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Like-charge attractions in metastable colloidal crystallites

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Sub-micrometre charged latex spheres can be suspended in water to form regular arrays known as colloidal crystals. In contrast to most conventional solids, colloidal crystals can be forced into metastable superheated states. The structure and dynamics of these metastable crystals show evidence for strong, long-range attractions between the similarly charged spheres. Such attractive interactions are inconsistent with the accepted theory of colloidal interactions, and might influence the properties of many natural and industrial suspensions.

Charge-stabilized colloidal suspensions of extremely uniformly sized polymer spheres were developed in the 1950s as media for paints and other surface coatings. These suspensions have attracted considerable attention in recent years for their utility as model systems with which to study the mechanisms of structural phase transitions¹. Depending on their concentration and chemical environment, colloidal spheres can form up into regular crystalline arrays or devolve into fluid disorder. Transformations between the ordered and disordered states are phase transitions analogous to melting and freezing of atomic matter. Unlike atoms, however, colloidal spheres can be tracked with a conventional light microscope. Their structural transformations thus provide unparalleled opportunities to investigate the microscopic mechanisms of phase transitions.

Here we describe how the study of phase transitions sheds new light on the fundamental properties of colloidal suspensions. In particular, we find evidence in an exotic colloidal melting transition for long-range attractive interactions between like-charged microspheres. When combined with direct measurements of the spheres' pairwise interaction potential, these observations strongly suggest that such attractive interactions may be responsible for a variety of other unexplained phenomena observed over the past decade in bulk colloidal suspensions.

The most striking of these anomalies include large stable voids in otherwise homogeneous suspensions^{2,3} and equilibrium phase separation between colloidal fluids of different densities^{4,5}. Neither should be possible in a system with purely repulsive interactions, although explanations based on impurity effects⁶ have proved difficult to exclude. Persistent quantitative discrepancies between predicted^{7–11} and observed^{12,13} melting points of colloidal crystals are no less disturbing, but might reflect relatively minor shortcomings in the theory. The long-ranged attractions we observe would account naturally for these effects, but are qualitatively inconsistent with the long-accepted theory for colloidal interactions. We suggest, therefore, that the theory for colloidal interactions requires substantial revision.

Colloidal interactions and phase transitions

The experiments described below were carried out on suspensions of polystyrene sulphate spheres of diameter $2a = 0.652 \pm 0.005 \mu\text{m}$ dispersed in deionized water (catalogue number 5065A, Duke Scientific, Palo Alto, CA). These spheres are synthesized with a large number of ionizable sulphate salt groups chemically bonded to their surfaces. These groups dissociate in water, each leaving a single negative charge bound to its sphere's surface and a compensating positively charged counterion in solution. One sulphate group subtends roughly 10 nm^2 so that a micrometre-scale sphere has a titratable charge

of the order of 10^5 electron equivalents. Not all surface groups dissociate at once, though, so the effective charge number is typically much smaller. While these specially prepared spheres have consistent and highly uniform surface charges, many naturally occurring and industrially prepared colloids also acquire static surface charges¹. Results discussed here should pertain to them as well.

The interaction between an isolated pair of similarly charged spheres is purely repulsive and has been shown both theoretically^{14,15} and experimentally^{16–18} to adopt the screened-Coulomb form

$$\frac{U(r)}{k_B T} = Z^2 \lambda_B \left[\frac{\exp(\kappa a)}{1 + \kappa a} \right]^2 \frac{\exp(-\kappa r)}{r} \quad (1)$$

where r is the spheres' centre-to-centre separation. This expression for the interaction energy was originally derived by Derjaguin, Landau, Verwey and Overbeek (DLVO)^{14,15} and accounts approximately for the counterions' exclusion from the spheres' interiors. The range of the interactions is limited by the concentration n of simple ions in the water and is described by the Debye–Hückel screening length $\kappa^{-1} = (4\pi n \lambda_B)^{-1/2}$, where $\lambda_B = e^2/\epsilon k_B T$ is the characteristic separation between ions carrying a single electronic charge, e , at temperature T in a fluid of dielectric constant ϵ .

The complete DLVO theory includes a term accounting for van der Waals attractions. This term is neglected in the following discussion because it contributes less than $0.01 k_B T$ to the interaction potential for polystyrene microspheres immersed in water and separated by more than 100 nm (ref. 19).

The suspension at an initial volume fraction around $\phi = 0.02$ is contained in the space between two parallel glass walls separated by $28 \mu\text{m}$. The edges of this sample volume are hermetically sealed

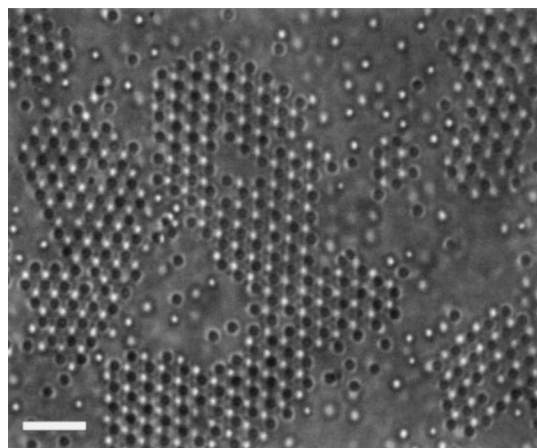


Figure 1 Metastable colloidal crystallites adrift in a colloidal fluid, after 10 minutes of melting. Scale bar, $5 \mu\text{m}$; field of view, $42 \times 35 \mu\text{m}$.

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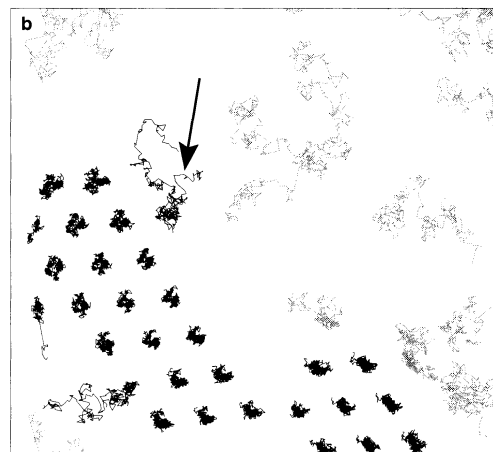
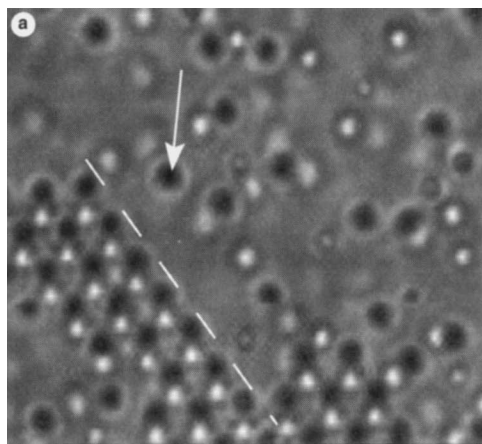


Figure 2 a, Video micrograph of the surface plane of a faceted colloidal crystal in contact with a dilute colloidal fluid. The dashed line demarks a (110) facet of the crystallite, while the arrow points out a sphere about to attach to the surface.

b, Trajectories of the spheres in **a** taken over 15 s. Heavy lines show trajectories that are part of the crystal, light lines show trajectories in the fluid.

against contamination by airborne CO_2 and make diffusive contact with reservoirs of ion exchange resin. We estimate the steady-state concentration of residual stray ions in this system to be less than $n = 5 \times 10^{-6} \text{ M}$. Such low ionic strengths provide for long-ranged electrostatic interactions with Debye–Hückel screening lengths extending to $\kappa^{-1} = 400 \text{ nm}$.

If we assume that the interactions among a collection of spheres can be built up by superposing pairwise repulsions of the form described by equation (1), then the phase diagram for the ensemble of spheres is well understood^{7–11}. In particular, a fluid interacting through screened-Coulomb repulsions can be frozen to a crystal of face-centred cubic (f.c.c.) or body-centred cubic (b.c.c.) symmetry by increasing the volume fraction of spheres in the suspension while leaving other parameters fixed. Transformations qualitatively consistent with this picture have been observed experimentally^{12,13} in charge-stabilized colloidal suspensions.

Conventional crystals are rigid enough to support themselves against gravity and so determine their own density. Colloidal crystals exist only within containers. Were they not confined, we might expect mutually repelling spheres to drift apart until the forces causing them to order were overwhelmed by randomizing thermal agitation. At this point, the crystal would melt. We have found, however, that some colloidal crystals made of like-charged spheres maintain their integrity even without confining walls. The structure and dynamics of these metastable crystals provide strong evidence for the influence of long-ranged attractions not accounted for in the DLVO theory.

Superheated crystals

We take advantage of forces which arise during low-frequency electrophoresis to compress a colloidal fluid past its freezing point²⁰. The latent heat of freezing is absorbed by the surrounding water whose heat capacity is comparatively so enormous that the suspension's temperature does not change. When the electric field is turned off, the suspension is free to return to its equilibrium fluid state so that any remaining crystals are superheated with respect to the fluid.

Parallel-plate gold electrodes patterned onto one of the sample volume's glass surfaces provide electrical contact to the suspension. A 60 Hz signal, 10 V peak-to-peak, is applied across the 1-mm gap and drives the spheres by electrophoresis. The interplay of this force and electro-osmotically driven bulk fluid flow engenders a Magnus force which pushes the spheres towards the walls and away from the sample volume's mid-plane. Similar forces drive spheres settling under gravity to the walls of fluidized beds²¹. The resulting increase in density induces freezing at the walls and produces several polycrystalline layers.

As we have previously described²⁰, superheated colloidal crystals in suspensions of moderate ionic strength melt at a rate limited only by diffusion of spheres away from the crystal surface. All traces of order in such suspensions typically disappear within 10 seconds. More thoroughly deionized suspensions at lower ionic strength display dramatically different behaviour, retaining residual metastable crystallites drifting through the fluid for as long as an hour. The examples in Fig. 1 are in a non-equilibrium ordered state 10 minutes after compression was stopped. The largest of these crystallites consist of five layers of spheres in a face-centred cubic packing. Individual spheres appear either light or dark depending on their distance from the focal plane of the microscope's $100 \times \text{NA } 1.4$ oil immersion objective. Dark spheres in Figs 1 and 2a constitute the layer closest to the glass wall, the brightest are in focus in the second layer, and the third layer is barely visible as light smudges. Nearest-neighbours are separated by $d = 1.8 \mu\text{m}$ or roughly three diameters.

That the melting rate changes dramatically with changing ionic concentration is not necessarily surprising. Increasing the screening length could push the ensemble of spheres close to their crystal–fluid coexistence line. In that case, the free-energy difference driving spheres from the crystal back into the fluid could be vanishingly small and the melting process correspondingly slow. Analysis of the crystals' structure, however, shows that other forces are at work.

Stable facets

The most prominent features of crystals such as those in Figs 1 and 2a are their well defined facets. A crystal's facets are stable against thermal capillary waves only if the latent heat of freezing per particle exceeds

$$L > 4k_{\text{B}} T \frac{z}{\eta} \quad (2)$$

where η is the coordination number of a particle at the surface and z is the bulk coordination number²². For low-index facets such as that in Fig. 2a, $z/\eta \approx 2$, so that the latent heat is at least $L = 8k_{\text{B}} T$ per particle.

This lower limit already is a factor of eight larger than the largest latent heat anticipated for spheres with purely repulsive pairwise interactions. Entropically stabilized hard-sphere crystals with short-range contact repulsions are predicted²³ to have a latent heat only as large as $1k_{\text{B}} T$ per particle. Longer-range repulsions lead to even smaller latent heats²⁴. The discrepancy with our observations is accounted for most easily by positing the existence of a long-range attractive interaction contributing to the crystal's cohesive energy in addition to the core electrostatic repulsion. The attraction cannot be attributed to van der Waals interaction as such fluctuation-induced forces are utterly negligible at the crystal's lattice spacing¹⁹. To account for the facets' stability, each nearest-neighbour 'bond' would have to reduce the system's free energy by of the order of $0.5k_{\text{B}} T$.

Interfacial kinetics

The kinetics of attachment and detachment at the interface provide further evidence of attractive pairwise interactions. Figure 2b shows the computer-measured trajectories¹⁷ followed by the spheres photographed in Fig. 2a. Spheres in the crystal simply rattle about their lattice positions with transit times comparable to the 1/30-second interval between video frames. For the most part, spheres in the neighbouring fluid roam freely.

The track we have emphasized near the centre of Fig. 2b follows a sphere which begins its trajectory as part of the fluid but joins the crystal interface for $\tau = 6$ s before resuming its random walk. In this time, the sphere wanders no further than $r_0 = 0.25 \mu\text{m}$ from its lattice position. The probability $P(r_0|\tau) = 1 - \exp(-r_0^2/(4D\tau))$ that a brownian sphere with the fluid's measured¹⁷ diffusion coefficient of $D = 0.15 \mu\text{m}^2 \text{s}^{-1}$ would remain so well localized is less than 0.02. Rather than being localized by chance, the sphere appears to be held in place by an energetic barrier to desorption over which it eventually escapes. If we estimate of the order of $N = 100$ unsuccessful attempts to leave the surface by thermal excitation, then the barrier height is at least $E_b = k_B T \ln N \approx 4k_B T$. the existence of a surface activation energy also would explain why only one other sphere detaches from the crystal during the 15 seconds for which the trajectories were traced.

Crystals made from mutually repulsive spheres should put up no barrier to detachment. The intersphere attraction of around $0.5k_B T$ per neighbour deduced from the crystals' faceted structure, however, would account naturally for the estimated E_b .

Smallest metastable clusters

As the initially large metastable crystallites melt, they create a population of smaller crystals. Eventually, these crystals shrink to the radius R^* at which their surface energy exceeds the binding energy holding them together and they dissociate. The critical radius for a face-centred cubic crystal with lattice constant d , latent heat per particle L , and surface tension γ is

$$R^* = \sqrt{2} \frac{\gamma d^3}{L} \quad (3)$$

The smallest metastable crystals thus allow us to set a lower limit on the surface tension of the crystal–fluid interface.

Figure 3 shows four stages in the dissociation of a minute crystal whose radius is one lattice constant. Very shortly after one additional sphere separates from the surface, the remaining spheres go on their separate ways. Although we regularly observe crystals such as that in Fig. 3a, we do not find smaller long-lived ordered clusters. If we identify $R^* = d$ and apply the above result for L , then we can estimate a lower limit for the surface tension: $\gamma > L/(\sqrt{2}d^3) \approx 5.6k_B T d^{-2}$. This value is about an order of magnitude larger than the largest surface tension anticipated for a system with purely repulsive pairwise interactions^{25–27}. Once again, the discrepancy is naturally explained by assuming a long-range attractive component in the pairwise interaction.

Measuring the interaction

These three experimental observations suggest that the metastable colloidal crystallites are bound together by a strong long-range attraction not accounted for by the DLVO theory. Recent direct measurements of the pairwise colloidal interaction potential^{16–18} demonstrate that no such attraction appears for isolated pairs of spheres. Attractions are observed, however, when spheres are rigidly confined to the plane by closely spaced parallel glass surfaces^{18,28,29}, although the mechanism for this attraction is not yet understood. As the metastable crystals form at glass walls, a wall-mediated interaction might explain our observations.

Two considerations stand in the way of this interpretation. First, the wall separation in the present experiments is roughly ten times larger than in the experiments for which pair attractions were

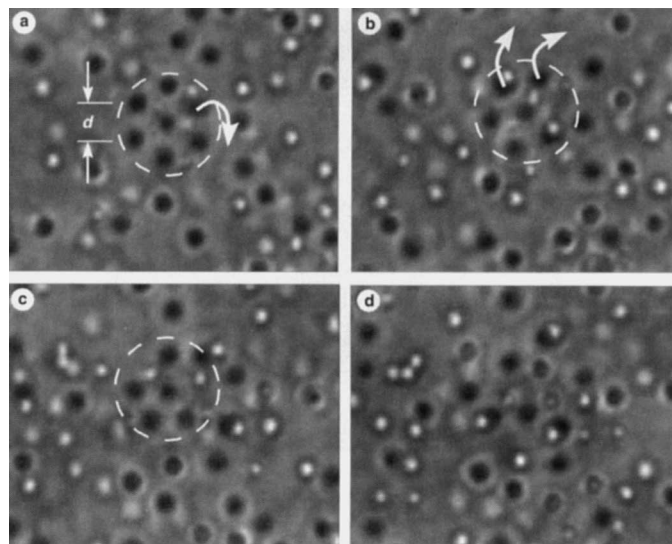


Figure 3 Metastable cluster of ten spheres against a glass wall. The appearance of clusters such as this, and the lack of smaller clusters, suggest that the maximum unstable radius is $R^* \approx 1d$. **a**, The initial ten-sphere cluster indicated by a dashed circle. The arrow indicates the direction in which a sphere will eventually leave the surface. **b**, The same cluster 6 seconds later when one sphere detaches. The crystallite has drifted in the interval. The next two spheres to detach are indicated by arrows. **c**, After another 2 seconds, the cluster is reduced to seven spheres. **d**, 1 second later, the crystal has completely dissipated.

measured, and the ability of a single wall to induce attractive interactions has not been demonstrated. Second, the walls' measured influence on colloidal interactions falls off with distance, h , from the wall¹⁸. Consequently, the effect might not extend far enough to stabilize the crystalline layers farthest from the wall.

To examine the range and magnitude of intersphere attractions mediated by a single glass wall, we performed direct interaction measurements in the same sample cell used to study the metastable crystals. The measurement technique is described in detail in ref. 16. Two optical tweezers are used to position a pair of spheres at fixed separations in the focal plane of the microscope. When the laser beam powering the traps is interrupted, the spheres move under the combined influence of random thermal forces and their mutual interaction. Blinking the traps on and off in synchrony with the video camera's shutter allows us to sample experimentally the markovian propagator for the master equation whose steady-state solution is the equilibrium pair distribution function for the spheres, $g(r)$. The pair distribution function is related to the pair interaction potential through Boltzmann's equation:

$$g(r) = \exp\left(-\frac{U(r)}{k_B T}\right) \quad (4)$$

Approximately 20,000 images of sphere pairs taken at 1/30-s intervals suffice to measure an interaction potential with 60-nm spatial resolution and $0.2k_B T$ energy sensitivity over a range of $6 \mu\text{m}$ and $5k_B T$, respectively. To avoid many-body contributions to the measurements, we diluted the suspension so that no other spheres wandered within $25 \mu\text{m}$ of the test pair.

The lower trace in Fig. 4 was obtained with the optical tweezers focused $h = 2.5 \pm 0.5 \mu\text{m}$ from the sample cell's upper glass wall. At this distance from the wall, the measured interaction potential has a strongly attractive minimum at a centre-to-centre separation of $3.5 \mu\text{m}$. This confirms that a single wall can induce an attraction between like-charged colloidal spheres comparable to that deduced from structural analysis of the metastable crystals. The range and strength of the attraction are too great to be accounted for by van der Waals attraction. Image charges in the nearby glass walls

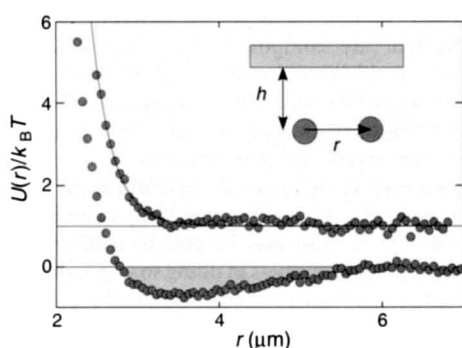


Figure 4 Interaction potential as a function of centre-to-centre separation for a pair of 0.65- μm -diameter polystyrene sulphate spheres near a charged glass surface. The experimental geometry is represented schematically in the inset. The upper curve was measured a distance $h = 9.5 \pm 1.0 \mu\text{m}$ from the nearest wall and has been offset by $1k_B T$ vertically for clarity. The dashed line is a fit to equation (1). The lower curve was acquired at $h = 2.5 \pm 0.5 \mu\text{m}$ and has an attractive minimum $\sim 0.7k_B T$ deep for spheres separated by more than five diameters.

similarly would exert too weak an influence. The attraction's dependence on distance from the wall suggests instead a counterion-mediated mechanism¹⁸.

No attraction is evident in the upper trace of Fig. 4 which was measured $h = 9.5 \pm 1.0 \mu\text{m}$ from the lower wall. As has been observed for spheres confined by a pair of closely spaced glass walls¹⁸, attractive interactions only appear when the spheres' ion clouds interact strongly with the glass wall's screening charge. These conditions are not considered in the formulation of the DLVO theory^{14,15}. The DLVO theory should apply, however, for isolated pairs of spheres far from the walls. The dashed curve in Fig. 4 is a three-parameter fit to equation (1) for the effective charge $Z = 7,300$, the Debye-Hückel screening length $\kappa^{-1} = 275 \text{ nm}$, and an additive offset.

The absence of an attractive minimum at $h = 9.5 \mu\text{m}$ suggests that the wall-induced attractive interaction alone cannot stabilize the fourth and fifth layers of crystals such as those in Fig. 1 which are at least $h = 7 \mu\text{m}$ from the wall. Furthermore, diluting the suspension for the interaction measurements probably reduced the electrolyte's ionic strength and increased not only the screening length but also the range of the wall-induced interaction. This seems likely because the centre-to-centre separation of both the attractive minimum and the repulsive core in $U(r)$ exceed the crystals' nearest-neighbour spacing of $1.8 \mu\text{m}$. In the higher ionic concentrations at which the metastable crystals were studied, the influence of the wall is likely to extend even less far than is indicated in Fig. 4. Interaction measurements in the confined geometry by Kepler and Fraden²⁸ also show that the range and strength of the wall-induced interaction depend strongly on the electrolyte's ionic concentration. They confirm, in particular, that higher ionic strengths lead to shorter-ranged attractions.

Attractive phenomenology

When combined with the results of direct interaction measurements, our observations on metastable colloidal crystals lead us to several insights into colloidal interactions. The structure and dynamics of the metastable crystals provide clear evidence for strong, long-range attractions acting between like-charged colloidal microspheres which are not explained by the standard DLVO theory. The attractive pair potentials measured in the presence of confining glass walls are strong enough to account for the crystals' properties, but do not extend far enough from the walls to stabilize their full three-dimensional structure. Their stability, therefore, suggests that the planes of charged spheres in the crystal act in a manner comparable to charged glass planes in providing the geometrical confinement apparently necessary for attractive interactions. A charged wall with its counterions indeed may resemble a

concentration of charge-stabilized spheres in a coarse-grained or mean-field description. If this is the case, then confinement-induced attractive interactions might arise in charge-stabilized colloidal suspensions even without glass walls. The nature and mechanism of this and the wall-mediated attraction are open questions and pose a formidable challenge to the theory of colloidal interactions.

Discrepancies between predictions of the DLVO theory and measurements on charge-stabilized colloidal suspensions have fuelled an active debate about alternatives to the DLVO theory for colloidal interactions. Such alternatives include the Sogami-Ise theory^{30,31}, which describes long-range pairwise attractions mediated by counterion distributions at least qualitatively similar to our observations. Very recent direct interaction measurements¹⁸, however, show that the Sogami-Ise theory does not correctly describe the interactions between unconfined pairs of spheres. It probably does not, therefore, explain the present observations.

The existence and behaviour of superheated colloidal crystals suggest instead that many-body effects may contribute an attractive component to the pairwise interactions between charged microspheres. Given the many useful, interesting and economically important properties which microscopic interactions impart to colloidal suspensions, this result has significance beyond the immediate application to non-equilibrium phase transitions. \square

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