

## Free polymer in a colloidal solution

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We provide a statistical-mechanical theory for a system of free polymer molecules in a colloidal solution. It is shown that three-body terms are required to obtain the shape of the polymer and the depletion-layer profile even when the dispersion medium is a good solvent for the polymer molecule. A semiquantitative analysis based on the density profile suggests that the addition of trace amounts (dilute) of free polymer induces the formation of weak flocs.

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The interaction between colloidal particles in a dispersion medium is important in many diverse areas [1-3]. Since the colloidal particles (assumed to be spherical here) are typically large, the long-range van der Waals interaction can be strong enough to lead to flocculation even when the volume fraction of the macroparticle is small [1]. The two most commonly accepted methods for achieving stability between colloids are through electrostatic stabilization and steric stabilization [1]. In the former case ionizable groups in the colloidal particle yield a large surface charge when suspended in an appropriate dispersion medium and the resultant electrostatic repulsion between the colloidal particles (well described by the Derjaguin-Landau-Verwey-Overbeek theory) prevents flocculation. In the case of steric stabilization the colloidal particles are either coated with an adsorbed polymer or polymer molecules are grafted onto them. The adsorbed polymers or the grafted polymers act as steric "bumpers" and hence give rise to the required repulsive interaction.

In addition to the above-mentioned mechanisms, Feigin and Napper [4,5] suggested that colloidal solution can, in principle, be stabilized by dissolving nonionic polymer molecules into the colloidal solution. They used a combination of Monte Carlo method and Flory-Huggins theory of polymer solution to argue that stability arises because of depletion of the concentration of free polymer at the surface of particles when they approach one another. Feigin and Napper find that for values of  $r$ , which is the distance between colloidal particles, such that  $R_F < r < 2R_F$  ( $R_F$  being the Flory radius of the added free polymer molecule) the interaction between the particles is purely repulsive. At smaller values of  $r$  there is an attractive force [6].

Most of the theoretical work has focused on the properties of adsorbed polymer solutions confined between two parallel plates under both equilibrium and nonequilibrium conditions [7-10]. In this Rapid Communication we present a complete statistical-mechanical theory of a free polymer in the presence of colloidal solution consisting of spherical particles as a step towards a microscopic theory of polymer-colloid interaction in semidilute solution. The theory represents a unification of the techniques used in

polymer physics [11,12] as well as methods familiar in the description of molecular liquids [13,14]. In order to expose the salient features of the theory we confine ourselves to the effect of one long polymer on the colloidal solution. The theory for semidilute solution, which is most directly related to the description of depletion stabilization, is treated in detail elsewhere [15]. Nevertheless, we argue that the essential physics leading to the lack of depletion stabilization is already found in the current analysis.

The polymer-colloid mixture is a ternary system consisting of the polymer molecule, the colloidal particles, and the continuous solvent phase. In our theory we approximate this as a binary system in which the interaction potentials are assumed to be renormalized by the solvent. The effective Hamiltonian for the system can be written as

$$H = H_{c-c}(\{R_i\}) + H_p(r(s)) + U_{p-c}(r(s), \{R_i\}), \quad (1)$$

where  $H_p(r(s))$  is the Hamiltonian corresponding to the polymer molecule which is taken to be the Edwards [14] model including three-body interactions. The first term in Eq. (1) represents the Hamiltonian for the colloidal particles. Here we assume that the interaction between colloidal particles can be modeled using hard-sphere potential. It should be emphasized that our theory is not restricted to colloidal particles that behave like hard-sphere systems. The input to the theory is the excess density-density correlation function,  $\chi_{c-c}(r)$ , in the absence of the polymer molecules. Thus if the effective interaction between the colloidal particles is not hard-sphere like the appropriate  $\chi_{c-c}(r)$  for the given potential has to be computed. The last term in Eq. (1) represents the interaction between the polymer molecule and the colloidal particles suitably renormalized by the solvent.

The partition function for the polymer-colloid system is

$$Z(L) = \int d[r(s)] \int d\{R_i\} \exp(-H). \quad (2)$$

After performing the trace over the coordinates of the colloidal particles using the standard Ursell-Meyer expansion techniques  $Z(L)$  becomes [15]

$$Z(L) \propto \int dr_0 \int_{r(0)=0}^{r(L)=r_0} D[r(s)] \exp(-H_{\text{eff}}), \quad (3)$$

where

$$H_{\text{eff}} = \frac{3}{2l} \int_0^L ds \dot{r}^2(s) + \rho_c \hat{c}(0) + \frac{1}{2} \int_0^L ds_1 \int_0^L ds_2 W(r(s_1) - r(s_2)) \\ + \frac{\omega_3}{3} \int_0^L ds_1 \int_0^L ds_2 \int_0^L ds_3 \delta(r(s_1) - r(s_2)) \delta(r(s_2) - r(s_3)) \quad (4a)$$

with  $\omega_3$  being the coefficient of the threebody term. In Eq. (4)  $L$  is the length of the polymer,  $l$  is the effective Kuhn length of the monomer units,  $\rho_c$  is the number density of colloidal particles,  $\hat{c}(k)$  is the Fourier transform of a direct correlation function  $c(r)$  (a renormalized potential) between the polymer and the colloidal particle and

$$W(r) = \omega_2 \delta(r) - \int dR_1 \int dR_2 c(R_1) \chi_{c-c}(|R_1 - R_2|) \\ \times c(R_2 - r) \quad (4b)$$

where  $\omega_2$  is the strength of the excluded volume interaction. We assume that  $c(r)$  can be obtained using the reference interaction-site (RISM) integral equation which for the homopolymer case considered here is given by [13,14,16]

$$\rho_c h_{p-c}(|r - R|) = \int dR_1 \int dr_1 \omega(r - r_1) c(r_1 - R_1) \\ \times \chi_{c-c}(R_1 - R), \quad (5a)$$

where  $g_{p-c}(r) = h_{p-c}(r) + 1$  is the polymer-colloid site-site radial distribution function, and  $\omega(r)$  is the intramolecular polymer structure factor which represents connectivity

$$Ll_1^2 \left[ \frac{1}{l} - \frac{1}{l_1} \right] = \frac{\omega_2}{l^2} \left[ \frac{24L^3}{\pi^3 l_1} \right]^{1/2} - \frac{1}{9} \left[ \frac{l_1}{l} \right]^2 L^4 \int dk \hat{c}(k) k^2 F(k^2 Ll_1/6) + L\bar{\omega}_3/l_1^2 l^3 \quad (6a)$$

where

$$F(x) = \frac{2}{x^2} \left[ e^{-x} \left( 1 + \frac{4}{x} + \frac{6}{x^2} \right) - \frac{6}{x^2} \right], \quad (6b)$$

and  $\bar{\omega}_3$  is a renormalized value of  $\omega_3$ . The approximate theory for the polymer-colloidal system is given by Eq. (6) together with the RISM equation for  $h_{p-c}(r)$  [cf. Eq. (5)].

We have solved Eqs. (5) and (6) numerically for a variety of situations. The natural parameters in the problems are  $L$ ,  $\rho_c$  (or equivalently the scaling variable,  $R_c \sim \rho_c^{-1/3}$ , the mean distance between the colloidal particles), and temperature  $T$  which can be related to the strength of binary interaction between monomers by,  $\omega_2 \propto (T - \Theta)/\Theta$ ,  $\Theta$  being the Flory temperature. For a given set of parameters the theory predicts the size of the polymer molecule  $R_p = (Ll_1)^{1/2}$ ,  $h_{p-c}(r)$  which can be used to obtain the thickness of the depletion layer. The numerical results have been obtained for values of  $\omega_2 = 0.3\sigma$ ,  $\bar{\omega}_3 = 0.22\sigma^3$ ,  $L = 6.1 \times 10^3 \sigma$ , and  $\sigma = 165l$ . Notice that in this case  $\sigma/R_c < 1$  and therefore theories for polymer molecules confined between two parallel plates are not applicable. The value of  $\omega_2$  was estimated from the experimental measurement of the second virial coefficient for poly(ethylene-oxide). In order to use the experimental results the osmotic pressure was expressed in powers of the mass density of monomers. The usual ex-

and other constraints. The Percus-Yevick-like closure relations are for the integral equation in Eq. (5) are [13,16]

$$g_{p-c}(r < \sigma/2) = 0, \quad c(r > \sigma/2) = 0, \quad (5b)$$

where  $\sigma/2$  is the radius of the colloidal particles. Thus once  $\rho_c$  (density of colloids),  $L$  (or molecular weight of the polymer),  $\chi_{c-c}$ , and the parameters  $\omega_2$  and  $\omega_3$  are specified the partition may be obtained using Eqs. (4) and (5). However, the calculation of the path integral for the theory given by Eqs. (4) and (5) is difficult, and one has to resort to approximate methods. In this paper we use the variational treatment of Edwards and Singh [11] to provide a simplified treatment. This basic methodology has been successful in providing qualitative treatment of several problems. The technical difficulty associated with this variational method for polymer problems is well recognized, and a proper treatment will require renormalization-group methods [15(b),17]. Assuming that the reference Hamiltonian is given by a Gaussian theory with an effective step length  $l_1$  it can be shown that the variational equation satisfied by  $l_1$  is given by [15(a)]

pression for the osmotic pressure given in Flory-Huggins theory is in terms of the number density of monomers. It is this difference that makes the value of  $\omega_2$  seem large. For this and other choices of the parameters  $R_p = Ll_1$  was obtained from Eqs. (5) and (6). Physically it is clear that for  $R_c \gg R_p$  the colloidal particles do not affect the size of the polymer chain. In the opposite limit there is a reduction in the entropy of the chain due to the volume occupied by the colloidal particles. This effectively induces an attractive interaction between the monomers. For sufficiently high colloid densities one expects a coil-globule-like transition where the polymer globule can be treated as an effective hard sphere. The results of the calculation are consistent with this physical picture and we find that  $R_p$  can be represented fairly adequately by the scaling function [18],

$$R_p \sim R_F f(R_c/R_F). \quad (7a)$$

The function  $f(x)$  is unity for large  $x$  but behaves like a power law for small  $x$  (high densities), i.e.,  $\lim_{x \rightarrow 0} f(x) = x^m$ . The exponent  $m$  can be obtained from the requirement that the polymer molecule collapses into a compact globule at high enough densities with  $R \propto N^{1/3}$  and it turns out to be  $\frac{4}{9}$ . Thus

$$R_p \sim N^{1/3} (R_c/l)^{4/9}. \quad (7b)$$

The numerical values of  $R_p$  obtained using our self-consistent mean-field theory are consistent with the tentative scaling picture presented above. It should be noted that even if the dispersion medium acts as a good solvent the presence of colloidal particles at high enough densities can render the solvent poor thus inducing the collapse of the polymer. It appears that when Eq. (7b) is obeyed ( $R_c \ll R_F$ ) one expects effective attraction between the colloidal particles. This would render the colloidal solution unstable leading to flocculation.

The most significant aspect of our calculation is the direct computation of the polymer-colloid radial distribution function,  $g_{p-c}(r)$ , the Fourier transform of which can, in principle, be measured by light-scattering techniques. In Fig. 1 a plot of  $g_{p-c}(r)$  as a function of  $r/\sigma$  is presented. This figure clearly shows the depletion effect, i.e., the probability of finding the monomers near the surface of colloids is considerably less than at distances greater than a certain depletion length,  $\xi$ . For all densities the depletion length is of the order of the size of the polymer molecules, i.e.,  $\xi \sim R_p$ . This prediction is consistent with experiments [19] and with previous RIS Monte Carlo analysis [4]. It appears that when the three-body interaction among the polymer molecule is taken into account, then the concentration profile of the polymer with respect to the colloidal particles can be adequately described by the usual van der Waals description of the interface profile between coexisting fluid phase of a binary mixture. However, this is not the case when  $\bar{\omega}_3 = 0$ . This is clearly seen from Fig. 1 which also shows  $g_{p-c}(r)$  for  $\bar{\omega}_3 = 0$  (corresponding to the symbol  $\square$ ) as a function of  $(r/\sigma)$  for  $\rho_c \sigma^3 = 0.1$ . For the highest densities where  $R_c/R_F \ll 1$  there is evidence for the formation of a colloid shell structure around the polymer molecule. This result can be understood by noting that at these high densities the polymer is in a globule-like state with the effective dimension  $R_F \sim \sigma$ . Thus the system can be represented as a collection of  $P+1$  hard spheres ( $P$  is the number of colloidal

particles corresponding to the density  $\rho_c$ ), which for  $\rho_c \sigma^3 = 0.1$  shows a mild solvent shell.

The computation of the potential of mean force between the colloidal particles mediated by the free polymer is, in principle, possible using theory advanced here. This, however, requires the development of an additional self-consistency equation to account for the renormalization of the bare colloid-colloid structure factor,  $\chi_{c-c}(r)$ . Nevertheless the depletion profiles presented in Fig. 1 can be used to develop a qualitative picture of the effect of free polymer in inducing depletion flocculation as the density of colloidal particles is varied. The arguments leading to this conclusion go as follows: At the densities considered here the polymer-colloid radial distribution function  $g_{p-c}(r)$  for the case when  $\omega_3 \neq 0$  can be approximately represented as

$$g_{p-c}(r) \sim (1 - e^{-(r-\sigma/2)/\xi}) \quad (8)$$

for  $r > \sigma/2$  with  $\xi$  being dependent on the colloid density. A potential of mean force between the polymer and the colloidal particle can be inferred by writing  $g_{p-c}(r) \sim e^{-\beta U_{MF}(r)}$ . The resulting potential  $U_{MF}(r)$  is weakly attractive for all values of  $r$ , and in particular  $U_{MF}(r) \sim -\ln(r/\xi)$  as  $r \rightarrow \sigma^+/2$ . Since  $\xi$  is a decreasing function of  $R_c$  in the density region considered here (see Fig. 1) it follows that at higher values of  $R_c$  there is sufficient attraction for  $r \sim \sigma/2$  that the colloidal particles crowd the polymer molecule, and consequently the mean distance between the colloidal particles would be less than  $R_c$ . This leads to the formation of weak flocs (weak because the strength of the driving force for this transition is mild). When  $\omega_3 = 0$  there is a primary minimum in  $U_{MF}(r)$  at large colloidal densities as can be seen from the curve in Fig. 1. Consequently weak floc formation, in this case, would be even more pronounced. The determination of the structure of the weak flocs requires the direct computation of the renormalized potential of mean force,  $U_{c-c}(r)$ , between the colloidal particles. If  $U_{c-c}(r)$ , which is attractive for  $r > \sigma/2$ , is stronger than  $U_{MF}(r)$  the system will phase separate. However, if reverse is the case then the weak flocs would have the structure of a "loose necklace" in which several colloidal particles are mildly attracted to the polymer chain. The precise situation will depend upon the parameters of the system. In either case it appears that when the concentration of the polymer is small then one can infer that free polymer induces the formation of weak flocs. The depletion stabilization picture of Feigin and Napper [4] only applies when the concentration of free polymer molecules is in the semidilute regime. The theory here has to be extended to this case before the notion of depletion stabilization can be completely ruled out.

The above analysis, based on the quantitative results of our theory can be used to provide a scenario for depletion stabilization in semidilute solutions. A complete description would require the calculation of the free energy of the ternary system. For colloid densities, such that  $R_c > \xi_p$  ( $\approx l\varphi_p^{-3/4}$  where  $\varphi_p$  is the volume fraction of the free polymer molecules) the free polymer induces the formation of weak flocs in analogy with the picture presented above. When  $R_c$  starts becoming comparable to  $\xi_p$  the interac-

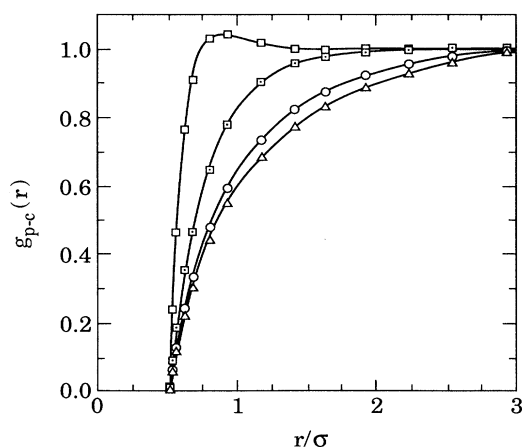


FIG. 1. Plots of polymer-colloid radial distribution function,  $g_{p-c}(r)$ , as a function of  $r/\sigma$ . The parameters for all the plots are given in the text. The plot labeled by  $\square$  corresponds to  $\bar{\omega}_3 = 0$ . The colloid density expressed as  $\rho_c \sigma^3$  for the plots are the following:  $\triangle$ — $10^{-5}$ ;  $\circ$ — $10^{-3}$ ;  $\square$ — $0.1$ ; and  $\square$ — $0.1$ .

tion with the colloidal particles modifies the size of the polymer and for  $R_c/\xi_p \sim 1$  the polymers may render stability to colloidal particles [4]. However, for  $R_c/\xi_p \ll 1$  the polymers should collapse into a compact structure and the system can then be adequately described as a binary mixture of hard spheres dispersed in a continuous solvent phase. It is well known that such a system will phase separate under appropriate conditions [20,21].

The major qualitative conclusion of the study is that the addition of trace amounts of free polymer to the colloidal solution induces the formation of weak flocs. This can be tested experimentally by adding free polymer to a suspen-

sion of hard-sphere-like colloidal particle-like polymethyl methacrylate in an inert organic solvent. From a theoretical point the complete description of the colloid-polymer mixture requires the inclusion of three-body interaction between polymer segments even when the dispersion medium is a *good solvent* for the polymer.

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