Perturbation analysis of droplet deformation under electrical double layer forces

S. J. Miklavcic*
Ian Wark Research Institute, University of South Australia, The Levels Campus, SA 5095 Australia
(Received 31 March 1997)

Fluid-liquid interface deformation by electrical double layer surface forces introduces several difficulties for the accurate interpretation of fluid-drop–particle interaction measurements. We investigate the source of these difficulties theoretically using a perturbation method. Relevant quantities, such as interface shape and droplet internal pressure, are expressed in series expansions in a dimensionless parameter $M=(n_0k_BT)/(\gamma/l)$, being the ratio of electrical double layer forces to surface tension, i.e., an effective double layer Bond number. Governing equations are truncated to first order in M, and solved for the deformation in droplet shape to leading order. Analytical and numerical results for the case of neutrally buoyant drops interacting with charged spherical particles allow for a quantitative examination of the extent of deformation. The case of drops experiencing finite buoyancy is also formulated in a linear theory, and a method of solution is outlined. [S1063-651X(98)07901-X]

PACS number(s): 47.55.Dz, 82.70.Dd, 68.10.−m, 83.50.−v

INTRODUCTION

The capture of small mineral particles in a heterogeneous colloidal dispersion by gas bubbles is the key to successful mineral flotation [1]. Two problems which arise in this process of separating specific particles of a mixture using bubbles are (i) knowing whether a favorable interaction exists between the two entities, and (ii) if not, whether modifications can be introduced to achieve the desired interaction. These issues were recently addressed in some experimental studies of the direct equilibrium interaction between a colloidal particle and a bubble using an atomic force microscope (AFM) [2–4]. Unfortunately, a new concern emerged from these experiments: the question of whether one can properly interpret the measured experimental data in the usual form of force-vs-intersurface separation, knowing that at least one of the surfaces—the fluid interface—suffers considerable deformation under the action of surface forces. In these circumstances, fluid-liquid deformation implies foremost that one has no direct knowledge of the instantaneous surface position associated with a given measured force. Second, the measured net force itself is an integral of an unknown induced surface stress distribution acting on a smooth but unknown varying surface. Without doubt these are two very important considerations. In short, one of the greatest drawbacks of using the AFM in its current form for this situation is that one is essentially working blind. Although efforts are being made to circumvent the problem, there has yet to be any direct experimental progress with regard to establishing the separation between the two surfaces or the shape of the fluid-liquid interface *in situ*, as there is with the surface forces apparatus [5].

One suggestion to be considered seriously in the meantime, as a means of deconvoluting the effect of deformation from the measurements, is to make direct use of theoretical calculations of equilibrium droplet shapes. The equation governing the interfacial profile is well known. Thus, given a form for the induced surface stress distribution, the shape function can be evaluated and the extent of deformation determined. The question we ultimately aim to answer is whether theory can make possible the determination of the intersurface distance during the measurement process. As was stressed in previous publications [6,7], surface deformation, occurring in colloid dispersions involving immiscible fluids, can lead to quite surprising behavior under otherwise well-understood conditions [8].

In this paper we model the important features of the interaction between a fluid drop and a colloidal particle as exist in the AFM experimental studies. We focus attention on analyzing the change in shape of the fluid drop induced by surface forces, using regular perturbation theory. The point of departure is the well-established, linear mean-field analysis of the electrical double layer about and between two spherical colloidal objects, which we have implemented to consider a range of surface potentials (up to 75 mV) and particle and droplet sizes (from 100 nm to 10 μm). We show that to first order the amount of deformation experienced by the droplet is dependent only on the electrical double layer stress distribution produced by the undeformed, spherical bodies. Numerical results for the extent of deformation are provided for cases involving both attractive and repulsive electrical double layer forces. What emerges from our analysis is, first, an explicit formula for shape deformation given an electrical double layer stress, [Eq. (22)]. Subsequently, there emerges the more long term possibility that one can utilize this formula to subtract the amount of deformation from measured data (which is in the form of force-vs-substrate displacement; see Refs. [2] or [3]), and so obtain quantitative force-vs-intersurface distance information, at least in the asymptotic regime.

The work presented here differs from our earlier efforts primarily in that we make no explicit appeal to the Derjaguin approximation to simplify determination of surface stresses (even though we are of the opinion that it is legitimate to do so in most practical situations). However, an approximate

*Present address: Department of Science and Engineering, ITN Campus Norrköping, University of Linköping, S-602 19, Norrköping, Sweden.

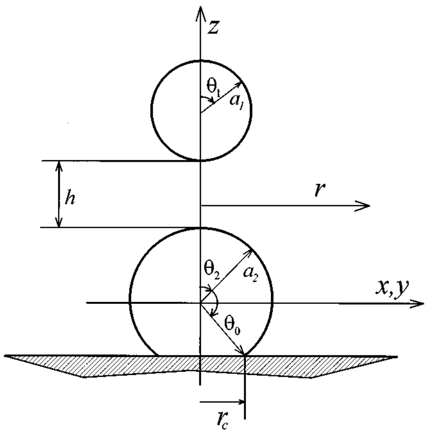

FIG. 1. Schematic diagram showing the geometry assumed for the interaction of a fluid drop and a spherical particle. For a neutrally buoyant drop, a bispherical coordinate system is appropriate. Polar angles θ_1 and θ_2 are represented by the line joining the two bodies, which we set as the z axis. The drop is pinned on a substrate along a contact circle of radius, r_c, which is established by specifying the polar angle θ_0. In this and subsequent figures, h denotes the distance of closest approach of the particle to the drop in its *undeformed* state. In all numerical, work θ_0 is held fixed at 120°.

asymptotic analysis is now emphasized, for which another set of constraints governs. The two themes are complementary. Before beginning the body of this paper, it is also appropriate to mention the works of Denkov and coworkers [9–11], who estimated the effects of soft interfacial deformation on the pairwise interaction of emulsion droplets, by invoking *a priori* simplifying assumptions about the geometry of the drops. On the other hand, Dungan and Hatton [12] took an exact but more numerical approach using a boundary integral formalism valid for linear differential systems to investigate the self-consistent interaction between a spherical ''protein'' particle and a flat deformable interface. These represent other potentially useful and alternative approaches to the one taken here.

LINEAR ANALYSIS OF NEUTRALLY BUOYANT DROPLETS

In the geometry of Fig. 1, we consider the problem of determining the shape of a fluid drop pinned along a fixed contact line on a flat solid surface, and interacting with a charged spherical particle via electrical double layer forces. In isolation, the particle, of radius a_1, has surface a potential ψ_1 (or equivalently, a surface charge σ_1) while the droplet has a surface potential ψ_2 (surface charge σ_2). The distance of their closest approach is denoted by h. At equilibrium, the interfacial profile of the drop must satisfy the extended Young-Laplace equation [6,13]

$$\gamma \nabla^* \cdot \mathbf{n} = \Delta P^* = -g\Delta\rho z^* + (P^* + \Sigma^*_{\mathrm{DL}}), \tag{1}$$

where $\mathbf{n}$ is the local unit outward normal vector to the surface. The latter then has local curvature $-\nabla^* \cdot \mathbf{n}$. ΔP^* is the *local* difference in static pressure across the interface. In Eq. (1), this is divided up into a contribution from gravity, a constant term which we refer to as the pressure excess, P^*, and a term representing the induced stress due to surface forces, Σ^*_{DL},

$$\Sigma^*_{\mathrm{DL}} = \mathbf{n} \cdot [(\Pi^*_{\mathrm{osm}} + \tfrac{1}{2}\varepsilon E^{*2})\mathbf{I} - \varepsilon \mathbf{E}^* \mathbf{E}^*] \cdot \mathbf{n}. \tag{2}$$

[In Eq. (1) and subsequent equations, dimensional variables are denoted by an asterisk superscript.]

In the quest for a perturbation analysis of droplet deformation, it is natural to consider the relative magnitudes of the various terms which appear in Eq. (1), especially its right hand side. One obvious length scale in this system is the radius of the *undeformed* drop, $l = a_2$ (see below). The stress and pressure scales are then γ/l. The first term in Eq. (2), the osmotic or kinetic term, scales as $n_0 k_B T$, where n_0 is the volume number density of a univalent salt in the bulk, k_B is Boltzmann's constant, and T is the absolute temperature. If we set the scale for the electrostatic potential to be $k_B T/e$ (e being the unit electric charge) then the electric field strength varies as $\kappa k_B T/e$, where $\kappa = \sqrt{(2e^2 n_0/\varepsilon_0 \varepsilon_r k_B T)}$ is the Debye screening parameter (κ^{-1} is the Debye screening length), ε_0 is the permittivity of free space, and ε_r is the relative permittivity of the electrolyte. This implies that the second and third terms of Eq. (2), the Maxwell stress terms, scale as $\frac{1}{2}\varepsilon\kappa^2 (k_B T/e)^2 (\varepsilon = \varepsilon_0 \varepsilon_r)$. That is, also as $n_0 k_B T$. With these natural scales in place we find that Eq. (1) reads

$$\nabla \cdot \mathbf{n} = -Gz + [K + M\Sigma_{\mathrm{DL}}], \tag{3}$$

where all terms are now dimensionless. In Eq. (3) we have introduced the dimensionless groups G and M, defined as

$$G = \frac{g\Delta\rho l^2}{\gamma} \quad \text{and} \quad M = \frac{l n_0 \; k_B T}{\gamma}. \tag{4}$$

Respectively, these are the gravitational Bond number which measures the relative strength of the gravitational (buoyancy) force to surface tension, and a surface stress ratio which measures the relative magnitude of the electrical double layer force to surface tension. In Eq. (3), $K = lP^*/\gamma$ is a dimensionless pressure constant which, in the present situation, is determined by the constraint on the droplet shape, $r(\theta)$, that the total volume contained within is equal to a known value, V,

$$V = \tfrac{2}{3}\pi \int_0^{\theta_0} r^3(\theta) \sin(\theta)\, d\theta. \tag{5}$$

In this section we shall make the simplifying assumption that the gravity force is negligible, i.e., $G = 0$, which therefore restricts the practical use of the equations below to systems involving immiscible fluids of equal density. In the absence of a double layer induced stress (equivalently, when the drop and particle are infinitely separated), the drop then assumes the shape of a truncated sphere of constant radius, a_2. The excess pressure in the drop above ambient is then $P^* = 2\gamma/a_2$, so that the dimensionless pressure excess is $K = 2$. From this initial state we study departures due to electrical double layer forces. Although our aim is for a general discussion of the changes in shape when electrical double layer influences are not negligible, the analysis below is restricted to the condition of relatively weak induced stresses, i.e., the double layer stress is small compared to surface tension: M is small. As we have said, the emphasis here is placed on examining the first order departure from sphericity.

If $r=1$ denotes the (dimensionless) shape of the drop in its undeformed state $(M=0)$, then the deformed drop can be described by the relation

$$r=1+\zeta(x_1,x_2,x_3), \tag{6}$$

where

$$\zeta=\sum_n \zeta^{(n)}(\mathbf{r})M^n \tag{7}$$

describes the departure from the perfect sphere. x_i are Cartesian coordinates that refer to the origin at the *center* of the undeformed drop. The Cartesian components of the surface normal are given by

$$n_i=\frac{(\boldsymbol{\nabla}F)_i}{|\boldsymbol{\nabla}F|}, \tag{8}$$

where $F=r-1-\zeta$. Thus

$$n_i=\frac{\dfrac{x_i}{r}-\dfrac{\partial\zeta}{\partial x_i}}{\left[1-2\dfrac{x_j}{r}\dfrac{\partial\zeta}{\partial x_j}+\left(\dfrac{\partial\zeta}{\partial x_j}\right)^2\right]^{1/2}}. \tag{9}$$

[In Eq. (9) and subsequent equations, we make use of the summation convention for terms with repeated indices.]

One can expand the denominator in Eq. (9), assuming ζ is small, to obtain the approximation

$$n_i=\frac{x_i}{r}-\frac{\partial\zeta}{\partial x_i}+\frac{x_ix_j}{r^2}\frac{\partial\zeta}{\partial x_j}-\frac{x_j}{r}\frac{\partial\zeta}{\partial x_j}\frac{\partial\zeta}{\partial x_i}-\frac{1}{2}\frac{x_i}{r}\frac{\partial\zeta}{\partial x_j}\frac{\partial\zeta}{\partial x_j}+\frac{3}{2}\frac{x_i}{r}\left(\frac{x_j}{r}\frac{\partial\zeta}{\partial x_j}\frac{x_k}{r}\frac{\partial\zeta}{\partial x_k}\right)+o(\zeta^3), \tag{10}$$

which, invoking Eqs. (6) and (7), leaves the Cartesian form of the fluid interface curvature expressed as the series

$$\begin{aligned}\boldsymbol{\nabla}\cdot\mathbf{n}=2&+\left(\frac{x_ix_j}{r^2}\frac{\partial^2\zeta^{(1)}}{\partial x_i\partial x_j}-\frac{\partial^2\zeta^{(1)}}{\partial x_i\partial x_i}+\frac{2x_i}{r}\frac{\partial\zeta^{(1)}}{\partial x_i}-2\zeta^{(1)}\right)M\\&+\left[\frac{x_ix_j}{r^2}\frac{\partial^2\zeta^{(2)}}{\partial x_i\partial x_j}-\frac{\partial^2\zeta^{(2)}}{\partial x_i\partial x_i}+\frac{2x_i}{r}\frac{\partial\zeta^{(2)}}{\partial x_i}-2\zeta^{(2)}\right.\\&-\frac{2}{r}\frac{\partial\zeta^{(1)}}{\partial x_i}\frac{\partial\zeta^{(1)}}{\partial x_i}+\frac{7}{r}\left(\frac{x_j}{r^2}\frac{\partial\zeta^{(1)}}{\partial x_j}\right)^2-2\frac{x_j}{r}\frac{\partial^2\zeta^{(1)}}{\partial x_j\partial x_i}\frac{\partial\zeta^{(1)}}{\partial x_i}\\&\left.+\frac{x_i}{r}\frac{\partial\zeta^{(1)}}{\partial x_i}\left(2\frac{x_kx_j}{r^2}\frac{\partial^2\zeta^{(2)}}{\partial x_k\partial x_j}-\frac{\partial^2\zeta^{(2)}}{\partial x_k\partial x_k}\right)\right]M^2+\cdots .\end{aligned} \tag{11}$$

Similar parameter expansions for the induced surface stress and the reference pressure can be developed. A simple scalar series expansion for the reference pressure is

$$K=\sum_{n=0}^{\infty} K^{(n)}M^n, \tag{12}$$

where $K^{(0)}$ is equal to 2, by definition. The Maclaurin expansion of the induced surface stress in powers of the surface perturbation,

$$\Sigma_{\rm DL}=\Sigma^{(0)}+(\boldsymbol{\nabla}\Sigma)_0\cdot\zeta\mathbf{r}+(\boldsymbol{\nabla}\boldsymbol{\nabla}\Sigma)_0:\zeta^2\mathbf{rr}+\cdots ,$$

can be converted using Eq. (7) into an expansion in terms of the parameter M:

$$\Sigma_{\rm DL}=\Sigma^{(0)}+\left(\frac{\partial\Sigma}{\partial r}\right)_0\zeta^{(1)}M+\left[\left(\frac{\partial\Sigma}{\partial r}\right)_0\zeta^{(2)}+\frac{1}{2}\left(\frac{\partial^2\Sigma}{\partial r^2}\right)_0\zeta^{(1)2}\right]M^2+\cdots , \tag{13}$$

in which the 0 subscripts and superscripts refer to the fact that the quantities concerned are to be evaluated on the undeformed droplet surface, i.e., on the truncated sphere.

It is more than likely that Eqs. (7)–(13) represent slowly converging series for any significant induced stress. If so, it is debatable whether a perturbation calculation going beyond first order will prove to be worthwhile when M is not small. Despite this, we persevere with a first order analysis which will nevertheless give an indicative measure of the asymptotic response of the droplet shape to double layer forces.

Substitution of Eqs. (11)–(13) into Eq. (3) leads to an inhomogeneous partial differential equation (p.d.e.) for the first order correction to the shape of the undeformed spherical shape: in Cartesian coordinates, this is

$$-\left(\frac{\partial^2\zeta^{(1)}}{\partial x_i\partial x_i}-2x_j\frac{\partial\zeta^{(1)}}{\partial x_j}-x_ix_j\frac{\partial^2\zeta^{(1)}}{\partial x_i\partial x_j}+2\zeta^{(1)}\right)=K^{(1)}+\Sigma^{(0)}. \tag{14}$$

As we assume that buoyancy effects are negligible so that the undeformed drop is spherical, it is appropriate that we rewrite the above p.d.e. in spherical coordinates. The governing equation becomes

$$-\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\zeta^{(1)}}{\partial\theta}\right)-\frac{1}{\sin^2(\theta)}\frac{\partial^2\zeta^{(1)}}{\partial\phi^2}-2\zeta^{(1)}=K^{(1)}+\Sigma^{(0)}. \tag{15}$$

This p.d.e. is more general than is necessary for our purposes, as we presume perfect axisymmetry which relieves ζ of any dependence on the azimuthal coordinate ϕ. We presume this also to be the situation in most if not all AFM experiments. Adopting the variable change $\mu=\cos(\theta)$, the governing equation is then the inhomogeneous Legendre differential equation of degree 1,

$$\frac{\partial}{\partial\mu}\left((1-\mu)^2\frac{\partial\zeta^{(1)}}{\partial\mu}\right)+2\zeta^{(1)}=-\Sigma^{(0)}-K^{(1)}\equiv R(\mu). \tag{16}$$

The homogeneous form of Eq. (16) has two linearly independent solutions,

$$P_1(\mu)=\mu, \quad Q_1(\mu)=\tfrac{1}{2}\mu \ln\left(\frac{1+\mu}{1-\mu}\right)-1. \tag{17}$$

Using these we can construct a solution to Eq. (16) which satisfies the appropriate boundary conditions on $\zeta^{(1)}$. The conditions on $\zeta^{(1)}$ are the fixed contact line condition at the drop's base and axisymmetry:

$$\zeta^{(1)}(\theta_0)=0, \quad \left.\frac{\partial \zeta^{(1)}}{\partial \theta}\right|_{\theta=0}=0. \tag{18}$$

Rather than using the homogeneous solutions (17) directly, we use the following combinations which, respectively, satisfy the conditions given in Eq. (18):

$$y_1(\mu)=P_1(\mu), \quad y_2(\mu)=P_1(\mu)Q_1(\mu_0)-P_1(\mu_0)Q_1(\mu). \tag{19}$$

In Eq. (19), we introduced $\mu_0=\cos(\theta_0)$. The perturbation $\zeta^{(1)}$ can be found using the Green function method, or, equivalently, using the method of variation of parameters. Using the latter, we find that

$$\zeta^{(1)}(\mu)=-y_1(\mu)\int_{\mu_0}^{\mu}\frac{y_2(\xi)R(\xi)}{(1-\xi^2)W(y_1,y_2)}\,d\xi + y_2(\mu)\int_{\mu}^{1}\frac{y_1(\xi)R(\xi)}{(1-\xi^2)W(y_1,y_2)}\,d\xi, \tag{20}$$

where W is the Wronskian of the two solutions,

$$W(y_1,y_2)=y_1(y_2)'-(y_1)'y_2=-\frac{P_1(\mu_0)}{(1-\mu^2)}. \tag{21}$$

Explicitly, in terms of Legendre functions, the solution becomes

$$\zeta^{(1)}(\mu)=P_1(\mu)\,\frac{Q_1(\mu_0)}{P_1(\mu_0)}\left(\int_{\mu_0}^{1}P_1(\xi)R(\xi)d\xi - 2\int_{\mu}^{1}P_1(\xi)R(\xi)d\xi\right)-P_1(\mu)\int_{\mu_0}^{\mu}Q_1(\xi)R(\xi)d\xi + Q_1(\mu)\int_{\mu}^{1}P_1(\xi)R(\xi)d\xi, \tag{22}$$

where R is given by the right hand side of Eq. (16). The constant $K^{(1)}$ is determined by the constant volume constraint derived from Eq. (5),

$$\int_{\mu_0}^{1}\zeta^{(1)}(\mu)d\mu=0. \tag{23}$$

It is simply

$$K^{(1)}=-\frac{I(\Sigma^{(0)})}{I(1)}, \tag{24}$$

where I is the sum of two integrals;

$$I(x)=\int_{\mu_0}^{1}y_1(\mu)\left(\int_{\mu_0}^{\mu}y_2(\xi)x(\xi)d\xi\right)d\mu-\int_{\mu_0}^{1}y_2(\mu)\times\left(\int_{\mu}^{1}d\xi y_1(\xi)x(\xi)\right)d\mu. \tag{25}$$

DOUBLE LAYER STRESS TENSOR FOR TWO SPHERICAL PARTICLES

Our interest in determining departures from spherical form of a charged droplet due to the stress induced by a nearby rigid charged spherical particle suggests using what is already available in the literature in regard to the double layer interaction between two spherical charged bodies [14–18]. In particular, we implement the results derived by Carnie, Chan, and Gunning [18] for the interaction of two spheres within the linear Poisson-Boltzmann approximation. The authors of Ref. [18] employed a bispherical coordinate system identical to that shown in Fig. 1, to produce a formula for the double layer force between two spherical rigid particles. The force can be given by integration of the total stress over the surface of either particle. Here it is the normal component of the stress on the particle (drop) surface itself which is of more interest to us, and is given in our notation by

$$(\Sigma_{\text{tot}}^{(0)})^* \equiv \sigma_{nn}^* = \mathbf{n}\cdot[(\Pi_{\text{osm}}^*+\tfrac{1}{2}\varepsilon E^{*2})\mathbf{I}-\varepsilon\mathbf{E}^*\mathbf{E}^*]\cdot\mathbf{n} = \frac{1}{2}\,\varepsilon(\kappa^2\psi^{*2}+E_\theta^{*2}-E_r^{*2}), \tag{26}$$

where

$$E_\theta^*=-\frac{1}{r^*}\frac{\partial\psi^*}{\partial\theta} \quad \text{and} \quad E_r^*=-\frac{\partial\psi^*}{\partial r^*}, \tag{27}$$

respectively, are the polar and radial components of the electric field in the double layer around the particles (the azimuthal component being zero). The electrostatic potential from which the field is derived can be shown to have the following simple form:

$$\psi^*=\sum_{0}^{\infty} d_n^*(r)P_n(\cos(\theta)). \tag{28}$$

The coefficients of this expansion are determined in a straightforward although tedious manner. The reader is referred to Ref. [18] for the necessary details. The normal component of the stress tensor evaluated on the drop's undeformed surface is evaluated by substitution of Eq. (28) into Eq. (27), and into Eq. (26), and evaluating the latter at $r=a_2$,

$$(\Sigma_{\text{tot}}^{(0)})^*=\tfrac{1}{2}\varepsilon\kappa^2\left(\frac{kT}{e}\right)^2\sum_{n,m=0}^{\infty}\Bigg\{P_n(\mu)P_m(\mu)\times[d_n(\kappa a_2)d_m(\kappa a_2)-d_n'(\kappa a_2)d_m'(\kappa a_2)] + \frac{(1-\mu^2)}{(\kappa a_2)^2}\,d_n(\kappa a_2)d_m(\kappa a_2)P_n'(\mu)P_m'(\mu)\Bigg\}. \tag{29}$$

The contents within parentheses are nondimensional, and the factor out front is the correct scaling of the double layer stress using the potential scaling of k_BT/e, discussed in the previous section. The sum on the right hand side is therefore related to the dimensionless external stress distribution $\Sigma^{(0)}$ appearing in Eq. (16).

This normal stress distribution is distance dependent through the coefficients, d_n. However, it includes a spherically symmetric stress contribution associated with the charged drop's double layer which remains even when the second particle is absent. This contribution is given by the $m=n=0$ term in the above infinite sum, in the limit of $h\to\infty$. Explicitly, this is given by

$$(\Sigma_{\text{unif}}^{(0)})^* = -\tfrac{1}{2}\varepsilon\kappa^2\left(\frac{kT}{e}\right)^2(1+2\kappa a_2)\,\frac{\overline{\psi_2^2}}{(\kappa a_2)^2}, \tag{30}$$

where $\overline{\psi_2}$ is the nondimensional potential on the *drop* surface. In this knowledge, the term to be inserted into Eq. (16) is the difference,

$$\Sigma^{(0)} = \Sigma_{\text{tot}}^{(0)} - \Sigma_{\text{unif}}^{(0)}, \tag{31}$$

rather than $\Sigma_{\text{tot}}^{(0)}$ itself [23].

We have solved the double layer problem for two spheres in the manner outlined in Ref. [18] for the case of constant but unequal surface potentials. The net stress contribution, Eq. (31), has been implemented in Eq. (22) to give the deformation to first order. Results of these calculations are discussed in the next section.

NUMERICAL RESULTS FOR NEUTRALLY BUOYANT DROPS

For the common salt concentration of $10^{-3}M$, we expect, on the basis of the parameter M, that the perturbation formulation presented in this paper will hold valid for quite generous values of the drop radii. For instance, consider the case of air bubbles in water, the bubble radii can be as large as 30 μm before the theory can be expected to break down. For a salt concentration of $10^{-5}M$, the bubble radius limit increases to 3 mm. Naturally, with the possibility that in practice either surface can have a potential larger than k_BT/e ($\approx$25 mV at 25 °C), the coefficients in the series expansion for K and ζ may themselves be sufficiently large to slow the convergence of the series or even cause it to diverge. This possibility is given consideration in the figures below where the coefficients $K^{(1)}$ and $\zeta^{(1)}$ are studied for their dependence on surface potentials ψ_1 and ψ_2, radii and the separation between the spherical particle and the *undeformed* fluid drop h. The reader should remain conscious of the fact that these results are nondimensional. Dimensionally meaningful quantities are the shape function $r^*(\theta)$ and the pressure excess, written as

$$r^*(\theta) = a_2 + a_2\zeta^{(1)}(\theta)M \tag{32a}$$

and

$$P^* = \frac{2\gamma}{a_2} + \frac{\gamma}{a_2}K^{(1)}M. \tag{32b}$$

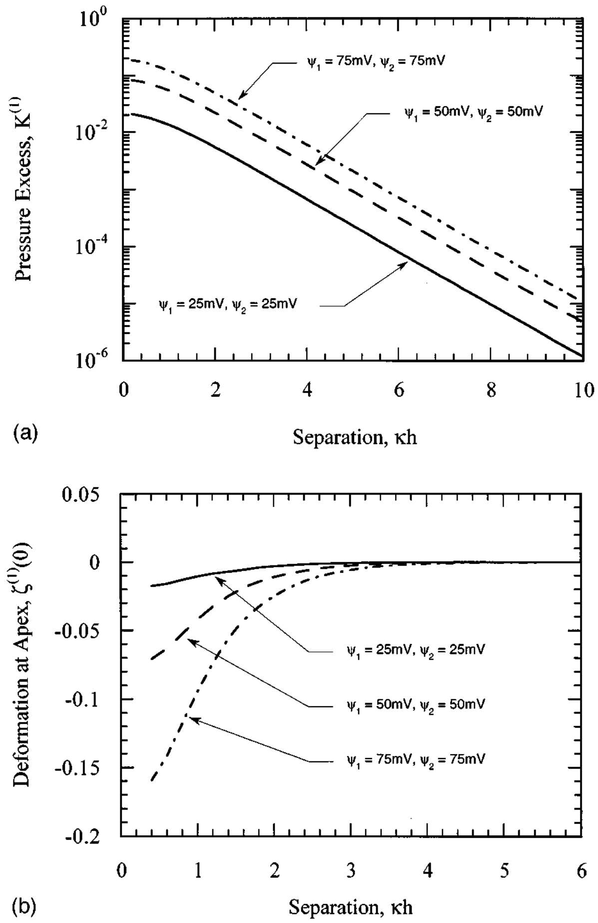

FIG. 2. Deformation effects in a neutrally buoyant, charged drop due to double layer forces as a function of minimum separation between the spherical particle and the *undeformed* drop. (a) demonstrates the typical response of the pressure excess inside the drop to double layer stresses. (b) shows the corresponding values of the shape deformation at the apex of the drop (the point of closest approach). All quantities shown are dimensionless. Parameters assumed in the calculations are as follows. Radii: $a_1=10$ nm, $a_2=100$ nm; salt concentration: $n_0=10^{-3}M$, giving a Debye length of $\kappa^{-1}=9.62$ nm; surface tension is $\gamma=72.8$ mN/m appropriate for an air-water interface. These parameters lead to a value of $M=0.34\times10^{-2}$. Values of the surface potential for the different cases are shown in the figure.

Alternately, the quantities $K^{(1)}$ and $\zeta^{(1)}$ can be judged for their physical significance when multiplied by M and compared with unity and 2, respectively (see Fig. 4).

It stands to reason that a repulsive double layer force will lead to a flattening of the drop, while an attractive double layer force will cause an elongation. This is of course borne out in our results. For example, monotonically repulsive forces are generated when the surface potentials are equal. Figure 2 represents such cases for three different sets of surface potentials. Even the largest set of potentials ($\psi_1=\psi_2=75$ mV) give no great cause for concern for convergence, and this is likely to stay the situation even at higher potentials, although the nonlinear Poisson-Boltzmann should really be implemented at that stage. A negative value of $\zeta^{(1)}$ implies a displacement of the surface below the spherical form, giving rise to a pressure increase in the drop denoted by a positive value of $K^{(1)}$. Qualitatively, both the pressure

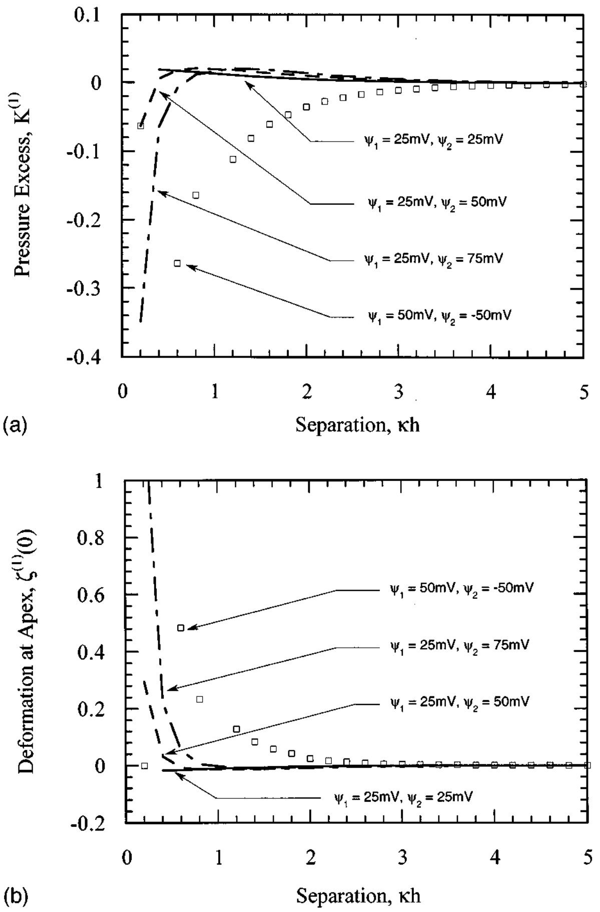

FIG. 3. As for Figs. 2(a) and 2(b), but for increasing unequal values of surface potential (indicated on the figures). Note that positive pressure excesses imply an increase in pressure inside the drop, negative values imply pressure decreases. Negative (positive) values of $\zeta^{(1)}$ imply displacement of the surface below (above) spherical form. Quantities shown are dimensionless.

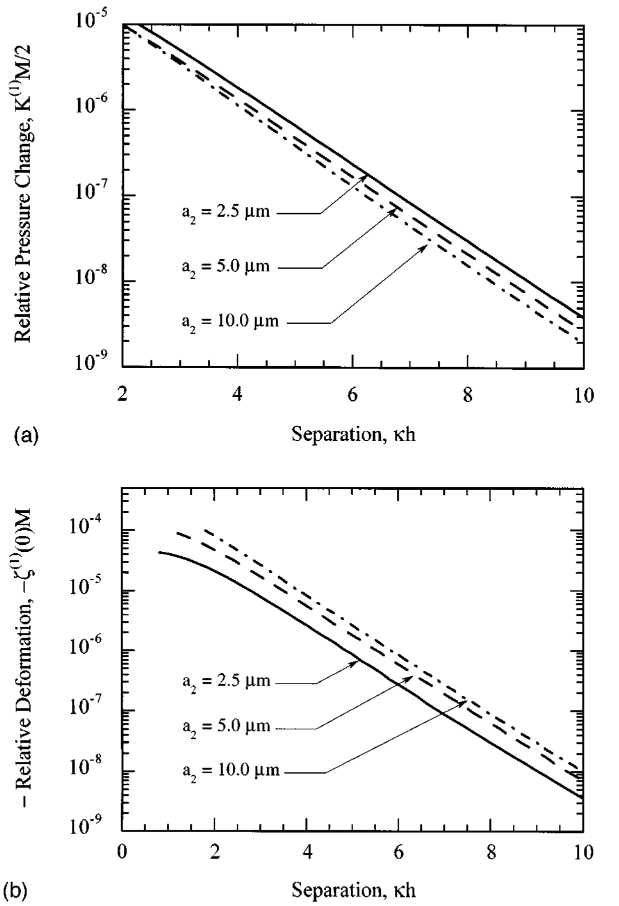

FIG. 4. Deformation effects in a neutrally buoyant, charged drop due to double layer forces as a function of minimum separation between the spherical particle and the *undeformed* drop: consideration of initial droplet size. (a) shows pressure excess variation with separation, while (b) shows the corresponding variation in apex deformation. By definition, relative pressure difference, and relative deformation are dimensionless quantities. Parameters assumed in the calculations are as follows. Particle radius $a_1=1\ \mu$m, surface potentials $\psi_1=\psi_2=50$ mV, and salt concentration $n_0=10^{-5}M$, giving a Debye length of $\kappa^{-1}=96.2$ nm; the surface tension is $\gamma=72.8$ mN/m, appropriate for an air-water interface. These parameters lead to values of $M=0.841\times10^{-3}$, 0.17×10^{-2}, and 0.34×10^{-2}, for drop radii $a_2=2.5$, 5, and 10 μm, respectively. These values of the drop radius a_2 are shown in the figure.

and the deformation increase with increased surface potential and decay exponentially with separation. Exponential decay in deformation was also calculated by this author in an earlier publication [6]. In more general cases of unequal surface potentials, we expect to see more diverse behavior [7] (Fig. 3). If the potentials are of the same sign, then a repulsive double layer force is predicted at large separations, while an attraction is predicted at short separations. If they are of opposite sign then a monotonic attraction is expected. The magnitudes and signs of the values of deformation and pressure excess shown in Fig. 3 reflect the induced stresses in these respective circumstances.

Increasing the size of the drop and particle and decreasing the salt concentration in such a way that κa_1 and κa_2 remain the same, e.g., decreasing κ by an order of magnitude (decreasing salt concentration by two orders of magnitude) and increasing a_1 and a_2 each by the corresponding order of magnitude, returns the values of $K^{(1)}$ and $\zeta^{(1)}$ shown in Fig. 2. However, doing so leaves M reduced by a factor of 10. Thus, in dimensional terms [Eq. (32)] the same amount of absolute deformation results in an absolute pressure excess change which is down by a factor of 100, and a relative change down by a factor of 10. Considering more general circumstances, the variation in the relative difference in shape and pressure, $\zeta^{(1)}M$ and $K^{(1)}M/2$, with droplet size is shown in Fig. 4, for three droplet radii under purely repulsive double layer forces.

One particular point of interest is the effect of surface forces on the internal pressure induced by a neighboring particle. The assumption that the pressure excess remains constant was made in recent calculations of the extent of deformation by colloidal forces [5–8]. It seems reasonable that any pressure change accompanying deformation will be negligible for microscopic to macroscopic fluid drops. Since the surface forces act only over a length scale of the Debye length κ^{-1}, one would not expect much variation in the drop volume and therefore pressure excess, when the droplet size is many orders of magnitude larger than κ^{-1}. This reasoning is now vindicated by the results in Fig. 4. As the figure also shows, $K^{(1)}M/2$ decreases monotonically with increasing size of the original drop. $\zeta^{(1)}M$, on the other hand, increases, all the while remaining quite small on the scale of the actual drop (unity). That the dimensional magnitudes of deformation are also quite modest on the scale of the separation between the bodies, is in line with the conditions of the perturbation calculation. Naturally, assuming a lower energy surface than the air-water interface, $\gamma = 72$ mN/m which is used as the basis for this data, will of course lead to greater deformation. The same can be said of using a larger surface potential. It has been shown elsewhere [6] that outside the restrictions of the perturbative regime ($M \geqslant 1$), which is the trend indicated in Fig. 4, the predicted values of deformation are comparable to the surface separation, which then makes it a matter of significance for the interpretation of direct surface force experiments.

ACCOUNTING FOR THE INFLUENCE OF DROP BUOYANCY

When the two immiscible fluids have different densities, the isolated pinned drop will no longer assume a spherical shape but will take either the form appropriate for a sessile or hanging drop depending on the sign of the density difference, under the influence of gravity. If a charged particle is then brought into its vicinity the drop surface will diverge from this sessile shape. Although more demanding, a perturbation analysis can still be performed, and we outline the details in this section without explicit calculations.

The equation of relevance is again Eq. (3), now with $G \neq 0$. Since the drop in the absence of surface forces is nonspherical, no special advantage can be taken of a spherical coordinate system (although it can nevertheless be adopted, if desired). Here we adopt a cylindrical coordinate system, once more assuming axisymmetry. The deformed drop shape is given by

$$z(r) = \zeta(r) = \zeta_0(r) + \xi(r), \tag{33}$$

where ζ_0 is a function of r, describing the isolated sessile drop, and ξ represents the perturbation due to the action of surface forces. The normal vector to the surface is given in cylindrical coordinates by

$$\mathbf{n} = \frac{\hat{z} - [\zeta_0'(r) + \xi'(r)]\hat{\mathbf{r}}}{\sqrt{1 + (\zeta_0' + \xi')^2}}. \tag{34}$$

The local curvature is then the divergence of this vector normal,

$$\begin{aligned} -\boldsymbol{\nabla} \cdot \mathbf{n} &= \frac{\zeta_0''(r) + \xi''(r)}{[1 + (\zeta_0' + \xi')^2]^{3/2}} + \frac{1}{r} \frac{[\zeta_0'(r) + \xi'(r)]}{\sqrt{1 + (\zeta_0' + \xi')^2}} \\ &\approx \frac{\zeta_0''(r)}{[1 + (\zeta_0')^2]^{3/2}} + \frac{1}{r} \frac{\zeta_0'(r)}{\sqrt{1 + (\zeta_0')^2}} \\ &\quad + \frac{1}{r} \frac{d}{dr} \left(\frac{r\xi'(r)}{[1 + (\zeta_0')^2]^{3/2}} \right) + O(\xi^2). \end{aligned} \tag{35}$$

The last expression is correct to first order in ξ, and assumes it is small compared with the overall length scale of the drop. The first two terms are familiar as expressions for the two principle curvature of the sessile drop. To leading order only the third term comes into a consideration of the effect of surface forces. The governing equation for the perturbation is derived from Eq. (3) by substitution of Eqs. (33) and (35), taking heed of the fact that to leading order ξ is formally proportional to M by construction, and should be identified with $\zeta^{(1)}$ of the previous section. The governing equation is then

$$-\frac{1}{r} \frac{d}{dr} \left(\frac{r\xi'(r)}{[1 + (\zeta_0')^2]^{3/2}} \right) = -G\xi(r) + K^{(1)} + \Sigma^{(0)}(r). \tag{36}$$

Although linear in ξ, it is difficult to solve Eq. (36) analytically in general, as the coefficients are functions of radius and likely only to be known as numerical data. If homogeneous solutions were known, then a solution analogous to Eq. (22) can be written down.

The problem could be simplified somewhat if surface forces were known only to act over a region near the apex where the sessile drop has low curvature. Equation (36) can then be simplified by assuming $\zeta_0'(r) \ll 1$. This leads to an inhomogeneous Bessel equation

$$\xi''(r) + \frac{1}{r}\xi'(r) - G\xi(r) = -K^{(1)} - \Sigma^{(0)}(\mathbf{r}), \tag{37}$$

describing the perturbation in this region, while, far from the source of external surface stress, where the curvature can be more significant, the perturbation must satisfy

$$-\frac{1}{r} \frac{d}{dr} \left(\frac{r\xi'(r)}{[1 + (\zeta_0')^2]^{3/2}} \right) = -G\xi(r) + K^{(1)}. \tag{38}$$

These equations are supplemented, as before, by appropriate boundary conditions of symmetry at the apex, and of a pinned contact line at some set radius, r_c,

$$\xi'(0) = 0, \quad \xi(r_c) = 0, \tag{39}$$

together with matching conditions of value and slope of the two solutions of Eqs. (37) and (38) at some appropriate radius, r_{match}

$$\xi_{\text{I}}(r_{\text{match}}) = \xi_{\text{II}}(r_{\text{match}}), \quad \xi_{\text{I}}'(r_{\text{match}}) = \xi_{\text{II}}'(r_{\text{match}}). \tag{40}$$

(Subscripts I and II denote the low and high curvature regions, respectively.) The pressure variation is again given by condition (23).

While the above mathematical model has relevance to systems involving *surface bound* charged drops with density different to the surrounding bulk phase, considerably more numerical effort is involved in the calculations compared with the case of neutrally buoyant drops. (For unattached drops, the shapes are much more likely to be spherical as the drops move through the continuous phase.) For consideration of the AFM experiments on interactions between a colloidal particle and a bubble or an oil droplet [2–4,19,20], or our own surface force experiments involving mercury drops [5], if one is to follow the above scheme one must first determine the original sessile drop shape by (numerical) integration of Laplace's equation, obtain the numerical solution of Eq. (36)

[or Eqs. (37) and (38)], and subsequently evaluate the pressure constant, $K^{(1)}$. All of these steps are performed with the proviso that one has a quantitative description of the double layer stress distribution over the original sessile surface. But again, since the sessile drop shape is likely to be known only numerically, the best scenario (i.e., invoking the Derjaguin approximation) will involve numerical double layer stress data, which then enforces further numerical integration. For this reason we do not see any advantage of this method, at this time, over a full and direct numerical integration of modified Laplace equation when both buoyancy and surface forces are present, as we have performed in the past [6,7]. We therefore make no further use of the analysis of this section.

SUMMARY AND FINAL REMARKS

We presented a linear perturbation study of fluid-liquid interfacial deformation due to electrical double layer forces of drops. The problem of a neutrally buoyant drop pinned on a solid surface interacting with a spherical particle was formulated in detail. While the resultant governing equation describing axisymmetric departures from spherical form, Eq. (16), has appeared in the literature previously [13,21,22], the equations for more general deformations, Eqs. (14) and (15), do not seem to be as familiar in the literature. An analytical solution to the axisymmetric problem was given, and subsequently investigated numerically for explicit dependences on surface and solution conditions. The mathematical model, covering the more general situation of a buoyant drop, again appears to be new to the literature, and may be useful to readers interested in either equilibrium or dynamic problems involving deformable drops in other circumstances. It was not explicitly studied here.

While the perturbation analysis and numerical results provided are correct, we remark, finally, that numerical inaccuracies do arise for certain combinations of parameters other than those used to produce the figures herein. The difficulties are associated with the fact that in this problem there are *two* clearly defined length scales, the Debye screening length κ^{-1}, and the size of the drop, $l=a_2$. As we have already pointed out, double layer forces act on the length scale of the former, while shape changes are based on the droplet size. This suggests that, when these length scales differ considerably (beyond the values assumed here), an analysis based on the method of matched asymptotic expansions would be more appropriate than the straightforward expansion method adopted here. Although it will certainly be valuable to pursue a matched asymptotic analysis valid for very large drops, the results given here have their place in colloidal situations.

ACKNOWLEDGMENTS

I am grateful to the Australian Research Council for financial support.

[1] K. L. Sutherland and I. W. Wark, *Principles of Flotation* (Australasian Institute of Mining and Metallurgy, Melbourne, 1955).
[2] M. L. Fielden, R. A. Hayes, and J. Ralston, Langmuir **12**, 3721 (1996).
[3] W. A. Ducker, Zh.-H. Xu, and J. N. Israelachvili, Langmuir **10**, 3279 (1994).
[4] H.-J. Butt, J. Colloid Interface Sci. **166**, 109 (1994).
[5] R. G. Horn, D. J. Bachmann, J. N. Connor, and S. J. Miklavcic, J. Phys. Condens. Matter **8**, 9483 (1996).
[6] S. J. Miklavcic, R. G. Horn, and D. J. Bachmann, J. Phys. Chem. **99**, 16357 (1995).
[7] D. J. Bachmann and S. J. Miklavcic, Langmuir **12**, 4197 (1996).
[8] S. J. Miklavcic, Phys. Rev. E **54**, 6551 (1996).
[9] N. D. Denkov, D. N. Petsev, and K. D. Danov, Phys. Rev. Lett. **71**, 3226 (1993).
[10] K. D. Danov, D. N. Petsev, N. D. Denkov, and R. Borwanker, J. Chem. Phys. **99**, 7179 (1993).
[11] N. D. Denkov, D. N. Petsev, and K. D. Danov, J. Colloid Interface Sci. **176**, 189 (1995); **176**, 201 (1995).
[12] S. R. Dungan and T. A. Hatton, J. Colloid Interface Sci. **164**, 200 (1994).
[13] O. A. Basaran and L. E. Scriven, J. Colloid Interface Sci. **140**, 10 (1990).
[14] G. M. Bell, S. Levine, and L. N. McCartney, J. Colloid Interface Sci. **33**, 335 (1970).
[15] A. B. Glendinning and W. B. Russel, J. Colloid Interface Sci. **93**, 95 (1983).
[16] J. W. Krozel and D. A. Saville, J. Colloid Interface Sci. **150**, 365 (1992).
[17] S. L. Carnie and D. Y. C. Chan, J. Colloid Interface Sci. **155**, 297 (1993).
[18] S. L. Carnie, D. Y. C. Chan, and J. S. Gunning, Langmuir **10**, 2993 (1994).
[19] S. Basu and M. M. Sharma, J. Colloid Interface Sci. **181**, 443 (1996).
[20] P. Mulvaney, J. M. Perera, S. Biggs, F. Grieser, and G. W. Stevens, J. Colloid Interface Sci. **183**, 614 (1996).
[21] M. Strani and F. Sabetta, J. Fluid Mech. **141**, 233 (1984).
[22] M. Strani and F. Sabetta, J. Fluid Mech. **189**, 397 (1988).
[23] In Ref. [18] no account of the double layer stress on an isolated sphere was required, as the authors of that paper were interested in the force between the two objects along the direction of the line joining them, the z direction. Because of symmetry, the z component of this stress integrated over the surface is zero.