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POLYMER-INDUCED DEPLETION INTERACTION AND ITS EFFECT ON COLLOIDAL SEDIMENTATION IN COLLOID-POLYMER MIXTURES

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The study of motions of small particles suspended in a fluid has always been an interesting subject in physics.¹ The dynamics of the particles is determined by the statistical properties of the random forces resulting from interactions between the particle and the surrounding fluid molecules. Brownian diffusion of small particles in a fluid at thermal equilibrium is one of the classical and best understood examples. Sedimentation, wherein heavy particles fall under the action of gravity through a fluid in which they are suspended, on the other hand, represents a "self-induced hydrodynamic diffusion".² The character of the sedimentation depends upon the interplay between long-range hydrodynamic forces, random Brownian forces and direct inter-particle forces.³ The main objectives of our NASA research projects carried out at Oklahoma State University are: (1) study motions of colloidal particles under different random forces in the carrier fluid, and (2) understand the effect of gravity on the particle motion when the density of the particles is different from the carrier fluid.

In this paper we focus on the polymer-induced depletion attraction and its effect on colloidal sedimentation in colloid-polymer mixtures. We first report a small-angle neutron scattering (SANS) study of the depletion effect in a mixture of hard-sphere-like colloid and non-adsorbing polymer. Then we present results of our recent sedimentation measurements in the same colloid-polymer mixture. A key parameter in controlling the sedimentation of heavy colloidal particles is the inter-particle potential $U(r)$, which is the work required to bring two colloidal particles from infinity to a distance r under a given solvent condition. This potential is known to affect the average settling velocity of the particles,³ and experimentally one needs to have a way to continuously vary $U(r)$ in order to test the theory. The interaction potential $U(r)$ can be altered by adding polymer molecules into the colloidal suspension. In a mixture of colloid and non-adsorbing polymer, the potential $U(r)$ can develop an attractive well because of the depletion effect⁴, in that the polymer chains are expelled from the region between two colloidal particles when their surface separation becomes smaller than the size of the polymer chains. The exclusion of polymer molecules from the space between the colloidal particles leads to an unbalanced osmotic pressure difference pushing the colloidal particles together, which results in an effective attraction between the two colloidal particles. The polymer-induced depletion attraction controls the phase stability of many colloid-polymer mixtures, which are directly of interest to industries.

It has been shown that the potential $U(r)$ has the form⁴

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

where σ is the particle diameter, Π_p is the osmotic pressure of the polymer molecules, and R_g is their radius of gyration. The volume of the overlapping depletion zones between the two colloidal particles is given by⁴

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

where $v_p = (4\pi/3)R_g^3$ is the volume occupied by a polymer chain and $\lambda = 1 + 2R_g/\sigma$. In the experiment, we measure the colloidal (partial) structure factor, $S_c(Q)$, which is directly related to the interaction potential $U(r)$. An advantage of using SANS is that one can eliminate the undesirable scattering from the polymer chains by using isotopically mixed solvents. (In the discussion below the subscripts c and p will be used to refer to colloid and polymer, respectively.)

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.⁵ Our recent SANS and SAXS measurements revealed that the particle has a core radius, $R_0 = 2.0 \text{ nm}$, and a monolayer thickness, $\delta = 2.0 \text{ nm}$. Previous dynamic light scattering experiment⁶ has shown that the colloidal particles are relatively monodispersed with $\sim 10\%$ standard deviation in particle radius. The polymer used in the study was hydrogenated polyisoprene (poly-ethylene-propylene or PEP), a stable model polymer. The molecular weight of the PEP was $M_p = 26,000$. Decane has been found to be a good solvent for both the colloid and PEP.⁶ 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 that the polymer chains have a radius of gyration $R_g = 8.3 \text{ nm}$ and their second virial coefficient $A_2 M_p = 44.4 \text{ (cm}^3/\text{gm)}$. 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 $R_{hs} = 4.8 \text{ nm}$, which agrees well with our previous light scattering measurement.⁶ 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.⁶ 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 $\lambda_0 = 7.05 \pm 0.4 \text{ \AA}$, and the usable range of the scattering wave number $Q [= (4\pi/\lambda_0) \sin(\theta/2)]$, with θ being the scattering angle] was $0.007 \text{ \AA}^{-1} \leq Q \leq 0.15 \text{ \AA}^{-1}$. The structure factor $S_c(Q)$ was obtained using the equation $S_c(Q) = I(Q)/[\rho_c P_c(Q)]$, where $I(Q)$ is the scattered intensity of the mixture samples, 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 $S_c(Q) = 1$. All the scattering measurements were conducted at room temperature.

To reduce the fitting ambiguity and pinpoint the control parameters for the depletion effect we prepared three series of mixture samples with the colloid volume fraction $\phi_c = 0.146$, 0.086 and 0.038 , respectively. For each series of the samples, ϕ_c was kept the same and the polymer concentration $C_p \text{ (gm/cm}^3\text{)}$ 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. Fig. 1 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 into the colloidal suspension 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. 1 show the calculated $S_c(Q)$ using $U(r)$ in Eq. (1). Note that there are four fitting parameters in the calculation: the diameter σ , the volume fraction ϕ_c , the dimensionless interaction amplitude $\tilde{P} = \Pi_p v_p / k_B T$, and the range parameter λ . The first two parameters are used to describe the hard core part of $U(r)$ and the last two parameters are used for the attractive tail. It is found from the fitting that for a fixed colloid concentration, the fitted values of σ and ϕ_c for the mixture samples do not change

very much with C_p , 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 $\lambda = 1 + R_g/(R_0 + \delta) = 3.07$. 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} .

Figure 2a 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.⁷ 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 . It is seen from Fig. 2b that once ϕ_p is scaled by the calculated $\alpha(\phi_c)$,⁸ the three curves in Fig. 2a collapse into a single master curve. The solid curve in Fig. 2b 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 $U(r)$ as in Eq. (1) but change the sign of $U(r)$ for $r > \sigma$ to fit the repulsive tail for the pure colloidal samples.) The linear coefficient should be unity for non-interacting 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 over-estimated. 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 compute 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. Fig. 2b clearly shows that the polymer-polymer interaction tends to reduce the depletion attraction. Similar suppression effects are also found in recent theoretical calculations of the depletion attraction between two parallel plates immersed in an interacting polymer (or particle) solution.⁹

The above SANS measurements clearly demonstrate the effectiveness of using a non-adsorbing polymer to control the magnitude as well as the range of the interaction between the colloidal particles. It is shown that the amplitude of the potential $U(r)$ is controlled by the polymer concentration C_p , and the range of $U(r)$ is proportional to the radius of gyration R_g of the polymer chains. Because the depletion potential $U(r)$ can be continuously varied in the experiment, the colloid-PEP mixture becomes an ideal system for the study of the interaction effect on the colloidal sedimentation. In the experiment to be described below, we measure the average settling velocity $v_c(C_p)$ of the colloidal particles as a function of C_p . The addition of the polymer molecules into

the colloidal suspension can have two competing effects on $v_c(C_p)$. It can either reduce $v_c(C_p)$ because the viscosity of the mixture solution is increased, or increase $v_c(C_p)$ because the depletion attraction between the particles is increased. Experimentally, one can separate the two effects by changing the colloid concentration. For sufficiently dilute colloidal mixtures, the distance between the colloidal particles is so large that their mutual interaction can be ignored. In this case, adding polymer into the colloidal suspension only affects the viscosity of the solution. The effect of $U(r)$ on $v_c(C_p)$ can be studied in the concentrated colloidal mixtures, once the sedimentation of the individual particles through a polymer solution is understood.

We now discuss the measurements of $v_c(C_p)$ in the dilute colloidal mixtures. The $CaCO_3$ particles have a hydrodynamic radius, $R_h = 5.0 \text{ nm}$, and their density $d_c \simeq 2.0 \text{ gm/cm}^3$. The density of the PEP is $d_p = 0.856 \text{ gm/cm}^3$. The solvent (decane) density is $d_s = 0.73 \text{ gm/cm}^3$ and its viscosity $\eta_0 = 0.84 \text{ cp}$ (at $T = 25^\circ C$). The Stokes velocity of the particle, determined by the balance between the accelerational force and the viscous drag, is

$$v_c(C_p) = \frac{2R_h^2(d_c - d_s)\mathcal{A}}{9\eta_c(C_p)}, \quad (3)$$

where \mathcal{A} is the acceleration and $\eta_c(C_p)$ is the viscosity experienced by the colloidal particles in the polymer solution at the concentration C_p . Because the particles are very small, their sedimentation under earth gravity ($\mathcal{A} = g$) is unobservable. To increase the settling velocity of the particles, we used a commercial ultracentrifuge, Beckman Model L8-70M. The sample cells were made of Ultra Clear solid polymer and their size (diameter \times height) was $14 \times 95 \text{ mm}$. The distance between the middle of the sample cell and the center of rotation was $\bar{r} = 11.3 \text{ cm}$. All the samples were centrifuged at the rotation speed $f = 35,000 \text{ rpm}$ for 4 to 6 hours depending on the sample viscosity. The corresponding centripetal acceleration $\mathcal{A} = (2\pi f)^2 \bar{r}$ was $1.5 \times 10^8 \text{ cm/s}^2$ ($1.5 \times 10^5 g$), which was large enough to cause the colloidal particles to settle 1 to 6 cm towards the bottom of the cell. After the centrifugation, a clear interface could be observed by eye in the initially uniform solution. This interface separated the upper clear solvent region from the lower dark-brown colloid-rich region. The travelling distance h of the interface was measured by a low-magnification microscope mounted on a translational stage controlled by a micrometer. The settling velocity was computed from the measured h via $v_c(C_p) = h/t$, where t is the running time. All the measurements were conducted at $22^\circ C$. Because the polymer density is very close to that of the solvent, the sedimentation of the polymer molecules was negligible. Therefore, the colloidal particles settled through a uniform PEP/decane solution at rest. To reduce systematic errors in the experiment, we present the sedimentation data in terms of the velocity ratio $R_c \equiv v_c(C_p = 0)/v_c(C_p)$. As shown in Eq. (3) $R_c = \eta_c(C_p)/\eta_0$ for the dilute colloidal mixtures.

Figure 3 shows the measured R_c as a function of C_p at $\phi_c = 0.014$. The molecular weight of the PEP was $M_p = 17,500$ and its $R_g \simeq 5.8 \text{ nm}$.¹⁰ It is seen that the measured $R_c(C_p)$ first increase linearly with C_p up to $C_p^c \simeq 0.07 \text{ gm/cm}^3$ and then it turns up sharply. Similar behavior was also observed for the measured $R_c(C_p)$ with other molecular weights. The crossover concentration C_p^c is found to be independent of M_p . With this value of C_p^c , we estimate the correlation length (or the mesh size) of the polymer solution to be $\xi \simeq R_g(C_p/C^*)^{-3/4} \simeq 3.5 \text{ nm}$, which is close to the size of the colloidal particles. The solid curve in Fig. 3 shows the macroscopic viscosity of the same polymer solution measured independently by Davison et al. with a capillary viscometer.¹ The functional form of the solid curve is $\eta_p/\eta_0 = 1 + [\eta]C_p + k_H([\eta]C_p)^2$, with the coefficient $[\eta] = 25 \text{ cm}^3/\text{gm}$ and $k_H = 0.335$. The dashed line is the linear plot $\eta_p/\eta_0 = 1 + [\eta]C_p$. Fig. 3 thus

reveals that the colloidal particles in the polymer solution feel the single-chain viscosity when their size is smaller than ξ . The particles experience the macroscopic viscosity of the polymer solution when their size become much larger than ξ .

We now discuss the effect of the colloidal interaction on $R_c(C_p)$. Fig. 4 shows the measured R_c vs. C_p for different ϕ_c . It is seen that for the two lowest colloid concentrations ($\phi = 0.014$ and 0.02), the measured $R_c(C_p)$'s superimpose with each other, indicating that the interaction between the colloidal particles is negligible and thus the velocity ratio R_c equals the viscosity ratio $\eta_c(C_p)/\eta_0$. As ϕ_c increases, the colloidal particles feel more and more depletion attraction and, therefore, their settling velocity at a fixed C_p is increased (R_c is reduced). For a fixed ϕ_c , the depletion attraction between the particles also increases with increasing C_p . Consequently, the colloidal settling velocity is increased. This is seen in Fig. 4 once the effect of increasing viscosity is divided out from the measured R_c vs. C_p . For the first time, the experiment provides a quantitative relationship between the settling velocity $v_c(C_p)$ and the inter-particle potential $U(r)$. Further theoretical calculation of $v_c(C_p)$ using the depletion potential $U(r)$ is underway. The above measurements reveal a great potential of using sedimentation to measure the interaction between the colloidal particles and other macromolecules in complex fluids.

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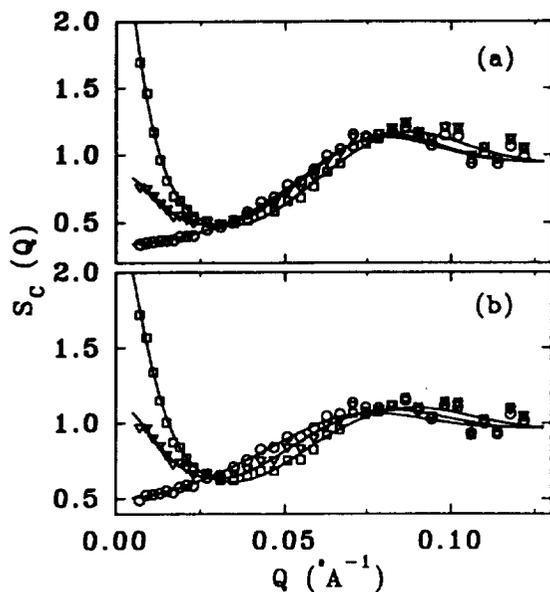


Fig. 1 - Measured $S_c(Q)$ of the colloid-PEP mixtures for different C_p when (a) $\phi_c = 0.146$ and (b) $\phi_c = 0.086$. The values of C_p (gm/cm^3) in (a) are: 0.0039 (circles), 0.0165 (triangles), 0.0308 (squares), and those in (b) are: 0.0038 (circles), 0.0233 (triangles) and 0.0652 (squares). The solid curves are the calculated $S_c(Q)$ using $U(r)$ in Eq. (1).

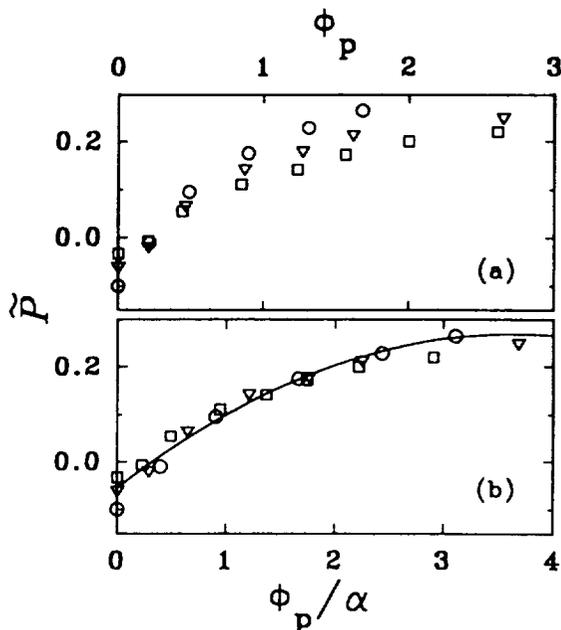


Fig. 2 - Fitted \tilde{P} as a function of (a) $\phi_p = C_p/C^*$ and (b) ϕ_p/α . The values of ϕ_c in the mixture samples are: 0.146 (circles), 0.086 (triangles) and 0.038 (squares). The solid curve in (b) is the fitted function $\tilde{P} = -0.054 + 0.178(\phi_p/\alpha) - 0.0245(\phi_p/\alpha)^2$.

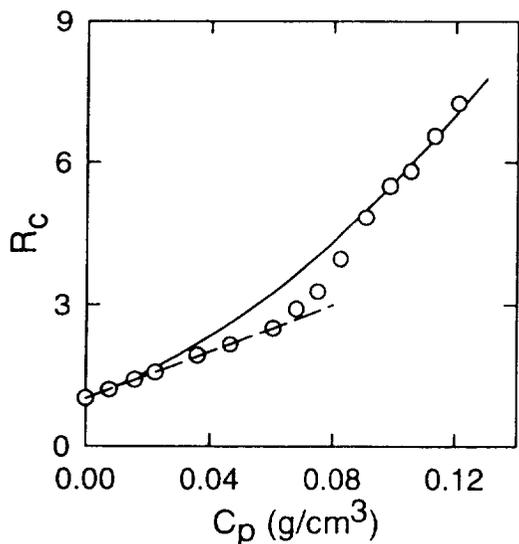


Fig. 3 - Measured R_c as a function of C_p at $\phi_c = 0.014$. The solid curve is $\eta_p/\eta_0 = 1 + [\eta]C_p + k_H([\eta]C_p)^2$ with $[\eta] = 25 \text{ cm}^3/gm$ and $k_H = 0.335$. The dashed line is the linear plot $\eta_p/\eta_0 = 1 + [\eta]C_p$.

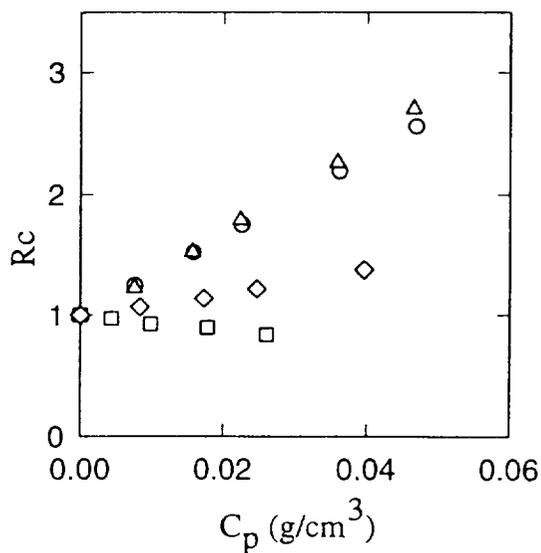


Fig. 4 - Measured R_c vs. C_p for different ϕ_c . The values of ϕ_c are: 0.014 (triangles), 0.02 (circles), 0.086 (diamonds), and 0.146 (squares).