

Chao-Yang Li, Shuang Zhang, Jian-Hua Huang and Meng-Bo Luo*

Size and diffusion of polymer in media filled with periodic fillers

Abstract: The effect of nanosized fillers on the equilibrium and dynamic properties of a single polymer chain has been studied by using off-lattice Monte Carlo (MC) simulation. Fillers of identical size are arranged periodically in the system and the Lennard-Jones (LJ) interaction is considered between the polymer and fillers. Our results show that the statistical size and dynamic diffusion properties of the polymer are not only dependent on the size of the polymer relative to the size of fillers and the distance between fillers, but also dependent on the interaction between the polymer and filler. The statistical size of the polymer can increase or decrease. Normal diffusion is always observed for long polymers and small fillers, whereas a transition from a desorbed state to an adsorbed state is observed for short polymers and large fillers. Finally, the size and diffusion of the polymer on an infinitely large surface are studied for comparison.

Keywords: diffusion; nanofiller; polymer; simulation; size.

*Corresponding author: Meng-Bo Luo, Department of Physics, Zhejiang University, Hangzhou 310027, China, e-mail: luomengbo@zju.edu.cn

Chao-Yang Li: Department of Physics, Hangzhou Normal University, Hangzhou 310036, China

Shuang Zhang: Department of Physics, Zhejiang University, Hangzhou 310027, China

Jian-Hua Huang: Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou 310018, China

1 Introduction

Polymer nanocomposites are materials in which nanoscopic inorganic particles are dispersed in a polymeric matrix. It is well known that the performance properties of the polymeric materials can be improved by adding nanosized filler particles (1–5). Computer simulations showed that the size and mobility of the fillers play a very important role in the reinforcement of polymer systems and that small particles are more effective (6, 7). The mobility is a complex function of the size of the filler and the interaction between the polymer and the filler. The existence of fillers can change the glass transition temperature (8) of

the polymer and can slow the diffusion of polymer chains (9, 10). Experiments found that the thermal and mechanical properties of polymethyl methacrylate/carbon nanofibers were significantly enhanced when compared to polymethyl methacrylate with no carbon nanofibers (11). Moreover, it was found that a normal diffusion of polymer in dilute solution will change to a sub-diffusion in media with random distributed fillers (12). In addition, the translocation of the polymer was dependent on the properties of fillers (12, 13). Fillers like dendrimers may play important roles in the delivery of DNA or drug in biological systems (14).

How nanosized fillers influence the chain dimension, which is usually characterized by the mean square end-to-end distance $\langle R^2 \rangle$, or the mean square radius of gyration $\langle R_g^2 \rangle$, is still not clear. Based on the rotational isomeric state theory, Monte Carlo (MC) simulations of poly(dimethylsiloxane) chains and randomly arranged non-attractive fillers found that $\langle R^2 \rangle$ of poly(dimethylsiloxane) chains increases for long chains and small fillers, but it decreases for short chains and large fillers (7). A small angle neutron scattering experiment supported this finding (15). The results were explained on the basis of the excluded volume effect of the fillers (7, 15). However, when the weak interaction between the polymer and the filler is taken into account, Vacatello (9, 10) found that $\langle R^2 \rangle$ in the presence of filler was always smaller than that in the unperturbed state without filler. Lattice MC simulation on long polymer chains with small random distributed fillers showed that $\langle R^2 \rangle$ was also dependent on the attraction strength of the fillers (16). With the increase in the attraction strength, $\langle R^2 \rangle$ decreases at first, then goes up slowly and at last saturates at strong attraction (16). Therefore, polymer-filler interaction is also important in affecting the dimension of polymer chains and plays an important role in the reinforcement of polymer systems (6).

In the present paper, we study the effect of size and attraction strength of the fillers on the equilibrium and dynamic properties of a single polymer chain. In our off-lattice MC simulations, fillers are arranged periodically in the system. A periodical system is an ideal model system, but is good for analyzing simulation results. It was pointed out that the most important characteristic of

the system is the length of polymer chains relative to the size and the distance between filler particles (7). In our simulation system, the distance between filler particles can be well defined and controlled. We find that both the equilibrium and dynamic properties of a single polymer chain are not only strongly dependent on the size and attraction strength of the fillers, but also dependent on the mean radius of gyration R_{G0} of the polymer in dilute solution. Our simulation results show that the dimension of polymer chains can increase or decrease, which is dependent on R_{G0} relative to the size of filler and the distance between fillers and the interaction strength between polymer and filler.

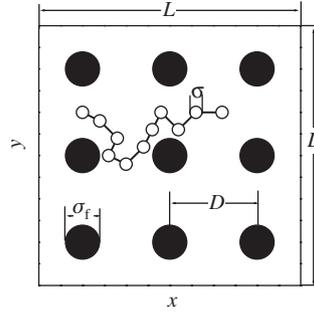


Figure 1 A two-dimensional sketch of our three-dimensional simulation system of size $L \times L \times L$ in the x , y , and z directions. Fillers represented by solid circles are placed in the system with a period D . Polymer is represented by connected open circles. The diameters of the monomer and the filler are σ and σ_f , respectively.

2 Model and calculation method

The polymer is modelled as a linear polymer chain with $N=64$ identical monomers. Monomers of mass m , separated by a distance r , interact via a generalized Lennard-Jones (LJ) potential of the form $V(r)=\varepsilon[(\sigma/r)^{12}-2(\sigma/r)^6]$ for $r < r_c = 2.5\sigma$ and 0 otherwise. Here ε and σ are the characteristic energy and length scales, respectively. Bond monomers are connected via a finitely extensive nonlinear elastic (FENE) anharmonic spring potential:

$$V_{\text{FENE}} = \begin{cases} -\frac{k_F}{2} (r_{\text{max}} - r_{\text{eq}})^2 \ln \left[1 - \left(\frac{r - r_{\text{eq}}}{r_{\text{max}} - r_{\text{eq}}} \right)^2 \right], & 2r_{\text{eq}} - r_{\text{max}} < r < r_{\text{max}} \\ \infty & \text{otherwise} \end{cases} \quad [1]$$

where the equilibrium bond length $r_{\text{eq}}=0.7$, the maximum bond length $r_{\text{max}}=1.3$, and the elastic coefficient $k_F=100$.

The nanosized filler is modelled as a sphere with a length scale denoted by σ_f . Here σ_f can be regarded as the diameter of the filler. The interaction between the polymer and the filler is described by another LJ potential of the form $V(r)=\varepsilon_{\text{fp}} \{[\sigma/(r-s)]^{12}-2[\sigma/(r-s)]^6\}$, where ε_{fp} is the interaction strength between the polymer and the filler and $s=(\sigma_f + \sigma)/2$ (6). The potential is set as 0 if $r-s > r_c = 2.5\sigma$.

Our simulation system is a cube of size $L \times L \times L$ in the x , y , and z directions. Periodical boundary conditions (PBC) are adopted in all the three directions. The fillers of identical size are periodically arranged in a simple cubic lattice structure in the system, i.e., q^3 fillers are set in the system with a period $D=L/q$. Moreover, all fillers are identical and motionless. A two-dimensional sketch of our three-dimensional simulation system is presented in Figure 1.

At the beginning of the simulation, we generate a polymer randomly without overlapping the fillers, i.e., the distance between monomer and filler $r > (\sigma_f + \sigma)/2$. Then, we randomly select a monomer and move it a small distance with dx , dy , and dz in the x , y , and z directions. All dx , dy , and dz are random values within $(-\Delta, \Delta)$. We use a small $\Delta=0.05\sigma$ in the simulation. This trial move will be accepted if the Boltzmann factor $\exp(-\Delta E/k_B T) > p$, where p is a random number within $(0,1)$ and ΔE is the energy shift due to the movement of the monomer. Here, T is the temperature and k_B is the Boltzmann constant. Afterwards, we run a sufficient long period of simulation to equilibrate the polymer system. We monitor the variation of polymer size during the process, and assume the system reaching equilibrium if the fluctuation of the time averaged size over three sequential time windows is $<10\%$. Finally, we calculate the statistical properties and self-diffusion of the polymer over a long simulation time. The statistical time is at least five times longer than the equilibrium time. The time unit used in this work is the MC step (MCS). In MC simulations, time unit MCS is arbitrarily defined, but can be rescaled to real time unit by experiment or molecule dynamics simulation. In this work, we define one MCS during which all monomers attempt to move 100 steps. In addition, $k_B T=1$ and $\sigma=1$ are used as units of energy and length, respectively. Here, the time window to monitor polymer equilibrium is set as 1000 MCS.

In the present simulations, the main variable is the LJ interaction strength ε_{fp} between polymer and fillers. The statistical dimension and dynamic diffusion of a linear polymer are calculated and the results are averaged over 1000 independent runs. The standard errors of our simulation data are found to be small and mostly can be neglected.

3 Results and discussion

At first, we simulated the conformational properties of the polymer without fillers, i.e., the polymer in a dilute solution. A weak monomer-monomer interaction $\varepsilon=0.2$ is considered in this work. We find that the polymer can be characterized by a self-avoiding walk chain with the Flory exponent $\nu\approx 0.6$ for such a weak monomer-monomer interaction. The $\langle R^2 \rangle_0 \approx 104$ and the $\langle R_G^2 \rangle_0 \approx 17$ for the polymer with length $N=64$. Here, the subscript 0 means the polymer in dilute solution without filler. The mean radius of gyration R_{G0} of $N=64$ is about 4. Then, we simulated the conformational properties and diffusion of the polymer with $N=64$ in a system with periodic fillers. We consider three typical regimes: (1) $R_{G0} > D > \sigma_f$, (2) $D > R_{G0} \sim \sigma_f$ and (3) $D > \sigma_f > R_{G0}$ in this work.

For the first regime $R_{G0} > D > \sigma_f$, we use $D=3$ and $\sigma_f=1$. Thus, $N_f=10^3$ quenched fillers are used in the system of size $L=30$, i.e., the fillers volume fraction is about 2%. Figure 2 shows the dependence of $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ of the polymer on the interaction strength ε_{fp} of the fillers. Here, $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ have the same behavior. We find that there are three regions: (1) Region I at small ε_{fp} , where the polymer size decreases with the increase in ε_{fp} , (2) Region II at moderate ε_{fp} where the polymer size increases with the increase in ε_{fp} , and (3) Region III at large ε_{fp} , where the polymer size decreases with the increase in ε_{fp} . We can see $\langle R^2 \rangle$ bigger than $\langle R^2 \rangle_0$ in a large interaction region of ε_{fp} from 0 to 5, which is consistent with experimental observation for the similar case that the polymer chain is much larger than fillers (15). The behaviors of the polymer in Regions I and II are in agreement with the simulation

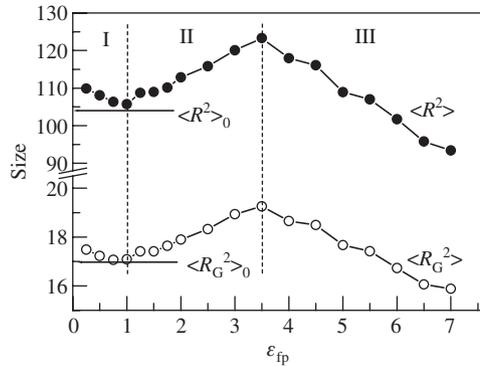


Figure 2 The dependence of mean square end-to-end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_G^2 \rangle$ of polymer on the interaction strength ε_{fp} of filler. Polymer length $N=64$, filler number $N_f=10^3$, filler size $\sigma_f=1$, and system size $L=30$. Two horizontal arrows indicate the values of $\langle R^2 \rangle_0$ and $\langle R_G^2 \rangle_0$, respectively. The error bar of data is smaller than the size of the symbol, which is the same for the following figures.

results of the polymer in a media with random fillers (16), which can be explained from the competition between the excluded volume and attraction of the fillers.

$\langle R^2 \rangle > \langle R^2 \rangle_0$ at small ε_{fp} because of the excluded volume effect of the fillers, but the attraction can compensate the excluded volume that decreases the size $\langle R^2 \rangle$. Thus, we find that the polymer dimension increases, but it decreases with ε_{fp} in Region I. At moderate ε_{fp} , the polymer tries to contact with more fillers, resulting in extending of the polymer configuration. We calculated the contact number of monomers N_{mc} with the monomer-filler distance $<1.5\sigma$ and the number of fillers N_{fc} that the polymer is in contact with. The dependences of N_{mc} and N_{fc} on ε_{fp} are presented in Figure 3. We find that N_{mc} increases monotonically with ε_{fp} , indicating that more monomers contact with fillers at larger ε_{fp} in order to reduce the energy of the polymer chain. However, the behavior of the polymer in Region III is different from the result of the polymer in the media with random distributed fillers, where the polymer size is roughly independent of ε_{fp} at large ε_{fp} (16). At large ε_{fp} , although N_{mc} still increases with ε_{fp} , we observe that N_{fc} decreases with ε_{fp} . This is because a coiled configuration can reduce the interstitial monomers among fillers, thus N_{fc} decreases at large ε_{fp} , but N_{mc} still increases. As a result, the polymer dimension decreases with ε_{fp} at large ε_{fp} . For the polymer in the media with random distributed fillers (16), the polymer might contact with fillers at a large local concentration, thus the polymer size increases with ε_{fp} , as we will discuss for the case of the polymer in the third regime.

For the second regime $D > R_{G0} \sim \sigma_f$, we use $D=15$ and $\sigma_f=5$. Thus $N_f=2^3$ fillers are used in the system of size $L=30$, i.e., the fillers volume fraction in this regime is also about 2%. The results of $\langle R^2 \rangle$ at different polymer-filler interaction strengths ε_{fp} are presented in Figure 4. $\langle R_G^2 \rangle$ has similar

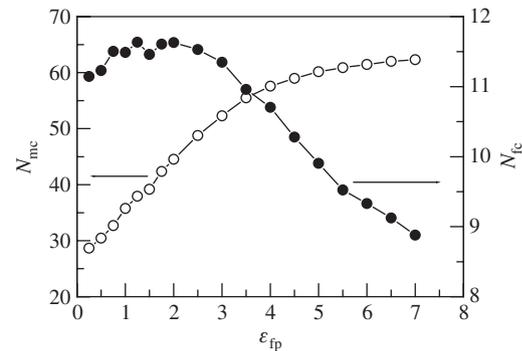


Figure 3 Plot of contact number of monomers N_{mc} and the number of contacted fillers N_{fc} vs. the interaction strength ε_{fp} of fillers. Polymer length $N=64$, filler number $N_f=10^3$, filler size $\sigma_f=1$, and system size $L=30$.

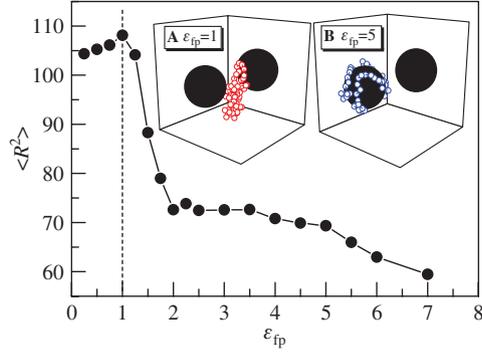


Figure 4 The dependence of the mean square end-to-end distance $\langle R^2 \rangle$ of polymer on the polymer-filler interaction strength ε_{fp} . Polymer length $N=64$, filler number $N_f=2^3$, filler size $\sigma_f=5$, and system size $L=30$. Insets (A) and (B) present the snapshots of the polymer at $\varepsilon_{fp}=1$ and $\varepsilon_{fp}=5$, respectively.

behavior and is not shown here. We find that $\langle R^2 \rangle$ starts to decrease at $\varepsilon_{fp} \sim 1.0$, indicating that there is a transition from a desorbed state (inset A in Figure 4) to an adsorbed state (inset B in Figure 4). At small ε_{fp} , the polymer locates in the large interstitial space among the fillers, so we have $\langle R^2 \rangle \approx \langle R^2 \rangle_0$ when ε_{fp} tends to 0. However, the fillers nearby will attract the polymer that increases $\langle R^2 \rangle$ at small ε_{fp} , whereas the size $\langle R^2 \rangle$ decreases with ε_{fp} if the polymer is adsorbed on the surface of one of the fillers at large ε_{fp} . The results indicate that there is a critical adsorption for polymer in this regime, and the critical adsorption point is at $\varepsilon_{fp}^* = 1.0$. In this regime, $\langle R^2 \rangle$ increases slowly with ε_{fp} at $\varepsilon_{fp} < \varepsilon_{fp}^*$, then it decreases by approximately 30% after ε_{fp}^* , and finally, it decreases slowly at ε_{fp} much larger than ε_{fp}^* . Such a decrease in polymer dimension at $R_{G0} \sim \sigma_f$ is consistent with experiment (15).

The mean square displacement of the center of mass of the polymer:

$$\langle \Delta r^2 \rangle = \langle [\mathbf{r}_{c.m.}(t) - \mathbf{r}_{c.m.}(0)]^2 \rangle \quad [2]$$

is calculated at different simulation times for the first and second regimes. Here, $\mathbf{r}_{c.m.}(t)$ is the position vector of the center of mass at time t . Figure 5A presents the evolution of $\langle \Delta r^2 \rangle$ of the polymer at different polymer-filler interactions for the first regime with filler size $\sigma_f=1$, and Figure 5B presents that for the second regime with filler size $\sigma_f=5$. It is clear that different diffusion properties are found for the two regimes. In the first regime $R_{G0} > D > \sigma_f$, normal diffusion $\langle \Delta r^2 \rangle \propto t$ is always observed at long time scale, even at large ε_{fp} . Such behavior is different from the subnormal diffusion of a polymer in a crowding environment with random fillers (12). At strong polymer-filler interactions, although the diffusion of the polymer is slow, the normal diffusion survives at a long time scale after $\langle \Delta r^2 \rangle = \langle R_G^2 \rangle$.

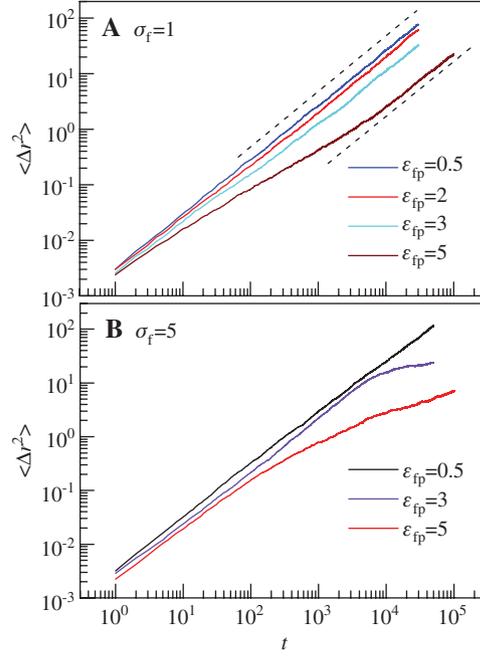


Figure 5 Log-log plot of the mean square displacement $\langle \Delta r^2 \rangle$ vs. the simulation time at different polymer-filler interactions for filler size $\sigma_f=1$ and filler number $N_f=10^3$ (A) and for filler size $\sigma_f=5$ and filler number $N_f=2^3$ (B). Polymer length $N=64$ and system size $L=30$. Two dashed straight lines show normal diffusions with exponent equal to 1.

In the second regime $D > R_{G0} \sim \sigma_f$, normal diffusion $\langle \Delta r^2 \rangle \propto t$ is only observed at small ε_{fp} before the adsorption. At large ε_{fp} , such as at $\varepsilon_{fp}=3$ and 5, we find that the polymer does not diffuse away from the fillers after the polymer is adsorbed. For this case, $\langle \Delta r^2 \rangle$ does not increase at long time scales.

We simulated a third regime with $D > \sigma_f > R_{G0}$, where the polymer can only be adsorbed on one filler. Simulations are carried out in a system of size $L=50$, with a large filler of diameter $\sigma_f=20$ at the center of the system. Then, we have $D=50$ as PBCs are adopted, while the polymer length is set as $N=64$. Here, the filler volume fraction is about 3.4%. For the case $D > \sigma_f > R_{G0}$, the value of filler volume fraction is trivial, since now the polymer can only contact with one filler. The diffusion of the polymer is similar to that of the polymer in the second regime, as shown in Figure 5(B), that is, normal diffusion is only observed at small ε_{fp} before the adsorption. However, the behavior of size is different from that of the polymer in the second regime, as shown in Figure 4. The results of $\langle R^2 \rangle$ and $\langle R_G^2 \rangle$ at different polymer-filler interaction strengths ε_{fp} are presented in Figure 6. At small ε_{fp} near 0, we have $\langle R^2 \rangle \approx \langle R^2 \rangle_0$ as the polymer locates away from the filler, like the case in the second regime. We find that the size of the polymer is approximately independent of ε_{fp} at $\varepsilon_{fp} < \varepsilon_{fp}^* = 1.0$, but it

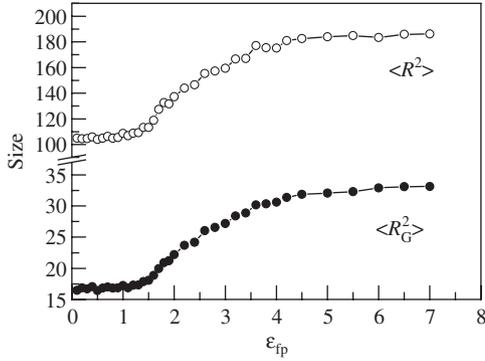


Figure 6 The dependence of mean square end-to-end distance $\langle R^2 \rangle$ and mean square radius of gyration $\langle R_G^2 \rangle$ of polymer on the interaction strength ε_{fp} of filler. Polymer length $N=64$, filler number $N_f=1$, filler size $\sigma_f=20$, and system size $L=50$.

then increases obviously with ε_{fp} at $\varepsilon_{fp} > \varepsilon_{fp}^* = 1.0$ and tends to be saturated at about $\varepsilon_{fp} > 4.0$.

We also calculated the average interaction energy $\langle E_{pf} \rangle$ between the polymer and filler at different ε_{fp} . The results of $\langle E_{pf} \rangle$ and value $-\langle E_{pf} \rangle / \varepsilon_{fp}$ are presented in Figure 7. $\langle E_{pf} \rangle$ begins to decrease while $-\langle E_{pf} \rangle / \varepsilon_{fp}$ begins to increase at $\varepsilon_{fp}^* = 1.0$, clearly indicating that the adsorption of polymer starts at ε_{fp}^* . Also, from about $\varepsilon_{fp} = 4.0$, we find that the value $-\langle E_{pf} \rangle / \varepsilon_{fp}$ starts to be saturated, indicating that the polymer is firmly adsorbed on the filler at large attraction strength.

From our simulation results in the second regime $D > R_{G0} \sim \sigma_f$ and the third regime $D > \sigma_f > R_{G0}$, it is clear that the size of polymer is strongly dependent on the size of filler when the polymer is adsorbed by the filler. Both show an adsorption transition which takes place at about $\varepsilon_{fp}^* = 1.0$.

Finally, we simulated the adsorption of polymer on an infinitely large surface. For this case, the polymer is confined between two flat surfaces with a separation

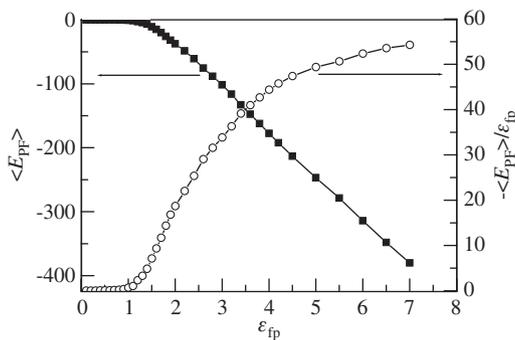


Figure 7 Plot of the average interaction energy $\langle E_{pf} \rangle$ and value $-\langle E_{pf} \rangle / \varepsilon_{fp}$ vs. the polymer-surface interaction strength ε_{fp} . Polymer length $N=64$, filler number $N_f=1$, filler size $\sigma_f=20$, and system size $L=50$.

distance D much larger than R_{G0} , to ensure that the polymer can only be adsorbed on a single surface (17). In the simulation, we use $D=50$ and 80×80 along surfaces for polymer of length $N=64$. The dependence of $\langle R^2 \rangle$ and its parallel component $\langle R^2 \rangle_{xy}$ and perpendicular component $\langle R^2 \rangle_z$ on the polymer-filler interaction strength ε_{fp} is presented in Figure 8. There is a minimum of $\langle R^2 \rangle$ at about $\varepsilon_{fp} = 1.0$, which indicates the place of the critical adsorption point (18). It is clear that $\langle R^2 \rangle_{xy}$ increases, whereas $\langle R^2 \rangle_z$ decreases after $\varepsilon_{fp} = 1.0$, indicating that polymer begins to be adsorbed at $\varepsilon_{fp} = 1.0$. The value of the critical adsorption point $\varepsilon_{fp}^* = 1.0$ is quite close to $\varepsilon_c = 0.98$ for a bond-fluctuation polymer model on the simple cubic lattice (19, 20), indicating that the bond-fluctuation polymer model is close to our non-lattice polymer model. However, the critical adsorption point $\varepsilon_{fp}^* = 1.0$ is smaller than $\varepsilon_c = 1.9$ of the similar non-lattice polymer model with a square well potential (21). It is clear that the long distance attractive interaction in our model can attract the polymer more efficient, therefore the critical adsorption point is lower in our model. We also find that the increase of $\langle R^2 \rangle$ after adsorption on a flat surface is much larger than that for the adsorption on a filler with diameter $\sigma_f=20$. This again indicates that the adsorbed polymer configurations are strongly dependent on the size of fillers.

We checked the diffusion of the adsorbed polymer along the surface, i.e., the dependence of parallel displacement $\langle \Delta r^2 \rangle_{xy}$ on the simulation time. We found that the diffusion along the surface was always normal at $\varepsilon_{fp} > \varepsilon_{fp}^*$, which is consistent with the simulation results for the lattice polymer model (17). This indicates that the polymer can diffuse randomly, even if it is adsorbed. However, the diffusion rate decreases with the increase in the attraction strength.

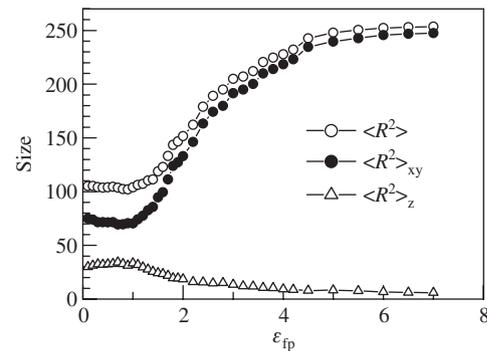


Figure 8 The dependence of the mean square end-to-end distance $\langle R^2 \rangle$ and its parallel component $\langle R^2 \rangle_{xy}$ and perpendicular component $\langle R^2 \rangle_z$ of polymer on the polymer-surface interaction strength ε_{fp} . Polymer length $N=64$.

In fact, there are more size regimes than the three typical regimes we studied in this work. However, the three typical regimes are interesting and attracted a lot of attention. The first regime $R_{G0} > D > \sigma_f$ is analogous to a long chains and small fillers case, while the second regime $D > R_{G0} \sim \sigma_f$ is analogous to a short chains and large fillers case, used in earlier studies (7, 10, 15). The third regime $D > \sigma_f > R_{G0}$ corresponds to short chains with large fillers, which is ubiquitous in biosystems. For example, ligands are attached to cell surfaces through flexible tether chains in many biological systems (22, 23), and DNA interacts with dendrimers for gene transfection (16, 24).

4 Conclusion

The effects of nanosized fillers on the equilibrium and dynamic properties of a single polymer chain were studied for three regimes: (1) $R_{G0} > D > \sigma_f$, (2) $D > R_{G0} \sim \sigma_f$ and (3) $D > \sigma_f > R_{G0}$. Here, R_{G0} is the mean radius of gyration of the polymer in dilute solution, D is the center-to-center distance of two nearest neighbor fillers, and σ_f is the diameter of fillers. In all three regimes, the statistical size and diffusion properties of the polymer are dependent on the polymer-filler interaction ε_{fp} . The statistical size ($\langle R^2 \rangle$ and

$\langle R_G^2 \rangle$) of the polymer chain can increase or decrease with ε_{fp} , but the behavior is strongly dependent on the relative sizes of R_{G0} , D , and σ_f . Besides the polymer dimension, different diffusion behaviors are observed for the polymer. In the first regime, normal diffusion is always observed for the polymer even if the polymer-filler interaction is strong, whereas in the second and third regimes, a transition from a desorbed state to an adsorbed state is observed. The polymer is adsorbed on the surface of the filler and does not diffuse away at strong polymer-filler interactions. Our simulation shows that there is an adsorption transition at the critical adsorption point $\varepsilon_{fp}^* = 1.0$. For the second and third regimes. At $\varepsilon_{fp} > \varepsilon_{fp}^*$, $\langle R^2 \rangle$ of the polymer decreases with ε_{fp} for the moderate fillers in the second regime, whereas it increases with ε_{fp} for the big fillers in the third regime.

Acknowledgements: This work was supported by the National Natural Science Foundation of China under Grant Numbers 21171145 and 21174132. Computer simulations were carried out in the High Performance Computing Center of Hangzhou Normal University, college of Science.

Received September 30, 2013; accepted November 14, 2013; previously published online January 7, 2014

References

- Dewimille L, Bresson B, Bokobza L. Synthesis, structure and morphology of poly(dimethylsiloxane) networks filled with in situ generated silica particles. *Polymer*. 2005;46(12):4135–43.
- Zhu ZY, Thompson T, Wang SQ, von Meerwall ED, Halasa A. Investigating linear and nonlinear viscoelastic behavior using model silica-particle-filled polybutadiene. *Macromolecules*. 2005;38(21):8816–24.
- Dionne PJ, Ozisik R, Picu CR. Structure and dynamics of polyethylene nanocomposites. *Macromolecules*. 2005;38(22):9351–8.
- Mark JE, Abou-Hussein R, Sen TZ, Kloczkowski A. Some simulations on filler reinforcement in elastomers. *Polymer*. 2005;46(21):8894–904.
- Paul DR, Robeson LM. Polymer nanotechnology: nanocomposites. *Polymer*. 2008;49(15):3187–204.
- Gersappe D. Molecular mechanisms of failure in polymer nanocomposites. *Phys Rev Lett*. 2002;89(5):058301.
- Yuan QW, Kloczkowski A, Mark JE, Sharaf MA. Simulations on the reinforcement of poly(dimethylsiloxane) elastomers by randomly distributed filler particles. *J Polym Sci, Part B: Polym Phys*. 1996;34(9):1647–57.
- Starr FW, Schroder TB, Glotzer SC. Effects of a nanoscopic filler on the structure and dynamics of a simulated polymer melt and the relationship to ultrathin films. *Phys Rev E*. 2001;64(2):021802.
- Vacatello M. Monte Carlo simulations of polymer melts filled with solid nanoparticles. *Macromolecules*. 2001;34(6):1946–52.
- Vacatello M. Chain dimensions in filled polymers: an intriguing problem. *Macromolecules*. 2002;35(21):8191–3.
- Guadalupe N-VM, Francisco R-de VL, Ernesto HH, Ivan Z-G. Surface modification of carbon nanofibers (CNFs) by plasma polymerization of methylmethacrylate and its effect on the properties of PMMA/CNF nanocomposites. *e-Polymers*. 2008;162:
- Cao WP, Sun LZ, Wang C, Luo MB. Monte Carlo simulation on polymer translocation in crowded environment. *J Chem Phys*. 2011;135:174901.
- Yu WC, Luo KF. Chaperone-assisted translocation of a polymer through a nanopore. *J Am Chem Soc*. 2011;133(34):13565–70.
- Tian WD, Ma YQ. Theoretical and computational studies of dendrimers as delivery vectors. *Chem Soc Rev*. 2013;42(2):705–27.
- Nakatani AI, Chen W, Schmidt RG, Gordon GV, Han CC. Chain dimensions in polysilicate-filled poly(dimethyl siloxane). *Polymer*. 2001;42(8):3713–22.
- Huang JH, Mao ZF, Qian CJ. Dynamic Monte Carlo study on the polymer chain in random media filled with nanoparticles. *Polymer*. 2006;47:2928–32.

17. Li H, Qian CJ, Wang C, Luo MB. Critical adsorption of a flexible polymer confined between two parallel interacting surfaces. *Phys Rev E*. 2013;87(1):012602.
18. Li H, Qian CJ, Sun LZ, Luo MB. Conformational properties of a polymer tethered to an interacting flat surface. *Polymer J*. 2010;42:383–5.
19. Descas R, Sommer JU, Blumen A. Static and dynamic properties of tethered chains at adsorbing surfaces: a Monte Carlo study. *J Chem Phys*. 2004;120:8831.
20. Lu WQ, Luo MB. Monte Carlo study on the critical adsorption point of bond-fluctuated polymer chains tethered on adsorbing surfaces. *Chin J Polym Sci*. 2009;27:109.
21. Milchev A, Binder K. Static and dynamic properties of adsorbed chains at surfaces: Monte Carlo simulation of a bead-spring model. *Macromolecules*. 1996;29(1):343–54.
22. Wong JY, Kuhl TL, Israelachvili JN, Mullah N, Zalipsky S. Direct measurement of a tethered ligand-receptor interaction potential. *Science*. 1997;275(5301):820–22.
23. Jeppesen C, Wong JY, Kuhl TL, Israelachvili JN, Mullah N, Zalipsky S, Marques CM. Impact of polymer tether length on multiple ligand-receptor bond formation. *Science*. 2001;293(5529):465–8.
24. Maiti PK, Bagchi B. Structure and dynamics of DNA–dendrimer complexation: role of counterions, water, and base pair sequence. *Nano Lett*. 2006;6(11):2478–85.