Nanoparticle Diffusion in Polymer Nanocomposites

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(Received 11 September 2013; revised manuscript received 26 November 2013; published 12 March 2014)

Large-scale molecular dynamics simulations show that nanoparticle (NP) diffusivity in weakly interacting mixtures of NPs and polymer melts has two very different classes of behavior depending on their size. NP relaxation times and their diffusivities are completely described by the local, Rouse dynamics of the polymer chains for NPs smaller than the polymer entanglement mesh size. The motion of larger NPs, which are comparable to the entanglement mesh size, is significantly slowed by chain entanglements, and is not describable by the Stokes-Einstein relationship. Our results are in essentially quantitative agreement with a force-level generalized Langevin equation theory for all the NP sizes and chain lengths explored, and imply that for these lightly entangled systems, activated NP hopping is not important.

DOI: 10.1103/PhysRevLett.112.108301 PACS numbers: 82.35.Np, 47.57.Ng, 83.80.−k

The transport properties of nanoparticle-polymer mixtures have been the focus of much recent attention [1–11]. There is good understanding of the motion of very large or very small colloidal particles of radius $R_{\mathrm{NP}} \equiv \sigma_{\mathrm{NP}}/2$ in a polymer melt or solution. The nanoparticle (NP) diffusion coefficient (D) in the large particle limit follows the Stokes-Einstein (SE) relation, $D = k_B T/(f \pi \eta R_{\mathrm{NP}})$, where k_B is Boltzmann's constant, T is the absolute temperature, η is the solvent viscosity, and $f = 4$ or 6 for slip or stick boundary conditions, respectively [6]. The corresponding behavior of small NPs, comparable to the size of a monomer, is also described by the SE relationship but with a length-scale-dependent viscosity that is smaller than the macroscopic value [10,12]. Specifically, the relevant apparent viscosity is controlled by subsections of chains with an end-to-end distance comparable to the NP size, as has been verified by molecular dynamics (MD) simulations [13] and theory [2]. In contrast to these well-defined limits, the behavior of NPs of diameter $\mathcal{O}(1)$ times the entanglement mesh size in long chain environments, d_T, is controversial [1,5,14–16]. Brochard-Wyart and de Gennes [12] argued that the NP diffusion constant follows normal SE behavior essentially immediately when its size becomes bigger than d_T, the entanglement mesh size. Such a sharp size-dependent crossover to SE has been seen by Szymanski *et al.* [17]. However, the recent work by Cai *et al.* [2] implies that the motion of these intermediate sized NPs should be faster than SE behavior since diffusion can be facilitated by hoplike motions through the polymer's entanglement mesh. Faster transport is also predicted by a microscopic force-level theory, but based on the idea that chain relaxation and local entanglement mesh fluctuations ("constraint release") dominate over hopping [18]. Thus, these two very different ideas suggest that SE behavior would only be seen for NPs bigger than the entanglement diameter, i.e., $\sigma_{\mathrm{NP}} > 2\text{–}10 d_T$. In the spirit of the entanglement dominated picture, Saxton showed, through simulations of NP motion in the presence of fixed obstacles, that the mean-squared displacement (MSD) follows an anomalous $\Delta r^2 \sim t^\beta$, $\beta < 1$ behavior [15]. While such anomalous behavior has been seen recently by Guo *et al.* [5], Omari *et al.* [9], Wong *et al.* [16], and Amblard *et al.* [1], these last workers emphasize that their results represent the coupling (or interaction) of the NP and the stiff F-actin polymers. Such an interaction dominated picture has also been suggested by Wang *et al.* [19] and Vagias *et al.* [20]. The transport behavior of NPs in this crossover size limit thus appears to be complicated by hopping effects, length-scale-dependent entanglement forces and dynamics, and the interaction of polymers and NPs. No clear understanding exists of the various competing mechanisms, and we use large-scale MD simulations to examine the role of entanglements on NP dynamics in this crossover regime.

We simulate weakly interacting mixtures of NPs of diameter $\sigma_{\mathrm{NP}} = 1\text{–}15$ (in units of σ, the monomer diameter) and bead-spring polymer melts of fixed chain length N in the range 10–400 (see Supplemental Material [21]) [22]. The interactions between two nonbonded polymer segments are described by the Lennard-Jones potential truncated at $r_c = 2.5\sigma$. For this polymer model the entanglement chain length $N_e \sim 45$, and d_T (in units of σ) is in the range $d_T \sim 7$ based on the transient caging of the polymer center-of-mass motion [7], and $d_T \sim b\sqrt{N_e} \sim 10$ where b is the Kuhn length, based on the entanglement chain length [20]. The NPs are modeled as bare smooth spheres made up of uniformly distributed monomers of the size of a polymer segment with a number density $\rho_{\mathrm{NP}}\sigma^3 = 1$. The NPs are athermal relative to each other, while the polymer-NP interaction is tuned to be attractive enough to permit miscibility [23]. The particle volume fraction is $\varphi_{\mathrm{NP}} = \sigma_{\mathrm{NP}}^3 M_{\mathrm{NP}}/(\sigma_{\mathrm{NP}}^3 M_{\mathrm{NP}} + \sigma^3 N M_C) = 0.1$, where M_{NP} and M_C are the numbers of NPs and polymer chains, respectively. Molecular dynamics simulations are carried out using the Large Scale Atomic Molecular Massively Parallel Simulator (LAMMPS) software [24]. The initial configurations of neat and NP-filled polymers are prepared at random at a constant number density while allowing for overlaps. The overlaps are removed by initially using a soft potential, and then by gradually increasing the strength of the potential [25]. After all overlaps are removed, the system, which now has its full interactions, is allowed to adjust its density at pressure $P^* = 0$ (a good mimic for atmospheric pressure) and temperature $T^* = 1.0$ using the isothermal-isobaric ensemble. The systems are then run at constant volume with a Langevin thermostat with a weak damping constant $\Gamma = 0.1\tau^{-1}$ to maintain temperature. For larger N, $P^* = 0 \pm 0.05$, whereas for shorter N, $P^* = 0 \pm 0.1$. Diffusion coefficients are estimated from $D = \lim_{t\to\infty}\langle[r_{cm}(t) - r_{cm}(0)]^2\rangle/6t = (1/6)d\langle[r_{cm}(t) - r_{cm}(0)]^2\rangle/dt$, which uses the mean-squared displacement (MSD) of the center of mass of the appropriate species. Both formulas gave identical results within uncertainty for NP diffusion coefficients.

A caveat is in order about finite size effects. While the largest boxes we consider have a lateral size $L = 66\sigma$, previous work [26–28] suggests that $D(L) = D(L \to \infty) -2.837\frac{kT}{6\pi\eta L}$ due to long-range hydrodynamic effects for particles larger than the fluid molecules. The corresponding expression for particles smaller than the chains is not available, and a detailed analysis is precluded by the relatively large computational effort required even for one L. Thus, while we estimate that our results for large particles and short chains are 30%–50% smaller than in the thermodynamic limit, we do not correct any of our results for the sake of consistency.

The diffusion coefficients of nanoparticles smaller than $d_T \sim 7$–10 [i.e., $\sigma_{\rm NP} = 1$, 3 and 5, respectively, Fig. 1(a)] in long chain melts show that the relevant viscosity corresponds to a section of the chain with $N_{\rm NP}$ monomers that satisfies $\sigma_{\rm NP}^2 = N_{\rm NP}\sigma^2$. Using the SE equation with the Rouse model viscosity $\eta = \eta_1 N_{\rm NP}$ (where η_1 is the viscosity of a monomer fluid at the same density) yields that $D_{\rm NP}^*\sigma_{\rm NP}^3$ should be a constant, independent of chain length, which is what is found [2,13]. For shorter chains the data can be described by the Stokes-Einstein relationship with the macroscopic viscosity of the chain fluid, i.e., $D_{\rm NP}^* = (kT/f\pi\eta\sigma_{\rm NP}) = (kT/f\pi\eta_1 N\sigma_{\rm NP})$, where we use $\eta = \eta_1 N$ and $f \sim 4$ [solid line in Fig. 1(a)]. An alternative approach of using the melt viscosity rather than $\eta = \eta_1 N$ is presented in Fig. 1(c), where $\eta_{\rm filled}$ is the viscosity of the filled melt [22]. The data for $\sigma_{\rm NP} = 3$ and 5 overlap for the short chains, while the data for $\sigma_{\rm NP} = 1$ are a little higher.

Our results for these smaller NPs are in good agreement with the predictions of the generalized Langevin equation (GLE) theory of Yamamoto and Schweizer [Fig. 2(a)]. The GLE approach is based on the mode-coupling idea that the relevant slow dynamical variable is the bilinear coupling of the NP and the collective polymer density fluctuations. The original approach [18] was not self-consistent since it assumed that the constraining forces on a particle relax entirely due to the length-scale-dependent motions of the polymer melt (constraint release regime). For entangled melts, this is an accurate simplification when particles are larger than d_T, and SE behavior is predicted to be recovered when the particle diameter reaches $\sim 10d_T$, which is well beyond the chains lengths simulated in this work. However, to treat the opposite limit of small particles, where relaxation of the entanglement network is not required for transport, the GLE approach has been extended to self-consistently allow forces to also be relaxed by Gaussian particle motion (see Supplemental Material [21]). The important consequence of this refined approximation is that the $D_{\rm NP}^*\sigma_{\rm NP}^3 = {\rm const}$ result is obtained naturally for long chains and small NPs [Fig. 2(a)].

More interesting are our data for NPs with sizes of order of the entanglement mesh length ($d_T \sim 7$–10), i.e., for $8 \le \sigma_{\rm NP} \le 15$. Figure 1(b) shows that the data for these NPs in the longer chain melts no longer follow the “universal” plateau seen for small NPs. Apparently, for long chains there are additional factors involved. Figure 1(c) shows that the SE scaling of the diffusivity is not found for any of these NPs, i.e., that $D_{\rm NP}^*\sigma_{\rm NP}\eta_{\rm filled}$ is not a constant. This behavior, especially for the intermediate sized particles ($8 \le \sigma_{\rm NP} \le 15$), disagrees with the ansatz of Brochard-Wyart and de Gennes [12] that particle motion is essentially fully coupled to chain motion, and hence SE-like behavior is recovered, as soon as the particle diameter exceeds d_T. While the SE behavior is not recovered here, the chain length dependence of the NP diffusion data is well described by the GLE theory [Fig. 2(b)] across this intermediate NP size range for all chain lengths.

These results for nanocomposites suggest that the chain-scale dynamics do not control NP diffusion (no SE scaling). However, the fact that the large N diffusivity of these intermediate sized NPs does not reach the same plateau as the small NPs [Fig. 1(b)] suggests that another effect, such as entanglements, plays a critical role. To understand the role of entanglements, we performed a series of simulations by allowing the chains to cross each other while leaving the NP-polymer interactions unaffected. The “chain-crossing” simulations (see Supplemental Material [21]) were performed at the same densities as the entangled chain model, and show that the diffusion of NPs of $\sigma_{\rm NP} = 10$ [open diamonds in Fig. 1(b)] track the universal behavior for small NPs. This conclusively demonstrates that the extra slowing down for these NPs and longer “noncrossing” chains is due to chain entanglements.

As discussed in the introduction, some recent theoretical ideas suggest that NPs with diameters ~ 1–$2d_T$ may undergo hopping controlled transport due to local, rare fluctuations of the entanglement network [2]. We now explore such hopping effects. As a first point, Fig. 1(d) shows results for the time-dependent NP MSD for a series of particle sizes. One sees an intermediate time non-Fickian

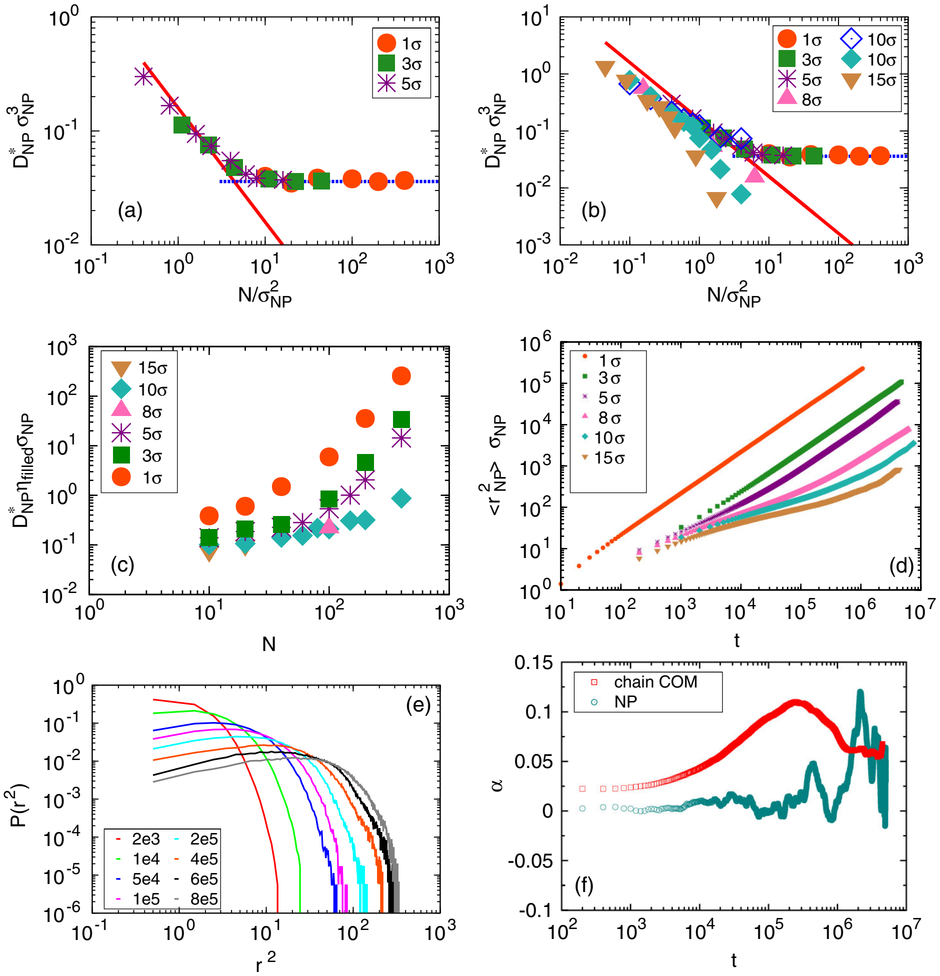

FIG. 1 (color online). (a)–(c) Terminal diffusion coefficient of NPs of different size, $D^*_{\rm NP}$, in melts of different N plotted in a scaled form as discussed in the text. (a) NPs that are smaller than the entanglement mesh size. The blue line was fit to the large N and small NP values with the prediction $D^*_{\rm NP}\sigma^3_{\rm NP} = 2kT\sigma^2/f\pi\eta_1$. (b) All of the NP data—in comparison to (a) the additional data are for larger NPs, and $\sigma_{NP} = 10\sigma$ in melts that allow for chain crossing (open diamonds). The $D^*_{\rm NP}$ values for the chain crossing model are scaled by a factor of 2 in order to compare with the noncrossing model (closed diamonds). (c) Data plotted in a Stokes-Einstein inspired form. (d) Mean-squared displacement of NPs of sizes $\sigma_{NP} = 1$–15 in polymer melts of length $N = 400$. (e) Probability distribution of mean-squared displacement of NPs during different time intervals from $t = 0$ for $N = 200$ and $\sigma_{\rm NP} = 15$ with time increasing going from left to right. (f) The non-Gaussian parameter α for both the chains and NPs for the system discussed in (e). The longest relaxation times of these chains are $\tau_1 \sim 2.6 \times 10^5$ from a Rouse mode analysis, which corresponds to the first peak of α.

regime though there is no extended power law scaling behavior. The minimum apparent exponent, defined locally as MSD $\sim t^x$, varies from $x \sim 1$ for the smallest particle to ~ 0.4 for the largest particle. This behavior is reminiscent of transient caging in supercooled liquids [29–36], but here arises from transient trapping and slowing down of particle motion due to emerging entanglement constraints. However, from a supercooled liquid perspective where activation barriers are high, a value of $x \sim 0.4$ is not small, and the NP is far from the idealized localization situation where the MSD displays a transient plateau. In the same vein, the probability distributions of particle displacement [Fig. 1(e)] show no peaks at distances associated with a jump-like motion, and the time-dependent non-Gaussian parameter $\alpha = \frac{3}{5}\frac{\langle r^4\rangle}{\langle r^2\rangle^2} - 1$ is very small, with an amplitude typical of normal, not supercooled, liquids [Fig. 1(f)] [29–36]. Additionally, it is much smaller than the non-Gaussian parameter for the melt chains. Thus, while particle motion is characterized by an anomalous power law dependent MSD at intermediate times, there is no evidence of NP hopping (or any form of non-Gaussian dynamics) for these weakly interacting polymer-NP mixtures. Thus, we conclude that spontaneous fluctuations of the entanglement mesh (constraint release) in these moderately long chain melts may be the most important mode of NP transport.

These physical conclusions are fully consistent with the dynamically Gaussian GLE theory. A detailed study will be presented elsewhere, but briefly we find that the GLE predictions agree qualitatively with all aspects of the simulation MSD data. This includes the prediction of subdiffusive behavior, which becomes more pronounced as

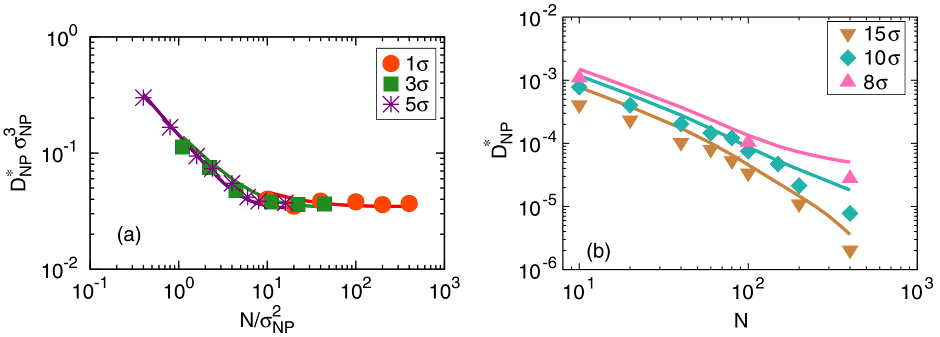

FIG. 2 (color online). Predictions of the GLE theory (solid lines) compared with simulation results. (a) $\sigma_{NP} < d_T$. (b) $\sigma_{NP} \geq d_T$. Note that a slip boundary condition was assumed.

particle size increases, no wide power law regimes, and the minimum value of the apparent exponent varying from $x \sim 1$ (Fickian) to ∼0.4 as the particle diameter grows from 1 to 15. There are no divergences or glass transitions of any kind (e.g., as in the Lorentz model) since forces on a particle always decay to zero at long times due to relaxation of the polymer liquid.

For crosslinked networks, or in the hypothetical $N \to \infty$ limit of polymer melts, the dynamical constraint release motions arising from chain relaxations would be quenched, and hence hopping should become the dominant channel of transport when particles are larger than the entanglement mesh length. Indeed, as will be discussed in a future publication, NP motion shows clear signs of "quantized" hopping in randomly crosslinked networks, where the constraint release channel is fully eliminated. For experimentally realizable entangled melts, the following combination of conditions appears to be necessary for hopping to dominate: particles are sufficiently large that barriers are well in excess of thermal energy, but not so large that this activated and exponentially slow process is slower than dynamical constraint release. Whether this is achievable for real entangled melts with practical values of N/N_e is a quantitative question with no a priori obvious answer. Regardless, we believe that considerable interest remains in simulating much longer N for NPs with diameters comparable to the tube or entanglement mesh size to examine if such hopping phenomena control NP motion in these circumstances.

We have also measured the chain diffusion constant by following the polymer center-of-mass dynamics. Although the N dependence of chain diffusivity is strong [Figs. 3(a) and 3(b)], adding the two largest NP sizes $\sigma_{NP} = 10$ and 15 only has a small effect on the polymer chain diffusion [Fig. 3(c)]. Smaller particle sizes cause, at most, a 40% change in the chain diffusion coefficient, implying that chain motion is not significantly affected by the addition of

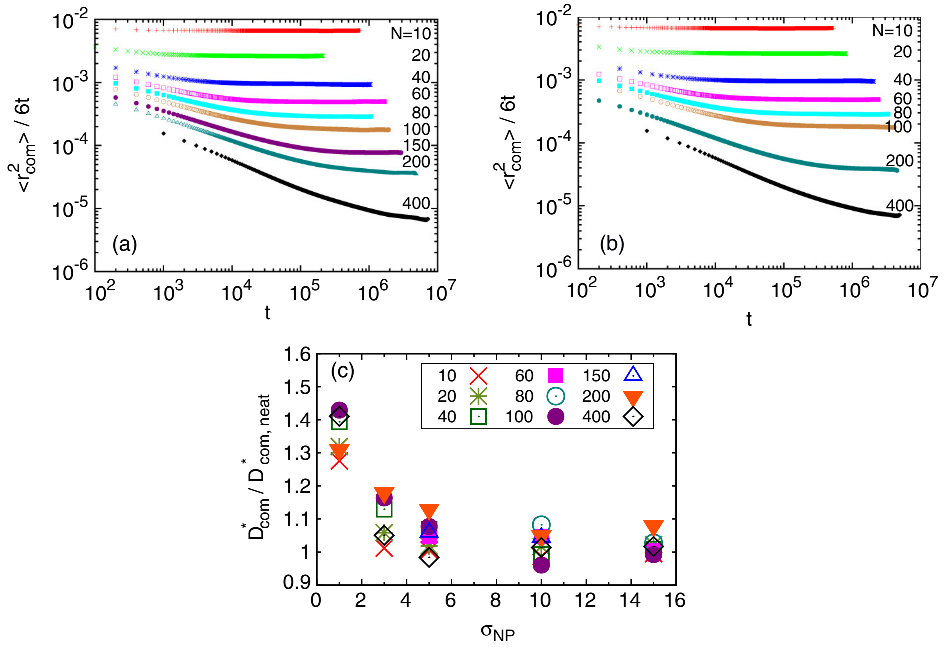

FIG. 3 (color online). Mean-squared displacement of chain center of mass as a function of time for different chain lengths in nanocomposites (a) $\sigma_{NP} = 10\sigma$ and (b) $\sigma_{NP} = 15\sigma$. (c) Normalized chain diffusion coefficients as a function of NP size. The data at various chain lengths are shown on the same plot.

NPs. For the most interesting larger particle sizes, note there is virtually no change of the ensemble-averaged polymer diffusion constant upon adding particles, consistent with the fact that our particle loadings are small. This also justifies an underlying theoretical approximation of the GLE approach [18] for dilute NP systems. Presumably, larger particle loadings and/or higher degrees of polymer entanglement should lead to chain slowing as has now been seen in several experiments [37].

In conclusion, our results clearly show that we have an excellent understanding of the motion of NPs smaller than the polymer's entanglement mesh size for weakly interacting NP-polymer systems. It is for sizes comparable to the entanglement mesh where NP diffusion is strongly coupled to entanglement dynamics. For these NP sizes we see no conclusive evidence for hopping-controlled transport. Rather, NP diffusion in this regime can be understood essentially quantitatively based on the GLE theory where polymer dynamical constraint release and length-scale-dependent entanglement forces control NP mobility. However, the hopping mechanism may play an important role for NPs comparable to the entanglement mesh size if they are dissolved in more strongly entangled melts, or maybe when the NP-polymer interactions become attractive, as found in some experiments. Future simulations and theory development are required to answer this question.

J. T. K., S. K. K., and G. S. G. gratefully thank Michael Rubinstein for many detailed discussions. J. T. K. and S. K. K. acknowledge financial support from the U.S. National Science Foundation (DMR-1006514). K. S. S. and U. Y. acknowledge financial support from the Division of Materials Science and Engineering, U.S. Department of Energy, Office of Basic Energy Sciences via Oak Ridge National Laboratory. This research used resources obtained through the Advanced Scientific Computing Research (ASCR) Leadership Computing Challenge (ALCC) at the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the United States Department of Energy under Contract No. DE-AC02-05CH11231. This work was performed, in part, at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Basic Energy Sciences user facility. Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

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