Capillary Attraction of Colloidal Particles at an Aqueous Interface

Alois Würger*

CPMOH, CNRS-Université Bordeaux 1, 351 cours de la Libération, 33405 Talence, France

Lionel Foret

Department of Physics, Kyoto University, Kyoto 606-8502, Japan

Received: April 25, 2005; In Final Form: June 15, 2005

We study the capillary forces arising from charged colloidal particles trapped at an oil−water interface. Since it is quadratic in the electric field, the electric stress acting on the interface cannot be written as the superposition of one-particle terms. Indeed, we find that the interfacial pressure is dominated by two-particle terms, which induce capillary forces involving one, two, three, or four particles. The dominant interaction is attractive and varies with the inverse cube of the particle distance.

Introduction

Besides their electrostatic repulsion that prevents coagulation,[1] charged colloidal particles at a liquid phase boundary are subject to an effective interaction that is mediated by the deformation of the interface. The formation of colloidal aggregates at an air−water interface suggested that this additional force was attractive;[2,3] its existence has been confirmed for micron size poly(methyl methacrylate) (PMMA) particles on water droplets in oil, by recording particle trajectories trapped at the interfaces of a water-in-oil microemulsion and evaluating their pair correlations.[4] Several attempts to explain this experimental finding in terms of an electric-field-induced capillary interaction remained unsuccessful.[4−8]

Quite generally, capillary phenomena arise from the balance of an external force, $P(\mathbf{r})$, and the interface tension, γ, inducing a deformation, $u(\mathbf{r})$, that is, in linear approximation, determined by the Young−Laplace equation $\gamma \Delta u(\mathbf{r}) + P(\mathbf{r}) = 0$. The total force field of two nearby particles depends on their distance, ρ, and so does the interfacial energy

$$F = -\frac{\gamma}{2}\int dS (\nabla u)^2 \tag{1}$$

The distance dependent part of the deformation free energy, F, constitutes a capillary interaction.

In most cases, the total pressure is a sum of two single-particle terms, $\hat{P}(\mathbf{r}) + \hat{P}(\mathbf{r} + \rho)$, and so is the deformation field, $\hat{u}(\mathbf{r}) + \hat{u}(\mathbf{r} + \rho)$. As a consequence, the capillary interaction reads

$$-\gamma \int dS (\nabla \hat{u}(\mathbf{r}) \cdot \nabla \hat{u}(\mathbf{r} + \rho))$$

A simple example is provided by the aggregation of cereal on a cup of milk, where the gravitational force, mg, on each of the grains deforms the liquid surface. The superposition of the dimples of nearby particles gives rise to an attractive energy, $F = (m^2 g^2 / 2\pi\gamma) \ln \rho$.[9] A similar situation arises from a force acting both on the particle and on the surrounding interface; for example, a polymer grafted on a membrane pulls at the point of attachment but exerts an opposite pressure on an area of the size of one gyration radius.[10] Still, the total force field is the sum of one-particle terms, and the elastic interaction is given as a sum of pair potentials.

In this paper, we show that a fundamentally different situation arises for the electric-field-induced capillary interaction of charged colloidal particles at an interface. Their electrostatic properties are to a large extent determined by the incomplete screening at an electrolyte−insulator boundary that has been studied extensively in the domains of classical Coulomb plasmas and colloid science.[11−14] In a bulk electrolyte of salinity n_0 and dielectric constant ϵ_w, the counterions are confined to a screening cloud of the size of one Debye length, $\kappa^{-1} = \sqrt{\epsilon_w k_B T / 2e^2 n_0}$, and result in an effective Yukawa type electrostatic potential, $\varphi(\mathbf{r}) = (Q/4\pi\epsilon_w r)e^{-\kappa r}$. For a particle trapped at an oil−water interface, a fraction, $\epsilon_{oil}/\epsilon_w$, of the counterions spread along the interface and lead to an effective potential that shows, at lateral distances, r, well beyond the Debye length, a power law dependence[11,12]

$$\varphi(r, z) = \frac{\epsilon_{oil}}{\epsilon_w{}^2} \frac{Q}{2\pi\kappa^2 r^3} e^{-\kappa z}$$

and that decays exponentially in the normal direction. The electrostatic free energy of two trapped particles, $V(r) = Q\varphi(r, 0)$ gives rise to a repulsive force that exceeds the attractive dispersion forces and thus stabilizes two-dimensional colloidal suspensions.[1,13]

Interfacial Pressure and Capillary Interaction

The charged particle is the source of electric-field lines which penetrate in the oil phase and end at the counterions that are spread along the interface. Because of the mismatch of dielectric constants, $\epsilon_{oil} \neq \epsilon_w$, the electric-field energy is discontinuous at the phase boundary and thus exerts a stress on the interface. The total interfacial pressure

$$P = k_B T \delta n + \mathcal{T}_{oil} - \mathcal{T}_w \tag{2}$$

comprises an entropic term due to the excess density, δn, of mobile ions at the aqueous side of the interface and an electrostatic term given by the discontinuity $\mathcal{T}_{oil} - \mathcal{T}_w$ of the

normal component of the Maxwell tensor $\mathscr{T}_{\alpha\beta} = \epsilon(E_\alpha E_\beta - \frac{1}{2}\mathbf{E}^2\delta_{\alpha\beta})$.[14] Contrary to the case of gravity that exerts a net force on the interface, the integral of the charge-induced pressure vanishes, $\int dSP = 0$.[5,6] It turns out that the normal component of the electric field is by a factor of κr larger than the parallel one and thus dominates the electric stress. When retaining the normal component, $E_w = \kappa\varphi$ only, and expanding the ion excess density, δn, to second order in φ, one finds that the entropic pressure cancels the Maxwell tensor at the aqueous side, $k_B T\delta n - \mathscr{T}_w = 0$.

As a consequence, the interfacial pressure is given by the electric stress at the insulating side, $\mathscr{T}_{oil} = (\epsilon_{oil}/2)E_{oil}^2$. The normal component of the electric field is obtained from the boundary condition for the displacement vector $\mathbf{D} = \epsilon\mathbf{E}$. For a single particle at the origin, one has the asymptotic expression

$$E_{oil}(\mathbf{r}) = -\frac{Q}{2\pi\epsilon_w\kappa r^3} \tag{3}$$

that holds at distances beyond the particle size, a, and the Debye length. The electric stress, $\mathscr{T}_{oil}(\mathbf{r})$, induces an interface deformation that is readily integrated, $u \propto r^{-4}$.[6]

In the case of N particles at positions $\mathbf{r}_i$, the electric field, $\sum_i E_i$, is a linear superposition of single-charge fields,

$$E_i = E_{oil}(\mathbf{r} - \mathbf{r}_i)$$

as shown in Figure 1a. The resulting stress

$$\mathscr{T}_{oil}(\mathbf{r}) = \sum_{i,j}\mathscr{T}_{ij}, \quad \mathscr{T}_{ij} = \frac{\epsilon_{oil}}{2}E_iE_j \tag{4}$$

comprises one-particle and two-particle terms. It turns out that the spatial variation and the physical meaning of the diagonal parts, $\mathscr{T}_{ii}$, differ significantly from those of the off-diagonal ones, $\mathscr{T}_{ij}$. Because of the linearity of the Young−Laplace equation, we may put

$$\gamma\Delta u_{ij}(\mathbf{r}) + \mathscr{T}_{ij}(\mathbf{r}) = 0 \tag{5}$$

and relate each stress term to a corresponding deformation field, u_{ij}. The deformation fields, u_{ij}, with $i \neq j$ cannot be attributed to a single particle. Thus, the electric-stress-induced capillary interaction is fundamentally different from the effective pair potentials arising from gravity and other single-particle forces. When inserting $u(\mathbf{r}) = \sum u_{ij}$ in eq 1,

$$F = -\frac{\gamma}{2}\sum_{ijkl}\int dS(\nabla u_{ij}\cdot\nabla u_{kl}) \tag{6}$$

we obtain contributions involving one, two, three, or four particles. Those with at least two different indices depend on the distance of the corresponding particles and induce an effective interaction.

One-Particle Stress and Diagonal Approximation

We discuss the relative magnitude of the diagonal and off-diagonal stress. In terms of the relative coordinate

$$\hat{\mathbf{r}}_i = \mathbf{r} - \mathbf{r}_i$$

the electric field of particle i varies as $E_i \propto 1/\hat{r}_i^3$. As a consequence, $\mathscr{T}_{ij} \propto 1/(\hat{r}_i\hat{r}_j)^3$ (with $i \neq j$) is much smaller than $\mathscr{T}_{ii} \propto 1/\hat{r}_i^6$ close to particle i and much smaller than $\mathscr{T}_{jj}$ close to particle j; note the scaling factor in Figure 1. From this
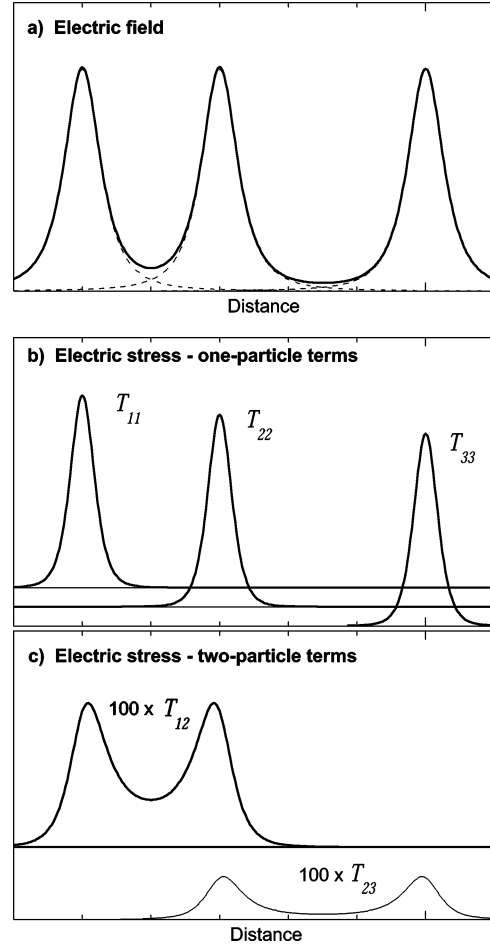
Figure 1. (a) Electric field at the interface. The dashed lines give the single-particle fields, and the solid line gives their superposition for three particles, with a short-range cutoff at $r = 0.1$. (b) The electric stress, $\mathscr{T}_{ii}$, arising from each of the particles $i = 1, 2, 3$. (c) Two-particle contributions to the electric stress. We show $\mathscr{T}_{12}$ and $\mathscr{T}_{23}$ that arise from particles at relative distances of $r_{12}/r_{23} = 2/3$. Note the magnification of the vertical axis by a factor of 100 with respect to the single-particle stress shown above.

observation, it was, more or less explicitly, concluded that the cross-terms were negligible;[5,6] this "diagonal approximation" consists of retaining the single-particle stress, $\sum_i \mathscr{T}_{ii}$, and deformation field, $\sum_i u_{ii}$, only. The capillary energy

$$F_D = -\frac{\gamma}{2}\sum_{ik}\int dS(\nabla u_{ii}\cdot\nabla u_{kk})$$

contains an induced interaction of particles i and k at distance ρ_{ik}. The unphysical divergence at $r = 0$ is regularized in terms of a cutoff radius, a; performing the surface integral, one finds the pair potential

$$f_D(\rho) = \frac{1}{2^7\pi\gamma}\left(\frac{\epsilon_{oil}}{\epsilon_w^2}\frac{Q^2}{2\pi\kappa^2}\right)^2\frac{1}{a^2\rho^6}$$

which is repulsive.[6] Note the explicit dependence on a; for typical colloidal particles, the cutoff radius takes a value close to the particle size.

Two-Particle Stress

Now we go beyond the diagonal approximation and consider two-particle deformation fields, u_{ij}. The cross-terms of the stress, $\mathscr{T}_{ij}$, are particular insofar as they are large at *both* positions $\mathbf{r}_i$

Capillary Attraction of Colloidal Particles

J. Phys. Chem. B, Vol. 109, No. 34, 2005 **16437**

and $\mathbf{r}_j$. This two-peak structure shown in Figure 1 turns out to be crucial for the capillary forces. Equation 5 cannot be integrated as it stands. However, since the surface integral in F is dominated by a small area close to each particle, we may use an approximate expression for ∇u_{ij} that is valid at short distances. Close to particle i, we have $\hat{r}_i \ll \hat{r}_j$, and $\hat{r}_j$ may be replaced by the distance ρ_{ij}; in the vicinity of particle j, we have $\hat{r}_i \gg \hat{r}_j$, and $\hat{r}_i \approx \rho_{ij}$. Then, eq 5 is readily integrated

$$u_{ij} = \frac{\epsilon_{oil}Q^2}{8\pi^2\gamma\epsilon_w{}^2\kappa^2\rho_{ij}{}^3}\left(\frac{1}{\hat{r}_i} + \frac{1}{\hat{r}_j} + \mathcal{O}(1/\rho_{ij})\right)$$

Close to each particle, the deformation field, u_{ij}, varies as the inverse distance, and the gradient reads $\nabla u_{ij} = \hat{r}_i/(\hat{r}_i\rho_{ij})^3 + \hat{r}_j/(\hat{r}_j\rho_{ij})^3$; corrections are given in powers of $\hat{r}_i/\rho_{ij}$. The surface integral in $\int dS(\nabla u_{ij}\cdot\nabla u_{kl})$ is dominated by the area close to the particles. The unphysical singularities occurring for $\hat{r}_i \to 0$ disappear when cutting the integrals at the particle size, a.

First, consider terms such as $-\gamma \int dS\nabla u_{ij}\cdot\nabla u_{ij}$. They give an attractive contribution that has the same form as the diagonal approximation f_D but is by a factor of 32 larger. Although attractive, the resulting interaction is of little interest, since f_D is small in any case.

It turns out that the dominant contributions to the capillary energy, F, stem from the superposition of one-particle and two-particle deformations such as u_{ii} and u_{ij}. Permuting labels and collecting identical terms, we find the effective two-particle interaction

$$f(\rho_{ij}) = -4\gamma \int dS(\nabla u_{ii}\cdot\nabla u_{ij}) \tag{7}$$

When introducing the particle size, a, as a cutoff and neglecting small corrections of the order a/ρ, the surface integral is readily evaluated

$$f(\rho) = -\frac{1}{2^7\pi\gamma}\left(\frac{\epsilon_{oil}}{\epsilon_w{}^2}\frac{Q^2}{2\pi\kappa^2}\right)^2\frac{1}{a^5\rho^3} \tag{8}$$

and gives an attractive interaction that varies with the inverse cube of the distance. It is by a factor of $2(\rho/a)^3$ larger than the result of the diagonal approximation $f_D(\rho)$.

Finally, we consider interactions involving three or four particles, that is, with three or four different indices in eq 6. These terms are only relevant at a sufficiently high density of colloidal particles and depend on the relevant orientation of the particles. One finds that they vary as a^{-2} with the partcile size and thus are of the same order of magnitude as the diagonal term f_D. We may conclude that interactions of three and four particles are small as compared to $f(\rho)$.

Discussion

The resulting two-particle interaction $f(\rho)$ varies with distance as ρ^{-3}, like the repulsive electrostatic potential $V(\rho) = Q\varphi(\rho)$. In terms of their ratio $\xi = f(\rho)/V(\rho)$, a net attraction arises if $\xi > 1$. We briefly discuss the observed attractive force of PMMA particles on water droplets dispersed in oil.[4] Inserting the values $\epsilon_{oil}/\epsilon_w \sim 1/30$, $\gamma \sim 40$ mJ/m^2, $\kappa^{-1} \sim 0.3$ μm, and $a = 0.75$ μm, we obtain the order of magnitude $\xi \sim 10^{-14}Z^2$; thus, the capillary attraction exceeds the electrostatic repulsion for $Z > 10^7$.

The formal surface charge density of these particles is of the order of 1/nm^2 and thus would allow such a large value for the valency. For bulk colloids, it is well-known that the long-range properties are described by an effective charge, $Z^* = 4(1 + \kappa a)a/l_B$,[15] which is, for micron sized particles and the Bjerrum

length in water, $l_B = e^2/(4\pi\epsilon_w kT)$, by more than 2 orders of magnitude smaller than the bare value, Z. This small effective valency, Z^*, of bulk colloids is related to the formation of a layer of condensed counterions; its thickness is given by the Gouy−Chapman length which is of the order of nanometers. However, this picture does not apply to the present situation of a strongly charged macroion at an oil−water interface; one expects that the condensed layer partly covers the interface close to the particle, that is, that the number of the counterions spread along the oil−water phase boundary significantly exceeds that obtained from the Debye−Hückel theory with the effective valency, Z^*. These remarks suggest that neither the bare charge, Z, nor the bulk effective value, Z^*, can be safely used in the above expression for the pair potential. We conclude that, at present, it is difficult to assess whether the charge-induced capillary attraction of colloidal particles exceeds their direct electrostatic repulsion.

The asymptotic power law $E_{oil} \propto r^{-3}$ for the electric field (eq 3) holds at distances beyond the particle size and the Debye length; at shorter distances, one finds a weaker variation, $E_{oil} \propto r^{-2}$. Following previous workers, we restrict the surface integrals to the range of validity of eq 3 by introducing a cutoff radius, a. For the experiments mentioned above, the particle diameter is about 1 μm, and the Debye length $\kappa^{-1} \sim 200$ nm, leading to a cutoff, a, of the order of 1 μm. Thus, eq 3 and the corresponding relations for the electric stress may be used for particles at distances significantly larger than a; in particular, our results apply to the case encountered in ref 4 where the distance of nearest neighbors is 6 μm. We stress that taking into account the modified electric stress close to the particles would not affect the power law behavior of the pair interaction but would slightly change its numerical prefactor.

Finally, we justify the linear treatment of capillarity, which corresponds to a small-gradient approximation for the deformation field and thus requires $|\nabla u| \ll 1$. Putting $|\nabla u| = 1$, we find that eq 5 ceases to be valid at distances shorter than $r_c = (\xi/5)^{1/5}a$. Since this value is close to the particle radius, the linearized theory is expected to give correct results. However, one should note that the an overall attractive potential, $f(\rho) + V(\rho)$, requires $\xi > 1$; in this case, treating capillarity at a linear level breaks down close to the particle, where $|\nabla u|$ approaches unity. This possibly indicates that the charge-induced attraction cannot exceed the direct electrostatic repulsion.

Summary

We briefly summarize the results of our study of the capillary properties of charged colloidal particles at an aqueous interface.

(i) The linear superposition of the electric field gives rise to an electric stress on the interface that comprises single-particle and two-particle terms. Thus, the interfacial pressure cannot be written as a sum of single-particle forces. In this respect, the charge-induced capillary phenomena are fundamentally different from those arising from gravity.

(ii) It turns out that the two-particle stress is essential for the capillary attraction on a flat interface. Previous work based on the one-particle pressure thus missed the dominant contribution to the pair interaction.

(iii) Since little is known about the counterion distribution close to strongly charged interfacial colloids, it is not clear whether one should use the bare valency, Z, the bulk effective value, Z^*, or some intermediate expression. Thus, we cannot, at present, conclude whether the capillary attraction obtained in this paper exceeds the electrostatic repulsion and whether it is relevant for the experiment reported in ref 4.

References and Notes

(1) Pieranski, P. *Phys. Rev Lett.* **1980**, *45*, 569.

(2) Ghezzi, E.; Earnshaw, J. C. *J. Phys.: Condens. Matter* **1997**, *9*, L517.

(3) RuizGarcia, J.; Gamez Corrales, R.; Ivlev, B. I. *Phys. Rev. E* **1998**, *58*, 660.

(4) Nikolaides, M. G.; Bausch, A. R.; Hsu, M. F.; Dinsmore, A. D.; Brenner, M. P.; Gay, C.; Weitz, D. A. *Nature* **2002**, *420*, 299.

(5) Megens, M.; Aizenberg, J. *Nature* **2003**, *424*, 1014.

(6) Foret, L.; Würger, A. *Phys. Rev. Lett.* **2004**, *92*, 058302.

(7) Danov, K. D.; Kralchevsky, K. D.; Boneva, M. P. *Langmuir* **2004**, *20*, 6139.

(8) Oettel, M.; Dominguez, A.; Dietrich, S. *Phys. Rev. E* **2005**, *71*, 051401.

(9) Kralchevsky, P. A.; Nagayama, K. *Adv. Colloid Interface Sci.* **2000**, *85*, 145.

(10) Bickel, T.; et al. *Phys. Rev. E* **2000**, *62*, 1124.

(11) Jancovici, B. *J. Stat. Phys.* **1982**, *28*, 42.

(12) Hurd, A. J. *J. Phys. A* **1985**, *18*, 1055.

(13) Aveyard, R.; et al. *Phys. Rev. Lett.* **2002**, *88*, 246102.

(14) Russel, B. W.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: 1989.

(15) Trizac, E.; Bocquet, L.; Aubouy, M. *Phys. Rev. Lett.* **2002**, *89*, 248301.

(16) Oettel, M.; Dominguez, A.; Dietrich, S. Preprint 2005.