

# Breakdown of the Continuum Stokes–Einstein Relation for Nanoparticle Diffusion

Anish Tuteja and Michael E. Mackay\*

*Department of Chemical Engineering and Materials Science,  
Michigan State University, East Lansing, Michigan 48824*

Suresh Narayanan

*Advanced Photon Source, Argonne National Labs, Argonne, Illinois 60439*

Subashini Asokan and Michael S. Wong

*Department of Chemistry, Rice University, Houston, Texas 77251*

*Received January 24, 2007; Revised Manuscript Received March 9, 2007*

## ABSTRACT

Cadmium selenide nanoparticles are found to diffuse approximately 200 times faster in a polymeric liquid than predicted by the Stokes–Einstein relation. This remarkable behavior is hypothesized to be due to the nanoparticles being smaller than the entanglement mesh to create a frictional drag that does not follow continuum expectations, in line with a theoretical calculation presented before. This is one of the first demonstrations of X-ray photo correlation spectroscopy applied to polymeric liquids, which we use to explain the simultaneous 60% viscosity reduction of the mixture through a proposed constraint release mechanism.

The assembly of inorganic nanoparticles in polymer matrices and block copolymers has been widely studied with the aim of tailoring their magnetic, mechanical, electrical, or optical properties.<sup>1–4</sup> “Self-healing” nanocomposites are now being envisioned based on the diffusion of nanoparticles to the various defect points in the composite (like cracks that develop as a result of environmental changes) to restore up to 75% of their original modulus.<sup>5,6</sup> Other nanoparticles found in nature (bionanoparticles), including tobacco mosaic virus and cowpea mosaic virus, have also been functionalized with various synthetic polymers for the objective of directing them into self-assembled, ordered structures to tailor vehicles for drug delivery.<sup>7,8</sup>

We consider the diffusion of nanoparticles here because any study targeting the spatial assembly of nanostructures requires an understanding of the nanoparticle dynamics to delineate the kinetics. In addition, the movement of proteins, DNA, and other naturally occurring nanoscale particles within the cytoplasm and the nucleus<sup>9,10</sup> are expected to emulate the nanoparticle–polymer matrix interaction, at least to some degree. Moreover, with many important experimental techniques moving toward smaller length scales and

sample volumes, such as microrheology,<sup>11–13</sup> which uses the generalized Stokes–Einstein (SE) relation to determine the shear modulus and viscosity, an accurate description of nanoscale dynamics becomes essential for data interpretation. In this work, we report the results for successful, direct measurement, of the diffusion coefficients of sub-10 nm diameter nanoparticles in polymer melts by using X-ray photon correlation spectroscopy (XPCS or dynamic X-ray scattering)<sup>14</sup> and find that the SE relation is no longer applicable.

The diffusion coefficients of the nanoparticles were found to be as much as 200 times faster than the prediction from the continuum SE relation based on the measured viscosity ( $D_{SE} = k_B T / 6\pi\eta a$ , here  $D_{SE}$  is the diffusion coefficient,  $k_B$  is the Boltzmann constant,  $\eta$  is the macroscopic polymer melt viscosity,  $T$  is the temperature, and  $a$  is the radius of the particle). This unusually fast diffusion is certain to influence the kinetics of self-healing, self-assembly, and possibly the polymer transport properties, as exemplified through a large decrease in the polymer viscosity on the addition of nanoparticles, as we<sup>15,16</sup> and others<sup>17</sup> have found previously. The viscosity is also reduced by a large factor in the present work, again contradicting Einstein’s century old prediction of the suspension viscosity given by  $\mu[1 + 2.5\phi]$ , where  $\phi$  is the particle volume fraction.<sup>18</sup> Note that the viscosity

\* Corresponding author. E-mail: mackay@msu.edu. Web page: [www.nanoeverything.com](http://www.nanoeverything.com).

decrease we measure is not enough to describe the increase in  $D_{SE}$  we subsequently report.

Deviations from the SE relation have been observed before, especially when the particle radius is close to the size of the solvent molecule or when the particle is about the same size as a polymer molecule in solution.<sup>19</sup> Edward<sup>20</sup> reviewed the literature and found that the SE relation could not be applied to diffusion of molecular penetrants in simple fluids such as water and carbon tetrachloride. Indeed, when the penetrants' radius became 2–3 times that of the suspending liquids', deviations from the SE relation were quite evident. So, as may be expected, XPCS was recently used to measure the translational diffusion coefficient of  $\sim 70$  nm polystyrene (PS) spheres in glycerol at various volume fractions of the particles,<sup>14</sup> in good agreement with the SE relation. Yet, previous simulations report the applicability of the SE relation on the atomic level,<sup>21</sup> while more recently, Vergeles et al.<sup>22</sup> discussed that the SE relation can serve as a qualitative approximation for particle sizes comparable to the solvent depending on the type of flow.

Complicated results are still apparent as evidenced from simulations of Heyes et al.,<sup>23</sup> who found the translational diffusion coefficients for nanoparticles are lower than the SE prediction while the rotational diffusion coefficients are higher than that calculated from the Stokes–Einstein–Debye relation. Similarly, Somoza et al.<sup>24</sup> found the local viscosity for rotation of dissolved anthracene ( $\sim 0.6$  nm in radius) to be orders of magnitude lower than the measured viscosity of the poly(dimethylsiloxane) and poly(isobutylene) solvents. All of the above simulations depend on the intricacies of their models and serve to show the difficulty in performing such studies as well as the potential unusual effects that may occur.

Naïvely, and despite the above complex results, one may expect the SE relation in polymeric liquids to be applicable only for  $a \gg l$ , which is the correlation length for a polymer, generally taken as the size of a monomer unit or polymer segment.<sup>25,26</sup> Yet, an interesting prediction, reported by Brochard-Wyart and de Gennes,<sup>27</sup> is that the friction coefficient will depend drastically on the nanoparticle size at much larger length scales. For example, when the particle size becomes smaller than the Navier extrapolation (slip) length,<sup>28–32</sup> then drag on the particle is reduced by the amount contributed through friction drag and so by a factor of  $2/3$ .<sup>33</sup> Slip is frequently graded by the slip length that is numerically obtained by taking the velocity profile and extrapolating it within the substrate (or particle) until the velocity is zero, with the distance equal to the slip length. de Gennes<sup>28</sup> calculated it by considering the rubbing of monomer units on the substrate and is of order  $r \times \mu/\mu_1$ , where  $r$  is the monomer size and  $\mu_1$  the viscosity of equivalent monomer units. Because the viscosity of an entangled polymer melt is so large, the slip length can be of the order of 1  $\mu\text{m}$ , or even larger.

For smaller and smaller particles, the friction remains constant until its size is less than the “tube” diameter<sup>34,35</sup> and a precipitous drop is expected. At this point, the friction is concentrated to a layer of monomer units rubbing next to

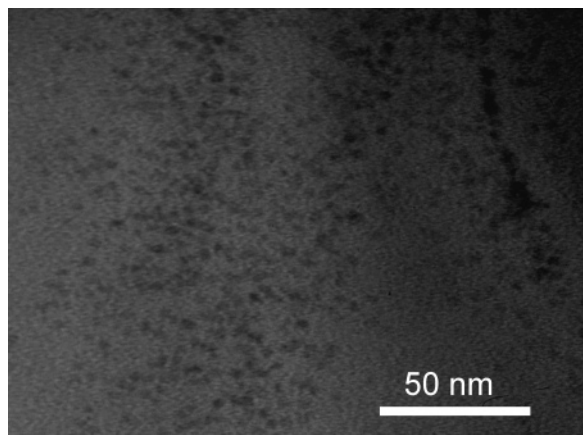
the nanoparticle surface, making it proportional to the nanoparticle area. The local viscosity ( $\mu_{LOC}$ ) due to this friction is expected to scale as  $n_0 r^2 \xi_0 \times [a/r]^2$ , where  $n_0$  is the number of monomer units per unit volume, and  $\xi_0$  is the monomeric friction coefficient. The collection of quantities  $n_0 r^2 \xi_0$  is merely the viscosity of an equivalent melt of monomer units,  $\mu_1$ .

The fall in the drag coefficient is expected to be extreme and of the order of  $\mu_{LOC}/\mu$  or numerically approximately 1/1000 to 1/10 000. The polymer melt's viscosity is given by reptation theory<sup>34,35</sup> as  $\sim \mu_1 N_c \times [N/N_c]^3$ , where  $N$  is the number of monomer units and  $N_c$  is the number of monomer units at the critical molecular mass for entanglements<sup>35,36</sup> ( $\sim 310$  for polystyrene) to elucidate why the drag coefficient is so small when compared to continuum expectations. Another interesting prediction of this theory is that the diffusion or friction coefficient is independent of the polymer's viscosity and hence molecular mass and so depends only on the particle size. We are not able to test the details of the theoretical predictions here; rather, we discuss whether the large drop in friction is possible, which was also predicted in the interesting work of Ganesan et al.<sup>25</sup> It is important to note that, in our study, the nanoparticles are larger than the correlation length but about the same size as the tube (mesh) size<sup>37</sup> and smaller than the polymer radius of gyration ( $R_g$ )<sup>25,26</sup> because we use small quantum dots dispersed in an entangled polymer melt.

Recently, addition of quantum dots (QDs) to polymers has received the attention of a number of research groups, mainly because of their extraordinary range of potential applications including electronic materials<sup>38,39</sup> and biosensors.<sup>40,41</sup> Many QD's have a covering of tri-*n*-octylphosphine oxide (TOPO) ligands on their surface to make them soluble in simple organic liquids. However, dispersion of quantum dots in various polymer matrices has proven to be quite difficult unless the TOPO ligands are replaced by either the matrix polymer or another polymer that is miscible with the matrix polymer.<sup>42</sup>

In our recent work,<sup>43</sup> we showed that dispersion of organic nanoparticles is possible in various polymer matrices, despite chemical dissimilarity, as long as the radius of the nanoparticle is less than the matrix polymer  $R_g$ . In accord with our experimental results, a simple Flory theory was developed, and we of course note that there are other theoretical studies that consider the thermodynamics of nanoparticle blends and attack the problem in a different manner to our simple theory.<sup>44–52</sup> Regardless of the mechanism or theoretical predictions, we extend our experimental study in this area by dispersing *inorganic* nanoparticles in polystyrene (PS), although we note that they are oleic acid stabilized CdSe quantum dots,<sup>53</sup> see Figure 1. On the basis of the nanoparticle concentration and size, as well as the sample size, there should be several thousands of nanoparticles visible in the micrograph, as seen.

The hydrodynamic radius of the quantum dots is 4.7 nm (as determined through dynamic light scattering in toluene at 35 °C), with a QD core radius of 2.2 nm, as determined from the analysis of multiple TEM micrographs, while the



**Figure 1.** Quantum dots can be dispersed in polymer matrices using rapid precipitation, as demonstrated by this TEM micrograph of an 8 vol % blend of oleic acid capped quantum dots dispersed in polystyrene (molecular mass, 393 kD).

$R_g$  of 393 kD PS is  $\sim 17$  nm (polydispersity index is 1.16). The quantum dots are miscible for the volume fraction studied here ( $\sim 8$  vol % in Figure 1) without any specific chemical modification of the nanoparticle surface.<sup>51,54,55</sup> Indeed, linear oleic acid is expected to have an unfavorable mixing energy with the polystyrene matrix to cause phase separation. However, it is believed that this unfavorable process is offset by an enthalpy gain due to an increase in molecular contacts at dispersed nanoparticle surfaces.<sup>43</sup> It should be pointed out that the method of blend preparation, rapid precipitation, is quite critical to ensure dispersion of nanoparticles.<sup>43,56</sup> This blend can then be drawn into fibers and stretched to prepare a thin polymer film, which can be useful for a wide variety of applications.<sup>57</sup>

Our XPCS measurements were carried out at the 8-ID-I beamline at the Advanced Photon Source (APS) with QDs chosen for this study because they provided a large contrast for X-ray scattering. XPCS is a relatively new technique for the determination of condensed matter dynamics and is in essence the extension of dynamic light scattering into the X-ray regime.<sup>58</sup> The primary requirements for the technique are the availability of a high-brilliance synchrotron radiation source and that the X-ray beam has to be made partially coherent, with the detector size matched to the size of the coherent speckles scattered by the sample.<sup>59</sup> Fluctuations in the speckle intensity are then directly related to the sample dynamics, as discussed elsewhere.<sup>14</sup>

Dynamic properties of the blends were characterized via autocorrelation of sequences of CCD images, like the one shown in Figure 2a, and normalized to the circular average of the CCD scattering at each wave vector. This allowed for determination of the normalized intensity–intensity autocorrelation function,  $g_2(q,t)$ , which is related to the field autocorrelation function,  $g_1(q,t)$ , by

$$g_2(q,t) = 1 + \alpha \times [g_1(q,t)]^2 \quad (1)$$

Here  $t$  is the delay time,  $q$  is the wave vector ( $= 4\pi/\lambda \sin(\theta/2)$ ),  $\lambda$  is the wavelength of the X-rays, and  $\theta$  is the

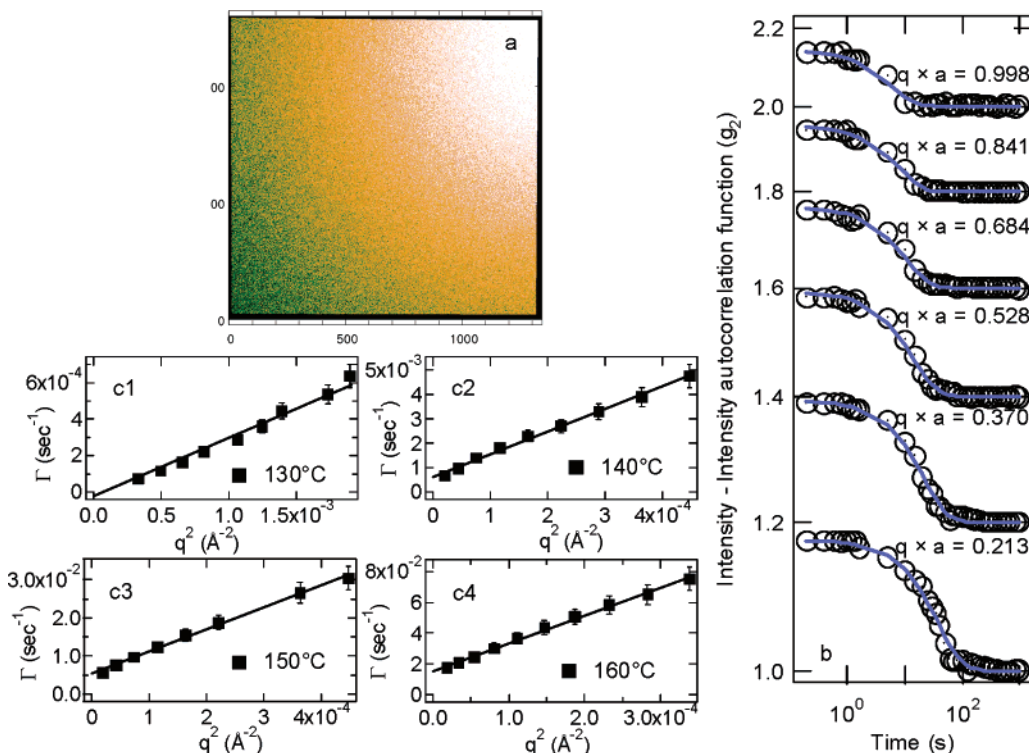
scattering angle), and  $\alpha$  is the instrument dependent contrast factor ( $\approx 0.15$  for our measurements), with

$$g_1(q,t) = \exp(-\Gamma t) \quad (2)$$

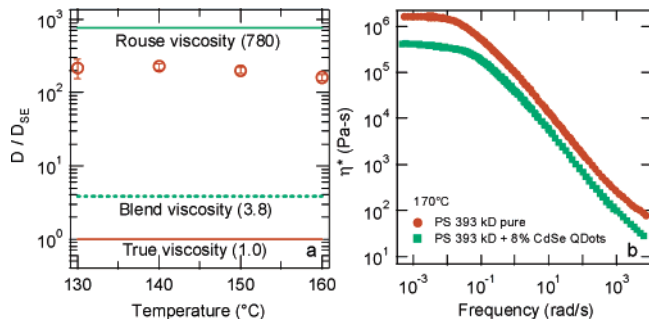
for diffusive motion, where  $\Gamma = q^2 D$  and  $D$  is the measured diffusion coefficient. Because the CdSe core is small, intraparticle scattering effects will be minimal and so correction using the form factor is not warranted or required. It is important to realize that the type of experiment we are performing does not have selectively labeled particles, and so the equivalent of the self-intermediate scattering function is not measured;<sup>60</sup> rather, scattering occurs from each of the particles.

Typical data obtained for the intensity–intensity autocorrelation function as a function of the delay time are shown in Figure 2b. This data could be fitted to a single exponential (eqs 1–2), with  $\alpha$  and  $\Gamma$  as the two fitting parameters; even allowing  $\alpha$  to be a variable parameter, it was found independent of  $q$  while  $\Gamma$  was not. The fits are shown as the solid lines in Figure 2b. A plot of  $\Gamma$  versus  $q^2$  is a straight line, as shown for various temperatures in Figure 2c1–2c4. The fact that all the data can be described by a straight line suggests that the nanoparticles demonstrate normal Brownian diffusion within the polymer melt at all temperatures with a slope equal to the diffusion coefficient.

The ratio  $D/D_{SE}$  is shown in Figure 3a for the CdSe Quantum dots in linear 393 kD PS as a function of temperature (it should be noted that the glass transition temperature for PS is  $\sim 106$  °C), with values given in Table 1. From the figure, it is immediately clear that the nanoparticles diffuse almost 200 times faster than the prediction from the SE relation based on the viscosity of pure PS. This is equivalent to stating that the local viscosity experienced by nanoparticles is much less than the macroscopically measured viscosity as speculated by Brochard-Wyart and deGennes.<sup>27</sup> The solid line shown on the graph, labeled “Rouse viscosity”,<sup>61</sup> is the value of the ratio assuming particles at infinite dilution and in the absence of any entanglements. The Rouse viscosity was determined by scaling the viscosity at the critical molecular weight for entanglement coupling (32.7 kD) with the molecular weight to the first power:  $292 \text{ Pa-s} \times [M_w/32.7 \text{ kD}] \times a_T$ , where  $a_T$  is the shift factor given by  $\log(a_T) = -7.65 \times [T(^{\circ}\text{C}) - 170]/[T(^{\circ}\text{C}) - 28.1]$ , valid for  $140\text{--}170$  °C. The viscosity for the entangled polymer was also found from similar data<sup>62,63</sup> and is given by  $292 \text{ Pa-s} \times [M_w/32.7 \text{ kD}]^{3.68} \times a_T$ . The diffusion coefficient is inversely proportional to the viscosity, and so if no entanglements are present, the “Rouse viscosity” curve is given by  $\mu/\mu_R = [M_w/32.7 \text{ kD}]^{2.68}$  to yield a value of 780 for our system. It should be pointed out that, for the calculation of  $D_{SE}$ , we have used a radius of 5 nm for the QDs; a radius of  $\sim 25$  nm would be required for the ratio to follow the Rouse viscosity curve, while a radius of  $\sim 0.05$  nm is needed for the SE relation to be valid. Clearly, neither of these limits is possible, and so the nanoparticles behave as if they are in a medium with viscosity between an entangled and unentangled melt.



**Figure 2.** (a) Single frame (CCD image) obtained from the X-ray diffraction of 8 vol % quantum dots in polystyrene (393 kDa). For each sample, 400–500 frames were taken at each temperature at intervals of 0.1 s. (b) Each frame was divided into equally spaced  $q$  regimes, based on their angular distance from the upper right-hand corner of the frame (the center of the X-ray beam), and analyzed to find the intensity–intensity autocorrelation function ( $g_2(q,t)$ ). The data was then fitted to a single exponential (the solid blue line) to obtain  $\Gamma$  as a function of  $q$ , which we normalize with the particle radius ( $a$ ) in the figure. The data sets have been offset by adding 0.2 to the previous set. (c1–c4) Graphs of  $\Gamma$  vs  $q^2$  for the quantum dots in PS at four different temperatures (130–160 °C) to determine the diffusion coefficient.



**Figure 3.** (a) Ratio of the measured diffusion coefficient to the diffusion coefficient calculated from the SE relation for the quantum dots in polystyrene. Different viscosity values were assumed to calculate the SE diffusion coefficient: the pure polymer viscosity (true viscosity), the pure polymer viscosity without entanglements (Rouse viscosity), and the viscosity of the blend determined in Figure 3b (blend viscosity). (b) The complex viscosity as a function of frequency for pure polystyrene and its blend with quantum dots to show a ca. 60% viscosity decrease in the blend.

Previous work suggests that the size and shape of particles are critical parameters for their diffusion.<sup>64</sup> Here, the nanoparticles are about the same size as the tube diameter or the entanglement mesh length<sup>65</sup> in entangled polystyrene ( $\sim 8$ – $9$  nm).<sup>37</sup> We find the  $D/D_{SE}$  ratio is always greater than one and less than the calculated ratio based on the Rouse viscosity in Figure 3a, suggesting that the nanoparticles' motion is influenced by some but not all of the entanglements in the system, as discussed above, leading to these extremely high diffusion coefficients. Yet, as discussed below, entanglements

**Table 1.** Diffusion Coefficients That Are Measured ( $D$ ) and Calculated, Based on the Stokes–Einstein Relation ( $D_{SE}$ ), for 5 nm Radius Quantum Dots Diffusing in 393 kD Polystyrene Melt as a Function of Temperature<sup>a</sup>

$T$ (°C)	viscosity (Pa·s)	$D_{SE}$ (nm <sup>2</sup> /s)	$D$ (nm <sup>2</sup> /s)	$D/D_{SE}$
130	$4.50 \times 10^8$	$3.94 \times 10^{-4}$	$2.90 \times 10^{-2}$	271
140	$1.59 \times 10^8$	$1.21 \times 10^{-3}$	$8.79 \times 10^{-2}$	230
150	$2.62 \times 10^7$	$6.20 \times 10^{-3}$	$4.78 \times 10^{-1}$	202
160	$6.30 \times 10^6$	$1.76 \times 10^{-2}$	$1.64 \times 10^0$	162

<sup>a</sup> The measured values for the terminal viscosity of pure polystyrene ( $M_w = 393.4$  kD, PDI = 1.16) as well as the values for the  $D/D_{SE}$  ratio are also tabulated.

may not play a role at all. We have also considered the effect of shear thinning and elasticity on the calculated Stokes–Einstein coefficient (i.e.,  $D_{SE}$ ) by using relations developed before to account for these effects.<sup>66,67</sup> One can estimate that the particles' frequency of movement is in the shear thinning regime; however, if the above relations are used, then one would find the calculated diffusion coefficient is indeed even smaller making the effect shown in the figure larger. Thus, these effects are neglected to give the minimum ratio.

Quite significantly, the diffusivity ratio is found to be independent of temperature (Figure 3a), in contrast to deviations from the SE relation observed previously near the glass-transition temperature due to the presence of “hopping” particles having excessively high mobility compared to ideal Brownian motion.<sup>68</sup> The temperature independence also

suggests that an activated process other than that associated with the polymer melt is not present, which is in agreement with the Brochard-Wyart and deGennes theory<sup>27</sup> (as well as continuum expectations). We realize that numerical coefficients are not available for their theory,<sup>27</sup> so the  $D/D_{SE}$  ratio will scale as  $N_c \times [N/N_c]^3 \times [r/a]^2$ , which will be  $310 \times [3780/310]^3 \times [0.3 \text{ nm}/5 \text{ nm}]^2$  or 2000, which is too large. Of course, some care in defining the parameters will change this value, for example, assuming  $N_c$  is the number of statistical segments reduces the value to 400, while including some of the known numerical factors according to reptation theory further reduces it to 160 (a factor of 20/48 can be used in the polymer melt viscosity relation). This is the correct order of magnitude, although we note that the viscosity scaling of  $N^3$  is not correct in the polymer melt viscosity expression and in the future we hope to measure the diffusion coefficient with various molecular mass polymer matrices to determine if it is in fact independent of  $N$ , i.e.,  $D = k_B T / 6\pi\eta_0 \zeta_0 a^3$ . In the present study, we have, however, confirmed the essence of the Brochard-Wyart–de Gennes prediction; there is a large drop in the friction coefficient, resulting in a huge increase in the diffusivity.

We believe this effect produces the viscosity reduction seen by us<sup>15,16</sup> and others<sup>17,69,70</sup> due to the separation of the relative times scales for network relaxation and nanoparticle diffusion. In agreement with these studies, addition of quantum dots to polystyrene also causes a large reduction in the melt viscosity of the nanocomposite (~60%, see Figure 3b) at all frequencies despite Einstein's relation predicting a ~20% increase in viscosity. Note that, because the nanoparticles reduce the melt viscosity of the polymer, the dotted line labeled "blend viscosity" has been added in Figure 3a, showing the maximum calculated value of  $D/D_{SE}$  using the nanoparticle–polymer blend viscosity and assuming infinite dilution. So, the viscosity reduction does not rationalize the rise in the diffusivity.

The relaxation time scale for 393 kD linear polystyrene is 50–150 s at 160 °C, while the diffusion coefficient for the QDs is ~1 nm<sup>2</sup>/s at the same temperature, suggesting a time scale for movement over a particle or tube diameter of ~20 s. Because of this, we suggest that the nanoparticles do not participate in the entanglement network dynamics and instead contribute to a constraint release phenomena,<sup>71–75</sup> allowing a fall in the viscosity. This was seen in the relaxation time spectra by Tuteja et al.<sup>16</sup> through a truncation of longer relaxation modes without significant reduction in the plateau modulus. Basically, the proposed mechanism is that the nanoparticles diffuse faster than the entangled mesh and so do not participate in its dynamics. They merely occupy space to provide a constraint release mechanism via dilution. Indeed, a more thorough theoretical investigation into this phenomenon was addressed in parallel and independent to our study by Curro and Frischnecht,<sup>76</sup> to reveal that constraint release through this mechanism is a viable explanation. We also note that introduction of free volume via perturbation of the packing structure within the polymer melt also appears to be an effect in these systems.<sup>15,16</sup>

**Acknowledgment.** We acknowledge NSF CTS-0400840, NSF NIRT ECS-0506309 and NSF CTS-0417640, EEC-0118007, NSF EEC-0647452, 3M Nontenured Faculty Award, Advanced Aromatics, and the Smalley–Curl Innovation Award for partial support of this project. We also thank Alicia Pastor for all her help with TEM and also Professor Ken Schweizer, Alec Sandy, and Michael Sprung for valuable discussions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357.

## References

- (1) Lopes, W. A.; Jaeger, H. M. *Nature* **2001**, *414*, 735–738.
- (2) Li, M.; Schnablegger, H.; Mann, S. *Nature* **1999**, *402*, 393–395.
- (3) Lin, Y.; Boker, A.; He, J. B.; Sill, K.; Xiang, H. Q.; Abetz, C.; Li, X. F.; Wang, J.; Emrick, T.; Long, S.; Wang, Q.; Balazs, A.; Russell, T. P. *Nature* **2005**, *434*, 55–59.
- (4) Bockstaller, M. R.; Lapetnikov, Y.; Margel, S.; Thomas, E. L. *J. Am. Chem. Soc.* **2003**, *125*, 5276–5277.
- (5) Gupta, S.; Zhang, Q. L.; Emrick, T.; Balazs, A. C.; Russell, T. P. *Nat. Mater.* **2006**, *5*, 229–233.
- (6) Smith, K. A.; Tyagi, S.; Balazs, A. C. *Macromolecules* **2005**, *38*, 10138–10147.
- (7) Raja, K. S.; Wang, Q.; Gonzalez, M. J.; Manchester, M.; Johnson, J. E.; Finn, M. G. *Biomacromolecules* **2003**, *4*, 472–476.
- (8) Johnson, J. E.; Chiu, V. *Curr. Opin. Struct. Biol.* **2000**, *10*, 229–235.
- (9) Seksek, O.; Biwersi, J.; Verkman, A. S. *J. Cell. Biol.* **1997**, *138*, 131–142.
- (10) Lukacs, G. L.; Haggie, P.; Seksek, O.; Lechardeur, D.; Freedman, N.; Verkman, A. S. *J. Biol. Chem.* **2000**, *275*, 1625–1629.
- (11) Lu, Q.; Solomon, M. J. *Phys. Rev. E* **2002**, *66*, 061504.
- (12) Chen, D. T.; Weeks, E. R.; Crocker, J. C.; Islam, M. F.; Verma, R.; Gruber, J.; Levine, A. J.; Lubensky, T. C.; Yodh, A. G. *Phys. Rev. Lett.* **2003**, *90*, 108301.
- (13) Papagiannopoulos, A.; Waigh, T. A.; Fluerau, A.; Fernyhough, C.; Madsen, A. J. *Phys.: Condens. Matter* **2005**, *17*, L279.
- (14) Lurio, L. B.; Lumma, D.; Sandy, A. R.; Borthwick, M. A.; Falus, P.; Mochrie, S. G. J.; Pelletier, J. F.; Sutton, M.; Regan, L.; Malik, A.; Stephenson, G. B. *Phys. Rev. Lett.* **2000**, *84*, 785–788.
- (15) Mackay, M. E.; Dao, T. T.; Tuteja, A.; Ho, D. L.; Van Horn, B.; Kim, H. C.; Hawker, C. J. *Nat. Mater.* **2003**, *2*, 762–766.
- (16) Tuteja, A.; Mackay, M. E.; Hawker, C. J.; Van Horn, B. *Macromolecules* **2005**, *38*, 8000–8011.
- (17) Kopesky, E. T.; Haddad, T. S.; Cohen, R. E.; McKinley, G. H. *Macromolecules* **2004**, *37*, 8992–9004.
- (18) Einstein, A. *Ann. Phys. (Leipzig)* **1906**, *19*, 371–381.
- (19) Liu, J.; Gardel, M. L.; Kroy, K.; Frey, E.; Hoffman, B. D.; Crocker, J. C.; Bausch, A. R.; Weitz, D. A. *Phys. Rev. Lett.* **2006**, *96*, 118104–1–118104-4.
- (20) Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261–270.
- (21) Alder, B. J.; Gass, D. M.; Wainwright, T. E. *J. Chem. Phys.* **1970**, *53*, 3813–3826.
- (22) Vergeles, M.; Keblinski, P.; Koplik, J.; Banavar, J. R. *Phys. Rev. E* **1996**, *53*, 4852–4864.
- (23) Heyes, D. M.; Nuevo, M. J.; Morales, J. J. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1625–1632.
- (24) Somoza, M. M.; Sluch, M. I.; Berg, M. A. *Macromolecules* **2003**, *36*, 2721–2732.
- (25) Ganesan, V.; Pryamitsyn, V.; Surve, M.; Narayanan, B. *J. Chem. Phys.* **2006**, *124*, 221102-1–221102-4.
- (26) Kim, J.; Keyes, T. *J. Phys. Chem. B* **2005**, *109*, 21445–21448.
- (27) Brochard-Wyart, F.; deGennes, P. G. *Eur. Phys. J. E* **2000**, *1*, 93–97.
- (28) deGennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827–863.
- (29) Henson, D. J.; Mackay, M. E. *J. Rheol.* **1995**, *39*, 359–373.
- (30) Mackay, M. E.; Henson, D. J. *J. Rheol.* **1998**, *42*, 1505–1517.
- (31) Migler, K. B.; Hervet, H.; Leger, L. *Phys. Rev. Lett.* **1993**, *70*, 287–290.
- (32) Mhetar, V.; Archer, L. A. *Macromolecules* **1998**, *31*, 8607–8616.
- (33) Happel, J.; Brenner, H., *Low Reynolds Number Hydrodynamics*; Springer: New York, 1981; p 570.
- (34) deGennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572–579.

- (35) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.
- (36) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley & Sons: New York, 1980.
- (37) Graessley, W. W. *J. Polym. Sci.* **1980**, *18*, 27–34.
- (38) Huynh, W. U.; Peng, X. G.; Alivisatos, A. P. *Adv. Mater.* **1999**, *11*, 923.
- (39) Lee, J.; Sundar, V. C.; Heine, J. R.; Bawendi, M. G.; Jensen, K. F. *Adv. Mater.* **2000**, *12*, 1102.
- (40) Pathak, S.; Choi, S. K.; Arnheim, N.; Thompson, M. E. *J. Am. Chem. Soc.* **2001**, *123*, 4103–4104.
- (41) Michalet, X.; Pinaud, F. F.; Bentolila, L. A.; Tsay, J. M.; Doose, S.; Li, J. J.; Sundaresan, G.; Wu, A. M.; Gambhir, S. S.; Weiss, S. *Science* **2005**, *307*, 538–544.
- (42) Skaff, H.; Ilker, M. F.; Coughlin, E. B.; Emrick, T. *J. Am. Chem. Soc.* **2002**, *124*, 5729–5733.
- (43) Mackay, M. E.; Tuteja, A.; Duxbury, P. M.; Hawker, C. J.; Van Horn, B.; Guan, Z.; Chen, G.; Krishnan, R. S. *Science* **2006**, *311*, 1740–1743.
- (44) Hooper, J. B.; Schweizer, K. S. *Macromolecules* **2006**, *39*, 5133–5142.
- (45) Hooper, J. B.; Schweizer, K. S. *Macromolecules* **2005**, *38*, 8858–8869.
- (46) Hooper, J. B.; Schweizer, K. S.; Desai, T. G.; Koshy, R.; Keblinski, P. *J. Chem. Phys.* **2004**, *121*, 6986–6997.
- (47) Starr, F. W.; Douglas, J. F.; Glotzer, S. C. *J. Chem. Phys.* **2003**, *119*, 1777–1788.
- (48) He, G.; Ginzburg, V. V.; Balazs, A. C. *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 2389–2403.
- (49) Lin, Y.; Boker, A.; He, J. B.; Sill, K.; Xiang, H. Q.; Abetz, C.; Li, X. F.; Wang, J.; Emrick, T.; Long, S.; Wang, Q.; Balazs, A.; Russell, T. P. *Nature* **2005**, *434*, 55–59.
- (50) Thompson, R. B.; Ginzburg, V. V.; Matsen, M. W.; Balazs, A. C. *Science* **2001**, *292*, 2469–2472.
- (51) Ginzburg, V.; Singh, C.; Balazs, A. *Macromolecules* **2000**, *33*, 1089–1099.
- (52) Ginzburg, V.; Balazs, A. *Adv. Mater.* **2000**, *12*, 1805–1809.
- (53) Asokan, S.; Krueger, K. M.; Alkhalil, A.; Carreon, A. R.; Mu, Z. Z.; Colvin, V. L.; Mantzaris, N. V.; Wong, M. S. *Nanotechnology* **2005**, *16*, 2000–2011.
- (54) Chen, H.; Schmidt, D. F.; Pitsikalis, M.; Hadjichristidis, N.; Zhang, Y. M.; Wiesner, U.; Giannelis, E. P. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 3264–3271.
- (55) Vaia, R. A.; Giannelis, E. P. *MRS Bull.* **2001**, *26*, 394–401.
- (56) Du, F. M.; Fischer, J. E.; Winey, K. I. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 3333–3338.
- (57) Fendler, J. H. *Chem. Mater.* **1996**, *8*, 1616–1624.
- (58) Grubel, G.; Zontone, F. *J. Alloys Compd.* **2004**, *362*, 3.
- (59) Lurio, L.; Lumma, D.; Sandy, A.; Borthwick, M.; Falus, P.; Mochrie, S.; Pelletier, J.; Sutton, M.; Regan, L.; Malik, A.; Stephenson, G. *Phys. Rev. Lett.* **2000**, *84*, 785–788.
- (60) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, 1989; p 525.
- (61) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272–1280.
- (62) Fox, T. G.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2384–2395.
- (63) Fox, T. G.; Flory, P. J. *J. Polym. Sci.* **1954**, *14*, 315–319.
- (64) Gisser, D. J.; Johnson, B. S.; Ediger, M. D.; Vonmeerwall, E. D. *Macromolecules* **1993**, *26*, 512–519.
- (65) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1–179.
- (66) Acharya, A.; Mashelkar, R. A.; Ulbrecht, J. *Rheol. Acta* **1976**, *15*, 454–470.
- (67) Chhabra, R. P.; Uhlherr, P. H. T.; Boger, D. V. *J. Non-Newtonian Fluid Mech.* **1980**, *6*, 187–199.
- (68) Kumar, S. K.; Szamel, G.; Douglas, J. F. *J. Chem. Phys.* **2006**, *124*, 214501.
- (69) Kopesky, E. T.; Haddad, T. S.; McKinley, G. H.; Cohen, R. E. *Polymer* **2005**, *46*, 4743–4752.
- (70) Yu, T. S.; Lin, J. P.; Xu, J. F.; Ding, W. W. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3127–3134.
- (71) Viovy, J. L. *J. Phys.* **1985**, *46*, 847–853.
- (72) Marrucci, G. *J. Polym. Sci.* **1985**, *23*, 159–177.
- (73) Tsenoglou, C. *Macromolecules* **1991**, *24*, 1762–1767.
- (74) Larson, R. G. *The Structure and Rheology of Complex Fluids*; Oxford University Press: New York, 1999.
- (75) des Cloizeaux, J. D. *Europhys. Lett.* **1988**, *5*, 437–442.
- (76) Curro, J. G.; Frischknecht, A. L. **2006**, in preparation.

NL070192X