Chemical Physics Letters 687 (2017) 96–100

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Diffusion dynamics of nanoparticle and its coupling with polymers in polymer nanocomposites

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ARTICLE INFO

Article history:
Received 9 August 2017
In final form 2 September 2017
Available online 8 September 2017

Keywords:
Polymer/nanoparticle composite
Nanoparticle diffusion
Non-Gaussian
Nanoparticle/polymer coupling

ABSTRACT

Diffusion dynamics of nanoparticles in polymer nanocomposites is investigated by coarse-grained molecular dynamics simulations. We report a strong polymer chain length dependent non-Gaussian diffusion of nanoparticles (NPs) in entangled polymer melt. By analyzing the NP motion and the polymer relaxation at different length and time scales, we find that the non-Gaussian diffusion of NPs originates from a dynamic coupling at a specific length scale with the melt polymer chain segments that possess similar size with NP. Our results provide a microscopic understanding of the complex particle environment interactions and a detailed mechanism for nanoparticle diffusion in entangled polymer melt.

1. Introduction

Over the past decades, tremendous efforts in theory [1–6], simulation [7–10], and experiments [11–14] have been made to understand the dynamics of nanoparticles (NPs) in both polymer solutions and melts. In polymer solution, the NP diffusion coefficient can be largely influenced by NP size, polymer concentration and the polymer chain length [6]. While in the polymer melt, depending on the relative size of the diameter of the NP (d_{NP}) compared to that of the Edwards tube of melt polymers (d_T) there is a length scale dependent dynamical coupling between NP and polymer chains. For $d_{NP} < d_T$, the motion of NP is coupled to the unentangled dynamical modes of local chain segments with the radius of gyration up to $\sim d_{NP}$. For $d_{NP} > d_T$, according to the scaling analysis by Brochard-Wyart and de Gennes [1], NPs have to wait for the complete relaxation of surrounding entangled polymers to diffuse. On the other hand, theoretical works of Dell and Schweizer [3] and Cai et al. [5] predict that the NPs move by hopping diffusion mechanism and therefore the NPs can have a fast diffusion and they don't have to wait for the polymer chains to completely relax (also see discussions in Ref. [10]). However, such hopping diffusion process was not seen in recent MD simulations for NPs weakly interacting with polymers even when $d_{NP} > d_T$ [8]. In contrast, small fullerene particles are observed to diffuse via a hopping mechanism in a conjugated polymer melt [9].

Although the NP diffusivity and its melt polymer chain length (N) dependence has been well investigated in the aforementioned literature, NP diffusivity only provides one piece of information, namely the second-order cumulants of NP displacement. From the dissusivity of the NPs alone, it is hard to distinguish more detailed diffusion mechanism of the NP. For instance, deviations in the displacement probability distribution (DisPD) from a Gaussian distribution, characterization of which needs information of higher order cumulants of NP displacement, has been widely observed in the diffusive motion of particulate matters not only for nanoparticles [14,15], but also for colloid particles [16,17] and proteins [18,19] in soft matter and biology systems. In these systems, the slowly-varying large-scale environmental fluctuations (EFs) which occur on time-scales similar as or slower than that of the random walk diffusion of particles, are considered as the direct cause of non-Gaussian diffusion [20,21]. However, a quantitative description of both length and time scales for EFs is hard to obtain since the environment has a much slower relaxation which is beyond the time window of experimental measurements [21]. Although different theoretical models have been developed, e.g., the continuous-time random walk model [22,23], the fractional Brownian motion model [24–26] and the diffusing diffusivity model [27], none of these models claim general applicability for all possible experimental cases. Therefore, the statistical nature of the dynamic coupling between NP and polymer melt and a detailed exploration of the underlying mechanism for such non-Gaussian diffusion process remain open questions.

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http://dx.doi.org/10.1016/j.cplett.2017.09.010
0009-2614/

2. Coarse-grained models and simulation details

In this work, large-scale coarse-grained (CG) MD simulations are performed for a polymer/NP composite (PNC), where all length and time scales for both NP diffusion and melt polymer chain relaxation can be well characterized. Our simulated PNC systems are composed of single-chain polystyrene (PS) NPs in linear PS melts, where enthalpic interactions are reduced to a minimum due to the same chemical composition of both polymer chains and NPs [28–31]. Experimentally, such NPs are fabricated from intramolecular cross-linking reactions in ultra-dilute solution [32]. CG potentials in our model are developed from iterative Boltzmann inversion method [33]. In order to closely mimic the experimental condition our NP model is fabricated in dilute solution via intra-chain cross-linking reactions, details for both models of linear PS chain and NPs are referred to our previous works [33,34]. Each styrene unit is coarse-grained into one CG bead, stereochemistry of the PS chain is described by two different types of bonds and three angle potentials [33]. Melt chains composed of $N = 10-720$ styrene units and NPs composed of 250 and 1300 styrene units, respectively, are considered. Mimicking the condition in experiment [30,31], each NP contains 20% cross-linking units. These NPs are denoted as NP250 and NP1300 and they have a radius of 2.0 nm and 3.4 nm respectively, these NP sizes are in good agreement with experimental measurements [35], they are also both smaller than $d_T = 7.5$ nm of melt polymers obtained from the primitive path analysis by using Z1 code [36–38]. Although previous simulations [39–42] have shown that such NPs prepared from cross-linking reactions in dilute solution may have different conformations, NPs in our simulation on average adopt spherical shape as indicated by the calculated form factor (plotted in Fig. S1 in Supporting Information). All simulated composite systems have a NP volume fraction of 10% unless otherwise stated, system details are listed in Table 1. Initial configurations are prepared by a random walk model, to ensure the full relaxation and sufficient sampling, all the systems are well-equilibrated via repeated annealing cycles between 500 and 1000 K [34]. The production run are performed under NPT condition up to 40 μs, which takes 120 days parallelized on 4 NVIDIA GTX980 gpus. All simulations are performed by using GALAMOST package [43]. Note that calculated radius distribution functions between NPs in systems with different chain length and different NP loadings (shown in Fig. S2) show that NPs are well dispersed in the system.

3. Results and discussions

Pioneering experimental works [28,30] have shown that adding cross-linked single-chain polystyrene (PS) NPs into PS melts can lead to a non-Einstein like viscosity reduction. Although the underlying mechanism is still under debate [44], our recent simulations [34] predicted an acceleration effect in the vicinity of NP surface due to its softness and deformability. Fig. 1(a) shows the diffusion coefficient D_{NP} of NPs in PS melts with different chain lengths N. It shows that D_{NP} has a strong N–dependence at short N while it turns to a constant for long chains, which is in good agreement with our previous results [45] where only one single NP is used. It indicates that the interaction between NPs has almost no impact on their own dynamics. Our results are also in good agreement

Table 1
Simulated systems. n_{NP} is the number of NPs, n_{PS} is the number of polystyrene chains, each system has approximately 2.6×10^5 styrene monomers in total. ϕ(%) is the NP loading and t is the total simulation time. Systems 'NP250/PS500' and 'NP250/PS720' both have 2 parallel simulations, as noted in the time column.

System	n_{NP}	n_{PS}	t (μs)	ϕ (%)
NP250/PS10	104	23400	1	10
NP250/PS50	104	4680	1	10
NP250/PS100	104	2340	1	10
NP250/PS150	104	1569	1	10
NP250/PS250	104	936	2	10
NP250/PS350	104	668	3	10
NP250/PS500	104	468	5, 10	10
NP250/PS720	104	325	20, 40	10
NP250/PS864	104	270	2	10
NP1300/PS500	20	468	5	10
NP250/PS500	21	509	5	2
NP250/PS500	312	364	5	30
NP250/PS500	520	260	5	50
NP250/PS720	21	353	20	2
NP250/PS720	208	288	20	20
NP250/PS720	416	216	20	40

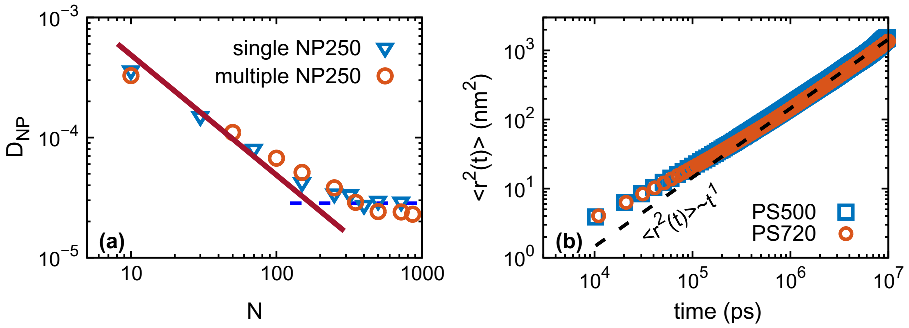

Fig. 1. (a) Diffusion coefficient of NP250, D_{NP}, in composites with different melt polymer chain lengths N. Red solid and blue dash lines are drawn to guid the N-dependence and N-independence of D_{NP}, respectively; (b) MSD curves for NP250 in PS500 and PS720. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)