Entropy dominated behaviors of confined polymer–nanoparticle composites*

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Stretched polymers will lose their possible configurations if they are mixed with nanoparticles or touch a hard wall, which leads to a strong depletion attraction responsible for the enrichment of nanoparticles near substrates. Moreover, it is found that there exists a sacrifice mechanism in confined pure polymer samples or polymer–nanoparticle mixtures, that part of the polymers, in order to reach a minimum free energy for the total system, are adsorbed on hard walls even though they lose their conformation. The current study provides a simple yet effective approach for the design of thin polymer composites.

Keywords: conformation entropy, nanoparticle, depletion attraction, thin polymer layer

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1. Introduction

The increasing capability of producing precisely sized particles accelerates the development of polymer–particle composite engineering which enables people to find composites that exhibit advantageous electrical, magnetic, optical, and mechanical properties.[1,2] As part of a renewed interest in nanocomposites, people have been trying to design new functional materials which combine the desirable properties of nano-size particles (nanoparticle) and polymers.[3] However, controlling materials at the nano-scale is one of the greatest challenges in modern interdisciplinary science. One obstacle to a broader application of polymer nanocomposites that still remains is the limited understanding of the relationship between nano-scale properties and mesoscopic structure.[3] In general, such systems involve a complicated combination of entropic and enthalpic interactions between different components. So far, researchers have established a means of harnessing both enthalpic and entropic interactions to control the distribution of nanoparticles in the polymer matrix and, thereby, tailor the macroscopic behaviors of the composites.[4,5]

In the present paper, we focus on the entropic effects in polymer–nanoparticle composites, and the influence of their interplay on final phases. We first make a consideration about the mechanism by which polymers interact with a hard sphere and a wall. Then we conclude the phase behaviors of confined polymer–nanoparticle composites in different polymer and nanoparticle concentrations. Finally, based on current understanding, we provide a method which could be used for constructing thin polymer films.

2. Simulation

In our study, the polymers were modeled as bead-spring chains without explicitly twisting or bending deformation. Each chain was connected by anharmonic springs, and modeled with a finite extensible nonlinear elastic (FENE) potential[6,7]

$$U_{\mathrm{FENE}}(r) = -0.5\kappa {R_0}^2 \ln\left[1 - \left(\frac{r}{R_0}\right)^2\right], \ (r < R_0), \quad (1)$$

where $\kappa = 30\epsilon/{\sigma_{\mathrm{M}}}^2$ is the spring constant, and $R_0 = 1.5\sigma_{\mathrm{M}}$ is the maximum extension between neighboring repeating units (monomers) in the same chain so as to avoid breaking. Here σ_{M} stands for the repeating unit size (length unit). We also designate the size of the nanoparticle as σ_{NP}. The pair interactions including nanoparticle–nanoparticle,

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nanoparticle–monomer, and monomer–monomer were modeled as the Lennard–Jones (LJ) potential given by

$$U_{\rm LJ}(r) = 4\epsilon\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] - 4\epsilon\left[\left(\frac{\sigma_{ij}}{r_{\rm c}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{\rm c}}\right)^{6}\right], \quad (2)$$

with σ_{ij} being the mean size of the two particles (ith and jth) involved in the pair interaction, and ϵ the interaction strength (for simplicity, we set $\epsilon = 1$). The parameter $r_{\rm c}$ is the cutoff distance used in the simulations. To make sure that the system is in a thermal state, we cut the potential at its minimum, $r_{\rm c} = r_{\rm min} = 2^{1/6}\sigma_{ij}$, thereby removing the attractive tail of the pair interaction and leaving it fully repulsive.[8] In addition, an LJ potential

$$U_{\rm Wall}(d) = 4\left[\left(\frac{\sigma_i}{d+\sigma_i/2}\right)^{12} - \left(\frac{\sigma_i}{d+\sigma_i/2}\right)^{6}\right] - 4\left[\left(\frac{\sigma_i}{d_0}\right)^{12} - \left(\frac{\sigma_i}{d_0}\right)^{6}\right], \quad (3)$$

was implemented for the two walls at positions of $z = -10$ and $z = 10$ to deliver a confinement effect to the system. The d is the vertical distance between the wall surface and the particle (including the monomer and the nanoparticle), and $d_0 = 2^{1/6}\sigma_i$ with σ_i is the size of the ith particle. The boundary conditions in both the x and y directions are periodic to mimic an infinitely extended film-like geometry. The simulations are carried out using the open source LAMMPS molecular dynamic package.[8] The equation of motion for the displacement of particles with an index i is given by the Langevin equation

$$m_i\frac{{\rm d}^2\boldsymbol{r}_i}{{\rm d}t^2} = -\nabla_i U - m_i\Gamma\frac{{\rm d}\boldsymbol{r}_i}{{\rm d}t} + \boldsymbol{F}_i(t), \quad (4)$$

where U is the total potential energy acting on the ith particle, for a monomer $U = U_{\rm LJ} + U_{\rm FENE} + U_{\rm Wall}$, and for a nanoparticle $U = U_{\rm LJ} + U_{\rm Wall}$. The quantity $\boldsymbol{F}_i(t)$ is a stochastic force that is related to the friction coefficient by the fluctuation-dissipation theorem. All the simulations in this work were carried out at a constant temperature $T = 1$ (in LJ units).

In the simulations, we first let polymers and nanoparticles completely mix in a large box with two fixed walls in the z direction after running for a sufficiently long time. In the x and y dimensions of the simulation box, we use shrink-wrapped boundaries that can change the box sizes. Then, we compress the box to a certain size which results in the total volume fraction that we want to consider. Finally, we change the boundary conditions in the x and y dimensions into periodic ones. The corresponding conformation is taken as the initial conformation for further studies.

3. Results and discussion

The addition of polymer chains to nanoparticles induces an entropic inter-particle depletion attraction.[9] Such an entropic depletion attraction force comes from the stretching of polymer chains when they pass around nanoparticles as a result of a mixture with large-size particles. Dispersed particles swell the linear polymer chains, resulting in a polymer radius of gyration that grows with the particle volume fraction. Figure 1 shows the radius of gyration of polymer chains as a function of the particle volume fraction. The square radius of gyration $R_{\rm g}$ is defined as the average square distance between monomers in a given conformation (with i-th monomer position vector $\boldsymbol{R}_i$) and polymer's mass center (position vector $\boldsymbol{R}_i$): $R_{\rm g}^2 = N^{-1}\sum(\boldsymbol{R}_i - \boldsymbol{R}_{\rm cm})^2$. We mixed the polymers and particles in a bulk state, and then slowly increased the volume composition of the particles. The result shown in Fig. 1 clearly indicates that the size of chains is stretched, and such an effect is enhanced by the increasing number of dispersed particles. As a result, each particle is surrounded by a depletion zone where there is essentially no polymer centers of mass, due to the high entropic cost of configurational distortion.

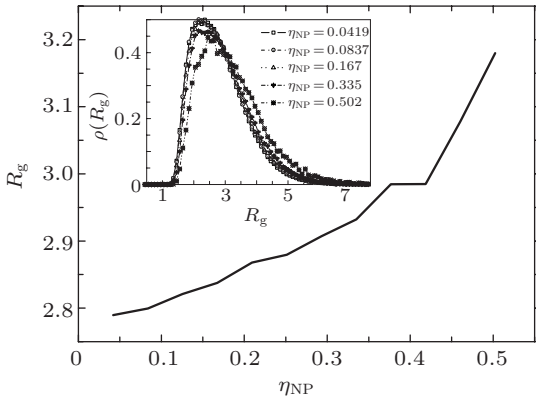


Fig. 1. Average radius of gyration $R_{\rm g}$ of polymer chains as a function of volume fraction $\eta_{\rm NP}$ of particles in a bulk state. Here, we fix the total volume fraction $\eta = 0.53$, and the size of particle $\sigma_{\rm NP}$ is twice that of the monomer $\sigma_{\rm M}$. The insert gives the probability distribution of $R_{\rm g}$ at different $\eta_{\rm NP}$ values.

As the two depletion zones belonging to different particles overlap with each other, there is a net osmotic pressure pushing the two particles together, which is called the entropic depletion attraction effect. Although enthalpic interactions are usually dominant,[4,10] entropic interactions also play a critical role in dictating the equilibrium structures of polymer–particle composites. Traditionally, the existence of entropic depletion attraction brings difficulty to the dispersion of particles in polymeric materials, especially for those with a large size asymmetry between nanoparticles and polymer segments. In experiments,[11] the researchers concluded that the range and depth of this entropic depletion attraction force can be tuned independently by altering the polymer's molecular weight and concentration, respectively, which has an important influence on the final states. The phase of particles with the addition of polymers can be gas–liquid coexistence, gas–liquid–crystal coexistence, or gas–crystal coexistence, depending on the strength of the depletion attraction at moderate volume fractions.[12,13]

The presence of a plane surface can significantly complicate the phases developed in polymer nanocomposites. Computational and experimental studies on filled polymers near a surface showed that as polymers melt they also induce an entropic depletion attraction between the particles and the surface.[5,14,15] To understand how polymers interact with a hard wall and nanoparticles, we first investigate the behavior of pure polymer samples in confinement. In line with our expectations, there exists a depletion region near the surface with no mass center of chains. However, the size of such a depletion region, corresponding to the distance between the wall surface and the most approaching mass center of polymers, decreases with increasing polymer concentration. Such a depletion region will completely disappear as the polymer concentration is larger than a certain value (and will be different depending on the polymeric degree of chains), and considerable part of the chains will touch on the wall and flatten against the surface. It is quite different from the phase in a dilute sample, where polymers should keep away from hard walls so as to save the lost configurational entropy. Figure 2 shows the density distribution of the mass center of polymers, and the distributions of radius of gyration in perpendicular ($R_{\rm g}^{\top}$) and parallel ($R_{\rm g}^{\parallel}$) directions (relative to wall surface), respectively. The two peaks of mass center distribution show that polymers concentrate in the vicinity of the walls. In such an aggregation zone, the corresponding value $R_{\rm g}^{\top} = 0$. Namely, these polymers can only stretch in a two-dimensional way parallel to the wall surface, but are compressed in a perpendicular direction. On the other hand, the almost unchanged value of $R_{\rm g}^{\parallel}$ of central region polymers shows that the hard walls have no influence on their size in a perpendicular direction. That is to say, as the density of pure polymer melt in confinement approaches or exceeds a certain value (about $\eta_{\rm M} = 0.4$ when the chain length $L_{\rm C} = 20$), part of the polymer will contact the walls and flatten against the surfaces as a sacrifice. Even this "sacrifice process" leads to the loss of configurational entropy of these chains, and the system's entropy gains more as a whole due to the fact that the major part of the polymer staying in the central region gets more freedom for position and movement.

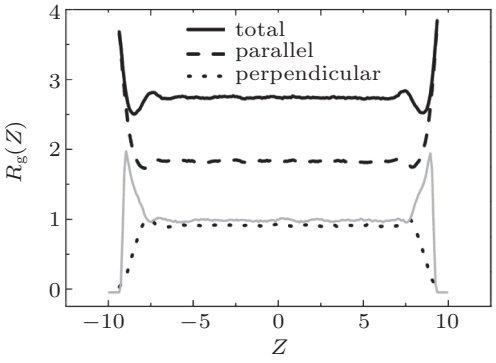


Fig. 2. In a confined pure polymer sample, the development of the radius of the gyration of chains along a direction perpendicular and parallel to the wall surfaces. The gray line shows the corresponding density distribution of polymer mass center. Here the total volume fraction is 0.5, the size ratio between the nanoparticle and monomer $\sigma_{\rm NP}/\sigma_{\rm M} = 2.0$, and the polymer chain length $L_{\rm c} = 20$.

For polymer–nanoparticle composites confined between two substrates, the depletion regions are existent both on the plane surface and around nanoparticles as mentioned above. A strong attraction force occurs between the walls and nanoparticles if the two depletion regions overlap. By using the classical density functional theory (DFT), theoretical calculations showed that entropy-driven forces expel polymers away from the plane surface, but attract nanoparticles to the wall sides.[16,17] Via both experimental and computational studies, researchers also found that such an entropic depletion attraction force can even drive nanoparticles into defects existing on the substrate.[3,18] More insights into the physics of polymer nanocomposites can be gained by computa-

tional studies which enable one to isolate the individual interactions that are implemented in simplified models.[5,14] In systems at a dense liquid state with few nanoparticles, both nanoparticles and polymers exhibit pronounced peaks near the substrates.[16] As shown in Fig. 3, most of nanoparticles are attracted on the hard walls and form a singer layer beside the surface due to the strong depletion attraction. The existence of peaks at the two borders in the distribution of polymers comes from the "sacrifice process" as the polymer is the dominant composition. If we increase the number of nanoparticles while keeping the total volume fraction unchanged, the peaks near the substrates in the distribution of polymers become weaker and finally disappear. As shown in Fig. 3, in a sample with $\eta_{\rm NP} = 0.454$ and $\eta_{\rm M} = 0.091$, a crystallized structure of nanoparticles is clearly seen at the two borders, but polymers are only centralized in the middle-region, indicating that nanoparticles prefer to be situated near the walls because of the polymer induced depletion attraction between the nanoparticles and the walls.

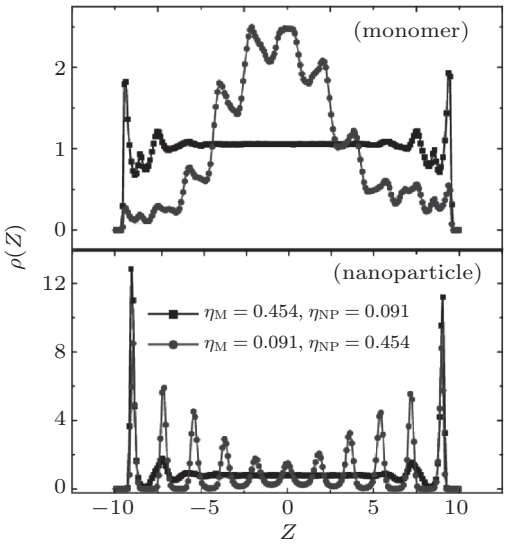


Fig. 3. Density profiles of (a) monomers and (b) nanoparticles along the direction perpendicular to the surface in a confined polymer–nanoparticle composite. Here the polymer chain length $L_{\rm c} = 20$, and $\sigma_{\rm NP} = 2\sigma_{\rm M}$, with $\sigma_{\rm NP}$ and $\sigma_{\rm M}$ being the sizes of the nanoparticle and the monomer, respectively. $\eta_{\rm NP}$ and $\eta_{\rm M}$ are the volume fractions of nanoparticles and monomers, respectively.

In general, polymer films created through the spin coating process[19,20] are in a non-equilibrium state that is stabilized by delivering high viscosities and long relaxation times[21] due to their high polymeric degree. For polymers melt or polymer–nanoparticle composites under confinement, part of polymers attach and flatten against the hard walls. This provides us with a feasible method to construct a thin polymer film by enhancing the efficiency of the sacrifice of the polymers' conformation, simultaneously counteracting the depletion effect to nanoparticles. That is to say, we need to carefully control the interplay between the depletion attraction and the effect of the "sacrifice process". Here, as a simulation prediction, we make a modification to the interaction between hard walls and monomers, that is

$$U_{\rm Wall}(d) = 4\left[\left(\frac{\sigma_{\rm M}}{d+\sigma_{\rm M}/2+\Delta d}\right)^{12} - \left(\frac{\sigma_{\rm M}}{d}+\sigma_{\rm M}/2+\Delta d\right)^{6}\right] - 4\left[\left(\frac{\sigma_{\rm M}}{d_0}\right)^{12} - \left(\frac{\sigma_{\rm M}}{d_0}\right)^{6}\right], \quad (5)$$

but keep the interaction between walls and nanoparticles

$$U_{\rm Wall}(d) = 4\left[\left(\frac{\sigma_{\rm NP}}{d+\sigma_{\rm NP}/2}\right)^{12} - \left(\frac{\sigma_{\rm NP}}{d+\sigma_{\rm NP}/2}\right)^{6}\right] - 4\left[\left(\frac{\sigma_{\rm NP}}{d_0}\right)^{12} - \left(\frac{\sigma_{\rm NP}}{d_0}\right)^{6}\right], \quad (6)$$

unchanged. Here Δd is supposed to be an artificial gap which can be added by polymer segments but is forbidden for larger nanoparticles, and is used here as an order parameter to measure the phase behaviors. The non-neutral feature of hard walls prevents the overlap between two depletion regions of one around nanoparticles and one closed to the wall surface, resulting in the degradation of attraction between walls and nanoparticles. On the other hand, the additional free gap strengthens the effect of the "sacrifice process", which attracts most of the polymers inside the gap simultaneously in order to save more free space in the central region for nanoparticles. Naturally, the ratio of polymers situated inside the gap over the total number increases with respect to increasing Δd. As shown in Fig. 4, polymers are completely expelled out of the central region, and stretched out as two-dimensional films near the walls. In this way, a perfect polymer thin film (nano-scale) is predicted. The predicted "sandwich polymer-nanoparticle composites" could offer a simple and effective approach to prepare stable polymer films.

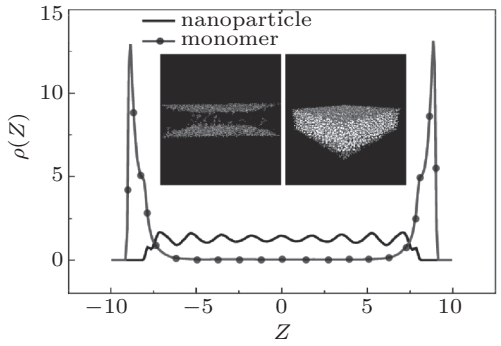


Fig. 4. Density profiles of monomers and nanoparticles along the direction perpendicular to the walls in a confined polymer–nanoparticle composites sample, with preferential wall boundary condition ($\triangle d = 0.5$). Here, the size of the nanoparticles is twice that of the monomers, $\eta = 0.5$, and the volume ratio between nanoparticles and polymers is 6.0. The two inset snapshots show the equilibrium distribution of components in the sample, with polymers in grey and nanoparticles in white.

4. Conclusion

In summary, our work takes a step towards identifying and clarifying the subtle interplay among different kinds of entropic contributions. The polymers lose conformation entropy by both the stretching of large size nanoparticles and the hard plane. This leads to a strong depletion potential that is responsible for the enrichment of nanoparticles near substrates. Moreover, we revealed the sacrifice mechanism that part of polymers flatten against hard walls even with losing conformation entropy, in order to maximize the total entropy (minimum free energy) in pure polymer samples or polymer–nanoparticle composites. Based on this understanding, we provide a simple but effective approach that can be used for the construction of thin polymer film.

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