

The Interaction of Colloidal Particles Collected at Fluid Interfaces

D. Y. C. CHAN,* J. D. HENRY, JR.,† AND L. R. WHITE*

*Department of Applied Mathematics, Research School of Physical Sciences, Institute of Advanced Studies, Australian National University, Canberra, Australian Capital Territory 2600, Australia, and

†Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

Received February 26, 1980; accepted June 12, 1980

Simple approximate expressions are derived for the meniscus forces acting between spherical and cylindrical bodies at a fluid interface using a superposition approximation due to Nicolson (*Proc. Cambridge Philos. Soc.* **45**, 288 (1949)). These expressions are correct to lowest order in the Bond number, $B = (\rho_B - \rho_A)gR^2/\gamma_{AB}$, and are applicable to bodies that may be dissimilar in Bond number and wetting characteristics. Our results compare very favorably with the exact numerical calculations of Gifford and Scriven (*Chem. Eng. Sci.* **26**, 287 (1971)) for parallel cylinders (for $B \leq 10^{-1}$). The small Bond number expressions derived herein are directly applicable to the interaction between particles of colloidal dimensions collected at fluid interfaces. Some sample calculations are given to illustrate the importance of capillary forces in interfacial coagulation processes. The extension of the theory to higher Bond number is discussed briefly.

1. INTRODUCTION

The importance of capillary forces in surface coagulation phenomena, e.g., scum formation and froth flotation processes, is well established.

The exact calculation of such forces involves considerable numerical effort and is only possible in the simplest geometries. The case of identical infinite parallel cylinders has been considered in detail by Gifford and Scriven (2) who calculated the force per unit length required to hold the cylinders at a fixed distance apart. They observed that "Remarkably the (log(Force) vs separation) curves are nearly—but not exactly—straight and parallel and fall on top of one another" for Bond numbers $B < 0.5$. They went on to say that "there apparently is no obvious way from the original equations to a justification of this striking result." However, in 1949, Nicolson (1) derived an analytic expression for the capillary force between floating bubbles by an approximate method which we discuss below. We shall show in this paper that the

"remarkable" results found by Gifford and Scriven can be explained using Nicolson's method which gives the force to leading order in the Bond number. The method is of wider validity and can be used to calculate the capillary forces between bodies of arbitrary shapes and physical properties. However, in this paper we restrict ourselves to the relatively simple geometries of planes and surfaces of revolution in order that the physical content is not obscured by complex mathematics.

In the next section we discuss the Nicolson approximations (i) to the shape of the fluid interface near solid bodies and (ii) to the consequent capillary forces acting between them. In Section 3, we derive expressions for the capillary force and interaction energy between floating bodies; the interaction between floating bodies and fixed boundaries are also considered. In Section 4, we discuss the extension of such calculations to large Bond numbers and the relevance of "exact" numerical calculations, such as those of Gifford and Scriven (2), to the dynamics of interacting systems.

Some typical numerical results for the interaction energy between two spherical colloidal particles collected at the air-water interface are also given.

2. THE NICOLSON METHOD

(a) *Interfacial Profiles*

We consider first a fluid interface with surface tension γ_{AB} separating an upper fluid A (density ρ_A) and a lower fluid B (density ρ_B) near a solid body. Far from the body the interface is planar and normal to the direction of gravity. Near the body, the interface is curved in general due to the thermodynamic requirement that the interface must meet the solid body at a given angle—the contact angle (given by Young’s equation (3) provided the solid surface is chemically homogeneous and molecularly smooth). The position of the interface is measured by the coordinates z and \mathbf{r} where z is the vertical height of the interface (measured relative to the planar interface at infinity) at vector position \mathbf{r} in the plane (measured relative to some arbitrary origin). If, at the position \mathbf{r} , we choose a Cartesian coordinate system (x_1, x_2) in the plane parallel to the principal sections of curvature of the interface, the principal radii of curvature $R_i(\mathbf{r})$ are given by the expression

$$\frac{1}{R_i(\mathbf{r})} = \frac{\partial^2 z(\mathbf{r})}{\partial x_i^2} \left(1 + \left(\frac{\partial z(\mathbf{r})}{\partial x_i} \right)^2 \right)^{-3/2} \quad (i = 1, 2). \quad [1]$$

When the disturbance of the interface due to the presence of the body is “small,” the principal radii of curvature can be approximated by

$$\frac{1}{R_i(\mathbf{r})} = \frac{\partial^2 z(\mathbf{r})}{\partial x_i^2} \quad (i = 1, 2). \quad [2]$$

The errors involved in neglecting the first derivative in [1] will be discussed later in this section.

The jump in pressure (i.e., the Laplace pressure) in crossing the interface from

fluid A to fluid B at \mathbf{r} is

$$\begin{aligned} \gamma_{AB} \left(\frac{1}{R_1(\mathbf{r})} + \frac{1}{R_2(\mathbf{r})} \right) & \approx \gamma_{AB} \left(\frac{\partial^2 z(\mathbf{r})}{\partial x_1^2} + \frac{\partial^2 z(\mathbf{r})}{\partial x_2^2} \right) \\ & = \gamma_{AB} \nabla^2 z(\mathbf{r}). \end{aligned} \quad [3]$$

The invariance of the two-dimensional Laplacian operator ∇^2 to rotation of the axis system means that the Laplace pressure can be approximated by [3] in any convenient system of coordinates which need not necessarily coincide with any principal axis system of the curved interface.

The hydrostatic pressure in fluid A just above the interface at \mathbf{r} is $-\rho_A g z(\mathbf{r})$ (where g is the gravitational acceleration) relative to the pressure at the plane interface infinitely far from the floating body. Just below the interface, in fluid B, the hydrostatic pressure is $-\rho_B g z(\mathbf{r})$ relative to the same origin. The Laplace pressure jump across the interface balances the change in hydrostatic pressure. Therefore, we have

$$\nabla^2 z \approx \lambda^2 z, \quad [4]$$

where

$$\lambda = [(\rho_B - \rho_A)g/\gamma_{AB}]^{1/2} \quad [5]$$

defines a length scale λ^{-1} on which the disturbance will decay to zero.

We shall consider cases in which the floating body and fluid interface form a horizontal contact line which is either straight (e.g., cylinders lying parallel to the fluid interface) or circular (e.g., spheres). For the case of an infinitely long straight contact line, the surface profile is a function only of the horizontal distance x measured normal to the contact line. In this case, [4] becomes

$$\frac{d^2 z}{dx^2} = \lambda^2 z \quad [6]$$

with a solution of the form

$$z(x) = Ae^{-\lambda x} \quad [7]$$

since the height of the interface $z \rightarrow 0$ as

$x \rightarrow \infty$. For later use, we choose to determine the constant A in terms of the slope

$$\dot{z}_c = \left. \frac{dz}{dx} \right|_{x_c}$$

of the interface at the contact line ($x = x_c$); thus the surface profile near a straight contact line can be written as

$$z(x) = -\frac{\dot{z}_c}{\lambda} e^{-\lambda(x-x_c)} \tag{8}$$

For the case of a floating axisymmetric body with a vertical symmetry axis, the contact line is horizontal and circular when viewed from above. In this case, the interfacial profile is a function only of the radial coordinate r measured horizontally from the symmetry axis and [4] takes the form of Bessel's equation (4),

$$\frac{d^2z}{dr^2} + \frac{1}{r} \frac{dz}{dr} = \lambda^2 z \tag{9}$$

The appropriate solution for the profile $z(r)$ is of the form

$$z(r) = AK_0(\lambda r) \tag{10}$$

where $K_n(x)$ is a modified Bessel function of the second kind of order n (4). We shall need the general result (4)

$$\frac{dK_0(x)}{dx} = -K_1(x) \tag{11}$$

and the asymptotic results (4)

$$K_0(x) \sim -\ln x + O(1) \tag{12}$$

$$K_1(x) \sim 1/x + O(x \ln x) \tag{13}$$

for small x ($\ll 1$), and

$$K_n(x) = \left(\frac{\pi}{2x}\right)^{1/2} e^{-x} \left(1 + O\left(\frac{1}{x}\right)\right) \tag{14}$$

for large x ($\gg 1$).

With the aid of [11], we determine the constant A in [10] in terms of the slope

$$\dot{z}_c = \left. \frac{dz}{dr} \right|_{r_c}$$

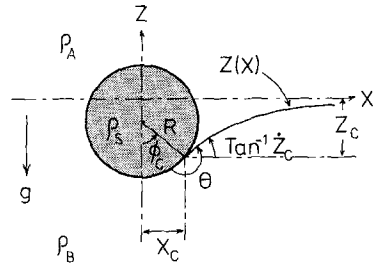


FIG. 1. The geometry of the floating horizontal cylinder at the AB interface. (Sphere is identical with x replaced by r .)

of the interface at the contact circle $r = r_c$. Therefore the surface profile around an axisymmetric body has the form

$$z(r) = -\frac{\dot{z}_c}{\lambda} \frac{K_0(\lambda r)}{K_1(\lambda r_c)} \tag{15}$$

We now return to the question of the validity of ignoring first derivatives in the Young-Laplace equation [3] by first considering the case of a single infinitely long horizontal floating cylinder of radius R (see Fig. 1). From the condition of vertical force balance on the floating cylinder, we shall show that \dot{z}_c (and therefore \dot{z} for all x) tends to zero as the Bond number

$$B = \frac{(\rho_B - \rho_A)gR^2}{\gamma_{AB}} \tag{16}$$

tends to zero. It follows that z_c^2 can be neglected when compared with unity for sufficiently small Bond number. This serves to delineate the region of validity of the linear interfacial profile equation [4].

The vertical force per unit length acting on the horizontal floating cylinder has three components: (i) the weight per unit length $-\pi R^2 \rho_s g \hat{z}$, (ii) the vertically resolved part of the interfacial tension γ_{AB} acting on unit length of the contact line given by (see Fig. 1)

$$2\gamma_{AB} \sin(\tan^{-1} \dot{z}_c) \hat{z} = 2\gamma_{AB} \dot{z}_c (1 + \dot{z}_c^2)^{-1/2} \hat{z} \tag{17}$$

and (iii) the upthrust per unit length U obtained by integrating the vertically resolved

part of the hydrostatic pressure acting on the surface of the cylinder, given by (see Fig. 1)

$$\begin{aligned}
 U &= -2Rg\hat{z} \left\{ \rho_B \int_0^{\phi_c} d\phi H(\phi) \cos \phi \right. \\
 &\quad \left. + \rho_A \int_{\phi_c}^{\pi} d\phi H(\phi) \cos \phi \right\} \\
 &= \{ \pi R^2 \rho_A g - 2(\rho_B - \rho_A) R^2 g [(z_c/R) \sin \phi_c \\
 &\quad + (1/2) \sin \phi_c \cos \phi_c - (1/2) \phi_c] \} \hat{z}, \quad [18]
 \end{aligned}$$

where

$$H(\phi) = z_c + R(\cos \phi - \cos \phi_c) \quad [19]$$

is the vertical coordinate of the cylinder surface at angle ϕ . From simple geometry we have the identity

$$\phi_c = \pi - \theta + \tan^{-1} \dot{z}_c, \quad [20]$$

where θ is the contact angle (see Fig. 1).

With the aid of [17], [18], and [20] the vertical force balance on the cylinder in equilibrium gives

$$\begin{aligned}
 2\dot{z}_c &= B(1 + \dot{z}_c)^{1/2} \left\{ \pi D - \pi + \theta - (1/2) \sin 2\theta \right. \\
 &\quad + \frac{\dot{z}_c^2 \sin 2\theta}{1 + \dot{z}_c^2} + \frac{2z_c \sin \theta}{R(1 + \dot{z}_c^2)^{1/2}} \\
 &\quad - \tan^{-1} \dot{z}_c + \frac{\dot{z}_c \cos 2\theta}{1 + \dot{z}_c^2} \\
 &\quad \left. - \frac{2z_c \dot{z}_c \cos \theta}{R(1 + \dot{z}_c^2)^{1/2}} \right\}, \quad [21]
 \end{aligned}$$

where the density ratio D is given by

$$D = \frac{\rho_s - \rho_A}{\rho_B - \rho_A}. \quad [22]$$

The form of Eq. [21] suggests, for small \dot{z}_c , that \dot{z}_c is of order B . Assuming this to be true, we see from [8] that (z_c/R) is of order $B^{1/2}$ (or $\dot{z}_c^{1/2}$) reflecting the physically obvious result that as B vanishes the interface becomes flat ($z_c/R \rightarrow 0$). Thus when \dot{z}_c is small, terms on the right-hand side of [21] involving (z_c/R) and \dot{z}_c as well as their

products may be neglected in comparison with the constants, so that as $B \rightarrow 0$ [21] becomes

$$\dot{z}_c = \frac{B}{2} \left\{ \pi D - \pi + \theta - \frac{1}{2} \sin 2\theta \right\} + O(B^{3/2}). \quad [23]$$

It therefore follows that in the expression for the interfacial curvature [3], first derivatives may be neglected in comparison to unity when the Bond number is sufficiently small so that the errors in the linear equation for the curvature [4] are of order B^2 .

The corresponding analysis for a floating sphere of radius R and density ρ_s yields

$$\text{weight} = -\frac{4\pi}{3} R^3 \rho_s g \hat{z}, \quad [24]$$

vertically resolved surface tension force

$$= 2\pi R \gamma_{AB} \frac{\dot{z}_c \sin \phi_c}{(1 + \dot{z}_c^2)^{1/2}} \hat{z}, \quad [25]$$

$$\begin{aligned}
 \text{upthrust} &= \left(\frac{4\pi}{3} R^3 \rho_A g - 2\pi R^3 (\rho_B - \rho_A) g \right. \\
 &\quad \times \left. \left\{ \frac{1}{2} \left(\frac{z_c}{R} + \cos \phi_c \right) \sin^2 \phi_c \right. \right. \\
 &\quad \left. \left. - \frac{1}{3} (1 - \cos^3 \phi_c) \right\} \right) \hat{z}. \quad [26]
 \end{aligned}$$

Vertical force balance on the floating sphere yields, to lowest order in B ,

$$\begin{aligned}
 \dot{z}_c \sin \phi_c &= B \left(\frac{2}{3} D - \frac{1}{3} - \frac{1}{2} \cos \theta + \frac{1}{6} \cos^3 \theta \right) \\
 &\quad + O(B^{3/2}). \quad [27]
 \end{aligned}$$

Once again, we see that first derivatives in [3] may be neglected in comparison with unity when the Bond number is sufficiently small.

(b) The Horizontal Force

In the Nicolson method, the horizontal force between floating particles is obtained

as follows. As shown above, the differential equation for the fluid interface is linear for small Bond numbers. The interfacial profile around two floating particles in close proximity can be written as a linear combination of the profile functions appropriate to the isolated particles. The coefficients are determined by the boundary condition on the surface of each particle. For particles not too close together, the interfacial profile is just the *sum* of the profiles around each particle at infinite separation. This is the superposition approximation and although it is a solution of the differential equation [4], it does not satisfy the contact line boundary conditions exactly (except at infinite separation). However, for small Bond numbers, where the gradient of the profile function is small, the superposition approximation will hold to quite small separations. Indeed, the superposition approximation yields the interfacial profile correct to leading order in the Bond number.

Consider two floating particles as they approach each other. As particle 2 moves along the interfacial profile imposed by particle 1, it will experience a change in gravitational potential energy (relative to infinite separation) as well as changes in energy due to changes in interfacial areas. The gravitational energy change is given by the product of the net weight of particle 2 and the height of its center of mass relative to its height at infinite separation. Within the superposition approximation, this change in height is given by $z_1(l)$, the displacement of the fluid interface at distance l from particle 1 in isolation. To this order, the net weight of particle 2 is its net weight at infinite separation. From the vertical force balance condition on the isolated particle, this is just the vertically resolved surface tension force. Changes in interfacial energies are of higher order in the Bond number. Therefore, within the superposition approximation which is correct to leading order in the Bond numbers the interaction energy between particles 1 and 2 is just

$$E(l) = \left\{ \begin{array}{l} \text{vertically resolved surface} \\ \text{tension force on 2 at infinity} \end{array} \right\} \times z_1(l). \quad [28]$$

The horizontal force on particle 2 can be calculated from the general result

$$\begin{aligned} F(l) &= - \frac{\partial E(l)}{\partial l} \\ &= - \left\{ \begin{array}{l} \text{vertically resolved surface} \\ \text{tension force on 2 at infinity} \end{array} \right\} \times \dot{z}_1(l). \quad [29] \end{aligned}$$

We note that the Nicolson approximation outlined above yields the horizontal force correct to leading order in the Bond number. To this order, the force is independent of the contact line boundary condition during approach, and consequently invariant to whether the contact angle remains constant or the position of the contact line on the particle surface remains fixed during interaction. For infinite horizontal floating cylinders, it is possible to show by a tedious algebraic argument that changes in interfacial energies are higher order in the Bond number than changes in the gravitational energy.

A similar argument in the more complicated geometry of interacting spheres is not feasible. We have therefore adopted the policy of first verifying the validity of the Nicolson approximation in the regime of low Bond numbers by comparison with the exact calculations of Gifford and Scriven (2) for horizontal parallel cylinders. That the approximation is valid in more complicated geometries is then inferred as there is no physical reason to suppose that the Nicolson approximation is a function of geometry.

3. RESULTS

With the aid of Eqs. [8], [15], [23], [27]–[29] we can obtain expressions for the interaction energy and force correct to leading order in the Bond number for the following geometries.

(a) *Infinite Parallel Cylinders*

For infinite horizontal parallel cylinders (denoted 1 and 2) at a horizontal distance l between the axes, the interaction energy per unit length is

$$E(l)/L = -\frac{\gamma_{AB}}{2} (R_1 R_2)^{1/2} (B_1 B_2)^{3/4} \times (C_1 C_2) e^{-\lambda l} \quad [30]$$

and the force per unit length is

$$F(l)/L = -\frac{\gamma_{AB}}{2} (B_1 B_2) (C_1 C_2) e^{-\lambda l}, \quad [31]$$

where

$$C_i = \pi(D_i - 1) + \theta_i - (1/2) \sin 2\theta_i \quad (i = 1, 2). \quad [32]$$

Since, for small Bond number,

$$e^{\lambda x_c} = 1 + O(B^{1/2})$$

we have replaced $e^{\lambda x_c}$ by unity in the derivation of [30] and [31] because we are only calculating the energy and force to leading order in the Bond number. The expression [31] is in exact agreement with the limiting form observed in the numerical work at Gifford and Scriven (2) on identical cylinders.

The exponential force law obtained above is correct to leading order in the Bond number. However, from the numerical work of Gifford and Scriven (2), it would appear that the force law is exponential even for $B = 0.5$, although the preexponential factor predicted by [31] is about 30% too small at this Bond number. At $B = 0.137$, Eq. [31] underestimates the force by less than 5%, and at $B \approx 0.01$, Eq. [31] is essentially exact.

(b) *Sphere-Sphere*

For floating spheres (denoted 1 and 2) of radii R_1 and R_2 at a horizontal distance l between centers, the interaction energy and horizontal force are

$$E(l) = -2\pi\gamma_{AB}(R_1 R_2)(B_1 B_2) \times (S_1 S_2) K_0(\lambda l) \quad [33]$$

and

$$F(l) = -2\pi\gamma_{AB}(R_1 R_2)^{1/2}(B_1 B_2)^{5/4} \times (S_1 S_2) K_1(\lambda l), \quad [34]$$

where

$$S_i = \frac{2}{3} D_i - \frac{1}{3} - \frac{1}{2} \cos \theta_i + \frac{1}{6} \cos^3 \theta_i \quad (i = 1, 2). \quad [35]$$

In the derivation of [33] and [34], we have replaced $K_1(\lambda r_c)$ by its asymptotic form $1/\lambda r_c$ (see Eq. [13]). Since (see Fig. 1)

$$\lambda r_c = B^{1/2} \sin \phi_c, \quad [36]$$

it is not consistent to retain terms in $K_1(\lambda r_c)$ to higher than the leading order.

(c) *Sphere-Infinite Cylinder*

The interaction energy and force between an infinite horizontal floating cylinder and a sphere of radius R_s whose center is at a horizontal distance l measured normally from the cylinder axis are

$$E(l) = -\pi\gamma_{AB} R_s^2 B_s^{1/2} B_c S C e^{-\lambda l}, \quad [37]$$

$$F(l) = -\pi\gamma_{AB} R_s B_s B_c S C e^{-\lambda l}, \quad [38]$$

where the sphere and cylinder functions S and C are given by [32] and [35].

(d) *Large Bond Number Systems*

The Nicolson expressions [28] and [29] for the energy and force are still applicable when only *one* of the particles has a small Bond number. In this case, $z_1(l)$ must be taken to be the profile around the isolated large Bond number particle. Further, $z_1(l)$ must be evaluated from the full nonlinear Laplace equation since we are no longer able to linearize. The force so obtained is correct to leading order in the smaller Bond number.

In this respect, the force exerted by a wall on a floating particle is just a special case of the above calculation where $z_1(l)$ is the interfacial profile in the neighborhood of the wall.

4. DISCUSSION

We have derived analytic expressions for the capillary force between floating bodies of spherical and cylindrical geometries. Our results are only valid to leading order in the Bond numbers of the particles. However, comparison with the exact numerical calculations of Gifford and Scriven (2) for identical cylinders shows that the approximate expression for cylinders is excellent for $B < 10^{-1}$. By inference, we expect similar accuracy for *all* the cases discussed above.

To extend our results to larger Bond numbers, an analysis of the order of complexity of that of Gifford and Scriven (2) would be required at the very least. The analysis for spheres would involve in part the solution of a partial nonlinear differential equation for the interfacial profile.

It should be noted that Gifford and Scriven's analysis, for all its complexity, is a *static* calculation, i.e., it yields the horizontal force required to hold the two bodies stationary at a given separation. Strictly speaking, this is not the force that enters in the equation of horizontal motion for one body moving under the influence of the other. If we denote the heights of the center of mass of the bodies above the horizon by h_1 and h_2 and the horizontal separation of the bodies by l , then the equations of motion are

$$m_1 \frac{d^2 h_1}{dt^2} = F_{v1}(l, h_1, h_2), \quad [39]$$

$$m_2 \frac{d^2 h_2}{dt^2} = F_{v2}(l, h_1, h_2), \quad [40]$$

$$\left(\frac{m_1 m_2}{m_1 + m_2} \right) \frac{d^2 l}{dt^2} = F_H(l, h_1, h_2), \quad [41]$$

where F_{v1} and F_{v2} are the vertical forces and F_H the horizontal force acting on the bodies. If we assume that the system is inertially limited and omit hydrodynamic drag, the calculation of these forces as functions of l , h_1 , and h_2 is straightforward given the interfacial profile as determined by the

Laplace equation and the contact line boundary conditions. Equations [39]–[41] must be solved as coupled differential equations in order to determine exactly the dynamical behavior of the bodies. Clearly the vertical force balance condition applicable in the *static* calculation of Gifford and Scriven (2), that is,

$$F_{v1}(l, h_1, h_2) = 0 = F_{v2}(l, h_1, h_2), \quad [42]$$

will *not* yield the correct dynamical behavior. However, it is not difficult to show that for parallel cylinders the magnitudes of $(d^2 h_1/dt^2)$ and $(d^2 h_2/dt^2)$ are of order B^3 so that the relationships between l , h_1 , and h_2 obtained from [42] are accurate to order B^3 . It follows therefore that to leading order in the Bond number, the calculation of Gifford and Scriven (2) as well as our expressions for the horizontal force are equally applicable to *both* the static and the dynamic cases.

Let us examine the case of interacting spheres in closer detail. In terms of the fundamental physical parameters, the interaction energy between two spheres [33] has the form

$$E(l) = - \frac{2\pi R_1^3 R_2^3}{\gamma_{AB}} \times (\rho_B - \rho_A)^2 S_1 S_2 K_0(\lambda l). \quad [43]$$

A further simplification is possible when the density ratios $D_i \gg 1$ so that we can use approximation¹

$$S_i \equiv \frac{2}{3} D_i + \frac{1}{6} \cos^3 \theta_i - \frac{1}{2} \cos \theta_i - \frac{1}{3} \approx \frac{2}{3} D_i \quad [44]$$

to reduce [43] to

$$E(l) = - \frac{8\pi R_1^3 R_2^3}{9\gamma_{AB}} (\rho_{s1} - \rho_A)(\rho_{s2} - \rho_A) \times K_0(\lambda l). \quad [45]$$

¹ The quantity $[(1/6) \cos^3 \theta - (1/2) \cos \theta - (1/3)]$, cf. Eq. [35], varies monotonically from 0 at $\theta = \pi$ to $-2/3$ at $\theta = 0$.

TABLE I
Interaction Energy between Spheres

Radius (μm)	Interaction energy $E(l)$ (ergs)	
	Contact	10 diameters
2.0	-1.43×10^{-16}	-0.92×10^{-16}
3.0	-1.53×10^{-15}	-0.95×10^{-15}
4.0	-8.19×10^{-15}	-4.95×10^{-15}
5.0	-3.01×10^{-14}	-1.77×10^{-14}
6.0	-8.69×10^{-14}	-4.99×10^{-14}
7.0	-2.13×10^{-13}	-1.20×10^{-13}
8.0	-4.62×10^{-13}	-2.54×10^{-13}
9.0	-9.11×10^{-13}	-4.92×10^{-13}
10.0	-1.69×10^{-12}	-0.90×10^{-12}
30.0	-9.53×10^{-10}	-3.75×10^{-10}

Now we see that in the limit $D_i \gg 1$, the interaction energy is independent of the density difference between the fluid phases as well as the contact angle θ (or wetting characteristics of the particles). We also note from [43] that the sign of the interaction energy (attraction or repulsion) is controlled by the factors S_1 and S_2 and that the magnitude of the interaction varies inversely with the interfacial tension γ_{AB} . The degree of distortion of the interface by a particle will increase as γ_{AB} decreases and the depth of the gravitational well into which a second particle would fall will therefore increase. Hence the interaction energy would be expected to increase with decreasing γ_{AB} . However, [43] does not imply that the interaction energy is infinite at $\gamma_{AB} = 0$, for when γ_{AB} is sufficiently small, the assumption of *small* Bond numbers needed to derive [43] will break down. It must be remembered that [43] is valid only under the constraint of small Bond numbers.

Another interesting feature of the interaction energy between spheres [43] is the extreme sensitivity to particle size $\sim (R_1 R_2)^3$ whereas the size dependence of van der Waals or electrical double layer forces between colloidal particles ($\sim 1 \mu\text{m}$) is $\sim R_1 R_2 / (R_1 + R_2)$. This point is illustrated in the numerical results of Table I.

The distance dependence of the energy

also deserves comment. At large separations ($\lambda l \gg 1$), we use the large argument form [14] for the Bessel functions to rewrite [43] as

$$E(l) \approx - \frac{2\pi^{3/2}}{\gamma_{AB}} R_1^3 R_2^3 (\rho_B - \rho_A)^2 \times S_1 S_2 \frac{e^{-\lambda l}}{(2\lambda l)^{1/2}}, \quad \lambda l \gg 1. \quad [46]$$

The most striking feature of this result is the range of the interaction characterized by λ^{-1} . For the air-water interface ($\gamma_{AB} = 70 \text{ erg cm}^{-2}$, $(\rho_B - \rho_A) = 1 \text{ g cm}^{-3}$), $\lambda^{-1} = 0.27 \text{ cm}$. Therefore at separation of order λ^{-1} the capillary interaction will dominate all other interparticle forces. When the separation between the spheres is of the order of the sphere diameter, then $\lambda l \sim O(B^{1/2}) \ll 1$ and we can use the small argument formulas [12] and [13] to rewrite [43] as

$$E(l) = \frac{2\pi R_1^3 R_2^3}{\gamma_{AB}} (\rho_B - \rho_A)^2 S_1 S_2 \ln(\lambda l), \quad \lambda l \ll 1. \quad [47]$$

For separations in the colloidal regime, [47] is the appropriate limiting expression. We note the slow logarithmic dependence on particle separation.

For an appreciation of the magnitudes of the capillary interaction energy we tabulate $E(l)$ for *identical* spheres of varying sizes (density $\rho_s = 3.0 \text{ g cm}^{-3}$). The function S for $\rho_s = 3.0 \text{ g cm}^{-3}$ is relatively insensitive to the contact angle so all calculations were performed with $\theta = 60^\circ$, i.e., $S = 1.44$. The extreme sensitivity of the dependence of $E(l)$ on particle size may be noted from Table I.

A final result of interest is the time for two identical spheres to come together under the influence of capillary forces. Starting at rest from an initial separation l_0 and under the assumption that the system is inertially limited and that $\lambda l_0 \ll 1$ we have from [47]

$$F_H(l) = - \frac{\partial E(l)}{\partial l} = F_H(l_0) \left(\frac{l_0}{l} \right) \quad [48]$$

and from [41]

$$\frac{d^2l}{dt^2} = \frac{2l_0 F_H(l_0)}{m} \frac{1}{l} \quad [49]$$

Integrating this equation we get

$$t = \left[\frac{\pi m l_0}{4 |F_H(l_0)|} \right]^{1/2} \operatorname{erf} \left(\left(\ln \frac{l_0}{l} \right)^{1/2} \right) \quad [50]$$

For $l_0 \gg l$, the time is given by

$$t \approx \left[\frac{\pi m l_0}{4 |F_H(l_0)|} \right]^{1/2} \quad [51]$$

$$= \left[\frac{3\pi \rho_s \gamma_{AB} l_0^2}{8(\rho_s - \rho_A)^2 g^2 R^3} \right]^{1/2} \quad [52]$$

which is linear in the initial separation distance. For particles of radius 10 μm , density 3.0 g cm^{-3} , collected at the air-water interface at $l_0 = 100$ diameters apart, the time required for them to come into contact is of the order of 3 sec.

In conclusion, we note that the analysis in this paper contains the implicit assumption that the range of the interaction λ^{-1} is much smaller than the dimensions of the vessel holding the fluids. This is not a trivial point since for typical ranges of physical parameters λ^{-1} can be of the order of centimeters. At the singular limit $\lambda = 0$, which can come about if the densities of the fluid phases become equal, $\rho_A = \rho_B$, or in zero gravity, $g = 0$, the interaction will have infinite range. In this limit a proper analysis must take into account the total volume of each fluid phase as well as the shape, dimensions, and wetting characteristics of the vessel that holds the fluid.

APPENDIX: NOMENCLATURE

<i>B</i>	Bond number; subscripts: c, cylinder; s, sphere; 1, 2, bodies 1 or 2
<i>C_i</i>	cylinder constant, Eq. [32], for bodies <i>i</i> = 1, 2
<i>D</i>	density ratio, $D = (\rho_s - \rho_A)/$

	$(\rho_B - \rho_A)$; subscripts 1, 2, bodies 1 or 2
<i>g</i>	acceleration due to gravity
<i>h₁, h₂</i>	height of center of mass of bodies 1, 2 relative to horizon
<i>l</i>	horizontal separation between center of mass of bodies
<i>r</i>	radial coordinate
<i>r_c</i>	radius of contact circle
<i>R</i>	radius; subscripts: c, cylinder; s, sphere; 1, 2, bodies 1 or 2
<i>S_i</i>	sphere constant, Eq. [35], for bodies <i>i</i> = 1, 2
<i>t</i>	time
<i>x</i>	Cartesian coordinate
<i>x_c</i>	position of contact line
<i>z</i>	height of fluid interface relative to horizon
<i>z_c</i>	slope of fluid interface at contact line

Greek Symbols

γ_{AB}	interfacial tension of fluids A, B
ϕ_c	contact line position (see Fig. 1)
λ	$[(\rho_B - \rho_A)g/\gamma_{AB}]^{1/2}$
ρ_A, ρ_B, ρ_s	density of fluid, liquid, and solid, respectively
θ_i	contact angle at bodies <i>i</i> = 1, 2 measured through lower liquid phase

ACKNOWLEDGMENT

Joseph D. Henry, Jr. was on leave from the Department of Chemical Engineering at West Virginia University. We acknowledge his support by the United States-Australian Scientific Co-operative Exchange Program.

REFERENCES

- Nicolson, M. M., *Proc. Cambridge Philos. Soc.* **45**, 288 (1949).
- Gifford, W. A., and Scriven, L. E., *Chem. Eng. Sci.* **26**, 287 (1971).
- Dussan, V. E. B., *Annu. Rev. Fluid Mech.* **11**, 371 (1979).
- Abramowitz, M., and Stegun, I. A., (Eds.), in "Handbook of Mathematical Functions." Dover, New York, 1965.