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Long-range attraction in aqueous colloidal suspensions

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Abstract

Long-range attractions in aqueous suspensions were observed between polymeric microspheres and also between microspheres and a gel bead. Attractive displacements were consistently seen even between like-charged entities, and they were observed over spans as large as 2 mm. Such behaviors are unexpected, and may reside in a long-range attraction mechanism.

Keywords

Long-range attraction; colloidal particles; aqueous suspensions

1. INTRODUCTION

Electrostatic interactions between charged particles have attracted sustained cross-disciplinary interest because of their fundamental role in governing the properties of many systems, including soft matter, colloidal suspensions, polyelectrolyte solutions, and various biological systems.^{1–5} In solution, such interactions are usually limited in strength by screening, as charged surfaces will attract a thin atmosphere of oppositely charged counterions, resulting in a sandwich often called an electric double layer.⁶ Based mainly upon this double layer, DLVO (Derjaguin-Landau-Verwey-Overbeek) theory was introduced to describe colloidal particle behavior in water.⁷ This theory includes both a repulsive force and a van der Waals attractive force. The latter is quite weak and decays rapidly with increasing separation; hence, it is commonly neglected when particle separation is more than 100 nm.⁸ Thus, electrostatic interactions in solution are normally considered to be short-ranged and typically inconsequential at separations larger than 100 nanometers.

However, many observations on colloidal systems cannot be explained quantitatively or qualitatively by the standard DLVO theory.^{10–30} An alternative description of the basic governing forces was put forward by Langmuir in 1938.⁹ Focusing on long-range attractions, Langmuir hypothesized that the attractive forces among like-charged colloidal particles were fundamentally electrostatic in nature, arising from the arrangement of counterions between particles. Based on this mechanism, Feynman coined the term “like-likes-like” through the intermediary of unlikes.²⁰ Ise et al.’s experimental observations in the 1980’s and 1990’s,^{10–15} Sogami’s theory,¹⁶ and Smalley’s reports^{17–19} also did not fit in with DLVO theory, and showed a much longer attractive force range.

Extending over many micrometers, the attractive force has been pursued extensively by Ise et al., whose experimental results implied that the attraction drove a reversible phase transition between the disordered isotropic state and the liquid crystalline state.^{21–26} Attractive forces over distances of 100 to 1000 nm were also found by Grier et al. using different approaches.^{27–30} In a recent review, McBride and Baveye pointed out that although DLVO theory adequately describes repulsive interactions between isolated like-charged particles, explaining multi-particle interactions in suspensions with low electrolyte concentration and high particle charge must require some long-range attractive force,¹ in concordance with the pioneering views of Langmuir and Feynman.

On the other hand, the concept of long-range attraction has not gone unchallenged. In particular, the theory developed by Ise and Sogami has been challenged both by Overbeek³¹ and by Woodward.³² However, vigorous responses have been put forth,³³ arguing that Overbeek's criticism was based on miscalculation of Gibb's free energy, and that Woodward had erroneously insisted that the inhomogeneity of microions caused by the presence of macroions invalidates Sogami's assumption that the Gibbs free energy is a first-order homogeneous function of the particle number. Hence, while long-range attractions not widely acknowledged, the defenders of that concept have responded to the criticisms thus far lodged, and long-range pairwise attractions have recently been directly confirmed experimentally.³⁴

The long-range attractive behaviors observed experimentally by Ise, Grier, and others extend to distances on the order of several micrometers. Here we report attractive forces extending up to the millimeter range. Such long-range attractions were found not only for entities of opposite charge, but also for entities of like charge.

2. EXPERIMENTAL METHODS

The experimental chamber was made of a 2-mm thick rectangular plastic block with a vertically oriented 1-cm diameter cylindrical hole cut in the middle. The bottom of the hole was sealed with a No.1 glass microscope cover slip (150 μm thick), through which the sample could be observed. Prior to each experiment all surfaces were cleaned thoroughly with ethanol and de-ionized water.

The suspensions under study consisted of three components: a single ion-exchange-resin bead (Bio-Rex MSZ 501(D) resin), microspheres, and distilled, de-ionized water. The ion-exchange-resin beads used were $600 \pm 100 \mu\text{m}$ in diameter and came in two types: anionic and cationic. Only one bead was used in each experiment, either positively charged or negatively charged. Prior to use, beads were washed with ethanol, and then washed again several times with de-ionized water from a Barnstead D3750 Nanopure Diamond purification system (type I HPLC grade (18.2 M Ω) 2 μm , polished).

The microspheres used in this study were principally surfactant-free sulfate, white, polystyrene-latex, 2 μm in diameter (product number 1–2000, Interfacial Dynamics Corporation, Portland, OR). Particles of this size undergo vigorous Brownian motion in water, and are sufficiently large to be imaged with a conventional light microscope. The microspheres are synthesized with a large number of sulfate groups chemically bound to their surfaces. These groups dissociate in water, each having a single negative charge bound to the microsphere surface and giving a compensating positively charged counterion in solution. Therefore, the sulfate microspheres used in experiments were negatively charged. All experiments were conducted on a Melles Griot isolation bench to shield against ambient vibration.

We pursued three categories of experiment: (i) one positively charged bead and negatively charged microspheres; (ii) one negatively charged bead and negatively charged microspheres; (iii) controls. For each experiment, a single bead was first placed in the chamber. Then, an aqueous microsphere suspension with a volume fraction of approximately 0.08 was added. Once the bead settled firmly to the bottom, the chamber was sealed carefully with a No.1 microscope cover slip and put on the sample stage of an inverted Zeiss Axiovert-35 optical microscope, used in the bright-field mode with either a $10\times$, $5\times$, or $2.5\times$ objective lens depending on the goal of the particular experiment. An attached color digital camera (Scion Corporation, CFW-1310C) was used to record images and videos. Track* Version 1.0 (© 2001 Penn State University) was used to track the trajectories and coordinates of the microspheres. Radial velocity was then calculated as a function of distance from the bead surface, and the results were plotted.

In the controls, different negatively charged microspheres ($2\text{ }\mu\text{m}$ carboxylate, Polysciences, Inc. Cat #18327) were used to test if the attraction might be the consequence of the specific surface-functional group that was ordinarily used. As another control, we replaced the ion-exchange bead with another charged surface, Nafion, to test whether unanticipated ion-exchange action might have caused the attraction. Nafion-117 is composed of a carbon-fluorine backbone with perfluoro side chains containing sulfonic acid groups, fabricated from a copolymer of tetrafluoroethylene and perfluorinated monomers. A $600\text{-}\mu\text{m}$ diameter Nafion grain was used in place of the bead. Third, extremely diluted concentrations of microspheres were used to determine whether the long-range attraction still exists when microsphere-microsphere distance increases sufficiently. We employed the lowest practical concentration (1/200 normal) — one that just barely allowed the required measurements to be made. Finally, some of the experiments were repeated in a chamber made solely from polycarbonate to rule out artifacts due to glass surfaces at top and bottom.

3. RESULTS

3.1 Positively charged bead and negatively charged microspheres

For these experiments, one positively charged bead was placed in a solution of negatively charged microspheres (see Figure 1). Immediately after the chamber was placed on the microscope stage, microspheres were observed to be moving toward the bead surface from all directions. These movements continued for up to three hours. The motion occurred throughout the chamber towards the bead from all directions, as illustrated by the arrows in Figure 1. At distances of $200\text{ }\mu\text{m}$ from the bead surface, microspheres moved consistently toward the bead at a speed of about $1\text{ }\mu\text{m/s}$.

Attractive movements were found even at distances of up to 2 mm from the bead surface (Figure 2). Data points obtained from four orthogonal directions were assembled into a single figure for comparison. All data were recorded just after the microsphere suspension had been added to the chamber. The resulting velocity-vs.-distance trends are similar in all four curves. At distances farther than $400\text{ }\mu\text{m}$ from the bead surface, velocity remained invariant at a value of $\sim 0.3\text{ }\mu\text{m/s}$. At positions closer than $\sim 200\text{ }\mu\text{m}$, velocity began to noticeably increase approximately exponentially, up to a value of $\sim 5\text{ m/s}$ at the bead surface, implying a distance-dependent attractive force. On the other hand, the fact that microspheres still moved toward the bead at distances of $2,000\text{ }\mu\text{m}$ or farther implies that attractive interactions extend over an extremely long range.

With increasing time, microspheres accumulated progressively at the surface of the bead, and after one hour, a bead-surface cluster could be readily detected (Figure 3). Figure 3a is the image of the bead surface at the start of the experiment. In Figure 3b, taken after one hour, the bead surface appears darker because more microspheres had deposited. In order to

examine more details of microsphere deposition on the bead surface, smaller microspheres ($D: 0.47 \mu\text{m}$) were substituted for the $2\text{-}\mu\text{m}$ spheres ordinarily used. The surface structure could then be seen as a colloidal crystal (see Figure 3c). Possibly, an element of crystallinity was present with the larger microspheres as well, but less conspicuous because of irregularities in layered structure and the presence of fewer layers. A more detailed report on these self-assembled colloidal crystals has been published elsewhere.³⁵

Microsphere movements were tracked in several different focal planes, above, below, or the same as, the bead's equatorial plane. Irrespective of the plane, microspheres behaved similarly — moving toward the bead and moving faster when within $200 \mu\text{m}$ of the bead surface. Eventually, all microspheres settled on the bead surface.

3.2 Negatively charged bead and negatively charged microspheres

For these experiments one negatively charged bead was used in conjunction with negatively charged microspheres. In contrast to the former setup with the positively charged bead, the negatively charged bead was ultimately surrounded by a clear “exclusion zone” devoid of microspheres (Figure 4). Such exclusion zones have been reported in detail in earlier work.^{36,37} The exclusion zone first grew with time, and finally became stable after approximately 10 minutes. It extended roughly $300 \mu\text{m}$ from the bead surface, similar to previous observations.³⁷

During the formation of the exclusion zone, microspheres were progressively excluded from the vicinity of the bead, translocating to positions beyond the exclusion zone. Once the exclusion zone was fully established, microspheres became attracted to its far edge from all directions, as illustrated by the arrows in Figure 4. Such attraction is unexpected, as microspheres and bead have the same (negative) charge polarity.

The dependence of velocity on distance from the exclusion-zone edge is shown in Figure 5. Positive values of velocity imply attraction between negatively charged microspheres and negatively charged bead surface. The figure confirms that microspheres were attracted towards the bead from every direction, and from distances as large as 2 mm from the edge of the exclusion zone. The velocities were lower than in the case with positively charged bead, and remained at more or less the same value of $\sim 0.3 \mu\text{m/s}$ throughout the effective range of up to 2 mm from the exclusion-zone edge (with some diminution close to the exclusion-zone edge; see Discussion), indicating the presence of a long-range attractive force in the direction of the bead, even though the bead and microspheres are of the same charge polarity.

Upon examining different focus planes, we found that as microspheres moved closer to the bead, they also moved toward the lower focal plane. Most of them accumulated on the glass surface at the bottom of the chamber, near the point where the bead touched the floor of the chamber. Immediately above the chamber floor and near to the bead, some microspheres translated away from the bead as others from above moved toward the bead, as though there were some minor circulation within a zone of about $150 \mu\text{m}$. For the most part, however, microspheres progressively accumulated at the bottom, near the bead.

The pictorial time course of accumulation is shown in Figure 6 with a negatively charged bead sitting at the bottom of the chamber. The pictures were taken at a focal plane lower than bead's equatorial plane. The region of sediment around the bottom of the bead grew with time, as can be seen by the progressive growth of the white area. Furthermore, after 24 hours, the suspension itself appeared much clearer, indicating fewer microspheres remaining in suspension - most of them having already settled at the bottom near the negatively charged bead.

3.3 Controls

We substituted carboxylate microspheres in order to rule out the possibility that the attraction was related to some specific feature of the sulfate microspheres used regularly. The results were similar. The negatively charged carboxylate microspheres were attracted to the negatively charged bead in all planes out to a distance of more than 2 mm from the exclusion-zone edge. Likewise, attraction to the positively charged bead took place at a velocity of $0.3 \mu\text{m/s}$ when microspheres were farther than $400 \mu\text{m}$ from the bead surface; and, beginning at a distance of $\sim 200 \mu\text{m}$ from the bead surface velocity increased exponentially to a terminal value of $4 \mu\text{m}$ per second at the bead surface.

Hence, in terms of the long-range attraction to both positively and negatively charged beads, carboxylate microspheres behaved in the same way as sulfate microspheres.

We also checked the bead for possible artifacts. In order to test for some unanticipated ion-exchange effect of the particular bead material, we substituted a grain of Nafion. Similar to the negatively charged bead, the grain of Nafion also developed an exclusion zone, which grew to $300 \mu\text{m}$ within 20 min. Measured just after that time, microspheres translated towards the edge of the exclusion zone at a velocity of $\sim 0.3 \mu\text{m/s}$, quantitatively similar to the behavior observed with the negatively charged bead. Hence, the nature of the “attractor” material seemed to play no decisive role.

Experiments were also carried out using a reduced concentration of microspheres to see whether long-range attraction still exists when the separation of microspheres is very much increased. At the lowest practical concentration (1/200 normal), the mean distance between adjacent microspheres was $\sim 200 \mu\text{m}$. Surprisingly, long-range attractive behavior persisted. Figure 7a and b show representative curves, respectively, of distance vs. velocity around positively and negatively charged beads with reduced microsphere concentration. Positive values of velocity indicate attraction. In both cases, microspheres move toward the bead throughout the 2-mm range. The shapes of these curves are similar to those in Figures 2 and 4, respectively, although the velocities are lower and there is considerable scatter. Despite such extreme distances between microspheres, long-range attraction was still evident.

To test whether the chamber material itself might be causing artifacts, a chamber was constructed completely of polycarbonate surfaces, as opposed to the glass-bottomed chamber used before. The glass cover slips used to seal the sample were also replaced with polycarbonate cover slips. Using a negative resin bead and negatively charged $2\text{-}\mu\text{m}$ sulfate microspheres, we found results consistent with standard experiments. In the focus plane of the bead's equator, microspheres translated towards the edge of the bead's exclusion zone uniformly from all directions. At distances ranging from $200 - 600 \mu\text{m}$ from the exclusion-zone edge, microspheres moved towards the exclusion zone edge at velocity of approximately $0.3 \mu\text{m/s}$ (Figure 8). Closer to the bead, at distances as small as $100 \mu\text{m}$ or nearer, average velocities were lower, approaching $0.1 \mu\text{m/s}$. In addition to the equatorial plane of the bead, videos were also taken in a range of focal planes down to the floor of the chamber, with no essential difference in results.

4. DISCUSSION

The results have demonstrated unexpectedly long-range attractive forces between colloidal entities. Whereas currently prevailing theory posits electrostatic forces over spans on the order of nanometers — and perhaps micrometers under extreme circumstances — the results obtained here show attractive behaviors over distances that are several orders of magnitude larger. Further, these attractive forces were observed not only between unlike-charged entities, but also between like-charged entities, thereby compounding the apparent anomaly.

4.1 The existence of long-range attractions

To test for potential artifacts, various control experiments were carried out. First, the seemingly attractive forces might have been observed merely because some fortuitous plane was investigated, a plane that happened to show attractive movements secondary to displacements elsewhere arising from phenomena such as thermally induced movements. In other words, the attractive movements may not have been primary. To test for this trivial explanation, representative planes were investigated throughout the chamber volume, both for the positively charged bead case (like-unlike) and the negatively charged bead case (like-like). In both situations, attractive movements toward the central bead from all directions were recorded throughout. Further, when the bead was removed from the chamber after some time, a dense residue of microspheres was always observed to have collected beneath the bead, reaffirming the primary movement of microspheres toward the bead. This was seen irrespective of microsphere concentration.

Other control experiments were carried out to determine whether the results might have been specific to the unique types of specimens studied. For example, some unknown substance might have been released into the suspension by the microsphere or the bead, which then induced attractive movements. To test this possibility, we replaced the gel bead with a grain of Nafion and found essentially similar results. Substituting the sulfate microspheres for carboxylate microspheres produced essentially similar results as well, as did replacing the glass-bottomed chamber with an all-polycarbonate chamber.

Hence, the long-range attractions found here seem to exist over a range of materials and situations. The fact that microspheres always — without exception — accumulated in time near or on the bead, reinforces the notion that what has been observed is indeed a long-range attraction.

4.2 Origin of long-range attractive forces

While short-range interactions have abundant theoretical underpinning,^{38–42} long-range interactions remain poorly understood. When like-charged colloidal particles are suspended in aqueous solution, they ordinarily attract one another.^{5,34} As the particles draw close enough, the attractive forces become balanced by repulsive forces between the like-charged entities. At that point, particles occupy quasi-stable sites and form colloid crystals, in which the surface-to-surface distance between particles is on the order of particle size.^{5, 23, 26}

Although appreciable effort has been devoted to such attractive forces, there is still no common agreement on the mechanism. Following an early suggestion by Langmuir,⁹ Feynman suggested that the reason for such unexpected long-range attractions was an intermediate of unlike charges.²⁰ In other words, long-range attraction between negatively charged entities arose because of positively charged intermediates: “like-likes-like because of an intermediate of unlikes.” This idea was extended in detail by Sogami and Ise et al.,^{10–16} who experimentally demonstrated many features of the attraction that were consistent with this concept.

Recent results from this laboratory have provided understanding of the source of the required “unlikes.” Adjacent to many hydrophilic surfaces such as those studied here, extensive regions of water with altered characteristics are observed.^{36, 37} These regions can extend up to hundreds of micrometers from the respective surface, and because they exclude solutes, they have been referred to as “exclusion zones.” Exclusion zones next to most hydrophilic surfaces are negatively charged, apparently through expulsion of positively charged entities, which then lie in the regions beyond.⁴³ Thus, abundant positively charged entities may well constitute Feynman’s “unlikes.”

Additional experiments from this laboratory confirm not only the presence of unlikes, but also that pairwise attractions can occur over macroscopic separations.³⁴ In this recent report, pairs of like-charged gel beads were placed in a chamber at initial surface-to-surface separations up to 0.5 mm. When gently dislodged from the chamber floor, the beads consistently approached one another and eventually wound up touching. These studies also used microelectrodes and pH-sensitive dyes to demonstrate the presence of unlike charges lying in between the charged beads, and this was true whether the beads were positively charged or negatively charged.

The key to explaining the long-range attraction could lie in the abundance of exclusion-zone-generated unlikes. In both types of experiment reported here, like-like and like-unlike, the microspheres themselves are of uniform charge polarity. Each microsphere is expected to have its own exclusion zone, with positive cloud beyond. Because of the abundance of these positive unlikes, microspheres may be perpetually attracted toward one another, conferring a cohesion on the microsphere array. The array then effectively acts as a unit. Hence, any attractive force applied to array microspheres closest to the bead may be felt as well by array microspheres extremely distant. Indeed, microspheres 2-mm distant from the bead moved toward the bead at velocities similar to those much less distant (Figure 5; and Figure 2, flat portion), confirming the cohesion — the underlying basis of which must be attractive interactions.

If the like-likes-like concept is correct, then one might expect that like-charged microspheres might ultimately aggregate. However, that is neither expected nor found. As particles approach one another, repulsive forces between particles will increase; once attractive and repulsive forces are in balance, the system remains stable.²³ This feature is amply evidenced in studies of colloid crystals.^{5,26} Thus, the like-likes-like mechanism does not necessarily anticipate aggregation.

On the other hand, the extreme distance over which such attractive interactions can apparently act was unexpected. When microsphere concentration was reduced so that microspheres were as far as 200 μm apart, the attraction was maintained; microspheres continued to move toward the bead as a unit. The velocities were indeed lower than normal (Figure 7), but at a far enough distance from the bead, microspheres still translated toward the bead at a consistent velocity irrespective of distance from the bead. Hence, the attractive forces necessary to maintain cohesion persisted even at these extreme inter-microsphere separations.

In sum, attractive interactions could be detected at distances up to 2 mm. In part, the extreme range stems from the fact that the colloidal particles that are being attracted act as a unit, held by cohesive forces.

4.3 Attractive forces near the bead

In the discussion above, we considered the microsphere array, focusing on the reason why velocities could be independent of distance from the bead. On the other hand, at distances closer than $\sim 200 \mu\text{m}$ from the bead in the like-unlike situation, microspheres translated toward the bead with higher velocity — the magnitude increasing with increasing proximity. An important question arises from this observation: If microspheres acted as a cohesive unit, why should the velocity be higher closer to the bead and lower farther away?

A possibility is that the attractive force very close to the bead is indeed high. This is not surprising with positive bead attracting negative microspheres. If such attractive force exceeds the cohesive force holding together the microspheres, then microspheres of the array will pull progressively apart. This is observed: microspheres farther away do not move

toward the bead as rapidly as those closer. The primary attractive force should then diminish with radial spread — ultimately falling to the point at which it equals the inter-microsphere force holding together the array. At that point, the array will translate as a unit, the velocity at the near edge equaling the velocity at the far edge. Hence, the observed velocity distribution is not entirely surprising.

4.4 Exclusion zones: an additional source of long-range forces

Results obtained with a negative bead and negative microspheres were essentially similar to the results with positive bead and negative microspheres with one notable difference: the presence of a 300- μm exclusion zone surrounding the bead. This zone contained no microspheres at all. Microspheres nevertheless moved consistently toward the bead, right up to the exclusion zone's far edge. It is as though an attractive force between like-charged entities projected across this large empty zone from the bead to the microsphere array.

The explanation may once again follow from the like-likes-like phenomenon. Around the bead, the exclusion zone is negatively charged³⁷ whereas the region beyond has low pH, indicating excess protons and positive charge.⁴³ These proton unlikes will attract negatively charged microspheres, which will then confer the attractive movements onto the entire microsphere array, as observed.

One may notice that when the microspheres approached the edge of the exclusion zone, they did not speed up as they did in the positively charged bead case. The situation here is quite different. In the case of the positively charged bead, the primary attraction was from the bead surface — a well-defined positively charged feature. In the present case the attractor is diffuse; it is a cloud of protons, which may be spread diffusely over the solution. Hence, the situation is quite different, and the force vs. distance relation is not necessarily expected to be the same.

A point of perhaps secondary significance is that microsphere velocity appeared to decrease somewhat as microspheres approached the edge of the exclusion zone. The diminution could be a real effect; however, it almost certainly stems at least in part from an asymmetry — the fact that the bead rests on the bottom of the chamber. The exclusion zone is thus somewhat egg-shaped and microspheres translating into its vicinity moved in a partially downward direction, resulting in the sediment patterns shown in Figure 6. Hence, the velocity as viewed from above will be a vector component of the actual velocity, and thus lower than that measured farther away where no downward component existed.

4.5 Mechanistic Considerations

Overall, the results reported in this paper appear counter-intuitive on a number of counts. First, only nanometer-scale interactions are predicted by standard DLVO theory (although micrometer-scale interactions have been amply observed; see citations above). Much of conventional physical chemistry is based on interactional limits extending over relatively short ranges. By contrast, the attractive interactions reported here extend to distances on the sub-millimeter scale, orders of magnitude larger than anticipated. A second and perhaps even more counter-intuitive point is that the attraction exists even when the protagonists have the same charge. As demonstrated, the explanation of these counterintuitive observations appears to be the like-likes-like mechanism.

A potential alternative explanation is that of an electrophoretic cell, wherein an electrical potential draws microspheres toward the bead. Thus, the central bead might generate a potential difference around itself, attracting the microspheres toward it. However, such potential differences have been directly measured; they extend over a span of only about 200

μm ,³⁷ whereas the attractive force extends an order of magnitude farther. Moreover, the attractive movement was seen even when bead and microspheres were of the same polarity.

5. CONCLUSION

The results presented in this paper show evidence for long-range of interactions between charged beads and microspheres. The evidence comes from two experimental configurations: like-unlike and like-like. In the former, the apparent long range is in part a consequence of attractive forces between microspheres, conferring cohesiveness on the array, which then moves as a more-or-less cohesive body. However, the cohesiveness itself is long range, the underlying attractive force remaining apparent even when the inter-microsphere distance is increased to the experimentally practical limit of $\sim 200 \mu\text{m}$.

In the like-like case, the attractive force appears to arch over an existing exclusion zone, drawing microspheres toward the bead. However, the true drawing force may derive from the more proximate protons beyond the exclusion zone, and as such, is not genuinely long range. Yet, the protons themselves are created only because of a long-range exclusionary force extending over $300 \mu\text{m}$.

Hence, both configurations show long-range effects extending several hundred micrometers, well beyond conventional theoretical expectations.

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Figure 1. Positively charged gel bead immersed in suspension of 2- μm sulfate microspheres. Arrows indicate the direction of microsphere movement.

Figure 2. Microsphere velocity vs. distance from the positively charged bead surface. Each trace obtained from one of the four orthogonal directions. Exponential curve fit to guide the eye.

Figure 3. Positively charged ion-exchange bead and 2- μm sulfate microspheres, obtained at (a) $t = 0$; and (b) $t = 1$ h. (c) smaller microspheres ($D: 0.47 \mu\text{m}$) showing self-assembled colloidal crystal layers formed around positively charged bead.

Figure 4. Negatively charged gel bead immersed in suspension of 2- μm sulfate microspheres. Arrows indicate the direction of microsphere flow.

Figure 5. Microsphere velocity vs. distance from edge of exclusion zone around negatively charged bead surface.

Figure 6.

Images of vicinity of negatively charged bead obtained as function of time. Growing white area indicates region of microsphere accumulation, on chamber floor near bead. Increasingly clear dark background indicates diminished scattering, consistent with diminishing number of microspheres remaining in suspension.

Figure 7. Highly diluted (200x) suspensions. (a) Microsphere velocity vs. distance from positively charged bead surface. (b) Microsphere velocity vs. distance from edge of exclusion zone around the negatively charged bead surface. Exponential curve fit to guide the eye.

Figure 8.

Results of control experiments using an all-polycarbonate chamber, a negative bead, and negative microspheres, showing microsphere velocity vs. distance from edge of the exclusion zone, with curve fit to guide the eye. Data represent combined results from orthogonal sides.