Colloidal Stabilization by Adsorbed Gelatin

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The stabilizing effect of adsorbed polyampholyte on colloidal dispersions is quantified through small angle neutron scattering measurements of the structure of concentrated dispersions. Gelatin is adsorbed onto colloidal acrylic latex particles of like net charge to provide both steric and electrostatic stabilization. The extent and structure of the adsorbed gelatin corona is measured using dynamic light scattering (DLS) and small angle neutron scattering (SANS) and dilution viscometry (DV). The SANS spectra from concentrated dispersions of bare and gelatin-coated colloidal particles are modeled via integral equation theory using pair potentials that superimpose an electric double layer and a simple model of steric repulsion, where all the parameters are determined a priori. Our results demonstrate for the first time that the stabilizing forces arising from the adsorbed gelatin can be predicted quantitatively from a simple combination of Derjaguin–Landau–Verwey–Overbeek (DLVO) theory and a model for the adsorbed polymer brush. These results agree with previous studies of the surface forces of gelatin adsorbed onto mica cylinders and are important for understanding colloidal stabilization imparted by adsorbed polyampholytes.

1. Introduction

Understanding the nature of gelatin adsorption and relating it to the conformation of gelatin molecules is a problem of wide interest in food processing,† photography,‡ biology, implant medicine, and engineering. The importance of understanding protein and polypeptide adsorption and a general review of the area has been presented by Möbius and Miller.4 Gelatin is a well-known stabilizer used in both suspensions and emulsions.6 Stabilization of the former systems is accomplished by the adsorbed gelatin as a steric barrier, whereas emulsions stabilization is achieved by modification of interfacial properties. This study is partly motivated by the goal of understanding gelatin stabilization of colloidal latex particles, which is technically important in controlling gelatin-containing formulations.

This work is also motivated by the complexity of polyampholyte–colloid interactions. The conformation of gelatin in solution and its adsorption onto surfaces is controlled by a delicate balance of the amphotolytic nature of the polypeptide, polymer character, hydrophobic forces, and polydispersity. Consequently, numerous variables can be expected to affect the adsorbed amount and the structure of the adsorbed layer, such as, temperature, ionic strength, pH, gelatin molecular weight and distribution, surface chemistry, solvent quality, and possibly surface geometry. Some recent experimental investigations of gelatin adsorption onto model colloidal particles provide a review of the field to date.7,8

Several methods have been used to study the stabilizing effects resulting from gelatin adsorption.9 Most relevant for the work performed here are the direct measurements of the forces between layers of gelatin adsorbed on mica cylinders through the use of the surface forces apparatus (SFA). Kawaniishi et al.10 explored the force between layers of gelatin adsorbed to mica surfaces both above and below its isoelectric point (pH = 5.1) using a SFA. The adsorbed amount of gelatin was calculated from the mean refractive index of the medium between the mica sheets. The authors reported a dependence of the adsorbed amount and the range of the layer interactions on the pH and ionic strength of the solutions. The measured force vs distance curves were fit with a linearized, constant-potential electrostatic interaction.11

Kamiyama and Israelschvili12 performed adsorption and SFA measurements on gelatin adsorbed onto mica from aqueous NaCl solutions. Particular attention was paid to the effect of ionic strength and pH on the excess adsorbed gelatin and on the force between the plates as a function of their separation. They found that the amount of added salt has a marginal effect on the adsorption properties, but a rather pronounced effect on the force between the plates: for high salt concentrations, the force is dominated by the steric effects, that is, the compression energy between two overlapping gelatin layers, which is very well described by the Alexander-de Gennes equation.13,14 On the other hand, if the salt concentration is low, the electrostatic double-layer repulsion between the plates is not screened and the forces display long-range tails quantifiable via an electrostatic repulsion.11

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Because of recently reported molecular scale measurements of the structure and amount of gelatin adsorbed onto model surfaces using X-ray reflectometry, it is now possible to provide a detailed molecular-level description of polyampholyte adsorption onto macroscopic surfaces and the consequent colloidal forces. Other methods have been attempted to quantify the forces acting between more microscopic surfaces, such as the rheology measurements of Howe et al. They characterized the viscosity of oil in water emulsions stabilized with gelatin and used a phenomenological model to extract pair potentials. Although the results for the stabilizing force due to adsorbed gelatin were within the realm of expectation, the method relied on phenomenological modeling and hence it was not predictive. To date, no method has been proposed to predict quantitatively the interparticle potential resulting from adsorbed gelatin.

Questions remain regarding the adsorption properties of gelatin onto highly curved surfaces, such as afforded by colloidal latex particles, and the resultant interaction between two such coated particles. Recently, it has been demonstrated that accurate measurements of the structure of gelatin adsorbed on colloidal particles can be achieved through a combination of methods that includes dynamic light scattering, small angle neutron scattering, (SANS), viscometry, densityometry, and solution depletion with fluorescent labeled gelatin. In this article, we investigate the consequence of gelatin adsorption onto well-characterized, model, spherical polymer colloids by resolving the dispersion structure factor over a range of concentrations. Statistical mechanics provides a rigorous link between the structure of a colloidal dispersion as measured by scattering methods and the direct interaction potential between the particles. SANS measurements are performed on concentrated solutions of bare and gelatin-coated latex particles and compared with integral equation theory, which provides an exact method for predicting scattering spectra based on parameters determined from independent measurements. We demonstrate that a simple superposition of interaction potentials for electrostatic repulsion and polymer brush steric forces suffices to predict the observed scattering data, in agreement with expectations from the measurements surface forces.

This article is organized as follows. In the next section we describe the experimental methods and the theoretical methods required to predict the dispersion structure after that we present and discuss the results of the SANS measurements. Then we compare the predictions and measurements and draw conclusions from analysis of the results.

2. Experimental Section

Materials. Acrylic-based latex (dynamic light scattering (DLS) radii of 330 ± 30 Å and 450 ± 40 Å) and lime-processed, deionized bone gelatin (Mn = 100 000, Mw = 160 000, Bloom: 295 ± 6.7% w/v gel at 10 °C, isoelectric point at pH = 5.1) were provided by Eastman Kodak Company and have been investigated previously. Hydrodynamics sizes were determined from velocity auto correlation functions (VACF) obtained on a 164-channel BI-9000AT digital correlator using 488-nm laser light scattered from diluted (~0.03% weight fraction) dispersions. The single particle diffusivity was extracted from a second-order cumulant analysis of the autocorrelation function and hydrodynamic radius (Rd) of the particles is calculated by the Stokes-Einstein relation. Polydispersity is determined from the ratio of second to first cumulant. Note that the neutron scattering length density of latex was determined previously by contrast variation to be 6.9 × 10^9 cm^-2.

The SANS experiments were performed on the NG3 SANS line at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD, in 1-mm-thick banjo cells at 40 °C. Thermal neutrons of 6 Å and 14.7% full width at half-maximum (fwhm) were used at detector distances of 5 and 13 m, resulting in a momentum transfer between 0.0047 and 0.0945 Å^-1. All solutions were prepared in 10 mM pH 5.7 sodium acetate buffer made with either H2O or D2O, depending on the nature of the experiment. In the experiments involving adsorbed gelatin, colloidal latex-gelatin mixtures were incubated at 40 °C for 8–10 h. The samples used in shell contrast experiments were equilibrated, centrifuged, and then re-suspended in clear, contrast matching aqueous buffer.

The collected SANS data are reduced according to the standard procedures recommended by NIST. Corrections for the empty cell, detector efficiency, and sample transmission are applied with software provided by NIST. The data are placed on an absolute scale by ratioing with scattering obtained by NIST-calibrated standards. Finally, the data are angle-averaged and Porod plots (I ∝ Q^-4 vs Q^-4) generated to determine the incoherent background scattering. The spectra reported here have had the incoherent background removed. However, no deconvolution of the instrument "smearing" function has been performed, because we prefer to smear the theoretical predictions with the known instrument smearing function for direct comparison with the data.

The cited electrophoretic mobility was determined by use of a Brookhaven ZetaPlus over a range of pH and added salt values encompassing those of the SANS measurements. Experimental procedures for the remainder of the cited data have been published by Vaynberg et al.7

3. Theoretical Predictions of the SANS Scattering from Gelatin-stabilized Colloidal Particles

In this section we present the method of generating the theoretical predictions that will be compared with the SANS measurements of both dilute and concentrated solutions of bare (electrostatically stabilized) and gelatin-coated latex particles. At low concentrations, the correlations between different particles are very weak and can be ignored; the scattering intensities result from scattering from a single particle and they allow us to determine important parameters such as the particle size and the extent of the adsorbed gelatin layer ("corona"). These parameters are necessary for the theoretical predictions of the scattering at high concentrations where correlations between particles become important.

Neglecting interparticle scattering contributions, the coherent macroscopic scattering intensity of a SANS experiment I(Q) is given by the expression:

\[ I(Q) = \frac{N}{\sqrt{2}} |A(Q)|^2 \]  

Here, Q is the scattering vector which is given by 4π sin(θ/2)/λ.

\( \theta \) is the scattering angle and \( i \) is the neutron wavelength. Moreover, \( N_s \) is the number of scatterers in the volume \( V \), and \( A(Q) \) is the scattering amplitude from a single particle. In the expression above it is assumed that the incoherent background scattering has been subtracted off and no instrument smearing is present.

The subscript on the left-hand side of eq 1 denotes the fact that the scattering intensity given by this equation is, at this stage, still a theoretical quantity; to have a direct comparison with experimental data, the finite resolution of the experimental apparatus has to be taken into account (i.e., instrument "smearing"). This is achieved by making a convolution of the quantity \( I_{\text{th}}(Q) \) with the resolution function \( R(Q, Q_0) \) as:

\[
I(Q) = \int_0^\infty dQ_0 I_{\text{th}}(Q_0)R(Q, Q_0)
\]  

(2)

For the instrument NG3 at NIST, the resolution function is modeled as triangular with the given mean and fwhm. The quantity \( I(Q) \) is then directly comparable with absolute SANS data with the incoherent background subtracted off.

For spherical scatterers having a core–shell structure, the scattering amplitude \( A_{C,\text{Sh}} \) can be written as follows:

\[
A_{C,\text{Sh}}(Q) = (\rho_{\text{sh}} - \rho_s)F(Q; R_M) + (\rho_c - \rho_{\text{sh}})F(Q; R_C)
\]  

(3)

where \( F(Q; R_M) \) and \( F(Q; R_C) \) are the form factors of the coated particle, which have radius \( R_M \), and of the core, which has radius \( R_C \), respectively. Moreover, \( \rho_c, \rho_{\text{sh}}, \) and \( \rho_s \) are the scattering length densities of the core, the shell, and the solvent, respectively. The scattering length density \( \rho_i \) of the component \( i \) in the mixture is calculated as

\[
\rho_i = \sum b_i v_i
\]  

(4)

where \( b_i \) is the coherent scattering length of an atom in the solvent or of a repeat unit in a polymer molecule and \( v_i \) is the respective volume the sum is carried, hence, over all atoms in a molecule or in the repeat unit.

The scattering length density of aqueous solvents can be varied by substituting heavy water, that is, D₂O for water. The scattering length density of a H₂O/D₂O mixture is given as:

\[
\rho_s = \phi_{\text{H}_2O}\rho_{\text{H}_2O} + (1 - \phi_{\text{H}_2O})\rho_{\text{D}_2O}
\]  

(5)

with \( \phi_{\text{H}_2O} \) denoting the volume fraction of H₂O in the isotopic water mixture. \( \rho_{\text{H}_2O} = -0.562 \times 10^{10} \text{ cm}^{-2} \) and \( \rho_{\text{D}_2O} = 6.404 \times 10^{10} \text{ cm}^{-2} \) denote the scattering length densities of the pure solvents. In this way, one can fulfill either the condition \( \rho_{\text{sh}} = \rho_s \) or the condition \( \rho_c = \rho_s \). The first case is denoted as core contrast and the second as shell contrast. The dilute limiting scattering results for core contrast are identical with the case of bare (uncoated) particles. Shell contrast provides a method to determine the extent of the gelatin layer. We examine the cases of core and shell contrast in more detail below.

### 3.1 Core Contrast or Bare Particles

In this case, where shell and solvent scatter neutrons in the same way, only the core is visible and eq 3 takes the form:

\[
A_{C,\text{Sh}}(Q) = (\rho_c - \rho_s)F(Q; R_C)
\]  

(6)

Combining eqs 1 and 6, we obtain for the scattering intensity the expression:

\[
I_{\text{th}}(Q) = n_c(\rho_c - \rho_s)^2F^2(Q; R_C)
\]  

(7)

where \( n_c \) is the number density of the colloidal particles.

For spherical particles having radius \( R_c \) and volume \( V_c = 4\pi R_c^3/3 \), the form factor \( F(Q; R_c) \) is analytically known in the Rayleigh–Gans–Debye limit:

\[
F(Q; R_c) = 3V_c \sin(QR_c) - QR_c \cos(QR_c) / (QR_c)^3
\]  

(8)

Using eqs 2, 7, and 8 above, we can determine the size of the bare latex particles by fitting the intensity data at low concentration and using the radius \( R_c \) of the particles as the only free parameter, where the scattering length density of the particles is either calculated from the known structure and density, or determined independently from contrast matching experiments.

### 3.2 Shell Contrast

In this case, where the solvent and the core scatter neutrons in the same way and only the corona is visible, we obtain from eq 3:

\[
A_{C,\text{Sh}}(Q) = (\rho_{\text{sh}} - \rho_c)F(Q; R_M) - F(Q; R_C)
\]  

(9)

Hence, the total scattering intensity is now given by the expression:

\[
I_{\text{th}}(Q) = n_c(\rho_{\text{sh}} - \rho_c)^2[F(Q; R_M) - F(Q; R_C)]
\]  

(10)

Once again, we obtain a comparison with SANS data by means of convolution of \( I_{\text{th}}(Q) \) with the resolution function. The form factor \( F(Q; R_M) \) is given by eq 8 above, after replacing \( R_c \) by \( R_M \) and \( V_c \) by \( V_M \).

Once the bare particle radius has been determined, for example, by the method outlined in section 3.1, the shell contrast procedure can be applied to low-concentration solutions using now \( R_M \) as the only free parameter to obtain the thickness \( L = R_M - R_c \) of the adsorbed layer. Note that this analysis is based on the assumption, as in previous work, that the gelatin density is uniform in the corona. Further, as our focus is on structural effects that are manifest at lower scattering vectors, to be discussed next, in this and in the preceding section we have neglected any effects of fluctuations in the adsorbed layer, an effect that has been treated in depth in ref 8. Finally, the adsorbed amount, which is measured independently via solution depletion and fluorescence labeling (see ref 7), can be determined in principle from a Guinier analysis (see, e.g., ref 8); however, the range of scattering vectors probed here and the size of the corona precludes an accurate determination of the adsorbed amount directly from SANS.

### 3.3 Scattering from Concentrated Dispersions

When the concentration of the colloidal particles in the solution increases, spatial correlations between the colloids become evident in the scattering patterns. Because the total scattering intensity obtained in a SANS experiment is strongly influenced by the interactions between the particles and the measured SANS profiles, and these correlations can be traced directly to the effective pair potential between the scatterers, SANS provides a method to resolve pair interaction potentials directly in concentrated dispersions.

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The starting point of a theoretical approach\textsuperscript{25,26} to the problem is to assume a pairwise additive interaction potential between the particles, which we denote by \( V(r) \), \( r \) being the separation between the particle centers. In the modern theory of the liquid state,\textsuperscript{27} a large variety of so-called integral equation theories have been developed, which allow for the evaluation of the radial distribution function \( g(r; n) \) of a dense liquid having number density \( n \), once the pair potential is known. The radial distribution function is proportional to the probability of finding a particle in the liquid at a distance from a given, reference particle, taken to be located at the origin. Associated with the radial distribution function is the total correlation function \( h(r) = g(r) - 1 \), the Fourier transform of which yields the structure factor \( S(Q) \) as

\[
S(Q) = 1 + n \int dr \exp[-iQ \cdot r] h(r) \quad (11)
\]

For atomic liquids, it has long been known that the structure factor establishes a bridge between theory and experiment. For such liquids the form factor is just the square of the volume of the scatterer and so the scattering intensity yields \( S(Q) \) directly. For a colloidal suspension, whose constituent entities are large particles, the form factor of the individual particles has to be considered.\textsuperscript{25,28} Furthermore, the complication of size, shape, and scattering length density polydispersity must be considered.\textsuperscript{15,26} In this work, because our particles are nearly monodisperse, we can ignore polydispersity effects and treat the scattering from monodisperse dispersions. For a concentrated, monodisperse dispersion, eq 1 becomes:

\[
I_{\text{th}}(Q) = \frac{N_c}{2} \left( A(Q) \right)^2 S(Q) \quad (12)
\]

where it is evident that the structure factor \( S(Q) \) becomes uncoupled from the determination of the form factor. The effects of polydispersity\textsuperscript{25,26} and finite size polydispersity\textsuperscript{26,28} on the scattering are well documented, but will not be included here. The primary effect of polydispersity in the range of scattering vectors considered here is to “smear” the minima in the form factor, as seen in the comparisons that follow.

Three factors permit this simplification for our system. First, the colloids are nearly monodisperse, because the polydispersity is less than 7\%, as determined by photon correlation spectroscopy. Second, the presence of instrument smearing tends to mask small amounts of polydispersity of this magnitude by SANS. Finally, our comparison with theory is for wavevectors around or greater than the first maximum, whereas the most significant effect of polydispersity is for wavevectors much lower than the primary peak in the structure factor.

For the concentrated dispersions, no contrast matching was performed and the form factor is taken to be that of the measured, dilute colloidal particle. Because the adsorbed mass of gelatin is very small in relation to the mass of the colloidal particle (~1% weight fraction), the contribution of the gelatin corona to the form factor scattering is negligible away from core contrast matching. Hence, we determined it is sufficiently accurate to use the same form factor for all the scattering predictions of the concentrated dispersions. Thus, for both bare and coated particles, the theoretical scattering intensity is given by the equation:

\[
I_{\text{th}}(Q) = n_c (\rho_c - \rho_s)^2 F^2(Q; R_c) S(Q) = \quad (13)
\]

\[
= I_0 \left( \frac{\sin(QR_c) - Q R_c \cos(QR_c)}{(QR_c)^3} \right)^2 \quad (14)
\]

where we have defined the prefactor \( I_0 \), which depends only on the density of the sample, the scattering length densities of the colloids and the solvent, and the size of the colloidal particle:

\[
I_0 = n_c (\rho_c - \rho_s)^2 V_c^2 \quad (15)
\]

Differences in scattering between the bare and coated particles at equal concentration can be traced directly back to a difference in the pair interaction potential, which affects the structure factor \( S(Q) \). Again, to have a direct comparison with experimental data, the above-obtained theoretical intensity \( I_{\text{th}}(Q) \) must be convoluted with the resolution function of the experimental apparatus, (see eq 2). We now propose interaction potentials suitable for describing the bare and gelatin-coated latex particles.

### 3.4. Bare Particle Interaction Potential
The acrylic latex particles used in this study are negatively charged and are suspended in a sodium acetate buffer of 10 mM. For the purpose of calculation, we estimate the number of surface charges \( Z \) from the measured value of the zeta potential (~77 mV), which we take to be the surface potential \( \psi_0 \) and the following relationship\textsuperscript{11}:

\[
\psi_0 = \frac{Ze}{4\pi\epsilon \epsilon_r R_c (1 + k_b T)} \quad (16)
\]

In eq 16, \( \epsilon_0 = 8.84 \times 10^{-12} \) (SI) is the dielectric constant of vacuum, \( \epsilon_r \) is the dielectric constant of the solvent (\( \epsilon_r = 81 \) for water), \( k_b \) is Boltzmann's constant, and \( T \) is the absolute temperature. The inverse Debye length \( \kappa \) gives the electrostatic screening length and is given by\textsuperscript{11}:

\[
\kappa = \frac{1}{\sqrt{\sum \epsilon_{\text{eff}} \kappa_b^2}} \quad (17)
\]

The sum is carried over all ion species present in the solution except for the colloidal particles themselves; \( n_c \) and \( z \) are the solution phase concentration and charge of the \( i \)th species. Using the known value of the colloid radius \( R_c \) and eq 17 with \( n_c = 0 \) and eq 16, we obtain the value \( Z = 1227 \) for the surface charge of the latex particles having hydrodynamic radius \( R_h = 330 \) A.

It is generally accepted that the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of charged interfaces accurately describes the effective interaction between charged colloids in an ionic environment.\textsuperscript{11} For these values of ionic strength, surface charge, and particle size we neglect the attractive influence of London–van der Waals forces. The functional form of the electrostatic interaction depends on the value of the dimensionless parameter \( \kappa R_c \). For small values of \( \kappa R_c \), a Yukawa form is suitable. In Table 1 we present the values of \( \kappa R_c \) for four mixtures we studied. The high concentration of salt present in the
mixtures makes this quantity large, typically \( \approx 10 \), and very weakly dependent on \( n_c \). For such large values, the effective potential between the colloidal particles is given by the nonlinear solution of the Poisson–Boltzmann equation as:\(^{11}\)

\[
\beta V_{\text{elec}}(r) = \begin{cases} 
U_0 \ln\{1 + \exp[-\kappa(r - 2R_C)]\}, & r < 2R_C; \\
0, & r > 2R_C,
\end{cases}
\]  

where

\[
U_0 = \frac{(Ze)^2}{8\pi k_B T e}\frac{1}{(1 + \kappa R_C)^2}
\]  

The values of \( U_0 \) for the four mixtures are shown in Table 1.

To determine the structure factor resulting from this interaction potential, a numerical solution of the Ornstein–Zernike equation with the Rogers–Young closure\(^{18}\) was performed as a function of colloid concentration. The Rogers–Young closure is “thermodynamically consistent”\(^{19,20,27}\) thus yielding a very accurate prediction of the structure factor that can be considered exact. Consequently, deviations from the measured structure factor can be attributed to deviations from the assumed form of the pair potential, all other factors being equal.

### 3.5. Gelatin-Coated Particles Interaction Potential

The surface potential of gelatin-coated \( R_m = 330 \) Å particles was measured to be \( \psi_s = -27 \) mV, corresponding to an effective particle charge of \( Z = 431 \). For simplicity, we neglect this charge at the surface of the colloid, ignoring both the complexity of the actual charge distribution in the corona and the interpretation of the measured electrophoretic mobility.

For separation distances less than twice the gelatin corona length \( L \), the effective interaction between coated particles also includes a steric repulsion resulting from the concentration of gelatin between the approaching particles. In previous work, Kamiyama and Israelachvili\(^{12}\) demonstrated that the Alexander–de Gennes potential described their surface forces measurements of gelatin adsorbed to macroscopic mica cylinders at similar solution conditions. Further, the gelatin layers were stable and could be considered “anchored” for purposes of interpreting the experiment. Thus, we follow the same approach here and we show that the above-mentioned potential can also describe the effective interaction, suitably modified for the spherical colloidal geometry, for our system.

Our starting point is the Alexander–de Gennes expression\(^{13,14}\) for the repulsive pressure \( P \) between two brush-bearing planar surfaces, each coated with a brush layer of thickness \( L \), expressed as a function of the interplate separation \( D \):
solutions of the Ornstein–Zernike–Rogers–Young (OZ-RY) equation for direct comparison with the measured SANS scattering spectra.

4. Results and Discussion

In this section, we proceed by first determining the particle form factor, which yields $R_C$, from SANS measurements of the dilute scattering from bare latex particles. Then, we show results of contrast matching experiments on dilute gelatin-coated latex to determine the extent of the gelatin corona, i.e., the parameter $L$. Then, using the known scattering length densities and solution compositions we compare a priori predictions for the SANS scattering for concentrated charge-stabilized dispersions to show the validity of the proposed electrostatic potential model. We then extend the analysis to gelatin-coated latex, where we use the known gelatin adsorption isotherms to again make a priori predictions for the scattering spectra of concentrated dispersions with varying gelatin coverage. Finally, these results are extended to a second latex of slightly larger radius with a fixed gelatin coverage, studied as a function of total gelatin/colloid concentration.

Results have been published for the dilute limiting scattering from these latex particles with and without adsorbed gelatin. These results are briefly reproduced and discussed below as a prelude to the analysis of the concentrated latex dispersions.

This procedure outlined above is performed at 1% weight latex concentration; the solvent composition is given in Table 1. The fits are shown in Figure 1, yielding $R_C = 282.5$ Å for the latex-particle radius. As shown, multiple minima and maxima can be fit successfully by a spherical, homogeneous sphere model. This value compares well with the hydrodynamic radius as determined from dynamic light scattering (330 ± 30 Å), which is usually observed to be slightly greater than SANS radii for most polymer lattices. Independent analysis using a polydisperse form factor shows that the value of polydispersity is on the order of 6%, in agreement with the DLS measurements.

<table>
<thead>
<tr>
<th>mixture</th>
<th>latex (%)</th>
<th>gelatin (%)</th>
<th>H2O (%)</th>
<th>D2O (%)</th>
<th>net gelatin (mg/m²)</th>
<th>adsorbed gelatin (mg/m²)</th>
<th>s (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9.8</td>
<td>0.1</td>
<td>83.3</td>
<td>6.8</td>
<td>0.12</td>
<td>0.07</td>
<td>48.90</td>
</tr>
<tr>
<td>II</td>
<td>9.8</td>
<td>1.0</td>
<td>82.4</td>
<td>6.8</td>
<td>1.0</td>
<td>0.5</td>
<td>18.25</td>
</tr>
</tbody>
</table>

*The percentages shown correspond to weight fractions.*

Table 2. Composition of Mixtures Containing both $R_C = 282.5$ Å Latex and Gelatin

Figure 1. SANS measurements of the bare particle form factor for 330 Å acrylic latex at 1% weight latex, where interparticle correlations can be ignored. The lines are theoretical fits to the data according to eq 7, used to extract the particle radii. Results for two different values of the sample–detector distance $L_2$ are shown: (a) $L_2 = 13$ m; (b) $L_2 = 5$ m.

any contributions caused by fluctuations, as discussed in ref 8. The uncertainty in the corona thickness is determined by a visible worsening of the theoretical fits of the data. As can be seen from Figure 2, good agreement is achieved within the core–shell model. Both fits yield the same net coated particle size, $R_u = 390 ± 20$ Å. Hence, the gelatin corona has thickness $L = 107.5$ Å.

We solved the OZ-RY equation with the pair potential parameters shown in Table 1 to obtain the structure factor $S(Q)$ and the total scattering intensity according to eq 14 for the concentrated, electrostatically stabilized latex dispersions with composition given in Table 1. The theoretical results are shown in comparison with the experimental data in Figure 3. Because the value of the prefactor $I_0$ (see eq 15) is also fixed, our approach contains no free fit parameters. Excellent agreement between
theory and SANS data is obtained by using the electro-
static pair potential, eq 18, for the bare latex particles.
Deviations are seen for the highest concentration at the
longest detector distance and at lowest scattering vector,
just next to the beam stop. This may be a consequence of
finite polydispersity, but is equally likely to be a conse-
quence of combined detector smearing and poor statistics
in circular averaging over a limited number of detection
cells.

Because of the high concentration of salt, the electro-
static potential is strongly screened and, therefore, the
hard core plays the most important role. A truly rigorous
test of the potential would also include variation in the
added salt concentration and the colloid concentration,
but this is beyond the scope of this study. In fact, it would
also be possible to describe theoretically the present SANS
data by performing a mapping of the electrostatic potential
to an effective hard sphere system.27

For the gelatin-coated particles, using the composite
interaction potential of steric plus electrostatic repulsion
and solving the OZ-RY equation yields the theoretical
results for the total scattering intensities shown in Figure
4. The solution properties are listed in Table 2. The good
quality of the agreement between theory and experiment
demonstrates the validity of this effective pair potential.
In Figure 5 we also show the bare structure factors for the
two solutions. Note that the average density of colloidal
particles is the same for both solutions; they only differ
in the amount of gelatin adsorbed and thus on the
steepness of the steric repulsive potential. This is mani-
fested in the shape of \( S(Q) \) for the higher gelatin
concentration, which displays more structure at higher
adsorbed gelatin. In this analysis we assume that
the layer thickness is constant and that only the prefactor
of the steric potential changes. Moreover, the dispersion
with higher adsorbed amount has its peak at a slightly
smaller \( Q \)-value than the dispersion with the lower
adsorbed amount, pointing to the fact that particles with
a dense gelatin coating are more repulsive and thus
separate further on average.

The relative contributions of the electrostatic and steric
repulsions to the stability of the gelatin-coated latex are
demonstrated in Figure 6a, for 0.1% weight gelatin, and
in Figure 6b for 1.0% weight gelatin. In the same figures,
we show separately the electrostatic and steric contribu-
tions. As can be seen, for the lower gelatin concentration,
the steric contribution is negligible compared with the
electrostatic one, whereas for the higher concentration
the two contributions are similar. The additional steric
repulsion between the adsorbed gelatin layers provides

\[ \text{(a)} \]

\[ \text{(b)} \]

**Figure 2.** SANS-measured scattering from the gelatin corona on 330 Å acrylic latex: (a) nearly contrast matched in equilibrium with 0.1% weight gelatin; (b) contrast matched in equilibrium with 0.2% weight gelatin. The lines are fits according to eq 10 with \( R_c = 282.5 \text{ Å} \) and \( R_M = 390 \text{ Å} \); The latex concentration was 0.36 wt % for both samples.

**Figure 3.** SANS-measured scattering from bare latex solutions (points) and the corresponding theoretical results (lines). Data from two different values of the sample–detector distance \( L_2 \) are shown: (a) \( L_2 = 13 \text{ m} \); (b) \( L_2 = 5 \text{ m} \).
the major stabilizing effect between the colloidal particles and causes the main peak in the structure factor to shift to higher Q-values, as shown in Figure 5. Apart from these quantitative remarks, we can also see from Figure 6 that, because of the high salt concentration, the effective interaction between the colloidal particles is short-ranged, which agrees with previous results by Kamiyama and Israelachvili on slightly curved cylindrical mica surfaces.12

To further investigate the validity of the above-mentioned effective pair potential for gelatin-coated colloids, we performed the same theoretical procedure for another set of SANS data, taken this time on mixtures of fully coated latex colloidal particles having a larger radius, $R_C = 400 \text{ Å}$, at four different colloidal concentrations. The ratio of adsorbed gelatin to colloid is held fixed in this series of experiments. We denote these mixtures III–VI and summarized their properties in Table 3. The parameter $s$ has been calculated as described above, and the thickness of the adsorbed gelatin layer $L$ is assumed to be independent of the size of the latex particles, i.e., we take again $L = 107.5 \text{ Å}$.

Without introducing any fit parameters, again we solve the Rogers–Young closure to calculate the structure factor and compare the theoretical results with the measured scattering intensities. The results for the intensities are shown in Figure 7 and the bare structure factors in Figure 8. Once more, the agreement between theory and experi-
The adsorption of polyampholytic gelatin onto colloidal acrylic latex of like net charge proceeds with relatively weak adsorption strength (on the order of a few $k_B T$ per molecule) to a saturation of only a few mg/m$^2$. The adsorption is thought to be primarily driven by charge-induced electrostatic polarization.\textsuperscript{7,15} The SANS measurements presented here demonstrate that this weakly adsorbed layer provides a significant steric stability. Further, our study shows that the naive superposition of a simple electrostatic repulsion with an equally simple model for polymer steric stabilization is able to accurately represent the interaction static potential between colloidal surfaces with adsorbed gelatin. This conclusion agrees with previous SFA studies; however, here we independently determine all the potential parameters and compare a priori predictions to direct SANS measurements of the colloidal microstructure. Indeed, we have shown that one can predict a priori the liquid structure of concentrated colloidal dispersions resulting from gelatin adsorption by this simple approach.

One technologically important use of gelatin is in providing shear stability during processing, such as in pharmaceutical and color film manufacturing, for example. The experiments and analysis shown here demonstrate that is should be possible to predict a priori the stabilization properties of gelatin from the known adsorbed amounts, gelatin corona thickness, and solution pH and ionic strength. Preliminary studies in our laboratory suggest that gelatin is a very effective stabilizer at these solution physicochemical conditions against shear-induced aggregation, qualitatively confirming the strong steric repulsion afforded by the relatively minor gelatin layer. Despite these successes, the accuracy of this simple, potential approach to modeling the complex interactions of weakly adsorbed polyampholyte layers is expected to break down when dynamical properties are considered. In particular, dispersion rheology and dense dispersion diffusion may be expected to be sensitive to the details of the adsorbed layer structure and its dynamics, in contrast to the static SANS measurements studied here. Consequently, further work is warranted to examine the details of the dynamical colloidal interactions imparted by adsorbed polyampholytes, as well as other interactions, such as bridging, that may play a role at solution physicochemical conditions other than those studied here.

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**Table 3. Composition of Mixtures Containing Both Latex and Gelatin for the Samples Containing Latex Particles of Radius $R_C = 400\,$Å\textsuperscript{a}**

<table>
<thead>
<tr>
<th>mixture</th>
<th>latex (%)</th>
<th>$H_2O$ (%)</th>
<th>$D_2O$ (%)</th>
<th>adsorbed gelatin (mg/m$^2$)</th>
<th>s (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>0.3</td>
<td>52.8</td>
<td>46.9</td>
<td>1.5</td>
<td>10.5</td>
</tr>
<tr>
<td>IV</td>
<td>1.2</td>
<td>52.4</td>
<td>46.4</td>
<td>1.5</td>
<td>10.5</td>
</tr>
<tr>
<td>V</td>
<td>3.9</td>
<td>50.9</td>
<td>45.2</td>
<td>1.5</td>
<td>10.5</td>
</tr>
<tr>
<td>VI</td>
<td>8.4</td>
<td>48.5</td>
<td>43.1</td>
<td>1.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The percentages shown correspond to weight fractions.