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Dynamic Monte Carlo study on the polymer chain in random media filled with nanoparticles

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Abstract

The effect of nanoparticles on the dynamic and configurational properties of a single polymer chain has been studied by using dynamic Monte Carlo simulation. An attractive potential, ε, is considered between fixed nanoparticles and polymer beads. The diffusion coefficient of the polymer D remains constant for weak interactions, i.e. small $\beta = -\varepsilon/k_B T$, and then gradually drops to zero at a critical value β_D^*. However, the mean square end-to-end distance $\langle R^2 \rangle$ shows a different behavior with an increase in the attractive interaction. $\langle R^2 \rangle$ decreases at small β and reaches a minimum at β_R^*, then goes up slowly and at last saturates at strong interaction. The values β_D^* and β_R^* scale with the concentration of nanoparticles. Interesting findings are: (1) a chain has its minimum size before the chain stops its diffusion, and (2) a chain continues its configuration adjustment even for $\beta > \beta_D^*$.

Keywords: Polymer chain; Nanparticle; Dynamic Monte Carlo simultation

1. Introduction

Significant enhancements in mechanical, rheological, dielectric, optical and other properties of polymer materials can be achieved by adding nano-size particles in polymer materials [1–3], driving an increased interest in understanding the changes in the structural and dynamic properties of polymer systems at the molecular level. The added nano-size particles are often referred as 'nanoparticles' or 'fillers'. Many of computer simulations on polymer systems in random media with randomly distributed nanoparticles have been performed [4–11]. It was found that the size of the filler particles play a very important role in the reinforcement of polymer systems [12,13] and small particles are more effective [12,13]. More reports can be found in a recent review [14].

Fillers slow the diffusion of polymer chains [6,15,16], and interactions between the polymer and particles also play an important role in influencing the diffusion of the polymer. Lee and Chakraborty [17] studied the dynamics of polymers in the random medium using kinetic Monte Carlo methods and found that, above a threshold temperature, polymers bearing monomers that are attracted to the disordered medium translocate faster through the medium than those bearing neutral or repulsive monomers.

However, the influence of particles on the chain dimension, characterized by the mean square end-to-end distance $\langle R^2 \rangle$, is more complicated. For a system filled with small particles, Monte Carlo simulations of poly(dimethylsiloxane) (PDMS) found that chain dimensions increase with increasing filler concentration [13]. In their simulation, no interaction between the filler and the chain is considered. Later, small angle neutron scattering (SANS) experiment supported this finding [18]. However, when the interaction between the polymer and the filler is taken into account, Vacatello [6,15,16] found that $\langle R^2 \rangle$ in the presence of filler is always smaller than that in the unperturbed state without filler. He pointed out that the increased dimensions found in recent SANS experiments [18] cannot be explained on the basis of simple excluded-volume arguments. He contributed such a behavior to effects that are presently not understood, for example, unexpectedly strong preferential interactions between PDMS and the nanoparticles used in the experiments. Feng and Ruckenstein [19] investigated the complexation between a polyampholyte and

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a charged nanoparticles using Monte Carlo simulations. Their simulated results revealed that the charge density and the nanoparticles size have significant effect on the conformation of such complex. Block copolymers provide a self-assembled template for the synthesis of nanoparticles, and SANS experiments showed the strong interparticle interaction between iron oxide nanoparticles may influence the copolymer microphase separation [20].

In this paper, we consider an attractive interaction ε between polymer beads and filler nanoparticles and examine the effect of the reduced interaction $\varepsilon/k_{\mathrm{B}}T$ on the dynamics and dimension of a single polymer chain. Because fillers of small size more strongly reinforce polymer systems, we focus on small fillers in this paper. We model the filler as having the same size as a polymer monomer, and both are located on a simple cubic lattice. The reduced interaction $\varepsilon/k_{\mathrm{B}}T$ can be changed by varying temperature T or the species of the polymers or nanoparticles, so it can be easily controlled in experiments. By using the dynamic Monte Carlo method, the dependences of the diffusion coefficient and the mean-square end-to-end distance on the reduced attractive interaction $\varepsilon/k_{\mathrm{B}}T$ are studied.

This paper is organized as follows: In Section 2, we describe the model and dynamic Monte Carlo simulation method. In Section 3, we focus on the dynamic properties and the configurational changes of the polymer chain induced by the attractive nanoparticles. Brief conclusions are presented in Section 4.

2. Model and simulation method

Dynamic Monte Carlo simulations are carried out on a simple cubic lattice box with periodic boundary conditions. At first, N_{NP} nanoparticles are randomly placed in the simulation box. Each nanoparticle occupies one lattice and is kept immobile. A single polymer chain of length n is comprised of n identical beads consecutively linked with bond lengths ranging from 1 to $\sqrt{3}$ (in the unit of lattice) on the SC lattice. Each bead occupies one site of the lattice. The bond between successive beads along a chain is taken from the 26 allowed bond vectors obtained from symmetry operations on the set {(1,0,0), (1,1,0), (1,1,1)}. In this model, the beads do not correspond to specific atoms in a polymer but rather to small groups of atoms, and the bonds do not represent specific covalent bonds between two atoms but instead the linkages between beads [21,22].

Interactions between polymer beads and between polymer beads and nanoparticles are considered. The only polymer bead–bead interaction is self-avoidance, that is, one lattice point cannot be occupied by more than one bead simultaneously. For a polymer bead–nanoparticle interaction, we introduce a nearest neighbor attractive interaction in addition to self-avoidance. A negative interaction strength $\varepsilon<0$ is applied for any nearest neighbor polymer bead and nanoparticle pair. A polymer bead can have more than one interaction if it has more than one nearest neighbor nanoparticle.

The Brownian movement of the polymer chains contains local and global movements [23]. The local movement involves the change of spatial configuration from choosing a bead randomly and attempting to move it one lattice spacing in one of the six randomly selected directions: $\pm x$, $\pm y$, $\pm z$. The global movement, reptation, leads to the whole chain worming one lattice unit ahead. The reptation is only tried for the two end beads, with each end being selected for a trial reptation move with a probability of 0.5. Either of the above trial moves will be accepted if the following four conditions are satisfied: (1) self-avoidance is obeyed, (2) the new bond vector still belongs to the allowed bond set, (3) two bonds do not intersect, and (4) the Boltzmann factor $\exp(-\Delta E/k_{\mathrm{B}}T)$ is greater than a random number uniformly distributed in the interval (0, 1), where ΔE is the change in energy due to the trial move. The time unit used in the work is a MC step (MCS). One MCS includes n bead trial movements.

The concentration of the nanoparticles C_{NP} is an important parameter. $C_{\mathrm{NP}}=N_{\mathrm{NP}}/L^3$ represents the ratio of the nanoparticles to the total lattice sites, here L is the system size in all three directions. In this paper, $L=40$ and C_{NP} varies from 0 to 0.125. Another important parameter is the reduced attractive interaction $\varepsilon/k_{\mathrm{B}}T$ which varies from 0 to -6. For simplification, we use a positive parameter $\beta=-\varepsilon/k_{\mathrm{B}}T$ in the paper instead of $\varepsilon/k_{\mathrm{B}}T$.

Quantities such as the mean square displacement of the center of mass, the mean-square end-to-end distance $\langle R^2\rangle$, and the energy of the simulation system are calculated by averaging over 10^5 independent realizations of the disordered medium of nanoparticles and initial chain configurations. For each independent realization, the first 10^5 MCS are discarded and the sequential 5×10^5 MCS are used to monitor the diffusion of the polymer chains. The last configuration is used to calculate the energy E and the end-to-end distance R. We have investigated the effects of the concentration C_{NP} of the nanoparticles and the attractive interaction $\varepsilon/k_{\mathrm{B}}T$ on the static and dynamic properties of the polymer chains.

3. Simulation results and discussion

3.1. Self-diffusion of polymer chain

To measure the self-diffusion coefficient of the chain, we calculate the mean square displacement of the center of mass of the chain $D_{\mathrm{cm}}(t)\equiv<|\vec{R}_{\mathrm{cm}}(t)-\vec{R}_{\mathrm{cm}}(0)|^2>$, where $\vec{R}_{\mathrm{cm}}(t)$ is the center position of the chain at time t. The mean square displacement $D_{\mathrm{cm}}(t)$ increases linearly with time t as shown in the insert of Fig. 1. The self-diffusion coefficient of the center-of-mass is defined as $D=\lim_{t\to\infty}(1/6)((D_{cm}(t))/t)$ and is estimated by the long time limit of $D_{\mathrm{cm}}(t)/6t$ at $t=5\times10^5$ MCS. In Fig. 1, we present the variation of the self-diffusion coefficient D with the parameter $\beta=-\varepsilon/k_{\mathrm{B}}T$ at different concentrations of the nanoparticles C_{NP}.

It shows that D remains roughly constant at very weak attractive interactions and then drops down to zero at a critical

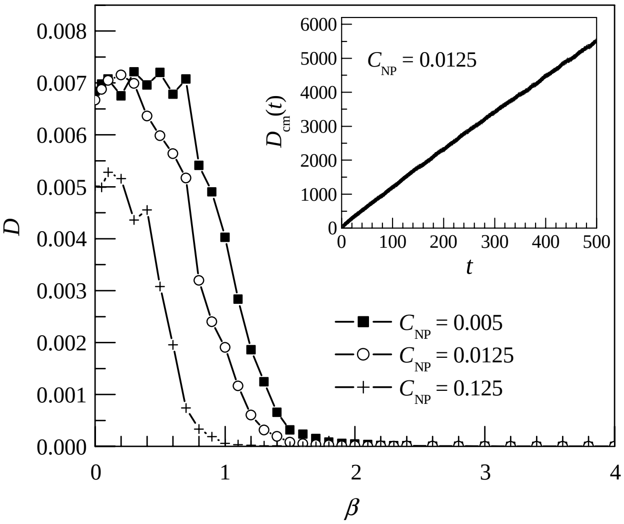

Fig. 1. Dependence of the self-diffusion coefficient D on the attractive interaction β at various concentrations of nanoparticles C_{NP}. The dependence of the mean square displacement $D_{\mathrm{cm}}(t)$ on time t is presented in the insert for $C_{\mathrm{NP}}=0.0125$ at $\beta=1$. The parameter $\beta=-\varepsilon/k_{\mathrm{B}}T$ and the chain length $n=100$.

attractive energy. This observation is in general agreement with the results of Monte Carlo simulations [9,15,16]. When the attractive interaction is weak, the attractive energy is small compared to the thermal energy, so D varies little with the attractive interaction. With an increase in the attractive interaction, the attractive interaction dominates and the polymer beads will approach the frozen nanoparticles as much as possible to reduce the system energy, resulting in the formation of bridge, train and loop subchains as found in Ref. [8], making it harder to detach a bead from the nanoparticles, so chain mobility is slowed until the chain becomes immobile at a critical attractive energy. From the snapshot in Fig. 2, we find one nanoparticle is surrounded by several polymer beads when β is big. In order to distinguish them clearly, here we only present the snapshot of the system for which the concentration of nanoparticles is as small as 0.002. Similarly, the diffusion coefficient decreases with the increase of the concentration of the nanoparticles.

We find there exists a critical attractive energy beyond which D equals zero. The critical attractive energy β_D^* is determined to be the attractive energy at which $D=0.0001$. The critical attractive energy β_D^* decreases with an increase in the concentration of nanoparticles C_{NP}. At small $\beta<\beta_D^*$, chains can diffuse in the system though the diffusion rate is affected by the nanoparticles; while at large $\beta>\beta_D^*$, chains are localized by the nanoparticles. Fig. 3 presents the non-localized and localized phase boundary for the polymer chain in random media with nanoparticles. The dependence of β_D^* on the concentration of nanoparticles C_{NP} can be roughly expressed as $\beta_D^*=0.70C_{\mathrm{NP}}^{-0.18\pm0.01}$. The non-localized and localized phase boundary was investigated previously with a scaling argument, however, it was presented in terms of chain stiffness and disorder strength [24].

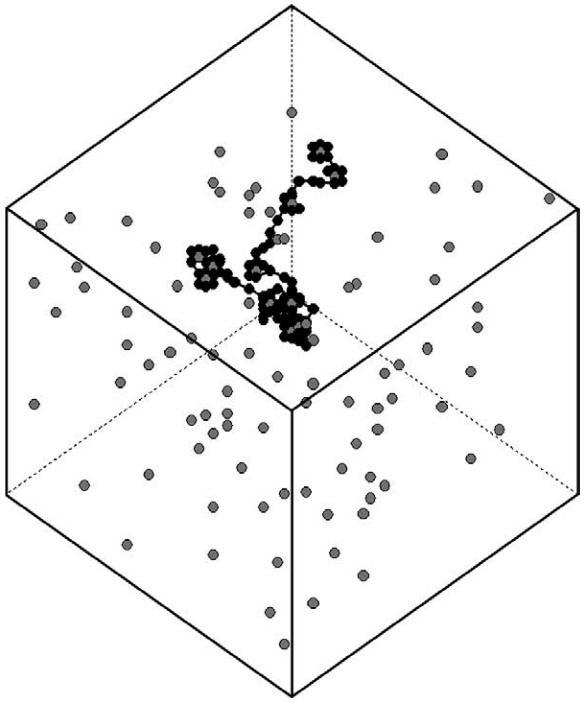

Fig. 2. Snapshot of the system with $C_{\mathrm{NP}}=0.002$ and the attractive energy $\beta=-\varepsilon/k_{\mathrm{B}}T=4.0$. The dark and grey circles represent polymer beads and nanoparticles, respectively. Simulation box size is 40×40×40.

3.2. Configuration of polymer chain

The spatial configuration of the polymer chain is also influenced by the nanoparticles. Fig. 4 presents the dependence of the mean square end-to-end distance $\langle R^2\rangle$ of the polymer chain on the attractive interaction β at different concentrations of nanoparticles C_{NP}. We find that $\langle R^2\rangle$ decreases gradually at small β, then goes up slowly and at last saturates at large β.

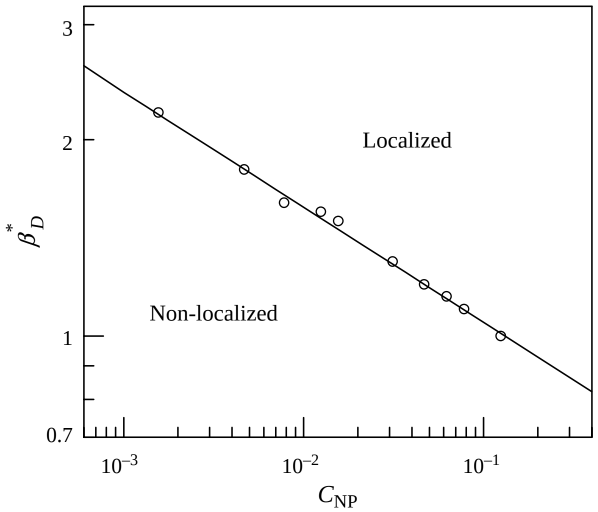

Fig. 3. Phase boundary of localized and non-localized phases. The values of the critical attractive energy β_D^* are plotted in double logarithmic with the concentration of nanoparticles C_{NP}. The straight line is a linear best fitting $\beta_D^*=0.70C_{\mathrm{NP}}^{-0.18\pm0.01}$.

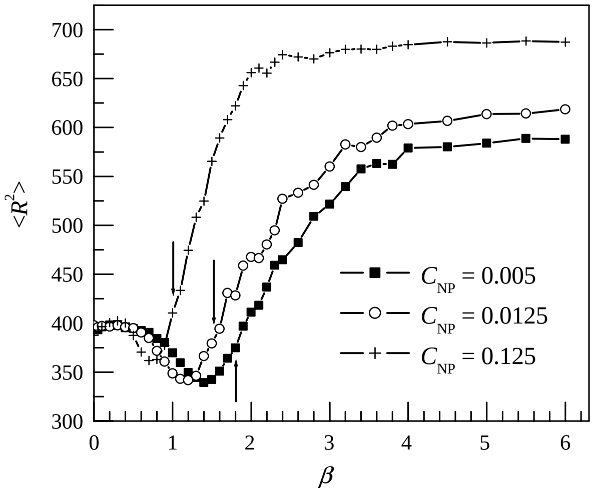

Fig. 4. Plots of $\langle R^2\rangle$ versus the parameter β for systems with the concentration of nanoparticles C_{NP} is 0.005, 0.0125 and 0.125, respectively. Three arrows indicate β_D^* for the three C_{NP}.

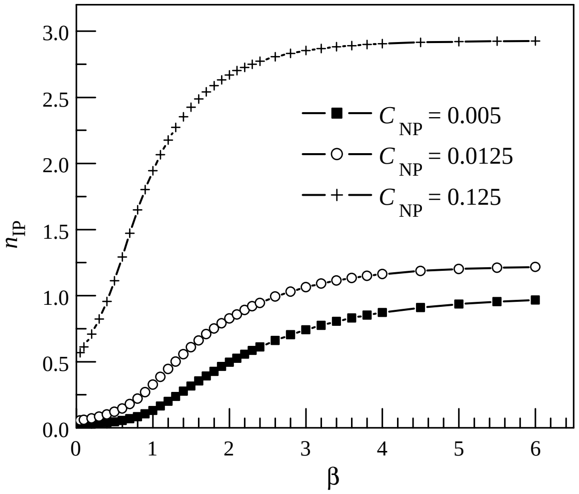

Fig. 5. Dependence of the mean interaction pairs on the interaction parameter β for several concentrations of the nanoparticles C_{NP}.

In this work, we consider a polymer system with a relatively low concentration of nanoparticles. The biggest concentration is 0.125. At $\varepsilon=0$, the configuration of the chain is roughly independent of the concentration, and the chain is a flexible coil with a relatively small value of $\langle R^2\rangle$, see Fig. 4. However, the dynamic properties, such as self-diffusion constant D, depend on the concentration of nanoparticles, as shown in Fig. 1.

At small β, there is a region where one can see $\langle R^2\rangle$ decreases with concentration C_{NP}, which is in agreement with the previous finding that $\langle R^2\rangle$ decreases gradually with disorder strength [19] and the simulated results obtained by Vacatello [6,15,16]. Vacatello's simulation was carried out at quite a high temperature, $T=400$ K, thus the reduced interaction ε/k_BT is about 0.125 [15]. However, in most cases, especially at large β, one can see that $\langle R^2\rangle$ increases with the concentration C_{NP}, and the increases are much larger than the desreases that precede them. In this region, nanoparticles help to enlarge chain's spatial dimension. In the experiment of Ref. [15], we expect there is a strong interaction between polymer and filler [23]. In the intermediate interaction region β, one will find $\langle R^2\rangle$ first decreases with filler concentration and then increases with filler concentration. Therefore, we conclude the polymer–filler interaction plays an important role in controlling chain dimension. Detailed results will be presented elsewhere.

When we consider the interaction in the system, equilibrium properties can be explained by free energy $F=U-TS$. We have calculated the number of the nearest neighbor interaction pairs per polymer bead, n_{IP}. The value n_{IP} is the average number of nanoparticles one polymer bead is in contact with. The system energy U can be obtained from n_{IP} as $U=n\times n_{IP}\times\varepsilon$ since each interaction pair contributes energy ε. The dependence of n_{IP} on the parameter β is presented in Fig. 5. We find that n_{IP} increases with the attractive energy and reaches a saturated value at strong interaction. n_{IP} also increases with an increase of C_{NP}.

At very small β, the energy U is very small and the system is dominated by the configuration entropy S. Snapshots of polymer chain configurations at $\beta=0$ and 0.8 are presented in Fig. 6(a) and (b). In this small β region, the configuration is small and the interaction pair n_{IP} is also small, so configuration entropy S dominates. Chains diffuse quickly and sometimes are in contact with very few nanoparticles. When one polymer bead contacts a nanoparticle, the nanoparticle will try to attract nearby polymer beads, making the chain a little smaller. Therefore, we find $\langle R^2\rangle$ decreases with the increase of interaction parameter β. For the same reason, $\langle R^2\rangle$ also decreases with the increase of concentration C_{NP} at very small β since chains will easily find a nanoparticle during random diffusion.

With an increase in the attractive interaction, the energy U gradually decreases and chains spend more time in contact with nanoparticles. Thus, a competition between the energy and the

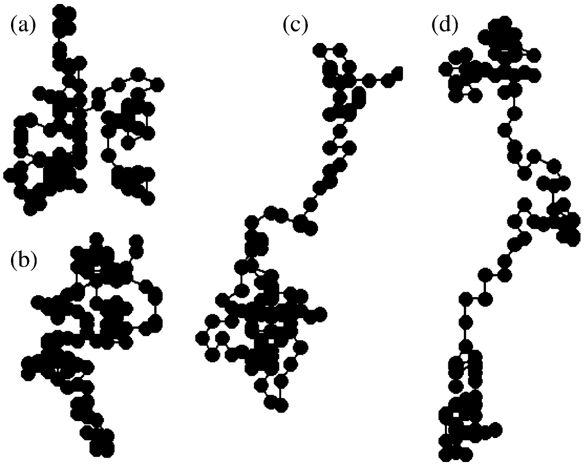

Fig. 6. Snapshots of polymer chain configurations at different attractive energies: (a) $\beta=0$; (b) $\beta=0.8$; (c) $\beta=1.2$; and (d) $\beta=6.0$. The nanoparticles are omitted in the figure for clarity. The concentration of nanoparticles is $C_{NP}=0.125$, chain length $n=100$ and simulation box size is 40×40×40.

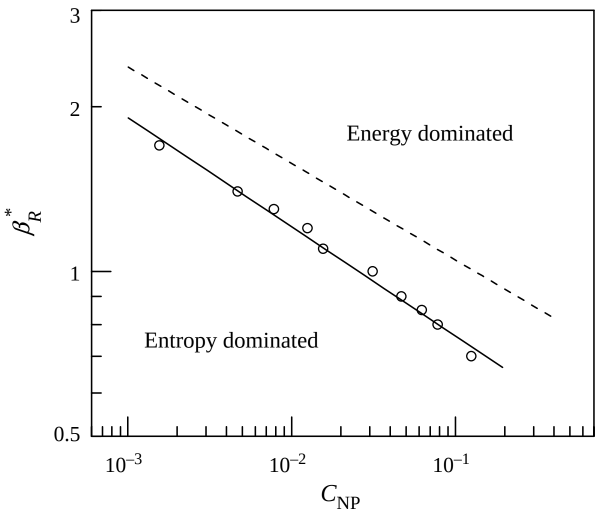

Fig. 7. Log–log plot of the values of the critical attractive energy β^*_R versus the concentration of nanoparticles C_{NP}. The straight solid line is a linear best fitting $\beta^*_R = 0.49C_{NP}^{-0.2\pm0.01}$, which separates the entropy dominating region and energy dominating region. The straight dashed line represent the critical value β^*_D at which chain is localized, $D=0$.

configuration entropy creates with the increase of interaction. At last, the attractive interaction dominates and the polymer beads try to contact as many nanoparticles as possible, while avoiding the bead−bead overlap and the intersection of the bonds, resulting in the extending configuration, so $\langle R^2\rangle$ becomes bigger, as shown in Fig. 6(c) and (d).

We define a critical reduced interaction β^*_R at which $\langle R^2\rangle$ is minimum. The dependence of β^*_R on the concentration of nanoparticles C_{NP} is plotted in Fig. 7. Like the relationship of β^*_D with C_{NP}, we find β^*_R can be roughly expressed as $\beta^*_R = 0.49C_{NP}^{-0.2\pm0.01}$. We find the value β^*_R is smaller than β^*_D, indicating the chain reaches its minimum dimension before it stops diffusion. At small $\beta < \beta^*_R$, entropy dominates the system, so the chain dimension decreases with β. While at large $\beta > \beta^*_R$, energy dominates the system, so the chain dimension increases with β.

In Fig. 4, we find that chains continue their configuration adjustments even for $\beta > \beta^*_D$, that is, the chains still undergo changes in configuration through the local bead movement to further reduce the system energy.

4. Conclusions

Dynamic Monte Carlo simulation has been used to study the effect of nanoparticles on the dynamic and the configurational properties of a polymer chain based on the bond-fluctuation lattice model. An attractive potential, ε, is considered between the fixed nanoparticle and polymer bead. The diffusion coefficient D remains constant for weak interactions, i.e. small $\beta = -\varepsilon/k_BT$, and then gradually drops to zero at a critical value β^*_D. However, the mean square end-to-end distance $\langle R^2\rangle$ shows a different behavior with an increase in the attractive interaction. $\langle R^2\rangle$ decreases at small β and reaches minimum at β^*_R, then goes up slowly and at last saturates at strong interaction. The values β^*_D and β^*_R scale with the concentration of nanoparticles C_{NP}: $\beta^*_D = 0.70C_{NP}^{-0.18\pm0.01}$ and $\beta^*_R = 0.49C_{NP}^{-0.2\pm0.01}$.

Our results show that $\langle R^2\rangle$ decreases with the concentration C_{NP} at small β and increases with the concentration C_{NP} at large β. Our results also show that (1) a chain has its minimum size before the chain stops its diffusion, and (2) a chain continues its configuration adjustment even for $\beta > \beta^*_D$.

Acknowledgements

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