Interactions and Dynamics in Charge-Stabilized Colloid

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Abstract:

A wide variety of natural and technologically important colloidal suspensions rely on electrostatic interactions for their useful and interesting properties. Recent advances in experimental probes of colloidal interactions reveal new phenomena apparently at odds with the conventional theory. In particular, they suggest that like-charged colloidal particles experience strong and long-ranged electrostatic attractions for each other, at least under some circumstances. The same mechanisms responsible for these attractions may affect processes as diverse as stabilization of industrial suspensions, protein crystallization, and self-assembly of semiconductor nanoclusters.

Perhaps the most remarkable observation on can make about colloidal suspensions is that the exist at all. Particles dispersed in a fluid medium have a natural tendency to aggregate under the influence of van der Waals attraction. And yet the fortunes of a great many natural an industrial processes require colloidal particles to remain dispersed, or at least to aggregate at a controlled rate. The existence of colloidal suspensions as varied as milk, inks and metallic sols attest to the efficacy of a variety of stabilizing mechanisms. As early as 1809, Reuss realized that many naturally occurring colloidal particles are charged [1]. By the end of the century, Schultz and Hardy demonstrated that the resulting electrostatic repulsions were strong enough to stabilize their suspensions against flocculating. This mechanism - arguably the best understood - continues to yield new surprises despite more than a century of analysis. The most recent burst of activity has been driven by the development of new and quite general techniques for measuring colloidal and macromolecular interactions. Its counterintuitive result, that like-charged particles sometimes attract each other, may have ramifications in areas as diverse as protein crystallization, self-assembly of nanostructures, and the stabilization of industrial suspensions. This article touches briefly on the well-established theory of electrostatic

stabilization in colloidal suspensions. The emphasis here is on the approximations which have provided the community with an analytical theory at the expense of overlooking recently discovered effects. Far from challenging the foundations of colloid science, our aim is to show that the conventional theory works remarkably well, even beyond its nominal domain of applicability. We then discuss experimental evidence for attractive interactions among like-charged colloidal spheres and introduce the new techniques that make such measurements possible. Finally, we address some of the most recent theoretical advances that promise to explain the still-anomalous observations and also to suggest in what contexts the newly recognized effects should be apparent.

Colloidal electrostatic interactions

Figure 1: Schematic view of the components of a charge-stabilized colloidal suspension. Ionizable surface groups dissociate in solution, leaving charges bound to the spheres' surfaces and counterions in solution. These counterions are augmented by other simple ions already in solution. Electrostatic interactions among all of these species result in an effective interaction between the spheres.
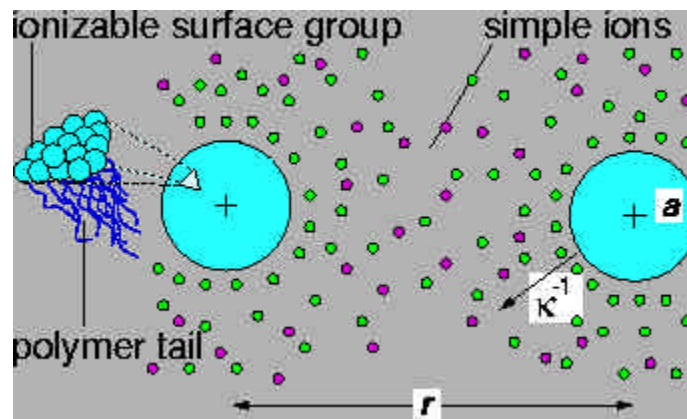
The electrostatic coupling among charged colloidal particles results from a hierarchy of many-body interactions. In general, charged colloidal particles interact not only with each other, but also with a sea of surrounding ion, some with the same charge called coions, and others with opposite charge called counterions, as shown schematically in Fig. 1. Charge-stabilized colloidal particles tend to carry much larger charges than the counterions and coions and also tend to by physically much larger. Often, they are referred

to as macroions, a class that includes charged polymer strands (polyelectrolytes and polyampholytes) and their aggregates such as membranes and vesicles. Steric exclusion of simple ions from the macroions' interiors adds complexity to an already busy picture.

Macroions influence the distribution of simple ions. These in turn mediate and moderate the interactions between the macroions. To make matters even more complicated, macroions and simple ions also interact with molecules in the suspending fluid. When viewed in this way, the availability of any analytical theory for colloidal interactions is remarkable. That such a theory can accurately describe the behavior of richly complex suspensions is extraordinary.

Despite everything, the conventional theory of colloidal electrostatic interactions is quite straightforward to formulate. We treat the suspending fluid with its simple ions as an ordinary electrolyte. The local electric potential, $\Phi(\mathbf{r})$, depends on the concentration, $n_i(\mathbf{r})$, of ions of type i, each with charge $z_i e$, through Poisson's equation,

$$\nabla^2 \Phi(\mathbf{r}) = -\frac{4\pi}{\epsilon} \sum_{i=1}^{N} z_i e\, n_i(\mathbf{r}), \tag{1}$$

where ϵ is the fluid's dielectric constant. Unfortunately, the ionic concentrations themselves depend on the local electric potential in an intrinsically nonlinear manner described in the mean-field approximation by the Boltzmann distribution,

$$n_i(\mathbf{r}) = n_i^{(0)} \exp\left(-\frac{z_i e \Phi(\mathbf{r})}{k_B T}\right), \tag{2}$$

where k_B is Boltzmann's constant and T is the system's temperature. $n_i^{(0)}$ is the ionic concentration for species i far from the spheres. Putting Eqs. (1) and (2) together yields the nonlinear Poisson-Boltzmann equation which has served as the basis for our understanding of electrolyte and macroionic behavior for more than 70 years. This equation, however, has only been solved analytically for a very restricted set of geometries, parallel charged plates, for example. Solutions for more general geometries such as pairs of spheres have proved elusive.

Even this intractable model involves a dramatic simplifying approximation. The suspending fluid appears in Eqs. (1) and (2) only through its dielectric constant, ϵ. This so-called primitive model completely neglects effects due to the structure of the solvent, an approximation which fails when the separation between macroions becomes comparable to a few molecular radii.

Derjaguin, Landau, Verwey and Overbeek (DLVO) pushed the field forward in the 1940's by applying approximations from the Debye-Hückel theory of electrolyte structure [2,3]. In particular, they Taylor expanded the exponential in Eq. (2), retaining only the linear term, and invoked electroneutrality to obtain the linearized Poisson-Boltzmann equation,

$$\nabla^2 \Phi = \kappa^2 \Phi, \tag{3}$$

where $\kappa^2 = \frac{4\pi e^2}{\epsilon k_B T} \sum_{i=1}^{N} z_i^2 n_i^{(0)}$. The screening length, κ^{-1}, describes how the simple ions' correlations with the macroions fall off with distance due to screening of the electric field.

In 1933, Onsager [4] pointed out that the nonlinear equation is not thermodynamically self-consistent since the work required to move two dissimilar ions into a suspension appears to depend on the order in which they are introduced. Remarkably, the linearized Poisson-Boltzmann equation does not suffer from this defect. Rather than engendering confidence in Eq. (3), though, Onsager's observation raises concern about the nonlinear equation from which it is approximated. The linearized theory is worth pursuing, however, since it is tractable and its shortcomings are believed to be both understandable and controllable [5].

Even so, a few more approximations are required before a straightforward analytical theory for colloidal electrostatic interactions emerges. Since the macroions are so big, they presumably move much more slowly than simple ions. Thus, it seems reasonable to treat the macroions as if they were fixed in space and work out the potential (and the distribution of simple ions) as a boundary value problem. Linearly superposing the fields due to two spheres gives the effective macroion interaction averaged over the simple ions' degrees of freedom. The result is a screened Coulomb repulsion. For pairs of spheres, each of radius a and charge number Z, it has the form

$$U(r) = \frac{Z^2 e^2}{\epsilon} \left[\frac{\exp(\kappa a)}{1 + \kappa a} \right]^2 \frac{\exp(-\kappa r)}{r}, \tag{4}$$

where the term in square brackets accounts for exclusion of the simple ions from the spheres' interiors. This electrostatic repulsion is balanced against van der Waals attraction [6],

$$V(r) = -\frac{A}{6} \left(\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln \frac{r^2 - 4a^2}{r^2} \right), \tag{5}$$

arising from sympathetic fluctuations in the particles' electron distributions. The scale for

the attraction is set by the Hamaker constant, A, which depends on the dielectric constant mismatch between the particles and the surrounding fluid. Typically, $A = \mathcal{O}(10^{-20})$ J $\approx 2\, k_B T$ [7] for latex particles in water. Equations (4) and (5) together constitute the DLVO theory for colloidal interactions.

Approximations invoked in deriving the DLVO potential limit its domain of applicability. For instance, the primitive model description of the solvent restricts it to describing phenomena at scales larger than a few nanometers. Furthermore, the linear form of Eq. (3) is only valid in regions where the local potential is small compared with the thermal energy scale. This cannot be true near the surface of a highly charged spheres.

Nonlinear effects usually are assumed to be confined to a thin surface layer around each sphere. Outside this layer's imaginary boundary, the linear DLVO theory should apply. The spheres' effective charge as seen in this linear domain is likely to be smaller than its bare value because of nonlinear screening in the boundary layer. But by how much? A variety of models have been proposed [8,9,10,11,12,13,14] to account for this charge renormalization in hopes of salvaging a quantitative model for colloidal interactions. This effort is doomed to failure if the interactions are not pairwise additive.

Combining single-sphere solutions of Eq. (3) into the pair potential of Eq. (4) is only possible if the distribution of simple ions around one sphere is not disturbed by the presence of the other. Linear superposition must be invoked once again in order to use the DLVO pair potential to describe the many-body structure of a suspension. These approximations and assumptions are likely to be reasonable for weakly charged spheres whose separations are much greater than the screening length, i.e. for weakly interacting suspensions.

For simplicity's sake, we will further assume that the simple ions each carry a single charge ($|z_i| = 1$). Polyvalent simple ions are responsible for many important processes in charge-stabilized suspensions. For instance, a doubly-charged counterion can for a bridge between singly-charged surface sites on two different macroions and thereby facilitate flocculation. Such effects are beyond the scope of the following discussion. As we will see, even suspensions with monovalent simple ions display phenomena that cannot be explained within the framework of the DLVO theory.

Finally the DLVO theory foundation in mean field theory [Eq. (2)] renders it incapable of describing fluctuations in the simple ion distributions, an obvious source of interesting phenomena. The mean field approximation should be reasonable in suspensions with high concentrations of simple ions. Relative fluctuations in local simple ion concentrations should be relatively small in such systems. Suspensions at low ionic strength, on the other hand, challenge DLVO on this front as well.

These caveats notwithstanding, the DLVO theory accounts for many properties of charge-stabilized colloidal suspensions such as their stability and aggregation rates [1,2,3,15]. Consequently, it has come to be accepted as one of the cornerstones of colloid science. Its limitations, all too often forgotten, have begun to assert themselves as research efforts push beyond its approximations' domain of validity. The ramifications of venturing into this uncharted realm have been most apparent in model suspensions of uniform spheres.

Interactions and the behavior of bulk suspensions

Highly charged and beautifully monodisperse colloidal spheres became widely available in the 1950's with the development of new techniques in emulsion polymerization [16,17]. While most industrial applications for colloidal do not require particularly stringent control over particle size dispersion, monodisperse spheres have found applications as precision spacers and as size standards in electron microscopy and light scattering. Their remarkably uniform properties also have sparked a new an exciting field of research. Interacting microspheres undergoing Brownian motion in a suspending fluid can be viewed as macroscopic ``atoms'' [18]. When thermal forces dominate their interactions, they move randomly and independently, much as the atoms in a fluid. When their interactions dominate, they organize themselves into rigidly ordered ranks like the atoms in a crystal. Depending on the spheres' charge and concentration and the electrolyte's screening length, charge-stabilized colloidal crystals adopt either face-centered cubic or body-centered cubic structures [19,20]. The analogy between colloidal disorder-order transitions and conventional freezing is extremely exciting because, unlike atoms, each sphere in a colloidal crystal can be tracked using a conventional light microscope [13,21,22,23].

Figure: Trajectories of charge-stabilized
colloidal spheres at the crystal-fluid
interface measured by digital video
microscopy. A density gradient was imposed
on this suspension of 0.352 μm diameter

spheres to form this near-equilibrium
interface. Trajectories sampled at 1/30 sec
intervals over 3 seconds highlight both the
structural and dynamical differences
between the two thermodynamic phases.
Data from C. A. Murray, D. G. Grier, and
W. O. Sprenger (unpublished).
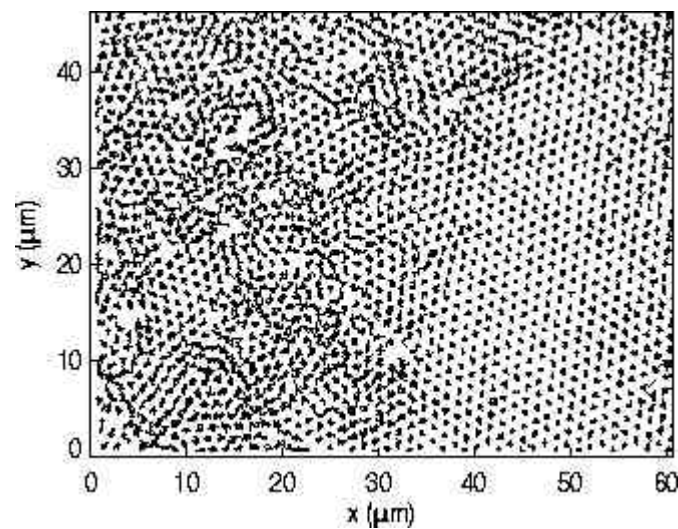
Here, then, is a system whose interactions are presumably well understood, and whose
phase transitions can be studied with ``atomic'' resolution - the very model of a model
system with which to study the microscopic mechanisms of structural phase transitions.
All we have to assume is that the DLVO pair potential is appropriate for describing
interactions in a many-body system. Under this assumption, the experimentally
determined phase diagram for bulk colloidal suspensions [19,20] has been found to
resemble that obtained from molecular dynamics simulations of particles interacting with
screened Coulomb repulsions [24,25]. Quantitative discrepancies have been ascribed quite
reasonably to uncertainty in the experimental control parameters. Even the elastic
properties of colloidal crystals seem consistent with the DLVO theory [26,27].

This qualitative agreement should not be cause for complacency, however. The
still-evolving theory of phase transitions tells us that materials' phase behavior depends
only weakly on the qualitative form of the pair potential. After all, colloidal phase
transitions resemble atomic phase transitions even though their pair potentials are quite
different. Perhaps the quantitative discrepancies in bulk behavior could indicate
qualitative misunderstanding of the microscopic energetics.

The announcement by Sogami and Ise [28,29] of an alternative to the DLVO theory inspired a successful search for anomalous behavior in charge-stabilized colloidal suspensions [30,31,32,33,34,35,36,37]. One interpretation of these and many other experimental observations is that like-charged colloidal particles can sometimes attract each other strongly and at very long range. This contradicts the predictions of the DLVO theory. It is consistent, however, with the predictions of the Sogami-Ise theory. Even among researchers who agree on the appearance of like-charge attractions, a controversy rages regarding their origins [38,39,40]. The remainder of this Article focuses on the evidence for like-charge colloidal attractions, possible explanations, and possible ramifications for practical processes which rely on colloidal stability.

Force measurements at the femtonewton frontier

Given the broad importance of understanding and being able to control colloidal interactions, it might seem puzzling that the DLVO theory was not tested by direct measurement years ago. Three characteristics of colloidal interactions have stood in the way. Typically, colloidal particles are small, maybe on a fraction of a micron in diameter. Sensitive mechanical transducers such as force balances usually rely for their accuracy and sensitivity on large sample volumes. To make matters worse, colloidal interactions involve fabulously small forces, typically on the order of tens of femtonewtons. Until the invention of the surface forces apparatus (SFA) in the 1970's [7] and the atomic force microscope in the 1980's [41], measuring such tiny forces was almost unimaginable. As a final complicating feature, colloidal particles are immersed in a delicately structured chemical environment which not only reacts sensitively to perturbations, but also generates obscuring noise.

Rather than attempting to bypass these intrinsic properties of the colloidal domain, newly developed experimental techniques take advantage of them. The result over the past five years has been the first direct measurements of colloidal interactions between free spheres. Some have reaffirmed long-held beliefs. Others have yielded surprises.

Deflection measurements of surface forces

The SFA measures the interactions between a pair of atomically smooth mica cylinders crossed at right angles [7]. Their interaction is dominated by forces engendered at the point of closest approach. Forces as small as tens of piconewtons can be gauged through the deflection of one of the cylinders, measured interferometrically. Such measurements have qualitatively confirmed predictions of the DLVO theory for the crossed cylinder geometry [42]. In particular, they provide direct mechanical measurements of the

Hamaker constant, *A*, which otherwise has to be estimated indirectly.

At particularly small separations, the SFA also has detected the discrete molecular structure of the solvent, and thus the breakdown of the primitive model [43]. Not surprisingly, correlations in the solvent lead to alternating attractions and repulsions as solvent layers are included or excluded from the gap. Such effects are relevant below the nanometer scale and contribute to processes such as adhesion and lubrication. They most likely are not significant for more widely separated particles.

The AFM offers a complementary view of the electrostatic interactions between colloidal spheres, at least in the high energy tail. The AFM also uses cantilever deflections to gauge surface forces. By using a single sphere as a probe on the end of the cantilever, the AFM can be used to measure sphere-sphere and sphere-surface interactions with a resolution limited by the detection threshold for deflections. Even with micromachined cantilevers, however, this threshold corresponds to piconewton forces. In this relatively high force regime, AFM measurements also have proved consistent with the DLVO theory [44,45].

Neither the SFA nor the AFM is sensitive enough to resolve colloidal interactions around the thermal energy scale. Thermal energy, however, sets the scale for all of the anomalous behavior at the focus of the current debate regarding colloidal electrostatic interactions. Fortunately, colloidal particles' sensitivity to exactly these forces makes possible quantitative measurements of interactions in this regime. Discerning the influence of pair interactions in an overwhelming background of thermal noise might seem impossible. These interactions are encoded in the spheres' dynamics. The Rosetta stone for this problem is provided by the theories of simple liquids [46] and of stochastic processes [47]. Starting in 1994, its secrets have been revealed through a combination of digital video microscopy and optical tweezer manipulation.

Structure as a force transducer

Even particles smaller than the wavelength of light can be observed with a conventional light microscope and their motions recorded with a conventional video camera. Digitizing and then analyzing a sequence of video micrographs makes possible very precise measurements of particle trajectories. Individual particles' centers can be located and tracked with spatial resolution approaching 10 nm at time intervals limited by the imaging device, typically 1/60 sec for NTSC cameras [13]. The resulting trajectories,

$$\rho(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)), \tag{6}$$

of *N* particles in the field of view offer a clear view of the spheres' structure and dynamics.

The time-averaged distribution of spheres in a low density suspension reflects pair interactions in a particularly simple way. The experimentally measured pair correlation function,

$$g(\mathbf{r}) = \frac{1}{\tau} \int_0^\tau dt \, \frac{1}{\rho^2} \int d\mathbf{x} \, \rho(\mathbf{x} - \mathbf{r}, t)\rho(\mathbf{x}, t), \tag{7}$$

is related to $U(r)$ through the Boltzmann distribution,

$$g(r) = \exp\left(-\frac{U(r)}{k_B T}\right), \tag{8}$$

in the limit that $\rho \to 0$. Low densities are necessary to prevent many-body correlations from obscuring the pair potential in Eq. (8). Acquiring good enough statistics on a low density suspension to accurately measure $U(r)$ requires care. Furthermore, video microscopy only provides images of thin layers in a three-dimensional system whose thickness is limited to the microscope's depth of focus. The resulting two-dimensionally sampled $g(r)$ differs subtly from the full three-dimensional structure [48]. Even with these caveats, measurements on an optical slice through a dilute three-dimensional suspension yielded good qualitative agreement with the DLVO theory for micron-diameter spheres separated on average by several screening lengths [49].

Better statistics and fewer observational artifacts can be obtained by examining the structure of monolayers of spheres sandwiched between parallel walls. Confinement removes perspective errors and prevents spheres from moving out of the field of view. Provided the ion clouds are not too badly distorted by the confining walls, we might expect the measured potential to be comparable to that for free spheres. Instead, the first such measurements by Kepler and Fraden [50] yielded a tremendous surprise.

Kepler and Fraden's observations on confined colloidal monolayers revealed an attractive minimum in the pair potential almost 1 $k_B T$ deep at a center-to-center separation of two or three diameters. Van der Waals attractions is utterly negligible at such distances [6]. So the observation of strong and long-ranged attraction appears qualitatively inconsistent with the DLVO theory. Even after particular care was taken to account for the finite density of the monolayers, the attraction persisted [51,52,53,54].

The question remained, however, as to whether the observed attraction is an intrinsic and previously unrecognized part of the colloidal pair potential, whether it is a many-body correction to the distribution of simple ions, or whether it is somehow induced by the walls. Measurements on isolated pairs of spheres using optical tweezers have provided

some of the answers.

Optical tweezers and colloidal dynamics as force transducers

Figure 3: Schematic diagram of optical tweezer operation. An objective lens focuses a beam of laser light into the sample volume. Particles with higher dielectric constants than the surrounding medium are attracted to the intense electric field at the focus and are trapped. The same objective lens can be used to image the trapped particles.
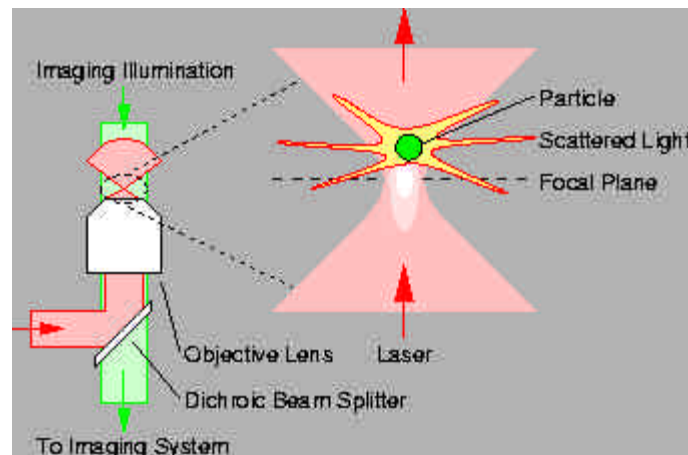

Optical tweezers use forces engendered by focused beams of light to trap and manipulate particles in three dimensions [55,56,57,58]. They can be used to position a pair of spheres at will within a microscope's focal volume. This ability has provided the basis for at least two methods to measure pair interactions directly.

Interactions between a pair of independently trapped particles can displace them within the potential wells of their traps. This displacement can be measured in a variety of manners and used to map out the pair interaction potential. Measurements using this approach have yielded good quantitative agreement with the DLVO theory, including the first direct measurement of van der Waals attraction for freely diffusing particles [59]. These measurements may be affected, however, by the perturbing influence of the intense tweezer illumination.

This perturbation can be eliminated by turning off the traps and tracking the spheres'

subsequent motion. An ensemble of such trajectories provides enough information to measure the pair potential precisely [60]. The existing record of such measurements reveals that isolated pairs of like-charged spheres do indeed repel each other [13,60,61,62]. Quantitative consistency with the DLVO theory, including linear superposition of single-sphere interaction parameters is recovered if the sphere charge and electrolyte screening length are treated as free parameters [61].

Figure 4: Pair interaction potentials measured with optical tweezers for three different sizes of polystyrene sulfate spheres dispersed in deionized water. Solid lines are fits to the DLVO potential for the spheres' effective charges and the electrolyte's screening length.
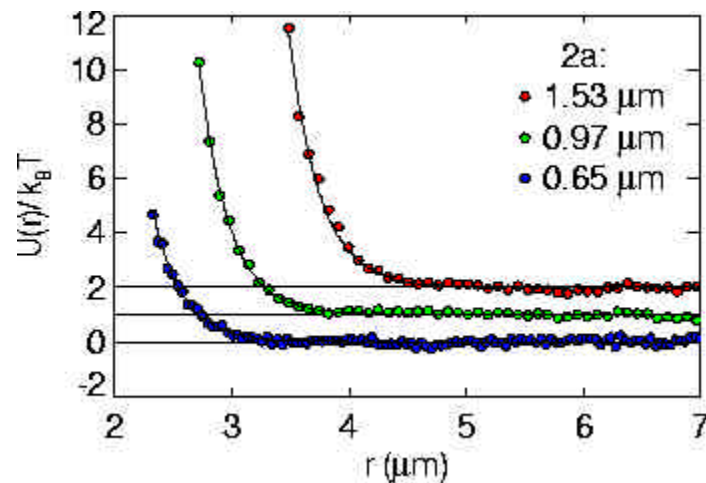
It is particularly noteworthy that the charge derived from interaction measurements differs from the electrokinetic charge measured electrophoretically and is only distantly related to the spheres' titratable charge. So even this victory for the beleaguered DLVO theory leaves open the important problem of assessing the control parameters responsible for suspensions' structure and dynamics.

The failure of optical tweezer measurements to observe attractions for isolated pairs of spheres strongly constrains candidate theories for colloidal electrostatic interactions which predict pairwise attractions. It is possible that experiments have not yet probed the parameter regime in which isolated pairs of spheres attract each other. Additional experiments are needed to rule out this possibility.

Although isolated pairs appear to repel each other, pairs of spheres confined by one or two glass walls develop strong and long-ranged attractive interactions [61,62]. This is consistent with the structure measurements on colloidal monolayers and strongly suggests

that walls induce attractions. But how do they do it? Several possibilities present themselves.

Geometric confinement and like-charge attractions

Confinement-induced attractions could have a simple geometric origin. Counterion clouds distorted into a superposition of multipole moments might somehow lead to attraction [53]. On the other hand, clean glass surfaces in contact with pure water develop a large negative surface charge density [63]. The attraction might involve the glass' charge and its associated counterions. Either way, the answer could bear strongly on our understanding of suspensions' properties in the presence of confining surfaces. The existing data sets offer tantalizing clues.

Figure 5: Pair potentials measured with optical tweezers for polystyrene sulfate spheres confined between parallel glass walls.
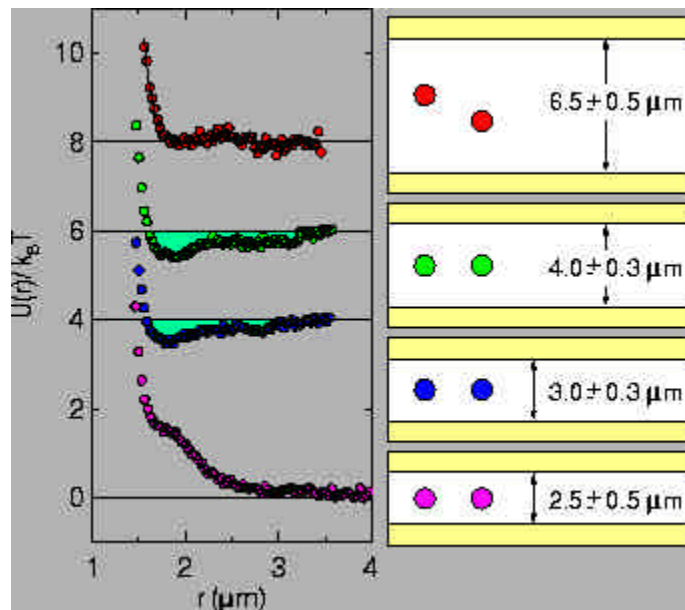
Simply superposing DLVO solutions for charged spheres between charged walls in the slit-pore geometry does reduce the repulsion between the spheres. The walls' counterions help to screen the spheres' interaction. The additional screening does not lead to an overall attraction, however. This result is echoed by recent numerical studies of charged spheres between neutral walls in the linearized Poisson-Boltzmann approximation. Together, these results all suggest that the attraction's origin will not be found in the standard form of the

DLVO theory. Rather we ought to consider effects left out of the DLVO theory, including ionic fluctuations, nonlinearity, and solvent structure.

Solvent structure seems a very unlikely candidate. While SFA measurements reveal solvent-induced attractions at the nanometer scale, the anomalous attraction extends to microns. Its dependence on ionic strength further counterindicates a simple geometric mechanism.

Comparing measured potentials for confined and unconfined pairs suggests that the core screened Coulomb repulsion is not significantly modified by confinement, but rather that confinement induces an additional attractive interaction. Observing further that the attraction is longer ranged than the repulsion rules out the entire class of mechanisms based ionic fluctuations. A straightforward argument makes this point clear.

Fluctuations in the ion cloud around one sphere might result in transient electric multipole moments whose fields would induce sympathetic fluctuations in neighboring spheres' ion clouds. Such sympathetic fluctuations always result in attractive interactions. Moreover, they would not affect the underlying screened repulsion which arises from time-averaged distributions. At first glance, fluctuations seem a natural mechanism for the anomalous behavior. Fluctuations in the electronic distribution, for example, are responsible for van der Waals attraction. And van der Waals attraction, although weak, is longer ranged that the screened Coulomb repulsion. Ionic fluctuations, however, should only give rise to short-ranged attractions [64,5]. The difference arises because electronic multipole fluctuations occur a high enough frequencies that their influence passes unscreened through the surrounding electrolyte. Ionic fluctuations, on the other hand, occur on diffusive time scales. The field due to one sphere's fluctuation is screened once by ionic redistributions before it reaches its neighbor and once again before the neighbor's sympathetic multipole field can return to the original sphere. This rule-of-thumb argument is borne out by recent calculations of fluctuating ion cloud interactions [64,5]. This class of mechanisms, therefore, cannot explain the observed long-ranged attraction.

Even if fluctuating multipoles could induce a long-ranged attraction, additional work would be required to explain why unconfined pairs of spheres seem only to repel each other. Although fluctuating multipoles may not induce long-ranged attractions, they ought to contribute to spheres' interactions at small separation. Why, then, have no colloidal interaction measurements observed them? This is an important question since fluctuating ionic multipole attractions ought to influence the stability of colloidal suspensions in a manner that cannot be predicted by mean field theories.

Spheres might develop static dipole moments if their ion clouds were distorted by a confining wall. These moments would tend to be aligned, however, and induce repulsions rather than attractions. Perhaps if on sphere moved toward one wall while its neighbor moved toward the other, opposing distortions could induce an attraction [50,53]. The

observation that even one wall induces an attraction rules out such mechanisms [62].

Image charges in the glass walls also might lead to a long-ranged attraction. It seems unlikely, however, that a mechanism closely tied to the geometry of the boundary conditions could be the final explanation. After all, a variety of observations suggest that attractions also crop up in bulk suspensions far from confining walls [30,31,32,33,34,35,36,37,62].

Nonlinearity seems to be the best remaining possibility. Its role in a mean field theory would be to modify the correlations among ions and macroions away from predictions of the linearized DLVO theory. Fully accounting for the Poisson-Boltzmann equation's nonlinearity, however, is an unsolved problem. Three approaches immediately assert themselves: numerical solution of the nonlinear equations, molecular dynamics simulations, and a search for an alternate theory. All three approaches have borne fruit.

Bowen and Sharif [65] have reported numerical solutions of the nonlinear Poisson-Boltzmann equation for two charged spheres on the axis of a charged cylindrical shell. Although this geometry does not exactly replicate the experimental setup, its additional symmetry greatly simplifies the computation. The dimensions and surface potentials were all chosen to be comparable to those for the optical tweezer measurements on isolated pairs of spheres. And when the cylinder diameter was reduced to the level of the experimental plate separation, the calculated interaction developed a long-ranged attractive tail. Unconfined spheres repelled each other in good agreement both with the DLVO theory and with experiment.

Experimental measurements of the pair interaction potential offer no direct information on the distribution of simple ions. Numerical results [65], on the other hand show that confinement within a cylindrical pore induces correlations in the simple ion distribution not anticipated by the DLVO theory. In particular, an excess of counterions is found clustered on the midplane between the two spheres. These counterions presumably were driven into this region by the walls of the charged pore and are responsible for the attraction. The two spheres still repel each other; they are attracted to the pore's counterions.

But are the preliminary numerical results simply artifacts of the Poisson-Boltzmann formulation of the problem? Systematic numerical studies have yet to be reported. Until they are, the stationary counterion-induced attraction seen in this model must be viewed as only a tantalizing clue.

However, this numerical result is consistent with a liquid structure theory recently proposed to address phase separation in strongly interacting colloidal suspensions [66]. The idea here is to treat the simple ions as a slightly non-ideal gas moving in a mean field created by the highly charged spheres. Van Roij and Hansen [66] treat the resulting

correlations to lowest non-trivial order, with self-consistency conditions ensuring that simple ions are excluded from the spheres' interiors. The resulting free energy for a many-sphere system has two interesting contributions. One is a pairwise screened Coulomb repulsion among the spheres - the DLVO result! The other is a many-body cohesive energy whose stabilizing influence increases as the density of spheres increases. This additional cohesive energy is not predicted by the DLVO theory and is likely to reflect non-monotonic sphere-ion correlations such as those found in the charged pore calculations. These correlations are not calculated directly in the mean field treatment, however, so direct comparisons are not possible.

In this regard, the most recent theoretical results echo the seldom-referenced Kirkwood-Hastings theory [67]. Hastings applied the Kirkwood theory of electrolyte structure [68] to a system with three components: large highly charged spheres, singly-charged counterions, and singly charged coions. The resulting theory predicts a critical point in the simple ions' phase diagram at which sphere-ion correlation cross over from repulsive monotonic decays to cohesive oscillations. The initial report [67] mistakenly suggested that the resulting sphere-sphere attractions might be responsible for all colloidal crystallization. While this conclusion is clearly false (repulsive spheres also crystallize), the Kirkwood-Hastings crossover might correspond to the onset of long-range like-charge attractions in bulk suspensions.

The overall result is consistent both with experimental observations and with numerical results: even though isolated pairs of spheres repel each other, appropriately dense clusters in an appropriately dilute electrolyte can develop a many-body cohesion. More importantly, this cohesive energy can drive structural phase transitions such as vapor-liquid condensation [30,31,69,70] not generally thought possible for systems with underlying pair repulsions.

This final point lends credence to the suggestion that the same mechanism may be responsible both for the attraction experienced by confined pairs of spheres and for the anomalous phase behavior of bulk colloidal suspensions.

Theoretical investigations have centered on the parameter regime for which experiments have identified interesting behavior. Naturally, they also all involve approximations and simplifying assumptions. Molecular dynamics simulations of the particles and their associated simple ions promise a peek into these systems' inner workings without such limitations. The vast number of ions associated with each sphere and the long range of their Coulomb interactions make such studies particularly difficult. The only one published to date [12] involves spheres arrayed in a BCC lattice, each carrying 100 charges and surrounded by 100 counterions. The simulated sizes and charge concentrations are thus an order of magnitude smaller than in the other studies. Even so, obtaining reliable statistics required taking advantage of the crystal's symmetry and following the motions of the ions in a single unit cell. The osmotic pressure of simple ions

at the unit cell's boundary provided a measure of the inter-sphere interaction. Since the measured pressures remained positive for all conditions explored, the authors concluded that the interaction was purely repulsive, although the repulsion appeared weaker than predicted by the DLVO theory.

Explaining the apparent discrepancy between the mean field numerical studies and the molecular dynamics simulations will be an important step toward a complete theory of colloidal interactions.

Conclusions

Research on interactions between charged colloidal spheres is a small part of the recent resurgence of interest in macroionic systems in general. This interest stems from a desire to understand how form an function arise in biological systems. It reflects the potential for new breakthrough technologies based on the self-assembly of colloidal and macromolecular arrays. And it signals a new advance toward the centuries-old goal of being able to predict the behavior of a very common class of natural systems. A more immediate and practical outcome of this research is likely to be new methods for assessing and controlling the stability of industrial suspensions in real time through direct measurements of sampled particles' properties. Learning how simple electrolytes mediate complex interactions between charged spheres is one important part of this program.

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