Interaction forces between colloidal particles in a solution of like-charged, adsorbing nanoparticles

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A B S T R A C T

We have measured the force between a weakly charged micron-sized colloidal particle and flat substrate in the presence of highly charged nanoparticles of the same sign under solution conditions such that the nanoparticles physically adsorb to the colloidal particle and substrate. The objective was to investigate the net effect on the force profile between the microparticle and flat substrate arising from both nanoparticle adsorption and nanoparticles in solution. The experiments used colloidal probe atomic force microscopy (CP-AFM) to measure the force profile between a relatively large (5 μm) colloidal probe glass particle and a planar glass substrate in aqueous solutions at varying concentrations of spherical nanoparticles. At very low nanoparticle concentrations, the primary effect was an increase in the electrostatic repulsion between the surfaces due to adsorption of the more highly charged nanoparticles. As the nanoparticle concentration is increased, a depletion attraction formed, followed by longer-range structural forces at the highest nanoparticle concentrations studied. These results suggest that, depending on their concentration, such nanoparticles can either stabilize a dispersion of weakly-charged colloidal particles or induce flocculation. This behavior is qualitatively different from that in nonadsorbing systems, where the initial effect is the development of an attractive depletion force.

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1. Introduction

Interparticle interactions in bidisperse particle suspensions have received significant interest by numerous colloidal researchers. Some of the earliest, and certainly the most cited, work was that of Asakura and Oosawa [1,2], who showed theoretically that the addition of small, nonadsorbing spheres to a solution of larger spheres could produce an attractive force between the larger particles – the well-known depletion force. For purely hard wall systems, Asakura and Oosawa derived a simple algebraic expression for this force by calculating the increase in free volume accessible to the small spheres when the excluded volume shells of the larger spheres overlapped. (An identical expression can be derived by consideration of the osmotic pressure difference between the gap region between the larger particles and the bulk when the gap becomes small enough to exclude the smaller particles [3].)

One of the appealing features of the depletion interaction is the ability to fine-tune the range and magnitude of the interaction by controlling separately the concentration and size of the smaller particles. This capability is useful, for example, to scientists interested in studying crystallization, gellation, and self-assembly of colloidal particles [4,5]. Since the work of Asakura and Oosawa, significant theoretical, computational and experimental work has been performed to better understand both the depletion force and the structural force produced by ordering of the nanoparticles under confinement at higher nanoparticle concentrations. (A recent review of work in this area was published by Walz [6].)

Traditionally, both theoretical and experimental studies of the depletion and structural forces, especially in systems involving nanoparticles in solution, have focused on systems in which the added material displayed little, if any, adsorption. Specifically, theoretical models typically assume no adsorption, while experimental studies have used components where adsorption was a minimum. For example, Walz and coworkers [7–19] performed a number of experimental studies investigating the effect of highly charged nanoparticles on the interaction force and energy profile between highly-charged, micron-sized colloidal particles. In these systems, adsorption of the nanoparticles was hindered by the strong electrostatic repulsion between the micro- and nanoparticles. The authors found that the initial effect of the nanoparticles was to create an attractive depletion force between the microparticles. As the nanoparticle concentration increased, pronounced oscillatory force profiles arose due to ordering of the nanoparticles around the interacting surfaces. Other experiments using nanoparticles as the depletant species were performed by Drelich et al. [20] and McNamee et al. [21], while a recent review of work performed using polymers was given by Kleshchanok et al. [22].

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It should be noted that for systems involving polymers, adsorption means that both steric and depletion forces can exist, possibly even simultaneously. Models for describing the net interparticle interaction in such systems were developed by Vincent and coworkers [23–25], Feigin and Napper [26], Van Lent et al. [27], and Seebergh and Berg [28].

In this paper, we extend our previous studies with non-adsorbing nanoparticles to investigate the effect of weakly adsorbing nanoparticles on the interaction force profile between larger, colloidal particles. Our objective is to address the following two questions:

1. What is the initial effect of adding the nanoparticles to the solution?

In our previous work with highly charged, non-adsorbing nanoparticles, we found that the initial effect of the nanoparticles was to create a depletion attraction between the larger particles, which was shown to be capable of inducing aggregation of micron-sized particles. With adsorption of the nanoparticles, the question is whether this initial depletion attraction is overwhelmed by the increased electrostatic repulsion between the decorated microparticles.

2. Are depletion and structural forces observed as the nanoparticle concentration is increased?

It is hypothesized that as the nanoparticle concentration increases, a depletion attraction will form at separations beyond the electrostatic repulsion between the colloidal surfaces. At higher nanoparticle concentration, longer-range oscillatory structural forces are expected to form.

The measurements were performed using the colloidal probe atomic force microscopy technique (CP-AFM) developed by Ducker et al. [29,30] and Butt [31], in which the force profile is measured between a single probe particle attached to an AFM cantilever and a planar substrate in aqueous solution. The probe particles and substrates in the current experiments were borosilicate glass, and the pH of the solutions was close to the glass iep (≈2.4) such that the surfaces were weakly charged. The nanoparticles were either zirconia (ZrO₂) or polystyrene. For the experiments with zirconia, solutions were conducted at solution pH values that were slightly below the glass iep such that the glass was slightly positively charged while the zirconia was highly negatively charged. The experiments with polystyrene were run with pH values of either 2.5 or 3.0, such that the glass was slightly negatively charged while the polystyrene was highly negatively charged (electrophoresis measurements of the polystyrene nanoparticles at these pH values yielded zeta potential of approximately –60 mV). Thus although the sign of the charge on the substrate, probe particle, and nanoparticles was the same in all experiments, the relatively weak charge on the probe particle and substrate allowed some deposition of the nanoparticles to occur.

It should be emphasized that although this system is similar to those used by Lewis and coworkers [32–34] to probe the nanoparticle-cle halo effect, there is one significant difference. Lewis and coworkers used pure silica particles in their experiments, while the experiments presented here were conducted using glass (borosilicate glass for the probe spheres, and water white glass microscope slides for the substrates). Unlike silica, glass can contain significant amounts (on the order 20–25% by weight) of additives, such as potassium, aluminium, calcium, and magnesium. It is believed that such impurities can create a nonuniform surface charge on the surface, such that although the average zeta potential of the surface could be slightly negative or positive, depending on the material and solution pH, oppositely charged patches would also exist, which would enhance adsorption. By comparison, Lewis and coworkers assumed that very little deposition of the nanoparticles would occur.

It should also be mentioned that Hong and Willing [35] performed similar CP-AFM experiments on the silica-zirconia system at nanoparticle concentrations of 10⁻⁶, 10⁻⁵, 10⁻⁴ and 10⁻³. The authors observed a slight ‘dip’ in the repulsive force-vs.-distance curve at 10⁻⁵ nanoparticle volume fraction which was attributed to nanoparticle haloing. However, this feature was not observed at 10⁻⁴ or 10⁻³ volume fractions, and even at 10⁻² volume fraction it was only observed in slightly more than half of the measured force curves.

We present here the experimental results as a function of both solution pH and ionic strength. We also compare our measured results with predictions made using a simple model developed by Piek and Walz [10] for describing the depletion interaction in charged systems.

2. Experimental

2.1. Materials

The water used for preparing all solutions was purified using an Easypure UV system and had a resistivity of 18.2 MΩ-cm. AFM force measurements were made between a glass slide (Fisher Scientific, product #12-544-12) and a borosilicate glass sphere with radius of 5 μm (Thermo Scientific, product #9010). The spheres were attached to silicon nitride cantilevers (Asylum Research, Santa Barbara, CA, product #TR400PSA, manufacturers’ listed spring constant, k, equal to 0.02 N/m) using UV curable glue (Norland Products, Cranbury, NJ, product #123L06). The glass slides had an RMS roughness of 0.26 nm over and area of 5 μm², as determined by AFM imaging. The nanoparticles used were either zirconia (ZrO₂, Nyacol, Ashland MA, product #ZR10/20, radius 5–10 nm) or polystyrene latex (Interfacial Dynamics Co., Eugene OR, product #S37200, radius ∼11 nm). The zirconia particles were supplied as a 20% by weight suspension at a pH of 0.5 with a net positive charge. The latex suspension was supplied as an 8% by weight suspension at a pH of 6 with a net negative particle charge owing to sulfate charges at the interface. Once the appropriate volume fraction suspensions were prepared, the dispersions were dialyzed using an ion exchange resin (Bio-Rad, Hercules, CA, product #143-7425). The pH of the suspensions was controlled using HNO₃ (Sigma Aldrich, product #84380). Images of the surfaces were obtained using silicon nitride, tapping mode cantilevers (Asylum Research, Santa Barbara, CA, Bio-Lever).

2.2. Methods

Solutions were prepared by adding an appropriate volume of the nanoparticle suspension to water. The solutions were then exposed to the ion exchange resin for three days, with intermittent mixing. During dialysis, slight aggregation of the nanoparticles was typically observed. After removal of the ion-exchange resin, nitric acid was added to control the pH. The suspensions were then sonicated for approximately 10 min to disrupt aggregates formed during the dialysis step. The solutions were passed through a 0.450 μm syringe filter (Fisher Scientific, product #09-719B) and allowed to equilibrate to room temperature (22–25 °C) before use.

Zeta potentials of the zirconia and polystyrene nanoparticles were measured using a Zetasizer Nano-ZS (Malvern Instruments Ltd., Worcestshire, UK). To estimate the zeta potential of the glass microparticle and substrate, the zeta potential of a 2 μm diameter borosilicate glass sphere, also purchased from Thermo Scientific, was measured using a Micro-Electrophoresis Apparatus Mk II (Rank Brothers Ltd., Cambridge, England).

AFM force measurements were conducted using an Asylum Research AFM (Asylum Research, Santa Barbara, CA, model MFP-3D). The borosilicate glass slides were cleaned using an oxygen plasma (SPI Supplies, West Chester, PA, PlasmaPrepII) and the glass
particles were cleaned using UV/ozone (BioForce Nanosciences, Inc., Ames, IA, UV/Ozone ProCleaner) once they had been attached to cantilevers. UV/ozone was used because plasma cleaning the cantilevers can cause deformation. All spring constants were measured prior to addition of glass spheres using thermal calibration (software provided by Asylum Research). AFM images of the surfaces were also obtained using the Asylum MFP-3D AFM.

Because of the low cantilever spring constants (0.02 N/m) used in the measurements, the measured forces show significant thermal noise. This can be seen in Fig. 1, where the red circles indicate the data obtained in one approach of the microparticle to the plate. To obtain smoother curves, an averaging procedure was utilized. Each force curve was discretized into separation distance steps of 0.2 nm, and all forces located within ±0.3 nm of each step were averaged together. The result of this averaging is represented by the black diamonds in Fig. 1. Finally, 10 such curves were averaged together to produce the final curve represented by the open blue circles. Forces between the sphere and flat plate, \( F_{sp} \), were converted to an energy per unit area between two flat plates, \( E_A \), using the relationship obtained from Derjaguin’s approximation.

\[
E_A = \frac{F_{sp}}{2\pi R}
\]

where \( R \) is the sphere radius.

3. Results

3.1. Composition of the glass substrate and probe particle

To quantify the composition of both the glass substrate and glass probe particle, elemental analysis measurements were performed using energy dispersive X-ray spectroscopy (Bruker AXS, MiKroanalysis GmbH, Berlin, Germany). The glass slide showed a normalized mass composition of 27.06% Si, 6.21% K, 5.62% Zn, 4.53% Na, 2.89% Ti, 2.56% Al, 51.14% O; while for the borosilicate glass probe particle, the composition was 21.02% Si, 15.18% Ca, 7.87% Al, 1.86% Na, 0.55% Mg, 53.52% O. For each sample, analyses were obtained at three different locations and the results were all similar. (By comparison, a measurement made on a pure silica slide showed only silicon and oxygen.)

3.2. Zeta potentials

Shown below in Table 1 are estimates of the average zeta potential for each of the materials used in these experiments at the relevant pH values. The values reported for the zirconia and polystyrene nanoparticles were measured on a sample of the materials used in the AFM force experiments, while the value for the glass microparticle and substrates are estimates based on the measured zeta potential on a 2 μm diameter borosilicate glass sphere purchased from the same supplier as the sphere used in the force measurements.

As seen, in the glass/zirconia experiments (performed at pH 1.5), the microparticle and substrate have a slight positive charge while the zirconia nanoparticles have a relatively high positive charge. By comparison, in the glass/polystyrene experiments (performed at pH 2.5 and 3.0), the glass is essentially at its isoelectric point at pH 2.5 and slightly negatively charged at pH 3.0. By comparison, the polystyrene nanoparticles have a relatively large negative charge at both pH values.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Average zeta potential values of the materials used in these experiments at the relevant pH values.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Zeta potential (mV)</td>
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<tr>
<td></td>
<td>pH 1.5</td>
</tr>
<tr>
<td>Glass microparticle and substrate</td>
<td>+4.4</td>
</tr>
<tr>
<td>Zirconia nanoparticles</td>
<td>+40</td>
</tr>
<tr>
<td>Polystyrene nanoparticles</td>
<td>−</td>
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</table>
3.3. Effect of dialyzing the nanoparticles

Figs. 2 and 3 demonstrate the effect of dialysis on the forces measured in the presence of nanoparticles. Fig. 2 is a plot of ln \( (E_A/m^2) \) vs. separation measured at pH 3.5 with and without polystyrene nanoparticles at \( \phi = 0.001 \) (\( \phi \equiv \) nanoparticle volume fraction). When the latex is introduced, the measured decay length, \( \lambda \), length drops well below the Debye length for a pH = 3.5 solution (\( \kappa^{-1} = 17.2 \text{ nm} \)), indicating an increasing ionic strength. Solution Debye lengths were determined by fitting the electrostatic repulsive force predicted at large separations (black lines, constant charge and constant potential) on a natural log plot. The predicted forces were calculated using the algorithm of Chan et al. [36], which calculates the electrostatic force between two identically charged solids in water by numerical solution of the Poisson–Boltzmann equation. Fig. 3 shows a similar experiment (same as Fig. 2, except the pH was 3.0), however in this experiment the solution with nanoparticles was dialyzed prior to adjusting the

![Fig. 2](image1.png)

**Fig. 2.** Natural log plots of \( E_A \) vs. separation (\( k = 0.026 \text{ N/m} \)) in the presence of an undialyzed suspension of polystyrene latex nanoparticles (red diamonds) and in the absence of nanoparticles (blue circles). Both solutions were at a pH of 3.5. The plot clearly shows that the addition of nanoparticles to the solution increases the ionic strength of the solution to a value above what is expected for a pH 3.5 solution. The solid lines are fits to the data from the nanoparticle solution made using a decay length, \( \lambda \), of 11.3 nm. By comparison, the theoretical Debye length, \( \kappa^{-1} \), at pH 3.5 is 17.04 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

![Fig. 3](image2.png)

**Fig. 3.** Natural log plots of \( E_A \) vs. separation (\( k = 0.026 \text{ N/m} \)) for the same glass/polystyrene system of Fig. 2. The solution containing nanoparticles (red diamonds) has been dialyzed prior to pH control. The blue circles represent a solution with no nanoparticles at the same pH as the solution containing nanoparticles. The measured decay length is in agreement the Debye length for both solutions (\( \kappa^{-1} = 9.59 \text{ nm} \) at pH 3.0). The increased magnitude of the electrostatic repulsive force can thus be attributed directly to the presence of the added nanoparticles and not indirectly to a change in solution ionic strength. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
pH. It is clear that the ionic strength of the solution containing the latex nanoparticles is now identical to the solution containing no latex, meaning that any changes in the measured force profile would be directly due to the nanoparticles themselves and not an indirect effect arising from a change in ionic strength. These results were collected from the polystyrene latex system and will be described in greater detail following the presentation of the results for the ZrO2 system, which was the first system studied. All subsequent force curves presented used nanoparticles suspensions that had been dialyzed.

### 3.4. Results from glass/zirconia system

The force between two glass surfaces as a function of pH and constant volume fraction of ZrO2 is shown in Fig. 4A. The force between the two glass surfaces without added nanoparticles (black diamonds) shows no electrostatic or van der Waals contributions when the pH is 1.5; a repulsive steric/hydration interaction is observed beginning at approximately 3–4 nm. While it may seem surprising that no van der Waals forces were detected, it should be noted that this is consistent with AFM measurements made on the silica–water–silica system by other researchers [30,37,38].

When zirconia nanoparticles at a volume fraction of 0.001 are introduced at a pH of 1.5, a repulsive force becomes apparent (red triangles in Fig. 4A). A plot of the natural log of the force vs. separation is found to be linear at large separations (Fig. 4B) and the decay length obtained from the slope in this linear region \( \lambda = 1.70 \text{ nm} \) is equal to the Debye length \( \kappa^{-1} = 1.70 \text{ nm} \). Similar results are found when the pH is increased to 1.75 and 2.0 at a constant nanoparticle volume fraction. These results clearly suggest that the zirconia nanoparticles are depositing to the surface of the glass microparticles, leading to an electrostatic repulsion between them. No evidence of a long-range attraction, such as a depletion attraction, is observed at these nanoparticle volume fractions.

Fig. 5 shows the effect of increasing the nanoparticle volume fraction on the force profile at a constant pH value of 1.5. Again, for a system with no nanoparticles, only repulsive steric/hydration forces are detected and adding zirconia nanoparticles at a volume fraction of \( \phi = 0.001 \) produces an exponentially-decaying repulsion with a decay length \( \lambda = 2.0 \text{ nm} \) approximately equal to the bulk Debye length. (Note that the force profile with no added nanoparticles in Fig. 5A is slightly different from that in Fig. 4A because these curves were obtained from different experiments with different materials. The steric or hydration forces causing this short-range repulsive force are surface-dependent and, because of their very short range nature, are difficult to measure accurately in these experiments.) When the nanoparticles volume fraction is increased to 0.01, the electrostatic repulsive force increases in magnitude, however the decay length of the force remains unchanged (shown in Fig. 5B which plots the natural log of force vs. separation). These

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![Fig. 4.](image)

**Fig. 4.** \( E_A \) vs. separation (k = 0.023 N/m) between two glass surfaces as a function of pH at constant volume fraction of ZrO2 (\( \phi = 0.001 \)). The decay lengths obtained from the slopes of the linear region of the curves in Fig. 4B are consistent with the known Debye lengths of the system. Note that since no electrostatic force was observed for the pH 1.5 solution without nanoparticles (black diamonds), this data is not presented in Fig. 4B. The Debye lengths, \( \kappa^{-1} \), at pH 2.0, 1.75 and 1.50 are 3.03 nm, 2.27 nm and 1.70 nm, respectively.

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![Fig. 5.](image)

**Fig. 5.** \( E_A \) vs. separation (k = 0.031 N/m) between two glass surfaces at constant pH and increasing volume fraction of zirconia nanoparticles. Addition of the nanoparticles results in an increasing electrostatic repulsion between the two glass surfaces with a decay length equal to the known Debye length. No long-range depletion forces are observed. The Debye length, \( \kappa^{-1} \), at pH 1.5 is 1.70 nm.
constant surface potential. As shown by Liu and Luijten [39], for when both are of the same sign, under the boundary conditions of between surfaces that have very dissimilar surface potentials, even should be mentioned is an electrostatic attraction that can arise creates favorable regions for adsorption. Another possibility that or that non-uniformity in the distribution of charge on the surface charge density of the glass does not present a significant barrier charge sites exists. Our results suggest that either the positive tion, and a slight excess of positive charge sites relative to negative

Fig. 6. AFM images of a glass substrate at pH 1.5, in the absence (left) and presence (right) of ZrO2 nanoparticles. The cross-section topography plots indicate additional protrusions on the sample in solutions containing the nanoparticles, and the size of these protrusions are consistent with the known diameter of the zirconia nanoparticles. The images were obtained in tapping mode with a Bio-Lever cantilever (k = 0.006 N/m).

A major advantage of the glass/polystyrene system, relative to the glass/zirconia system, is that experiments can be done on the high-pH side of the glass isoelectric point where the surface has a slight negative charge and the polystyrene has a strong negative charge. The higher pH values means that the Debye length of the solution is significantly greater and that measurable electrostatic forces can be detected between the glass surfaces even in the absence of any added nanoparticles. Thus experiments were conducted at pH values of 2.5 (k^-1 = 5.39 nm) and 3.0 (k^-1 = 9.59 nm).

Figs. 7A and 8A show the energy/area profiles measured at pH 2.5 and 3.0, respectively, in both the absence and presence of polystyrene nanoparticles. Measurements in both systems are qualitatively similar. As in the glass/zirconia system, the introduction of nanoparticles at low concentrations results in an increased, exponentially-decaying repulsive force. Plots of the natural log of the energy vs. separation distance (Figs. 7B and 8B) at low nanoparticle concentrations are linear at large separations with a decay length equal to the bulk Debye length. This again suggests that the nanoparticles are simply depositing onto the glass surfaces, increasing the effective surface charge density and producing an electrostatic repulsion that increases with increasing nanoparticle concentration.

Further evidence of such deposition is given by the SEM images shown in Fig. 9. Each of these images was obtained by immersing one of the glass slides in a polystyrene latex solution (φ = 0.006) at either pH 2.5 (Fig. 9A) or 3.0 (Fig. 9B) for a period of 30 min. After removal, each slide was gently rinsed with water that had been ti- trated to the same pH as the adsorption solution in order to remove free particles, and then allowed to dry in air. SEM images of the slides was obtained using a field emission scanning electron microscope (SEM, LEO1550, Carl Zeiss Microlmaging Inc., Thornwood, NY). As seen, significant deposition of the nanoparticles is observed at both pH values.

At higher nanoparticle concentrations (φ = 0.006), longer-ran- ged attractive depletion forces are observed, causing a local mini- mum in the energy profile at approximately 40 nm separation for pH 2.5 and 52 nm separation for pH 3.0 (inset to Figs. 7A and
8A). In addition, at pH 3.0, longer-range structural forces are clearly evident when the nanoparticle volume fraction increases to 0.01. The natural log plots at the highest concentration (Figs. 7B and 8B) show significant deviation from linearity at these higher nanoparticles concentrations since the depletion and structural forces are comparable to the electrostatic component, especially at the largest separations.

4. Discussion

The results obtained in both the glass/zirconia and glass/polystyrene systems paint a consistent and straightforward picture of the effects of highly charged nanoparticles on the interaction force or energy profile between weakly-charged glass surfaces. When the nanoparticles are introduced, strong adsorption onto the weakly-charged glass surfaces occurs. Although both the nanoparticles and glass surfaces are like-charged, it appears that the magnitude of the electrostatic repulsion, combined with a heterogeneous surface charge due to impurities in the glass, is insufficient to prevent the nanoparticles from depositing and adhering due to strong van der Waals forces. Thus the net result of adding nanoparticles to the system is an increased electrostatic repulsive force with a characteristic decay length equivalent to the solution Debye length. As the nanoparticle concentration is increased, the degree of deposition increases, producing a stronger electrostatic repulsion. However, since the Debye length of the solution remains essentially unchanged, the characteristic decay length of the interaction remains constant. Clearly, any depletion interaction that is also present at these concentrations is too weak to alter the Debye length significantly.

At sufficiently high nanoparticle concentrations, a long-range, attractive depletion interaction appears. Although the strong electrostatic repulsion between the probe particle and substrate remains, and possibly even strengthens as the bulk nanoparticle concentration increases, the depletion attraction forms at larger distances where the electrostatic repulsion is significantly weakened. This attractive force arises from the exclusion of the nanoparticles from the gap region between the charged nanoparticle-covered microparticle and plate when the separation distance becomes sufficiently small to exclude the nanoparticles. Although this depletion interaction is present at even the lowest nanoparticle concentrations, it is too small to be detected in the AFM measurements. To first order, the magnitude of the depletion interaction scales with the bulk number density of the nanoparticles, as shown by Walz and Sharma [3], in charged solutions, the magnitude of the depletion interaction is also very sensitive to the solution Debye length of the system (the range and magnitude of the interaction increases with the bulk Debye length). This trend explains why the depletion interaction is much more pronounced
at pH 3.0 for the glass polystyrene system ($k^{-1} = 9.59$ nm) than at pH 2.5 ($k^{-1} = 5.39$ nm) for equal nanoparticle volume fractions.

Piech and Walz [10] found that the depletion interaction in charged systems could be approximated using the hard-sphere model of Asakura–Oosawa but with an adjusted nanoparticle size. Specifically, for two hard microspheres of radius $R$ separated by gap $h$ in a solution of hard nanospheres of radius $a$ and bulk number density $\rho$, the Asakura–Oosawa interaction force between the two microspheres can be written as:

$$F_{ss}(h) = \frac{\pi a^2}{2} + \frac{2aR}{h}$$

for $0 < h < 2a$

$$F_{ss}(h) = 0$$

for $h > 2a$ \hspace{1cm} (2)

where the negative sign indicates that the force is attractive. For cases where the microparticle size, $R$, is much greater than the nanoparticle size, $a$, such as in the measurements presented here, the corresponding force between a particle and flat plate ($F_{sp}$) will be approximately twice the force predicted by this expression, which is based on the Derjaguin approximation. Piech and Walz [10] showed that the correct effective nanoparticle radius to use in charged systems is the distance, measured from the center of the nanoparticles to the surface of the microparticle, at which the nanoparticle–microparticle electrostatic repulsion becomes equal to $0.5 kT$. Even though the exact value of this distance depends on several factors, including the surface potential of the micro- and nanoparticle, a very rough estimate was the nanoparticle radius plus $5k^{-1}$ (this value is also consistent with experimental observations made by Odiachi and Prieve [41].)

Using this approach, we calculated the depletion interaction for the glass/polystyrene system at pH 2.5 and nanoparticle volume

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Fig. 9. SEM images of glass slides that had been immersed in a 0.006 volume fraction polystyrene nanoparticle solution at either pH 2.5 (9A) or 3.0 (9B) for 30 min and then washed with a nanoparticle-free solution at the same pH. Substantial deposition of the nanoparticles is observed.
fraction of 0.01. The result is represented by the solid line in Fig. 7A and B, which also includes an electrostatic repulsive force between the large particle and plate calculated using a Debye length of 5.8 nm and surface potential of −12 mV. The effective nanoparticle radius and volume fraction of solution used to obtain this result was 38 nm (hard sphere radius plus 4.7 radius and volume fraction of solution used to obtain this result as simply the wavelength of this interaction could be closely approximated at nanoparticle concentrations below approximately 8% volume, surfaces. Piech and Walz [15] and Tulpar et al. [17] showed that particles upon confinement into layers parallel to the interacting dent. This structural interaction arises from ordering of the nano-

5.8 nm and surface potential of the large particle and plate calculated using a Debye length of 0.01. The result is represented by the solid line in Fig. 7A

At the highest concentrations of polystyrene nanoparticles at pH 3.0 (Fig. 8), an oscillatory structural interaction is clearly evi-
dent. This structural interaction arises from ordering of the nano-
particles upon confinement into layers parallel to the interacting surfaces. Piech and Walz [15] and Tulpar et al. [17] showed that at nanoparticle concentrations below approximately 8% volume, the wavelength of this interaction could be closely approximated as simply \[ \rho^{-1/3} \], where \( \rho \) is the bulk number density of nanoparticles (#/volume). For 11 nm radius nanoparticles at a volume fraction of 0.01, \( \rho^{-1/3} \) is 82 nm. By comparison, the wavelength of the oscillation in Fig. 8 at 0.01 volume fraction is measured to be 70 nm, which is a reasonable agreement considering the uncertainty in the number density (e.g., due to polydispersity in the nanoparticle size).

5. Conclusions

We have measured the forces between weakly charged glass particles and substrates in the presence of highly charged nanoparticles of ZrO₂ and polystyrene latex. Due to the weak charge and impurities in the glass, both types of nanoparticles adsorbed to the glass. We find that in both systems, the measured surface forces are consistent with adsorption of nanoparticles to the glass surfaces, leading to an increased electrostatic repulsion between the surfaces at low nanoparticle volume fractions with a character-

istic length equal to the bulk Debye length. For the glass/polysty-
rene system, longer-range depletion interactions were detected at nanoparticle volume fractions, \( \phi \), of 0.006, and oscillatory struc-
tural forces at \( \phi \approx 0.01 \) and pH 3.0. For the glass/polystyrene sys-
tem, the measured force profile could be described reasonably well using a simple hard wall approach in which an effective size of the nanoparticles, representing the range of the electrostatic repulsion was used in place of the actual size.

This observed trend in the nature of the force profile is substan-
tially different from that seen in systems where little deposition of the nanoparticles occurs. Specifically, in the latter systems, the initial effect of the nanoparticles is the formation of a depletion attraction, which can be strong enough to induce flocculation. Our current results suggest that with weakly charged microparti-
cles, the increased electrostatic repulsion that arises upon addition of the nanoparticles could potentially further stabilize a weakly-

stable dispersion (i.e., a dispersion consisting of weakly-charged particles). However, aggregation could then result at higher nano-

particle concentration upon the development of the depletion attraction.

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