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Effective interaction of a charged colloidal particle with an air–water interface

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Abstract

Within the framework of linear and non-linear Poisson–Boltzmann theory, we study the effective interaction of a single charged colloidal sphere in an aqueous electrolytic solution with an air–water interface. The effects of varying the salt concentration and the colloidal surface charge density on the effective interaction are being investigated, with a view to understanding some physical phenomena, which include electrostatic adsorption and trapping at the air–water interface. Results show an electrostatic double-layer barrier to the colloid's approach to the interface which can be lowered considerably by increasing the salt concentration. For enough added salt, the charged colloid should be able to suddenly pop up at the air–water surface, an effect which has actually been observed in recent experiments. We discuss the relevance of our results to other experimental observations, and emphasize the close analogy between the problem considered here and the classical problem of the interaction of two colloids in a bulk suspension.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Charged colloidal particles can be trapped at the interface between two fluids. Experimental studies of such two-dimensional (2D) colloidal systems are very instructive as they afford the possibility of investigating in two dimensions such interesting problems as crystallization, aggregation, and melting. Pieranski [1] was the first to report a direct microscopic observation of 2D colloidal crystals trapped at the air–water interface, for polystyrene spheres. Kesavamoorthy *et al* [2], also working with polystyrene spheres at the air–water interface, reported the observation of a sudden collapse of the 2D crystal into a compact structure. The instability of the crystalline phase was attributed to enhanced attractive interparticle interaction at the interface. Stamou *et al* [3], offering a theoretical explanation, have proposed a mechanism for attractive interaction between colloids trapped at an air–water interface, which is based on non-uniform wetting causing an irregular shape of the particle meniscus. There are other important works on 2D crystallization and melting [4] of charged colloids at the air–water

interface, including that by Terao and Nakayama [5] who made computer simulations and found two-stage melting of colloidal crystal and the existence of a hexatic phase at certain conditions. There are a good number of papers dealing with aggregation and clustering of colloidal spheres at the air–water interface [6–10] with a view to understanding their structures, growth, and dynamics. We also mention novel experimental studies [11] on 2D systems of superparamagnetic colloids at the air–water interface which have shed new light on quite a few rather fundamental properties of 2D systems.

The study of colloids at the air–water interface is useful also with respect to some biologically oriented questions, revealing some aspects of the crystallization of proteins, which in a first primitive approach can be regarded as charged colloids. Protein structure determination by classical x-ray crystallography requires three-dimensional crystals that are difficult to obtain for most proteins [12]. An alternative has been to grow 2D crystals by adsorbing proteins at the air–water interface for synchrotron radiation diffraction analysis [13]. Adsorption of proteins generally at fluid–fluid interfaces and their behaviour in the adsorbed state also play an important role in the formulation and stabilization of different foam-based and emulsion-based products in the food and drug industries [14–16].

Most of the above-cited studies deal mainly with the various interparticle interactions between particles located *already at the interface*, which lead to the observed structures (crystals, aggregates, etc) and behaviour (e.g. denaturing of proteins). But very few reliable studies have been reported on particle–interface interaction leading to adsorption and trapping. The present study is focusing on just these particle–interface interactions, and here, in particular, on the electrostatic effective interaction between charged colloidal particles with an air–water interface.

Hurd [17], who investigated the effective pair interaction potential of trapped charged colloids, has defined interfacial colloids as consisting of particles dispersed on an interface between two fluid media and held there by surface tension. This definition follows perhaps from the work of Pieranski [1], who calculated the surface energy (capillary) well in which a charged polystyrene latex sphere can be trapped and showed that it dominates, by many orders of magnitude, any thermal or gravitational fluctuations present. The influence of electrostatic forces for a charged latex particle, however, was totally ignored in Pieranski's analysis as regards the trapping.

We will show in the present work that since the electrostatic contribution to keeping a colloid at the interface is very small compared to the surface energy trap, this neglect is easily justifiable if one is interested only in the behaviour of particles already trapped. Electrostatics is, however—and this is essential in our context—the key to understanding the particle–interface interaction, i.e., those quantities that govern the physical processes of colloidal particles which are approaching the air–water interface, but which are not yet trapped. The question that originally suggested this study was: if it is energetically advantageous for a charged colloid to be at the air–water interface, what prevents all other colloids of the suspension popping up to the surface?

The answer to this question is simple: any charged object approaching a neutral interface between two media of different dielectric constants experiences repulsive image-charge forces if it approaches it from the medium with the higher dielectric constant [18, 19]. This applies also to the highly charged colloids in an aqueous electrolyte solution approaching an air–water interface (dielectric constant ratio: 1:80). The existence of further charges, the microions of the electrolyte solution, can change this picture only quantitatively, and not qualitatively [20, 21]. They introduce screening, and thus just reduce the image-charge repulsion, leading to a salt-dependent repulsive energy barrier which prevents the bulk colloids approaching the interface from appearing at the interface. This electrostatic energy barrier is the focus of this work.

We calculate its height and salt dependence within the framework of Poisson–Boltzmann (PB) theory (linear and non-linear).

Simple as our explanation of a repulsive energy barrier might first appear, the situation in the literature on this point is most confusing. This confusion can be traced back to the paper of Stillinger [22] who calculated the electrostatic potential of a colloidal point charge at an interface between an electrolyte and a neutral substrate of different dielectric constant. He then considered the limiting case in which the point macroion is adsorbed directly on the substrate, and calculated the work done in bringing the point charge from infinity (the bulk solution) to this position. This work turned out to be negative, and Stillinger concluded that adsorption of the ion at the substrate is energetically favoured. The result is correct, the conclusion however not. Indeed, a point charge directly at the interface has a negative electrostatic (trapping) energy, but on its way to this energetically favourable position it has to overcome an infinitely large energy barrier which for a colloid of finite size reduces to the finite barrier that we have just discussed; it therefore cannot adsorb. Earnshaw [23] must have misapplied Stillinger's potential in attempting to describe a mechanism of trapping from an electrostatic viewpoint, pointing out that the electrostatic trap can compete with or even exceed the surface energy trap for highly charged latex particles. Earnshaw's result seems to suggest an electrostatic double-layer force driving the macrosphere from the bulk of the electrolyte solution to the interface. This result is incorrect: Stillinger's potential, correctly applied [21], leads to the same screened image-charge repulsion, already analysed not only in other recent studies [20], but already in some of the earliest investigations on this field [24, 25].

2. Exposition of the problem

2.1. The effective interaction in non-linear Poisson–Boltzmann theory

We consider a charged spherical particle which could be colloidal or macromolecular in dimension, in the vicinity of a planar boundary between an aqueous electrolytic solution of dielectric constant ϵ and a bounding medium, specifically air, of dielectric constant ϵ' . For air, $\epsilon' = 1$ is so low compared to that for water, $\epsilon = 80$, that we can approximate the ratio ϵ'/ϵ as zero. It can be shown [24, 25] that the relative error in calculated quantities (e.g. the interaction potential) due to this approximation is of the order of $2/(\epsilon + 1)$. We shall hereafter refer to the boundary between air and the aqueous solution as the air–water interface or just the interface. The electrolyte is assumed to be unbounded, i.e., there is a reservoir of salt ions coupled to the system, so the number of ions is not fixed. The fixed thermodynamics variables are: the temperature T , the chemical potential μ_s for a given monovalent salt-ion concentration c_s ($\beta\mu_s = \log c_s \Lambda^3$, with $\beta = k_B T$, k_B being the Boltzmann constant and Λ^3 the thermal wavelength), and the volume of the electrolyte region V . Our system is then in the grand canonical ensemble with the grand potential, Ω , being the relevant thermodynamic function.

The grand potential of the system is determined for a given particle–interface distance h by using the solution of the mean-field PB equation for the electrostatic potential ψ . The PB equation can be written as

$$\nabla^2 \phi = \kappa^2 \sinh \phi \quad (1)$$

where $\phi = e\beta\psi$ (e being the elementary charge) is the normalized potential. $\kappa^2 = 8\pi\lambda_B c_s$ is the screening parameter related to the salt-ion concentration and $\lambda_B = e^2\beta/\epsilon$ is the Bjerrum length. The colloidal particle of radius a is assumed to bear a fixed surface charge density, $-e\sigma$; when totally immersed in water ($h \geq a$) it bears $Z (=4\pi a^2\sigma)$ fixed negative homogeneously distributed charges, while the confining air–water interface bears no surface charges.

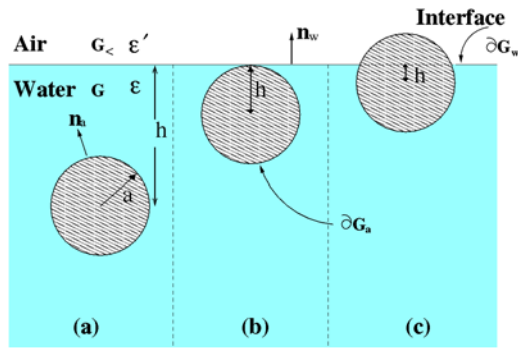


Figure 1. Our system: a colloidal sphere of uniform surface charge density $-e\sigma$ and radius a inside an electrolyte (water) of dielectric constant ϵ , and a distance h from an interface formed by air of dielectric constant ϵ' . (a) The colloid is completely immersed in the electrolyte ($h > a$), (b) the colloid just touches the interface ($h = a$), and (c) the colloid emerges at the interface ($h < a$).

There is the controversial claim that the air–water interface can be associated with some electrostatic surface potential. This is supposedly due to the preferred orientation of interfacial water molecules. It has been reported that as a result of this orientation, a thin electrical double layer at the interface is established with the outermost portion (facing the gas phase) of the double layer being negative and the innermost part (facing the liquid phase) being positive [26–28]. Sengupta and Damodaran [14] calculated and gave the value of the inner potential as about 184.7 mV which lies between previous experimentally measured values (100–200) mV [28]. On the other hand, works involving air bubbles in water report that the bubble–water surface potential (facing the liquid phase) is negative and of value -25 ± 10 mV [29]. Ducker *et al* [30], lamenting the uncertainty in the exact magnitude of the potential (air–water interface), assumed values from zero to -25 mV. Even if we assume an air–water interface of oppositely charged layers, the electric flux through any surface enclosing such layers is zero and hence it is more accurate to assume that the interface is neutralized and bears no net surface charges, as we have in this work. It is also noteworthy that Wagner [24] and Onsager and Samaras [25] also treated the air–water interface as being neutral.

We denote the boundary given by the Cartesian $z = 0$ interface by ∂G_w , the surface of the particle by ∂G_a , the region of the electrolytic solution by G (with the volume of the colloid excluded!), and the negative $z < 0$ half-space by $G_<$; see figure 1.

The fixed charges on the colloidal sphere, in contrast to the mobile salt ions, enter the problem through the boundary conditions in the PB boundary value problem (BVP). We employ the constant-charge boundary condition requiring that at ∂G_a the normal component of the electric field be proportional to the particle surface charge density σ . We also assume a vanishing dielectric constant for both air and the particle so that $\epsilon'/\epsilon \approx 0$ and so that the potential vanishes at infinity. Since the dielectric constants of the particle and air are taken to be zero, we do not have to solve for the potentials inside these regions. The BVP can then be summarized as follows:

$$\begin{aligned}
 \nabla^2 \phi &= \kappa^2 \sinh \phi & r \in G \\
 \mathbf{n}_a \cdot \nabla \phi &= 4\pi \lambda_B \sigma & r \in \partial G_a \\
 \mathbf{n}_w \cdot \nabla \phi &= 0 & r \in \partial G_w \\
 \phi &= 0 & r \rightarrow \infty
 \end{aligned} \tag{2}$$

where \mathbf{n}_a and \mathbf{n}_w are the outward unit normal vectors on the particle surface and the interface respectively; see figure 1. The boundary conditions in equation (2) have been considerably simplified by the assumption of vanishing dielectric constants for air and the colloid, and the treatment of the air–water interface as uncharged. For example, at the boundary, ∂G_w , the boundary condition should read $\epsilon \mathbf{n}_w \cdot \nabla \phi|_{z=0+} - \epsilon' \mathbf{n}_w \cdot \nabla \phi|_{z=0-} = 4\pi \epsilon \lambda_B \sigma_w$, where $\sigma_w = 0$ is the charge density at the interface.

The BVP is solved for three stages of the particle position relative to the air–water interface in different coordinate systems suitable for the geometry of the problem:

- (a) Particle in solution and close to the interface ($h > a$): bispherical coordinates (figure 1(a)).
- (b) Particle in solution but just touching the interface ($h = a$): tangent-sphere coordinates (figure 1(b)).
- (c) Particle partly in solution and partly in air ($0 < h < a$): toroidal coordinates (figure 1(c)).

The bispherical coordinate system has been used repeatedly for describing effective interaction between two charged spheres in solution [31–33], and recently by us [21] for calculating the interaction between a charged sphere and a charged/uncharged planar interface. A full description can be found in the latter reference. The toroidal and tangent-sphere coordinates procedures are new here and are detailed in the appendix. The advantage of choosing different coordinate systems is mainly a technical one: in this way the complex shape boundaries of the system are transformed, for all three situations in figure 1, into 2D rectangular form; this then simplifies the numerical procedure for solving the BVP enormously.

Once ϕ is known, we proceed to calculate the grand potential, Ω_h , of the system which can be written in its final form [21]:

$$\beta \Omega_h = -\frac{\sigma}{2} \int_{\partial G_a} dS \phi_h + c_s \int_G dV (\phi_h \sinh \phi_h - 2 \cosh \phi_h + 2). \quad (3)$$

The first term gives the electrostatic energy due to the fixed colloidal charges on ∂G_a , while the second term incorporates the entropic and electrostatic contributions of the mobile ions in G . The subscript h is intended to emphasize the parametric h -distance dependence of ϕ and then Ω . Equation (3) can alternatively be written as

$$\beta \Omega_h = \frac{1}{8\pi \lambda_B} \int_G dV [(\nabla \phi)^2 + 2\kappa^2 (\phi_h \sinh \phi_h - (\cosh \phi_h - 1))], \quad (4)$$

in the region G . The effective particle–interface interaction $\beta V(h)$ can now be defined as the total change in the grand potential when the particle is brought to a finite distance h (near the interface) from infinity (in the electrolyte far from the interface):

$$V(h) = \Omega_h - \Omega_\infty. \quad (5)$$

Ω_∞ is determined by solving the PB problem for an isolated particle in the bulk of the electrolytic solution in the spherical coordinate system. It can also be obtained from solution in bispherical coordinates by taking a sufficiently large particle–interface separation ($h \rightarrow \infty$).

It is important to emphasize that equation (5) accounts only for the energy stored in the double layer. As long as $h \geq a$, this is indeed equal to the total energy of interaction between the colloid and the interface. However, when the colloidal particle breaks through the air–water interface, i.e. if $h < a$, additional contributions to the interaction energy must be included. The most important of these additional energy terms—we denote it by E_s —is due to capillary forces and is estimated further below. Other terms arise due to the fact that a part of the colloidal surface is exposed to air when $h < a$. Estimating these terms requires knowledge of some subtle details about the dewetted colloid surface. We can only speculate about the precise state of charge of the dewetted surface. Two cases mark the extremes: the dewetted part remains

fully charged; or it completely discharges by binding some ions either from the air or from water. Let us first consider the former case. The charges on the dewetted parts of the colloidal particles are then transferred from a region of high dielectric constant to one of low dielectric constant. There is an energy penalty known as Born repulsion for transferring charges from a high- to a low-dielectric-constant region [34]. The repulsion would in fact be high enough to make it virtually impossible for any colloid to break through the interface. This, however, would contradict all the experimental observations reporting stable 2D colloidal suspensions trapped at the air–water interface [1, 2, 35].

The alternative, namely a discharging of the dewetted surface, costs energy as well. A colloidal particle put in the bulk of an aqueous solution would become spontaneously charged: its solvation energy U_{sol} is negative. If $p_{dewet}(h)$ is the fraction of the colloidal surface that is dewetted, then $-U_{sol}p_{dewet}(h)$ could, in principle, be used to estimate the energy cost of discharging the particle. Being however a quantity that depends heavily on the microscopic details of the solvation process, U_{sol} would vary from colloid to colloid. Since we here wish to keep our considerations as general as possible, we assume in the following the case of full discharging of the dewetted surface, but completely ignore the energy contribution due to this discharging and concentrate instead on the only safe piece of information, that is, the energy change that goes along with the changes of the double layer near the wetted surface as the particle goes through the interface. We will find that this energy is at least an order of magnitude smaller than the surface capillary energy E_s . We finally note that full discharging of the dewetted part of the colloid implies that ∂G_a for $h < a$ in equations (2) and (3) refers to only that part of the colloidal surface that is exposed to water.

2.2. The effective interaction in the limit of zero salt concentration

The PB-BVP, equation (2) and hence equation (3) can be solved numerically for various values of κ . An exception is the case $\kappa = 0$ (no salt ions) when convergence problems occurred in our numerical scheme. Though highly unphysical, the case $\kappa = 0$ is still not uninteresting to us—not only as a limiting case, but also as an introduction to the following section.

The effective potential in the salt-free limit, $V^0(h)$, consists only of the self-energy of the particle's fixed charges in their own Coulomb potential:

$$V^0(h) = \Omega_h^{self} - \Omega_\infty^{self} \quad (6)$$

with the self-energy

$$\beta\Omega_h^{self} = -\frac{1}{2} \int_{\partial G_a} dS \sigma(\mathbf{r}) \phi_h^0(\mathbf{r}) \quad (7)$$

where ϕ_h^0 is the potential due to the colloidal surface charges. When $h \rightarrow \infty$, the potential has perfect spherical symmetry and, for a colloid with a constant surface charge density $-\sigma e = -Ze/4\pi a^2$, one obtains $\phi^0(a) = -Z\lambda_B/a$ and thus

$$\beta\Omega_\infty^{self} = \frac{Z^2\lambda_B}{2a}, \quad h \rightarrow \infty. \quad (8)$$

If the colloid is at a finite distance from the interface ($h \geq a$), the potential is no longer spherically symmetric since there is a jump in the dielectric constants at $z = 0$, requiring that $\nabla\phi = 0$ at $z = 0$ when $\epsilon'/\epsilon \rightarrow 0$. This boundary condition can conveniently be satisfied using the method of image charges. If $\epsilon'/\epsilon \rightarrow 0$ and if we approximate the colloid by a point charge, the colloidal image charge is of the same sign and magnitude as the colloidal charge, and located at $z = -h$. One then obtains

$$\beta\Omega_h^{self} = \frac{Z^2\lambda_B}{4h} + \beta\Omega_\infty^{self}. \quad (9)$$

The next stage is reached when the colloidal particle breaks through the air–water interface ($h < a$). We assume that the total charge on the particle falls as the surface is dewetted. Assuming uniform wetting or dewetting without meniscus, the now h -dependent total charge Z can be expressed as

$$Z_h = \frac{Z}{2}(1 + h/a), \quad |h| \leq a. \quad (10)$$

Ignoring for the moment the constraint $\nabla\phi = 0$ at $z = 0$, the electrostatic potential of this partially charged sphere reads

$$\begin{aligned} \phi_h^0(r, \theta, \varphi) &= -\frac{Z\lambda_B}{4\pi} \int_{\theta'_h}^{\pi} d\theta' \sin\theta' \int_0^{2\pi} \frac{d\varphi'}{\sqrt{\mathcal{R}}} \\ \mathcal{R} &= r^2 + a^2 - 2ar \cos\theta \cos\theta' - 2ra \sin\theta \sin\theta' \cos\varphi', \end{aligned} \quad (11)$$

where θ'_h is the contact angle of the colloid with the air–water interface. Interestingly, numerical integration of equation (7) with (11) substituted shows that the self-energy (for $h < a$) can reasonably be approximated as

$$\beta\Omega_h^{self} = \frac{Z_h^2\lambda_B}{2} \left(\frac{1}{2h'} + \frac{1}{a} \right), \quad (12)$$

where the total remaining charge Z_h , equation (10), is now assumed to be located at the centre of the wetted volume, h' from the interface. Collecting all pieces, we thus arrive at the following approximate effective potential:

$$\beta V^0(h) = \begin{cases} \frac{Z^2\lambda_B}{4h} & h \geq a \\ \frac{Z_h^2\lambda_B}{2a} \left(1 + \frac{a}{2h'} - \frac{Z^2}{Z_h^2} \right) & |h| < a \end{cases} \quad (13)$$

which our numerically calculated potentials should approach in the limit $\kappa \rightarrow 0$.

2.3. The effective interaction in linear Poisson–Boltzmann theory

The BVP, equation (2), can be solved only numerically due to the non-linearity of the PB equation. Analytical results may however be possible on linearization with further approximations, when the potential ϕ is everywhere less than one.

In [21], we have described how to obtain the effective particle–interface interaction from Stillinger’s [22] potential derived for a point charge in an electrolytic solution (ϵ) near a neutral dielectric substrate (ϵ') using the linearized PB equation ($\nabla^2\phi = \kappa^2\phi$). If $\epsilon'/\epsilon \rightarrow 0$, the following Yukawa-like interaction potential is found:

$$\beta V_{st}(h) = \frac{Z^{*2}\lambda_B}{4h} e^{-2\kappa h} \quad (14)$$

for $h \geq a$, where $Z^* = Ze^{\kappa a}/(1 + \kappa a)$ is the renormalized charge taking care of the finite size of the colloidal particle. This effective potential can be understood as the repulsive interaction of a point charge Z^* with its own *screened* image charge. For $h \rightarrow 0$, this potential diverges, resulting in an energy barrier of infinite height which prevents a point-like particle from adsorbing onto the air–water interface. It is immediately seen that equation (14) is consistent with (13), as the $\kappa = 0$ limit of (14) gives just the bare image-charge interaction $Z^2\lambda_B/4h$. The parameter regimes of validity of equation (14) have been tested extensively against the full PB result in [21] for $h > a$. There is no attempt here to extend the screened interaction as in (14) to the region $h < a$.

3. Results and discussion

3.1. The electrostatic energy barrier

We have solved the PB BVP in equation (2) numerically for a charged colloidal particle near and at an air–aqueous electrolyte interface, at finite salt-ion concentrations characterized by the Debye screening constant κ . The solution enabled us to determine the grand potential, equation (4), and the effective interaction, equation (5), between the charged particle and the air–water interface. Other relevant parameters that have gone into the problem are: the equilibrium temperature of the system characterized by the Bjerrum length λ_B , the colloid or particle radius a , the particle surface ion density σ , and the particle–interface distance h . We have then five input parameters; κ , λ_B , a , σ , and h that govern the interaction potential. By scaling all lengths by a and by furthermore scaling the interaction potential as $\tilde{\lambda}_B \beta \Omega$ (see equation (4)), we can reduce these parameters to just three independent input parameters: $\tilde{\kappa}$, \tilde{h} , and $\tilde{\sigma}$, where $\tilde{\lambda}_B = \lambda_B/a$, $\tilde{\kappa} = \kappa a$, $\tilde{h} = h/a$, and $\tilde{\sigma} = a\sigma\lambda_B$. The scaled form of the surface density is suggested by the first boundary condition in equation (2).

The reduced inverse screening length, $\tilde{\kappa}$, is varied from 0 to 3. The particle comes from the bulk solution where $\tilde{h} \gg 1$ to the surface, $\tilde{h} < 1$. $\tilde{\sigma}$ is varied from about 0.02 to 0.15 when we encountered severe convergence problems due to the enormous effect of the non-linearity in the PB equation. A sphere of radius $1 \mu\text{m}$ carrying $Z = 1000$ elementary charges corresponds to $\tilde{\sigma} \approx 0.057$ at room temperature. Because the fixed charges are assumed to be homogeneously distributed on the colloid, σ is constant and independent of h , but Z can vary with h when the particle pops out of water; see equation (10). The choice and range of these parameters will enable us to explore the linear and to some extent non-linear regimes of the potential ϕ_h .

Figure 2 shows the plot of the scaled grand potential $\tilde{\lambda}_B \beta \Omega(\tilde{h})$ as a function of the reduced particle–interface separation, \tilde{h} for various values of the reduced screening constant $\tilde{\kappa} = 0, 0.5, 1.0, \text{ and } 2.0$ at fixed $\tilde{\sigma} = 0.08$. The $\tilde{\kappa} = 0$ curve is obtained from limiting potentials, equations (9) and (12). All curves show a repulsive particle–interface interaction at $\tilde{h} > 1$ and a well-resolved peak at $\tilde{h} = 1$. For $\tilde{h} < 1$, the particle begins to dewet. The fraction of the colloidal surface exposed to water decreases and accordingly the double-layer energy goes down, resulting in an obvious minimum, $\beta \Omega(h \leq -a) = 0$, when the particle is completely discharged. This minimum is not shown in the plots. We reiterate that figure 2 shows just the double-layer interaction energy and that for $\tilde{h} < 1$ the energy contributions due to the discharging and the capillary forces have not yet been added. The figure reveals an electrostatic barrier to adsorption of the charged colloid to the interface from the bulk electrolyte. This barrier is lowered on increasing the salt content of the solution. Let us define the adsorption barrier height as

$$\tilde{\lambda}_B \beta V_{ad} = \tilde{\lambda}_B \beta [\Omega(\tilde{h} = 1) - \Omega(\infty)]. \quad (15)$$

There is also a double-layer barrier to pushing the particle from the interface to the bulk solution:

$$\tilde{\lambda}_B \beta V_{de} = \tilde{\lambda}_B \beta [\Omega(\tilde{h} = 1) - \Omega(-\infty)], \quad (16)$$

($\Omega(-\infty) = 0$) which for convenience we call the double-layer desorption barrier. Figure 3 shows the variation of these quantities with $\tilde{\kappa}$, for $\tilde{\sigma} = 0.05, 0.08, \text{ and } 0.10$. Both barrier heights decrease with increasing $\tilde{\kappa}$, i.e. increasing salt concentration. Note that both graphs, figures 3(a) and (b), are plotted to the same scale, showing that for a given $\tilde{\sigma}$, the desorption barrier is far higher than the adsorption barrier.

We now turn to the other forces that the colloid experiences at the interface. Most important are the forces resulting from the surface tension which lead to a trap for the colloidal particles at

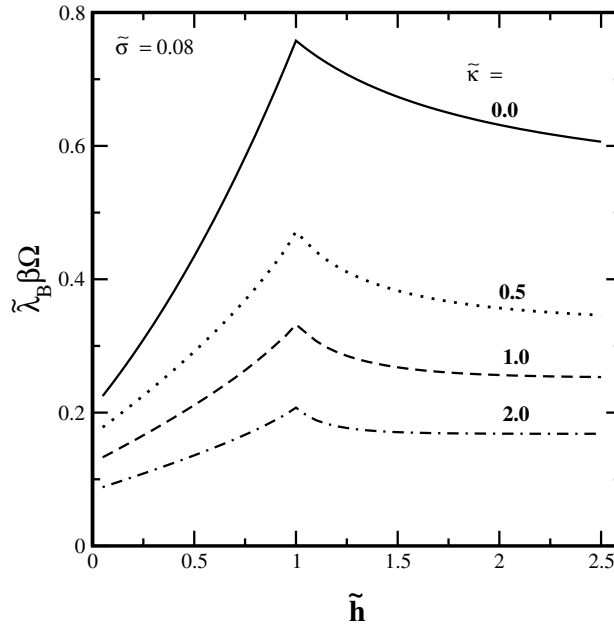


Figure 2. The grand potential given in the reduced form $\tilde{\lambda}_B \beta \Omega(\tilde{h})$ as a function of the interface–particle separation, \tilde{h} , for various values of the screening constant. The reduced colloid surface charge density, $\tilde{\sigma}$, is fixed at 0.08. The $\tilde{\kappa} = 0$ curve is obtained from the limiting case, equations (9) and (12), while the rest are obtained through numerical solution of the non-linear PB equation. All lengths are given in units of a .

the air–water interface. It is instructive to compare the depth of this trap with that resulting from the double-layer forces just considered. Pieranski [1] has reported that colloidal polystyrene particles are trapped in a surface energy well with a minimum when a particle is immersed to about two thirds of its diameter in suspension ($\tilde{h} \approx 1/6$). The surface energy is made up of three contributions; the surface energy of the particle–air interface, the surface energy of the particle–water interface, and the negative surface energy of the missing air–water interface. The total energy can be expressed as [1]

$$\beta E_s(\tilde{h}) = \beta \pi a^2 \gamma_{aw} (\tilde{h}^2 + 2(\bar{\gamma}_{pw} - \bar{\gamma}_{pa})\tilde{h} + 2(\bar{\gamma}_{pa} + \bar{\gamma}_{pw}) - 1), \quad (17)$$

where $\bar{\gamma}_{pa} = \gamma_{pa}/\gamma_{aw}$, $\bar{\gamma}_{pw} = \gamma_{pw}/\gamma_{aw}$; γ_{pw} , γ_{pa} , and γ_{aw} are respectively the surface tensions of the particle–water, particle–air, and air–water interfaces. For the minimum energy, one obtains

$$\beta E_s(\tilde{h}_{min}) = \beta \pi a^2 \gamma_{aw} (2(\bar{\gamma}_{pw} + \bar{\gamma}_{pa}) - (\bar{\gamma}_{pw} - \bar{\gamma}_{pa})^2 - 1) \quad (18)$$

with $\tilde{h}_{min} = (\bar{\gamma}_{pa} - \bar{\gamma}_{pw})$ found from minimizing (17). The corresponding desorption barrier, βE_{de} , for the surface energy is then given by

$$\beta E_{de} = \beta E_s(\tilde{h} = 1) - \beta E_s(\tilde{h}_{min}). \quad (19)$$

Dividing the surface energy desorption barrier by a^2 , we obtain a quantity $\beta E_{de}/a^2$ that is constant for all particle sizes. On the other hand, the double-layer desorption barrier reduced in the same manner, $\beta V_{de}/a^2$, still depends on the sphere radius as well as the surface charge density and the screening constant. To compare the two types of barrier for a polystyrene sphere, we have to resort again to the unreduced parameters, namely a , λ_B , κ , and σ . Figures 4(a)–(c)

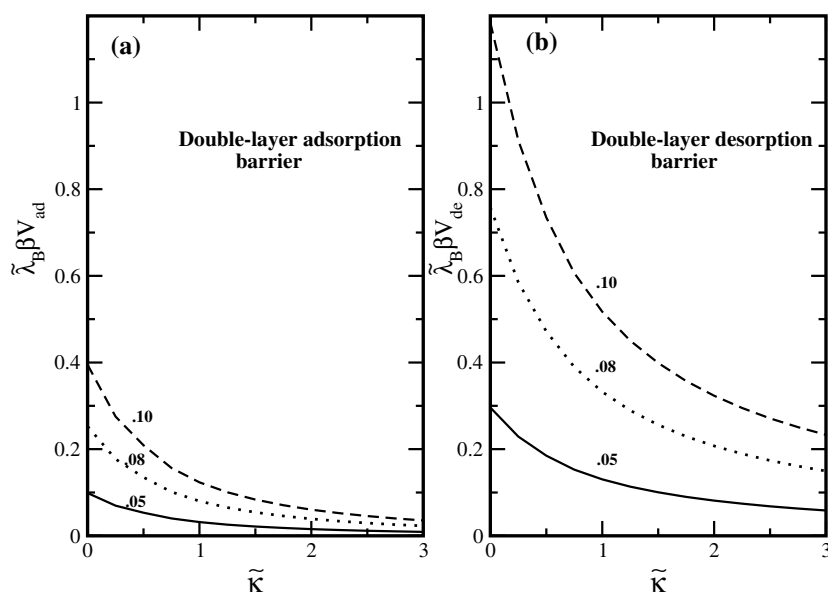


Figure 3. (a) The height of the double-layer energy barrier to colloid adsorption to the air–water interface from the electrolyte, $\tilde{\lambda}_B \beta V_{ad}$ defined in equation (15), as a function of the inverse screening length, $\tilde{\kappa}$, for various scaled surface charge densities, $\tilde{\sigma}$ (numbers labelling the curves). (b) The height of the analogous barrier to desorption back to the electrolyte from air, $\tilde{\lambda}_B \beta V_{de}$ defined in equation (16), also as a function of $\tilde{\kappa}$.

show the variation of the double-layer desorption barrier per a^2 with the surface charge density $|e\sigma|$ for three particle radii $a = 50, 100,$ and 200 nm and for (a) $\kappa = 0.01$ nm $^{-1}$, (b) $\kappa = 0.005$ nm $^{-1}$, and $\kappa = 0$. λ_B is fixed at its room temperature value in water (0.715 nm). The straight line in figure 4 is $\beta E_{de}/a^2$ ($\times 10^{-2}$). The values for γ_{pa} , γ_{pw} , and γ_{aw} are taken from [1]. The figure shows that $\beta V_{de}/a^2$ increases with increasing a , increasing $|e\sigma|$, and decreasing κ . However, for the highest surface charge density and largest particle investigated here, the surface energy trap still leads the electrostatic trap by more than an order of magnitude. But for highly charged particles of micrometre dimension, the electrostatic contribution to the overall barrier may become significant.

We next wish to compare the approximate interaction potential, $\beta V_{st}(h)$, equation (14) based on Stillinger’s linearized PB equation, with the exact potential based on the numerical solution of the non-linear PB equation. Such a comparison, shown in figure 5, reveals the parameter regime in which the more handy linear theory is valid. In the figure, the curves labelled ‘Full-PB’ and ‘Linear’ are the exact and approximate potentials respectively. Figure 5(a) shows the particle–interface interaction, $\tilde{\lambda}_B \beta V(\tilde{h})$, as a function the particle–interface separation, \tilde{h} , for various reduced surface charge densities, $\tilde{\sigma}$, at a fixed screening constant $\tilde{\kappa} = 1.0$; and figure 5(b) shows the adsorption barrier height, $\tilde{\lambda}_B \beta V_{ad}$, versus $\tilde{\sigma}$ for different values of $\tilde{\kappa}$. Both figures show that the linear theory tends mostly to underestimate the potential but has better agreement with the exact potentials at large separation $\tilde{h} \gg 1$ and small $\tilde{\sigma}$. Figure 5(b) further shows that increasing the salt content, i.e. increasing $\tilde{\kappa}$, does not seem to affect the accuracy of the linear theory with regard to the adsorption barrier height. All three sets of curves (for $\tilde{\kappa} = 0.5, 1.0, 2.0$) have about the same error margin.

Figure 6 is meant as a summary of the preceding considerations. Presented is a schematic drawing of the total interaction energy of a charged colloid near and at an air–water interface,

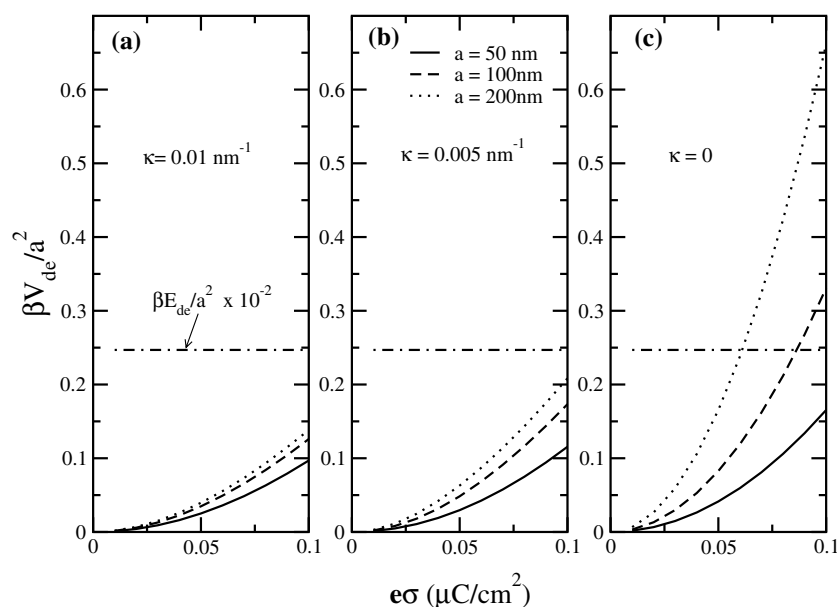


Figure 4. Comparing height of the double-layer barrier to desorption with that for the surface energy, specifically for polystyrene spheres, and with unscaled parameters (a , λ_B , κ , $e\sigma$). Dividing both the double-layer barrier height, βV_{de} , and the surface energy barrier height, βE_s , by a^2 , $\beta E_s/a^2$ remains constant while $\beta V_{de}/a^2$ varies with a , κ , and σ . The axes labels are the same for the three plots.

i.e., the sum of the electrostatic contributions of equation (4) and the force derived from the surface tension, equation (17). Gravitational forces are not included. The energy contribution due to the (possibly only partial) discharging of the dewetted colloid surface at $\tilde{h} < 1$ is also not included. The force on a colloid, approaching the interface from bulk where $\tilde{h} \gg 1$, is repulsive, but for a particle of finite size the repulsive energy barrier has a finite height. This barrier height at $\tilde{h} = 1$ is larger for higher colloidal surface charge or lower salt content of the electrolyte. When the colloidal particle breaks through the air–water interface, i.e., when $\tilde{h} < 1$, surface tension forces become important and hold the colloid in a trap that is orders of magnitude deeper than the height of the double-layer barrier.

It is an interesting observation that this picture of the interaction between a charged colloid and an air–water interface resembles our classical understanding of the effective colloid–colloid interaction in bulk (Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [36]): in both cases, there is a repulsive and salt-dependent energy barrier at large distances that prevents particles from being pulled into an attractive well at shorter distances that is orders of magnitudes larger (van der Waals attraction in DLVO theory, attractive surface tension force in our case). This, for instance, means that just in the same way as one can induce an initially stable colloidal suspension to aggregate by adding salt (‘salting-out’ effect), one should be able to cause colloids to pop up to the air–water interface by reducing the energy barrier through adding salt.

It is necessary to point out again that the terms, adsorption and *desorption*, used in this study are only convenient terms for describing the behaviour of the particle in the vicinity of the interface. The complete picture of ion adsorption or desorption is a complex process which should include the explicit structure of the solvent (water) molecules. For similar reasons also, the potentials used in the analysis are regarded as *effective*, in that contributions from

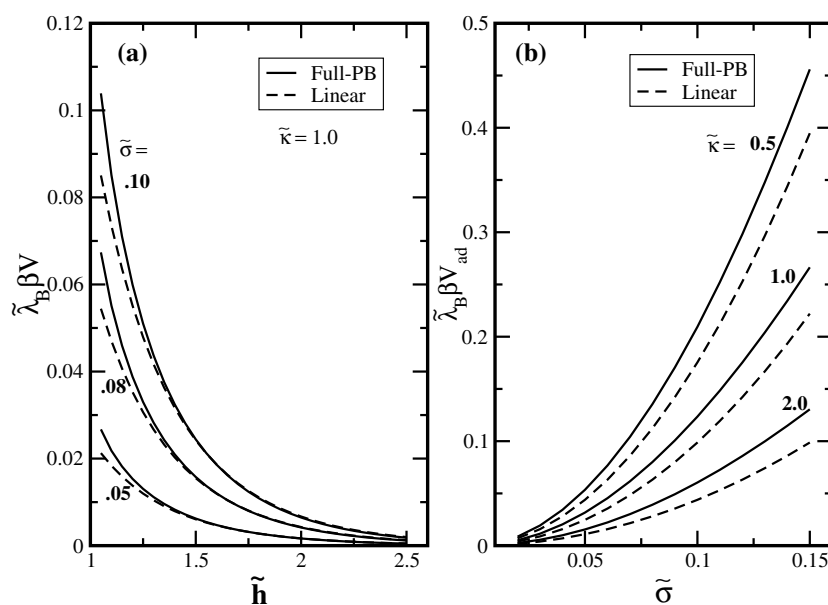


Figure 5. Comparison between the particle–interface interaction energies based on numerical solution of the non-linear PB equation (‘Full-PB’) and that based on a linear potential (‘Linear’), equation (14). (a) The interface–particle interaction ($\tilde{h} > 1$), $\tilde{\lambda}_B \beta V(\tilde{h})$, as a function of the interface–particle separation, \tilde{h} , for reduced surface charge densities $\tilde{\sigma} = 0.05, 0.08$, and 0.10 . (b) The double-layer adsorption barrier height, $\tilde{\lambda}_B \beta V_{ad}$, as a function of $\tilde{\sigma}$ for screening constants $\tilde{\kappa} = 0.5, 1.0$, and 2.0 .

solvent interactions (particle–solvent, air–solvent) and contributions from lateral interactions (particle–particle) are not included.

3.2. Relevance to experiments

The foregoing results can be applied to explain qualitatively some experimental observations.

- (i) As mentioned earlier, Kesavamoorthy *et al* [2] have described the observation of a layer of 2D hexatic polystyrene crystals in a thin suspension film confined between glass and air. Below the air–water interface, the crystalline particles are separated by about two times the particle diameter. But on exposing the film to an intense laser light, some water is drained from the suspension and some particles suddenly pop out at the air–water interface, and subsequently collapse into a compact 2D structure. The sudden emergence of the particles at the interface can be explained in the light of our results: on draining water from the film, the salt concentration is increased, increasing the screening constant κ , and thereby reducing the electrostatic adsorption barrier height, $\tilde{\lambda}_B \beta V_{ad}$. The particles can then overcome the barrier and are subsequently trapped in both electrostatic and surface (tension) energies, but most dominantly in the latter, as we have shown in figure 4.
- (ii) The adsorption rates of some charged proteins at interfaces have been observed to increase with increasing ionic strength of the solvent. MacRitchie and Alexander [37], quite a long time ago, studied experimentally the rate of adsorption of the charged globular proteins bovine serum albumin and lysozyme at the air–water interface. On varying the electrostatic potential by addition of NaCl, the rate of adsorption was found to increase as the potential was decreased. This is in agreement with our result in which the particle–

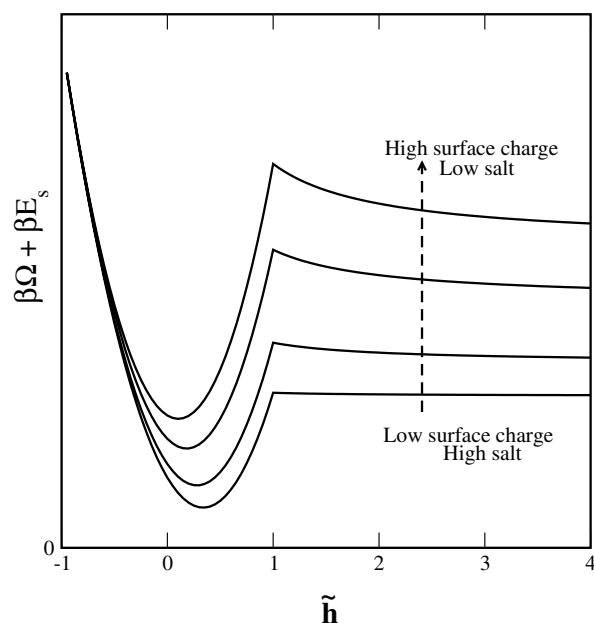


Figure 6. A schematic plot of the total interaction energy of a charged colloidal particle at the air–water interface with a repulsive double-layer energy barrier at large distances and an attractive well resulting from surface tension forces at shorter distances.

interface interaction potential is decreased with increased screening, resulting in lowering of the adsorption barrier. Furthermore, the much-talked-about non-reversibility of proteins on adsorption at air–water interface, which has been attributed largely to denaturing once at the interface [15], may well also be due to the trapping of the protein at the interface.

- (iii) A recent atomic force microscope (AFM) experiment [38] involving a direct measurement of the force of interaction between an air bubble attached to the base of the AFM piezo-stage and a single polystyrene sphere attached to the AFM cantilever, all in an aqueous electrolyte, shows some barrier (suspected to be of electrostatic origin) to the particle approach to the air–water (bubble–water) interface. However, direct comparison of data from AFM experiments with theoretical results such as ours is not quite straightforward for the following reason: the conversion of the directly measurable AFM stage position and the cantilever deflection to the more relevant particle–interface separation is problematic due to the deformability of the bubble interface. That is, the position of the interface shifts as the particle approaches the interface. A good deal of information about the AFM experiments for particle–air/water interface interaction can be found in [30, 39] and in appendix B, where we have also given a simple procedure for obtaining the particle–interface distance from the AFM observables.

4. Summary and conclusions

The present work is essentially a numerical study of the interaction of a singly charged colloidal particle of radius a with an air–water interface, where special emphasis has been put on the electrostatic aspect of this problem. On the basis of the PB equation, we calculated the effective electrostatic double-layer interaction for all particle–interface distances h , including the case

where the particle breaks through the air–water interface. The PB BVPs could be solved numerically using geometry-adapted coordinate systems for the three situations $h > a$, $h = a$, and $h < a$. For $h > a$ the colloid experiences a repulsive double-layer force which becomes attractive for $h < a$. The resulting double-layer energy barrier has its maximum value at $h = a$. We studied its dependence on the colloidal surface charge density and the salt concentration of the electrolyte, and compared it with the depth of the surface tension trap, located directly at the air–water interface. For the system experimentally studied in [1], the energy contributions due to surface tension forces are some orders of magnitude larger than those resulting from electrostatic forces. The electrostatic aspects of the problem are therefore mainly important in the distance regime where the colloid has not yet touched the interface, i.e., at $h > a$. In the distance regime $h < a$, a thorough calculation of the interaction potential is still awaited; it must take account of (a) the detailed discharging process of the dewetted part of the colloidal surface, and (b) the capillary forces, with a realistic description of the meniscus.

An interesting analogy that we have mentioned in this work is that between the DLVO problem of two colloids in bulk and our problem of a colloid near the air–water interface. From an electrostatic viewpoint, this analogy is obvious from the image-charge concept: a charged colloidal particle a distance $z = h$ from the air–water interface behaves as if there were another colloidal particle of the same charge at $z = -h$ (apart from a factor $1/2$ in the interaction potential). The resulting interaction is repulsive. But the analogy to the classical DLVO picture extends a little further: in both cases, electrostatic double-layer repulsion at large distances contrasts with a much stronger attraction at smaller distances. It is due to dispersion forces in the DLVO case, and caused by surface tension forces in our case. It is important that the repulsive double-layer barrier, preventing the particle from being pulled into the attractive well, is salt dependent, and can thus be easily manipulated experimentally. In the same way as a colloidal suspension can be caused to become unstable, a colloidal particle can be induced to pop up to the air–water interface—by adding salt. Experiments in which this interesting effect has actually been observed are mentioned and discussed in the text.

Acknowledgments

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Appendix A. Solution of the PB equation and the grand potential in the various coordinate systems

In our numerical scheme, the PB equation and the grand potential for the problem have been written and solved in different coordinate systems. They include bispherical, toroidal and tangent-sphere coordinates. Each coordinate system is suited to a particular interface–particle configuration (figure 1). They enable the complex system boundaries to be transformed into 2D rectangular forms. The bispherical coordinate system is suitable when the particle is some finite distance away from the interface and has been described elsewhere for a similar problem [21]. The tangent-sphere and toroidal systems for touching and penetrating configurations, respectively, are described here in a similar manner.

The general procedure is to express the Laplacian appearing in the BVP equations in the appropriate coordinates. The mildly non-linear elliptic BVP, in which the non-linearity arises solely through the potential function, is reduced to a sequence of linear elliptic problems by the Newton–Raphson iteration method [40, 41]. Each iteration requires the solution of a linear

elliptic problem, achieved using HERMCOL [41], a publicly available code. This method uses a fourth-order discretization based on collocation with bicubic Hermite basis functions. The resultant linear equations are solved with a band solver. And the resulting potential in every iteration is used in the numerical integration for the grand potential, equation (3), now expressed in the appropriate coordinates. This continues until the iteration converges to the desired accuracy.

Under the constant-charge boundary condition, the BVP equation (2) can be written as

$$\begin{aligned}
 \nabla^2 \phi &= \tilde{\kappa}^2 \sinh \phi & \mathbf{r} \in G \\
 \mathbf{n}_a \cdot \nabla \phi &= 4\pi \tilde{\sigma} & \mathbf{r} \in \partial G_a \\
 \mathbf{n}_w \cdot \nabla \phi &= 0 & \mathbf{r} \in \partial G_w \\
 \phi &= 0 & \mathbf{r} \rightarrow \infty
 \end{aligned}
 \tag{A.1}$$

where all lengths including the Laplacian have been scaled by the particle radius a ; $\tilde{\kappa} = \kappa a$, $\tilde{\sigma} = a\sigma\lambda_B$. Henceforth any reduced length will be indicated by the tilde (\sim) symbol.

Toroidal coordinates

The toroidal coordinate system (η, θ, φ) is related to the rectangular coordinates (x, y, z) by [42]

$$\begin{aligned}
 x &= \frac{b \sinh \eta \cos \varphi}{\cosh \eta - \cos \theta} \\
 y &= \frac{b \sinh \eta \sin \varphi}{\cosh \eta - \cos \theta} \\
 z &= \frac{b \sin \theta}{\cosh \eta - \cos \theta} \\
 \eta \in [0, \infty]; \quad \theta &\in [-\pi, \pi]; \quad \varphi \in [0, 2\pi].
 \end{aligned}
 \tag{A.2}$$

The coordinate surfaces are: two intersecting spherical bowls ($\theta = \pm \text{constant}$), a toroid ($\eta = \text{constant}$), and a half-plane ($\varphi = \text{constant}$). To make the system adaptable to our problem, one spherical bowl is assumed to be the particle that has penetrated the air–water interface and the other is its image (figure A.1(a)). Because of the cylindrical symmetry about the line joining the two spherical bowls, the coordinates reduce to (η, θ) and are related to the cylindrical coordinates (ρ, z) where $\rho = \sqrt{x^2 + y^2}$; thus,

$$\begin{aligned}
 \rho &= \frac{b \sinh \eta}{\cosh \eta - \cos \theta} \\
 z &= \frac{b \sin \theta}{\cosh \eta - \cos \theta}.
 \end{aligned}
 \tag{A.3}$$

The equation of the coordinate surface of interest, the spherical bowl, is then

$$\rho^2 + (z - b \cot \theta)^2 = \frac{b^2}{\sin^2 \theta}.
 \tag{A.4}$$

The particle of radius a , centred at h , is a surface of constant θ , θ_c , with the following important relations:

$$\begin{aligned}
 a &= b / \sin \theta_c \\
 h &= b \cot \theta_c \\
 h/a &= \cos \theta_c.
 \end{aligned}
 \tag{A.5}$$

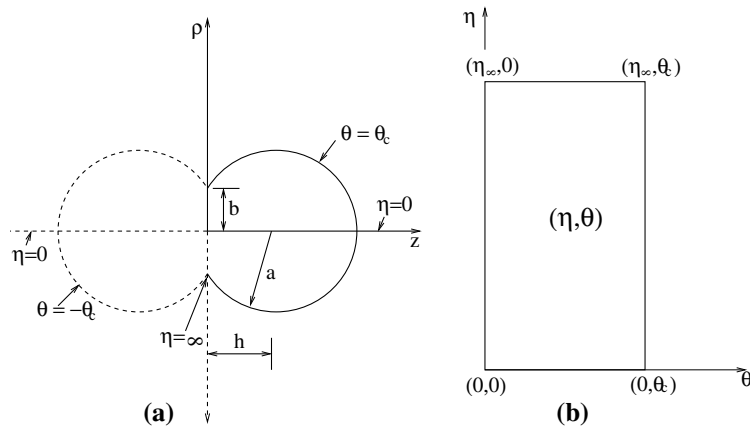


Figure A.1. The toroidal coordinate system: the boundaries of the colloid (full line sphere) and the electrolyte system in (a) are mapped to the (η, θ) rectangle in (b).

We proceed to express (A.1) in the (η, θ) coordinates, starting with boundary condition on the four sides of the rectangle (figure A.1(b)):

$$\begin{aligned}
 \partial_\eta \phi(\eta_\infty, \theta) &= 0 \\
 \partial_\theta \phi(\eta, 0) &= 0 \\
 \partial_\eta \phi(0, \theta) &= 0 \\
 \partial_\theta \phi(\eta, \theta_c) &= \left(\frac{b}{\cosh \eta - \cos \pi} \right) (-4\pi \tilde{\sigma}).
 \end{aligned} \tag{A.6}$$

The Laplacian in the PB equation transforms as

$$\begin{aligned}
 \nabla^2 \phi &= \frac{\delta^3}{b^2 \sinh \eta} \left\{ \frac{\partial}{\partial \eta} \left(\frac{\sinh \eta}{\delta} \frac{\partial \phi}{\partial \eta} \right) + \sinh \eta \frac{\partial}{\partial \theta} \left(\frac{1}{\delta} \frac{\partial \phi}{\partial \theta} \right) \right\} \\
 &= \frac{\delta^3}{b^2} \left\{ \frac{1}{\delta} \frac{\partial^2 \phi}{\partial \eta^2} + \frac{1}{\delta} \frac{\partial^2 \phi}{\partial \theta^2} + \frac{(1 - \cosh \eta \cos \theta)}{\delta^2 \sinh \eta} \frac{\partial \phi}{\partial \eta} - \frac{\sin \theta}{\delta^2} \frac{\partial \phi}{\partial \theta} \right\}
 \end{aligned} \tag{A.7}$$

where $\delta = \cosh \eta - \cos \theta$. The grand potential, equation (3), can finally be written as

$$\begin{aligned}
 \tilde{\lambda}_B \beta \Omega(h) &= -\pi \tilde{\sigma} \int \phi_h \frac{\tilde{b}^2 \sinh \eta}{(\cosh \eta - \cos \theta_c)^2} d\eta \\
 &\quad + \frac{\tilde{\kappa}^2}{4} \int d\eta \int d\theta [\phi_h \sinh \phi_h - 2(\cosh \phi_h - 1)] \frac{\tilde{b}^3 \sinh \eta}{(\cosh \eta - \cos \theta)^3}
 \end{aligned} \tag{A.8}$$

with $\tilde{b} = b/a$.

Tangent-sphere coordinates

The tangent-sphere coordinate system (μ, ν, φ) is similar to the toroidal coordinate system with the two fused spherical bowls now two tangent spheres. The relevant coordinate surfaces are the two tangent spheres of constant ν ($\pm \nu_c$) which are convenient for describing our system if the particle just touches the interface ($h = a$). Again, the second sphere is assumed to be

the particle image. The configuration has cylindrical symmetry and relates to the cylinder coordinates (ρ, z) thus:

$$\begin{aligned}\rho &= \frac{\mu}{\mu^2 + v^2} \\ z &= \frac{v}{\mu^2 + v^2} \\ \mu &\in [0, \infty], \quad v \in [-\infty : \infty]\end{aligned}\tag{A.9}$$

The surfaces of constant μ are toroids without centre openings. The equation of the tangent sphere can be written as

$$\rho^2 + \left(z - \frac{1}{2v}\right)^2 = \frac{1}{4v^2}.\tag{A.10}$$

That gives, as in (A.5), the following relations:

$$\begin{aligned}a &= 1/2v_c \\ h &= 1/2v_c \\ h/a &= 1.\end{aligned}\tag{A.11}$$

The BVP can be summarized in the following equations:

$$\begin{aligned}\gamma^2 \frac{\partial^2 \phi}{\partial \mu^2} + \gamma^2 \frac{\partial^2 \phi}{\partial v^2} + \gamma \frac{(v^2 - \mu^2)}{\mu} \frac{\partial \phi}{\partial \mu} - 2\gamma v \frac{\partial \phi}{\partial v} &= \sinh \phi; \\ \partial_\mu \phi(\mu_\infty, v) = 0; \quad \partial_v \phi(\mu, 0) = 0; \quad \partial_\mu \phi(0, v) = 0; \\ \partial_v \phi(\mu, v_c) &= \left(\frac{1}{\mu^2 + v_c^2}\right)(-4\pi\tilde{\sigma})\end{aligned}\tag{A.12}$$

where $\gamma = \mu^2 + v^2$. The grand potential in this coordinate system can be derived as

$$\begin{aligned}\tilde{\lambda}_B \beta \Omega(h) &= -\pi\tilde{\sigma} \int \phi_h \frac{\mu}{(\mu^2 - v_c)^2} d\mu \\ &+ \frac{\tilde{\kappa}^2}{4} \int d\mu \int dv [\phi_h \sinh \phi_h - 2(\cosh \phi_h - 1)] \frac{\mu}{(\mu^2 - v^2)^3}.\end{aligned}\tag{A.13}$$

Appendix B. The atomic force microscope (AFM)

The interaction of solid colloidal particles with fluid interfaces is often measured by the AFM. Ducker *et al* [30] measured forces across water between a silica probe particle attached to the AFM cantilever and an air bubble sitting on the piezo-driven stage. Similar experiments have been reported by other workers [38, 43–45]. Chan *et al* [39], basing their study on AFM experiments, have recently probed the effect of disjoining pressure on particle–fluid interface interaction in an analytic manner to describe the total force exerted on the probe particle as a function of the distance of the piezo-stage. They also displayed numerical results based on the solution of the PB equation using the Derjaguin method [36], a reasonable method in the limit where the interface–particle separation is much smaller than the particle radius, as for the AFM probe particle ($a \sim 1\text{--}3 \mu\text{m}$).

The difficulty in analysing AFM results lies mainly in converting the particle–piezo-stage distance, l , and the cantilever deflection d (see figure B.1(a)) to the particle–interface minimum separation, D_0 (in our study $D_0 = h - a$), a major parameter in theoretical schemes. The difficulty arises because the air–water interface (or bubble interface) is no longer planar as the particle approaches the interface but is deformed according to the elasticity of the interface.

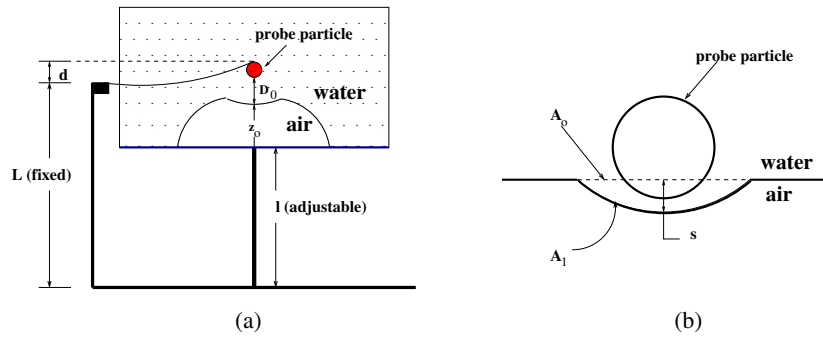


Figure B.1. (a) Geometry of the AFM measurement. (b) Estimating the bubble ‘spring constant’, k_b .

Sticking to the labels used by Chan *et al* [39] for the AFM set-up, we outline below a rather simple recipe for the conversion.

From figure B.1(a) we observe that D_0 can be written as

$$D_0 = d + l_0 - l \quad (\text{B.1})$$

where $l_0 = L - 2a - z_0$. The direct measurable quantities are: L , which is fixed as shown; l , the adjustable piezo-stage; a , the particle radius; and d , the cantilever deflection measured by the light reflection technique. l_0 and hence z_0 , the deformed height of the bubble, can be estimated from the elastic properties of the interface. If the interface is assumed linearly elastic, then we may write the force F exerted by the probe on the interface as

$$F = k_b(z_1 - z_0) \quad (\text{B.2})$$

where z_1 is the undeformed height of the bubble (also measurable [30]) and k_b is the effective ‘spring constant’ of the interface. We also have that

$$F = k_c d, \quad (\text{B.3})$$

with k_c the spring constant of the AFM cantilever. Hence from (B.2) and (B.3), we find that

$$z_0 = z_1 - \frac{k_c}{k_b} d \quad (\text{B.4})$$

or

$$l_0 = l_1 + \frac{k_c}{k_b} d, \quad (\text{B.5})$$

where $l_1 = L - 2a - z_1$.

What is now left is to estimate k_b . Consider the flat bubble surface deformed by the force on the particle, as shown in figure B.1(b). Because the bubble is so large compared to the particle, the particle sees a flat environment. The elastic free energy of changing the flat cross-sectional area, A_0 , to the depressed area, A_1 , can be written as

$$E(s) = \gamma_b(A_1 - A_0) \quad (\text{B.6})$$

where $s (=z_1 - z_0)$ is the height of the surface depression (figure B.1(b)) and γ_b is the bubble–water surface tension ($\gamma_b = 0.072 \text{ N m}^{-1}$). It is hence straightforward to show that

$$A_1 - A_0 = \pi s^2, \quad (\text{B.7})$$

and so we have

$$E(s) = \pi \gamma_b s^2. \quad (\text{B.8})$$

The corresponding force, $F(s)$, is then

$$F(s) = 2\pi\gamma_b s = 2\pi\gamma_b(z_1 - z_0). \quad (\text{B.9})$$

Comparing (B.9) and (B.2), we have

$$k_b = 2\pi\gamma_b, \quad (\text{B.10})$$

which remarkably turns out to be simple and solely dependent on the elasticity of the bubble–water interface characterized by the surface tension γ_b . Putting this all together, equation (B.1) now becomes

$$D_0 = (h - a) = \left(1 + \frac{k_c}{2\pi\gamma_b}\right)d + l_1 - l. \quad (\text{B.11})$$

This relation now enables us to compare the F -over- l force curves measured in an AFM experiment (with $F = k_c d$) with the forces considered in the present study given as a function of h .

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