When like charges attract: interactions and dynamics in charge-stabilized colloidal suspensions

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Abstract. Measured pair interactions among highly charged colloidal spheres dispersed in simple electrolytes yield several surprises. Isolated pairs of like-charged spheres are found to repel each other, much as predicted by conventional theory. The same spheres, however, can develop a strong and long-ranged attraction for each other when confined either by charged glass walls, or by neighbouring spheres. Such like-charge attractions are inconsistent with the mean-field theory for macroionic interactions. These and other experimental observations further constrain recently proposed extensions to the mean-field theory.

1. Introduction: the mean-field theory for macroionic interactions

The Coulomb interaction between charged colloidal particles dispersed in a polar solvent is moderated and mediated by a diffuse cloud of surrounding ions. These simple ions are much smaller than the macroionic colloidal particles, and carry much smaller charges. The resulting disparity in dynamical timescales encourages us to define an effective colloidal interaction averaged over the simple ions' degrees of freedom. How to define and interpret this effective interaction has inspired spirited debate for more than 50 years.

Experimental observations reported over the past few years have raised the surprising possibility that like-charged colloidal spheres may sometimes attract each other. If we view the spheres in isolation, their attraction seems counterintuitive. Recalling instead that the overall suspension is electroneutral suggests that unexpected features in the spheres' effective pair potential must reflect unanticipated dynamics in the simple ions' distributions. The phenomena discussed in the following sections are noteworthy because they appear to be inconsistent with existing mean-field theories. Such discrepancies raise concern about mean-field theory's broader application to macroionic problems as diverse as protein folding, DNA complexation, and the stability of industrial suspensions.

Since the goal of this article is to assess constraints on theory imposed by experimental measurements of colloidal interactions, it is worthwhile to review the theory's principal approximations.

Virtually all descriptions of macroionic interactions take advantage of the separation of timescales between the macroions' and simple ions' motions and describe the simple ions as moving in the field imposed by stationary macroions. The partition function in this Born–Oppenheimer approximation is

$$Q = Q_0 \int_\Omega \mathrm{d}\vec{r}_1 \, \cdots \, \mathrm{d}\vec{r}_N \, \exp[-\beta V(\{\vec{r}_i\})] \qquad (1)$$

where

$$V(\{\vec{r}_i\}) = \frac{1}{\epsilon} \sum_{i=1}^{N} q_i \phi(\vec{r}_i) \tag{2}$$

is the electrostatic potential energy for N simple ions with charges q_i arrayed at positions $\vec{r}_i$ in an electric potential $\phi(\vec{r})$. The prefactor Q_0 results from integrals over momenta and $\beta^{-1} = k_B T$ is the thermal energy at temperature T. All charged species in the system, including the fixed macroions, contribute to $\phi(\vec{r})$. The macroions also exclude simple ions from their interiors, so their volumes are excluded from the volume of integration Ω. Equation (2) implicitly adopts the primitive model, approximating the solvent's influence through a simple dielectric constant ϵ.

The partition function can be rewritten as a functional integral over all of the possible simple-ionic distributions

$$Q = Q_0 \int{}' Dn \, \exp(-\beta f[n]) \tag{3}$$

where

$$n(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \tag{4}$$

is one particular distribution whose activity is approximately given by

$$f[n] \approx V[n] + k_B T \int_{\Omega} n \ln n \, d\Omega. \tag{5}$$

The prime on the integral in equation (3) indicates that the populations of counterions are conserved:

$$\int_{\Omega} n \, d\Omega = N.$$

Equation (5) differs from the exact activity by terms accounting for higher-order correlations among simple ions. Dropping these terms, as we have in (5), yields a thermodynamically inconsistent theory [1], whose redeeming virtue is tractability. In particular, the conventional mean-field approximation replaces the functional integral in (3) with its integrand evaluated for the distribution n_0 with minimum activity, $f_0 = f[n_0]$. Minimizing (5) to implement the mean-field approximation yields the familiar Poisson–Boltzmann equation

$$\nabla^2 \phi = -\frac{4\pi}{\epsilon} \sum_{\alpha} n_\alpha q_\alpha \exp(-\beta q_\alpha \phi) \tag{6}$$

where the subscript α denotes the various species of simple ions. The fixed macroions provide boundary conditions for $\phi(\vec{r})$.

By considering only one possible ionic distribution, the mean-field approximation ignores contributions from fluctuations as well as higher-order correlations. Even this simplified formulation is intractable for all but the simplest geometries. In developing the classical theory for colloidal electrostatic interactions, Derjaguin, Landau [2], Verwey, and Overbeek [3] (DLVO) invoked the Debye–Hückel approximation, linearizing the Poisson–Boltzmann equation, and solved for the potential

$$\phi(r) = -\frac{Ze}{\epsilon} \frac{e^{\kappa\sigma}}{1 + \kappa\sigma} \frac{e^{-\kappa r}}{r} \tag{7}$$

outside a sphere of radius σ carrying charge $-Ze$. The decay of correlations within the simple-ion distributions is described by the Debye–Hückel screening length, κ^{-1}, given by

$$\kappa^2 = \frac{4\pi}{\epsilon k_B T} \sum_{\alpha} n_\alpha q_\alpha{}^2. \tag{8}$$

For the rest of this discussion, we will consider only monovalent simple ions: counterions carrying a single charge $+e$ and coions carrying $-e$.

The Debye–Hückel approximation cannot be valid near the surface of a highly charged sphere. The hope, however, is that nonlinear effects will be confined to a small region very near the sphere's surface and thus may serve only to renormalize the sphere's effective charge at longer length scales [4, 5].

We obtain the effective pair potential by integrating (7) over the surface of a second sphere separated from the first by a centre-to-centre distance r. This integration is facilitated by assuming that the second sphere's presence does not disrupt the first sphere's ion cloud. The resulting superposition approximation yields a screened Coulomb repulsion for the effective intersphere interaction,

$$U(r) = \frac{Z^2 e^2}{\epsilon} \left(\frac{e^{\kappa\sigma}}{1 + \kappa\sigma} \right)^2 \frac{e^{-\kappa r}}{r}. \tag{9}$$

The DLVO theory was developed principally to explain colloidal suspensions' stability against flocculation under van der Waals attraction. In general, $U(r)$ should include an additional term accounting for such dispersion interactions. However, their influence is negligible for the systems that we will consider [6, 7] and is omitted.

2. Repulsions between isolated pairs of colloidal spheres

Since its development, the DLVO theory has profoundly influenced the study of macroionic systems. Testing its predictions directly through measurements on pairs of spheres has only become possible quite recently with the development of new experimental techniques. These newly minted methods fall into three categories:

(1) measurements based on the equilibrium structure of low-density suspensions [8–10],
(2) measurements based on the nonequilibrium trajectories [11–14] of spheres positioned and released by optical tweezers [15], and
(3) measurements based on the dynamics of optically trapped spheres [7, 16].

All rely on digital video microscopy [17] to track the spheres' motions and consequently would not have been possible before computerized image analysis became readily available.

Methods (1) and (2) take advantage of the Boltzmann relationship

$$\lim_{\bar{\rho} \to 0} g(r) = \exp[-\beta U(r)] \tag{10}$$

between the spheres' pair potential and their equilibrium pair correlation function

$$g(r) = \left\langle \frac{1}{\bar{\rho}\Omega} \int \rho(\vec{x} - \vec{r}, t) \rho(\vec{x}, t) \, d\vec{x} \right\rangle \tag{11}$$

where $\rho(\vec{r}, t)$ is the distribution of spheres at time t, $\bar{\rho}$ is the mean concentration of spheres, and the angle brackets indicate an average over both time and angles. The two approaches differ in how they measure $g(r)$, but agree in their principal result: isolated pairs of spheres, far from walls and unconfined by their neighbours, repel each other.

Data from reference [12] for three sizes of anionic polystyrene sulphate spheres all dispersed in the same strongly deionized 1:1 electrolyte are reproduced in figure 1(a). Solid curves passing through the data points result from nonlinear least-squares fits to (9) for the spheres' effective charges and the electrolyte's screening length. As expected [4, 5], the effective charges are one or two orders of magnitude smaller than the spheres' titratable charges. The screening length of $\kappa^{-1} = 310 \pm 20$ nm is comparable to the spheres' diameters and corresponds to a total ionic strength of 10^{-6} M, a reasonable value for deionized water at $T = 25\,°$C. The apparent success of the screened Coulomb functional form does not validate the Debye–Hückel approximation, however, since Kjellander's analysis of the nonlinear mean-field theory also predicts a screened Coulomb repulsion under experimental conditions [18].

Comparable results were obtained by Vondermassen *et al* [8] from measurements on optical cross-sections of dilute suspensions at low ionic strength. Sugimoto *et al* [7] studied pairs of spheres at higher ionic strength trapped in optical tweezers and were able to measure van der Waals attraction's contribution to the interaction. In all cases, the measured pair potentials agree qualitatively and at least semi-quantitatively with predictions of the DLVO theory.

The observed pair repulsions at low ionic strength pose a challenge to theories predicting long-ranged pairwise attractions. For example, Sogami and Ise [19] proposed that the colloidal pair potential can develop an attractive tail in the grand canonical ensemble when the number N of simple ions is allowed to vary:

$$U_{SI}(r) = \frac{Z^2 e^2}{\epsilon} \left[1 + \kappa\sigma \coth\kappa\sigma - \frac{\kappa r}{2} \right] \frac{e^{-\kappa r}}{r}. \tag{12}$$

This controversial theory has been quoted widely as a possible explanation for a wide variety of colloidal phenomena. However, equation (12) fails to describe measured pair potentials such as those in figure 1(a), as can be seen from the overlaid nonlinear least-squares fits. Since (12) fails for isolated pairs of spheres, it cannot be expected to describe the behaviour of many spheres through superposition.

3. Attractions between confined pairs of spheres

The same spheres which repel each other in isolation can develop a strong and long-ranged attraction in the presence of one or two confining glass walls. Such attractions were first observed by Kepler and Fraden [9] in dilute suspensions sandwiched between parallel glass plates. Optical tweezer measurements [12] such as the examples in figure 1(b) confirmed the walls' role by demonstrating their influence on two otherwise isolated spheres. The challenge is to explain how nearby walls induce attractions between otherwise repulsive spheres.

The glass–water interfaces in these experiments develop negative surface charge densities comparable to the spheres'. Both the surfaces and their charges must distort the simple-ion distributions around nearby charged spheres. Complementary dipole distortions induced by parallel walls have been proposed [20] as a possible explanation for long-ranged colloidal attractions. The efficacy of a single wall [14], however, rules this out as a general mechanism.

Bowen and Sharif [21] suggested on the basis of numerical calculations that pair attractions arise naturally in confined geometries in the nonlinear mean-field approximation. However, Neu [22] and Sader and Chan [23] (NSC) have demonstrated that this result must be incorrect by proving that the nonlinear Poisson–Boltzmann equation can only yield repulsions in confined geometries. The NSC proof holds for constant-potential boundary conditions, at least some variants of constant-charge boundary conditions, and for confining pores of arbitrary cross-
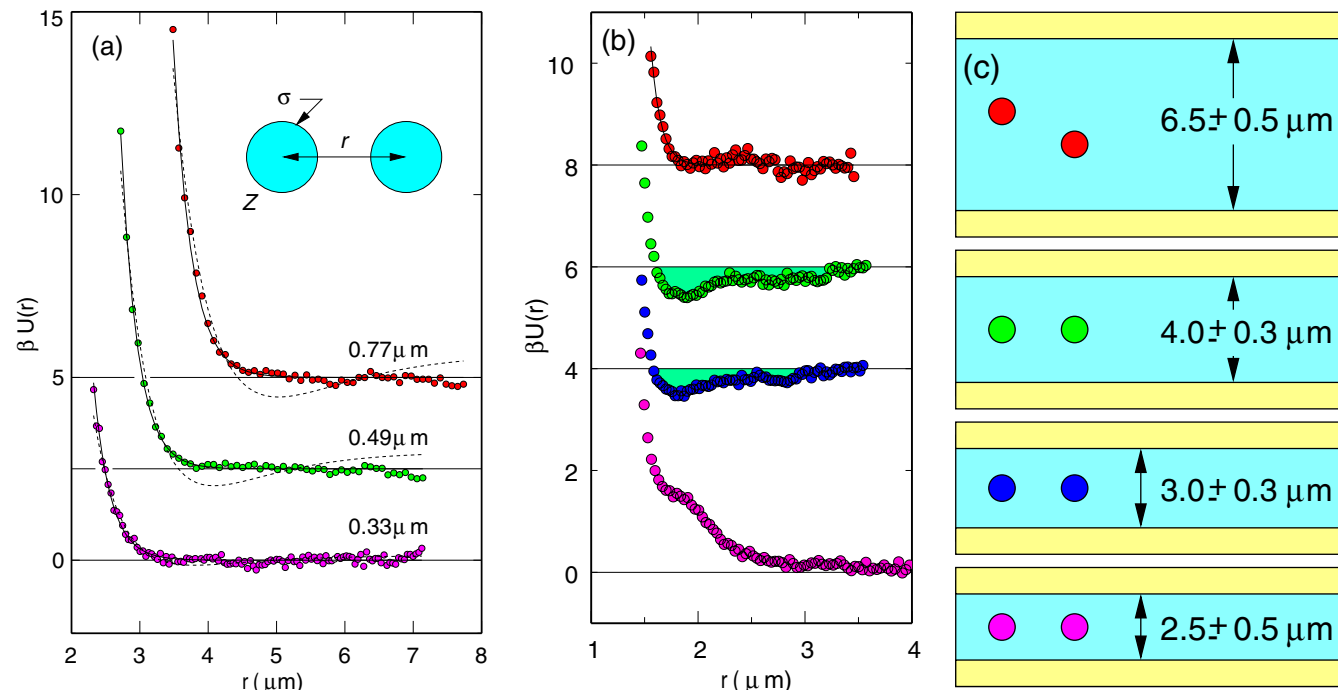
Figure 1. (a) Interaction potentials for pairs of polystyrene sulphate spheres dispersed in deionized water at $T = 25\,^{\circ}C$. Sphere radii are indicated next to each curve. Solid lines are nonlinear least-squares fits to (9). Dashed lines are fits to (12). (b) The pair potential for spheres of radius 0.327 μm confined between parallel glass walls as shown in (c). For large separations, spheres are free to move in all three dimensions and their pair potential resembles that for unconfined spheres. Once the spheres are confined to the mid-plane by electrostatic interactions with the walls, the pair potential has a minimum, indicating long-ranged attractions. At very small wall spacings, spheres also experience an unscreened repulsion due to field lines propagating through the dielectric glass walls.

section. This important result suggests that confinement-induced like-charge attractions are qualitatively inconsistent with the Poisson–Boltzmann formulation.

NSC also appear to contradict recent perturbation calculations [24] which find wall-induced attractions for constant-charge boundary conditions. The disagreement might hinge on details of the boundary conditions [24], in which case wall-induced attractions would seem to be a rather specialized phenomenon. Other experiments, however, point to a broader context for like-charged colloidal attractions and thus a more general mechanism outside of mean-field theory.

4. Metastability of superheated colloidal crystals

Suspensions of purely repulsive monodisperse spheres with pairwise additive interactions are believed to exist in three equilibrium phases: fluid, face-centred cubic (FCC) crystal or body-centred cubic (BCC) crystal. Experiments on charge-stabilized colloidal suspensions have revealed other states, however, including equilibrium liquid–vapour phase separation [25, 26], re-entrant solid–liquid transitions [27], stable void structures consistent with solid–vapour and liquid–vapour phase separation [26], and metastable superheated crystals [14, 28]. These additional states are most easily explained if the pair potential includes an attractive component [19, 20, 25–27, 29] or if the system develops a many-body cohesion [30].

Metastable crystals' structure and dynamics, in particular, reveal long-ranged attractions consistent in range and magnitude with the measured wall-induced attraction [14]. These crystals, an example of which is shown in figure 2, are made by compressing a low-density
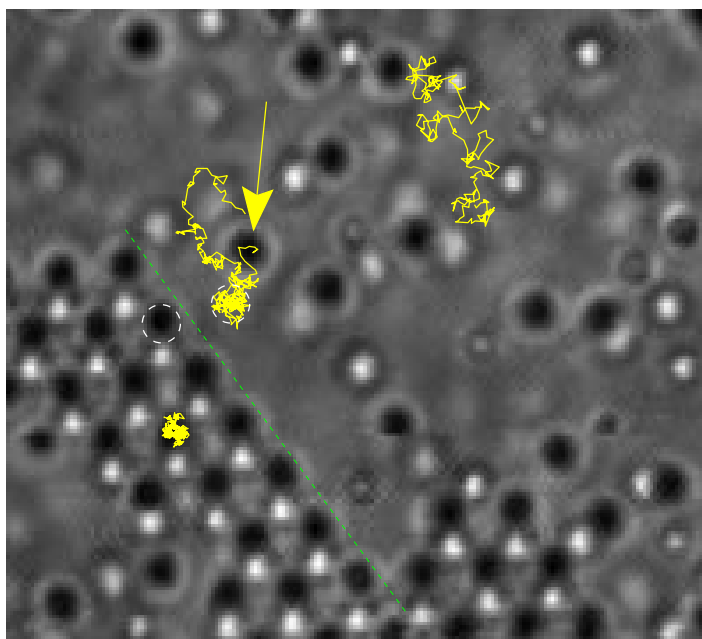

Figure 2. A video microscope view of the (110) face of a superheated metastable FCC colloidal crystal in contact with a low-density fluid. Superimposed traces indicate the trajectories of selected spheres in 1/30 s intervals. These trajectories clearly distinguish well-localized spheres in the crystal from freely diffusing spheres in the fluid. Some spheres, such as the one indicated with the arrow, collide with and temporarily attach to the crystal–fluid interface.

suspension of spheres against glass walls through an electrohydrodynamic instability [28]. The crystals should melt in a matter of seconds once the compressing field is turned off, at a rate limited only by diffusion. Instead, some crystalline regions persist for as long as an hour, their facets and interfacial fluctuations attesting to a large stabilizing latent heat.

These observations might seem only to confirm that nearby walls induce attractions among pairs of spheres since the crystals are formed against glass surfaces. These are three-dimensional crystals, however, and extend away from confining walls into the bulk of the suspension. Indeed, their surfaces are so far from the nearest walls that pair interaction measurements at comparable separations reveal no attraction [14]. Thus, the wall-induced attraction cannot be responsible for the crystals' three-dimensional structure. This is strong circumstantial evidence that the spheres themselves can engender a many-body cohesion whose range and strength are comparable to those of the wall-induced pair attraction.

The suggestion that bulk colloidal suspensions can experience many-body cohesions even in the absence of nearby bounding walls is consistent with observations of other anomalous phase transformations in bulk colloidal suspensions. It should not be viewed as evidence for *pairwise* attractions, however, since the direct interaction measurements described in section 2 largely rule out this interpretation.

In this sense, observations on metastable superheated colloidal crystals serve as a bridge between pair interaction measurements and measurements of bulk phase behaviour. They suggest that a similar mechanism may be responsible for the anomalous behaviour in both classes of experiments. If this is the case, then the failure so far to measure long-ranged attractions in isolated pairs of spheres suggests that all of the anomalous behaviour observed in bulk suspensions arises from the breakdown of pairwise additivity in macroionic interactions. The interesting thing about this failure is that it is not subtle—it leads to qualitatively new behaviour when compared with mean-field theory's predictions. It is evident even in systems for which the DLVO theory has long been assumed to be adequate.

5. Failure of linear superposition in equilibrium crystals

Despite its shortcomings, the DLVO theory is appealing in its simplicity. Even if it does not accurately describe pair interactions in strongly interacting suspensions, it might adequately describe suspensions' bulk properties, perhaps with appropriately renormalized interaction parameters. This approach has been invoked to reconcile experimentally observed fluid–FCC–BCC phase transitions with those seen in simulations on particles interacting with screened Coulomb pair repulsions [31, 32]. Superposition of effective pairwise interactions similarly has been used to account for colloidal crystals' elastic properties [4, 29, 33, 34]. Unfortunately, microscopic analysis of colloidal crystals' microscopic structure and dynamics reveals that such a parametrization fails to describe their bulk properties consistently [35]. In particular, no combination of effective interaction parameters simultaneously parametrizes the potential of mean force and the bulk modulus.

Figure 3(a) shows a cross-section through the potential of mean force for colloidal spheres in a FCC colloidal crystal at volume fraction $\phi = 0.026$. This crystal was grown from a suspension of polystyrene sulphate spheres of radius $\sigma = 0.327$ μm dispersed in deionized water in diffusive contact with mixed-bed ion-exchange resin. Its volume fraction was computed from a measured nearest-neighbour spacing of $a = 2.50 \pm 0.10$ μm. The potential of mean force, $W(\vec{r})$, describes a sphere's potential energy due to interactions with its neighbours and can be measured through the probability $P(\vec{r}) = \exp[-\beta W(\vec{r})]$ for finding spheres displaced by $\vec{r}$ from their equilibrium positions.

If spheres in the crystals repel each other according to (9), then the potential of mean force
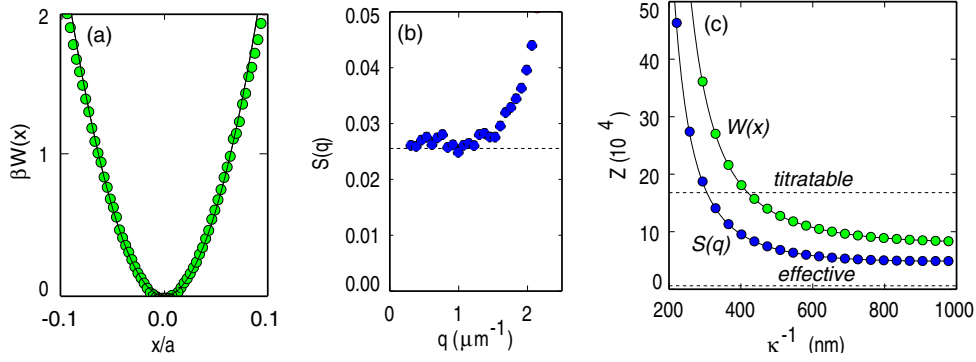
Figure 3. (a) The potential of mean force along an arbitrary direction for spheres in a colloidal crystal at $\phi = 0.026$. Distances are measured in units of the crystal's equilibrium lattice constant, a. The solid line is a fit to the form $W(x) = Ax^2$. (b) The structure factor calculated from spheres' measured locations together with an extrapolation to long wavelengths, $\lim_{q\to 0} S(q)$. (c) Possible values for Z and κ^{-1} derived from the data in (a) and (b). Dashed horizontal lines indicate sphere charges measured by conductimetric titration and by fitting the pair potential in figure 1(a).

can be built up by superposition of nearest-neighbour interactions [35]:

$$W(r) \approx 12U(a)\left(\frac{\sinh \kappa r}{\kappa r} - 1\right) \approx 2U(a)(\kappa r)^2 \tag{13}$$

for a 12-fold-coordinated FCC crystal. The quality of the quadratic fit to the data in figure 3(a) suggests that this might indeed be an adequate description of colloidal crystals' microscopic dynamics. Comparably good results are obtained for other crystals.

Measuring a single property leaves us with an entire family of possible values for Z and κ. Identifying a single (Z, κ) pair describing the crystal's collective properties requires a simultaneous measurement of an independent property.

Fourier transforming the crystal's pair correlation function $g(r)$ yields its angle-averaged static structure factor:

$$S(q) = 1 + 2\pi \int_0^\infty [g(r) - 1]J_0(qr)r \, dr. \tag{14}$$

A crystal's structure at small wavenumbers q is inversely proportional to its bulk modulus:

$$B = \lim_{q\to 0} \frac{\bar{\rho}k_B T}{S(q)} \tag{15}$$

which also can be related to an effective pair interaction [35]:

$$B = \frac{2\sqrt{2}}{3}\frac{U(a)}{a^3}[2(\kappa a)^2 + \kappa a + 1] \tag{16}$$

to yield a family of (Z, κ) values. The crystal's structure factor at small wavenumbers is shown in figure 3(b).

Rather than intersecting at a particular set of effective interaction parameters for the crystal, the families of values obtained by these two methods are disjoint, as can be seen in figure 3(c). Thus, this colloidal crystal's collective properties are not parametrized by (9) even though this effective potential nicely describes interactions between isolated pairs of its spheres. The breakdown of pairwise additivity is manifest not only in biphasic or strongly confined suspensions, but even in colloidal crystals' bulk properties, and even for quite weakly interacting crystals.

6. Discussion

The DLVO theory fails to account for the interactions, dynamics, and phase transitions in strongly interacting charge-stabilized colloidal suspensions. No consensus has yet emerged regarding which of its approximations is to blame for the discrepancies. Even the underlying Poisson–Boltzmann mean-field theory is now suspect. Consequently, no definitive statement is yet possible regarding possible ramifications for other macroionic systems. Although it is far from complete, the existing body of experimental evidence allows us to place constraints on the evolving theory.

So far, no interaction measurement on isolated pairs of spheres has found attractions inconsistent with the DLVO theory. And yet evidence for many-body attractions abounds when the number density of the same spheres is increased. On this basis, we provisionally rule out any of the existing theories which predict pairwise attractions for isolated spheres. A definitive statement awaits additional experimental evidence concerning the interaction's dependence on thermodynamic control parameters; such experiments are now ongoing.

Anomalous attractions are observed on length scales extending to several micrometres. It seems unlikely, therefore, that the discrete structure of the solvent or the discrete size of the simple ions can play a role in mediating the attraction. In other words, the primitive model should suffice.

Image charges in the confining walls, or sphere-induced changes in the walls' charge state could conceivably lead to attractions. The additional repulsion observed for tightly confined spheres (see, for example, the lowest curve in figure 1(b)) provides one counter-indication, however. Bulk phenomena such as the observed metastability of superheated colloidal crystallites further indicates that glass surfaces are not necessary to engender many-body colloidal attractions.

Fluctuations in ion density around the spheres seem another likely candidate. Existing calculations suggest that such fluctuations do indeed lead to attractions, but that they are doubly screened and thus short ranged [36]. Similarly, careful handling of the kinetics of ion adsorption onto colloidal surfaces leads to short-ranged attraction [37]. The experimentally observed attractions, on the other hand, are longer ranged than the singly screened pair repulsion. If ionic fluctuations are responsible, the mechanism must involve modes of fluctuation not yet considered.

Finally, we should not forget that the mean-field behaviour predicted by the Poisson–Boltzmann formulation need not reflect the true saddle-point behaviour of the system. High-order correlations neglected in (5), if they could be treated analytically, might lead to interesting new predictions not only for charge-stabilized colloidal suspensions but also for macroionic systems in general.

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