J. Phys. Chem. A **2002,** *106,* 689−696

Influence of Dissolved Gas on van der Waals Forces between Bubbles and Particles

N. Mishchuk[†]

Institute of Colloid Chemistry and Chemistry of Water, The National Academy of Sciences,
pr.Vernadskogo, 42, Kyiv 03142, Ukraine

J. Ralston,[*,‡] **and D. Fornasiero**[‡]

Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus,
Mawson Lakes, Adelaide, SA 5095, Australia

Received: May 14, 2001; In Final Form: November 12, 2001

The presence of dissolved gas, in the form of very small bubbles in the aqueous phase between a solid particle interacting with a microbubble, and/or on the surface of the particle, modifies the van der Waals interaction forces. The change in the character of the latter appears similar to the action of hydrophobic forces. Neglecting these changes can lead to the incorrect interpretation of experimental data, in particular to the overestimation of the role of any hydrophobic attraction.

1. Introduction

Interparticle forces depend to a large extent on the homogeneity, smoothness, and purity of the surfaces of interacting particles. The purity and homogeneity of the bathing liquid in the gap between these particles is equally important. One factor that strongly affects interparticle interaction is the presence of very small bubbles of gas (vapor) in the liquid and/or on the surface of the particles. The shape, size and location of these bubbles and, consequently their influence on interparticle interaction depends on the history of their origin as well as the dynamics of particle movement. For example, very small bubbles of gas may be present on the surface of particles, nucleated by their hydrophobic surface and/or through the availability of surface microfissures. Very small bubbles can form due to the cavitation of liquid in the gap between hydrophobic particles,[1,2] or from the interplay between the electrical double layers of interacting macrobodies.[3−7] In real systems, the various mechanisms may appear practically simultaneously, thus the observed interaction of hydrophobic macrobodies depends in some general way on the different forms of gas. Because the size, quantity, and position of these very small bubbles is continuously variable, one can only deal with an "averaged" system.[8,9] Note that in a system in contact with the atmosphere, dissolved gas will inevitably be present in the aqueous phase. A small component may be hydrated, as in the case of carbon dioxide, whereas the remainder will be present as individual molecules and/or very small bubbles. The arguments that follow are couched in terms of very small bubbles. Reference is made to dissolved gas, in molecular form, where appropriate.

Any theoretical analysis of the influence of dissolved gas on either homo or heterocoagulation depends on the characteristic size of the bubbles. Analyses presented in different publications to date (e.g., refs 10−12 generally concern relatively large bridging bubbles, with a characteristic size of some microns).[10−12] In this present paper, we limit our investigation by dealing only with the opposite case of very small gas bubbles, *whose size is in the nanometer domain*.

Very small bubbles of gas present in the gap between or on the surface of particles affect all components of the interparticle interaction: electrostatic, van der Waals, structural (hydrophobic), and hydrodynamic. In this work, we shall consider only their influence on van der Waals forces and show that the change in the character of the van der Waals forces can correspond qualitatively to that of the hydrophobic interaction. The neglect of these changes can lead to the incorrect interpretation of experimental data, in particular to the overestimation of the role of any hydrophobic attraction.

The mechanism of formation of very small bubbles of gas, either in the liquid or on the surface of macrobodies is essentially a nonequilibrium problem. We therefore start with the case when these very small bubbles or gas layers on the surface of macrobodies are already formed and maintain some quasi-stationary position. Although the existence of very small gas bubbles affects the interaction between macrobodies (for example, the interaction of a macrobubble and solid particle under conditions of microflotation[6] or the Brownian coagulation of dispersed particles[7,11]), the exact form of this interaction depends on the nature of the particular macrobodies. In the present article we shall confine ourselves to the consideration of a solid spherical particle, in particular quartz, interacting with a macrobubble.

We shall choose five special cases that, qualitatively, reflect the possible ways in which interaction may occur. In turn, we have a macrobubble interacting with the following:

- a clean particle through a homogeneous liquid;
- a clean particle through an inhomogeneous liquid containing very small bubbles;
- a particle, covered with a thin, homogeneous surface layer of gas, through a homogeneous liquid;
- a particle, covered with a thin, inhomogeneous surface layer of gas, through a homogeneous liquid;

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[*] To whom correspondence should be addressed. E-mail: john.ralston@unisa.edu.au.

[†] Institute of Colloid Chemistry and Chemistry of Water, The National Academy of Sciences, pr.Vernadskogo, 42, Kyiv 03142, Ukraine. mis@carrier.kiev.ua.

[‡] Ian Wark Research Institute, University of South Australia, Mawson Lakes Campus.

10.1021/jp0118221 CCC: $22.00

- a particle in a homogeneous liquid, but with one very small bubble attached to the particle.

The purpose of the present paper is not the development of the precise theory of van der Waals forces for these rather complicated systems, but rather to describe the main features of their dependence on the existence and location of gas mixtures. Therefore, for each of the special cases described above, we define the conditions under which rather exact calculations can be carried out on the basis of the existing theory of van der Waals forces. As is seen below, the various approximations used allow us to determine all of the interesting limiting cases, i.e., to demonstrate the main trends in the van der Waals forces for different situations where dissolved gas may be present.

2. Analysis

2.1 Interaction of a Macrobubble and Clean Solid Particle through a Homogeneous Liquid. For simplification, the retardation and screening of van der Waals forces by electrolyte are neglected. In this case, the interaction between a clean solid surface and a macrobubble can be described by the well-known expression for short-range van der Waals forces[13]

$$F_{\mathrm{CS}} = -K\frac{A}{12\pi h^2} \tag{1}$$

where the subscript CS means “clean surface“, and the coefficient

$$K = \frac{2\pi R_0 a_{\mathrm{p}}}{R_0 + a_{\mathrm{p}}} \tag{2}$$

takes into account the spherical shape of macrobubble and particle. R_0 and a_{p} are the radii of macrobubble and particle respectively and

$$A = A_{\mathrm{W}} - \sqrt{A_{\mathrm{W}} A_{\mathrm{P}}} \tag{3}$$

is the Hamaker constant for particle/macrobubble interaction through an aqueous medium. A_{W} and A_{P} are the Hamaker constants for water and the particle, whereas h is the shortest distance between the surfaces of the macrobubble and particle.

2.2 Interaction of a Macrobubble and a Clean Solid Particle through a Liquid that Contains Very Small Bubbles. The existence of very small bubbles in the space between a macrobubble and a particle changes the dielectric properties of water and, consequently, should change the force of interaction between the macrobodies. In this instance, the interaction of very small bubbles with the macrobodies is insignificant (e.g., the solid surface is hydrophilic) and, due to Brownian motion, the very small bubbles are distributed in the liquid practically uniformly.

In this case, one might anticipate that the existence of these very small bubbles could increase the repulsion between the interacting solid particle and the macrobubble. It is known, from numerous calculations of Hamaker constants, that the interaction of macrobodies through a layer of air is stronger than through a liquid, in particular through water. For example, according to calculations by Rabinovich and Churaev,[14] the interaction between particles of quartz through a vacuum is approximately 12 times larger than through a layer of tetradecane, and 6 times larger than through a layer of water. A similar situation occurs for the interaction of unlike particles. For example, the interaction of gold and quartz in a vacuum is 3.75 times larger than when water is the medium.

We expect that the introduction into water of very small bubbles of gas with a dielectric permittivity practically the same as that of a vacuum will increase the interaction forces. Recalling that for particle/particle and particle/bubble interaction, the signs of the respective Hamaker constants are opposite, an increase in interaction forces in the first case means an increase in attraction, whereas in the second case there is an increase in repulsion. Thus, the existence of very small bubbles should result in an increase in homocoagulaton and a decrease in particle/bubble heterocoagulation. At first sight, our conclusion about the decrease in heterocoagulation contradicts experimental data for microflotation efficiency.[6] Actually, this is not inconsistent, for our supposition about a uniform distribution of very small bubbles in the gap between a bubble and particle is unlikely to be realized and, of course, the particle surface is “clean” in the case considered here (no hydrophobic layer). A more realistic distribution of gas will be discussed later. In this present section, the anticipated quantitative changes of interaction forces assuming a homogeneous distribution of very small bubbles in the liquid, will be determined.

The first necessary condition for the evaluation of interaction forces through an interlayer containing microscopic objects is the condition of homogeneity. The latter is connected with a limit on the dimension of the very small bubbles, the diameter of which $2a$ (where a is the radius), should be less than the distance between surfaces of macrobodies in the narrowest part of the gap, h

$$2a < h \tag{4}$$

In this case, a large number of very small bubbles may be located in a gap. Due to Brownian motion their distribution will be uniform and, in this sense, it is possible to consider the liquid as quasi-homogeneous.

Because any analysis of surface forces is usually of interest for spacing intervals from several up to some tens of nanometers, very small bubbles need to be about several nanometers or so in diameter. Where these tiny bubbles are larger, their number in the gap between a particle and a bubble will be very small. In this instance, interaction calculations have to be performed by treating the particle, small bubble and macrobubbles as separate objects.

The limit on the upper size of the very small bubbles is a necessary condition for using existing formulas for van der Waals forces. The homogeneity of the fluid is important not only in connection with this aspect, but also in relation to the electromagnetic waves that give rise to the van der Waals forces. Thus, a necessary condition for liquid homogeneity is that the bubble size must be small when compared with the wavelength of the electromagnetic radiation, where the latter is typical for the absorption spectrum of interacting bodies in a medium. When considering the role of characteristic distance in the theory of van der Waals forces, $\lambda/2\pi$,[15] this condition can be written as

$$2a \ll \lambda/2\pi \tag{5}$$

As shown by Krupp[16] as well as Ninham and Parsegian,[17] for a reasonably good description of van der Waals forces, it is sufficient to take into account dipole relaxation with a frequency $\omega \approx (10^{10} - 10^{11})$ rad/sec as well as resonance absorption in the infrared ($\omega \approx (10^{13} - 10^{14})$ rad/sec) and short-range ultraviolet ($\omega \approx 10^{16} rad$/sec) regions of the spectrum. The shortest wavelength, $\lambda = 2\pi c/\omega$ (where c is the rate of propagation of an electromagnetic wave), corresponds to the ultraviolet region of the spectrum and is equal to about 150−

200 nm. This means that the condition $2a \ll 30$ nm is satisfied, corresponding well with condition (4) regarding the size of the very small bubbles in comparison with the characteristic distance between the relevant macrobodies.

The van der Waals forces are connected to the dielectric dispersion of macrobodies and the layer of intervening liquid. Calculation of these forces can be performed using eq 1, where the Hamaker constant for a liquid interlayer with a high dielectric permittivity can be obtained from[13,17]

$$A = \frac{3\hbar}{4\pi}\int_0^\infty \frac{(\epsilon_1(i\omega) - \epsilon_3(i\omega))(\epsilon_2(i\omega) - \epsilon_3(i\omega))}{(\epsilon_1(i\omega) + \epsilon_3(i\omega))(\epsilon_2(i\omega) + \epsilon_3(i\omega))}d\omega - \frac{3}{4}kT\frac{(\epsilon_{10} - \epsilon_{30})(\epsilon_{20} - \epsilon_{30})}{(\epsilon_{10} + \epsilon_{30})(\epsilon_{20} + \epsilon_{30})} \quad (6)$$

where $\hbar$ is Planck's constant, $\epsilon_i(i\omega)$ is the dielectric permittivity at an imaginary frequency $i\omega$ for the macrobodies (i = 1,2) and liquid interlayer (i = 3), ϵ_{i0} is the static dielectric permittivitiy in the limiting case of zero frequency, k is Boltzmann's constant, and T is the temperature. For calculations of the Hamaker constant in the absence of very small bubbles it is possible to use known data[13] concerning the dielectric dispersion for water and quartz, $\epsilon_i(i\omega)$ and to use the dielectric permittivity of air, $\epsilon_2(i\omega) = 1$.

For analysis of the change in the interaction force caused by the presence of microbubbles, we use the primary concept of the so-called adsorptive component of van der Waals forces. This takes into account changes in the properties of the medium caused by the presence of macromolecules in the liquid. Mixtures can be taken into account by the introduction of an additional component of complex dielectric permittivity[18,19]

$$\epsilon_3^*(i\omega) = \epsilon_3(i\omega) + \Delta\epsilon_3(i\omega) \quad (7)$$

where first term, $\epsilon_3(i\omega)$ is the dielectric permittivity of the pure liquid, whereas the second term is the change in dielectric permittivity caused by the macromolecules.

The theory of dielectric dispersion predicts,[20,21] that in a high-frequency electromagnetic field, the variation of the dielectric permittivity of a liquid, $\Delta\epsilon_3$, caused by a small quantity of spherical particles with dielectric permittivity ϵ^* is a linear function of the relative bulk concentration, v

$$\Delta\epsilon_3 = 3v\,\epsilon_3\frac{\epsilon^* - \epsilon_3}{\epsilon^* + 2\epsilon_3} \quad (8)$$

In particular, this expression was used[22] for an analysis of the adsorptive component of the van der Waals forces. In our investigation, it is important that eq 8 is correct for every possible size distribution of spherical particles. In the limiting case of individual dissolved gas molecules, the "bubble radius" will be that of a molecule. We take the dielectric permittivity of the gas to be independent of the bubble radius and, as a first approximation, neglect any possible deviation caused by the molecular form of the gas.

On the basis of eqs 7 and 8, the dielectric permittivity of a liquid containing very small bubbles can be presented as

$$\epsilon_3^*(i\omega) = \epsilon_3(i\omega)\left(1 + 3v\frac{1 - \epsilon_3(i\omega)}{1 + 2\epsilon_3(i\omega)}\right) \quad (9)$$

where the dielectric permittivity of the gas present in the very small bubbles is taken as $\epsilon^* = 1$ at every possible frequency. In the limiting case of zero frequency, it follows from eq 9 that the static dielectric permittivity can be represented as

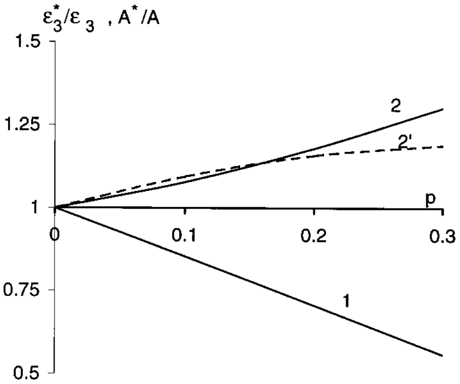

Figure 1. Changes in the dielectric permittivity of water (curve 1) and the Hamaker constant for quartz/quartz (curve 2) and quartz/air (curve 2′) interactions, caused by the presence of tiny gas bubbles with volume fraction α.

$$\epsilon_{30}^* = \epsilon_{30}\left(1 + 3v\frac{1 - \epsilon_{30}}{1 + 2\epsilon_{30}}\right) \quad (10)$$

Thus, the required Hamaker constant for the interaction between two macrobodies through a liquid interlayer in the presence of very small bubbles can be calculated on the basis of eq 6, in which $\epsilon_3(i\omega)$ is replaced by $\epsilon_3^*(i\omega)$ and ϵ_{30} by ϵ_{30}^* eq 13. We then obtain a correlation between the Hamaker constants, $A^*/A = A(\epsilon_3^*)/A(\epsilon_3)$, that is sufficient for describing the change in interaction forces.

The results of the calculation are shown in Figure 1 (curve 1 for ϵ_3^*/ϵ_3, curve 2 (particle/particle) and curve 2′ (particle/macrobubble) for A^*/A). The calculations are restricted by an upper limit on the volume fraction of very small bubbles in the liquid (0.05). There are various causes for this limit: at a larger volume fraction, the accuracy of eq 10 decreases and condition 5 specifying noninterference of the electromagnetic wave by the homogeneous fluid will not be valid at high volume fraction because of the complicated configuration of interbubble space.

In the case of identical dispersed particles, or rather small disperse particles near the surface of a large bubble under conditions of flotation, the efficiency of homo or heterocoagulation is connected to the stability coefficient W (e.g., ref 23). The latter depends exponentially on the height of the energy barrier $V_{\max} = V_W + V_E$. Here, V_W is the van der Waals energy, and V_E is the electrostatic energy in the region of energy barrier. It can be shown that even a 10−20% increase in the van der Waals energy can lead to considerable acceleration of coagulation. For example, $V_{\max} = 2kT$ is the sum of $V_W = -5KT$ and $V_E = 7KT$. For a 20% increase in the absolute value of van der Waals energy, V_W, the energy becomes equal to $V_{\max}^* = kT$, leading to an increase in W by almost a factor of 3: $W/W^* = \exp(V_{\max} - V_{\max}^*) = e \approx 2.7$.

In the case of large disperse particles of different sizes, which sediment with different velocities, or in the case of a macrobubble and such a particle, that move toward one another under microflotation conditions, the pressing hydrodynamic force is dominant.[24,25] Therefore, a 10−20% increase in repulsion will not strongly reduce the efficiency of heterocoagulation. In the case of particles that are genuinely in the colloid domain, either interacting with themselves or with a macrobubble, the effect of the Hamaker constant modification will be more pronounced. There is a decrease in aggregation efficiency in this system, instead of the increase observed for identical macrobodies.

One should also recognize that due to the large Laplace pressure, $P_L = 2\gamma/r$ (where γ is the surface tension, and r is the radius of the very small bubble), very small bubbles preserve their spherical shape, an important condition in terms of the accuracy of eq 10. However, due to the large Laplace pressure, the density of the gas in each bubble and its dielectric permittivity are larger than under atmospheric pressure. Moreover, these very small bubbles have to contain some quantity of liquid vapor, which also results in an increase in dielectric permittivity. The net effect is to change the results presented in Figure 1 and the influence of dissolved gas will be somewhat reduced.

2.3 Interaction of a Macrobubble and a Particle with a Thin Homogeneous Surface Layer of Gas through a Homogeneous Liquid. Another limiting case, indeed an extreme example, for the presence of dissolved gas is its localization on the surface of a solid particle and its absence in the liquid. This gas which appears on the surface of a particle is present there due to the poor wetting of the surface/or the existence of microfissures on it. There are some similarities in this behavior to the adsorption of gases onto solid surfaces[37] and at the aqueous solution-air interface.[42]

The analysis of the interaction between a macrobubble and a particle covered by layer of gas can readily be achieved using the well-known theory of van der Waals forces modified by the presence of adsorbed layers.[26−28] All versions of the theory give almost identical results when calculations are performed.

Differentiating the expression for the energy of interparticle interaction[25] and taking the Hamaker constant for the macrobubble interacting with the layer of air as zero, the required interaction force is

$$F_{GL} = -\frac{1}{12}[A_W F_1 - \sqrt{A_W A_P} F_2] \tag{11}$$

where F_{GL} refers to the force between the gas-covered particle and the macrobubble and

$$F_{1,2} = \left[\frac{y}{(x^2+xy+x)^2} + \frac{y}{(x^2+xy+x+y)^2} + \frac{2}{x^2+xy+x} + \frac{2}{x^2+xy+x+y}\right](2x+y+1)\frac{dx}{dh^*} \tag{12}$$

where x, y, and dx/dh^*, used in F_1 and F_2, are in the following form

$$\text{for } F_1\text{:}\quad x = \frac{h^*}{2(a_p+H)};\; y = \frac{R_0}{a_p+H};\; \frac{dx}{dh^*} = \frac{1}{2(a_p+H)} \tag{13}$$

$$\text{for } F_2\text{:}\quad x = \frac{h^*+H}{2a_p};\; y = \frac{R_0}{a_p};\; \frac{dx}{dh^*} = \frac{1}{2a_p} \tag{14}$$

where $h^* = h - H$ is the distance between the surfaces of a macrobubble and the external boundary of the adhering air layer, where the latter has thickness H.

For a comparison between the forces in eqs 1 and 11, it is necessary to simplify expression 11. The most relevant conditions for the parameters are $y \gg 1$, $x \ll 1$ and $xy \ll 1$, thus the expressions $F_{1,2}$ can be simplified to

$$F_{1,2} \approx \left[\frac{1}{yx^2} + \frac{1}{y} + \frac{2}{xy} + \frac{2}{y}\right]\frac{y\,dx}{dh^*} \approx \frac{dx}{x^2 dh^*} \tag{15}$$

As a result, F_{GL} in eq 11 can be presented in the form

$$F_{GL}(h) = -\frac{a_p}{6}\left[\frac{A_W}{h^{*2}} - \frac{\sqrt{A_W A_P}}{(h^*+H)^2}\right] = -\frac{a_p}{6}\left[\frac{A_W}{(h-H)^2} - \frac{\sqrt{A_W A_P}}{h^2}\right] \tag{16}$$

At $H = 0$ the force $F_{GL}(h)$ has the same expression as the force between a clean particle and a macrobubble (F_{CS} in eq 1).

Since it is usual for $A_P > A_W$ (refs 17, 18) at short distances the first term in eq 16 is larger than the second one. As a result, the force $F_{GL}(h)$ is attractive. At a certain distance

$$h_{0,GL}{}^* = -H\frac{A_W}{A}\left[1 + \sqrt{1 - \frac{A}{A_W}}\right] \text{ or } h_{0,GL} = H\left(1 - \frac{A_W}{A}\left[1 + \sqrt{1 - \frac{A}{A_W}}\right]\right) \tag{17}$$

both components of the force $F_{1,2}$ are equal in magnitude but opposite in sign and the force, $F_{GL}(h = h_{0,GL})$ equals zero. At larger distances $h > h_{0,GL}$ the second term prevails and the force $F_{GL}(h)$ becomes repulsive.

Under the condition where $dF_{GL}(h^*)/dh^* = 0$, the force takes its maximum value. This condition can be rewritten as

$$\frac{\sqrt{A_P/A_W}}{(h^*+H)^3} - \frac{1}{h^{*3}} = 0 \tag{18}$$

the solution of which is

$$h_{\max,GL}{}^* = \frac{H}{\sqrt[3]{(A_P/A_W)^{1/2}} - 1} \text{ or } h_{\max,GL} = H\left(1 + \frac{1}{\sqrt[3]{(A_P/A_W)^{1/2}} - 1}\right) \tag{19}$$

and describes the coordinate of the maximum.

One can therefore see that for both coordinates h_0^* and $h_{\max}^*$, the distance between them is a linear function of the thickness of the gas layer, H, and strongly depends on the correlation between A_P and A_W.

Figure 2 shows the results of calculations of van der Waals forces for particles with a clean surface (curve 1) and with a layer of air of thickness H (curves 2−4). At a certain distance between the macrobubble and the particle, the van der Waals force for the particle with a layer of air changes its sign. The coordinate of this change is equal to $h_{0,GL} = h_{0,GL}^* + H$, where $h_{0,GL}^*$ is calculated according to eq 17.

Figure 2 demonstrates that the change of force from a positive value to a negative one takes place over a rather short distance. Therefore, in the measurement of force between a macrobubble and a particle, this change can appear as a jump. Because the air layer is “invisible” in such a measurement, the coordinate of the jump is counted *from the particle surface* and hence lies between $h_{0,GL}$ and $h_{\max,GL}$.

Let us compare the results of calculations of F_{GL} with those for the hydrophobic force, typically presented as an exponential function[30]

$$F^{ph} = -KC_{ph}e^{-h/D_{ph}} \tag{20}$$

or as the sum of two exponential functions[31]

$$F^{ph} = -K(C_{ph}^1 e^{-h/D_{ph}^1} + C_{ph}^2 e^{-h/D_{ph}^2}) \tag{21}$$

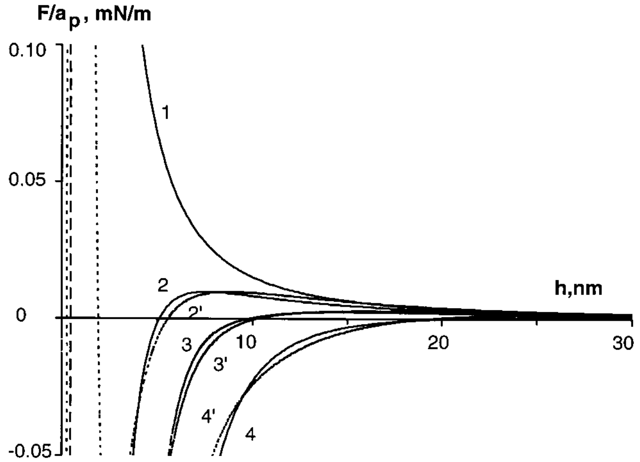

Figure 2. van der Waals forces for particle/bubble interaction as a function of particle-macrobubble distance and gas layer thickness: 0 nm (curve 1), 0.5 nm (curve 2), 1 nm (curve 3), 2 nm (curve 4) and the sum of van der Waals and hydrophobic forces for a clean "gas free" particle − $C^1_{\text{ph}} = 5 \times 10^{-5}$ J/m^2, $D^1_{\text{ph}} = 2.6$ nm, $C^2_{\text{ph}} = 4 \times 10^{-4}$ J/m^2, $D^2_{\text{ph}} = 1.05$ nm (curve 2′); $C^1_{\text{ph}} = 3 \times 10^{-5}$ J/m^2, $D^1_{\text{ph}} = 4.0$ nm, $C^2_{\text{ph}} = 2 \times 10^{-3}$ J/m^2, $D^2_{\text{ph}} = 1.05$ nm (curve 3′); $C^1_{\text{ph}} = 7 \times 10^{-5}$ J/m^2, $D^1_{\text{ph}} = 4.2$ nm, $C^2_{\text{ph}} = 4 \times 10^{-3}$ J/m^2, $D^2_{\text{ph}} = 1.05$ nm (curve 4′); $a_{\text{p}} = 35 \mu m$; $R_0 = 0.5$ mm; $A = -1 \times 10^{-20}$ J; $A_{\text{W}} = 4.38 \times 10^{-20}$ J; $A_{\text{p}} = 6.6 \times 10^{-20}$ J.

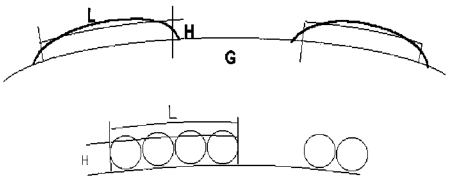

Figure 3. Schematic representation of a particle coated (a) with segments of gas (a) and (b) with group of tiny gas bubbles.

where C_{ph} and $C^{1,2}_{\text{ph}}$ are the amplitudes of the hydrophobic force for the solid surface/macrobubble interaction, whereas D_{ph} and $D^{1,2}_{\text{ph}}$ are the corresponding decay lengths.

The results of calculations of the van der Waals force for a particle without a layer of air (eq 1) to which the hydrophobic force (eq 21) is added for a specific set of parameters are shown in Figure 2 (curves 2′−4′). The amplitudes and decay lengths of the hydrophobic force were chosen to yield curves that appear similar to curves 2−4, calculated *exclusively* for van der Waals forces. The amplitudes and decay lengths fall within the range of values observed experimentally for particle−particle and particle-bubble interactions [e.g., refs 30−34].

We observe that the curves practically coincide. In experimental measurements of interparticle forces, it is possible that, without an appropriate analysis of van der Waals forces, the observed "jump into contact" may be incorrectly attributed to hydrophobicity.

2.4 Interaction of a Macrobubble and Particle with a Thin Nonhomogeneous Surface Layer of Gas through a Homogeneous Liquid. At present, let us suppose that very small bubbles take a certain quasi-stable position and size. The debate over the possible existence of very small bubbles and their stability is dealt with elsewhere [e.g., refs 5, 8, 9].

The model for a nonhomogeneous layer of air can be developed with certain assumptions. We suppose that the very small bubbles form a flat segment (Figure 3a)[38,43] or, alternatively, a dense group of spherical very small bubbles (Figure 3b)[39,40] with an average thickness *H*, distance between segments *G* and the length of each segment or group of very small bubbles *L*. We also assume that the thickness of the tiny bubble segments *H* (or the diameters of all spherical very small bubbles) are very similar. These two variations of the distribution of gas adsorption on the particle surface show, qualitatively, two limiting cases for hydrophobic and hydrophilic surfaces interacting with a macrobubble.

The mathematical description of the interaction can be simplified if the characteristic dimensions *G* and *L* along the particle surface are considerably larger than the dimension *H* in the direction perpendicular to the particle surface

$$G \gg H \text{ and } L \gg H \tag{22}$$

and larger than the characteristic distance for the electromagnetic wave $\lambda/2\pi$ for the van der Waals interaction

$$G \gg \lambda/2\pi \text{ and } L \gg \lambda/2\pi \tag{23}$$

The conditions stipulated in 22 allow us to investigate the interaction between separate segments of gas and a macrobubble, as well as between a clean surface of particle and a macrobubble, as two independent interactions. This permits us to neglect the deviation from this interaction in the relatively small transition region between the segment and the clean surface. The conditions given in 23 allow us to suppose that the electromagnetic wave cannot move around the gas segments nor around empty places on the particle surface. Thus, in the first approximation, we can describe the interaction between a particle and a macrobubble as the sum of the interactions between a clean particle and a macrobubble and between a particle with layer of air and a macrobubble. This approximation is rather primitive, nevertheless it allows us to identify the main contribution of the influence of either gas segments or a dense group or cluster of very small bubbles on the particle/macrobubble interaction.

Because the thickness of the gas layer *H* cannot be too large, the conditions specified in 23 are stronger than those in 22.

With these restrictions of conditions 22 and 23 in mind, the choice of specific values of *L* and *G* for different flat segments or groups of spherical very small bubbles is not important. Therefore the interaction can be described by the surface force F_{s} where

$$F_{\text{S}} = F_{\text{SG}} + F_{\text{CS}} \tag{24}$$

where $F_{\text{SG}} = F_{\text{SG}}\ (h, H, S_{\text{SG}})$ and $F_{\text{CS}} = F_{\text{CS}}\ (h, S_{\text{CS}})$ take into account the interaction between a macrobubble and segments of gas (SG) and between a macrobubble and a clean surface (CS) of the solid particle. S_{CS} is the area of a clean particle surface, S_{GS} is the area of a particle surface covered by gas segments.

Both components of the force can be calculated as usual, apart from the additional coefficients which must take into account the relative area of clean surface, αCS and gas-covered surface, α_{SG} where

$$\alpha_{\text{SG}} = \alpha = S_{\text{SG}}/S \text{ and } \alpha_{\text{CS}} = 1 - \alpha = S_{\text{CS}}/S \tag{25}$$

and *S* is the total area of particle surface.

As shown above, the presence of the gas layer changes the sign of the van der Waals force. Therefore, at a certain distance between a particle and a macrobubble, F_{SG} and F_{CS} could not only have different values, but also different signs. If very small bubbles or segments of gas cover all (or most) parts of the region of particle/macrobubble contact, the interaction force will be close to F_{GL} (eq 11). In the opposite case the interaction force will be close to F_{CS} (eq 1).

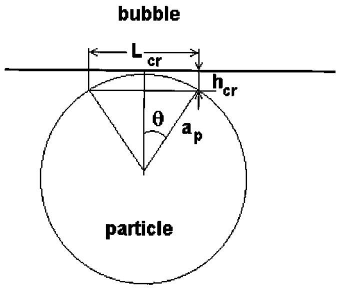

Figure 4. Schematic representation of gas macrobubble and particle.

However, eq 24 cannot readily be used to describe the case of very large L or very large G when, *in the contact region*, *either* only the gas segment/dense group of very small bubbles *or* only a clean surface occurs. Thus, it is necessary to introduce the additional conditions

$$G \ll L_{cr} \text{ and } L \ll L_{cr} \tag{26}$$

where L_{cr} is a certain critical value, which can be evaluated by analysis of the effective area of particle/macrobubble interaction. Analysis of van der Waals and electrostatic forces between two surfaces shows that strong interaction generally occurs at distances $h < h_{cr} = 5-25$ nm (e.g., 13). Taking into account the curvature of the particle surface and neglecting the curvature of macrobubble (the radius of macrobubble $R_0 \gg a_p$) we can evaluate the linear size of the region of interaction L_{cr}. On the basis of Figure 4 and the related geometry, the value of L_{cr} can be expressed through a_p and h_{cr} as

$$L_{cr} = \sqrt{8a_p h_{cr} - 4h^2_{cr}} \approx \sqrt{8a_p h_{cr}} \tag{27}$$

if second-order terms in h_{cr} are neglected. For example, for $a_p = 35\mu$m, used for the calculations presented in Figure 2, with $h_{cr} = 5$ nm and 30 the critical size of the gas segment L_{cr} equals 1200 and 2900 nm. Thus, the conditions specified in (26) are realized if the values of L and G are about 200−300 nm and 500−700 nm, respectively.

On the basis of the above analysis, one concludes that the model of interaction between a macrobubble and a particle covered by gas segments can be developed only for intermediate values of the parameter α because the limiting cases $\alpha \rightarrow 0$ and $\alpha \rightarrow 1$ do not satisfy the conditions (23) and (26) simultaneously. For example, at $\alpha \rightarrow 1$ it is impossible to satisfy condition (26) for the characteristic size of gas segments $G \ll L_{cr}$ and the condition (23) for characteristic size of clean segments $L \gg \lambda/2\pi$. On the other hand, at $\alpha \rightarrow 0$ it is impossible to satisfy the conditions $G \gg \lambda/2\pi$ and $L \ll L_{cr}$. Thus, our theoretical model can only be used for $0.3 \le \alpha \le 0.7$.

van der Waals forces between a macrobubble and a clean solid surface can be described by eq 1 with the coefficient $1 - \alpha$

$$F_{CS} = -(1-\alpha)K\frac{A}{12\pi h^2} \tag{28}$$

and between a macrobubble and segments of gas on the particle surface by eq 11 with coefficient α

$$F_{SG} = -\alpha\frac{1}{12}[A_W F_1 - \sqrt{A_W A_P} F_2] \tag{29}$$

where the functions $F_{1,2}$ are described by eq 12, or with the approximations $y \gg 1$, $x \ll 1$ and $xy \ll 1$ by eq 16

$$F_{SG} = -\alpha\frac{a_p}{6}\left[\frac{A_W}{h^{*2}} - \frac{\sqrt{A_W A_P}}{(h^* + H)^2}\right] = -\frac{a_p}{6}\alpha\left[\frac{A_W}{(h-H)^2} - \frac{\sqrt{A_W A_P}}{h^2}\right] \tag{30}$$

The most interesting case is related to the possibility of finding parameters for the region where repulsion is changed to attraction. This means that it is necessary to analyze the conditions $F_{SG} < 0$ and $|F_{SG}| > |F_{CS}|$. As shown above, the gas layer causes an attraction at small distances from its surface, $h^* < h_0$. Thus, we have to find a critical distance $h_{0,SG}$ that satisfies the condition $|F_{SG}| = |F_{CS}|$. Considering eqs 28 and 30 and a simplified version of eq 2, $K \approx 2\pi a_p$ ($R_0 \gg a_p$), this specific condition can be rewritten as the algebraic equation

$$-\alpha\left[\frac{A_W}{(h_o - H)^2} - \frac{\sqrt{A_W A_P}}{h_o^2}\right] = (1-\alpha)\frac{A}{h_o^2} \tag{31}$$

the solution of which is

$$h_{0,SG} = -H\left(1 - \alpha\frac{A_W}{A}\right)\left(1 + \sqrt{\frac{\alpha A_W}{A - \alpha A_W}}\right) \tag{32}$$

In the limiting case $\alpha = 1$ this solution gives the same value as expression (17), describing the gas layer $h_{0,GL}$.

Calculations were performed for a fixed value of the parameter $\alpha = 0.5$, different thicknesses of the gas segments H (Figure 5), and for two fixed thicknesses of gas segments H and different values of the parameter α (Figure 6). One can see that with increasing H and α, the attraction between the particle and the macrobubble increases. As in Figure 2, we found that the amplitude and decay length of the hydrophobic force, when combined with the van der Waals force for a clean particle (curves 2′−7′) gives approximately the same behavior as curves 2−7 for the particle, when the latter is covered by segments of gas. Increasing the parameter α demonstrates the transition from the particle without gas segments to a particle covered by an homogeneous layer of air.

This theoretical analysis was performed neglecting the deformation of the gas segment or the very small bubbles.[35] We propose that deformation is important only at short distances between the macrobubble and the gas segments on the particle surface, appearing only after the force barrier is overcome and the minimum reached. This approximation appears sound because due to the large Laplace pressure, the possibility of deformation of the very small bubbles is rather small.

2.5 Interaction of a Macrobubble and Particle in the Presence of a "Bridge" Formed by a Very Small Bubble. In this instance, we analyze the interaction of a macrobubble and particle with a very small bubble fixed on the particle surface. The size of the very small bubble results in a significant distance between the macrobubble and the clean particle surface, at which the van der Waals forces are already rather insignificant (e.g., a very small bubble represented as a hemisphere with a radius of 30 nm). In this case, the interaction between the macrobubble and "particle" is readily defined by the interaction between a macrobubble and a very small bubble. This results in an attraction between the "particle" and the macrobubble over a distance that is practically equal to the radius of the very small bubble (see curve 2 in Figure 7). As in Section 4, the deformation of the very small bubble is neglected.

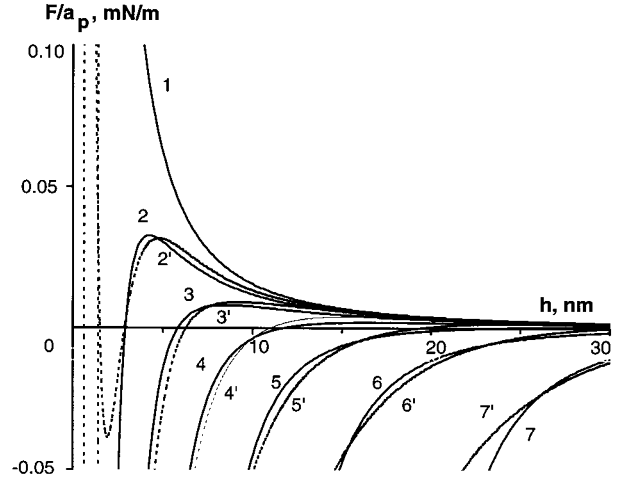

Figure 5. van der Waals forces for particle/bubble interaction in the presence of gas segments ($\alpha = 0.5$) with thickness of: 0 nm (curve 1), 1 nm (curve 2), 2 nm (curve 3), 4 nm (curve 4), 8 nm (curve 5), 16 nm (curve 6) and the sum of van der Waals and hydrophobic forces for a clean "gas free" particle − $C^1_{ph} = 1 \times 10^{-4}$ J/m^2, $D^1_{ph} = 3.0$ nm, $C^2_{ph} = 5 \times 10^{-4}$ J/m^2, $D^2_{ph} = 1.0$ nm (curve 2′); $C^1_{ph} = 5 \times 10^{-5}$ J/m^2, $D^1_{ph} = 2.6$ nm, $C^2_{ph} = 1.2 \times 10^{-3}$ J/m^2, $D^2_{ph} = 1.0$ nm (curve 3′); $C^1_{ph} = 1 \times 10^{-4}$ J/m^2, $D^1_{ph} = 2.8$ nm, $C^2_{ph} = 1 \times 10^{-3}$ J/m^2, $D^2_{ph} = 1.3$ nm (curve 4′); $C^1_{ph} = 1 \times 10^{-4}$ J/m^2, $D^1_{ph} = 3.8$ nm, $C^2_{ph} = 4 \times 10^{-4}$ J/m^2, $D^2_{ph} = 2.0$ nm (curve 5′); $C^1_{ph} = 2.5 \times 10^{-4}$ J/m^2, $D^1_{ph} = 4.5$ nm, $C^2_{ph} = 8 \times 10^{-4}$ J/m^2, $D^2_{ph} = 1.0$ nm (curve 6′); $C^1_{ph} = 2.5 \times 10^{-4}$ J/m^2, $D^1_{ph} = 6.2$ nm, $C^2_{ph} = 4 \times 10^{-4}$ J/m^2, $D^2_{ph} = 2.0$ nm (curve 7′).

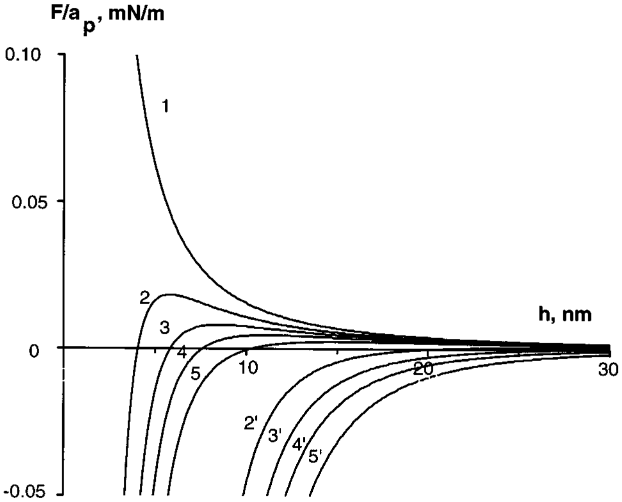

Figure 6. van der Waals forces for particle/bubble interaction without gas (curve 1), in the presence of gas segments with thickness of: 1 nm (curve 2−4) and 5 nm (curve 2′−4′) and in the presence of homogeneous layer of gas (curve 5 and 5′ with thicknesses 1 and 5 nm, respectively). Curves 2,2′ − $\alpha = 0.3$; curves 3,3′ − $\alpha = 0.5$ and curves 4,4′ − $\alpha = 0.7$.

To compare these interaction forces we show, in Figure 7, curve 3, calculated for the interaction of a particle coated by a homogeneous gas layer of the same thickness (30 nm). In this case, the attraction between a particle and macrobubble occurs through a set of very small bubbles, rather than just through one very small bubble. Naturally, the magnitude of the attractive force between the macrobodies increases. Curve 4, calculated for a particle coated by a continuous gas layer of the same thickness, shows a further increase in attraction.

The limiting case of such interaction is the interaction of a microbubble and "particle" that is formed by gas (without a solid core). In this case, the Hamaker constant changes its sign, and the van der Waals forces between the macrobubble and particle are attractive (curve 5). A gas layer of thickness 30 nm practically screens the field of a solid particle core (curve 4), therefore curves 4 and 5 almost coincide.

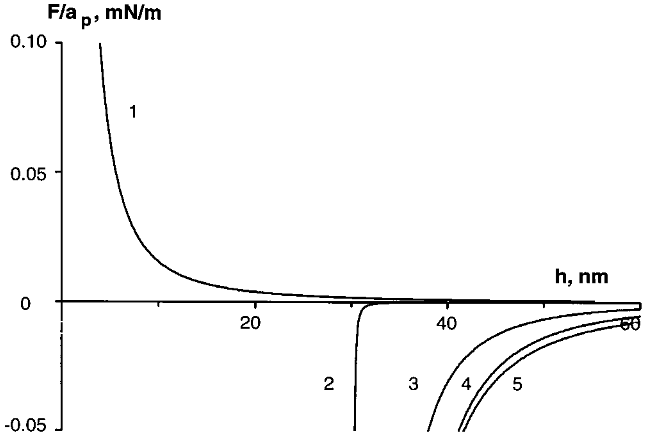

Figure 7. van der Waals forces for particle/bubble interaction without gas (curve 1), in the presence of a bridging gas bubble (hemisphere) with radius 30 nm (curve 2), in the presence of a layer of gas segments with thickness 30 nm and $\alpha = 0.5$ (curve 3), in the presence of a homogeneous layer of gas with thickness 30 nm (curve 4) and in the case when a particle is replaced by an air bubble (curve 5).

We note that the trends, magnitude and distance of action of the F/a_p versus h data are consistent with existing measurements of small hydrophobic particle-macrobubble interactions, specifically in connection with the attractive component of this interaction.[34,41,44]

3. Discussion

We have dealt with some general trends in the influence of dissolved gas on the van der Waals interaction forces between a particle and a macrobubble. Our analysis has shown that the presence of gas can lead to an increase in repulsion between macrobodies, or to the appearance of an attraction that, in many respects, appears similar to the action of hydrophobic forces.

The real situation is more complicated, because of the intrinsic instability of very small bubbles *and* because these bubbles may exist in the liquid between macrobodies and on their surfaces simultaneously. The real size and shape of very small bubbles or segments and their distribution on the particle surface may be quite different and change with time, behavior that can clearly have a strong influence on the van der Waals forces. The modeling of such a complicated situation requires a special, separate theoretical study.

There is also another open question. All of our conclusions were related to the possibility of heterocoagulation. However, the presence of very small bubbles can influence the rupture of the liquid film between a macrobubble and a particle. The heterogeneity of a film, owing to the presence of very small bubbles, and, especially, the capacity of small bubbles to implode with the ejection of a large amount of energy (the Laplace pressure in very small bubbles is many times greater than atmospheric pressure) should promote the rupture of the thin liquid film between a macrobubble and particle.[36] However, this rupture process occurs by a completely different mechanism than for an homogeneous film or for a film containing a stable dispersion of small particles. The appearance and disappearance of very small bubbles can thus dramatically vary the stability of a thin film between macrobodies.

The dissolution of gas promotes this process, because, in this case, cavitation and other mechanisms of bubble formation are enhanced. Thus, one expects that the influence of very small gas bubbles on thin film rupture should be essentially stronger than the influence of small disperse particles[26] because the presence of solid particles in a film of water is generally not accompanied by local pressure drops and fluid flows. The latter can also cause "jumps" in the measurement of interparticle interaction forces.

Acknowledgment. Financial support from the Australian Research Council, through the Special Research Centre scheme, is gratefully acknowledged by J. Ralston and D. Fornasiero.

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