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Effect of polydispersity on the depletion interaction in nonadsorbing polymer solutions

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The effect of polymer polydispersity on the depletion interaction between two plates immersed in a nonadsorbing polymer solution is studied by self-consistent-field theory. The depletion potential is calculated numerically for the Schulz molecular weight distribution. The results show that as the two plates approach the polymers with different chain lengths are excluded from the gap gradually for conformational entropy penalty, and the range of the depletion potential increases and the depth of the potential decreases with increasing polydispersity. For the case of two large spheres the Derjaguin approximation is used to study the effect of polydispersity. The result shows that the polydispersity has little effect on the contact potential. However, it induces more broad interaction than the monodisperse polymers.

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I. INTRODUCTION

The depletion effect between colloidal particles induced by nonadsorbing polymers attracts more and more attention recently due to its importance in biological and industrial applications, such as the phase separation of polymer-colloid mixtures, colloidal suspensions flocculation and protein crystallization [1,2]. From a theoretical viewpoint, it is valuable to investigate the conformational change of polymers in a strongly confined state when depletion occurs. In practical applications the depletion interaction possesses an outstanding feature, or, it can be tuned easily. We can control the range and the strength of the attractive depletion force between the colloidal particles by varying the characteristic of the added polymers, which have pronounced effects on the phase diagram of polymer-colloid mixtures.

Most studies focused on monodisperse polymers because of their simplicity [3–11]. However, in practice polymers are polydisperse and possess a distribution of molecular weight, which has a quantitative impact on the depletion interaction. In a dilute polymer solution of monodisperse polymers, the range of the depletion interaction is the same as the radius of gyration of the polymers, which is the characteristic length of the system. When the distance between the two plates (or spheres, etc.) is smaller than the size of the polymers, the polymers escape from the gap between the two objects to get more conformational and translational entropy. Thus, there exists a difference in osmotic pressure between the inside and the outside of the gap, which induces an attractive interaction and pushes the plates (or spheres) together. However, in the case of polydisperse polymers, there is no unique characteristic length in the system. As two objects approach, the penalty of entropy for longer chains is more than that for shorter chains, and the longer chains will move out from the gap first and then the shorter chains will move out gradually. We can expect that the range of the depletion interaction will be larger than that of monodisperse polymers. In semidilute solutions, polymers with different chain length entangle each other. In this case the correlation length (or the mesh size) of the solution is the most important quantity [12], and the polydispersity hardly affects the properties of the solution. Although in the depletion case, where the polymers with different lengths exhibit different behaviors for the spatial confinement, it can be expected that the overall effect of polydispersity is rather weak.

The common method is to treat polydisperse polymers as polydisperse penetrable hard spheres [13–16]. This oversimplified model can catch the main point of polydispersity, however, the material characteristic of chain connectivity is neglected and the interaction between polymer coils is crude. As a result, the description of the obtained depletion force is qualitative and not accurate. Tuinier and Petukhov extend the force method to calculate the interaction between two plates, and used the adsorption method with the product-function approximation to investigate the effect of polydispersity for two spheres in an ideal polymer solution [17]. The polydispersity was taken into account by averaging the correlated quantities with the distribution function. However, their method is phenomenological and cannot be applied to real polymers with excluded volume. On the other hand, we noticed that in the study of equilibrium polymers at interface, van der Gucht *et al.* found that the exact analytical solutions are possible for the exponential distribution of polymers

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length [26,27]. This distribution is a special case ($k=1$) in the Schultz distribution of the polymer chain lengths, and the corresponding results can be comparable.

The self-consistent-field theory (SCFT) and the corresponding numerical methods provide a useful tool in the studies of inhomogeneous polymers and complex fluid interfaces [18–21]. In polymer solutions the approximation of SCFT is proved to be successful in dealing with the homopolymer-solvent system, although the mean-field approximation breaks down in some cases where the fluctuation is enormous, such as in semidilute solutions with good solvents [22]. In this paper, we use the method developed by Fredrickson and Sides [23] to study the effect of polydispersity on the depletion interaction between two plates. In this method, the realistic continuous distribution of chain lengths can be incorporated into the SCFT models of polymer solutions. The equilibrium structure of the system, including the density profile of each component in the chain length distribution, can be calculated by an effective numerical method. We choose the Schulz distribution as the distribution function of polymer chain lengths. The merit of this method is that it is based on a microscopic description and that the polymer polydispersity is taken into account properly in the partition function. The developed formula will be exact and the results will be accurate enough even when we take some approximations in the calculation of the integrals appearing in the theory. The contribution from the chains with different length must be calculated accurately in view of the subtle effect on the depletion interaction. In order to compare with the monodisperse case, the polydisperse polymer solutions have the same bulk concentrations and the same number average chain length as the monodisperse polymer solutions.

The paper is organized as follows. In Sec. II we present the SCFT of polydisperse polymer solutions in the grand canonical ensemble frame and the corresponding method for solving the self-consistent-field equations for the Schulz molecular weight distribution. In Sec. III we present the results and discussions. In Sec. IV we give the conclusions.

II. THEORY

We consider a polydisperse polymer solution between two parallel plates to be in equilibrium with a reservoir. The distance between two plates is d, the area of each plate is A, and hence the volume of system is $V=Ad$. We adopt the grand canonical ensemble to describe the system. The grand partition function for the polydisperse polymer-solvent mixture is defined by

$$\Xi = \sum_{n_1,n_2,\ldots,n_N,\ldots=0}^{\infty} \sum_{n_s=0}^{\infty} e^{n_1\mu_1+n_2\mu_2+\cdots+n_N\mu_N+\cdots} \times e^{n_s\mu_s} Z(n_1,n_2,\ldots,n_N,\ldots;n_s). \tag{1}$$

In this expression, n_N and μ_N denote the number and the chemical potential of polymer chains with chain length N, respectively. n_s and μ_s denote the number and the chemical potential of solvent molecules, respectively. In the following, we take the statistical segment length of the polymer, b, as the unit of length, and k_BT as the unit of energy. For simplicity, we assume that the solvent molecules occupy the same volume as the monomers (statistical segments) of the polymer. The average monomer density is given by $\rho_0=1/b^3$. Z is the partition function for the system with fixed particle numbers $\{n_1,n_2,\ldots,n_N,\ldots;n_s\}$ given by

$$Z(n_1,n_2,\ldots,n_N,\ldots;n_s) = \frac{\text{const}}{n_s!\prod_i n_i!} \int \prod_j [d\mathbf{r}_s^j] \mathcal{D}\{\mathbf{R}_p\} \delta[\hat{\rho}_p(\mathbf{r}) + \hat{\rho}_s(\mathbf{r}) - \rho_0] \exp[-U_0(\mathbf{R}_p) - W(\mathbf{R}_p,\mathbf{r}_s)], \tag{2}$$

where the integration $\mathcal{D}\{\mathbf{R}_p\}$ denotes all path integrals over all possible conformations of the polymer chains. The integral of the momentum has been carried out and included in the constant term. We ignore the contribution from the kinetic energy since it has no impact on the thermodynamic properties. U_0 is the "Edwards Hamiltonian" of the polymers given by

$$U_0(\mathbf{R}_p) = \frac{3}{2b^2}\sum_i \int_0^{N_i} dt \left(\frac{\partial}{\partial t}\mathbf{R}_\mathbf{i}(t)\right)^2, \tag{3}$$

where the sum of i runs over all the chains, while the total number of chains is $n_1+n_2+\cdots+n_N+\cdots$. N_i is the chain length of the ith chain. The delta function embodies the incompressible condition of the polymer solution. The local densities are given by $\hat{\rho}_p(\mathbf{r})=\Sigma_i\int_0^{N_i}dt\,\delta[\mathbf{r}-\mathbf{R}_i(t)]$ and $\hat{\rho}_s(\mathbf{r})=\Sigma_{j=1}^{n_s}\delta[\mathbf{r}-\mathbf{r}_s(j)]$. $W(\mathbf{R}_p,\mathbf{r}_s)$ is the intermolecular potential. In terms of the local densities W can be described by a simple form

$$W(\mathbf{R}_p,\mathbf{r}_s) = b^3\chi \int d\mathbf{r}\,\hat{\rho}_p(\mathbf{r})\hat{\rho}_s(\mathbf{r}), \tag{4}$$

where χ is the Flory-Huggins parameter.

Equation (1) includes a two-body interaction. A Hubbard-Stratonovich transformation is introduced to decouple the two-body interaction. By defining the volume fraction (polymer concentration) $\hat{\phi}(\mathbf{r})=\hat{\rho}(\mathbf{r})/\rho_0$, we have $W=\rho_0\chi\int d\mathbf{r}\,\hat{\phi}_p(\mathbf{r})\hat{\phi}_s(\mathbf{r})$. Following Helfand [18], we can obtain the following expression of Ξ in terms of a functional integral representation:

$$\Xi = \int \mathcal{D}\phi_p \mathcal{D}\phi_s \mathcal{D}\omega_p \mathcal{D}\omega_s \mathcal{D}\eta \exp\left(\int d\mathbf{r}[\omega_p \phi_p + \omega_s \phi_s - \chi \phi_p \phi_s - \eta(\phi_p + \phi_s - 1)] \right) \times \sum_{n_s=0}^{\infty} \frac{(e^{\mu_s} Q_s)^{n_s}}{n_s!} \sum_{n_1=0}^{\infty} \frac{(e^{\mu_1} Q_1)^{n_1}}{n_1!} \sum_{n_2=0}^{\infty} \frac{(e^{\mu_2} Q_2)^{n_2}}{n_2!} \cdots \sum_{n_N=0}^{\infty} \frac{(e^{\mu_N} Q_N)^{n_N}}{n_N!} \cdots = \int \mathcal{D}\phi_p \mathcal{D}\phi_s \mathcal{D}\omega_p \mathcal{D}\omega_s \mathcal{D}\eta \exp(-G), \tag{5}$$

in which

$$G = \int d\mathbf{r}[\chi \phi_p \phi_s - \omega_p \phi_p - \omega_s \phi_s + \eta(\phi_p + \phi_s - 1)] - \sum_N e^{\mu_N} Q_N[\omega_p] - e^{\mu_s} Q_s[\omega_s]. \tag{6}$$

The quantity $Q_N[\omega_p]$ is the partition function of a single polymer chain with length N in a potential field ω_p and is given by

$$Q_N[\omega_p] = \int \mathcal{D}\mathbf{R} \exp\left[-\frac{3}{2b^2} \int_0^N dt \left(\frac{\partial}{\partial t} \mathbf{R}(t) \right)^2 - \int_0^N dt \omega_p[\mathbf{R}(t)] \right]. \tag{7}$$

Similarly the partition function of a solvent molecule in a field ω_s is given by

$$Q_s = \int d\mathbf{r} e^{-\omega_s(\mathbf{r})}. \tag{8}$$

Notice that in Eq. (6), the sum of N is only the sum over the different lengths (corresponding to different species). Using the continuous distribution of chain length N to replace the discrete distribution, the sum of N can be replaced by the integral over chain lengths and the second term in G becomes $\int_0^\infty dN e^{\mu_N} Q_N[\omega_p]$.

Using the saddle point approximation, the mean-field grand potential can be obtained. The self-consistent-field equations can be derived by the minimization of G with respect to ϕ_s, ϕ_p, ω_s, ω_p, and η. The results are as follows, respectively,

$$\omega_s(\mathbf{r}) = \chi \phi_p(\mathbf{r}) + \eta(\mathbf{r}), \tag{9}$$

$$\omega_p(\mathbf{r}) = \chi \phi_s(\mathbf{r}) + \eta(\mathbf{r}), \tag{10}$$

$$\phi_s(\mathbf{r}) = e^{\mu_s} e^{-\omega_s(\mathbf{r})}, \tag{11}$$

$$\phi_p(\mathbf{r}) = \int_0^\infty dN \left(e^{\mu_N} \int_0^N dt q_p(\mathbf{r},t) q_p(\mathbf{r},N-t) \right), \tag{12}$$

$$\phi_p(\mathbf{r}) + \phi_s(\mathbf{r}) = 1. \tag{13}$$

The propagator $q_p(\mathbf{r},N)$ satisfies the modified diffusion equation

$$\frac{\partial}{\partial t} q_p(\mathbf{r},t) = \frac{b^2}{6} \nabla^2 q_p(\mathbf{r},t) - \omega_p(\mathbf{r}) q_p(\mathbf{r},t) \tag{14}$$

with the initial condition $q_p(\mathbf{r},0)=1$ and the boundary conditions $q_p(\mathbf{r},t)=0$ at the surfaces of the plates. The partition function of the single chain $Q_N[\omega_p]$ can be evaluated by $Q_N[\omega_p]=\int d\mathbf{r} q(\mathbf{r},N)$. The volume fraction of monomers contributed by the chains with length N is given by

$$\phi_p(\mathbf{r},N) = e^{\mu_N} \int_0^N dt q_p(\mathbf{r},t) q_p(\mathbf{r},N-t). \tag{15}$$

Obviously, $\phi_p(\mathbf{r})=\int_0^\infty dN \phi_p(\mathbf{r},N)$. Equations (9)–(14) constitute a set of self-consistent-field equations, which can be solved numerically. In the above equations the chemical potentials μ_N and μ_s are unknown and can be determined from the bulk phase of the reservoir.

Consider a bulk system, in which the total volume is V and the total number of polymers chains is n_t. The chain length distribution function is denoted by $f(N)$. The quantity of $n_t f(N) dN$ represents the number of chains in the bulk phase with length between N and $N+dN$. The (number) average chain length is given by $\bar{N}=\int_0^\infty dN N f(N)$. The bulk concentration satisfies

$$\phi_p^0 = \frac{n_t b^3}{V} \int_0^\infty dN N f(N). \tag{16}$$

In the bulk homogeneous phase the polymer concentration and the mean-field potentials are constants denoted by subscript 0. Giving the polymer bulk concentration ϕ_p^0 of the reservoir, we can calculate the chemical potentials. Because the chemical potentials μ_N and μ_s are dependent on each other, we can choose $\mu_s=0$. From Eqs. (9)–(11) and Eq. (13), we obtain

$$\omega_s^0 = -\ln(1 - \phi_p^0), \tag{17}$$

$$\omega_p^0 = -\ln(1 - \phi_p^0) + \chi(1 - 2\phi_p^0). \tag{18}$$

Solving Eq. (14) with a constant potential ω_p^0, we can obtain $q_p(t)=e^{-\omega_p^0 t}$. Equation (12) can be expressed by

$$\phi_p^0 = \int_0^\infty dN e^{\mu_N} N e^{-\omega_p^0 N}. \tag{19}$$

Since Eqs. (16) and (19) must be equal, we have

$$\frac{n_t b^3}{V}\int_0^\infty dN N f(N) = \int_0^\infty dN e^{\mu_N} N e^{-\omega_p^0 N}. \qquad (20)$$

In fact we can find that for any up limit in the above integral Eq. (20) always holds. Combining Eq. (16) and Eq. (20) we can obtain

$$e^{\mu_N} = \frac{\phi_p^0 f(N)}{\int_0^\infty dN N f(N)} e^{\omega_p^0 N} = \frac{\phi_p^0 f(N)}{\bar{N}} e^{\omega_p^0 N}. \qquad (21)$$

Substituting these results into Eq. (6) yields the grand potential per unit volume in the homogeneous state as

$$g_0 = \frac{G_0}{V} = \ln(1-\phi_p^0) + \chi(\phi_p^0)^2 - \frac{\phi_p^0}{\bar{N}} - (1-\phi_p^0). \qquad (22)$$

Giving the chemical potentials, the polymer concentration and the grand potential can be calculated. As a realistic chain length distribution we adopt the Schulz distribution

$$f(N) = \frac{k^k}{\bar{N}\Gamma(k)}\left(\frac{N}{\bar{N}}\right)^{k-1} e^{-k(N/\bar{N})}, \qquad (23)$$

k is the polydispersity index. A smaller k corresponds to a more polydisperse distribution.

Using the transformation $M = kN/\bar{N}$, the total concentration of polymer segments is written by

$$\phi_p(\mathbf{r}) = \int_0^\infty dM \widetilde{\phi_p}(\mathbf{r},M). \qquad (24)$$

Here, the partial volume fraction coming from the chains with length M is

$$\widetilde{\phi_p}(\mathbf{r},M) = \frac{\phi_p^0 e^{\omega_p^0 \bar{N}M/k}}{\bar{N}} \frac{e^{-M}M^{k-1}}{\Gamma(k)} \times \int_0^{\bar{N}M/k} dt q_p(\mathbf{r},t) q_p(\mathbf{r},\bar{N}M/k - t). \qquad (25)$$

We can define the average volume fraction of polymers as a function of the separation of two plates, d, given by

$$\langle \phi_p(d)\rangle = \frac{1}{d}\int_0^d dx \phi_p(x). \qquad (26)$$

The grand potential of the system is

$$G = \int d\mathbf{r}[\chi\phi_p\phi_s - \omega_p\phi_p - \omega_s\phi_s] - \frac{\phi_p^0 \bar{N}}{\Gamma(k)}\int_0^\infty dM e^{\omega_p^0 \bar{N}M/k} e^{-M} M^{K-1} Q_{\bar{N}M/k}[\omega_p] - e^{\mu_s} Q_s[\omega_s]. \qquad (27)$$

In Eq. (25) the indefinite integrals of M can be performed by using a Gauss-Laguerre quadrature formula proposed by Fredrickson and Sides [23],

$$\int_0^\infty dM e^{-M} F(M) \approx \sum_{i=1}^{n_G} g_i F(M_i), \qquad (28)$$

where the abscissas M_i and weights g_i are tabulated by Abramowitz and Stegun [24]. This formula is efficient and converges quite rapidly. We find that only eight points ($n_G = 8$) are sufficiently accurate for all cases.

In order to calculate the depletion potential between two plates (per unit area), we define the excess grand potential with respect to homogeneous state as

$$\Omega(d) = G(d) - G_0. \qquad (29)$$

The pair potential between two plates (per unit area) at a separation d is given by

$$W(d) = \Omega(d) - \Omega(\infty). \qquad (30)$$

The iterative method is used to find the self-consistent solutions. The Crank-Nicholson semi-implicit scheme is employed to solve the modified diffusion equation. The longest chain has a length coinciding with the largest Gauss-Laguerre abscissa M_{n_G}.

III. RESULTS AND DISCUSSIONS

The mean-field theory is applicable for polymer solutions near the Θ point. In this paper, we restrict ourselves to ideal solutions, or, $\chi = 0.5$. The solvency will affect the depletion character, however, it has no qualitatively different effect. The effect of solvents with different solvency have the same trend on the depletion interaction [25]. Also, as we discussed in the introduction, in the semidilute solution the effect of the polydispersity is rather weak. Thus, we only consider the dilute case.

Throughout this paper, the number average chain length of the polydisperse polymers is $\bar{N} = 200$. To be a contrast, we also take $N = 200$ in the monodisperse polymer solution. All the distances are normalized by the radius of gyration, or $R_{g0} = b\sqrt{\bar{N}/6}$.

We first consider a polymer solution near a single plate. Being in a confined state, the polymers avoid approaching the surface for seeking more conformational entropy. There exists a depletion region, in which the polymer-monomer concentration is lower than the bulk concentration. The characteristic of depletion depends on the conformational entropy of polymers, which is governed by the chain length N. Thus, the polymers with different length will have different effects on the characteristic of depletion. In Fig. 1 we give the polymer-monomer concentration of monodisperse and polydisperse polymers in solution near a single plate. The depletion region is about $2R_{g0}$. The result shows that the effect of polydispersity will broaden the range of the depletion region and the broader the chain length distribution is, the broader the depletion region is. Therefore, we can conclude that the longer chains have more contribution to the depletion.

Now, we investigate a polymer solution between two plates. This situation is different from that near a single plate. Besides the conformational entropy, the translational entropy also comes into play. An expected effect of polydispersity is

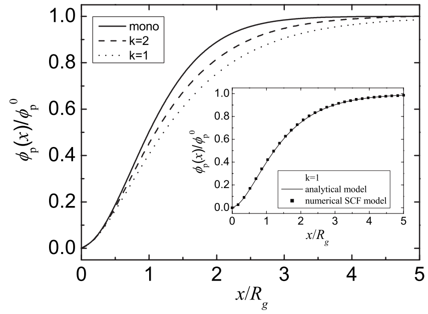

FIG. 1. Monomer volume fraction profiles of monodisperse and polydisperse polymers near a single plate. The parameters are taken as $\bar{N}=200$, $\phi_p^0=0.01$, $\chi=0.5$. The inset shows the comparison of the volume fraction profiles of the numerical SCFT calculation for the case of $k=1$ (symbols) and the analytical result (solid line).

on the local monomer concentration. In order to find how the chains with different length change in the region between two plates as the distance varies, we investigate the partial monomer concentration profiles changing with the distance d. In Fig. 2 we show the partial concentration profiles $\phi_p(x,N)$ for different d. Here, the parameters are chosen as $\chi=0.5$, $k=1$, $\phi_p^0=0.01$. We choose three typical chains with length $N_i=M_i\bar{N}$ coinciding with the first three Gauss-Laguerre abscissas for $n_G=8$: $M_1=0.170\,27$, $M_2=0.903\,70$, $M_3=2.251\,08$. The total monomer concentrations are also shown in those figures. If the separation between the two plates is large, the polymers with moderate length (M_2,M_3) contribute the main part of the monomers staying in the gap. As the separation decreases, the longer chains are preferentially excluded. Evidently, this is because the longer chains will lose more conformational entropy if they are in the gap. When $d=5b$, we can find that the main contribution of the polymers in the gap comes from the short chains, corresponding to M_1. The other polymers with longer length are hardly present in the gap.

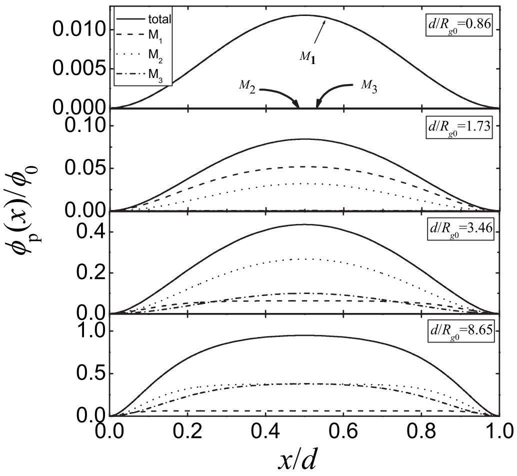

FIG. 2. The partial polymer volume fraction profiles $\phi_p(x,M_i)$ between two plates at four different separations $d/R_{g0}=0.86,1.73,3.46,8.65$ (corresponding to $d/b=5,10,20,50$, respectively), for the case of $\chi=0.5$, $\bar{N}=200$, and $k=1$. The reduced chain lengths, M_i, coincide with the first three Gauss-Laguerre abscissas for $n_G=8$: $M_1=0.170\,27$, $M_2=0.903\,70$, $M_3=2.251\,08$. The total monomer volume fraction $\phi_p(x)$ is also shown.

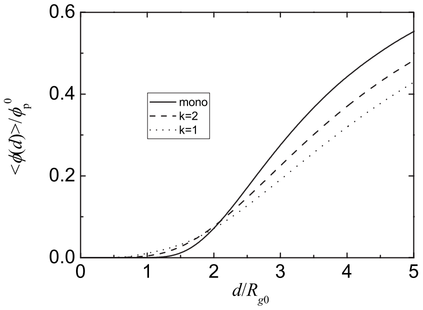

FIG. 3. The average monomer volume fraction profiles of monodisperse and polydisperse polymers in the gap as a function of the separation d. The parameters are taken as $\chi=0.5$, $\bar{N}=200$, $\phi_p^0=0.01$. Curves correspond to $k=1,2$ and monodisperse case.

Figure 3 gives the average volume fraction of monomers in the gaps as a function of the separation d for monodisperse and polydisperse polymers with $k=2$ and $k=1$. An interesting effect occurs for small separations. For $d>2R_{g0}$, the more disperse the polymer solution is, the lower the average monomer volume fraction is. For $d<2R_{g0}$, we find the opposite result. The effect comes from the fact that the short polymer chains can enter the gap more easily. The present result is the same as that of Tuinier and Petukhov [17].

Figure 4 gives the effect of polydispersity on the depletion interaction between two plates. With the increasing polydispersity the range of the interaction increases, while the depth of the potential decreases. The present result shows that the common conclusion, which states that the polydispersity makes the contact potential between two plates increase [16,17], is incorrect. Polydisperse polymer solutions include chains with different lengths, and the chains longer than $\bar{N}$ play a role even if the distance between the two plates is large. Thus, the range of the depletion interaction is broader in comparison with that for the monodisperse polymers. However, the effect of polydispersity is small.

As we mentioned in the introduction, if the chain length distribution is purely exponential, van der Gucht *et al.* actually obtained an exact analytical result [26,27]. This distribu-

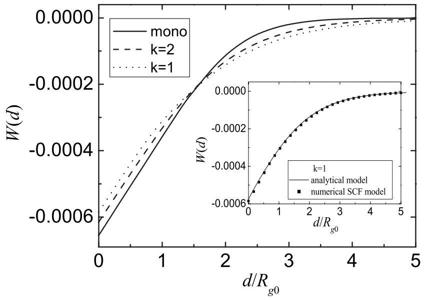

FIG. 4. The depletion potential between two plates as a function of the separation d for monodisperse case and polydisperse cases $(k=1,2)$. The parameters are taken as $\chi=0.5$, $\bar{N}=200$, $\phi_p^0=0.01$. The inset shows the comparison of the depletion potential obtained of the numerical SCFT calculation for the case of $k=1$ (symbols) and the analytical result (solid line).

tion corresponds to the case of $k=1$ in the present model, and we can compare our result for this case with theirs. For such an exponential distribution the Laplace transformation can be used to solve the propagator. The boundary condition of the propagator on the surface corresponds to $C\to\infty$ when the depletion of polymer occurs. Therefore, when two plates are infinitely far apart $(d\to\infty)$, the density of monomers near a single plate is given by [26,28]

$$\frac{\phi(x)}{\phi_p^0} = (1 - e^{-x/R_{g0}})^2.$$

The grand potential per unit area between two plates with a separation d is given

$$\Omega(d) = \sqrt{\frac{2}{3\bar{N}}}\phi_p^0 \tanh\left(\frac{d}{2R_{g0}}\right).$$

Thus, the depletion potential per unit area between two plates can be given by

$$W(d) = \Omega(d) - \Omega(\infty) = \sqrt{\frac{2}{3\bar{N}}}\phi_p^0\left[\tanh\left(\frac{d}{2R_{g0}}\right) - 1\right].$$

We can compare our numerical results with the analytical results given by the above expressions. The comparisons are shown in the insets of Figs. 1–4 for the volume fraction profiles and the depletion potential, respectively. One can find that the present SCFT calculation is in good agreement with the existing analytical results for the case of $k=1$.

It is useful to investigate the effect of polydispersity on two spheres, which relates to the stability of colloidal dispersions. In principle calculating the depletion potential between two spheres is possible using the SCFT in bispherical coordinates [29]. However, the procedure is rather complicated and it needs high performance computers because of the two-dimensional characteristic. Here, we adopt a simple method, namely the Derjaguin approximation [30], for large colloidal particles. In this approximation the force $f(D)$ between two spheres of radius R_c is related to the potential between two plates, $W(D)$, in the following way:

$$f(D) = \pi R_c W(D), \tag{31}$$

where D is the distance between the surfaces of the two spheres. Integrating the force yields the depletion potential $W^{\text{sph}}(D)$ between two large spheres

$$W^{\text{sph}}(D) = -\int_D^\infty f(x)dx = -\pi R_c\int_D^\infty W(x)dx. \tag{32}$$

The Derjaguin approximation is accurate when the spheres are large enough. Figure 5 gives the result. The depth of the interaction is hardly affected by the polydispersity, whereas the interaction range increases with increasing polydispersity. The polymer polydispersity has a more significant effect on the attractive interaction between two spheres than that between two plates. As a result the colloidal dispersions becomes more unstable. Thus, the polydispersity enhances the tendency of phase separation to polymer-colloid mixtures compared with monodisperse mixtures.

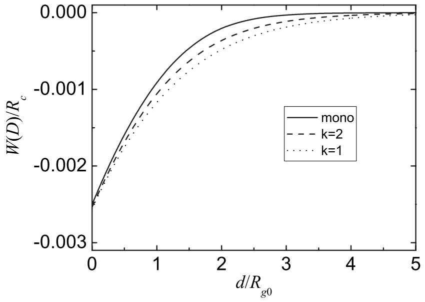

FIG. 5. The depletion potential between two large spheres as a function of the separation d for the monodisperse case and the polydisperse cases $(k=1,2)$. The parameters are taken as $\chi=0.5$, $\bar{N}=200$, $\phi_p^0=0.01$.

IV. CONCLUSION

We propose a SCFT based on a microscopic description to investigate the effect of polydispersity on the depletion interaction between two plates for nonadsorbing polymers. The continuous distribution of chain lengths can be incorporated into SCFT in the grand canonical ensemble. For the Schulz distribution an efficient numerical method, or Gauss-Laguerre quadrature formula, has been used to evaluate the total monomer volume fraction by approximating the continuous chain lengths distribution with a discrete distribution. The depletion interactions are calculated from the mean-field results of monomer concentrations and potential fields. Because of the conformational entropy the shorter polymer chains prefer to stay in the gap with the longer chains when the two plates approach. The present calculations show that the polydispersity increases the range of the potential between two parallel plates, while it decreases the depth of the potential. Also, the present numerical result for the case of $k=1$ is in good agreement with the analytical result obtained by van der Gucht *et al.* in the study of equilibrium polymers at the interface. Moreover, the Derjaguin approximation is used to evaluate the depletion potential between two large spheres. The effect of polydispersity increases the range of the interaction, but it has little impact on the contact potential between the two spheres. However, it increases the driving force towards phase separation. The present result also shows that polydisperse polymers have a weak effect on the depletion, whereas they can induce colloidal suspensions flocculation easier than monodisperse polymers.

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[28] Note that d, $\langle N_0\rangle$, R_0, and ρ_0 in Ref. [26] correspond to $d/2$, $\bar{N}$, R_{g0}, and ϕ_p^0 in the present model, respectively, and b and k_BT are the units of length and energy, respectively; one can easily obtain these results from the analytical results given in Table I in Ref. [26].

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