Neutron Scattering Study of Depletion Interactions in a Colloid-Polymer Mixture

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We report a neutron scattering study of depletion interactions in a mixture of colloid and nonadsorbing polymer. It is found that the measured colloidal structure factor can be well described by an effective interaction potential for the polymer-induced depletion attraction between the colloidal particles. The amplitude of the attraction is found to increase linearly with the polymer concentration but it levels off at higher polymer concentrations. [S0031-9007(96)00388-2]

The recent calculations [1] for the entropy-driven phase separation in binary mixtures of hard spheres have stimulated considerable experimental efforts to study the phase behavior of various binary mixtures of colloidal particles [2], surfactant aggregates [3], and polymer molecules [4]. While the phase behavior of these mixtures is generally in agreement with the theory, they are nevertheless not strictly hard-sphere systems. The colloidal particles used in these experiments were stabilized either by surface charges or by a layer of surfactant molecules, and hence the interparticle potential has a weak repulsive tail. The interaction potentials for the surfactant aggregates and polymer molecules are probably much softer than that of the hard spheres. Macroscopic phase measurements are useful in studies of the structure and phase behavior of the binary mixtures, but they are much less sensitive to the details of microscopic interactions in the mixtures. Direct measurements of the microscopic interactions, therefore, are needed in order to correlate then with the phase behavior of the mixtures.

In a mixture of hard spheres with two different sizes, small particles are expelled from the region between two large particles when the large particle surface separation becomes less than the size of the small particles. This depletion effect leads to an unbalanced osmotic pressure difference pushing the large particles together, which results in an effective attraction between the two large particles. At sufficiently high particle concentrations and large size differences, the depletion attraction can cause the mixture to segregate into two different phases [1,5,6]. The depletion attraction can be expressed in terms of an effective potential $U(r)$, which is the work required to bring the two large particles from infinity to a distance r in an environment of the small particles. It has been shown that $U(r)$ has the form [7]

$$U(r) = \begin{cases} +\infty & r \le \sigma, \\ -\Pi_p V_0(r) & \sigma < r \le \sigma + 2R_g, \\ 0 & r > \sigma + 2R_g, \end{cases} \quad (1)$$

where Π_p is the osmotic pressure of the small particles; σ and $2R_g$ are the diameter of the large and small particles, respectively. The volume of the overlapping depletion zones between the two large particles is given by [7]

$$V_0(r) = v_p \left(\frac{\lambda}{\lambda - 1} \right)^3 \left[1 - \frac{3}{2} \left(\frac{r}{\sigma \lambda} \right) + \frac{1}{2} \left(\frac{r}{\sigma \lambda} \right)^3 \right], \quad (2)$$

where v_p is the volume of a small particle and $\lambda = 1 + 2R_g/\sigma$. In this Letter we report a small-angle neutron scattering (SANS) study of the depletion attraction in a colloid-polymer mixture. In the experiment we measure the colloidal (partial) structure factor, $S_c(Q)$, which is directly related to the potential $U(r)$ between the colloidal particles. (In the discussion below, we will view the polymer molecules as the small particles mentioned above, and use the subscripts c and p for colloid and polymer, respectively.) An advantage of using SANS is that one can eliminate the undesirable scattering from the polymer chains by using isotopically mixed solvents. In addition to its fundamental importance in statistical physics, the study of colloid-polymer mixtures also has a myriad of industrial applications [5].

The colloidal particles used in the experiment consisted of a calcium carbonate ($CaCO_3$) core with an adsorbed monolayer of a randomly branched calcium alkylbenzene sulphonate surfactant. These particles have been well characterized previously using SANS and small-angle x-ray scattering (SAXS) techniques [8]. Our recent SANS and SAXS measurements [9] revealed that the particle has a core radius, $R_0 = 2.0$ nm, and a monolayer thickness, $\delta = 2.0$ nm. The colloidal suspensions were prepared by diluting known amounts of the concentrated suspension with the solvent, decane. The suspensions were then centrifuged at an acceleration of 10^8 cm/s^2 (10^5 g) for 2.5 h to remove any aggregates and dust. The resulting suspensions were found to be relatively monodispersed with

~10% standard deviation in the particle radius, as determined by dynamic light scattering [10].

The polymer used in the study was hydrogenated polyisoprene (poly-ethylene-propylene or PEP), a stable chain polymer. The PEP is a model polymer ($M_w/M_n < 1.1$), which has been well characterized previously using various experimental methods [11]. The molecular weight of the PEP was $M_p = 26\,000$ amu. Decane has been found to be a good solvent for both the colloid and PEP [10]. Because decane and PEP are both protonated, the polymer chains in the mixture are invisible to neutrons. Our Zimm analysis of the SANS data from the pure PEP/deuterated-decane solution has shown [9] that the polymer chains have a radius of gyration $R_g = 8.3$ nm and their second virial coefficient $A_2 M_p = 44.4$ cm^3/g. With the measured A_2 one can define an effective hard-sphere radius R_{hs} via $4(4\pi/3)R_{hs}^3 = A_2 M_p^2$. Thus we have $R_{hs} = 4.8$ nm, which agrees well with our previous light scattering measurement [10]. The light scattering experiment has revealed that the PEP chains do not adsorb onto the colloidal surfaces, and the phase separation in the colloid-PEP mixture samples occurs at the concentrations very close to the depletion prediction [10]. Because the basic molecular interactions are tuned to be simple, the SANS measurements in the colloid-PEP mixture can be used to critically examine the current depletion theory.

The SANS measurements were performed at the High Flux Beam Reactor in the Brookhaven National Laboratory. The incident neutron wavelength $\lambda_0 = 7.05 \pm 0.4$ Å, and the usable range of the scattering wave number Q [$= (4\pi/\lambda_0)\sin(\theta/2)$, with θ being the scattering angle] was $0.007 \le Q \le 0.15$ Å^{-1}. The scattering cells were made of quartz, and had a path length of 1 mm. The raw scattered intensity $I_r(Q)$ (counts/h) was measured at room temperature by a two-dimensional detector. The corrected intensity, $I(Q)$, was obtained by computing the azimuthal average and subsequently applying the standard corrections due to the background intensity, solvent scattering, and sample turbidity. The structure factor $S_c(Q)$ was obtained using the equation $S_c(Q) = I(Q)/\rho_c P_c(Q)$, where ρ_c is the colloid number density and $P_c(Q)$ is the scattering intensity per unit concentration measured in a dilute pure colloidal suspension, in which $S_c(Q) = 1$.

To fit the scattering data, we calculate the Fourier transform, $C(Q)$, of the direct correlation function, $C(r)$. When the potential $U(r)$ consists of a hard core plus an attractive tail as in Eq. (1), $C(r)$ can be obtained under the mean spherical approximation (MSA), which is a perturbative treatment to the Percus-Yevick equation [12]. Under MSA, we have

$$C(r) = \begin{cases} C_{hs}(r) & r \le \sigma, \\ -U(r)/k_B T & r > \sigma, \end{cases} \qquad (3)$$

where $k_B T$ is the thermal energy and $C_{hs}(r)$ is a known direct correlation function for the hard-sphere system [12]. Note that $C(r)$ is constituted by two parts: (i) a hard core

which involves the colloid diameter σ and its volume fraction ϕ_c, and (ii) an attractive tail with the dimensionless amplitude $\tilde{P} = \Pi_p v_p / k_B T$ and the range parameter λ. With the calculated $C(Q)$, we obtain the structure factor $S_c(Q)$ via the well-known relation [12]

$$S_c(Q) = 1/[1 - \rho_c C(Q)]. \qquad (4)$$

Figure 1 shows the measured $S_c(Q)$ of the pure colloidal suspension for two volume fractions: (a) $\phi_c = 0.146$ and (b) $\phi_c = 0.086$. The solid curves are fits by the simple hard-sphere structure factor [13], which can be obtained by taking $U(r) = 0$ for $r > \sigma$ in Eq. (3). In the fitting σ is found to remain constant for different colloid concentrations, and its best fit value is $\sigma = 7.7$ nm. This value is very close to the measured particle size $2(R_0 + \delta)$ ($= 8.0$ nm) as mentioned above. Because the surfactant shell of the colloidal particle is "soft," we expect its effective hard shell thickness to be slightly smaller than δ. It is also found that the ratios of the fitted ϕ_c agree well with the corresponding ratios of the known mass concentration of the colloidal samples [14]. It is seen from Fig. 1 that the hard-sphere model fits the data well, except in the small-Q region. Since the measured $S_c(0)$ is smaller than the hard-sphere value, the deviation in the small-Q region can be attributed to a weak repulsion between the soft surfactant shells. Because the deviation is small, the measured $S_c(Q)$ is found to be insensitive to the detail functional form of the soft repulsion in $U(r)$. To have a meaningful comparison with the fitting results for the mixture samples, we use the same $U(r)$ as in Eq. (1) but change the sign of $U(r)$ for $r > \sigma$. The dashed curves in Fig. 1 show the calculated $S_c(Q)$ for the hard spheres with the soft repulsion, which fits the data better than the hard-sphere model in the small-Q region. The fitted values of σ and ϕ_c are the same as
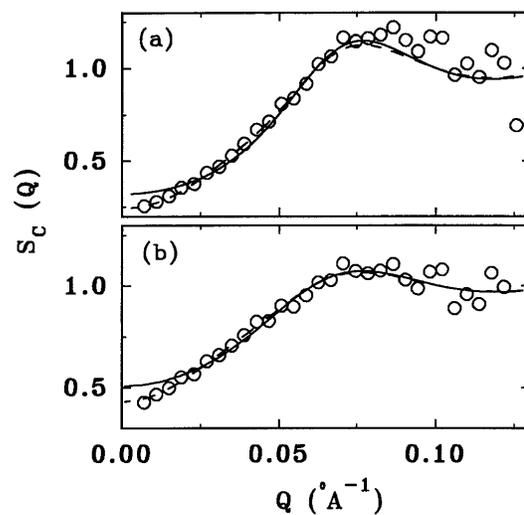

FIG. 1. Measured structure factor $S_c(Q)$ of the pure colloidal suspensions for two volume fractions: (a) $\phi_c = 0.146$ and (b) $\phi_c = 0.086$. The solid curves are the fits to the hard-sphere model, and the dashed curves correspond to a hard core potential with a repulsive tail.

those from the hard-sphere model. The fitting parameters for the repulsive tail will be discussed later together with the mixture data.

To reduce the fitting ambiguity and pinpoint the control parameters for the depletion effect, we prepared three series of mixture samples with $\phi_c = 0.146$, 0.086, and 0.038, respectively. For each series of the samples, ϕ_c was kept the same and the polymer concentration C_p (g/cm^3) was increased until the mixture became phase separated (except for the series with $\phi_c = 0.038$) with a visible interface, which separates the dark brown colloid-rich phase from the light brown colloid-poor phase. Figure 2 compares the measured $S_c(Q)$ for three values of C_p when (a) $\phi_c = 0.146$ and (b) $\phi_c = 0.086$. It is seen that the main effect of adding PEP is to increase the value of $S_c(Q)$ in the small-Q region, whereas the large-Q behavior of $S_c(Q)$ remains nearly unchanged. The solid curves in Fig. 2 show the fits by Eq. (4) using the potential $U(r)$ in Eq. (1). For a fixed colloid concentration, the fitted values of σ and ϕ_c for the mixture samples with different C_p do not change very much, and they are very close to those obtained from the corresponding pure colloidal suspensions. Furthermore, the fitted λ also remains constant for different ϕ_c and C_p, and its best fit value is $\lambda = 2.9$. This value is close to the calculated $\lambda = 1 + R_g/(R_0 + \delta) = 3.07$. Because polymer chains are penetrable, the actual colloid-polymer interaction radius [R_g was used as this interaction radius in Eq. (1)] should be in between the radius of gyration R_g and the effective polymer-polymer interaction radius R_{hs}. From the fitted value of λ, we find the effective

colloid-polymer interaction radius to be 7.6 nm, which is about 10% smaller than R_g but 60% larger than R_{hs}. With the above three fitting parameters fixed, we were able to fit all the scattering data from different mixture samples (19 samples in total) with only one free parameter—the interaction amplitude $\tilde{P}$.

It should be pointed out that in the above data analysis we have assumed the colloidal particles to be identical and ignored the small polydispersity in particle sizes. Because the colloidal parameters are the same for each series of the mixture samples with the same ϕ_c, the effect seen in Fig. 2 is solely due to the addition of PEP into the colloidal suspension. Furthermore, the main effect of the small polydispersity is to average out the oscillations of $S_c(Q)$ in the large-Q range beyond the first peak position, whereas the effect of adding polymer, as shown in Fig. 2, is to increase the value of $S_c(Q)$ in the small-Q range. Therefore, the small size polydispersity is unlikely to affect our analysis of the depletion effect.

Figure 3(a) shows the fitted $\tilde{P}$ as a function of the effective polymer volume fraction $\phi_p = C_p/C^*$, where $C^* = M_p/(4\pi/3)R_g^3$ is the polymer overlap concentration. It is seen that $\tilde{P}$ first increases linearly with ϕ_p up to $\phi_p \simeq 1$, and then it levels off. For a given ϕ_p, $\tilde{P}$ also depends upon ϕ_c. If the polymer molecules in the mixture are treated as an ideal gas, their osmotic pressure $\Pi_p = n_p k_B T$ and hence $\tilde{P} = \Pi_p v_p/k_B T = \phi_p$. Recently, Lekkerkerker et al. [4,6] pointed out that the polymer number density n_p should be defined as $n_p = N_p/V_f$, where N_p is the total number of the polymer molecules and $V_f = \alpha(\phi_c)V$ is the free volume not occupied by the colloidal particles and their surrounding depletion zones. They have calculated $\alpha(\phi_c)$ as a function of ϕ_c [6]. It is seen from Fig. 3(b)
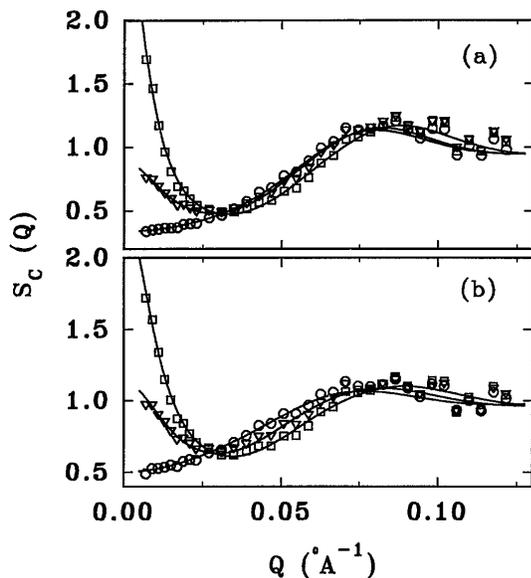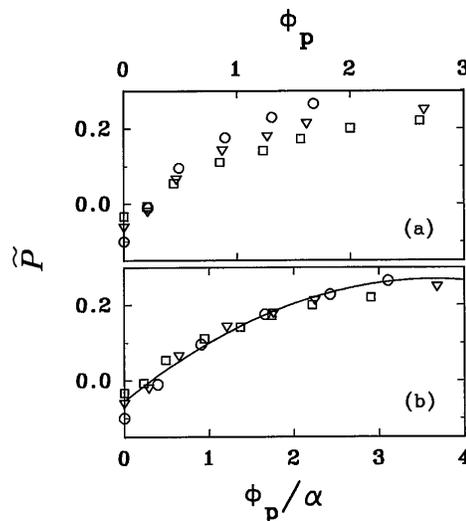

FIG. 2. Measured colloidal structure factor $S_c(Q)$ of the colloid-PEP mixtures for different polymer concentration C_p when (a) $\phi_c = 0.146$ and (b) $\phi_c = 0.086$. The values of C_p (g/cm^3) in (a) are 0.0039 (○), 0.0165 (▽), and 0.0308 (□), and those in (b) are 0.0038 (○), 0.0233 (▽), and 0.0652 (□). The solid curves are the fits by Eq. (4) using the potential $U(r)$ in Eq. (1).

FIG. 3. Fitted interaction amplitude $\tilde{P}$ as a function of (a) $\phi_p = C_p/C^*$ and (b) ϕ_p/α. The colloid volume fractions in the mixtures are $\phi_c = 0.146$ (○), 0.086 (▽), and 0.038 (□). The solid curve in (b) is the fitted function $\tilde{P} = -0.054 + 0.178(\phi_p/\alpha) - 0.0245(\phi_p/\alpha)^2$.

that once ϕ_p is scaled by the calculated $\alpha(\phi_c)$ [15], the three curves in Fig. 3(a) collapse into a single master curve. The solid curve in Fig. 3(b) is the fitted function $\tilde{P} = -0.054 + 0.178(\phi_p/\alpha) - 0.0245(\phi_p/\alpha)^2$.

The fitted $\tilde{P}$ consists of three terms. The small negative intercept indicates that there is a weak repulsive interaction between the soft surfactant shells of the colloidal particles. [To have a meaningful comparison with the fitted $\tilde{P}$ for the mixture samples, we used the same value of λ (= 2.9) to fit the repulsive tail for the pure colloidal samples.] The linear coefficient should be unity for noninteracting polymer chains (an ideal gas), but our fitted value is 0.178. One plausible reason for the deviation is that with the effective potential approach, the polymer molecules are assumed to be smaller than the colloidal particles and their number density should be much higher than that of the colloidal particles. In our experiment, however, these two assumptions are not strictly satisfied, and thereby the overlap volume $V_0(r)$ in Eq. (2) is overestimated. As a result, the fitted $\tilde{P}$ becomes smaller than its actual magnitude, because $U(r)$ in Eq. (1) is proportional to the product of $V_0(r)$ and $\tilde{P}$. Another possibility is that in calculating ϕ_p, a smaller characteristic length than R_g should be used for the polymer chains. For example, if R_{hs} is used to estimate ϕ_p, the linear coefficient will be increased by a factor of $(R_g/R_{hs})^3 \simeq 5.2$.

The polymer-polymer interaction, which gives rise to the quadratic term in the fitted $\tilde{P}$, can have two competing effects on the depletion attraction. It may either increase the osmotic pressure (and hence $\tilde{P}$) because the polymer chains have a positive second virial coefficient or reduce the depletion attraction because it requires the system to do more work to expel the polymer molecules from the depletion zones. Figure 3(b) clearly shows that the polymer-polymer interaction tends to reduce the depletion attraction. A similar suppression effect is also found in recent theoretical calculations of the depletion attraction between two parallel plates immersed in an interacting polymer (or particle) solution [16]. The suppression effect may be used to explain why it is easier to induce phase separation in colloid-polymer mixtures than in colloid-colloid mixtures under similar conditions. Because the colloidal particles have a larger second virial coefficient than the corresponding polymer molecules, the interaction amplitude $\tilde{P}$ in the colloid-colloid mixtures will start to level off at lower concentrations.

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