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Equilibrium and dynamical properties of polymer chains in random medium filled with randomly distributed nano-sized fillers

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The effect of randomly distributed nano-sized fillers on the equilibrium and dynamical properties of linear polymers is studied by using off-lattice Monte Carlo simulation. Lennard-Jones interactions between polymer and fillers are considered. Results show that the statistical dimension and dynamical diffusion of polymer are dependent on the polymer-filler interaction strength ϵ_{pf} . The mean square radius of gyration $\langle R_G^2 \rangle$ shows a minimum at a critical polymer-filler interaction ϵ_{pf}^* . The value of ϵ_{pf}^* decreases with the increase in the polymer length or the concentration of fillers. The exponent ν in $\langle R_G^2 \rangle \sim N^{2\nu}$ is a typical value of self-avoiding walking chain at small ϵ_{pf} but it increases sharply to a bigger value at $\epsilon_{\text{pf}} > \epsilon_{\text{pf}}^*$. The mean square displacement decreases with the increase in ϵ_{pf} . Moreover, the normal diffusion of polymer at weak interactions changes to the subnormal diffusion at moderate and strong attractions. We find that polymers diffuse in dilute filler regions at weak attraction and diffuse in dense filler regions at strong attraction.

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1. INTRODUCTION

It is well known that nano-sized fillers in polymer nanocomposites (PNC) can enhance prominently the physical properties of polymer matrices.¹⁻¹⁶ Nano-sized fillers can improve the mechanical, thermal, electrical, optical properties,¹⁷⁻²⁶ and so on. Nano-sized fillers change the physical properties of PNC through the coupling between polymer and fillers. It was observed that the addition of nano-sized ZnO in natural rubber increases the tensile strength and tensile modulus.²⁷ Moreover, the existence of fillers can change the dynamics of polymer and therefore shift the glass transition temperature.^{28,29} For instance, nano-sized fillers can slow down the diffusion of polymer chains.^{27,30,31} The viscosity of polymers can be affected by the loading of fillers. For example, Nusser *et al.* found a decrease of viscosity of Polydimethylsiloxane (PDMS)/polyhedral oligomeric silsesquioxane (POSS) as POSS content was increased.³² However, Anderson *et al.* found an increase in the viscosity of poly(ethylene oxide) (PEO)/silica with the increase in the silica content.³³ In addition, fillers like dendrimers may play important roles in the delivery of DNA or drug in biological systems.^{34,35} Thus the equilibrium and dynamical properties of polymer chains in the medium filled with fillers have attracted great attention in experiments, theories, and computer simulations.

The knowledge about how do nano-sized fillers impact the equilibrium properties of polymer chains is still in progress. The effect of fillers on the polymer chain is dependent on the fillers' size, shape, mobility, concentration, distribution, and polymer-filler interaction. However, inconsistent results were still observed in experiments as well as in simulations. Computer simulations showed an increase in the mean square radius of gyration $\langle R_G^2 \rangle$ of polymer in a medium with randomly distributed pure-repulsive fillers when the chain is long and, conversely, a decrease when the chain is short.³⁶ Experimental results observed the similar behavior for polymer in polysilicate/poly (dimethylsiloxane) nanocomposites, that is an increase in R_G when R_G is larger than the filler whereas a decrease when R_G is about the same size as the filler.^{37,38} The behaviors of polymer were explained from the exclude volume (EV) effect of the fillers.³⁶⁻³⁸ Therefore it is straight forward to expect the effect of

filler's concentration. However, Sen *et al.* showed that the polymer conformations of short or long polystyrenes (PS) chains were roughly independent of the concentration of nano-sized spherical silica fillers.³⁹ The possible reason is that the silica fillers aggregate at large filler concentration and leave a large void space for polymer in the experiment. Recently, it was observed that polymer conformation R_G of polymers in the presence of carbon nanotubes (CNTs) increases linearly with the concentration for small size CNT but decreases slightly for large size CNT.⁴⁰ However, simulation results showed that the polymer's size was very weakly dependent on the filler concentration in random or periodic medium filled with purely repulsive or weakly attractive fillers,^{41,42} since polymers stay in the intermediate region between fillers to avoid the EV effect of fillers. In contrast to the EV effect, the influence of polymer-filler interaction on the polymer conformation was much more significant. Simulation showed an expansion of chain dimension in filler/polymer systems with small fillers and attractive interactions between polymers and fillers.⁴³ Chain dimension is often represented by mean square end-to-end distance $\langle R^2 \rangle$ or mean-square radius of gyration $\langle R_G^2 \rangle$. Our recent Monte Carlo (MC) simulations showed that $\langle R_G^2 \rangle$ of polymers in medium with periodic fillers was significantly affected by the polymer-filler interaction strength ε_{pf} and the filler period d .^{42,44} Here d is the center-to-center distance of two nearest neighbor fillers. Value $\langle R_G^2 \rangle$ decreases with ε_{pf} at weak interactions and increases with ε_{pf} at moderate interactions. However, at strong interactions, $\langle R_G^2 \rangle$ decreases again for $2R_{G0} > d$ and tends to saturation for $2R_{G0} < d$. Here R_{G0} is the radius of gyration of polymer in dilute solution. The simulation results can be explained from the competition between EV effect and attraction of fillers. The polymer chain's statistical dimension was found to be strongly dependent on the attractive strength and the concentration of nano-sized fillers.

On the other hand, the diffusion of polymers can be affected by the loading of nano-sized fillers. Recently, many experiments demonstrated that the diffusion decreases with the loading of spherical particles.^{8,17,45-47} For instance, Gam *et al.* investigated the tracer diffusion of deuterated polystyrene (dPS) into PS mixed with

29 nm phenyl-capped silica nanoparticles.⁸ Results showed that the diffusion coefficient of dPS decreased rapidly in the region $2R_{G0} > d$. The effect of the attraction between polymer and fillers was studied in the deuterated poly(methyl methacrylate) (dPMMA) in PMMA/hydroxyl-capped silica system, but researches showed that the attractive interactions did not significantly alter the diffusion of macromolecules in PNCs.⁴⁶ While MC simulations found that a normal diffusion of polymer in dilute solution can be changed to a subnormal diffusion in medium with random distributed strong attractive fillers.⁴⁸ The results indicated that the concentration and the attraction strength of fillers are two important factors to influence the diffusion of polymer. It was found that the effect of fillers increases with the attraction strength of fillers.^{41,48} Our previous work also found the diffusion of polymer in the periodic medium was dependent on the relative size between polymers and fillers and the attraction of fillers.⁴⁴ In the regime $2R_{G0} < d$, the polymer has a transition from normal diffusion at weak polymer-filler interactions to being trapped by a few fillers at strong polymer-filler interactions. But in the regime $2R_{G0} > d$, though the diffusion constant decreases with the increase in the attraction strength, the polymer chain can always remain normal diffusion even if the polymer-filler interaction is strong.

In this work, the effects of randomly distributed nano-sized fillers on the statistical dimension and dynamical diffusion of a linear polymer are investigated by off-lattice MC simulations. The medium with randomly distributed fillers is closer to the environment of PNCs.⁴⁶ Fillers are immobile in this work to mimic the situation of short polymers in PNCs where fillers can be regarded as motionless in system.⁴⁶ Therefore the situation is different from that of fillers in solution where fillers are mobile.^{49,50} Since small fillers show significant effect on the polymer, the fillers in this work are chosen to be as the same size as polymer monomers. We therefore define a filler concentration C_f as the ratio of fillers number to the volume of simulation system. To compare with the polymer in the periodic medium with regime $2R_{G0} < d = 10$ and $2R_{G0} > d = 3$, we have chosen the same concentrations of fillers $C_f = 1/10^3$ and $C_f = 1/3^3$. And in order to better understand the behavior of polymer in the random

medium, an intermediate concentration of fillers $C_f = 1/5^3$ is also considered. We take the attractive interaction between polymer and fillers into account. In addition, the properties of polymer in the periodic medium and in the random medium are compared and discussed. We find that the statistical dimension and diffusion of polymer are not only dependent on the polymer-filler interaction strength but also dependent on the distribution of fillers. And the subnormal diffusion process of polymer in the random medium is also a process for polymer moving from sparse space to dense space. This can partially explain the different behaviors of polymers in the random medium and in the periodic medium.

2. MODEL AND CALCULATION METHOD

Off-lattice MC simulations are carried out in a system of size $L \times L \times L$ in the x , y , z directions. Periodic boundary conditions (PBC) are applied in all the three directions. And N_f fillers of identical size are randomly placed but without overlapping in the system.

The simulation is performed for a linear polymer with N identical monomers in our model. Monomers of mass m are modeled as spheres and interact via a Lennard-Jones (LJ) potential of the form

$$V(r) = \begin{cases} \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^6 \right] + V_c & \text{for } r < r_c, \\ 0 & \text{for } r \geq r_c \end{cases}, \quad (1)$$

where ε , σ and r are the depth of the LJ potential, the size of monomer, and the separation distance between monomers, respectively. Here, the potential $V(r)$ is truncated at the cut-off distance r_c and is shifted to 0 at r_c by setting

$V_c = -\varepsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - 2 \left(\frac{\sigma}{r_c} \right)^6 \right]$. We consider the long-range attraction between monomers

by setting $r_c = 2.5\sigma$. For the bonded monomers, finitely extensible non-linear elastic (FENE) interaction

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

is adopted with equilibrium bond length $r_{\text{eq}} = 0.8\sigma$, maximum bond length $r_{\text{max}} = 1.3\sigma$, and elastic coefficient $k_F = 100k_B T/\sigma^2$. In this paper we use $k_B T \equiv 1$ and $\sigma \equiv 1$ as units of energy and length, respectively. Here k_B is the Boltzmann constant and T is the temperature. A weak intrachain interaction $\varepsilon = 0.2$ between two non-bonded monomers is used in our simulations. We found that the polymer behaves as a self-avoiding walk (SAW) polymer chain in dilute solution at $\varepsilon = 0.2$, and the mean square radius of gyration $\langle R_G^2 \rangle_0 \approx 16.8$ for polymer with length $N = 64$ in dilute solution.⁴⁴ Therefore, the polymer-filler interaction is the most important factor in the system.

All the fillers are modeled as motionless spheres with a length scale denoted by σ_f , which is regarded as the diameter of the fillers. The interaction between the polymer and the fillers is described by expanded LJ potential of the form

$$V_{\text{pf}}(r) = \begin{cases} \varepsilon_{\text{pf}} \left[\left(\frac{\sigma}{r-s} \right)^{12} - 2 \left(\frac{\sigma}{r-s} \right)^6 \right] + V'_c & \text{for } r < r_c, \\ 0 & \text{for } r \geq r_c \end{cases}, \quad (3)$$

where ε_{pf} is the LJ interaction strength between the polymer and the filler, and parameter $s = (\sigma_f - \sigma)/2$.¹² Again, the potential $V_{\text{pf}}(r)$ is also truncated and shifted to 0 at the cut-off distance r_c by setting $V'_c = -\varepsilon \left[\left(\frac{\sigma}{r_c - s} \right)^{12} - 2 \left(\frac{\sigma}{r_c - s} \right)^6 \right]$. We also take the polymer-filler attraction into account by setting $r_c - s = 2.5\sigma$. The concentration of the fillers in the random medium is defined as $C_f = N_f/L^3$. In this paper, the system size $L = 60\sigma$ and the number of randomly distributed fillers N_f is 6^3 , 12^3 and 20^3 for $C_f = 1/10^3$, $1/5^3$ and $1/3^3$, respectively.

To obtain the statistical properties of polymer at different ε_{pf} , we adopt an annealing MC process by slowly increasing ε_{pf} from 0.1 to 6. Using the annealing method, the last equilibrium conformation at the previous ε_{pf} is used as the starting conformation for the next ε_{pf} . At first, the polymer is grown without overlapping the

fillers, *i.e.*, the distance between monomer and filler must be set as $r > (\sigma_f + \sigma)/2$. Next we select one monomer randomly and move it a very small step with dx , dy , and dz in the x , y , and z directions. All dx , dy , and dz are random values within $(-\Delta, \Delta)$. In this work, a small value $\Delta = 0.05\sigma$ is used. In addition, Metropolis algorithm is used in our simulation. That is, the move of monomer will be accepted with a probability $p = \min[1, \exp(-\Delta E/k_B T)]$, where ΔE is the energy shift due to the move. We find that the acceptance rate is about 0.6 for $\Delta = 0.05\sigma$, and the acceptance rate is dependent on the attraction strength of fillers. The time unit in our simulation is the Monte Carlo step (MCS). In this work, we define one MCS as the time duration during which every monomer tries to move 100 times.

It was found that the system can be equilibrated with short time using annealing method. Compared to normal MC simulation at separated temperature, the annealing method can significantly reduce the equilibrium time and therefore save simulation time.⁵¹⁻⁵³ Therefore, we run a time scale about $10N^2$ MCS to equilibrate the polymer at each ε_{pf} . At last, we calculate the equilibrium property represented by mean square radius of gyration $\langle R_G^2 \rangle$ and self-diffusion property represented by mean square displacement (MSD) of the center of mass of the polymer in a long simulation time scale.

In this paper, the fillers are set as having the same size as polymer monomer, *i.e.*, $\sigma_f = \sigma = 1$. The main variables in the simulations are the LJ interaction ε_{pf} between polymer and fillers and the concentration of fillers C_f in the system. The quantities such as $\langle R_G^2 \rangle$ and MSD are calculated by averaging over 1000 independent realizations of immobile fillers. In addition, the mean square radius of gyration $\langle R_G^2 \rangle$ are also averaged over 100 polymer configurations obtained in each realization of immobile fillers. During the simulation, we record 100 polymer configurations at a fixed time interval about N^2 MCS after equilibrium. For MSD, we run 10^6 MCS simulation from the equilibrium configuration of polymer. The standard errors of our simulation results are found to be quite small and mostly be negligible.

3. RESULTS AND DISCUSSIONS

In this work, we focus our study on the statistical dimension and dynamical diffusion of polymers in the random medium with randomly distributed immobile fillers. Five typical polymer lengths $N = 16, 32, 64, 96$ and 128 are considered for the scaling behavior between $\langle R_G^2 \rangle$ and N . Three filler concentrations, (1) $C_f = 1/3^3$, (2) $C_f = 1/5^3$, and (3) $C_f = 1/10^3$, are considered for the polymer with length $N = 64$. Here cases $C_f = 1/5^3$ and $C_f = 1/10^3$ correspond to that polymers are in the regime $2R_{G0} > d$ and in the regime $2R_{G0} < d$ in the periodic medium, respectively. While $C_f = 1/5^3$ lies somewhere between the two filler concentrations. All simulations are carried out in a large system with size $L = 60\sigma$, which is much larger than $R_{G0} \approx 6.0$ for the longest polymer $N = 128$ used in the simulations. Since $L \gg 2R_{G0}$ for all polymers, the size effect of our simulations is negligible.

3.1. Conformational size of polymer

At first, we have simulated the equilibrium properties of polymer chains. We have checked the effect of polymer-filler interaction and polymer length on the statistical size of polymers. The mean square radius of gyration, $\langle R_G^2 \rangle$, is calculated for different polymer lengths. Fig. 1 presents the dependence of $\langle R_G^2 \rangle$ on the interaction strength ε_{pf} for polymers in the random medium with $C_f = 1/5^3$. These results are obtained through an annealing process by slowly increasing ε_{pf} from 0.1 to 6. We find that all the behaviors of $\langle R_G^2 \rangle$ of polymers are similar. At small $\varepsilon_{pf} < 0.5$, $\langle R_G^2 \rangle$ remains a constant for small N , indicating that the confinement of nano-sized fillers on polymers is negligible. Whereas $\langle R_G^2 \rangle$ for $N = 128$ shows slightly increase at small $\varepsilon_{pf} < 0.5$. The reason is that a long polymer suffers strong EV effect of the fillers. Nevertheless, $\langle R_G^2 \rangle$ decreases gradually at moderate ε_{pf} and reaches a minimum at a critical value ε_{pf}^* . But at $\varepsilon_{pf} > \varepsilon_{pf}^*$, $\langle R_G^2 \rangle$ goes up slowly and at last tends to saturate at large ε_{pf} . The behaviors of $\langle R_G^2 \rangle$ in the random medium indicate that the nano-sized fillers play important roles in determining the equilibrium properties of polymer.

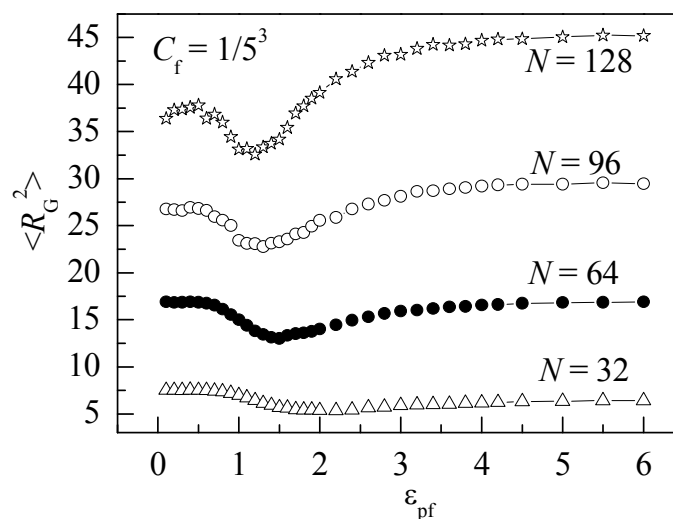


Fig. 1 Dependence of the mean square radius of gyration $\langle R_G^2 \rangle$ on the polymer-filler interaction strength ϵ_{pf} for polymers in the random medium with $C_f = 1/5^3$. Four different polymer lengths ($N = 32, 64, 96,$ and 128) are considered. Here filler size $\sigma_f = 1\sigma$ and system size $L = 60\sigma$.

It was found that the conformational size $\langle R_G^2 \rangle$ is minimum at the critical adsorption point for the case polymer adsorbed to a flat surface.⁵⁴ For the adsorption of polymer on flat surface, the perpendicular component $\langle R_G^2 \rangle_z$ decreases while the parallel component $\langle R_G^2 \rangle_{xy}$ increases with the increase in the attraction of surface. It was found that the decrease of $\langle R_G^2 \rangle_z$ takes place before the increase of $\langle R_G^2 \rangle_{xy}$, resulting in a minimum in $\langle R_G^2 \rangle$ near the critical adsorption point.⁵⁴ Here we suppose that the critical value ϵ_{pf}^* is somewhat related to the critical adsorption of polymer on filler surfaces. Polymers are in the desorption state at weak attraction $\epsilon_{pf} < \epsilon_{pf}^*$ and in the adsorbed state at strong attraction $\epsilon_{pf} > \epsilon_{pf}^*$. The desorption and adsorption state of polymer can be described by two numbers: N_{mc} -- the number of monomers that contact with fillers and N_{fc} -- the number of fillers that is contacted by polymer. Here we define a polymer-filler contact if the monomer-filler distance is less than $0.5\sigma_f + \sigma = 1.5\sigma$ as the interaction is strong in this region. The variation of N_{mc} and N_{fc} with ϵ_{pf} will be presented at the end of this subsection. However, the mechanism for the

minimum in $\langle R_G^2 \rangle$ is different from that on flat surface. Fig. 2 presents three snapshots of the equilibrium conformations of polymer at $\varepsilon_{\text{pf}} = 0.5$ ($\ll \varepsilon_{\text{pf}}^*$), $\varepsilon_{\text{pf}} = 1.2$ ($\sim \varepsilon_{\text{pf}}^*$), and $\varepsilon_{\text{pf}} = 5$ ($\gg \varepsilon_{\text{pf}}^*$), respectively. At $\varepsilon_{\text{pf}} = 0.5$, polymers are in random coil state. The numbers N_{mc} and N_{fc} are zero or very small, that is, polymers do not contact with fillers or temporarily contact with few fillers and look like in the free space without fillers. At $\varepsilon_{\text{pf}} = 1.2$, numbers N_{mc} and N_{fc} are relatively large and part of polymers are temporarily adsorbed on fillers, that effectively shorten the length of polymers. Thus $\langle R_G^2 \rangle$ decreases near $\varepsilon_{\text{pf}}^*$. Whereas at $\varepsilon_{\text{pf}} = 5$, polymers are strongly adsorbed on fillers. In order to decrease the energy, polymers are tried to connect with as many fillers as possible, thus the part between two fillers is stretched obviously.⁴⁴ Therefore $\langle R_G^2 \rangle$ becomes big at large ε_{pf} .

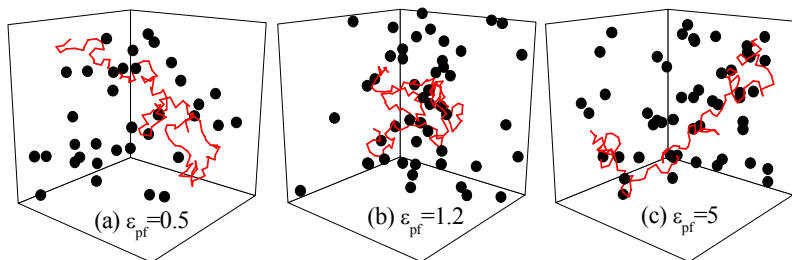


Fig. 2 (color online) Snapshots of the equilibrium conformations of polymer at $\varepsilon_{\text{pf}} = 0.5$ (a), 1.2 (b), and 5 (c), respectively. Red lines represent polymers while black solid circles represent fillers. The three plots have the same dimension.

We find that the critical value $\varepsilon_{\text{pf}}^*$ decreases with the increase in polymer length N as shown in Fig. 1. For example, $\varepsilon_{\text{pf}}^*$ is about 1.5 for $N = 64$ and about 1.2 for $N = 128$, respectively. The result shows that it is easy for long polymer to contact with fillers, therefore the place of minimum $\langle R_G^2 \rangle$ shifts to weaker attraction for longer polymer. Fig. 3 presents the dependence of $\varepsilon_{\text{pf}}^*$ on inverse polymer length N^{-1} . We find that the value $\varepsilon_{\text{pf}}^*$ can be approximately expressed as $\varepsilon_{\text{pf}}^*(N) = \varepsilon_{\infty}^* + bN^{-1}$ with $\varepsilon_{\infty}^* = 0.89 \pm 0.02$ for the polymer in random medium with $C_f = 1/5^3$. Here ε_{∞}^* is the critical value for infinitely long polymer. The dependence of ε_{∞}^* on the concentration C_f will be

investigated in future.

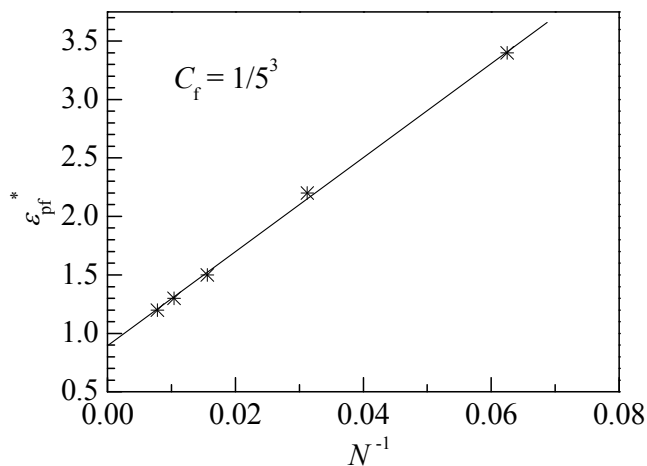


Fig. 3 Plot of the critical attraction strength ε_{pf}^* vs the reciprocal of polymer length N^{-1} with the filler concentration $C_f = 1/5^3$. The straight line is the linear best fitting.

In dilute solution, we find the scaling relation $\langle R_G^2 \rangle_0 \propto N^{2\nu}$ with Flory exponent $\nu = 0.59 \pm 0.02$ for the present model polymers. Since the exponent $\nu = 0.59 \pm 0.02$ is a typical scaling value for SAW polymers, our model polymers with weak intrachain interaction $\varepsilon = 0.2$ behaves as a SAW polymer chain.^{42,44} We have also checked the scaling relations for polymers in the random medium. The inset of Fig. 4 presents log-log plot of $\langle R_G^2 \rangle$ with N for polymers in the random medium with $C_f = 1/5^3$. The results show that $\langle R_G^2 \rangle$ still increases with N in the power-law relation $\langle R_G^2 \rangle \propto N^{2\nu}$ for N from 16 to 128. Here the exponent ν is estimated by a least-square fitting of the linear, long-length region in the log-log plot of $\langle R_G^2 \rangle$ vs. N . The dependence of exponent ν on ε_{pf} is presented in Fig. 4. We find that the exponent ν is dependent on the polymer-filler interaction strength ε_{pf} . At small $\varepsilon_{pf} < 1.0$, ν keeps a constant about 0.59, indicating that the confinement of nano-sized fillers on polymers is negligible at small ε_{pf} . However, at $\varepsilon_{pf} > 1.0$ ν increases steeply with ε_{pf} and tends to a saturation value 0.73 ± 0.01 . We find the value $\varepsilon_{pf} = 1.0$ lies between ε_{pf}^* ($N = 128$) and ε_∞^* . The deviation of $\varepsilon_{pf} = 1.0$ from ε_∞^* is possibly due to the estimate of the exponent ν is

dependent on finite polymer lengths up to $N = 128$. Therefore, our results show that there are two scaling exponents for polymer in random medium, i.e., a normal one for weak attraction medium and a large one for strong attraction medium. In strong attraction medium, the statistical size of longer polymers increases more obviously as shown in Fig. 1, thus the scaling exponent is larger. Our results indicate that the attraction of nano-sized fillers play an important role on the equilibrium properties of polymer.

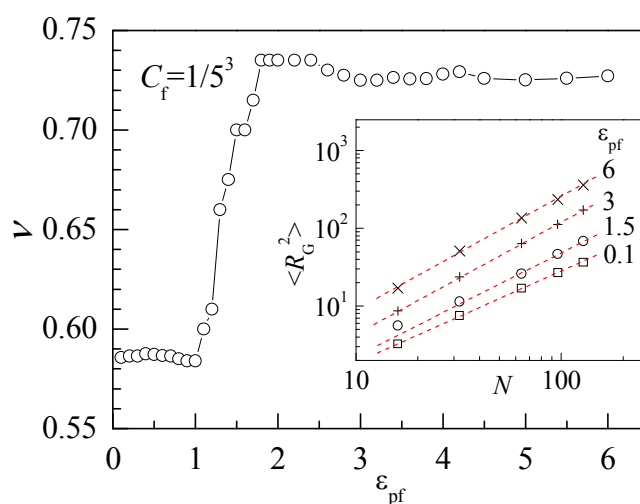


Fig. 4 Flory exponent ν in the power-law relation $\langle R_G^2 \rangle \propto N^{2\nu}$ versus polymer-filler interaction ε_{pf} for polymer in the random medium with filler concentrations $C_f = 1/5^3$. The inset shows log-log plots of $\langle R_G^2 \rangle$ versus polymer length N for polymer at different polymer-filler interactions ε_{pf} . For clarity in the inset, values of $\langle R_G^2 \rangle$ at $\varepsilon_{pf} = 1.5, 3$ and 6 are multiplied by $2, 4$ and 8 , respectively. The red dashed straight lines are linear fits of the data from polymer length $N = 32$ to 128 .

We then study the effect of the concentration of fillers on the statistical conformational size of polymer. We here consider a typical chain length $N = 64$ since polymers with different lengths show the same behaviors. Fig. 5a presents the dependence of $\langle R_G^2 \rangle$ on ε_{pf} in the random medium, while the results of polymer in the periodic medium are presented in Fig. 5b for comparison. All results are obtained

through an annealing process by slowly increasing ε_{pf} from 0.1 to 6. For polymer in the random medium, the behavior of $\langle R_G^2 \rangle$ with ε_{pf} can be divided into three regions. In region I with small ε_{pf} (less than about 0.5), $\langle R_G^2 \rangle$ is roughly equal to $\langle R_G^2 \rangle_0$ for polymers in the medium with small C_f , indicating that polymers are in large intermediate spaces where the confinement is negligible. The result is similar to that of polymer in the periodic medium with $C_f = 1/10^3$. Whereas for polymer in the random medium with large concentration $C_f = 1/3^3$, we find that $\langle R_G^2 \rangle$ is slightly larger than $\langle R_G^2 \rangle_0$, indicating that polymers in dense system experience strong EV effect of nano-sized fillers. Such a behavior is similar to long polymers in random medium as shown in Fig. 1 for $N = 128$. In region II with moderate ε_{pf} , $\langle R_G^2 \rangle$ decreases obviously with ε_{pf} . However, the place of the minimal $\langle R_G^2 \rangle$, $\varepsilon_{\text{pf}}^*$, and the minimum of size, $\langle R_G^2 \rangle_{\text{min}}$, are dependent on C_f . Value $\varepsilon_{\text{pf}}^*$ decreases with an increase in C_f . We find that, for polymer length $N = 64$, $\varepsilon_{\text{pf}}^*$ is about 1.8, 1.5, and 1.2 at $C_f = 1/10^3$, $1/5^3$, and $1/3^3$, respectively. In region III with $\varepsilon_{\text{pf}} > \varepsilon_{\text{pf}}^*$, $\langle R_G^2 \rangle$ increases with ε_{pf} and tends to saturation at large ε_{pf} . The saturation value of $\langle R_G^2 \rangle$ also increases with the increase in C_f . These behaviors are in agreement with previous lattice MC simulation of polymer in random medium but differ from that in the periodic medium as shown in Fig. 5b.⁴¹ These results clearly indicate that the distribution and concentration of fillers play important roles on the conformational properties of polymer.

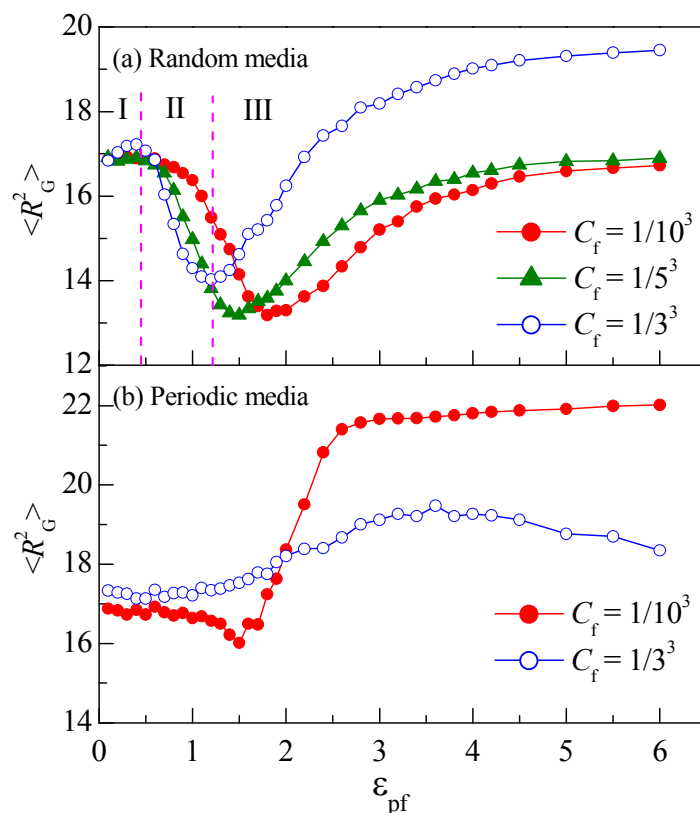


Fig. 5 (color online) Plots of the mean square radius of gyration $\langle R_G^2 \rangle$ of polymer in the random medium (a) and in the periodic medium (b) as a function of polymer-filler interaction strength ϵ_{pf} at different concentrations C_f of fillers. Two dotted red lines separate three regions (I, II, and III) for polymers in the random medium with $C_f = 1/3^3$. Polymer length $N = 64$, filler size $\sigma_f = 1\sigma$, and system size $L = 60\sigma$.

Fig. 5a also shows that polymer size $\langle R_G^2 \rangle$ is roughly independent of the concentration of fillers at weak polymer-filler interactions. But the behavior of $\langle R_G^2 \rangle$ in the moderate polymer-filler interaction region, say from $\epsilon_{pf} = 1$ to 2, is complicated. The results indicate that, at moderate polymer-filler interactions, the size of polymer chain can be increased or decreased by changing the concentration C_f of fillers. In fact, these behaviors have been observed in experiments.^{37,39,40,43}

The different behaviors of polymers in the random medium and in the periodic

medium can be explained qualitatively by the free energy $F = U - TS$ of polymer chains. Here U is the energy and S is the conformational entropy. The fillers can provide two main effects on the polymer. One is the EV effect which enlarges the size while decreases S of polymer. A small increase in $\langle R_G^2 \rangle$ at high $C_f = 1/3^3$ is due to the EV effect of fillers at weak attraction. Another is the attraction of fillers which decreases the energy U of polymer by adsorbing polymers.

To understand the attraction of fillers, we have calculated the number N_{mc} of monomers that contact with fillers and the number N_{fc} of fillers that is contacted by polymer. Fig. 6 presents the dependence of N_{mc} and N_{fc} on the interaction strength ε_{pf} for polymer in the random medium and in the periodic medium with $C_f = 1/10^3$ and $C_f = 1/3^3$. It is clear that N_{mc} increases with ε_{pf} and saturates at large ε_{pf} for all cases as shown in Fig. 6a and 6c, roughly independent of the medium and the filler concentration. It means that more and more monomers contacts with fillers in order to decrease its energy U with the increase in ε_{pf} . However, the dependences of N_{fc} on ε_{pf} are different for polymers in different medium, as shown in Fig. 6b and 6d. For polymer in the random medium, N_{fc} behaves similar to N_{mc} , that is, it increases with ε_{pf} and saturates at large ε_{pf} . But for polymer in the periodic medium, the behavior of N_{fc} is dependent on C_f . At small $C_f = 1/10^3$, N_{fc} increases up to 2 with the increase in ε_{pf} . But at large $C_f = 1/3^3$, N_{fc} decreases slowly at large ε_{pf} . These results indicate that the randomly distributed fillers have different attractive modes for polymer from the periodically distributed fillers. Our results clearly show that polymer in the random medium always decreases its energy by contacting with more fillers.

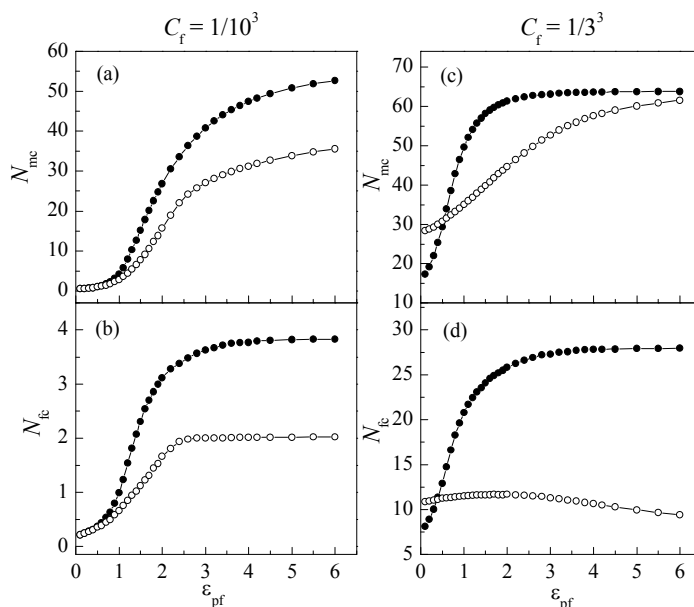


Fig. 6 Plots of the number N_{mc} of monomers contacted by fillers and the number N_{fc} of fillers contacted by polymer versus the interaction strength ϵ_{pf} for polymer in the random medium (solid circles) and in the periodic medium (open circles) with $C_f = 1/10^3$ (a and b) and $C_f = 1/3^3$ (c and d), respectively. Here the polymer length $N = 64$, filler size $\sigma_f = 1\sigma$, and system size $L = 60\sigma$.

In the random medium, the distribution of fillers is not uniform, instead there are dilute filler regions with large free space and dense filler regions with small free space. At small $\epsilon_{pf} < 0.5$, both N_{mc} and N_{fc} are very small as shown in Fig. 6 since the attraction of fillers is very weak. At weak attraction (Region I), the EV effect of fillers is dominant. Thus the polymer locates in the dilute filler regions and behaves like a random coil to avoid contacting with fillers. So the mean square radius of gyration $\langle R_G^2 \rangle$ of polymer is close to $\langle R_G^2 \rangle_0$ as shown in Fig. 5a. Similarly, $\langle R_G^2 \rangle$ of the polymer in the periodic medium with $C_f = 1/10^3$ at $\epsilon_{pf} < 0.5$, is also roughly equal to $\langle R_G^2 \rangle_0$. Thus at small $\epsilon_{pf} < 0.5$, the dependences of $\langle R_G^2 \rangle$ on ϵ_{pf} for polymer in the random medium and in the periodic medium with $C_f = 1/10^3$ are similar.

At moderate ϵ_{pf} from 0.5 to ϵ_{pf}^* (Region II), both N_{mc} and N_{fc} increase steeply with

ε_{pf} , clearly meaning that the attraction of fillers begins to play effects on the polymer. However, there is a competition between the EV effect and the attraction of fillers. With an increase in ε_{pf} , more monomers contact with fillers to reduce the system energy to compensate the EV effect of fillers. As some monomers are temporarily in contact with fillers, the polymer is shrank around the fillers and thus looks like a little shorter, therefore $\langle R_G^2 \rangle$ decreases with the increase in ε_{pf} and reaches its minimum when the competition balances in power at value ε_{pf}^* . Finally at large C_f (Region III), it is easy for polymer to contact with more fillers, so we can see that ε_{pf}^* decreases with the increase in C_f as show in Fig. 5a. As the attraction effect dominates when $\varepsilon_{pf} > \varepsilon_{pf}^*$, thus the polymer tries to contact with as many fillers as possible to reduce energy by extending polymer's conformation. Therefore, the parts of polymer between two fillers are stretched and we find that $\langle R_G^2 \rangle$ increases steeply with ε_{pf} in region III. Because polymer can contact with more fillers at larger C_f , $\langle R_G^2 \rangle$ increases with C_f at $\varepsilon_{pf} > \varepsilon_{pf}^*$. The behaviors of polymer in the random medium are similar to that in the periodic medium with $C_f = 1/3^3$.⁴⁴ These results imply that the polymer tends to enter dense filler regions at $\varepsilon_{pf} > \varepsilon_{pf}^*$. This is consistent with the results that N_{fc} of the random medium is much larger than that of the periodic one as shown in Fig. 6b and 6d.

At larger ε_{pf} , N_{fc} as well as $\langle R_G^2 \rangle$ increases very slowly with the increases in ε_{pf} for polymers in the random medium. The polymer may be adsorbed tightly on several fillers when the attraction of fillers is strong enough. However, the slightly changes in N_{fc} and $\langle R_G^2 \rangle$ imply that the polymer can still diffuse at larger ε_{pf} . The polymer always keeps looking for denser filler regions in order to contact with more fillers and further reduce the system energy. The behavior of polymer in the random medium is somewhat similar to that of polymer in the periodic medium in the dense filler region with $2R_{G0} > d$ but differs from that with $2R_{G0} < d$.⁴⁴ For polymer in the periodic medium with high $C_f = 1/3^3$ ($2R_{G0} > d$), polymer can diffuse in the medium at large ε_{pf} . But for polymer in the periodic medium with low $C_f = 1/10^3$ ($2R_{G0} < d$), the polymer is tightly adsorbed on two fillers and does not diffuse at large ε_{pf} .

3.2. Diffusion of polymer in random medium

In this subsection, we study the dynamical properties of polymer in the random medium filled with randomly distributed fillers at different ε_{pf} s and C_f s. Because the simulation time is excessively long at large ε_{pf} , we have to focus our simulations on the diffusion of polymers at relatively small ε_{pf} from 0.1 to 3. The dynamical property of polymer is measured by the time dependent MSD of the center of mass of polymers. MSD is defined as

$$\langle \Delta r^2 \rangle = \langle [\vec{r}_{cm}(t) - \vec{r}_{cm}(0)]^2 \rangle, \quad (4)$$

with $\vec{r}_{cm}(t)$ is the position vector of the center of mass at time t . Fig. 7 presents the evolution of the polymer of length $N = 64$ in the random medium with $C_f = 1/10^3$ and $C_f = 1/3^3$, respectively. It is clear that the MSD decreases with the increase in ε_{pf} , clearly showing that the attraction of fillers can reduce the diffusion of polymer.

Moreover, the diffusion property is also changed by the attraction of fillers. The normal diffusion ($\langle \Delta r^2 \rangle \propto t$) of polymers is observed for $C_f = 1/10^3$ at small $\varepsilon_{pf} < 0.8$ and for $C_f = 1/3^3$ at $\varepsilon_{pf} < 0.3$, respectively. With the further increase in ε_{pf} , the diffusion is obviously slowed down by attractive fillers and changes to a subnormal diffusion $\langle \Delta r^2 \rangle \propto t^\alpha$ with the exponent $\alpha < 1$ at long time scale for all polymers. We expect α will be a constant at sufficient long time. The behaviors are in agreement with the simulation results for polymer in crowded environment with random fillers,⁴⁸ but are different from the results of polymer in the periodic medium.⁴⁴

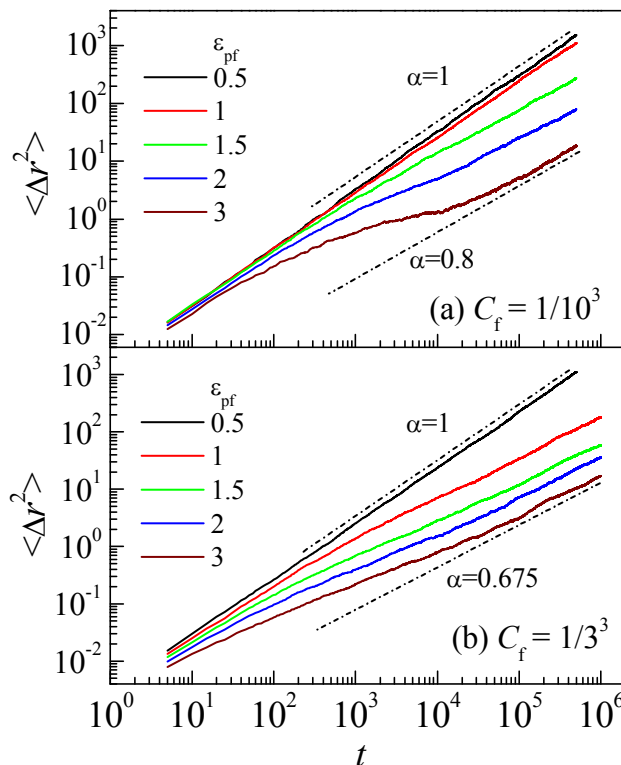


Fig. 7 (color online) Log-log plot of the MSD of center of mass $\langle \Delta r^2 \rangle$ versus the simulation time t at different polymer-filler interaction ε_{pf} s for filler concentration (a) $C_f = 1/10^3$ and (b) $C_f = 1/3^3$. The system size $L = 60\sigma$ and polymer length $N = 64$. Dashed straight lines show slopes of simulation data at long time scales.

For the diffusion of polymer in the random medium, we find that the exponent α is dependent on the attractive strength ε_{pf} of fillers. Fig. 8 shows the dependence of α on ε_{pf} for $C_f = 1/10^3$ and $C_f = 1/3^3$. The exponent α keeps a constant $\alpha = 1$ at small ε_{pf} . Then it decreases quickly with ε_{pf} at moderate ε_{pf} and at last tends to a saturation value. In addition, the value α of $C_f = 1/10^3$ is bigger than that of $C_f = 1/3^3$ at the moderate ε_{pf} region, since it is easier for polymer diffusing in the medium of smaller filler concentration. The value α tends to be about 1 as $C_f \rightarrow 0$.

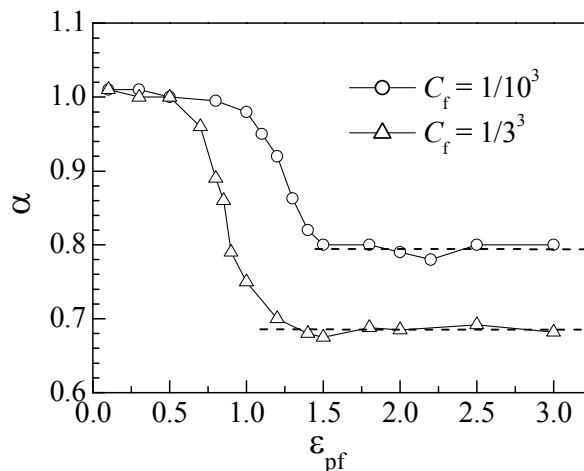


Fig. 8 The exponent α in the diffusion relation $\langle \Delta r^2 \rangle \propto t^\alpha$ versus polymer-filler interaction ϵ_{pf} for polymer $N = 64$ in the random medium with filler concentrations $C_f = 1/10^3$ and $C_f = 1/3^3$. Two dashed lines represent the plateau of α at large ϵ_{pf} region.

At small ϵ_{pf} , the effect of the attraction of fillers is weaker than the EV effect of fillers. Therefore the polymer diffuses in sparse space among fillers to avoid contacting with fillers. The exponent $\alpha \approx 1$ indicates that the polymer diffuses normally at small ϵ_{pf} . The normal diffusion region becomes narrower with the increase in C_f . At moderate ϵ_{pf} , the polymer starts to contact with a few fillers to reduce its contact energy. The contact between polymer and fillers retards the diffusion of polymer, resulting in a subnormal diffusion. Since it is easier for polymer to contact with fillers at larger C_f , the subnormal diffusion appears earlier at larger C_f . And polymer contacts more fillers at larger C_f , so the value of α becomes much smaller at larger C_f . Finally at large ϵ_{pf} , the attraction of fillers exceeds the EV effect, and the polymer tries to contact with fillers as many as possible to reduce the system energy. Thus the polymer moves in dense filler regions with even smaller diffusion rate. The exponent α decreases with the increase in C_f , indicating that polymer moves more slowly at larger C_f . However the exponent α is roughly independent of ϵ_{pf} in this region. And the starting attraction strength for the plateau is about $\epsilon_{pf} = 1.5$ is almost independent of C_f . Thus, at strong attraction region, the exponent α is roughly

independent of ϵ_{pf} , though MSD decreases with the increase in ϵ_{pf} as shown in Fig. 7.

Finally, we would like to point out that the diffusion behaviors of polymers in random media are different from the behaviors of polymers in the periodic medium, where polymers always keep normal diffusion for the case $2R_{G0} > d$ and are adsorbed on two or more fillers and stop diffusing for the case $2R_{G0} < d$. In the random media, there are dilute filler regions and dense filler regions. Our results show that polymers diffuse in dilute filler regions at weak attraction whereas it diffuses in dense filler regions at strong attraction.

From the equilibrium property shown in Fig. 6, we find that polymers contact with more fillers at larger filler attraction. That is, polymers are in dilute filler regions at weak attraction while they are in dense filler regions at strong attraction. To further confirm the diffusion mechanism of polymers in the random media, we have calculated the mean number of fillers around one monomer, N_{f25} , that describes the number of fillers fallen into the area within a radius of 2.5σ around one monomer of polymer. The value N_{f25} simply represents the concentration of fillers of the space near the polymer. We have calculated N_{f25} for polymers in the random media during the diffusion. The evolutions of N_{f25} for polymers in medium with $C_f = 1/3^3$ are presented in Fig. 9 for three values of ϵ_{pf} . We find that N_{f25} remains roughly constant with time but it increases obviously with ϵ_{pf} . At the weak attraction, e.g., $\epsilon_{pf} = 0.5$, the EV effect is important, thus polymers stay in the dilute filler regions with sparse space, that results in a small value of N_{f25} . Whereas at strong attraction, e.g., $\epsilon_{pf} = 3$, polymers are attracted towards fillers and thus polymers diffuse in the dense filler regions.

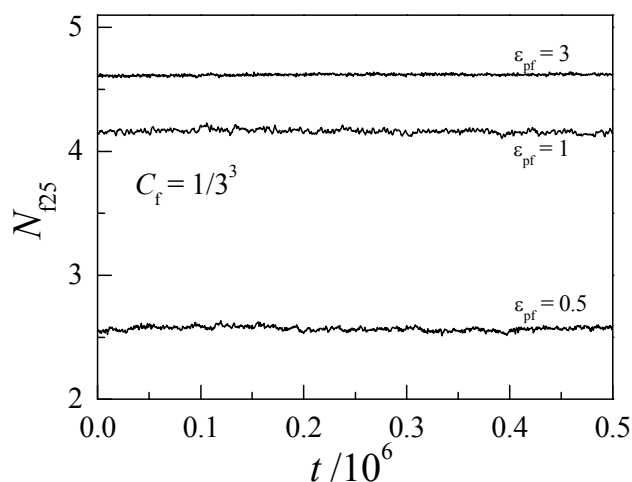


Fig. 9. Plots of the number N_{f25} of fillers fallen into the area within a radius of 2.5σ around one monomer of polymer versus the simulation time t for polymer in the random medium with $C_f = 1/3^3$ at different attractions $\epsilon_{pf} = 0.5, 1, \text{ and } 3$. Simulation parameters: The polymer length $N = 64$, filler size $\sigma_f = 1\sigma$, and system size $L = 60\sigma$.

4. CONCLUSIONS

The equilibrium and dynamical properties of polymer chains in the random medium with randomly distributed fillers are studied by Monte Carlo simulations. All the fillers are identical and immobile in the simulations. The polymer-filler interaction ϵ_{pf} is taken into account in the simulation as a main factor. The statistical size, e.g. the mean square radius of gyration $\langle R_G^2 \rangle$, and diffusion property of polymers are simulated. Results show that the equilibrium and dynamical properties of polymers are strongly depended on the polymer-filler interaction, concentration of fillers, and distribution of fillers. The effect of fillers increases with an increase in the concentration of fillers.

The statistical size $\langle R_G^2 \rangle$ is roughly unchanged at weak polymer-filler interactions. At moderate attraction, $\langle R_G^2 \rangle$ decreases with the increase in the attraction strength and reach minimum at ϵ_{pf}^* . The place of minimum ϵ_{pf}^* decreases with the increase in C_f . At $\epsilon_{pf} > \epsilon_{pf}^*$, $\langle R_G^2 \rangle$ increases with ϵ_{pf} and tends to saturation at large ϵ_{pf} . The saturation value of $\langle R_G^2 \rangle$ also increases with the increase in C_f . On the other hand, polymers in

the random medium diffuse normally in the low filler concentration regions when the attraction of fillers is weak. At strong attraction of fillers, polymers move in the high filler concentration regions and fillers retard the diffusion of polymers. As a result, we find that polymers in the random medium keep diffusing but a normal diffusion at weak filler attraction changes to a subnormal diffusion at strong attraction. Finally, by comparing the equilibrium and dynamical properties of polymers in the random medium with that in the periodic medium, we find that the effects of the randomly distributed fillers on polymer are different from that of the periodic distributed fillers.

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