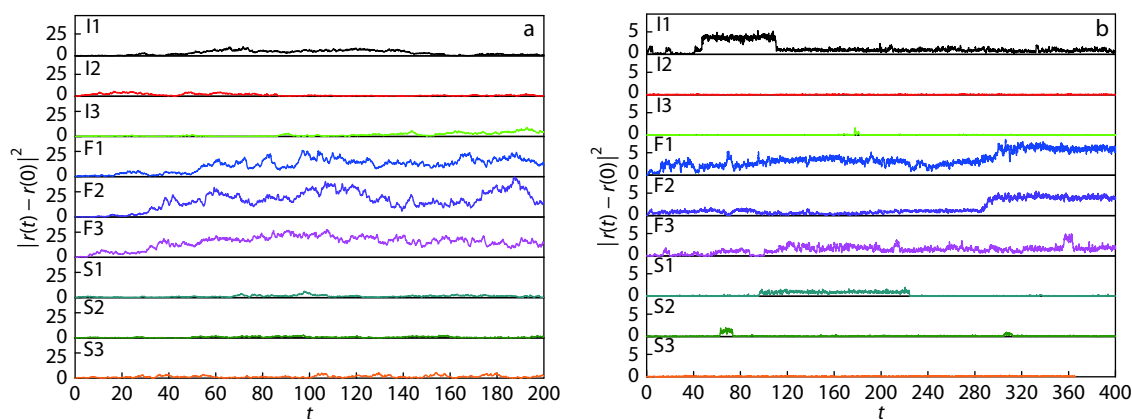


Fig. 6 Typical square displacement of fast, slow, and interfacial segments in PNCs with different particle loadings: (a) $\phi = 0.10$, (b) $\phi = 0.50$. In both panels, three randomly selected samples are given for each kind of segments (I1–I3 are interfacial segments, F1–F3 fast segments, and S1–S3 slow segments).

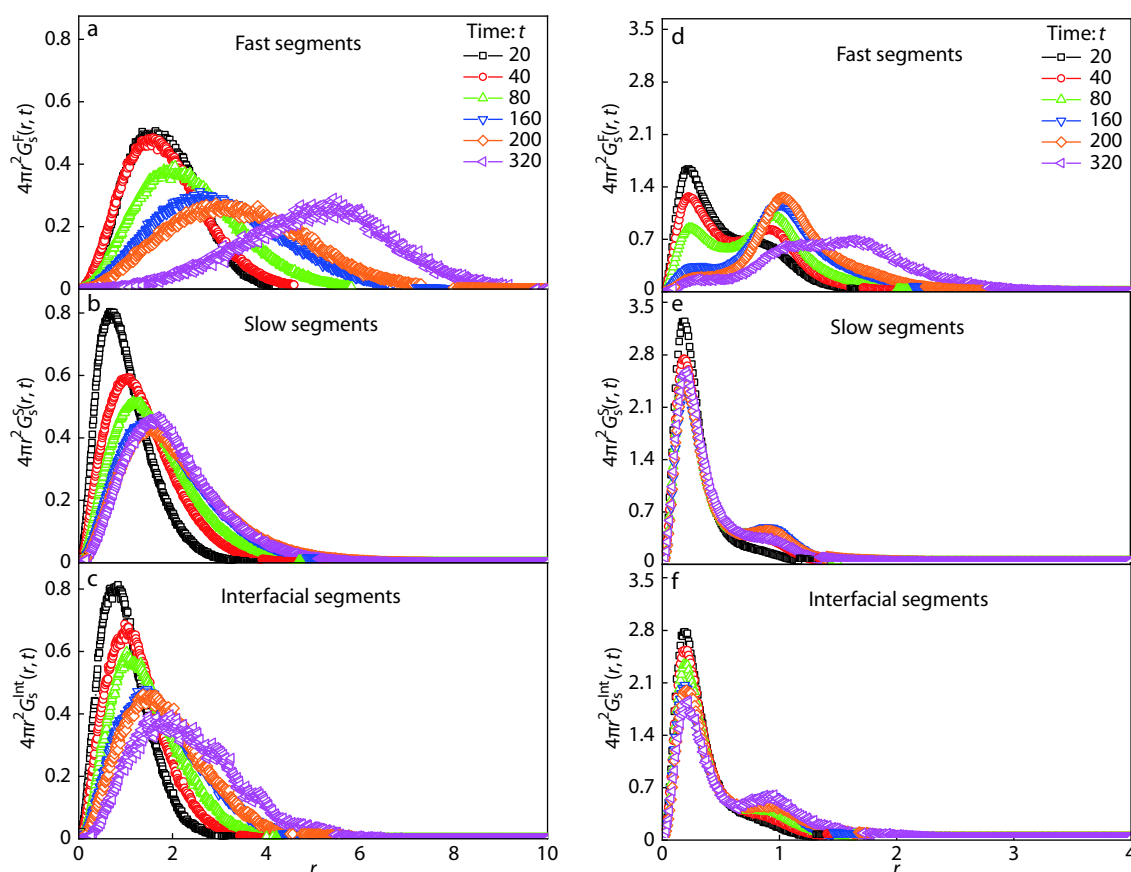


Fig. 7 Probability distribution of segment displacements $4\pi r^2 G_s(r, t)$ for (a, d) fast segments, (b, e) slow segments, and (c, f) interfacial segments in PNCs for (a–c) $\phi = 0.10$ and (d–f) $\phi = 0.50$. In each panel, the obtained curves of $4\pi r^2 G_s(r, t)$ for different time scales are designated by different colors.

similar to those of the interfacial segments for the system with both low and high particle loadings, implying that there may exist a close connection between slow segments and interfacial segments.

A more detailed understanding of the correlation between jump event and local environment can be derived from the distribution of displacements for different types of segments, as shown in Fig. 7. At $\phi = 0.10$ and the same time scale, the displacement distribution of fast segment is always wider, and the peak position of fast segment is always larger than that of slow and interfacial segments, indicating slow dynamics of slow and interfacial segments. In addition, the distribution of the interfacial segments exhibits a few, but less evident shoulders, while there is no apparent shoulder for that of fast and slow segments. This suggests that the intermittent motion or jump-like motion may occur near the surface of NPs, caused by the transient desorption-absorption transition due to weak attraction between segments and NPs. It is seen that the polymer size increases with increasing NP loading, as listed in Table 2. This implies that the polymer chain is stretched to deviate from its ideal state with adding NPs. Thus, the entropy loss caused by the addition of NPs will lead to desorption of segments from the surface of NPs, which may result in the jump-like motion of segments. At higher particle loading ($\phi = 0.50$), multiple peaks are found for all fast, slow, and interfacial segments, suggesting the emergence of intermittent motion. This is quite different from the random motion of fast segments and the slow motion of slow and interfacial segments at low volume fraction, which is probably due to the weak attraction and strong confinement caused by the increasing volume fraction of NPs. It should be noted that the “slow” motion of slow and interfacial segments in low ϕ system is still faster than that in high ϕ system. Moreover, for the distribution of fast segments, there exist some distributions on small r , which might result from that some originally defined fast segments may be transformed into other types since the calculation of the self-part of van Hove function of fast segment requires an average on different 0–80 time intervals in order to obtain good statistics. In this case, the intermittent motion of fast segments may also originate from the transformation from originally defined fast segments to slow or interfacial segments.

From above discussion, we guess that there may exist a close connection between slow segments and interfacial segments in our PNCs. Then we calculate the proportion of interfacial segments among all the slow (P_{SI})/fast (P_{FI}) segments and the proportion of interfacial segments (P_{IN}) among all the segments in the system for $t = 0-80$, as shown in Fig. 8. As expected, with increasing ϕ , P_{IN} increases, indicating that more segments are located near the surface of NPs as NP loading increases. Astonishingly, P_{SI} is less than 1.0 especially when the particle loading is low. This suggests that not all the slow segments come from the interfacial region and some slow segments are located in the bulk region of PNCs, which leads to slight difference between the distribution of slow segment displacement and the distribution of interfacial segment displacement. Note that the present interfacial segments are named when their initial position ($t = 0$) is near the surface of

NPs. We have also checked a more rigorous definition, *i.e.*, only those segments staying at the surface of NPs within the time scale $t = 0-80$ are designated as the interfacial segments. The qualitatively similar results are found, as shown in Fig. S2 (in ESI). Interestingly, P_{FI} also increases with increasing particle loading, suggesting that there are still some fast segments in the interfacial region, which might result from the increasing total number of interfacial segments. This can be well understood from the interparticle distance (ID), defined by:^[59]

$$ID = 2R \left[\left(\frac{\phi_{\max}}{\phi} \right)^{\frac{1}{3}} - 1 \right] \quad (6)$$

where $\phi_{\max} = 2/\pi$ is the random-close-packing volume fraction. ID represents the average spacing between the surface of neighboring NPs, assuming that NPs are randomly distributed in the polymer matrix.^[60] With ϕ increasing, ID decreases and goes to 1.46 when ϕ is 0.25, implying that more segments are in the surface of NPs. When ϕ is up to 0.44, P_{IN} goes to 1.0, indicating that the interfacial layers occupy the free space and then strong confinement induced by NPs dominates the motion of polymer segments.

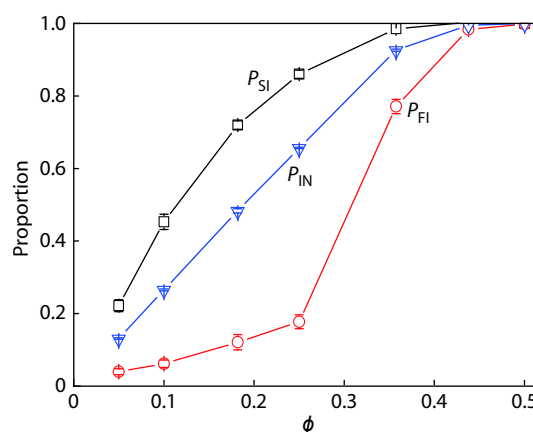


Fig. 8 The proportion of interfacial segments among all the slow (P_{SI})/fast (P_{FI}) segments and the proportion of interfacial (P_{IN}) segments among all the segments in the system for $t = 0-80$. The solid lines are guided to the eye, and the error bars are evaluated from at least 6 independent samples.

CONCLUSIONS

In this paper, we investigate the motion of polymer chain in the presence of NPs by employing a coarse-grained molecular dynamics simulation. We find that the slow dynamics of polymer segments is related not only to weak interaction between NP and polymer chain, but also to the confinement induced by NPs. By analyzing the distribution of probability displacement, particle trajectory, and the displacement of particle, we confirm the emergence of intermittent dynamics of polymer segments consisting of localized motion in short time scales and jump motion in long time scales, especially when the particle loading is high. We show that the displacement distribution of chain segments becomes non-Gaussian with the addition of NPs, and

exhibits an obviously exponential tail at larger distance, which may lead to the intermittent motion of segments. Moreover, we find that the transient adsorption-desorption transition leads to the intermittent dynamics of segments at low particle loadings, while the confinement caused by adding NPs dominates the intermittent dynamics of segments at high particle loadings.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2352-7>.

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