Interactions in mixtures of colloid and polymer

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Résumé. — Nous étudions la solution d’un colloïde stabilisé par des molécules tensioactives et d’un polymère — le polyisoprène hydrogené. À l’aide d’un développement du viriel, l’intensité aux petits angles est calculée en fonction des concentrations en polymère et en colloïde. Avec cette équation nous avons déterminé le volume exclu mutual entre une molécule polymérique et une particule colloïdale. En outre, nous avons détruit le deuxième coefficient du viriel des particules colloïdales dans la solution diluée de polymères. Cette méthode pour obtenir les paramètres d’interaction dans un mélange polymère-colloïde est capable de sonder les changements d’interaction effective de la suspension colloïdale due à l’introduction du polymère libre, c’est-à-dire, l’effet déplétion.

Abstract. — We report results of light scattering study of interactions in a mixture of a surfactant-stabilized colloid and hydrogenated polyisoprene polymer. With a virial expansion the small-angle scattering intensity from the mixture is calculated as a function of colloid and polymer concentrations. Using the obtained formula we measured the mutual excluded volume between a polymer molecule and a colloidal particle, and extracted the second virial coefficient of the colloidal particles in the dilute polymer solution. This scheme of obtaining interaction parameters in the polymer-colloid mixture is capable of probing the changes of the interaction potential for the colloidal suspension due to the addition of free polymer, the so-called depletion effect.

1. Introduction.

Recently the science and technology of colloidal suspensions have been greatly advanced to meet demands of modern industries for specific and sophisticated functions for various materials. A stable colloidal system is desired for this purpose because the entire system’s physicochemical properties directly reflect the properties of constituent particles. Many theoretical and experimental investigations have been carried out to study interactions of colloidal particles in simple aqueous and organic solutions [1-4]. These interactions may be expressed in terms of the potential $U(r)$, which is the work required to bring two colloidal

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particles from infinity to a separation $r$ under given solvent condition. The potential $U(r)$ determines the osmotic pressure of a stable colloidal dispersion. It also governs the stabilities of such systems.

There exist many even more complicated colloidal systems in reality, such as colloidal dispersion in a mixed solvent, or that coexisting with other macromolecules (e.g., polymers). To be more specific, we focus here on the colloidal suspension in polymer solutions. Needless to say, the study of such complex systems has great applications in industries. The complexity of these systems arises because of the formation of an adsorption (or depletion) layer of polymer at the surface of the colloidal particle. This adsorption (or depletion) layer changes both the hydrodynamics and the thermodynamics of the colloidal suspension [5, 6].

The hydrodynamic effect is that the adsorption layer slows down the Brownian motion of the adsorbed colloidal particle in the solution. Dynamic light scattering technique [7] has been used to estimate the apparent hydrodynamic thickness of an adsorbed layer of the polymer [8]. The hydrodynamic thickness is the difference between the Stokes' radius of the bare colloidal particle in the solvent alone and the value for the particle in the polymer solution. The experimental situation, however, is much complicated some times by effects that are peculiar to the system studied and lead to confusion in interpretation of the data [9].

The adsorption (or depletion) layer of polymer also affects the interaction potential $U(r)$ between the colloidal particles. For instance, when the free polymer is added to the colloidal suspension, the polymer molecules are expelled from the neighborhood of the colloidal particle due to the entropic repulsion. Therefore, the particle is surrounded by a depletion zone with a polymer concentration substantially lower than the bulk concentration of polymer. The free energy of the system is increased by the depletion effect. The system can reduce its free energy by grouping the colloidal particles together to share the depletion volume. This results in an effective attraction between the colloidal particles. If the attraction is large enough, a phase separation or flocculation of the colloidal particles occurs. The depletion effect was first recognized by Asakure and Oosawa [10], and later it was extensively discussed in a paper by Vrij [11]. In recent years, many theoretical and experimental studies of the depletion effect have been carried out in various aqueous and organic colloidal solutions [12].

The potential $U(r)$ influences various measurable properties of the colloidal suspension. In this paper we focus on the second virial coefficient, which can be obtained from the measurement of the concentration dependence of the light intensity scattered by the colloidal particles. With a virial expansion for the partial structure factors of binary mixtures given by Ashcroft and Langreth [13], the small-angle scattering intensity from the colloidal-polymer mixture is calculated as a function of colloid and polymer concentrations. Using the obtained formula one can measure the mutual excluded volume between a polymer molecule and a colloidal particle, and extract the second virial coefficient of the colloidal particles in the dilute polymer solution.

This scheme is useful for the microscopic study of changes in the interaction potential $U(r)$ of a sterically stabilized colloidal suspension due to the adsorption or the depletion. In contrast to many previous experimental studies [12], which mainly focused on the phase behavior of colloidal dispersions in a free polymer solution, we report here results of light scattering study of interactions in the mixture of colloid and polymer. Our light scattering measurements demonstrate that the above scheme is indeed capable of probing the interaction parameters in mixtures of polymer and colloid.

The colloidal particle chosen for the study consisted of a calcium carbonate (CaCO$_3$) core with an adsorbed monolayer of alkylbenzene sulphonate surfactant (CaSA). The polymer we used was hydrogenated polyisoprene (PEP), a very stable straight chain polymer. Both of
them were dispersed in the good solvent, decane. Such a non-aqueous dispersion is ideal for the present study because both the colloidal particles and the PEP polymer molecules can be approximately viewed as hard spheres of radius in the range between 4.5 nm and 11 nm.

In the next section, we describe the theoretical method used for obtaining the interaction parameters in the mixture of colloid and polymer. Experimental details appear in section 3, and the results are presented and analyzed in section 4. Finally, the work is summarized in section 5.

2. Theory.

2.1 Scattering from a Binary Mixture. — Consider the scattering medium to be made up of two kinds of macromolecular species. Each macromolecule contains $n_1$ (or $n_2$) subunits and the illuminated volume contains $N_1 + N_2$ molecules. Thus there are $n_1N_1 + n_2N_2$ subunits in the scattering volume. The scattering intensity from these subunits is given by [7]

$$I(Q) = \left( B/V \right) S(Q),$$

where $B = V [k^2 E_0 (n - n)/eR]^2$, and $V$ is the scattering volume. The scattering vector $Q = 2 k \sin (\theta/2)$, and $k = 2 \pi n/\lambda$, where $\lambda$ is the wavelength of the incident light, $n$ is the refractive index of the liquid solvent, and $\theta$ is the scattering angle. In the above, $R$ is the distance between the scattering source and the observation point, $e$ is the dielectric constant of the solvent, and $E_0$ is the intensity of the incident light. The unit vector $n_i(r_i)$ is the polarization direction of the incident (scattered) electric field. The structure factor $S(Q)$ has the form

$$S(Q) = \left\langle \left| \sum_{i=1}^{n_1} b_i e^{-iQ \cdot r_i} \right|^2 \right\rangle,$$

where $r_i$ is the position of the $i$-th subunit and $b_i$ is its scattering amplitude.

One can relabel the subunits with two subscripts $\ell$ and $j$ as follows:

$$S(Q) = \left\langle \left| \sum_{\ell=1}^{n_1} \sum_{j=1}^{n_{\ell}} b_{\ell j} e^{-iQ \cdot r_{\ell j}} + \sum_{\ell=1}^{n_2} \sum_{j=1}^{n_{\ell}} b_{\ell j} e^{-iQ \cdot r_{\ell j}} \right|^2 \right\rangle,$$

where $b_{\ell j}$ and $r_{\ell j}$ are the scattering amplitude and the position of the $j$-th subunit in the $\ell$-th molecule. Denoting the position of the center of mass of the $\ell$-th molecule by $R_\ell$, and the position of the $j$-th subunit in the molecule by $X_{\ell j}$, we have $r_{\ell j} = R_\ell - X_{\ell j}$. Then equation (3) becomes

$$S(Q) = \left\langle \left| \sum_{\ell=1}^{n_1} f_{1,\ell}(Q) e^{-iQ \cdot R_\ell} + \sum_{\ell=1}^{n_2} f_{2,\ell}(Q) e^{-iQ \cdot R_\ell} \right|^2 \right\rangle,$$

In the above,

$$f_{1,\ell}(Q) = \left( \sum_{j=1}^{n_{\ell}} b_{\ell j} e^{iQ \cdot X_{\ell j}} \right),$$

is the form factor of the first kind of molecules. The form factor for the second kind molecules has the same form.
If molecules in each summation in equation (4) are identical, the form factor \( f_1 \) (and \( f_2 \)) can be factored out from the summation. Expanding equation (4) we may write the intensity in equation (1) as

\[
I(Q) = B \left\{ \rho_1 f_1(Q) S_{11}(Q) + 2(\rho_1 \rho_2)^{1/2} f_1(Q) f_2(Q) S_{12}(Q) + \rho_2 f_2(Q) S_{22}(Q) \right\},
\]

where \( \rho \) is the number density of the scattering molecules, and the partial structure factor

\[
S_{ij}(Q) = (N_i N_j)^{-1/2} \sum_{\vec{r}} e^{-iQ \cdot (\vec{r}_i - \vec{r}_j - \vec{r})}.
\]

Here the summation runs over all molecules in the scattering volume. In the limit \( Q \to 0^+ \), equation (6) becomes

\[
I(0) = B \rho_1 f_1(0) S_{11}(0) + 2(\rho_1 \rho_2)^{1/2} f_1(0) f_2(0) S_{12}(0) + \rho_2 f_2(0) S_{22}(0).
\]

The structure factor \( S_{ij}(Q) \) is proportional to the Fourier transform of the radial distribution function \( g_{ij}(r) \) for the two-component mixture. From the Ornstein-Zernike equation one can relate \( S_{ij}(Q) \) with \( C_{ij}(Q) \), the Fourier transform of the direct correlation function \( C_{ij}(r) \). The final results given by Ashcroft and Langreth [13] are

\[
S_{11}(Q) = \left\{ 1 - \rho_1 C_{11}(Q) - \rho_1 \rho_2 C_{12}(Q) / [1 - \rho_2 C_{22}(Q)] \right\}^{-1},
\]

\[
S_{22}(Q) = \left\{ 1 - \rho_2 C_{22}(Q) - \rho_1 \rho_2 C_{12}(Q) / [1 - \rho_1 C_{11}(Q)] \right\}^{-1},
\]

\[
S_{12}(Q) = (\rho_1 \rho_2)^{1/2} C_{12}(Q) / [1 - \rho_1 C_{11}(Q)][1 - \rho_2 C_{22}(Q)] - \rho_1 \rho_2 C_{12}(Q).\]

The above equations may be compared with the corresponding expression for the one-component system

\[
S(Q) = \left\{ 1 - \rho C(Q) \right\}^{-1},
\]

The quantities \( S_{ij}(0) \) can be easily derived from the \( C_{ij}(0) \). Notice that \( C_{ij}(0) \) are concentration dependencies.

The light scattering intensity from optically isotropic molecules in dilute solution is given by [7]

\[
B' M \rho^2 / R(0) = 1 / S(0),
\]

where \( M \) is the molecular weight, \( \rho' = \rho M \) is the mass density (gm/cm\(^2\)) of the molecules, and \( B' = B f' \). Here \( f' = f / M \) is the polarizability per unit mass of the molecule. The excess intensity \( R(0) \) is defined as \( I(0) - I_0 \), where \( I(0) \) is the scattered light intensity from the solution at the mass concentration \( \rho' \), measured at the scattering angle \( \theta \to 0^+ \), and \( I_0 \) is the scattering intensity of the solvent alone (\( \rho = 0 \)). Equation (11) can be obtained from equation (8) when only one component is concerned. With the virial expansion for \( S(0) \) we have [14]

\[
B' M \rho^2 / R(0) = 1 + 2 h_2 \rho' / M + O(\rho'^2),
\]

where \( h_2 \) is the second virial coefficient defined as [15]

\[
h_2 = 2 \pi \int_0^\infty \left( 1 - e^{-r/v_M} \right) r^2 dr.
\]
In the above, $U(r)$ is the interaction potential. A straight line can be obtained at low
$p_r$ and when $p_f / R(0)$ is plotted against $p_f$. From the slope of the straight line one obtains the
second virial coefficient $b_2$. Comparing equation (12) with equations (10) and (11), we find
that $b_2 = -C(0)/2$.

2.2 SCATTERING FROM MIXTURE OF COLOIDAL AND POLYMER. — The above discussion on the
light scattering is general for any binary system. For example, one can study the interactions
of colloidal particles in a mixed solvent [16] or in a critical binary liquid mixture [17]. Another
example is a mixture of two polymers in a common solvent [18]. We focus here, however, on the
interactions in the mixture of colloid and polymer. As mentioned in Introduction, the
addition of free polymer to a stochiometrically stabilized colloidal dispersion can change the effective
interaction between the colloidal particles. We now describe, in this section, the detailed data
analysis procedure. In particular, we want to determine the interaction parameters
$C_{ij}(0)$ mentioned in the last section.

For our mixture the scattering from the colloidal particle is much stronger than that from the
polymer molecule, so that the polymer solution can be treated as a solvent. Then equation
(8) can be written as

$$B'M_1 \rho_f / R(0) = \left( S_{11}(0) + 2(p_f/p_1)^{1/2} (f_2/f_1) S_{12}(0) + (p_f/p_1)(f_2/f_1)^2 \Delta S_{22}(0) \right)^{-1}, \quad (14)$$

where the component 1 is denoted as the colloidal particle, $B' = B'_{mj}$; and $I_0$, is in the
definition of $R(0)$, now is the scattering intensity from the pure polymer solution. The quantity $\Delta S_{22}(0)$ is defined as $S_{22}(0, p_1) - S_{22}(0, p_f = 0)$, where $S_{22}(0, p_1)$ is the partial
structure factor for polymer molecules in the mixture, and $S_{22}(0, p_f = 0)$ is that in the pure
polymer solution. For low concentrations of colloid and polymer, one can make density expansions for the interaction parameters $C_{ij}(0)$. Here we define that

$$C_{11}(0) = C_{11} + p_f A_{1}/M_1 + p_1^2 A_{1}/M_2 + O(p_f^2),$$
$$C_{22}(0) = C_{22} + p_1 A_{1}/M_1 + p_1 B_{1}/M_1 + O(p_1^2),$$
$$C_{12}(0) = C_{12} + p_f B_{1}/M_1 + p_f E_{1}/M_1 + O(p_f^2). \quad (15)$$

Substituting equation (15) into equation (14) and making another density expansion, we have

$$B'M_1 \rho_f / R(0) = Y(\rho_2) + 2 \frac{\rho_2}{M_1} P(\rho_2), \quad (16)$$

where the intercept

$$Y(\rho_2) = 1 - \frac{\rho_2^2}{M_1} \frac{2 f_2}{f_1} C_{12} - \left( \frac{\rho_2^2}{M_2} \right)^2 \left[ \frac{2 f_2}{f_1} (C_{12} C_{22} + E_2') - \left( \frac{f_2}{f_1} \right)^2 (3 C_{12}^2 - B_1) \right] + O(\rho_f^2), \quad (17)$$

and the slope

$$P(\rho_2) = \frac{C_{11}}{2} - \frac{\rho_2^2}{M_1} \left( C_{12} A_2 + \frac{2 f_2}{f_1} (C_{12} C_{11} - E_1) \right) + O(\rho_f^3, \rho_1). \quad (18)$$

If the polymer is invisible ($f_2 = 0$), equation (16) becomes identical to equation (12) with
an effective second virial coefficient $b_{11}(\rho_i)$ of species 1 for a given polymer concentration $\rho_i$. This virial coefficient has the usual interpretation in terms of osmotic pressure derivatives. Comparing equations (18) and (16) with equation (12), one finds that the effective second virial coefficient $b_{11}(\rho_i)$ has the following form

$$b_{11}(\rho_i) = -\frac{C_{11}}{2} \frac{\rho_i^2}{M_2} \left( C_{12} + A_2 \right) + \mathcal{O}(\rho_i^2).$$  \hspace{1cm} (19)$$

As it stands, the interaction between a colloidal particle and a polymer molecule reduces the value of $b_{11}(\rho_i)$, and therefore the effective interaction between the colloidal particles may become attractive if enough polymer is added.

When the polymer is visible ($f_s \neq 0$), the interference between the two species changes both the intercept $Y$ and the slope $P$. From the measured $Y(\rho_i)$ the colloidal-polymer interaction parameter $C_{12}$ can be obtained using equation (17). Therefore, we can find quantitatively how the two species attract or repel. There is another parameter in equation (17), namely, the scattering amplitude ratio $f_s/f_1$. The scattering amplitude $f_s$ can be written as

$$f_s/M_i = (1/4 \pi) \left( \frac{\partial \varepsilon_i}{\partial \rho_i} \right)_{\rho_i=0} = (2 n_0/4 \pi) \left( \frac{\partial \eta_i}{\partial \rho_i} \right)_{\rho_i=0},$$  \hspace{1cm} (20)$$

where $n_0$ is the refractive index of solvent. The quantity $(\partial \eta_i/\partial \rho_i)_{\rho_i=0}$ can be measured by differential refractometry.

It should be emphasized that the above derivation for $b_{11}(\rho_i)$ in equation (19) is based on the partial structure factors (see Eq. (9)) for binary liquid mixtures given by Ashcroft and Langreth [13]. Equation (9) is general and independent of approximations for solving the structure factors. Therefore, equation (19) is valid for many colloid-polymer interactions. However, to obtain the exact functional form of $C_{ij}(0)$ one has to solve equations for $C_{ij}(0)$ from liquid theory. The exact functional form of $C_{ij}(0)$ has been obtained by the Percus-Yevick equation for binary hard-sphere systems [13, 19]. The Percus-Yevick equation is exact for low concentrations of hard spheres. With a virial expansion of the known $C_{ij}(0)$ we obtained the values of the expansion coefficients in equation (15) with $R_{11}$ and $R_{22}$ being the equivalent hard sphere radii of the colloidal particle and the polymer molecule respectively. Table I reports the final results. Therefore, the effective second virial coefficient $b_{11}(\rho_i)$ can be calculated using equation (19). The final result is

$$b_{11}(\rho_i) = \frac{16 \pi}{3} \frac{R_{11}^2}{M_2} \left( 1 - \frac{\rho_i^2}{\rho_i^2} \left( \frac{R_{22} + R_{11}^2}{6 R_{11}^2} \right) \right) .$$  \hspace{1cm} (21)$$

Table I. — The values of the expansion coefficients of $C_{ij}(0)$ in equation (15) for a binary hard-sphere system with $R_{11}$ and $R_{22}$ being the two hard sphere radii and $s = R_{11}/R_{22}$:

<table>
<thead>
<tr>
<th>$C_{ij}(0)$</th>
<th>$\frac{32 \pi}{3} R_{11}^2$</th>
<th>$\frac{160 \pi}{3} R_{11}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}(0)$</td>
<td>$\frac{32 \pi}{3} R_{11}^2$</td>
<td>$\frac{160 \pi}{3} R_{11}^2$</td>
</tr>
<tr>
<td>$C_{22}(0)$</td>
<td>$\frac{32 \pi}{3} R_{22}^2$</td>
<td>$\frac{160 \pi}{3} R_{22}^2$</td>
</tr>
<tr>
<td>$C_{12}(0)$</td>
<td>$\frac{4 \pi}{3} (R_{11} + R_{22})$</td>
<td>$\frac{16 \pi}{9} R_{11}^2 R_{22}^2 (1 + 6 s + 15 s^2 + 6 s^3 + s^4)$</td>
</tr>
<tr>
<td>$C_{21}(0)$</td>
<td>$\frac{4 \pi}{3} (R_{11} + R_{22})$</td>
<td>$\frac{16 \pi}{9} R_{11}^2 R_{22}^2 (1 + 6 s + 15 s^2 + 6 s^3 + s^4)$</td>
</tr>
</tbody>
</table>
where

\[ f(s) = 1 - \frac{s^3}{(1 + s)^3} \left( 8 + 15 s + 6 s^2 + s^3 \right). \]  

(22)

In the above, \( s = R_{11}/R_{22} \).

Another way to obtain the effective second virial coefficient \( b_{11}(\rho_i) \) is to directly calculate the effective interaction potential \( U(r) \) for colloidal particles in a polymer solution. Vrij and De Hek [11, 20] have derived an effective colloid-colloid interaction potential in the polymer solution by assuming that the colloidal particles are hard spheres, and that polymer molecules behave as hard spheres toward the colloidal particles, but can freely interpenetrate each other. With this potential they calculated the second virial coefficient for the colloidal particles in the polymer solution [11, 20]. In the dilute limit their \( b_{11}(\rho_i) \) turns out to be the same as that in equations (21) and (22). This is expected because the model proposed by Vrij and De Hek is essentially a binary hard-sphere model at least to the first order of the polymer concentration.

With the obtained \( b_{11}(\rho_i) \) one can estimate the stability limit (spinodal condition) for the colloidal particles in the polymer solution. At the limit of stability the system does not resist long-range fluctuations in concentration and the reciprocal osmotic compressibility goes to zero. Using the virial expansion of the osmotic pressure, one arrives at the spinodal condition [20]

\[ b_{11}(\rho_i) = -\frac{M_i}{2\rho_i}, \]  

(23)

for small \( \rho_i \). Substituting equation (21) into equation (23), we obtain the spinodal polymer concentration \( \rho_i^{*} \), at which the phase separation occurs:

\[ \rho_i^{*}/M_i = \frac{6 R_{11}^1}{\pi (R_{11} + R_{22})^6 f(s)} \left[ 1 + \frac{3 M_i}{32 \pi \rho_i^{*} R_{11}^1} \right]. \]  

(24)

3. Experimental

3.1 MATERIALS AND CHARACTERIZATION.—The colloidal system used in the study consisted of spherical calcium carbonate particles suspended in decane. The particles were stabilized by an adsorbed monolayer of a randomly branched calcium alkylbenzene sulfonate (CasA) surfactant. The synthesis procedures used to prepare the colloidal dispersion have been described by Markovic et al. [21]. These colloidal particles have been well characterized previously using small-angle neutron scattering technique [21], and are used as an acid-neutralizing aid in lubricating oils. Such a non-aqueous dispersion is ideal for the investigation attempted here since the colloidal system is approximately a hard-sphere-like system [22] (only short-range van der Waals and steric forces are important in this type of system).

The colloidal samples for scattering studies were prepared by dispersing known amounts of the concentrated material in decane. Decane (Aldrich Chemical Company, > 99 % pure) was used as received. Finally, the suspension (5.5 wt. %) was fractionated by ultracentrifugation for 2.5 hours at a nominal acceleration of \( 10^5 \) g (g = 980 cm/s²) to remove colloidal aggregates and dust. The obtained calcium carbonate dispersion was found to be relatively monodispersed with less than 10 % standard deviation in the particle radius, as determined by dynamic light scattering. Earlier dynamic light scattering investigations [23] of the same
colloid showed that the hydrodynamic radius of the particles was 5.0 nm. Under the assumption that the adsorbed layer of surfactant formed a concentric shell around the CaCO$_3$ core, the neutron scattering data gave a monolayer thickness of 1.8 nm [21]. The colloidal solution was stable over a period of months as monitored by the scattering intensity of the laser light.

The molecular weight $M_1$ of the colloidal particle was obtained by a sedimentation measurement. The sedimentation rate $v$ of the colloidal particle is related to the centripetal acceleration $\gamma$ via Stokes' law

$$ v = \left( \frac{M_1 - M_0}{6 \pi \eta R_0} \right) \gamma $$

(25)

Here $R_0$ is the hydrodynamic radius of the colloidal particle, $\eta$ is the solvent viscosity, and $M_0 = (4 \pi / 3) R_0^3$ is the mass of the displaced fluid. The true displaced fluid is probably slightly less than this value. The resulting estimate is $M_1 = 300,000 \pm 15\%$.

The polymer used in the study was hydrogenated polyisoprene, i.e., alternating polyethylene-propylene (PEP). The synthesis procedures used to prepare polyisoprene and the hydrogenation procedures have been described by Mays et al. [24, 25]. The polyethylene-propylene and its hydrogenated derivative PEP are model polymers, which have been well characterized previously using various experimental techniques [24-26]. Molecular weight characterization was carried out by size exclusion chromatography, which was made with a Waters 150-C SEC instrument using $\mu$Styragel columns and tetrahydrofuran as the elution solvent. The ratio $M_w/M_n$ were well below 1.1 for samples in the study. The PEP-decane solution was stable over a period of months as monitored by the scattering intensity of the laser light. It is found that decane is good solvent for both the colloid and the PEP polymer.

3.2 Light Scattering. — Light scattering measurements were performed using Brookhaven Instruments light scattering goniometer (BI-200SM). A 30-mW He/Ne laser (Spectra Physics, Model 127) illuminated a 10-ml sample tube in a index-matching vat. The laser intensity was stable within a few percent over a period of a month. Toluenes was used as an index-matching fluid to reduce background scattering from the cylindrical glass cell. All the measurements were conducted at the room temperature. The scattered light coming from well-defined scattering volume and angular aperture was collected by a photomultiplier (EMI 9863/350). Intensity measurements were accumulated automatically for two second periods at the scattering angles $\theta$ between 45° and 90°.

4. Results and discussion.

Figure 1 presents the scattering data from our colloidial particles in decane. The data is plotted as $K_1 \rho / f(\theta) / f_0 - 1$ versus $\rho / f_0$, where $f(\theta)$ is the scattering intensity from the colloidal solution at concentration $\rho / f_0$ (gm/cm$^3$), measured at the scattering angle $\theta$, and $f_0$ is the light intensity scattered from solvent alone ($\rho / f_0 = 0$). Since the size of our colloidal particles (5.0 nm in radius) is much smaller than the wavelength of the incident light (\(\lambda = 623.8 \text{ nm}\)), the scattering from these particles is isotropic. Therefore $f(\theta)$ is independent of $\theta$. This is shown in figure 1, where the data points measured at three different angles ($\theta = 45^\circ$, 60° and 90°) coincide with each other.

The value of $b_{11}/M_1$ ($\theta = 11$ and $M_1$ being the second virial coefficient and the mass of the colloidal particle, respectively) is determined from the slope of the fitted straight line using equation (12). It is found that for our colloidal particle in decane $b_{11}/M_1 = 3.8 \pm 0.5 \text{ cm}^3/\text{gm}$. The quoted uncertainty is only due to the scatter in the data [27]. With the measured $b_{11}$ one can define the radius $R_{11}$ of an equivalent hard sphere such that $4(4 \pi / 3) R_{11}^3 = b_{11}$. This gives
Fig. 1.—Plot of $K_i \rho_j / \langle I(\theta) / I_0 - 1 \rangle$ versus $\rho_j$ for CaCO$_3$ colloidal particles in decane. The scattering angles are 90° (open circles), 60° (closed circles) and 45° (triangles). The solid line is a linear fit to the data points of 90°-measurement.

$$K_i = 0.39 (b_{ij})^{1/3},$$

(26)

where the subscript $ij$ denotes the species. We have been using 1 for colloid and 2 for polymer.

With equation (26) we have $R_{12} = 4.8$ nm, which is close to the measured hydrodynamic radius of 5.6 ± 0.4 nm. Therefore, we conclude that the interaction between the colloidal particles is hard-sphere like. This conclusion is also supported by measurements of small-angle neutron scattering [22]. Our uncertainty in both the mass and the particle concentration is large enough to explain the difference between the measured and the expected values. It should be mentioned that the constant $K_1$ in the plot of figure 1 was chosen such that $K_1 \rho_j / \langle I(\theta) / I_0 - 1 \rangle = 1$ when $\rho_j = 0$. The constant $K_1$ equals $B' M_j / I_0$ when the notations in section 2 are used.

Similarly, $b_{22}/M_j$, $(b_{22})_2$ and $M_j$ being the second virial coefficient and the mass of the polymer, respectively, for PEP polymer in decane was measured. Figure 2 shows the plot of $K_2 \rho_j / \langle I(\theta) / I_0 - 1 \rangle$ versus the polymer concentration $\rho_j$ for PEP with molecular weights $(M_j)_L = 86000$ (Fig. 2a) and $(M_j)_b = 26000$ (Fig. 2b) (a subscript outside parentheses is used to identify a quantity related with different molecular weights of the polymer. Letters L, S, and T are used for «large», «small», and «tiny», same afterwards). Table II summarizes the characterizations of the PEP polymers and the colloidal particles in decane.

From equation (12) one expects that $(K_2)_L / (K_2)_b = (M_j)_L / (M_j)_b$, and indeed the measured $(K_2)_L / (K_2)_b = 3.1$, which is very close to the nominal value of $(M_j)_L / (M_j)_b = 3.3$. The ratio $(b_{22}/M_j)_L / (b_{22}/M_j)_b$ of the two virial coefficients should be equal to $(M_j)_L / (M_j)_b)^{0.764}$ according to theory [28] and recent experiment [26]. The measured $(b_{22}/M_j)_L / (b_{22}/M_j)_b = 2.27$, while the expected value is 2.37. Here the measured $(K_2)_L / (K_2)_b$ is used as the ratio of the two molecular weights. It is also known from equation (12) that the ratio $K_j / K_2 = f_2 f_j / f_1 f_2$, where $f_1$ and $f_j$ are the scattering amplitude of the colloidal particles (polymer chains). With this equation the value of $f_2 / f_1$ can be obtained. In Table II the measured values of $f_2 / f_1$ are listed for the polymer $(M_j)_L$ and the polymer $(M_j)_b$. Here we have used the fact that both $f_1$ and $f_j$ have the same sign (positive) relative to the solvent, which was checked using Chromatix KMX-16 laser differential refractometer.
Fig. 2. — Plots of $K_p \rho^2 / (I(\theta)/I_0 - 1)$ versus $\rho^2$ for PEP polymer in decane with molecular weights $(M_1)_0 = 86000$ (Fig. 2a) and $(M_2)_0 = 26000$ (Fig. 2b). The scattering angles are 90° (open circles), 60° (closed circles), and 45° (triangles). The solid lines are the linear fits to the data points of 90° measurements.

Table II. — Characterizations of the colloidal particle $(M_1)$ and the PEP polymers $(M_2)$ in decane $(i = 1$ for colloid, and $i = 2$ for polymer).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$b_i/M_i$ (cm$^3$/gm)</th>
<th>$R_i$ (nm)</th>
<th>$K_i \times 10^3$</th>
<th>$f_{2}/f_{1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(M_1)_0$</td>
<td>300 000</td>
<td>3.8</td>
<td>4.8</td>
<td>2.56</td>
</tr>
<tr>
<td>$(M_2)_0$</td>
<td>86 000</td>
<td>147.1</td>
<td>10.8</td>
<td>1.02</td>
</tr>
<tr>
<td>$(M_2)_1$</td>
<td>26 000</td>
<td>64.9</td>
<td>5.5</td>
<td>0.33</td>
</tr>
</tbody>
</table>

We now turn to the mixture of the colloid and the polymer. Figure 3 shows the scattering data from our colloidal particles in PEP/decane solution. The concentration of the polymer $(M_2)_0$ is 1.46% (gm/cm$^3$). The data is plotted as $K_1 \rho^2 I_0 / (I(\theta)/I_0 - 1)$ versus $\rho^2$, where $I_0$ and $K_1$ are the same as that in figure 1, and $I_0$ is the scattering intensity from the 1.46% PEP solution alone. The typical value of $I(\theta)/I_0$ varies from 3 to 13 in our working range of colloid concentrations. It is seen from figure 3 that the intercept $Y(\rho^2)$ of the straight line is larger than unity, and its slope $P(\rho^2)$ becomes negative.

It is found that both the intercept $Y(\rho^2)$ and the slope $P(\rho^2)$ change with the polymer concentration $\rho^2$. For small polymer molecules the interference between the polymer and the colloid is weak, and hence the change in the intercept $Y(\rho^2)$ is smaller. Figure 4a shows the measured $Y(\rho^2)$ as a function of $\rho^2$ for PEP with $(M_2)_0 = 1100$ (open circles) and $(M_2)_1$ (closed circles). It is seen that $Y(\rho^2)$ remains constant for the tiny polymer. The solid curve in figure 4a is the least-squares fitting curve

$$Y(\rho^2) = 1 + \rho^2 (15 \pm 2)$$

$$(cm^3/gm) - \rho^2 (145 \pm 90)$$

$$(cm^3/gm^2)$$

Figure 4b shows the measured $Y(\rho^2)$ as a function of $\rho^2$ for the polymer $(M_2)_1$. The large change in $Y(\rho^2)$ is expected because of the stronger interference signal ($f_2/f_1 = 0.34$). The solid curve in figure 4b is the least-squares fitting curve

$$Y(\rho^2) = 1 + \rho^2 (137.7 \pm 8.1)$$

$$(cm^3/gm) - \rho^3 (7304 \pm 645)$$

$$(cm^3/gm^2)$$

By comparing the fitting with equation (17) one obtains $C_{12}/M$. The second virial coefficient
Fig. 3. — Plot of $K_1 \rho_1 \ell_1 / (I(\theta) - I_0)$ versus $\rho_1$ for the mixture of the CaCO$_3$ colloid and PEP polymer in decane. The polymer concentration is 1.46% (gm/cm$^3$) with $(M_2)_h = 86,000$. The scattering angle is 90°, and the solid line is a linear fit to the data points.

Fig. 4. — Variations of the intercept $\gamma(\rho_2)$ as a function of the polymer concentration $\rho_2$ for PEP polymers with $(M_2)_h = 1100$ (open circles in Fig. 4a), $(M_2)_h = 26,000$ (closed circles in Fig. 4a), and $(M_2)_h = 86,000$ (Fig. 4b). The solid curves are the least-squares fits to equation (17).

$b_{12}$ between the colloidal particle and the polymer molecule is related to $C_{12}$ via $b_{12} = -C_{12}/(2\ell_1)$ (see Sect. 2). Finally, with equation (26) the equivalent radius $R_2$ of the mutual excluded volume between the colloid and the polymer can be found.

As shown in table III, the measured value of $(R_{12})_2 \approx 4.6$ nm for the small polymer is close to the expected hard sphere value $(R_{11} + (R_{22})_h)/2 = 5.1$ nm. However, the measured value of $(R_{12})_2 \approx 9.5$ nm for the large polymer is 22% larger than the hard sphere value $(R_{11} + (R_{22})_h)/2 = 7.8$ nm. These amounts to a 65% difference in the second virial coefficients since these radii vary as the cubic root of the virial coefficients. The experimental uncertainty for the measured virial coefficients is less than 20%. Therefore, we conclude that when the size of polymer molecules becomes larger than that of colloidal particles the hard sphere approximation breaks down. This can be understood by the fact that it is easier for polymer chains to interpenetrate than for a polymer chain and a hard sphere to do so. One would anticipate that this effect is more pronounced for larger polymer chains, and indeed
Table III. -- Interaction parameters in the mixture of the colloid and the PEP polymers. The experimental results (labeled by m) are compared with the hard-sphere predictions (labeled by h).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$(b_{12}/M_2)_m$ (cm$^3$/gm)</th>
<th>$(R_{12})_m$(nm)</th>
<th>$(R_{12})_h$(nm)</th>
<th>$(P(\rho_2)/b_{12}(0))_m$</th>
<th>$(P(\rho_2)/b_{12}(0))_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(M_2)_H = 26000$</td>
<td>37.5</td>
<td>4.6</td>
<td>5.1</td>
<td>1 - $5\rho_2$</td>
<td>1 - $4\rho_2$</td>
</tr>
<tr>
<td>$(M_2)_K = 86000$</td>
<td>101.3</td>
<td>9.5</td>
<td>7.8</td>
<td>1 - $107\rho_2$</td>
<td>$41 - 278\rho_2$</td>
</tr>
</tbody>
</table>

this was observed in our $R_{12}$ measurements. The above « osmotic effect » has been noticed many years ago by Vrij [11].

The variation of the slope $P(\rho_2)/M_2$ with the polymer concentration $\rho_2$ is shown in figure 5 for the polymer with $(M_2)_H$ (closed circles in Fig. 5a), $(M_2)_K$ (open circles in Fig. 5a), and $(M_2)_K$ (Fig. 5b). For the tiny polymer $P(\rho_2)/M_2$ remains constant. For the other two molecular weights, it is found that $P(\rho_2)/M_2$ can be fitted to a linear function $\alpha(1 - \beta\rho_2)$. The solid lines in figure 5 are the linear fits to the data. The quantity $\alpha$ is just $b_{11}(0)/M_2$ measured at $\rho_2 = 0$. The two values of $\alpha$ obtained from the fittings ($\alpha = 3.4$ cm$^3$/gm, and 3.6 cm$^3$/gm) are close to that obtained from figure 1. The measured values of $\beta$ are shown in table III.

The slope $P(\rho_2)$ for the binary hard-sphere system can also be calculated using equation (18) and table I. In table III we list the calculated $P(\rho_2)/b_{11}(0)$ for the two polymers with $(M_2)_H$ and $(M_2)_K$. Here $b_{11}(0) = 16\pi R_{12}^3/3$ is the second virial coefficient when $\rho_2 = 0$. In equation (18) the interference effect (the term proportional to $f_2/f_1$) has been included. For the mixture with $R_{12} = 5.5$ nm, $R_{11} = 4.8$ nm, $M_2 = 26000$, and $f_2/f_1 = 0.1$, the calculated interference contribution to the decay of $P(\rho_2)$ is 40% of the contribution from the polymer-colloid interaction. For the other hard-sphere system with $R_{12} = 10.8$ nm, $M_2 = 86000$, and $f_2/f_1 = 0.34$, the calculated interference contribution is 31%. It should be mentioned that for the hard-sphere system the interference effect always makes $P(\rho_2)$ smaller than that without the interference. This can be seen from equation (18) and table I. As shown in table III, for the small polymer $(M_2)_H$ the measurements agree well with the hard-sphere calculation. However, for the large polymer $(M_2)_K$ one can clearly see a

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Fig. 5. -- Variations of the slope $P(\rho_2)/M_2$ as a function of the polymer concentration $\rho_2$ for PEP polymers with $(M_2)_K = 1100$ (closed circles in Fig. 5a), $(M_2)_K = 26000$ (open circles in Fig. 5a), and $(M_2)_H = 86000$ (Fig. 5b). The solid lines are the linear fits to the data points. The dash line shows the expected $P(\rho_2) = 3.4$ (cm$^3$/gm)$(1 - \rho_2^2)$ (21 cm$^3$/gm) for the tiny polymer.
discrepancy between the calculated and the measured $P(\rho^*_I)/b_{11}(0)$. This is due to the non-hard-sphere behavior of the polymer molecule toward the colloidal particle.

For the tiny polymer ($M_{ZJ}$, there is no interference signal (see Fig. 4a), and also the measured $\beta = 0$ (see Fig. 5a). This is the case that $F(s)=0$ in equations (21) and (22) when $R_2 < R_{11}$. Since the equivalent hard sphere radius, $R_{22}$, of the polymer molecule scales [26] as $M_{ZJ}^{2/3}$, we estimate $(R_{22})_J = 0.8$ nm. The expected $P(\rho^*_I)/b_{11}(0) = 1 - \rho^*_I 2.1 \text{ (cm}^3/\text{gm})$. This is certainly too small to see in our working range of the polymer concentrations. The dash line in figure 5a shows the expected $P(\rho^*_I) = 3.4 \text{ (cm}^3/\text{gm}) [1 - \rho^*_I 2.1 \text{ (cm}^3/\text{gm})]$, which fits the data well.

The spinodal polymer concentration $\hat{\rho}^*_I$, at which the colloidal suspension phase separates, can be estimated using equation (24) together with the measured $R_{11}$ and $R_2$. For the small polymer ($M_{ZJ}$), the calculated $\hat{\rho}^*_I = 5.8 \text{ % (gm/cm}^3)$ when the colloid concentration $\rho^*_I = 9.8 \text{ % (gm/cm}^3)$. Phase separation occurred in our mixture when $\hat{\rho}^*_I = 4.8 \text{ % (gm/cm}^3)$ and $\rho^*_I = 9.8 \text{ % (gm/cm}^3)$. The colloidal particles precipitated out from the solution, and formed a dark brown colloid-rich phase on the bottom of the sample cell. As one can see, the measured spinodal polymer concentration $\hat{\rho}^*_I$ is close to the hard-sphere calculation from the second virial coefficient $b_{11}(\rho^*_I)$. For the large polymer ($M_{ZJ}$), the calculated $\hat{\rho}^*_I = 0.44 \text{ % (gm/cm}^3)$ when the colloid concentration is 15.2 % (gm/cm$^3$). The actual measured $\hat{\rho}^*_I = 1.9 \text{ % (gm/cm}^3)$, which is much larger than the calculated value from the hard-sphere model. This discrepancy supports our finding that these large polymer molecules do not behave as hard spheres in their interactions with the colloidal particles. We want to state, however, that no systematic study of the phase behavior of our mixture was intended here.

5. Conclusion.

With a virial expansion for the partial structure factors of binary mixtures given by Ashcroft and Langreth [13], the small-angle scattering intensity from a mixture of colloid and polymer is calculated as a function of colloid and polymer concentrations. Using the obtained formula one can extract interaction parameters in the mixture of polymer and colloid. This scheme shows how the scattering data provides information about changes of the interaction potential $U(r)$ for a colloidal suspension due to the addition of free polymer, the so called depletion effect. Our calculation demonstrates that the effective colloid-colloid interaction potential $U(r)$ proposed by Vrij and De Hek [11, 20] is consistent with the solution of the Percus-Yevick equation at least to the first order of the polymer concentration.

The light scattering technique is used to study interactions in the mixture of the CaSA surfactant stabilized CaCO$_3$ colloid and hydrogenated polyisoprene polymer. By measuring the concentration dependence of the scattered light from the colloid dispersion in the dilute polymer solution, we obtained the mutual excluded volume between the polymer molecule and the colloidal particle. Furthermore, the second virial coefficient of the colloidal particles is extracted for the polymer mixture with $(M_F) = 26,000$. The measurements suggest that the second virial coefficient linearly decreases to a negative value upon addition of the polymer when the polymer concentration is small. The dependence of the measured second virial coefficient on the polymer concentration agrees with the prediction for the depletion effect given by Vrij and De Hek [11, 20]. It is also found that when the size of polymer molecules becomes much larger than that of colloidal particles, the hard sphere approximation breaks down. The experiment suggests that our scheme of obtaining interaction parameters in the mixture of colloid and polymer is indeed capable of probing the changes of the interaction potential $U(r)$ for colloidal particles in the polymer solution.

Finally, we want to point out that the interpretation of our measurements for the effective second virial coefficient $b_{11}(\rho^*_I)$ is somewhat complicated by the interference effect between
the colloid and the polymer. The use of the neutron scattering with isotopically mixed solvents could eliminate the unwanted scattering from the polymer. Likewise, small-angle x-ray scattering could be used to complement the light scattering results. This is possible because x-ray and laser light will in general have different contrast ratios $f_j/f_s$, and by combining both types of scattering data one may in principle isolate the effect of the interference. We expect our method to be useful in the future for measuring the interactions between various polyatomic species in solution. It requires uniform samples without polydispersity or other heterogeneities. These species must also retain their identity upon mixing.

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[27] Some of the experimental uncertainty is from the error in the colloid concentration due to the centrifugation procedure, which removes some colloidal aggregates and dust. The measured value of $b_{11}/M$ varies with samples from different centrifugation batch within 15%. Here we take a value which is close to the average. We notice that the uncertainty of the colloid concentration has no effect on the measurements in the mixture as long as one uses the colloidal samples from the same centrifugation batch. This is because the measured quantities in the mixture are independent of the colloid concentration.