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To cite this article: A Karatrantos et al 2014 IOP Conf. Ser.: Mater. Sci. Eng. 64 012041

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Structure, entanglements and dynamics of polymer nanocomposites containing spherical nanoparticles

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Abstract. We investigate the effect of nanoparticles on polymer structure, nanoparticle dynamics and topological constraints (entanglements) in polymer melts for nanoparticle loading above percolation threshold as high as 40.9% using stochastic molecular dynamics (MD) simulations. An increase in the number of entanglements (decrease of $N_e$ with 40.9% volume fraction of nanoparticles dispersed in the polymer matrix) in the nanocomposites is observed as evidenced by larger contour lengths of the primitive paths. Attraction between polymers and nanoparticles affects the entanglements in the nanocomposites and alters the primitive path. The diffusivity of small sized nanoparticles deviates significantly from the Stokes-Einstein relation.

1. Introduction
The addition of nanoparticles to a polymer matrix can improve the electrical, thermal, mechanical, rheological and tribological properties [1]. We explore how nanoparticles can affect polymer structure when the polymer radius of gyration is larger than the nanoparticle radius (R). There is controversy as to whether the addition of nanoparticles to a polymer melt causes perturbed behaviour of polymers [2,3,4,5]. The quality of nanoparticle dispersion [3,4] can have an important effect on the polymer structure. However, we need to note that in the experimental area of polymer nanocomposites containing spherical nanoparticles, the role of monomer-nanoparticle interaction on polymer structure and nanoparticle dynamics is not clear yet.

The dynamics of long polymers is limited by entanglements, which are topological constraints imposed by the other chains. These can dramatically change the polymer’s viscosity, mechanical and tribological properties. We investigate how the spherical nanoparticles also affect the primitive path network of polymers by using topological algorithms [6-9]. An increase in the entanglement polymer density originates mechanical reinforcement in nanocomposites [10].

2. Simulation Details
In the stochastic MD method [14] a set of interacting particles is considered, whose time evolution is governed by Newton’s equation of motion. The Lennard-Jones potential $V_{ij}^{LJ}$, acting along the line between the centres of mass of two particles force [11] is given by:

$$V_{ij}^{LJ} = 4\varepsilon_{ij} \left( \frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^{6}}{r_{ij}^{6}} \right)$$

(1)

where $\varepsilon_{ij}=k_BT$ ($k_B$ is the Boltzmann constant, and $T$ is the absolute temperature) is the interaction energy between particle $i$ and particle $j$ (for monomers: $\varepsilon_m=\sigma_m=m=1$, for nanoparticles: $\varepsilon_p=1$, $\sigma_p=2R$, $m_p=0.85\cdot(4/3)nR^3$, $r_{ij}$ represents the distance between particles $i$ and $j$. For monomer (m)-
nanoparticle (p) interactions the combination rules: \( \varepsilon_{mp} = (\varepsilon_m \varepsilon_p)^{1/2} \), \( \sigma_{mp} = (\sigma_m + \sigma_p)/2 \), were used. The monomers (or nanoparticles) are modelled with the repulsive only part of Equation 1, with a cut off radius at \( r_c=2^{(1/6)} \sigma_m \) (\( r_c=2^{(1/6)} \sigma_p \) for nanoparticles). For attractive monomer - nanoparticle interaction (attractive nanoparticles) the cut off radius is \( r_c=2.4 \sigma_{mp} \), and for repulsive monomer-nanoparticle interaction (repulsive nanoparticles) \( r_c=2^{(1/6)} \sigma_{mp} \). Also, the monomers were connected using FENE potential [12]. The stiffness of the polymer chains is controlled by a cosine harmonic bending potential [13], which acts on three consecutive beads along the chain. By increasing the intramolecular stiffness of the polymer chain the entanglement length is decreased [14] to a value of \( N_e \approx 58 \).

\[
V_{ij}^{LJ} = \frac{1}{2} k_\theta \left( \cos(\theta_{ijk}) - \cos(\theta_0) \right)^2
\]

where \( \theta_{ijk} \) is the bending angle between three consecutive bonds. The equilibrium value is \( \theta_0 = 109.5 \), and the bending constant \( k_\theta = 25 \) [13].

The simulations of the polymer melt were performed at a monomer density \( \rho= (N_m/V) = 0.85 \) in a simulation cell of 60000 particles (where \( N_m \) is the total number of monomeric units in the system and \( V \) is the volume of the system) using the NVT ensemble. The pressure calculated for the \( N=200 \) polymer melt was \( P^*=P \cdot \sigma_m^3/\varepsilon_m = 4.864 \). That pressure was used to perform all the nanocomposite systems simulations in the NPT ensemble. To set the temperature at \( T^*=k_B T/\varepsilon_m = 1 \) and pressure at \( P^*=4.864 \) the Langevin thermostat and Berendsen barostat were used respectively. The equations of motion were integrated using the Leap frog algorithm [15] with a time step equal to 0.005\( \tau \) for polymer melts (a time step of 0.004\( \tau \) was used for nanocomposite simulations), where \( \tau=(m_m \sigma_m^2/ k_B T)^{1/2} \) is the LJ time unit. The duration of the simulation runs were between 4-20-10^6 steps depending on the length of the molecules. The equilibrium time is long enough for the polymer to move at least twice the radius of gyration of the polymer, \( R_g \), which is the equilibration criterion usually used [16,17]. For nanocomposites, we consider systems of spherical nanoparticles in a dense polymer melt.

**Figure 1.** Spherical nanoparticles dispersed in polymer matrix (\( \phi=31.6\% \)).

In the nanocomposite systems (see Figure 1) studied, a total number of \( N_t=23600 \) monomers were used in a cubic cell. Details of the nanocomposite systems studied are summarized in the Table 1:
### Table 1. Volume fraction $\phi\%$, number of nanoparticles $N_p$ of radius $R$

<table>
<thead>
<tr>
<th>$\phi%$</th>
<th>$N_p$ of radius $R=1$</th>
<th>$N_p$ of radius $R=2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>18.7</td>
<td>800</td>
<td>100</td>
</tr>
<tr>
<td>25.7</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>31.6</td>
<td>1600</td>
<td>200</td>
</tr>
<tr>
<td>40.9</td>
<td>2400</td>
<td>300</td>
</tr>
</tbody>
</table>

3. Estimators for entanglement length $N_e$

In polymer melts of sufficiently long flexible chain molecules, neighbouring chains strongly interpenetrate and entangle with each other [18], thus, the motion of polymers whose degree of polymerization becomes larger than the “entanglement length” $N_e$ is confined to a tubelike region. The $N_e$ can be determined by the estimator of Everaers (S-coil estimator) [19]. In addition, there are modified estimators that provide an upper bound for $N_e$, such as the modified S-coil [8], but they tend to overestimate $N_e$ for weakly entangled chains. In order to eliminate the systematic errors that appeared in the previous estimators [7,9] and to obtain an accurate $N$-independent value, we use an ideal $N_e$ estimator (M-coil) [8], which requires simulation of multiple chain lengths, using coil properties. The averages in our analysis are taken over the ensemble of all chains at each time step. Then the time average is taken for 250 saved configurations (at a time larger than the disentanglement time, $t>\tau$).

4. Results and discussion

#### 4.1 Polymer and nanoparticle structure

In Figure 2 we show the monomer-nanoparticle and nanoparticle-nanoparticle radial distribution functions $g(r)$ for repulsive and attractive nanoparticles ($R=1$) respectively for different volume fractions. As can be seen the high monomer density of the layers establishes a well defined interface between the nanoparticles and polymer melt whose structure differs from that of the amorphous polymer melt. Monomer packing effects become important as monomers form layers around the nanoparticle, which is illustrated by the oscillations of $g(r)$. A completely different behaviour of the nanoparticle structure due to the polymer nanoparticle interaction can be seen in Figures 2c, 2d.
Figure 2. Radial distribution functions in the nanocomposite systems at different volume fractions $\phi$ for $R=1$. 

(a) repulsive nanoparticles: monomer-nanoparticle, (b) attractive nanoparticles: monomer-nanoparticle, (c) repulsive nanoparticles: nanoparticle-nanoparticle, (d) attractive nanoparticles: nanoparticle-nanoparticle. i) 10.3% (black line), (ii) 25.7% (dotted line), (iii) 31.6% (dashed line), (iv) 40.9% (dashed-dotted line).

4.2 Nanoparticle dynamics

It is known that the dynamics of spherical particles (colloids) in a fluid can be predicted by the classic continuum Stokes-Einstein relation. For a large spherical particle of radius $R$ in a fluid of viscosity $\eta$ the diffusion coefficient $D$ of the particle is given by [20]:

$$D = \frac{k_B T}{4\pi\eta R} \quad \text{(3)}$$

However, in the case of nanoparticles dispersed in polymer melts and solutions, the validity of Equation (3) is questionable. The nanoparticle diffusivity of the simulated nanocomposite systems is calculated through the mean square displacement measurements and is given by [11]:

$$D = \lim_{t \to \infty} \frac{\langle (r_{cm}(t) - r_{cm}(0))^2 \rangle}{6t} \quad \text{(4)}$$

It can be seen from Figure 3 that the nanoparticle diffusivity for different polymer matrices deviates from the Stokes – Einstein relation for small nanoparticles of $R=1$. This behaviour is obvious in the dilute regime ($\phi=10.3\%$) for polymers with $N>20$. However, the nanoparticle diffusivity follows the Stokes-Einstein relation in nanocomposites containing short chains at the dilute regime. In addition, in the regime above the percolation threshold ($\phi_c=31\%$) the nanoparticles diffusivity is decreased dramatically.
4.3 Entanglement length

In Figure 4 we show the dependence of $N_e$ as calculated by the M-coil estimator [8,21] of nanocomposite systems, for repulsive and attractive nanoparticles. The polymer-nanoparticle interaction alters the number of entanglements for the high nanoparticle volume fractions studied, as can be seen in Figure 4a due to an increase of the contour length of the primitive path ($L_{pp}$) (Figure 4b). The addition of nanoparticles decreases the $N_e$ since there are more topological constraints that hinder the polymer chain diffusivity.

**Figure 3.** Nanoparticle (R=1) diffusivity estimated using Equation (4) for attractive spherical nanoparticles at different volume fractions $\phi$: i) 10.3% (spheres), ii) 18.7% (diamonds), (iii) 25.7% (squares), (iv) 31.6%, (v) 40.9% (stars), (vi) Stokes-Einstein relation (equation 3) (filled circles).

**Figure 4.** a) $N_e$ estimated using the M-coil estimator for polymer nanocomposites: (i) repulsive nanoparticles: R=1 (circles), (ii) attractive nanoparticles: R=1 (diamonds), (iii) repulsive nanoparticles: R=2 (squares). b) Contour length of the primitive path $L_{pp}$: (i) repulsive nanoparticles: R=1 (circles), (ii) attractive nanoparticles: R=1 (diamonds), (iii) repulsive nanoparticles: R=2 (squares).
5. Conclusions
The polymer structure, nanoparticle dynamics and topological constraints (entanglements) of polymers in melts and nanocomposites containing spherical nanoparticles were investigated by means of stochastic molecular dynamics simulations. We show that small sized nanoparticles can diffuse much faster than that predicted from the Stokes-Einstein relation. Also, we applied an ideal $N_e$ estimator for the calculation of the number of entanglements in our systems, and extracted the $N$--independent entanglement length $N_e$. We observe that the entanglement length decreases significantly with volume fraction of nanoparticle. This decrease of $N_e$ in the polymer melt with nanoparticles originates from the polymer/nanoparticle entanglements, because of the increase in contour length of the primitive path due to the addition of nanoparticles.

Acknowledgements
We thank Professor Martin Kroger for providing the Z1 algorithm and for useful discussions. This research was funded by the EPSRC/NSF Materials Network program EP/5065373/1 (EPSRC: NC, AK) and DMR-0908449 (NSF: KIW, RJC).

References