

Solvent Size Effect on the Depletion Layer of a Polymer Solution near an Interface

Jinglei Hu, Rong Wang,* and Gi Xue

Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received: October 20, 2005; In Final Form: November 29, 2005

By varying polymer concentration ϕ_p^0 and Flory–Huggins parameter χ , the effect of solvent size on the depletion interaction between polymer coils and a hard wall was investigated by the real-space version of self-consistent field theory (SCFT). The depletion profiles and depletion thickness indicated that the depletion effect is strong in less good solvent with large molecular volume. Through the analysis of the respective free energies of polymer coils and solvent molecules, we found that the increment in the translation entropy of the solvent is the key to strengthening the depletion interaction. On the basis of the SCFT results, we define a solvent with volume about one to six times that of the polymer segment as a “middle-sized solvent”. The density oscillations previously studied by Van der Gucht et al. and Maassen et al. were also observed in our simulation, and the addition of middle-sized solvent will magnify the amplitude of the oscillations. The solvent-size-dependent depletion interaction may be an explanation for the reduced entanglement and promoted crystallization behavior of polymer coils prepared from the solution with middle-sized solvent.

Introduction

Depletion interaction widely exists in polymer–colloid mixtures, at surfaces and interfaces, and has attracted increasing attention. Asakura and Oosawa¹ first described the depletion-induced attraction between two plates immersed in an ideal nonadsorbing polymer solution. In the Asakura–Oosawa–Vrij^{2,3} model, a polymer coil is mapped onto a penetrable hard sphere (PHS), which has a smaller radius R_g (or $2R_g/\sqrt{\pi}$) than a colloidal particle. In the so-called “colloid limit”, depletion force arises, since the smaller polymer coils are excluded from a narrow shell or depletion zone on the order of R_g around the larger particles. Considering the free volume accessible to the PHSs, Lekkerkerker⁴ introduced an osmotic equilibrium model for a PHS and colloid mixture based on the statistical semigrand canonical ensemble. By varying the size ratios of PHSs to colloidal particles, the phase diagram was calculated with perturbation theory. Meijer and Frenkel⁵ have carried out lattice Monte Carlo simulations of ideal polymer chains mixed with hard spheres. Bates and Frenkel⁶ simulated PHSs plus platelets to study the phase behavior. Their simulation results showed that for small size ratios of PHSs to colloidal particles the agreement with the free volume theory of Lekkerkerker is fairly good. However, deviations appear for larger size ratios.⁷

It has been pointed out that, when a polymer coil becomes larger than a colloidal particle, i.e., in the “protein limit”, the PHS model fails because it neglects the configuration entropy of polymer chains. The details of polymer physics should be described in a better way to quantify the depletion interaction.⁷ Eisenriegler⁸ calculated the depletion profile of the monomer density and the depletion force for two small spherical particles in a solution of ideal chains using field theoretical methods. Mean field theory first proposed by De Gennes et al.^{9,10} has proven to be a powerful tool to treat the depletion interactions in polymer solutions. Fleer et al.^{11–14} developed a numerical self-consistent field method that enables calculation of the polymer segment profiles near interfaces and takes into account

the chain length, polymer concentration, and solvency. However, the solvent size was overlooked by convention in most theoretical investigations.

Naughton and Matsen demonstrated that the solvent size must be sufficiently small so that the solvent distributes evenly throughout the mixture.¹⁵ Martin and Wang¹⁶ addressed the crossover from wet brushes to dry brushes as the molecular weight of the solvent increases. They concluded that the crossover is purely driven by the entropic effect. These results show that solvent size has a large effect on the phase behavior in polymer solution.

We have deviated from the standard convention for polymer solutions of setting the reference volume, ρ_0^{-1} , equal to the volume of a solvent molecule, v_s . The depletion effect near the hard wall is investigated by varying solvent size in the real-space implementation of the self-consistent field theory (SCFT).¹⁷

Theoretical Method

We consider a polymer solution near a hard wall, which is energetically neutral and impenetrable. There are n_p polymers with n_s solvent molecules in the system. Each polymer consists of N segments with the statistical length a . We assume the mixture is incompressible with each polymer segment occupying a fixed volume ρ_0^{-1} and each solvent molecule taking a volume v_s . Thus, the total volume of the system is $V = n_p N / \rho_0 + n_s v_s$, the volume fraction of polymer is $\phi_p^0 = n_p N / V \rho_0$, and the ratio of the solvent to polymer size is $\alpha = v_s \rho_0 / N$.

The free energy of the system is given by

$$F = -\phi_p^0 \ln \left(\frac{Q_p}{\phi_p^0 V} \right) - \frac{1 - \phi_p^0}{\alpha} \ln \left[\frac{Q_s \alpha}{(1 - \phi_p^0) V} \right] + \frac{1}{V} \int d\mathbf{r} \{ \chi N \phi_p(\mathbf{r}) \phi_s(\mathbf{r}) - w_p(\mathbf{r}) \phi_p(\mathbf{r}) - w_s(\mathbf{r}) \phi_s(\mathbf{r}) - \xi(\mathbf{r}) [1 - \phi_p(\mathbf{r}) - \phi_s(\mathbf{r})] \} \quad (1)$$

* Email: rong_wang73@hotmail.com.

Note that F is reduced by $k_B T \rho_0 V/N$ and is dimensionless. For the present system, there are two fields

$$w_p(\mathbf{r}) = \chi N \phi_s(\mathbf{r}) + \xi(\mathbf{r}) \quad (2)$$

$$w_s(\mathbf{r}) = \chi N \phi_p(\mathbf{r}) + \xi(\mathbf{r}) \quad (3)$$

acting on polymers and solvent molecules, respectively. Here, $\phi_p(\mathbf{r})$ and $\phi_s(\mathbf{r})$ are the standard dimensionless concentrations of these two respective components, and χ is the Flory–Huggins interaction parameter between solvent and polymer. Note that the field for each component has the contributions due to interaction with the other component, and a Lagrange multiplier field $\xi(\mathbf{r})$ to enforce the incompressibility assumption

$$\phi_p(\mathbf{r}) + \phi_s(\mathbf{r}) = 1 \quad (4)$$

The introduction of fields allows us to calculate the partition functions of the two different molecules. For the polymer, we must first parametrize the molecule with a variable s that increases from 0 to N over its length. This allows us to define a partial partition function, $q(\mathbf{r}, s)$, for the $(0, s)$ portion of the chain with the s th segment fixed at position \mathbf{r} . It is evaluated by solving the modified diffusion equation

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \frac{Na^2}{6} \nabla^2 q(\mathbf{r}, s) - w_p q(\mathbf{r}, s) \quad (5)$$

with the initial condition $q(\mathbf{r}, 0) = 1$. The boundary condition $q(z = 0, s) \equiv 0$ is used. In terms of this function, the total partition function for the polymer is $Q_p = \int d\mathbf{r} q(\mathbf{r}, N)$. Because the solvent molecule is treated as a point particle, its partition function is given by the simple expression $Q_s = \int d\mathbf{r} \exp[-\alpha w_s(\mathbf{r})]$.

The dimensionless concentrations are

$$\phi_p(\mathbf{r}) = \frac{\phi_p^0 V}{N Q_p} \int_0^N ds q(\mathbf{r}, s) q(\mathbf{r}, N - s) \quad (6)$$

$$\phi_s(\mathbf{r}) = \frac{(1 - \phi_p^0) V}{Q_s} \exp[-\alpha w_s(\mathbf{r})] \quad (7)$$

As in any mean-field calculation, the fields must be adjusted so that these concentrations satisfy the self-consistent eqs 2–4.

The numerical simulations are carried out on a one-dimensional lattice with size $L = 512$. The grid size is $\Delta z = 0.25$. The simulation is performed until the density profiles are stable and the free energy difference between two iterations is smaller than 10^{-6} , i.e., $\Delta F < 10^{-6}$. We select the concentration of the solution $\phi_p^0 \gg 1/N^{1/2}$ in order to avoid the strong fluctuation effect of the dilution solution.¹⁸ Without loss of generality, we set $N = 100$, and then $\phi_p^0 \gg 0.1$ makes a semidilute or concentrated solution.

Results and Discussion

The profile of the polymer segments in solvent with different sizes is shown in Figure 1, where z divided by the statistical length a denotes the distance from the planar wall, and $\rho(z)$ is the reduced polymer density, $\phi(z)/\phi_p^0$. Polymer segments are excluded from the surface because of conformational restrictions. Near the surface, the ϕ_p^0 -normalized polymer density persists downward with the increase in the size of solvent molecules. Larger solvent molecules have a greater tendency to translate to the surface¹⁵ and deplete more polymer segments. As is

shown in Figure 1a and b, the depletion zone where $\rho(z)$ is less than its bulk value 1 broadens with decreasing polymer bulk concentration ϕ_p^0 . With the quality of solvent molecules taken into account, Figure 1c and d shows the depletion density profiles at $\chi N = 5$ versus the athermal cases in Figure 1a and b, respectively. The qualitative difference caused by the solvencies is studied below, as indicated in Figure 3.

Using Scheutjens–Fleer¹³ theory, van der Gucht et al.¹⁹ found that the density profiles approach their bulk value in a nonmonotonic oscillatory way. Similar behavior was found in a recent Monte Carlo simulation of self-avoiding lattice walks by Bolhuis et al.²⁰ Maassen et al.²¹ also predicted the density oscillations based on mean field theory treatment. The region where the deviation from the bulk concentration starts is enlarged in Figure 2. It can be seen that the polymer density exhibits a maximum, which is too small to be visible on the scale of Figure 1. The amplitude of the oscillations decays quickly with increasing distance z from the surface. The decay length, measured for the range of order in the polymer solution caused by the surface,¹⁹ is independent of solvent size and concentration, as seen in Figure 2a and b. The decay length has the order of R_g , the radius of gyration of polymer coils, implying that the bump arises from correlations between polymer coils.²⁰ By analogy with hard-sphere fluids, the oscillatory behavior in segment density is associated with the liquidlike layering of polymer coils near the surface. The maximum amplitude dictated by the solid line in Figure 2a is the same as the corresponding case in ref 19. Increasing the solvent size will amplify the oscillation, and the position of the maximum amplitude shifts away from the planar wall. One can see that the amplitude decreases strongly with increasing concentration. An explanation is that the increasing overlap of polymer coils with increasing concentration suppresses inhomogeneities in the density profile.¹⁹

Depletion thickness δ is defined as the zeroth moment of the density profile, which takes the form^{11,14}

$$\delta = \int_0^\infty [1 - \rho(z)] dz \quad (8)$$

Figure 3 shows the dependence of the depletion thickness on the relative solvent size. At conventional solvent size, viz., $\alpha = 0.01$, the depletion thickness δ hardly changes when varying χN from 0 to 5 for $\phi_p^0 = 0.3$ and $\phi_p^0 = 0.7$. As shown in Figure 3, it is a well-known fact that the depletion effect is favored in dilute and semidilute solutions rather than in more concentrated solutions. One can also see that, for both semidilute and concentrated solutions, the depletion thickness δ increases with decreasing solvency (increasing χN). It can be easily understood by considering the decreasing osmotic pressure of the solution induced by less good solvent.¹¹ This tendency is more pronounced at large solvent size, resulting in a broad depletion zone and a great value of δ . In summary, the depletion interaction is strengthened in less good solvent with large molecular volume.

To elucidate the interesting behavior arising from solvent molecules with large size, we provide insight into the free energies of the solution, including entropic contributions and enthalpic interaction. The polymer entropic free energy is described by F_p as follows:

$$F_p = -\phi_p^0 \ln \left(\frac{Q_p}{\phi_p^0 V} \right) - \frac{1}{V} \int d\mathbf{r} w_p(\mathbf{r}) \phi_p(\mathbf{r}) \quad (9)$$

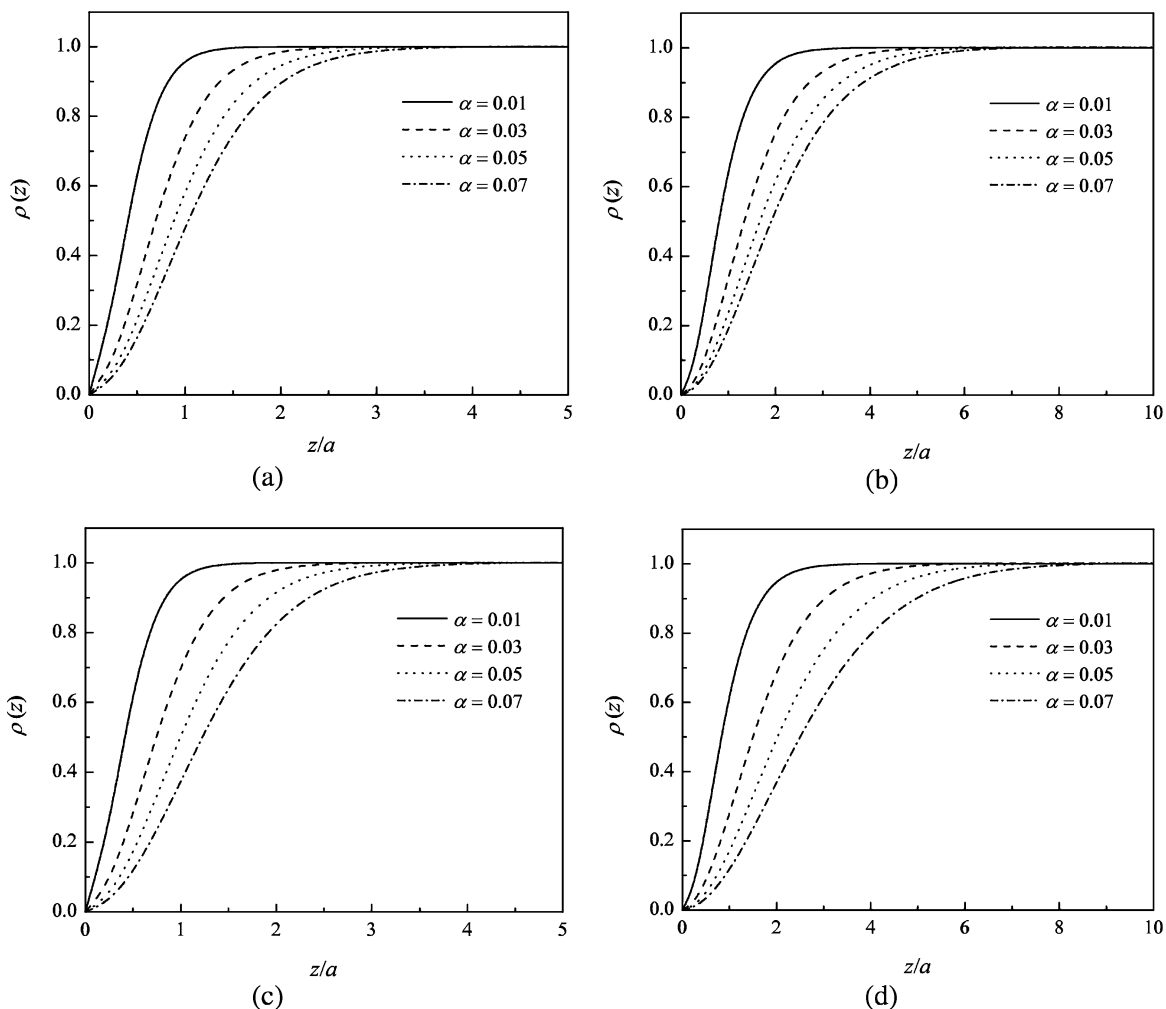


Figure 1. Reduced polymer density profiles $\rho(z) = \phi(z)/\phi_p^0$ in the solvent with different sizes ($\alpha = 0.01$, solid; $\alpha = 0.03$, dash; $\alpha = 0.05$, dot; $\alpha = 0.07$, dash-dot) vs the distance to the surface. (a) $\phi_p^0 = 0.7$, $\chi N = 0$; (b) $\phi_p^0 = 0.3$, $\chi N = 0$; (c) $\phi_p^0 = 0.7$, $\chi N = 5$; and (d) $\phi_p^0 = 0.3$, $\chi N = 5$.

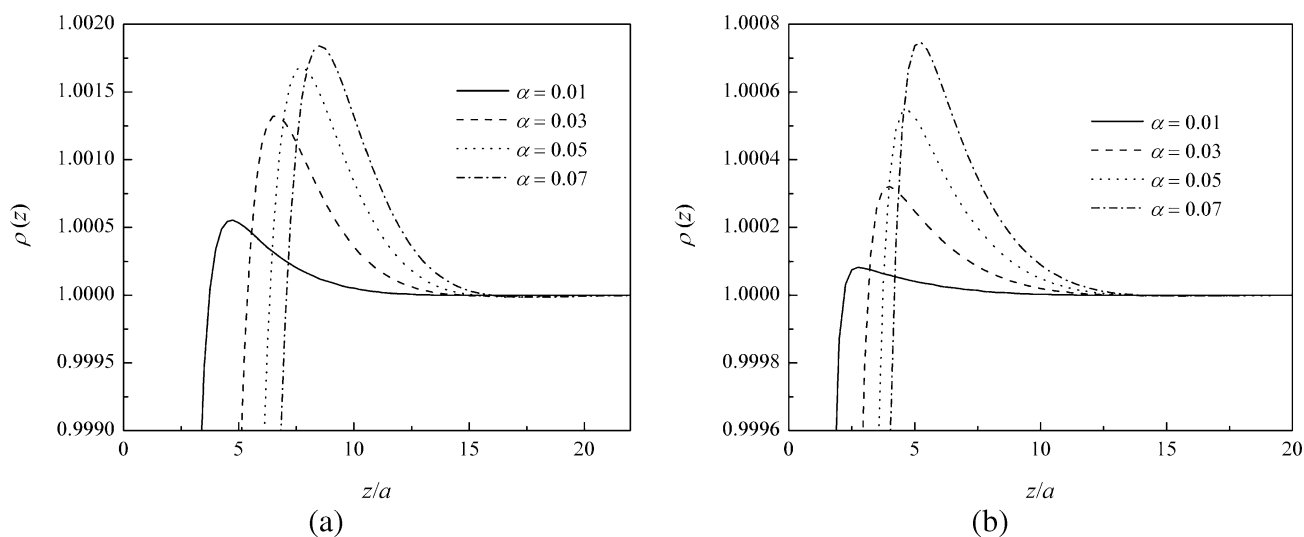


Figure 2. Oscillatory behavior of the polymer density profiles near the hard wall. Note the enlarged scale of the vertical axis. (a) $\phi_p^0 = 0.3$, $\chi N = 0$; (b) $\phi_p^0 = 0.7$, $\chi N = 0$.

F_s accounts for solvent entropic contributions to the free energy

$$F_s = -\frac{1 - \phi_p^0}{\alpha} \ln \left[\frac{Q_s \alpha}{(1 - \phi_p^0)V} \right] - \frac{1}{V} \int d\mathbf{r} w_s(\mathbf{r}) \phi_s(\mathbf{r}) \quad (10)$$

The term F_e details the enthalpic interactions between the

polymers and the solvent molecules

$$F_e = \frac{1}{V} \int d\mathbf{r} \chi N \phi_p(\mathbf{r}) \phi_s(\mathbf{r}) \quad (11)$$

Therefore, the total free energy of the system is $F_{\text{tot}} = F_p +$

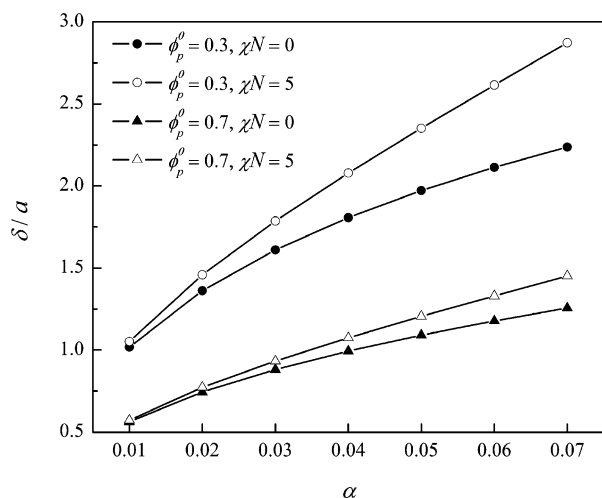


Figure 3. Dependence of depletion thickness δ reduced by a on the relative solvent size α .

$F_s + F_e$. The reference state is selected to be the state where the solvent volume equals the polymer segmental volume, i.e., $\rho_0^{-1} = v_s$.

In Figure 4, polymer entropic free energy F_p , solvent entropic free energy F_s , enthalpic interaction free energy F_e , and total free energy F_{tot} are shown as functions of solvent size at less good solvent condition ($\chi N = 5$). The polymer entropic free energy F_p decreases with increasing solvent size, see Figure 4a. The solvent with large molecular volume has great potential to drive the polymer from the hard wall, and thus, the polymer

can realize more configurations in the bulk to reduce its entropic free energy. We can see from Figure 4b that solvent molecules with large size will gain more translation entropy to lower the total free energy. It is evident that F_s contributes dominantly to the total free energy of the polymer solution, F_{tot} . The free energy consideration corroborates the simple physical origin of the depletion interaction.^{1,2,22,23} It is the competition between the translation entropy of the solvent and the configuration entropy of the polymer that results in the depletion of polymer segments from the hard wall. The total free energy persists all the way down when increasing the size of the solvent molecules. We also do the calculations with different polymer chain lengths. Shown in Figure 5 is the total free energy as a function of the relative solvent size. A closer look at Figure 4d and Figure 5 reveals that the free energy significantly decreases, as the solvent volume is up to sixfold larger than that of a segment. We term the solvent with this range in volume as a “middle-sized solvent”, which is inspired by the experimental results of Xue et al.^{24–27} It should be noted that, when the solvent size becomes even larger and comparable to the coil size, the solution should be a polymeric blend containing “fillers” and tends to phase separate, as is beyond our consideration.

As stated in the Introduction, the solvent with large molecular volume has received considerable attention. Much of the work of Xue et al.^{24–27} has been devoted to the exploration of the reduced entanglement and enhanced crystallizability of polymer chains in solvents with large molecular volumes, such as poly(ethylene glycol) (PEG) oligomers or dioctyl phthalate (DOP). Huber and co-workers²⁸ recently carried out an experiment on

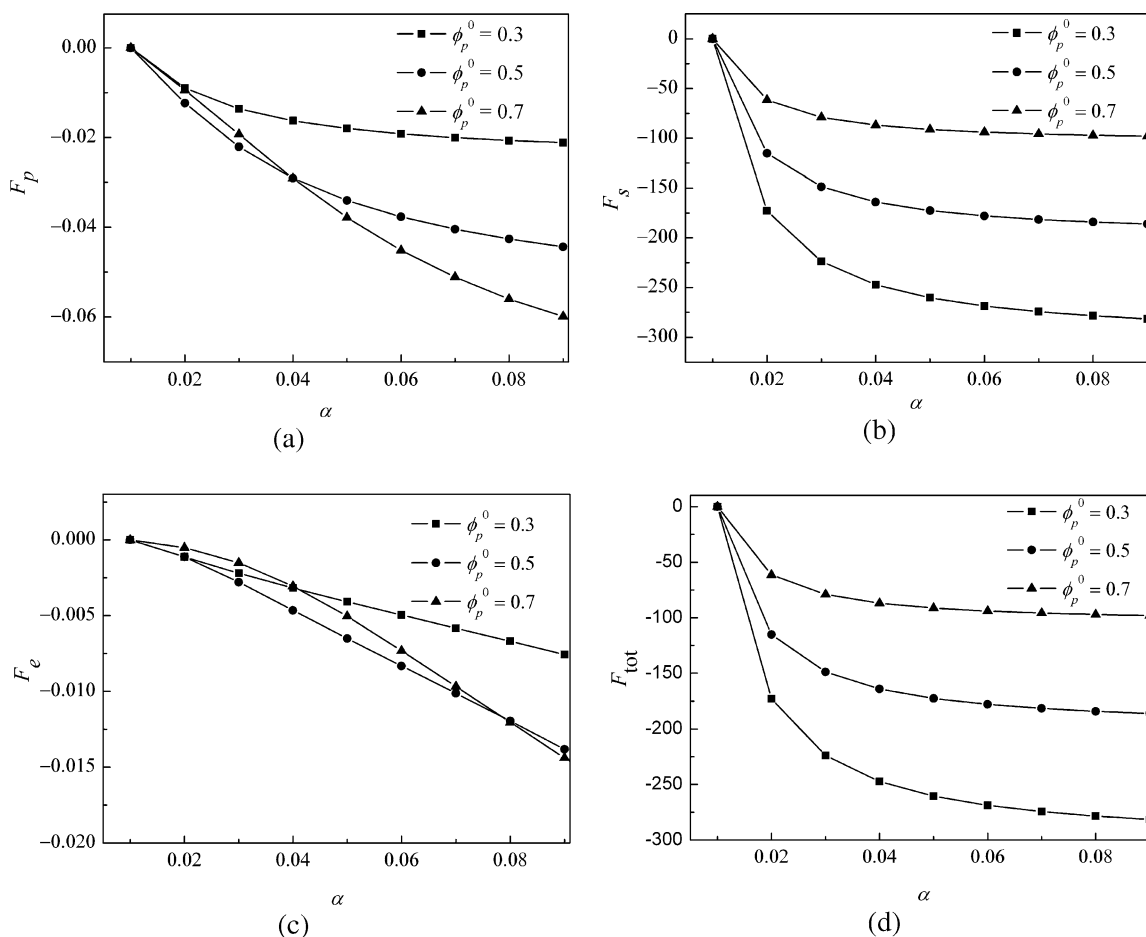


Figure 4. (a) Polymer configuration free energy F_p , (b) solvent translation free energy F_s , (c) enthalpic interaction energy F_e , and (d) total free energy F_{tot} as a function of the solvent size α for $\phi_p^0 = 0.3$ (solid), 0.5 (dash), and 0.7 (dot) at $\chi N = 5$.

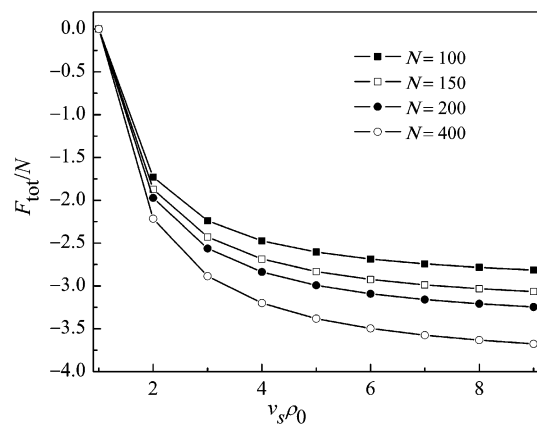


Figure 5. Total free energy F_{tot} reduced by polymer chain length N vs size ratio of solvent molecule to polymer segment for $\phi_p^0 = 0.3$ and $\chi N = 0$.

a polystyrene–silsesquioxane–toluene model system, where silsesquioxane (SILS) serves as a sub-colloidal or nanosized solvent. Light scattering and small-angle neutron scattering measurements for the mixture indicated a zone depleted of SILS. Our SCFT results bear some analogy to the above experimental investigations. A straightforward consideration should be as follows: Solvent molecules with increasing volume cannot evenly distribute in the solution because they are excluded from the center of the polymer coils, leading to a depletion zone; a partially ordered structure of polymer coils²⁹ will somewhat be formed to provide more free volume accessible to the solvent molecules. The depletion interaction mediated by solvent size is considered to represent the first principles of the mode of action of PEG or DOP used for obtaining disentangled chains with promoting crystallizability. We have to stress that our SCFT results can at best reflect part of the experiments because of the solvophobic effect involved.

Conclusion

We performed SCFT study on the solvent size effect of the depletion interaction between polymer coils and a hard wall. By varying polymer concentrations and solvencies, the depletion profile and the depletion thickness were calculated, revealing that the depletion effect is strong in semidilute solution with less good solvent. When increasing the solvent size, we found that solvents with large molecular volume intensify the depletion effect. On the basis of the free energy calculation, we term the solvent with volume about 1–6 times that of a single polymer segment as a “middle-sized solvent”. The translation free energy of the middle-sized solvent outweighs the polymer configuration free energy and the mutual interaction energy. The strengthened depletion effect is attributable to the significant gain in translation entropy of the added middle-sized solvent. It is believed that the depletion interaction mediated by solvent size is related to the improved crystallizability and/or partially ordered structure of polymer coils prepared from the solution

with large solvent molecules, although further experimental investigations are needed.

Another point we shall note is the amplified density oscillation induced by the middle-sized solvent. Increasing the solvent size will enlarge the amplitude of the density oscillation, and the position of the maximum amplitude shifts away from the planar wall. The decay length of the oscillations is independent of solvent size and has the order of R_g . It can be concluded that the liquidlike ordering localizes within a range of R_g near the hard wall, and the added middle-sized solvent enhances such ordering. The physical background behind the different positions of the maximum is not yet fully understood, but our observations suggest that it is related to the thickness of the depletion layer.¹⁹

Acknowledgment. We gratefully acknowledge financial support from National Natural Science Foundation of China (no. 20504013, 90403013, and 50533020), Nanjing University Talent Development Foundation (no. 0205004107), and Natural Science Foundation of Nanjing University (no. 0205005216).

References and Notes

- (1) Asakura, S.; Oosawa, F. *J. Chem. Phys.* **1954**, *22*, 1255.
- (2) Asakura, S.; Oosawa, F. *J. Polym. Sci.* **1958**, *33*, 183.
- (3) Vrij, A. *Pure Appl. Chem.* **1976**, *48*, 471.
- (4) Mao, Y.; Cates, M. E.; Lekkerkerker, H. N. W. *J. Chem. Phys.* **1997**, *106*, 3721.
- (5) Meijer, E. J.; Frenkel, D. *J. Chem. Phys.* **1994**, *100*, 6873.
- (6) Bates, M. A.; Frenkel, D. *Phys. Rev. E* **2000**, *62*, 5225.
- (7) Tuinier, R.; Rieger, J.; de Kruif, C. G. *Adv. Colloid Interface Sci.* **2003**, *103*, 1.
- (8) Eisenriegler, E. *J. Phys.: Condens. Matter* **2000**, *12*, A227.
- (9) de Gennes, P. G. *Scaling concepts in polymer physics*; Cornell University Press: Ithaca, New York, 1979.
- (10) Joanny, J. F.; Leibler, L.; de Gennes, P. G. *J. Polym. Sci. A* **1979**, *17*, 1073.
- (11) Fleer, G. J.; Skvortsov, A. M.; Tuinier, R. *Macromolecules* **2003**, *36*, 7857.
- (12) Fleer, G. J.; van Male, J.; Johnner, A. *Macromolecules* **1999**, *32*, 825.
- (13) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
- (14) Tuinier, R.; Fleer, G. J. *Macromolecules* **2004**, *37*, 8754.
- (15) Naughton, J. R.; Matsen, M. W. *Macromolecules* **2002**, *35*, 5688.
- (16) Martin, J. I.; Wang, Z.-G. *J. Phys. Chem.* **1995**, *99*, 2833.
- (17) Drolet, F.; Fredrickson, G. H. *Phys. Rev. Lett.* **1999**, *83*, 4317.
- (18) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727.
- (19) van der Gucht, J.; Besseling, N. A. M.; van Male, J.; Stuart, M. A. C. *J. Chem. Phys.* **2000**, *113*, 2886.
- (20) Bolhuis, P. G.; Louis, A. A.; Hansen, J. P.; Meijer, E. J. *J. Chem. Phys.* **2001**, *114*, 4296.
- (21) Maassen, R.; Eisenriegler, E.; Bringer, A. *J. Chem. Phys.* **2001**, *115*, 5292.
- (22) Yodh, A. G.; Lin, K. H.; Crocker, J. C.; Dinsmore, A. D.; Verma, R.; Kaplan, P. D. *Philos. Trans. R. Soc. London, Ser. A* **2001**, *359*, 921.
- (23) Poon, W. C. K. *J. Phys.: Condens. Matter* **2002**, *14*, R859.
- (24) Chen, J.; Xue, G.; Li, Y. *Macromolecules* **2001**, *34*, 1297.
- (25) Sun, Q.; Zhou, D.; Wang, X.; Xue, G. *Macromolecules* **2002**, *35*, 7089.
- (26) Zhou, D. S.; Li, L.; Che, B.; Cao, Q.; Lu, Y.; Xue, G. *Macromolecules* **2004**, *37*, 4744.
- (27) Zhou, D. S.; Li, L. A.; Li, Y. Q.; Zhang, J.; Xue, G. *Macromolecules* **2003**, *36*, 4609.
- (28) Kramer, T.; Schweins, R.; Huber, K. *Macromolecules* **2005**, *38*, 151.
- (29) Snir, Y.; Kamien, R. D. *Science* **2005**, *307*, 1067.