

Supporting Information

Simulation on diffusivity and statistical size of polymer chains in polymer nanocomposites

Jian-Hua Huang ^{1,*}, Dan-Dan Sun ¹, Rong-Xing Lu, Huan Zhang ¹, Raja Azhar Ashraaf
Khan ²

¹ *Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China.*

² *Department of Physics, Zhejiang University, Hangzhou 310027, China.*

1. Results of Monte Carlo simulation for the system with mobile nanoparticles

We have performed more Monte Carlo (MC) simulations for the polymer nanocomposite (PNC) system with mobile nanoparticles (NPs). Three kinds of NPs, including repulsive NPs (RNPs) and attractive NPs (ANPs) of interaction strengths $\epsilon_{pn} = 1.0$ and 2.5 , are considered in these simulations. The diameter and concentration of NPs are set as $\sigma_n = 5$ and $c_n = 0.125$, respectively, and the length of polymer chain is fixed as $N = 64$. It was pointed out that the diffusion rate of NPs is smaller than that of polymers due to the large mass of NPs.¹ To mimic the slow diffusion of NPs, the mobile probability, p_m , is set as 1 for polymer monomers while that of NPs is set much smaller than 1 in the MC simulation. When $p_m = 0.00015$, we find the diffusion rate of NP is about 1/40 of polymer in dilute solution, in accordance with the experimental report.¹

Fig. S1 shows the variation of the polymer diffusion coefficient D and the mean-square radius of gyration $\langle R_g^2 \rangle$ of polymer chains with the concentration of polymers c_p in different systems. These results are similar to those of immobile NPs present in Fig. 1, although the values of D and $\langle R_g^2 \rangle$ are changed due to the mobile of NPs and the minimum D is hard to be determined since the D values are very small at small c_p .

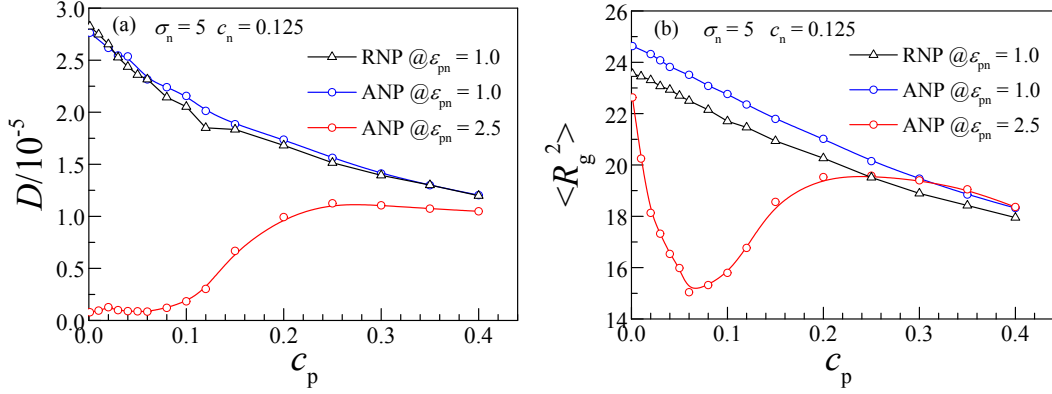


Fig. S1 Variation of the diffusion coefficient D (a) and the mean-square radius of gyration $\langle R_g^2 \rangle$ (b) of polymer chains with the concentration of polymers c_p for three different systems with mobile NPs.

For the system with orderly distributed immobile NPs, we can observe NP-polymer-NP bridges since we find a relatively large probability for one polymer chain contacting with two or more NPs (Fig. 2 for strong attraction strength $\epsilon_{pn} = 2.5$). If NPs are allowed to move, the bridging effect could cause the bridge narrow.² **Fig. S2** shows the evolution of NP-NP distance, d , for a typical case (initial $d = 10$). We find the two NPs are pulled by the polymer chain and d decreases from initial 10 to about 6, the latter equals to the plus of NP's and polymer monomer's diameter. The snapshots of NP-polymer-NP bridges with $d = 10$ and $d = 6$ are presented in the inset of **Fig. S2**.

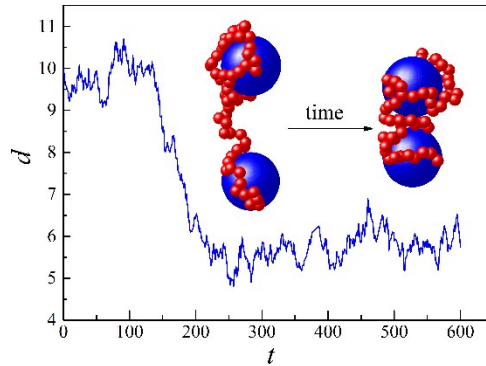


Fig. S2 Evolution of NP-NP distance d for the NP-polymer-NP bridge if NPs are allowed to move in polymer dilute solution. $\sigma_n = 5$ and $\epsilon_{pn} = 2.5$.

2. Results of molecules dynamics simulation using LAMMPS

Molecular dynamics (MD) simulations are performed using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software.³ The system is the same as that used in the dynamic MC simulation. However, the interactions adopted in the MD simulation are different slightly from MC.

In the LAMMPS simulation, the interaction between two monomers is purely repulsive which is described by a truncated and shifted WCA potential⁴

$$V_{\text{WCA-pp}}(r) = \begin{cases} 4\epsilon_{\text{pp}} \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r < 2^{1/6} \sigma \\ 0, & r \geq 2^{1/6} \sigma \end{cases}, \quad (1)$$

where ϵ_{pp} is the interaction strength. For bonded monomers, the finite extensible nonlinear elastic (FENE) potential⁵

$$V_{\text{FENE}}(b) = \begin{cases} -\frac{1}{2} K R_0^2 \ln \left[1 - \left(\frac{b}{R_0} \right)^2 \right], & b < R_0 \\ \infty, & b \geq R_0 \end{cases}. \quad (2)$$

is further considered. Here b is the bond length. The parameters adopted are: $K = 30\epsilon_{\text{pp}}/\sigma^2$, $R_0 = 1.5\sigma$. The equilibrium bond length $\langle b \rangle$ is about 0.97σ .

In this work the most important interaction is that between polymer and NP which is described by a modified Lennard-Jones (LJ) potential of the form⁶

$$V_{\text{pn}}(r) = \begin{cases} 4\epsilon_{\text{pn}} \left[\left(\frac{\sigma}{r-s} \right)^{12} - \left(\frac{\sigma}{r-s} \right)^6 \right] + V_c & \text{for } r < r_c \\ 0 & \text{for } r \geq r_c \end{cases}, \quad (3)$$

with $s = \frac{\sigma_n - \sigma}{2}$ and ϵ_{pn} the interaction strength between polymer and NP. We set $\epsilon_{\text{pn}} =$

ϵ_{pp} and $r_c - s = \sigma$ for repulsive NPs (RNPs), whereas we set $\epsilon_{\text{pn}} = 2.5\epsilon_{\text{pp}}$ and $r_c - s = 2.5\sigma$ for attractive NPs (ANPs). The potential V_{pn} is shifted to 0 at r_c by setting

$V_c = -4\epsilon_{\text{pn}} \left[\left(\frac{\sigma}{r_c - s} \right)^{12} - \left(\frac{\sigma}{r_c - s} \right)^6 \right]$. As NPs are immobile in our system, the interactions

between two NPs are trivial. $\sigma_n = 5\sigma$ is used in simulations.

The random motion of the polymer chains is described by Langevin equation^{7,8}

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\nabla_i \sum (V_{\text{WCA-pp}} + V_{\text{FENE}} + V_{\text{pn}}) - m_i \Gamma_i \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_r \quad (4)$$

Here, the first term of the right-hand side is the conservative forces in the system, the second term is the viscous damping force with Γ_i the frictional coefficient, and the last term \mathbf{F}_r is the random force.

All physical quantities are expressed in the standard LJ units. The length and energy are measured, respectively, in the units of σ and ε_{pp} , i.e., we set $\sigma = 1$ and $\varepsilon_{\text{pp}} = 1$. The mass of polymer monomer is set as $m = 1$, so that the reduced unit for time is $\tau_0 = \sqrt{\frac{m\sigma^2}{\varepsilon}}$. Simulations are carried out at temperature $k_B T = 1$ with k_B the Boltzmann's constant and T the temperature. The MD simulations are performed at constant number of particles, volume and temperature (NVT) with a Langevin thermostat with damping constant $\Gamma = 0.1 \tau_0^{-1}$.

The variation of the diffusion coefficient D and mean-square radius of gyration $\langle R_g^2 \rangle$ with the concentration of polymers c_p are plotted in **Fig. S3** for systems with RNPs and ANPs at $\varepsilon_{\text{pn}} = 2.5$. The concentration of NPs is set as $c_n = 0.125$. We find the results are similar to those of MC simulations shown in Fig. 1. The minima of D and $\langle R_g^2 \rangle$ are both located at $c_p = 0.064$, the same as that found in the MC simulation. We have also calculated the variation of D and $\langle R_g^2 \rangle$ with ANP concentration for the $c_p = 0.064$ case. The MD results presented in **Fig. S4** are generally in agreement with the MC results (Fig. 7 in the revised manuscript). That is, the results obtained from MC simulation can be verified by MD simulation.

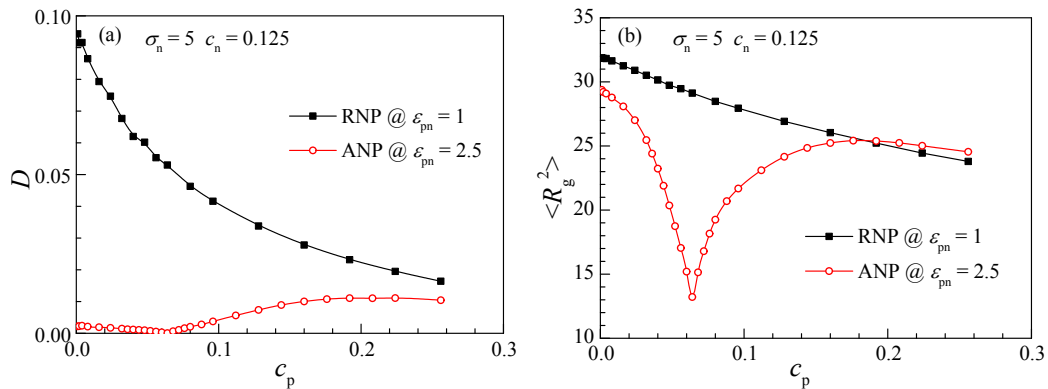


Fig. S3 MD results of the variation of the diffusion coefficient D (a) and mean-square radius of gyration $\langle R_g^2 \rangle$ (b) of polymer chains with the concentration of polymers c_p in systems with RNPs and ANPs at $\epsilon_{pn} = 2.5$.

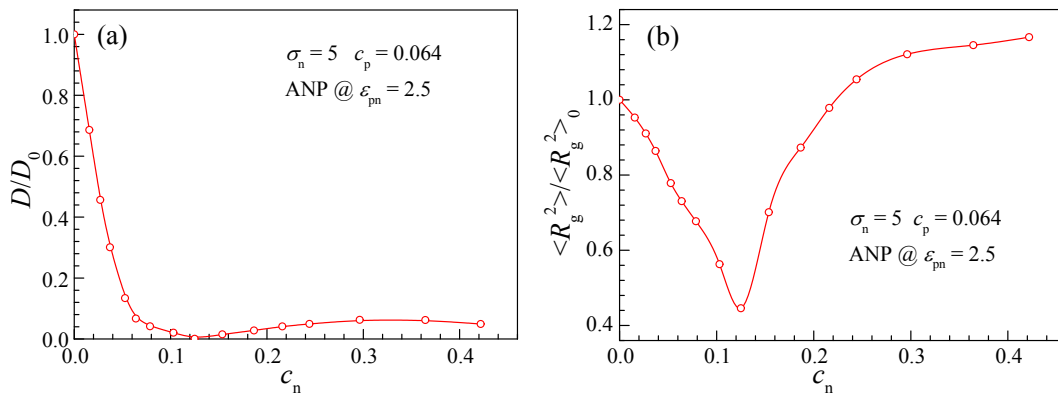


Fig. S4 MD results of D/D_0 (a) and $\langle R_g^2 \rangle / \langle R_g^2 \rangle_0$ (b) of polymer chains with the concentration of NP c_n in systems with immobile ANPs.

References

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