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## **STUDY OF PARTICLE – BUBBLE INTERACTION USING ATOMIC FORCE MICROSCOPY – CURRENT POSSIBILITIES AND CHALLENGES**

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Study of interaction forces between mineral particles and air bubbles is a key to understanding flotation processes. Measurement of such interaction forces has only recently been made possible with the introduction of the atomic force microscope (AFM) and the colloidal probe technique. Using AFM, interactions between a single particle attached to the AFM cantilever and an air bubble placed on a flat hydrophobic surface are measured in an aqueous environment. Interaction forces prior to rupture of the interfacial water film as a function of the hydrophobic surface state can be established, as shown in the present study. Additionally, the effect of the hydrodynamic force between approaching air bubble and particle is quantified. Despite the great potential of the AFM colloidal probe technique for studying particle – bubble interactions, several challenges pertaining to the AFM design, experimental procedure, and data analysis have to be addressed due to deformation of the air-water interface. For example, such issues as the range of the piezoelectric translator and cantilever deflection, determination of the bubble spring constant, and identification of the point of contact between bubble and particle are now under consideration.

*Key words: particle – bubble interaction, Atomic Force Microscopy (AFM), hydrophobic force, contact angle, hydrodynamic force*

### **INTRODUCTION**

Flotation is an important separation process used for the recovery of billions of tons of valuable minerals (Fuerstenau and Herrera-Urbina, 1989), for the recycling of paper and plastic (Drelich and Miller, 2001; Shen et al., 2002) and for the treatment of

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wastewater (Ramirez and Johnson, 1980; Odegaard, 2001). This complex process includes many physicochemical and hydrodynamic phenomena in a dynamic system composed from solid particles, air bubbles, and aqueous solutions of various chemicals. Although many of these phenomena have been successfully studied in the past and significant practical as well as fundamental knowledge has been gained, a complete understanding is still not developed. The particle – bubble interactions, leading to attachment are a key to flotation and have received much attention (Lekki and Laskowski, 1976; Chiang, 1983; Alekseev, 1991; Luttrell and Yoon, 1992; Yoon, 1992). It has been realized that these interactions are composed from DLVO forces, non-DLVO interactions and a hydrodynamic component. (Yoon, 1992; Skvarla and Kmet, 1993; Yoon and Mao, 1996; Yoon, 2000). In this view, a significant effort has been made to characterize such interaction forces by establishing Hamaker constants for mineral particles (Lins et al., 1995), and zeta potentials for both air bubbles (Laskowski et al., 1989) and mineral particles (Drzymala and Laskowski, 1980). However, in order to account for all the components in the system the direct measurement of the interaction force between a particle and an air bubble is necessary.

Although the direct force measurements have been possible for some time using the Surface Force Apparatus (SFA) (Israelachvili and Tabor, 1972; Derjaguin et al., 1978), only development of the Atomic Force Microscope (AFM) (Binnig et al., 1986) and the colloidal probe technique (Ducker et al., 1991) has made it possible to study interaction forces between a single particle of choice and a selected surface.

Using this method a single particle with diameter from 1 to 100  $\mu\text{m}$  is attached to the AFM cantilever and is moved toward the surface using a piezoelectric translator. During this movement the deflection of the cantilever is recorded by means of a reflected laser beam which serves as an optical lever. Using this data the profile of interaction force as a function of distance between the particle and the surface is obtained. Additionally, after contact, during retraction of the cantilever from the surface, the adhesion force between particle and surface can be measured.

This setup has been successfully used in the study of interaction forces between particles and solid surfaces, particularly in systems closely related to mineral processing (Rabinovich and Yoon, 1994; Biggs and Proud, 1997; Pazhianur and Yoon, 1997; Yoon et al., 1997; Toikka et al., 1998; Yoon and Pazhianur, 1998), and many important findings pertaining to the role of hydrophobic interactions, system stability, coagulation, influence of surfactants and flocculants, etc. were established. A significant number of these research initiatives pertain to flotation. Unfortunately experimental and theoretical difficulties of measurement involving the deformable air-water interface have forced researchers to consider model, solid hydrophobic particles to represent the air bubble. Different materials have been used as a model air bubbles including silanated glass (Pazhianur and Yoon, 1997) and polyethylene (Nalaskowski et al., 1998; Drelich et al., 2000). However, this approach although giving applicable results, is far from reality. Deformation of the air-water interface during particle approach and subsequent changes in charge density and surfactant adsorption density

cannot be reproduced with the use of solid hydrophobic particles as representation of air bubbles. Also, formation of the three-phase contact line (TPL) and the relaxation of air-water interface after attachment can only be observed when a real air-water interface is used during the experiment.

Fortunately, during the last few years significant progress has been made in this area, both with respect to instrumentation and experimental procedure. Further, advances in the theoretical analysis have been made as well. Several researchers have successfully conducted interaction force measurements between an air bubble and a solid particle using commercially available AFM systems (Ducker et al., 1994; Fielden et al., 1996), and specially designed, home-built instruments, closely related to the AFM design ((Butt, 1994; Preuss and Butt, 1998a; Preuss and Butt, 1999). Unfortunately, despite numerous significant contributions to the theoretical analysis of interaction forces between the solid particle and the deformable interface and the deformation of this interface during particle approach (Miklavcic et al., 1995; Miklavcic, 1998; Nguyen and Stechemesser, 1998; Ralston and Dukhin, 1999; Ralston et al., 1999; Nguyen et al., 2001; Nguyen and Evans, 2002), the geometry of the interface during approach must be considered during calculation of these interfacial forces. Despite some limitations, it has to be stated here, that significant progress has been made and AFM measurements can significantly contribute to the analysis of particle-bubble interactions in mineral processing science.

In this paper, examples of experimental data from the authors' research will be shown. Possibilities for the use of AFM for different studies as well as limitations of the technique will be discussed.

## EXPERIMENTAL SECTION

### MATERIALS

Glass spherical particles (Polysciences, Inc.) were carefully cleaned by subsequent sonication in acetone, methanol and RCA SC-1 cleaning solution composed of 5 vol. H<sub>2</sub>O, 1 vol. 29% NH<sub>3</sub>aq, and 1 vol. 30% H<sub>2</sub>O<sub>2</sub> at 80 °C (Kern and Puotiene, 1970), rinsed with deionized water and dried. The glass spheres, which were not cleaned with this procedure, were hydrophobic and had an estimated contact angle around 10 degrees. The liquid film between these particles and a bubble was unstable, leading to its rupture.

Spherical polyethylene (PE) particles were obtained using a procedure, which involves suspending a powder of polymeric thermoplastic materials, such as PE, in glycerol, heating the suspension above the melting point of the polymer, and then solidification of the dispersed polymeric droplets at a reduced temperature. After appropriate filtration and drying, this procedure was found not to change the surface properties of PE particles, which retained a high degree of hydrophobicity. These particles had a relatively smooth surface and were particularly useful for investigating



interaction forces using the AFM colloidal probe technique (Nalaskowski et al., 1999a).

Other materials include: highly ordered pyrolytic graphite (HOPG – Digital Instruments, Inc.), KCl (Malinckrodt, Inc.) and deionized water (Milli-Q Millipore system).

#### METHODS

The prepared spherical particles were glued to the AFM cantilever with a small amount of epoxy resin using a procedure described elsewhere (Ducker et al., 1991). Tipless triangular silicon nitride cantilevers having a spring constant of 0.12 N/m (Digital Instruments, Inc.) were used. The cantilever was placed under the CCD camera fitted with long distance lens giving a 500× magnification. A small amount of resin was transferred on the tip of the cantilever using a 50 μm diameter tungsten wire attached to a micromanipulator. After that, a selected sphere was picked up using a new tungsten wire and carefully placed on the cantilever using the micromanipulator. Cantilevers were ready for measurements after at least 24 hours of drying. Using this procedure, spherical particles with a diameter down to 1 μm could be precisely glued to the end of AFM cantilever, see Fig. 1.

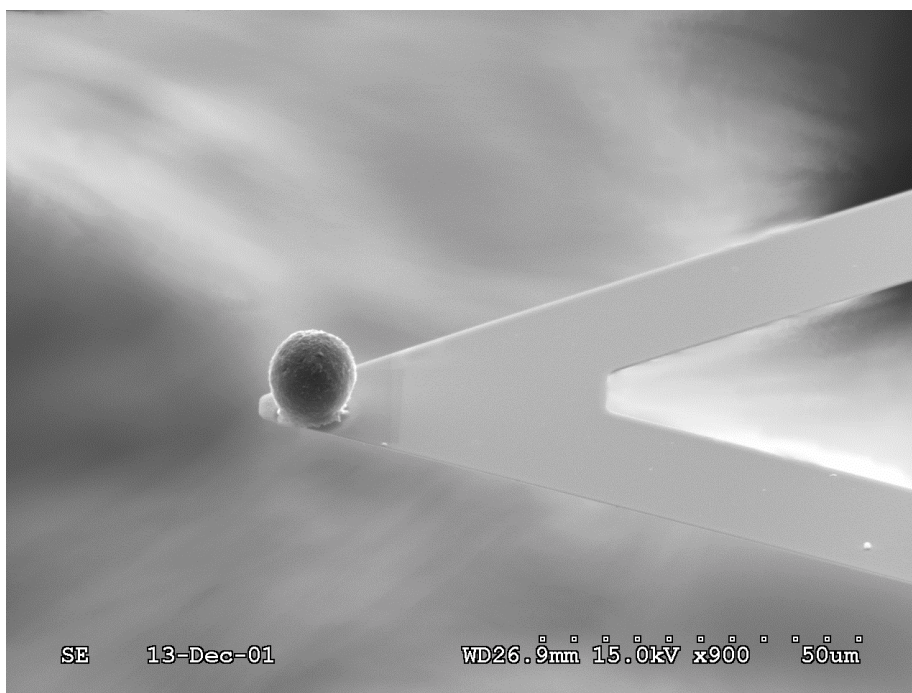


Fig. 1. SEM photograph of a spherical particle (14 μm diameter) glued to the end of AFM cantilever

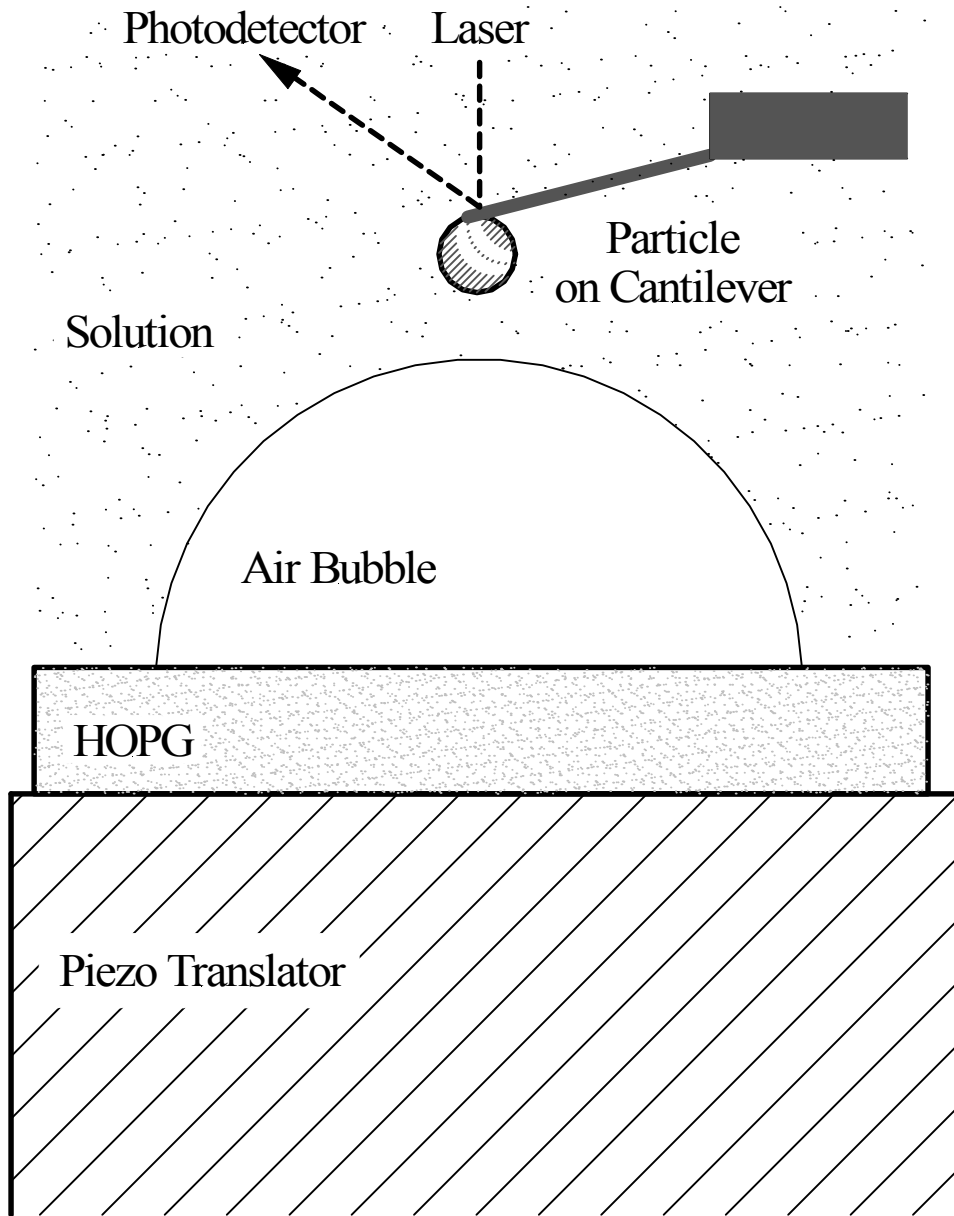


Fig. 2. Schematic of the AFM setup used for particle-bubble interaction force measurement

A Nanoscope IIIa atomic force microscope (Digital Instruments, Inc.) equipped with a fluid cell was used for the measurements. As shown in, a laser light is focused on the back of the cantilever to detect the cantilever's deflection as it interacts with the surface beneath it. The reflected light is directed onto a split photodiode detector, which produces a voltage signal proportional to the cantilever deflection. If the spring constant is known, the deflection of the spring can be converted to force using Hooke's law. Using such a setup the force acting on the cantilever can be determined with sensitivity greater than 0.1 nN. The sample beneath cantilever is moved using a piezoelectric transducer. In the force measurements, motion in the  $x$  and  $y$  directions is disabled and the piezoelectric tube is used to move the surface in the  $z$  direction and the cantilever deflection is continuously measured. The approach velocity of the surface can be accurately controlled and varied over three orders of magnitude.

A silicone o-ring was placed on the surface of the HOPG and filled with 1 mM KCl solution or deionized water. A hemispherical air bubble with a diameter from 400 to 600  $\mu\text{m}$  was formed on the graphite surface using a microsyringe. The air bubble attached to the hydrophobic graphite surface was stable for many hours. Such prepared sample was mounted on the top of the piezoelectric transducer of the AFM system and the prepared cantilever with attached particle in the quartz fluid cell holder was mounted above.

The particle on the cantilever was initially positioned, under optical microscope control, on the center of air bubble and roughly one micrometer above the bubble surface. Different speeds of approach were obtained by changing the scan rate of the piezoelectric translator and the cantilever deflection versus piezoelectric transducer displacement was recorded. At least 5 measurements were taken for each speed of approach. Subsequently, deflection was recalculated into force normalized with respect to particle diameter and separation distance was obtained based on constant compliance region.

## RESULTS AND DISCUSSION

Using the experimental setup previously described, many interesting and important properties of the particle-bubble system can be studied. Several possibilities are discussed below.

### PARTICLE CONTACT ANGLE AND MICROSHERE TENSIOMETRY

Wetting properties of micrometer-size particles are important in many industrial applications including paint, plastic, pharmaceutical and mineral processing industries. Measurement of the contact angle of small particles, which is the most common way to describe wetting characteristics, is unfortunately by no means an easy task. Usually different variations of the capillary rise method are employed (Bartell and Osterhof, 1927; Diggins and Ralston, 1993; Siebold et al., 1997). In these methods particles are packed into a tube, closed at the bottom by a porous plug. The bottom of the tube is



immersed into the studied solution and capillary rise of the liquid through the packed bed of particles is observed. Contact angle can be obtained from the speed of the capillary rise or from the pressure necessary to stop the rise. Unfortunately this method is strongly dependant on the packing of the particle bed and it is not easy to compare results when different procedures for particle bed preparation are employed. Additionally models of the capillary rise used for the contact angle measurements are not yet clear (Siebold et al., 2000). Finally, it has to be emphasized that only the average contact angle for the whole population of particles is obtained.

AFM can be easily used for measurement of the contact angle of single particles if their geometry is close to spherical. In such a measurement the particle is glued to the cantilever and the deflection of the cantilever due to the force acting between the particle and the air bubble is recorded in function of piezo translator displacement. An example of such force curves is given on Fig 3.

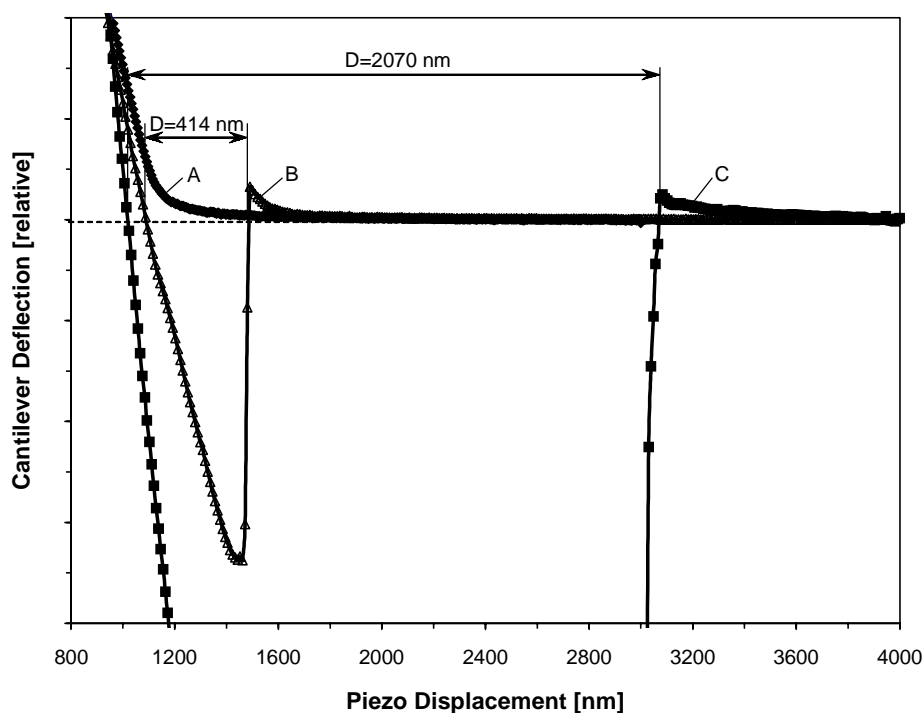


Fig. 3. Cantilever deflection versus piezo displacement for three different particles interacting with an air bubble in water. (A) - hydrophilic glass particle, (B) - slightly hydrophobic glass particle, (C) - highly hydrophobic PE particle. (D) denotes the distance at which particle penetrates the air bubble under the zero force



Three curves for three different particles with varying wettability are shown. The curve (A) is typical for a completely hydrophilic glass particle. In this case the interfacial water film between particle and bubble is thermodynamically stable and no attachment is observed as is evident by only repulsive interactions which are a net effect of repulsive electrostatic, van der Waals and hydrodynamic forces. The curves (B) and (C) are recorded for a slightly hydrophobic glass particle (B) and strongly hydrophobic PE particle (C). In the case of these particles the water film between the interfaces is unstable and jump to contact and formation of TPL occurs. At a certain point after attachment, during the continuous approach of particle there is a point where the force curve crosses zero. At this point no force is acting on the particle. The distance  $D$  (shown on Fig. 3) is a distance of particle penetration into the air bubble.

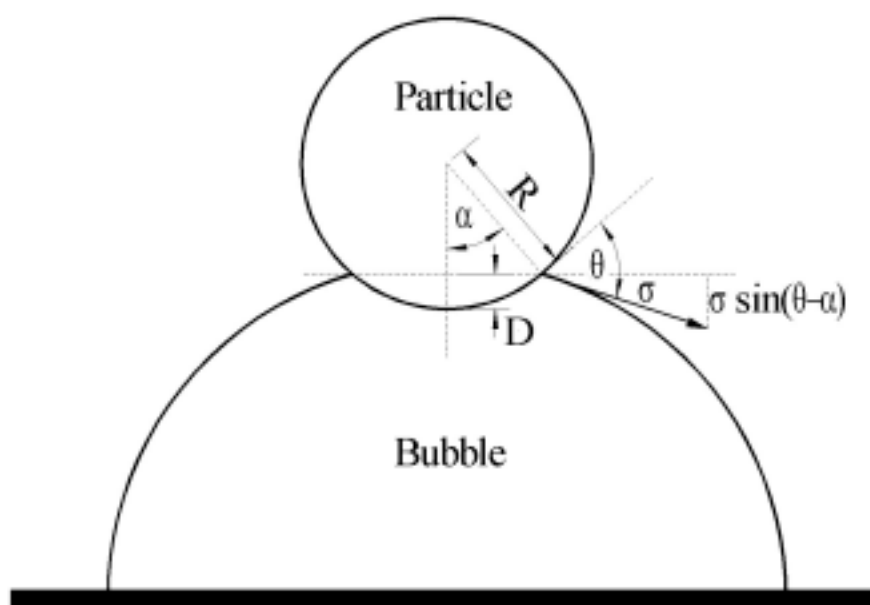


Fig. 4. The equilibrium state of a spherical particle at the air-water interface. ( $R$ ) – particle radius, ( $D$ ) – distance of penetration into air bubble, ( $\sigma$ ) – surface tension, ( $\alpha$ ) – central angle, and ( $\theta$ ) – contact angle

The equilibrium state of the particle at the air-water interface is shown on Fig. 4. The gravitational force acting on micrometer-size particle can be neglected and the interaction between the air bubble and particle after the jump to contact is dominated by a capillary force. For a spherical particle this force is given by: Eq. 1 (Scheludko et al., 1976)

$$F_C = 2\pi R\sigma \sin \alpha \sin(\theta_R - \alpha) \quad (1)$$





where  $R$  – radius of the particle,  $\sigma$  – air-water interfacial tension,  $\alpha$  – central angle and  $\theta_R$  is the receding contact angle, since the particle is moving into the air bubble and the liquid recedes on the particle surface. By resolving the (1) with respect to the vertical component  $D$  one can obtain:

$$\cos \theta_R = \frac{R - D}{R} \quad \text{Eq. (2)}$$

Using Eq. 2 then  $\theta_R$  can be easily obtained by measuring the distance  $D$  and knowing the radius of the particle. Although the interpretation of force/radius versus separation distance is complicated and still not a satisfactorily resolved issue for measurements between a particle and a deformable surface, it is not necessary to take all these problems into account for contact angle measurements. There is even no necessity of converting the obtained deflection versus piezo displacement curves which means that even knowledge of the spring constant for the system is not necessary.

The calculated receding contact angle  $\theta_R$  for the glass particle of radius  $27 \mu\text{m}$  (curve B) was  $10^\circ$ , while the  $\theta_R$  for the PE particle of radius  $9 \mu\text{m}$  (curve C) was  $39^\circ$ . The measured value for the PE particle is smaller than  $\theta_R$  measured for similarly treated planar PE surface which was equal  $67^\circ$  (Nalaskowski et al., 1999a). This difference can be explained by considering additional work required for formation of TPL which is known as a line tension. If work is required for an increase of TPL it will result in a decrease in the contact angle (Preuss and Butt, 1998b).

In a similar way the advancing contact angle  $\theta_A$  can be measured using a water drop instead of an air bubble (Ecke et al., 1999). Although the  $\theta_A$  can also be obtained with an air bubble by measuring the pull-off force during the retracting of particle from air-water interface (Preuss and Butt, 1998b) it is usually possible only with specially designed instruments – commercial AFM systems are not able to fully record cantilever deflection during the retraction of hydrophobic particle from the bubble. By measuring the pull-off force of a spherical particle with known contact angle air-water interfacial tension can be also obtained.

#### HYDROPHOBIC INTERACTIONS

The understanding of interaction forces between mineral particle and an air bubble is crucial for the understanding of the flotation process. It is widely accepted that the attachment of a particle to the bubble cannot be explained based on DLVO theory. This is because in most cases the electrostatic component is repulsive (air-water interface is negatively charged (Collins et al., 1978; Saulnier et al., 1996; Graciaa et al., 2000)) and the van der Waals interaction between particle and bubble is also repulsive (Hough and White, 1980; Nguyen et al., 2001). It is evident that an additional attractive non-DLVO force is involved. This so called long range



hydrophobic force existing between hydrophobic surfaces has been an object of extensive study for the last 20 years (Christenson and Claesson, 2001; Skvarla, 2001). The origin and nature of these interactions is not completely clear but it is accepted that they are related to the formation of submicroscopic bubble cavities between hydrophobic surfaces and the subsequent rupture of the water film (Christenson and Claesson, 1988; Parker et al., 1994; Nalaskowski et al., 1999b; Attard, 2000; Tyrrell and Attard, 2002). Since previous research was limited only to solid surfaces it was unclear how these long range attractive forces are manifested in particle-bubble interactions. Recently such measurements have been conducted for different particles in various surfactant solutions by several researchers (Ducker et al., 1994; Preuss and Butt, 1998a). They have showed that a long-range jump to contact between particle and the bubble exists, which is a manifestation of the long-range hydrophobic forces. This jump-to-contact distance is dependent on the hydrophobicity of the particle and the presence of adsorbed surfactants at the air-water interface as well.

Unfortunately, in comparison with solid-solid interactions, the theoretical approach to the measurement involving a deformable surface is difficult and still unclear. Several important matters should be taken into consideration.

The first important difference is that since we deal with a very “soft”, deformable surface of an air bubble the spring constant of the system,  $k$ , is no longer equal to the cantilever spring constant,  $k_C$ , but also constitutes the spring constant of the bubble,  $k_B$ , which acts as a second spring during the interactions. The total spring constant is given by (3):

$$\frac{1}{k} = \frac{1}{k_C} + \frac{1}{k_B} \quad (3)$$

The spring constant,  $k$ , can be obtained from the slope of constant compliance region of force curve – the linear part of the force curve after contact (assuming the calibration of photodetector response versus deflection of the cantilever has been performed and the deflection of cantilever is known). When the spring constant of the cantilever is measured using one of the known methods (Cleveland et al., 1993; Sader et al., 1995; Maeda and Senden, 2000) the bubble spring constant can be determined from (3). The spring constant of an air bubble of diameter 500  $\mu\text{m}$  in water was found to be  $k_B = 0.065 \text{ N/m}$  (Ducker et al., 1994). It has to be noted that this value is smaller than many of the commercially available cantilevers which means that the air bubble will deflect more than the cantilever itself. Additionally this spring constant is dependent on bubble size (smaller bubble – larger  $k_B$ ) and on the adsorption of surfactants on the air-water interface. Moreover, the assumption is usually made that  $k_B$  is constant during the approach and is not dependent on the interaction forces exerted at the interface due to the presence of the particle in the vicinity. The validity of this assumption is by no means obvious.



The second important difference between bubble-particle measurements and particle-solid surface measurements is the uncertainty of the real separation distance between the particle and bubble. This is related to the low spring constant of the bubble and contribution of the bubble to the deflection. Such a problem can be relatively easily addressed in the case of fully hydrophilic particles as shown in Fig. 5.

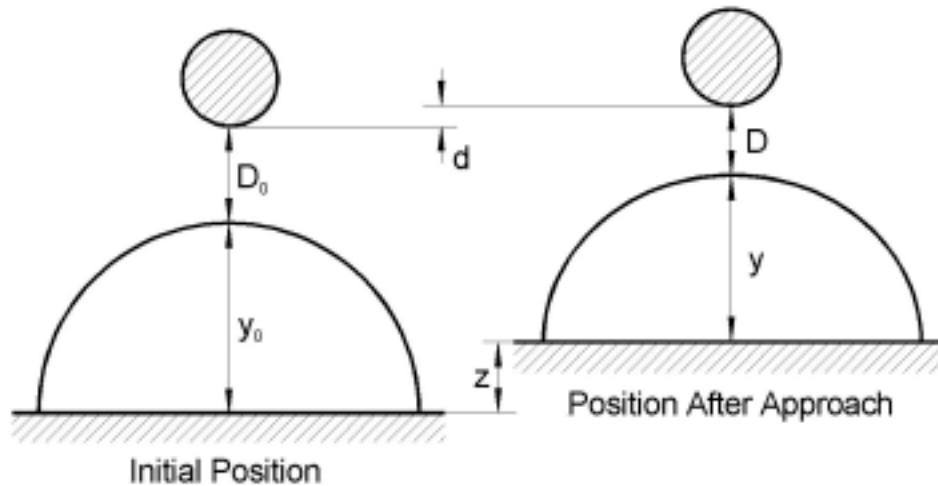


Fig. 5. Schematic of the relative positions of a particle and a bubble with surface deformation. ( $D_0$ ,  $D$ ) – initial and real separation distance, ( $y_0$ ,  $y$ ) – initial and real height of the air bubble, ( $z$ ) – piezo displacement, ( $d$ ) – cantilever deflection

The deflection of the cantilever,  $d$ , can be converted to force using Hooke's law:

$$F = k_C d \quad (4)$$

If the bubble behaves like a linear spring with a spring constant  $k_B$ , we can also obtain:

$$F = k_B (y_0 - y) \quad (5)$$

where  $y_0$  and  $y$  are the initial and actual heights of the bubble surface at the apex.

Solving (4 and Eq. 5 gives:

$$y_0 - y = d \frac{k_C}{k_B} \quad (6)$$



The distance balance yields:

$$D + y + z = D_o + y_o + d \quad (7)$$

In this equation,  $z$  is the position of the piezoelectric stage, which is experimentally determined from the applied voltage independently of the cantilever deflection,  $d$ , and the actual deformation,  $y$ , of the gas-liquid interface, the relative value of which is described by (6). The solution to (6) and (7) for the actual separation distance,  $D$ , gives:

$$D = d \left( 1 + \frac{k_C}{k_B} \right) - z + D_o \quad (8)$$

This equation is central to the conversion of the experimentally available data of the cantilever deflection,  $d$ , and the position,  $z$ , of the piezoelectric stage to the actual separation distance,  $D$ , between surfaces.

The initial separation distance,  $D_o$ , is usually not known precisely, but it can be eliminated from the conversion considering the “molecular” contact regime between surfaces. In this “hard sphere” interaction, the separation distance  $D$  is very small, and we can set-off the value of 0 for this distance (for solid surfaces, this value is about 0.2 nm). However, for generality we describe the separation distance in the contact regime by  $D_c$  and obtain from (8):

$$D_c = d_c \left( 1 + \frac{k_C}{k_B} \right) - z_c + D_o \quad (9)$$

Eliminating  $D_o$  from (8) and (9) gives:

$$D = D_c + (d - d_c) \left( 1 + \frac{k_C}{k_B} \right) - (z - z_c) \quad (10)$$

This equation allows the actual separation distance to be determined from the measured variables  $d$ ,  $d_c$ ,  $z$  and  $z_c$ .

However, other types of deformation at the air-water interface also can be possible as schematically shown on Fig. 6. Electrostatic and hydrodynamic repulsion may cause formation of a dimple on the surface, while attractive hydrophobic forces may cause formation of a bulge and finally TPL and neck formation. In this last case the particle will additionally penetrate the air bubble depending on the hydrophobicity as explained in the previous part of this paper. Furthermore, the presence of interfacial forces may change the spring constant of the bubble which may become distance

dependant. More detailed approaches to the problem of the surface deformation accounting for the presence of interaction forces are also available (Parker and Attard, 1992; Miklavcic et al., 1995; Miklavcic, 1998; Nguyen and Stechemesser, 1998). They are difficult to apply in practical systems and do not take into account many important factors like the presence of non-DLVO interaction forces, especially hydrophobic attraction.

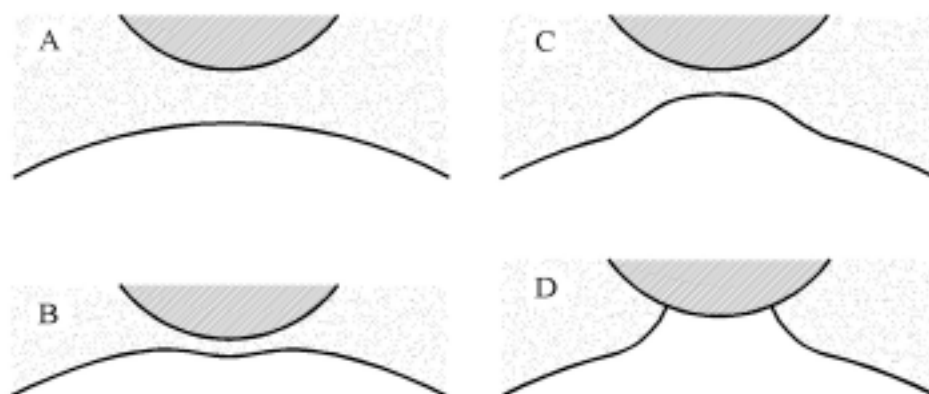


Fig.6. Schematic for the possible deformations of the bubble surface. (A) - particle far from bubble - no deformation; (B) - hydrophilic particle - dimple formation; (C) - hydrophobic particle - bulge formation; (D) - hydrophobic particle closer to the surface – formation of neck and TPL

Nevertheless, the AFM can successfully be used for the study of bubble-particle interactions. For example, the effect of particle hydrophobicity (natural, rendered by the silanization or the adsorption of surfactants) on the particle attachment can be studied (Butt, 1994; Ducker et al., 1994; Preuss and Butt, 1998a; Preuss and Butt, 1999). An example of such a study is shown on Fig. 7. It can be seen that in the case of a hydrophilic particle the water film between the particle and bubble is stable and only repulsive forces are observed, which involve at least three repulsive components: electric double layer, van der Waals and hydrodynamic forces. Hydrophobic particles jump to contact at a given distance and the TPL is formed. It can be seen that for strongly hydrophobic particle the jump-to-contact distance is much greater than that for a weakly hydrophobic particle. However it has to be noted that the separation distance is only relative here. The particles, after jump to contact, penetrate the air-water interface for a certain distance dependent on the particle hydrophobicity. Additionally, when the particle approaches, the air-water interface deforms due to the surface forces which are also dependent on particle surface chemistry. This problem cannot be resolved without measurement of real particle-bubble separation distance using an independent method (e.g. interferometry).



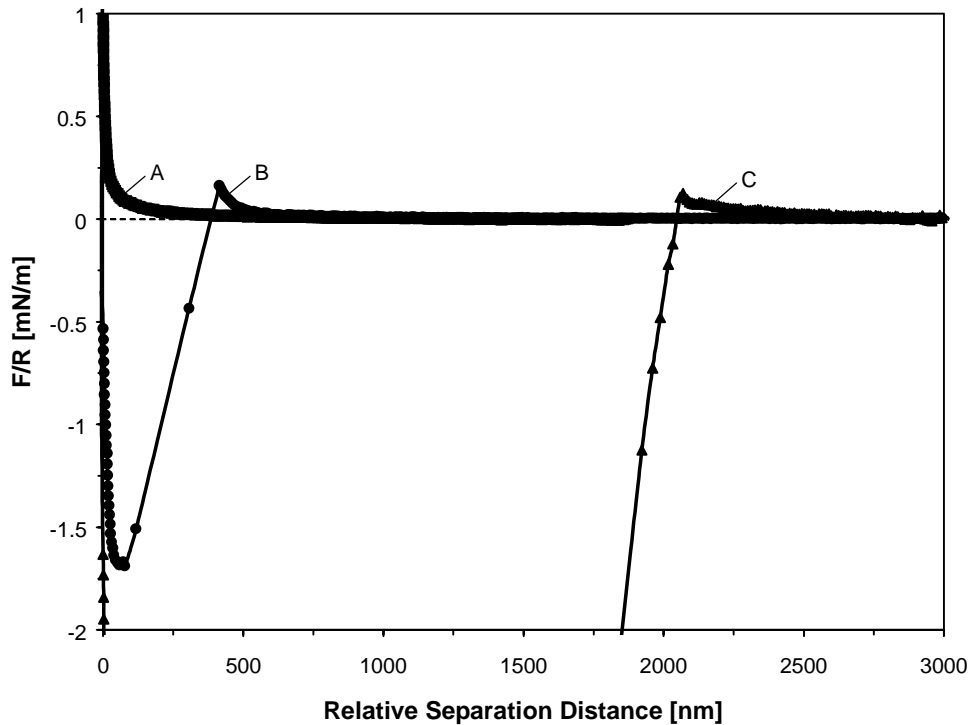


Fig. 7. Interaction forces between air bubble surface in water and spherical particles of different hydrophobicity. (A) - hydrophilic particle  $\theta_R = 0^\circ$ ; (B) - slightly hydrophobic particle  $\theta_R = 10^\circ$ ; (C) - strongly hydrophobic particle  $\theta_R = 39^\circ$

#### HYDRODYNAMIC FORCES

Another important force which has to be considered in the flotation process is the hydrodynamic force during the bubble-particle approach. These forces were of great interest in previous studies (Pugh et al., 1994; Dai et al., 1998; Nguyen, 1999; Ralston et al., 1999; Yoon, 2000). The AFM can be used for the study of hydrodynamic interactions between a mineral particle and an air bubble.

Typically, the force measurements are carried out with a very low speed of the piezoelectric translator such that the dynamic phenomena of the system can be ignored and the static analysis of the force curve can be applied. It is interesting to note that commercially available AFM systems are capable of operating in the highly dynamic regime. Therefore, a speed of the piezoelectric translator on the order of tens to hundreds of microns per second can easily be achieved. By changing the speed of piezoelectric translator the hydrodynamic component of the interaction force between a spherical particle and a solid surface can be measured (Craig and Neto, 2001). Using

a similar approach, the dynamic interaction between a bubble and a particle, which is close to the interactions expected in the flotation of mineral particles, can also be studied.

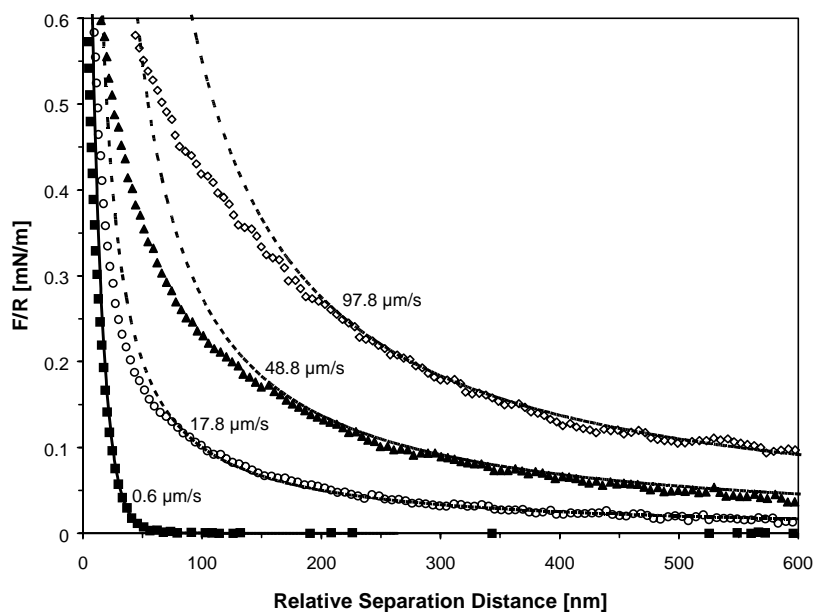


Fig. 8. Interaction force between hydrophilic glass particle and air bubble in  $1 \times 10^{-3}$  M KCl solution as a function of approach speed. Continuous line (at  $0.6 \mu\text{m/s}$ ) indicates theoretical DLVO repulsion for constant charge model ( $A = -1.0 \times 10^{-20}$  J,  $\Psi_B = -15$  mV,  $\Psi_P = -60$  mV), dotted lines indicate theoretical hydrodynamic forces

The force curves recorded between hydrophilic glass particle ( $27 \mu\text{m}$  radius) and an air bubble in  $1 \times 10^{-3}$  M KCl solution are shown in Fig. 8 as a function of approach speed. Only repulsive forces were found in this system. The range and magnitude of the force increase significantly with an increase in approach speed. The experimental values were fitted to DLVO theory using the constant charge model (Israelachvili, 1991):

$$F_{\text{DLVO}} / R = \frac{4\pi\sigma_B\sigma_P}{\epsilon\epsilon_0\kappa} e^{-\kappa D} - \frac{A}{6D^2} \quad (11)$$

where  $\sigma_B$ ,  $\sigma_P$  indicate the surface charge of bubble and particle, accordingly, calculated using the Graham equation (Israelachvili, 1991):



$$\sigma = 0.117[\text{KCl}]^{0.5} \sinh(\Psi / 51.4) \quad (12)$$

Other symbols indicate:  $\varepsilon$  – dielectric constant of medium,  $\varepsilon_0$  – the permittivity of free space,  $\kappa$  – reverse Debye length,  $A$  – Hamaker constant,  $D$  – separation distance and  $\Psi$  – surface potential.

Previous work has shown that a potential for the air bubble of  $\Psi_B = -15$  mV (Usui et al., 1981), and a surface potential for silica of  $\Psi_p = -60$  mV (Ducker et al., 1991) can be used. A nonretarded Hamaker constant  $A = -1.0 \times 10^{-20}$  J, calculated theoretically for silica/water/air system (Hough and White, 1980) was used in these calculations. Because of the uncertainty in the separation distance and zero separation value due to possible deformation, calculated values were shifted to correspond to those with relative zero separation distance.

The hydrodynamic force was calculated using the simplified Brenner's equation (Horn et al., 2000), which can be used when the separation distance between a sphere and the wall is much smaller than radius of the sphere:

$$F_{\text{HYDR}} / R = 6\pi\eta U \frac{R}{D} \quad (13)$$

where  $\eta$  is viscosity and  $U$  is the approach velocity.

It has to be noted that a very simplistic approach was used here – no deformation analysis was employed and the surfaces were treated as nondeformable and planar (in view of the fact that the diameter of the air bubble is orders of magnitude greater than the diameter of the particle). Nevertheless, the calculated results agree quite well with measured values. For higher approach speeds the hydrodynamic component of the repulsive force is predominant over the DLVO surface forces as can be concluded from the comparison with the force curve obtained for a low speed of approach (0.6  $\mu\text{m/s}$ ). Theoretical hydrodynamic forces, calculated using (13), show agreement with experimental data for larger separation distances, while deviate significantly at shorter distance. This may be related to the deformation of air-water interface due to the surface forces at closer separation distances.

In a similar way the hydrodynamic forces between hydrophobic particles and an air bubble can be studied. They have also repulsive character and strongly affect jump-to-contact distance and formation of TPL as it has been experimentally observed (Nguyen et al., 2002).

## CONCLUSIONS

The AFM can be used as a valuable tool for investigating particle-bubble interactions in mineral processing science. Despite many limitations with respect to the theoretical analysis of experimental data, important information about the particle-bubble system can be obtained, including contact angle for a single particle, surface

forces, and hydrodynamic forces. However in order to facilitate further progress in this area, important issues regarding the geometry of the system, particularly the real separation distance due to deformation, and the existence of strong hydrophobic interactions leading to formation of the TPL have to be addressed. Limitations of commercial AFM systems as a tool for particle-bubble interaction studies should also be recognized. These limitations include: short vertical distance of the piezo translators unable in most cases to fully retract the particle from the bubble after attachment, nonlinearity of the scanner, and small range/nonlinearity of position sensitive photodetector. It was evident that the commercial AFM system is not specifically designed for the study of particle-bubble interactions, which prevents measurement of the stability of particle-bubble attachment and simple measurement of the advancing contact angle, and finally results in a higher degree of uncertainty when compared with measurements between solid surfaces. In order to fully utilize the potential of AFM for studies of particle-bubble interactions, a specially designed instrument is recommended, based on the AFM design, as described in the literature (Butt, 1994). Further improvement of such designs by including an interferometer coupled with a high speed video camera for the measurement of separation distance and surface geometry will provide for further advances in the study of particle-bubble interactions.

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**Nalaskowski J., Nguyen A.V., Hupka J., Miller J.D.,** *Badania oddziaływań cząstka-pęcherzyk za pomocą mikroskopu sił atomowych – obecne możliwości i wyzwania*, Fizykochemiczne Problemy Mineralurgii, 36 (2002), 253-272 (w jęz. angielskim)

Badania oddziaływań pomiędzy cząstkami mineralnymi i pęcherzykami powietrza są kluczowe do zrozumienia przebiegu flotacji. Wykorzystanie mikroskopii sił atomowych (AFM) i techniki próbnika koloidalnego umożliwia pomiar takich oddziaływań. Przy użyciu AFM oddziaływania pomiędzy pojedynczą cząstką przymocowaną do dźwigni AFM i pęcherzykiem powietrza, umieszczonym na powierzchni hydrofobowej, mogą być mierzone w środowisku wodnym. Ważna jest znajomość sił występujących przed przerwaniem filmu międzyfazowego wody oraz hydrofobowość użytej cząstki jak wykazano w obecnej pracy. Zmierzono również siły hydrodynamiczne pomiędzy zbliżającym się pęcherzykiem powietrza i cząstką mineralną. Pomimo znaczących możliwości techniki próbnika koloidalnego i AFM w badaniu oddziaływań cząstka-pęcherzyk, istnieje szereg wyzwań związanych z modyfikacją konstrukcji instrumentu, procedurą pomiarową oraz analizą teoretyczną danych. Szczegółnej uwagi wymaga uwzględnienie zasięgu ugięcia dźwigni AFM oraz skanera piezoelektrycznego, wyznaczenie stałej sprężystości pęcherzyka, właściwego wyboru punktu kontaktu cząstki z pęcherzykiem oraz uwzględnienie deformacji powierzchni pęcherzyka.