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LETTER TO THE EDITOR

## The electrostatic interaction between interfacial colloidal particles

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**Abstract.** The electrostatic interaction between charged, colloidal particles trapped at an air-water interface is considered using linearised Poisson-Boltzmann results for point particles. In addition to the expected screened-Coulomb contribution, which decays exponentially, an algebraic dipole-dipole interaction occurs that may account for long-range interactions in interfacial colloidal systems.

Interfacial colloids consists of particles dispersed on an interface between two fluid media and held there by surface tension. A particularly interesting example is the system of polystyrene latex spheres at an air-water interface, since in this case, the particles are highly charged and therefore strongly interacting. Ordered and disordered phases have been observed in this system (Pieranski 1980), leading to speculations that interfacial colloids may be a model system for studying the physics of condensed, two-dimensional phases, such as melting, especially since the interaction appears to be long-range, extending over many Debye screening lengths. By varying the screening length via the ionic strength of the substrate, attractive van der Waals interactions can be made to dominate, allowing a wide variety of two-dimensional phenomena to be investigated. For example, diffusion-limited aggregation in a plane was recently studied by Hurd and Schaefer (1985).

Pieranski suggested on intuitive grounds that each charged particle and its asymmetric counterionic cloud form a dipole moment perpendicular to the interface, and that the particles interact *through the air* with an algebraic, dipolar force law. (Interactions propagating through the water substrate are screened by mobile ions, leading to an exponentially decaying force law.) A similar asymmetry effect was noticed by Jancovici (1982) in analysing a classical Coulomb plasma near a wall: along the wall, the pair correlation function exhibits a power-law decay attributable to non-vanishing electrical dipole interactions induced by the wall. Such soft potentials favour the formation of the proposed 'hexatic' phase (Halperin and Nelson 1978), through which the melting transition might be continuous in two dimensions, although simulations of the polystyrene-water system using algebraic potentials indicate a discontinuous transition (Kalia and Vashishta 1981).

The purpose of this letter is to place the speculations concerning dipole-dipole interactions at large separations between interfacial colloidal particles on a firm theoretical basis, and to clarify the facts of electrostatic interactions. Other possibilities for important interactions involving surface deformations in the substrate (attractive dimples, etc) are not treated in this letter.

Stillinger (1961), in studying the discrete adsorbed charge effect, found an integral expression for the electrostatic interaction between point charges at an electrolyte interface by solving the linearised Poisson-Boltzmann equation. His expression is the starting point for this letter. It is shown here that the interaction energy is dominated by exponential behaviour at small separations and by algebraic behaviour at large separations. These regimes are also illustrated by direct numerical integration.

The two major assumptions in Stillinger's work are those of point charge and the linearisation of the Poisson-Boltzmann equation. (The use of the Poisson-Boltzmann equation itself might be questioned; however, ion-ion correlations should be negligible for the dilute solutions considered here.) The point charge assumption is applicable when the particles are separated by distances much larger than their radii,  $r \gg a$ , which is just the desired limit. On the other hand, the linearisation assumption, which assumes that the electrostatic energy for a mobile ion in solution is everywhere much smaller than its thermal energy,  $e\psi \ll kT$ , is not rigorously justified near the highly charged colloidal particles. Nevertheless, since this assumption often holds in the far field, the form of the potential can be calculated within the framework of the linearised theory, and any difficulties concerning the true potential can often be rectified by the use of an effective charge. These details, while important in many real problems, are ignored here in the interest of simplicity.

Stillinger's expression for the interaction between two particles at an electrolyte-air interface, such as those in figure 1, is

$$U(r) = 2[(Ze)^2/\epsilon r]y(\kappa r), \quad (1a)$$

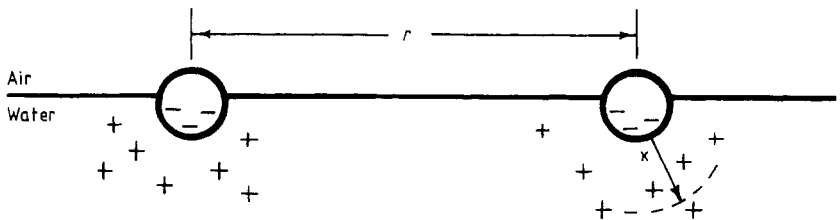
with

$$y(k) = \int_0^\infty \frac{xJ_0(x) dx}{(x^2 + k^2)^{1/2} + x/\epsilon} \quad (1b)$$

where  $Ze$  is the total charge on each interfacial particle,  $r$  is the distance between them,  $k$  equals  $\kappa r$  where  $\kappa^{-1}$  is the Debye screening length, and  $\epsilon$  is the dielectric constant of water. The factor of two in (1a) arises from the fact that the effective dielectric constant at the interface is just the average of the two media, in this case water and air,  $\frac{1}{2}(\epsilon + 1) \approx \frac{1}{2}\epsilon$ .

Because water has a large dielectric constant ( $\approx 80$ ), it is expedient to drop the term  $x/\epsilon$  in the denominator, a procedure which yields the familiar screened-Coulomb interaction via the identity

$$\int_0^\infty \frac{xJ_0(x) dx}{(x^2 + k^2)^{1/2}} = \exp(-k). \quad (2)$$



**Figure 1.** Schematic of charged particles at an electrolyte-air interface. The asymmetry of the counterionic clouds gives rise to electrical dipole moments that interact with long-range (power-law) forces.

(Similarly, for an infinitely dilute electrolyte,  $\kappa \rightarrow 0$ , a bare-Coulomb interaction emerges from (1b).) In this limit of large  $\epsilon$ , all of the electric displacement field is captured in the substrate where screening by mobile ions takes place.

The simplest approach to the full integral  $y(k)$  is to expand the denominator in powers of  $\epsilon^{-1}$ . The first term in the expansion is just the exponential screened-Coulomb term. The second term hints of more interesting interactions: it has an algebraic ( $r^{-2}$ ) form for large particle separations. In fact, all of the terms of order  $\epsilon^{-n}$  decay algebraically when  $n$  is odd and exponentially when  $n$  is even. (The exponential and algebraic regimes are separated more cleanly below.) In view of the role played by screening ions, it is tempting to assign the algebraic interactions to fields propagating in the air and the exponential interactions to fields in the substrate. If this picture is true, then  $\epsilon^{-1}$  acts as a coupling constant for propagators in each medium.

The important dipole-dipole contribution can be precisely extracted in one step by eliminating the radical form the denominator of (1b),

$$(y)k = \frac{\epsilon^2}{\epsilon^2 - 1} \int_0^\infty \frac{x J_0(x)}{(x^2 + k'^2)^{1/2}} \left( \frac{x^2 + k^2}{x^2 + k'^2} \right)^{1/2} dx - \frac{\epsilon}{\epsilon^2 - 1} \int_0^\infty \frac{x^2 J_0(x)}{x^2 + k'^2} dx, \quad (3)$$

where  $k'^2 = k^2/(1 - \epsilon^{-2})$ . The first integral corresponds to the screened-Coulomb interaction and the second to the dipole interaction as shown below. Adding and subtracting  $k'^2$  to the numerator of the second integral yields

$$\begin{aligned} \int_0^\infty \frac{x^2 J_0(x)}{x^2 + k'^2} dx &= \int_0^\infty J_0(x) dx - k'^2 \int_0^\infty \frac{J_0(x)}{x^2 + k'^2} dx \\ &= 1 - (\pi/2)k'(I_0(k') - L_0(k')), \end{aligned} \quad (4)$$

where  $I_0$  is the modified Bessel function of the first kind and  $L_0$  is the modified Struve function. The difference between these functions is tabulated in Abramowitz and Stegun (1972) where the asymptotic expansion is also listed,

$$I_0(k) - L_0(x) \sim \frac{2}{\pi} \left( \frac{1}{x} + \frac{1}{x^3} + \frac{1 \times 3}{x^5} + \dots \right).$$

Hence, the integral in (4) for large separations is

$$\int_0^\infty \frac{x^2 J_0(x)}{x^2 + k'^2} dx \sim -\frac{1}{k'^2} - \frac{1 \times 3}{k'^4} - \dots, \quad (5)$$

and the corresponding part of the electrostatic energy is obtained from (1a), (1b), (3) and (5)

$$U_{\text{dipole}} \sim 2(Ze/\epsilon\kappa)^2 r^{-3}. \quad (6)$$

The effective dipole moment of each interfacial colloidal particle and its associated counterionic cloud can now be identified as

$$\mu = Ze/\sqrt{\epsilon\kappa}. \quad (7)$$

Each dipole corresponds to charges  $\pm Ze$  separated by a distance  $(\sqrt{\epsilon\kappa})^{-1}$  in a medium with dielectric constant  $\epsilon$ . Equation (6) differs from Pieranski's assumed interaction by a factor  $\epsilon^{-1}$ .

It remains to be shown that the balance of the interaction energy is exponentially decaying and thus at large separations it becomes unimportant compared to the dipolar component. The remaining integral in (3) can be transformed into a rapidly converging

series by expanding the denominator around the value  $x^2 + k^2$ , then integrating term by term,

$$\int_0^\infty \frac{xJ_0(x)}{(x^2 + k^2)^{1/2}} \left( \frac{x^2 + k^2}{x^2 + k'^2} \right)^{1/2} dx = \sum_{m=0}^{\infty} (-1)^m \left( \frac{k'}{\varepsilon} \right)^{2m} \int_0^\infty \frac{xJ_0(x) dx}{(x^2 + k^2)^{m+1/2}} \quad (8)$$

This last integral, which is of the Hankel-Nicholson type (Abramowitz and Stegun 1972), is related to the modified Bessel function of the second kind  $K_n$ ,

$$\int_0^\infty \frac{xJ_0(x) dx}{(x^2 + k^2)^{m+1/2}} = \frac{2^{1/2-m}}{\Gamma(m+1/2)} \frac{K_{m-1/2}(k)}{k^{m-1/2}} \quad (9)$$

With these substitutions, the integral in (8) can be written as the absolutely convergent series

$$\left( \frac{2}{\pi} \right)^{1/2} \left( k^{1/2} K_{1/2}(k) - \sum_{m=0}^{\infty} \frac{(-1)^m (\alpha k)^{m+1} m!}{2^m (2m+1)!} k^{1/2} K_{m+1/2}(k) \right), \quad (10)$$

where  $\alpha = (\varepsilon^2 - 1)^{-1} \ll 1$ . The dominant exponential behaviour can be seen from the relation

$$k^{1/2} K_{m+1/2}(k) \sim (\pi/2)^{1/2} \exp(-k). \quad (11)$$

(A more rigorous approach is to calculate upper and lower bounds for (10) by making appropriate replacements for the factorial expressions in order to obtain summable series. In particular, the upper- and lower-bounding series can be shown to be exponentially decaying.) Finally, the screened-Coulomb part of the interaction energy is found from equations (1a), (1b), (3), (8), (10) and (11),

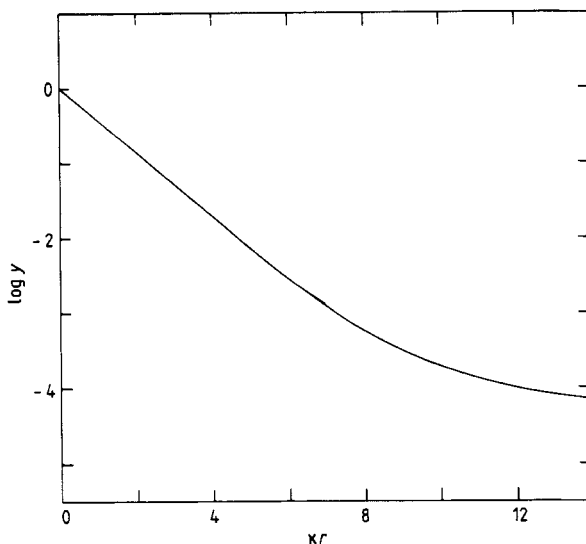
$$U_{\text{coulomb}} \sim 2[(Ze)^2/\varepsilon r] \varepsilon^2 (\varepsilon^2 - 1)^{-1} \exp(-\kappa r). \quad (12)$$

The two distinct contributions to the function  $y(k)$  in (4) and (12) can be seen graphically by integrating (1b) numerically, then plotting the results on log-linear and log-log scales. For calculational purposes, the integral was transformed into a series by splitting up the range of integration between the zeros of  $J_0(x)$  and performing each integral by Simpson's rule. The resulting alternating-sign series was terminated after 20 terms, and the remainder was estimated by Euler's transform (Abramowitz and Stegun 1972) using the last 10 terms. Accuracy was not characterised thoroughly, but by comparing with the large  $\varepsilon$  limit in (2), six-digit accuracy was routinely obtained. The results for  $\varepsilon = 80$  are plotted in figures 2 and 3, showing the exponential and algebraic behaviour, respectively.

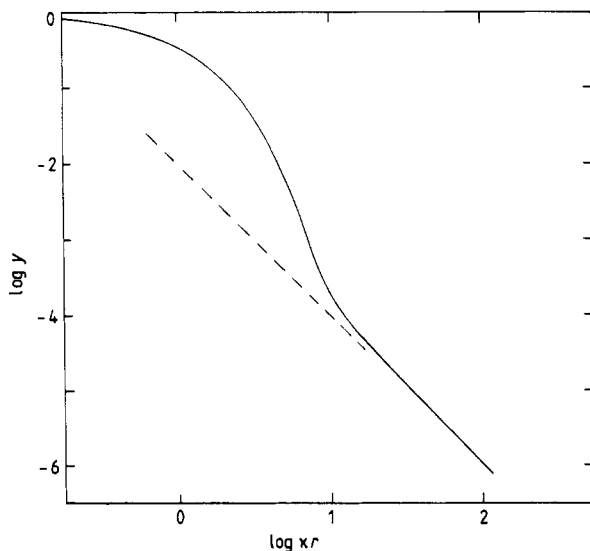
Above  $\kappa r \approx 10$ , the interaction is clearly dominated by the dipole-dipole term, which agrees with the relative magnitudes of the asymptotic forms

$$\frac{U_{\text{coulomb}}}{U_{\text{dipole}}} \sim \varepsilon \kappa^2 r^2 \exp(-\kappa r) |_{\kappa r=10} = 0.363.$$

Pieranski's observations indicate strong interactions occurring at 10  $\mu\text{m}$  separations, and, since  $\kappa^{-1} \approx 0.7 \mu\text{m}$  in distilled water,  $\kappa r$  is of the order of 14, well into the dipole-dipole regime. Moreover, for interfacial particles, even the screened-Coulomb interactions are stronger than for effects mentioned earlier. Whether the two-body potential, or more significantly the potential of mean force, is comparable to  $kT$  at these large separations depends largely on the charge of the floating particles. For



**Figure 2.** Interaction integral  $y(\kappa r)$  on log-linear scales. The exponential behaviour, characteristic of a screened-Coulomb interaction, is evident for small separations. The dielectric constant of the substrate is taken to be that of water,  $\epsilon = 80$ .



**Figure 3.** Interaction integral  $y(\kappa r)$  on log-log scales. Using the same results as in figure 1, the algebraic behaviour from dipole-dipole interactions is revealed for large separations.

$Kr \approx 10$ , the charge must be about  $Z = 5 \times 10^3$  for the dipole-dipole energy to be equal to  $kT$ . Although only a fraction (two thirds, say) of the particle's surface is wetted, this charge is not unreasonable. In the light of these findings, it is not surprising to find quite long-range repulsive interactions in charged interfacial colloidal systems.

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