Van Lierde A and Lesoille M (1991) Compared effectiveness of xanthate and mercaptobenzothiazole as gold and arsenopyrite collectors. In: *Proceedings of the XVII International Minerals Processing Congress*, Dresden, vol. IV, pp. 111-119.

the flotation of minerals using two kinds of collectors. In: Somasundaran P (ed.) *Fine Particle Processing*, American Institute of Mining, Metallurgical and Petroleum Engineers, New York, pp. 787-801.

Wakamatsu T and Numata Y (1979) Fundamental study on

# **Bubble**^**Particle Capture**

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### **Introduction**

Bubble–particle capture is the heart of froth flotation. For efficient capture to occur between a bubble and a hydrophobic particle, they must *first* undergo a sufficiently close encounter, a process that is controlled by the hydrodynamics governing their approach in the aqueous environment in which they are normally immersed. Should they approach quite closely, within the range of attractive surface forces, the intervening liquid film between the bubble and particle will drain, leading to a critical thickness at which rupture occurs. This is then followed by movement of the three-phase-line contact line (the boundary between the solid particle surface, receding liquid phase and advancing gas phase) until a stable wetting perimeter is established. This sequence of drainage, rupture and contact line movement constitutes the *second* process of attachment. A stable particle–bubble union is thus formed. The particle may only be dislodged from this state if it is supplied with sufficient kinetic energy to equal or exceed the detachment energy, i.e. a *third* process of detachment can occur.

The capture (or collection) efficiency *E* of a bubble and a particle may be defined as:

$$
E = E_{\rm C} \times E_{\rm A} \times E_{\rm S} \tag{1}
$$

where  $E_C$  is the collision efficiency,  $E_A$  is the attachment efficiency and  $E<sub>S</sub>$  is the stability efficiency of the bubble-particle aggregate. This dissection of capture efficiency into three parts was originally proposed by Derjaguin and Dukhin (1960–61) and focuses attention on the three zones of bubble-particle capture where, in order, hydrodynamic interactions, surface forces and forces controlling bubble-particle aggregate stability are dominant.

This article describes each of the substeps in the bubble-particle capture process. The individual processes and efficiencies are focused upon, since they provide the key to understanding the substeps. Our knowledge of the various efficiencies has been enhanced by six important publications, referred to in **Table 1**, each of which signalled major advances in our understanding and catalysed further research in this interdisciplinary field of colloid and flotation science.

## **Processes and Substeps**

### **Process 1: Collision Ef**\**ciency**

For a batchwise flotation process, the flotation recovery (the mass of particles recovered in a given time *t*) *R* is given by:

$$
R = 1 - \exp - t \left( \frac{3GhE_{\rm c}E_{\rm A}E_{\rm S}}{2d_{\rm b}V} \right) = 1 - \exp(-tk)
$$
\n[2]

where  $G$  is the volumetric gas flow rate of a swarm of bubbles of diameter  $d<sub>b</sub>$  passing through a particle suspension of volume *V* and depth *h*, and:

$$
k = \frac{3GE_{c}E_{A}E_{S}b}{2d_{b}V}
$$
 [3]

The flotation rate constant  $k$  is directly analogous to that obtained in chemical reaction kinetics. Its value will be partly determined by the substep(s) in bubble-particle collision, attachment and detachment processes, as well as by physical variables such as *G*. (For a constant *G* and constant bubble size distribution,  $d_b$  will be an appropriate average.)

Equation [2] has been shown to apply, for example, to a system of monodisperse polystyrene latex particles floating under batchwise conditions. A plot of  $\ln (1 - R)$  versus *t* yields the rate constant *k*. For systems that are polydisperse in particle size and/or in which particles of different hydrophobicities are present, the recovery then becomes the sum of a series of exponential terms and the plot of

**Table 1** Key papers in understanding fundamental flotation substeps (details of references are given in Further Reading)

Date	Area of research
1948	A fundamental paper by Sutherland on the kinetics of the flotation process appeared in Australia. This paper invoked induction time, described particle size effects in flotation, and catalysed other similar approaches. While it was preceded by other efforts, this paper was the first comprehensive effort to describe recovery, size and time data in a fundamental manner.
1960-61	In Moscow, Derjaguin and Dukhin produced a key paper on the theory of flotation of small and medium-sized particles. Hydrodynamics, surface forces and diffusiophoresis were all used in this theory. This seminal work resulted in an acceleration of fundamental flotation research worldwide.
1972	Blake and Kitchener, working together in London, published some very careful measurements of the thickness of aqueous films on hydrophobic quartz surfaces. Film thicknesses, measured as a function of salt concentra- tion, were shown to depend on the electrical double layer force. Film instability occurred on hydrophobic surfaces at film thicknesses less than about 60 nm. This value, which was smaller than the range of the electrical double layer force, represented the combined effects of hydrophobic force, surface heterogeneities and external disturbances. Blake and Kitchener's film thickness studies hinted at the length dependence of hydrophobic forces, information which was subsequently obtained by surface force experiments after 1982.
1976	Scheludko and colleagues in Bulgaria considered how particles might become attached to a liquid surface and developed the capillary theory of flotation.
1977	Anfruns and Kitchener published the first measurements of the absolute rate of capture of small particles in flotation. This was the first critical test of collision theory under conditions where the bubble and particle surface chemistry was characterized and controlled.
1983	Schulze published a key textbook on the physicochemical substeps that are important in flotation, drawing on a wide range of hydrodynamic, surface chemical and engineering information. Originally published in German, once translated into English the book captured an international audience.
$c.$ 1980-present	There has been a strong interest in developing reliable collision models (Dai et al., 1998). The surface force apparatus and, recently, the atomic force microscope colloid probe technique, have provided very useful insight into electrical double layer, van der Waals and hydrophobic forces (Israelachvili, 1985; Fielden et al., 1996). Thin film drainage has been investigated between a rigid and a deformable interface (Miklavcic et al., 1995). Attachment efficiencies have been measured (Hewitt et al., 1995). Reliable methods for measuring contact angles on particles have been developed (Diggins et al., 1990). Major theoretical and experimental advances in describing dynamic contact angles on well-defined surfaces have been made (Blake, 1993).

 $\ln (1 - R)$  versus *t* will show curvature, reflecting the different contributions to the recovery from the various particles present in the mixture.

In the metallurgical literature, *R* versus *t* data are frequently analysed by assuming that the pulp consists of 'fast' and 'slow' floating components, allowing the respective rate constants  $(k_f$  and  $k_s$ ) and fractions ( $f_f$  and  $f_s$ ) to be determined. Although this is a gross simplification of the real multicomponent situation, much valuable information may be gleaned from such an analysis. In fact the latter is frequently used to examine the flotation behaviour of particles of a specific size range in flotation circuits, where the behaviour of an individual flotation cell or bank of cells may be approximated to a batchwise process.

Derjaguin and Dukhin were the first to distinguish three zones of approach of a bubble and a particle on the basis of the different kinds of force in each zone (**Figure 1**). This model is a very useful one and helps to identify the various contributions to capture efficiency. However, it should not be taken to mean that there are well-defined boundaries between each zone; rather they grade into one another, the importance of the various contributing effects in each zone being more accurately identified as further information becomes available.

Zone 1 is a region far from the bubble surface where hydrodynamic forces are dominant, controlling  $E_c$  in eqn [1]. Hydrodynamic drag forces act to sweep the particle around the bubble, viscous forces tend to retard this relative motion between the two, while particle inertial and gravitational forces move the particle towards the bubble.



**Figure 1** Hydrodynamic (1), diffusiophoretic (2) and surface force (3) zones of interaction between a bubble and a particle. (Reproduced with permission from Derjaguin BV and Dukhin SS (1960–61). Theory of flotation of small and medium-size particles. Transactions of the Institute of Mining and Metallurgy 70: 221-246, Figure 1).

Broadly speaking, all models of collision efficiency predict that  $E<sub>C</sub>$  decreases with particle size at constant bubble size down to a particle diameter of about  $0.5 \mu m$ . Then, Brownian diffusion probably takes over as the predominant capture mechanism (although this has not been proven), the collision efficiency increasing with decreasing size as the tiny particles (virtually 'solute molecules') move towards the bubble surface. In 1948 Sutherland made the first significant contribution to the treatment of collision efficiency. His hydrodynamic treatment of the process of particle and bubble approach in zone 1 was carried out without any consideration of particle inertia, bubble deformation or film thinning, deficiencies that were in part recognized by Sutherland and Wark in 1955.

The Sutherland theory, based on potential theory or streamline flow, shows that the concentration,  $C$ , of mineral floated at a time  $t$  is related to its initial concentration,  $C_0$ , by the recovery,  $R$  as:

$$
R = \frac{C_0 - C}{C_0} = \left\{ 1 - \exp\left(-t \left[ \frac{3\pi \phi R_b R_p V_t N_B}{\cosh^2 (3 V_t \lambda / 2R_b)} \right] \right\} \right\}
$$
\n[4]

where  $R_b$  and  $R_p$  are the bubble and particle radii,  $V_t$  is the bubble-particle relative velocity,  $\lambda$  is the

induction time,  $N_B$  is the number of bubbles per unit volume, and  $\phi$  is the fraction of particles retained in the froth following bubble-particle attachment. The reader should note the relationship between eqns  $[2]$ ,  $[3]$  and  $[4]$ , which are the basis for a firstorder model, largely based on pulp microprocesses. Despite the deficiencies of the Sutherland model, his 'first approximation theory' yields results that are in fair agreement with experimental determinations of particle trajectories, touching angles and collision efficiencies, obtained from model experiments performed in a vertical flow tube with individual particles and a single bubble. For more detailed treatments of the hydrodynamic aspects of bubbleparticle collision the reader is referred to the extensive literature available.

The inability of collision theories to describe adequately the collection process between bubbles and smooth and angular particles was vividly demonstrated by Anfruns and Kitchener in 1977. Their experiments, the first measurements of absolute rate of capture, gave results in only fair agreement with collision theory, assuming every collision resulted in capture of their very hydrophobic particles.

#### **Process 2: Attachment Efficiency**

Derjaguin and Dukhin identified zone 2 in Figure 1 as that region where diffusion effects are important. A strong electric field exists in this zone, since the liquid flow around the moving bubble gives rise to a tangential stream at its surface that destroys the equilibrium distribution of adsorbed ions there. Where surfactant is present it is continually swept from the upper to the lower surface of the bubble. Transport of ionic surfactant to the moving bubble surface therefore takes place, leading to the establishment of a concentration gradient. A strong electric field of order  $3000 \text{ V cm}^{-1}$  is established when the cation and anion diffusion coefficients differ, as they generally do. Hence charged particles entering zone 2 will experience an electrophoretic force in precisely the same way as in an electrophoresis cell and will be either attracted towards, or repelled from, the bubble surface. The term 'diffusiophoresis' was coined for this phenomenon, i.e. the 'diffusiophoretic force' therefore acts on the particle as an additional force.

To date, however, evidence confirming the presence or absence of diffusiophoresis in flotation is equivocal and sparse. Apart from noting its possible contribution to capture efficiency, it is not pursued further here.

In zone 3, surface forces predominate once the thin film between the bubble and the particle is reduced

much below a few hundred nanometres. These forces can accelerate, retard or even prevent the thinning of the liquid film between the particle and the bubble. From a thermodynamic point of view, the free energy of a liquid film differs from the bulk phase from which it is formed. This excess free energy was originally called the 'wedging apart' or 'disjoining' pressure by Derjaguin and represents the difference between the pressure within the film,  $p^\mathrm{f}$ , and that in the bulk liquid adjacent to the solid surface,  $p^{l}$ . Note that for a bubble pushed against a flat solid surface, immersed in water,  $p^{\rm b}$ , the pressure within the bubble, is equal to *p*<sup>f</sup> . Derjaguin and his school, as well as Scheludko, performed experimental measurements of disjoining pressures, providing both the first real verification of the DLVO theory of surface forces (named after Derjaguin, Landau, Verwey and Overbeek), as well as the first accurate experimental estimates of the Hamaker constant. The disjoining pressure  $(\pi)$  depends on the Rlm thickness, *h*, and:

$$
\pi(h) = p^{\mathrm{f}} - p^{\mathrm{l}} \tag{5}
$$

For mechanical equilibrium in a stable film  $\pi(h) > 0$ and  $d\pi/dh < 0$ .

If the liquid film is stable at all thicknesses the liquid is said to wet the solid completely and the solid is said to be hydrophilic. This occurs, for example, when an air bubble approaches a clean silica surface  $immerged$  in water  $-$  in this instance the Hamaker constant is negative and the corresponding van der Waals force is repulsive for the silica-water-air triple layer. For an unstable film the thin film must drain, then rupture, and the resulting three-phase line of contact (tplc, vapour-water-solid) must expand to form a wetting perimeter before the particle can adhere to the bubble. Each of these events will have a characteristic time associated with it, the sum of which must be less than the contact time between the bubble and the particle if bubble-particle capture is to occur. The contact time is generally of the order of  $10^{-2}$  s or less. The induction time,  $\lambda$  (see eqn [4]) is normally taken as the time required for bubble-particle adhesion to occur, once the two are brought into contact, i.e. it is the sum of the thin film drainage and tplc spreading times  $(t_{\text{film}} + t_{\text{th}})$  and is synonymous with the attachment time. Rupture is a very fast process and is not a significant contributor to  $\lambda$ .

When a bubble is pressed against a solid surface, through water, the intervening film is generally not plane parallel. Rather the edge of the film thins quickly and a small, thicker dimple is trapped in the centre, because the bubble is deformable. This is essentially a kinetic phenomenon, caused by the outflow being greatest at the very edge of the film in the initial stages of drainage. The existence of this dimple has been detected experimentally. Hydrodynamic theories attempting to describe the profile and evolution of the dimple have been proposed but with very limited success in describing experimental data. Surface deformation of bubble surfaces can also occur under the influence of electrostatic interactions (and possibly other surface forces as well) aside from any kinetic effects.

An unstable film arises when there is a net attractive force between the particle and the bubble. This normally occurs when there is an attractive hydrophobic force involved, since the van der Waals and electrostatic forces are repulsive, except in rare circumstances. The measurement of this hydrophobic force, its length dependence and theoretical origins are subjects of intense research effort. In recent times it has become possible to measure the hydrophobic force, in a configuration relevant to the flotation process, by attaching a small particle to the cantilever in an atomic force microscope (**Figure 2**). The particle is then pressed against a captive bubble and the force-separation distance profile determined. In this fashion, the various surface forces may be explored.

Experimental evidence relating to film drainage in systems where soluble surfactants are present is rather equivocal. Adsorption and desorption processes coupled with possible molecular reorientation make any theoretical interpretation difficult. Unfortunately these are the very systems that are of primary interest to mineral processing. Furthermore additional complications ensue when one considers a particle approaching a bubble in flotation. The nature of the bubble surface (i.e. whether it is mobile or immobile) will influence the thinning of the thin film between bubble and particle. This makes any solution of the Navier-Stokes equation for film drainage difficult, particularly in the case of the



**Figure 2** Experimental arrangement for the measurement of forces between a particle and a bubble using the atomic force microscope colloid probe technique [from Fielden, Hayes and Ralston (1996), Langmuir, 12, 3721-3727, with permission].

angular particles that are normally present in flotation. It is worth recalling at this point the observations that smooth spheres float more slowly than angular particles under otherwise identical conditions, presumably because the asperities on the angular particles lead to increased film drainage rates and/or rupture.

The kinetics of movement of the tplc are of central importance in many processes, apart from flotation. During the movement of the tplc a dynamic contact angle is established. Irrespective of whether the 'surface chemical', 'hydrodynamic' or mixed 'surface chemical/hydrodynamic' approaches are used, there is as yet no general theory that adequately describes tplc kinetics on all surfaces. One cannot generally calculate *ab initio* what the spreading velocity of the tplc will be when an air bubble spreads over a mineral surface immersed in water in the presence of a surfactant. Part of the problem at least is due to the fact that poorly characterized experimental systems have been used where any generalization has been obscured by the same time-dependent adsorption/desorption/ molecular reorientation processes that complicate thin Rlm drainage rate studies. Physical and chemical surface heterogeneities on the particle surface also strongly influence the tplc kinetics.

At present only the crudest estimates of  $t_{\text{film}}$  and  $t_{\text{thle}}$  can be made. Hence various experimental methods for determining  $\lambda$  are frequently resorted to. A potentially valuable approach to the calculation of induction times, based on bubble deformation and restoration, has been developed.

These experimental methods for determining induction times are generally based on either pressing a bubble against a smooth mineral surface or against a bed of particles. The disadvantages of all current methods for determining  $\lambda$  include: (1) insufficient understanding of the process of bubble deformation and energy dissipation during bubble-particle  $collision$ ; (2) insufficient information concerning the behaviour of the attractive hydrophobic forces during the bubble-particle interaction (e.g. how the thin Rlm of liquid evolves during the time a particle slides or rolls around a bubble; it may well be incorrect to assume that bubble-particle interaction ceases when the particle passes the bubble equator); (3) the absence of data on  $t_{\text{film}}$ , e.g. influence of surfactant type and concentration on thin-film drainage mechanisms and rate; and (4) the absence of data on  $t_{\text{th}}$  as a function of hydrophobicity, physical and chemical surface heterogeneities and surfactant type.

The most appropriate method for determining induction times is probably through direct observation of bubble-particle interactions in a flotation cell under well-defined conditions. The necessary theory can then be developed. For the present the Sutherland and similar approaches (eqn [4]) serve as useful approximations in determining  $\lambda$  from experimental flotation data of the type normally generated.

Kinetic effects certainly have a strong influence on bubble-particle collision and attachment efficiencies. The latter provides the key to selective separations in flotation. Once attachment has occurred, the interplay between particle size and contact angle in the environment of the flotation cell becomes of paramount importance and is the next subject of our discussion.

#### **Process 3: Stability Efficiency and Detachment**

**Flotation limits for coarse particles** The essential problem in understanding bubble-particle aggregate stability is to determine whether or not the adhesive force, acting on the tplc, is large enough to prevent the destruction of the aggregate under the dynamic conditions that exist in flotation. It is important to understand the physics of the problem before moving on to a mathematical description. Let us consider a smooth spherical particle located at the fluid interface. Once the equilibrium wetting perimeter has been established following spreading of the tplc, the static buoyancy of this volume of the particle will act against the gravitational force (**Figure 3**). The hydrostatic pressure of the liquid column of height  $Z_0$  acts against the capillary pressure. The 'other detaching forces' require further discussion. Since they arise from the particle motion relative to the bubble, velocity-dependent drag forces will oppose the detachment of the particle from the bubble. An analysis of these forces is extremely complex and has not been reported to date. Therefore any force balance will necessarily be quasistatic and approximate.

The net adhesive force,  $F_{\text{ad}}$ , is equal to the sum of the attachment forces,  $F_a$ , minus the detachment forces,  $F_d$ , i.e.:

$$
F_{\rm ad} = F_{\rm a} - F_{\rm d} \tag{6}
$$



Figure 3 Location of a smooth spherical particle at a fluid interface. (From Schulze (1983) Physicochemical Elementary Processes in Flotation. Amsterdam: Elsevier.)

The particle will not remain attached to the bubble if *F*ad is negative but will be present in the liquid phase.

The mathematical description of the various forces that dictate the equilibrium position of particles at liquid-vapour or liquid-liquid interfaces has followed an evolutionary trail. Analogous processes of interest, for example, include pigment 'flushing', where a solid particle is induced to transfer from one liquid phase to another by appropriate surface modification with surfactants, and the stabilization of emulsion droplets by solid particles.

The actual problem of the balance of forces operating on a particle at a liquid-air interface has been considered by Sutherland and Wark, who considered the case of a gas bubble attached to a plane solid surface of infinite extent and used this as a model for bubble–particle adhesion in flotation. Since this work there have been other very notable contributions. It was Princen who proposed the first extensive and generalized treatment of the forces acting on a particle at fluid interfaces. This theory was developed further by Schulze in 1977 and expanded in 1983.

Consider the case of a spherical particle at a liquid-air interface. We assume that the system is in a quasistatic state and that the contact angle corresponds to that for a static system. The dynamic contact angle can depart significantly from the static value, depending in part on the velocity of the tplc. If the particle oscillates around its equilibrium position, the tplc would be expected to move to some extent. Hence a full analysis would need to account for the velocity-dependent drag forces mentioned above and link these to contact angle dynamics. Since this is an intractable problem at present, a simpler approach is necessary.

Let us suppose that a spherical particle of radius  $R_p$  is attached to a bubble of radius  $R_b$  where  $R_b$  is much greater than  $R_p$ , as shown in Figure 3. By understanding the forces that operate on the particle, it is possible to calculate the energy of detachment. The forces acting upon the particle are as follows:

• Capillary force,  $F_c$ , acting in the vertical direction along the tplc:

$$
F_c = 2\pi r_0 \gamma \sin \phi_0 = -2\pi R_p \gamma \sin \omega [\sin(\omega + \theta)]
$$
\n[7]

where  $\gamma$  is the liquid-vapour surface tension.

• Static buoyancy of the fractional volume of the immersed particle,  $F_b$ :

$$
F_{\rm b} = \frac{\pi}{3} R_{\rm p}^3 \rho_1 g [(1 - \cos \omega)^2 (2 + \cos \omega)] \qquad [8]
$$

 Hydrostatic pressure, *F*h, of the liquid column of height  $Z_0$  on the contact area:

$$
F_{\rm h} = -\pi r_0^2 \rho_1 g Z_0 = -\pi R_{\rm p}^2 (\sin^2 \omega) \rho_1 g Z_0 \quad [9]
$$

• Capillary pressure,  $F_p$ , in the gas bubble which acts on the contact area  $\pi r_0^2$ :

$$
F_{\rm p}=P_{\gamma}\pi r_0^2
$$

which for a spherical bubble is given approximately as:

$$
F_{\rm p} \approx \pi R_{\rm p}^2 \sin^2 \omega \left(\frac{2\gamma}{R_{\rm b}} - 2R_{\rm b}\rho_{\rm 1}g\right) \qquad [10]
$$

• Gravitational force,  $F_{\rm g}$ :

$$
F_{\rm g} = \frac{4}{3} \pi R_{\rm p}^3 \rho_{\rm p} g \tag{11}
$$

where  $\rho_p$  is the particle density.

 $\bullet$  Extra detaching forces,  $F_d$ , which are denoted approximately and generally as the particle mass multiplied by a generalized acceleration  $b_m$  in the flotation cell:

$$
F_{\rm d} \approx \frac{4}{3} \pi R_{\rm p}^3 \rho_{\rm p} b_{\rm m} \tag{12}
$$

It is worth remarking that it is bubble-particle aggregates that are actually accelerated in the flotation device, thus  $\rho_p$  is in fact an approximation  $(\Delta \rho = \rho_{\rm p} - \rho_1).$ 

At equilibrium, the sum of these forces,  $\sum F$ , must equal zero.

The energy of detachment,  $E_{\text{det}}$ , corresponds to the work done in forcing a particle to move from its equilibrium position,  $h_{eq}(\omega)$  at the liquid-vapour interface to some critical point,  $h_{\text{crit}}(\omega)$ , where detachment occurs and the particle moves into the liquid phase. The sum of the various forces,  $\sum F$ , is related to  $E_{\text{det}}$  by:

$$
E_{\text{det}} = \int_{b_{\text{eq}}(\omega)}^{b_{\text{crit}}(\omega)} \sum F \, \mathrm{d}h(\omega) \tag{13}
$$

Equation [13] may be solved by introducing the various forces and carrying out a numerical integration. The detachment process takes place when the kinetic energy of the particle equals  $E_{\text{det}}$ . The kinetic energy of the particle is given by  $\frac{2}{3}\pi R_p^3 \rho_p V_t^2$ , where  $V_t$  is the relative (turbulent) velocity of the particle, acquired due to stresses on the bubble-particle aggregate in the turbulent field of the flotation cell, as the aggregate collides with other bubbles or aggregates or due to other modes of excitation.  $V_t$  is determined experimentally as the velocity of gas bubbles in the flotation cell and  $\rho_p$  is the density of the particle.

The maximum floatable particle diameter based on the kinetic theory,  $D_{\text{max,K}}$ , is given as:

$$
D_{\text{max,K}} = 2 \left[ \frac{3}{2\pi \rho_p V_t^2} \int_{b_{\text{eq}}(\omega)}^{b_{\text{crit}}(\omega)} \left\{ \frac{2}{3} \pi R_p^3 \rho_1 g \right.\right.
$$
  

$$
\times \left[ 1 - \frac{2\rho_p}{\rho_1} - \cos^3 \omega + \frac{3b}{2R_p} \sin^2 \omega \right.
$$
  

$$
- \frac{3}{a^2 R_p^2} \sin \omega \sin(\omega + \theta) \right]
$$
  

$$
- \pi (R_p \sin \omega)^2 \left( \frac{2\gamma}{R_b} - 2R_b \rho_1 g \right) \right\} dh \Big]^{1/3}
$$
[14]

Equation [14] may be solved by numerical integration or by plotting each of the kinetic and detachment energies as a function of  $R_p$  at constant  $\gamma$  and  $\rho_p$  and specified  $V_t$ .  $\rho_1$  refers to the density of the fluid and  $\gamma$  is the surface tension at the liquid-vapour interface. This equation has been shown to describe adequately both the detachment of a sphere from a liquid-vapour interface and the behaviour of hydrophobic angular quartz particles between approximately 30 and  $120 \mu m$  in diameter under flotation conditions.

Flotation limits for fine particles The only theoretical study to date dealing with the limit of floatability of fine particles was published by Scheludko and co-workers in 1976. The limit is the critical work of expansion required to initiate a primary hole or threephase contact line during bubble-particle approach } a requirement that is met by the kinetic energy of the particles. The matching of these two quantities enables a minimum particle diameter,  $D_{\text{min,K}}$ , for flotation to be obtained:

$$
D_{\min,K} = 2 \left[ \frac{3\kappa^2}{V_t^2 \Delta \rho \gamma \{1 - \cos \theta\}} \right]^{1/3} \qquad [15]
$$

where  $\kappa$  is the line tension, opposing expansion of the tplc. Molecules that are present in a line have a free energy that is different from those at a surface  $-$  in fact there is an excess linear free energy and a linear tension in an analogous fashion to that of excess surface free energy and surface tension.

In fact,

$$
\kappa = \left(\frac{\partial F}{\partial L}\right)_{T,V,W} \tag{16}
$$

where *F* is the Helmholtz free energy, *L* is the contact line, *T* is the temperature, *V* is the volume and *W* is the thermodynamic work. The Young-Dupré equation becomes:

$$
\gamma_{S/V} - \gamma_{S/L} = \gamma_{L/V} \cos \theta \pm \frac{\kappa}{r}
$$
 [17]

The line tension is important for small contact radii and can oppose or reinforce  $\gamma_{L/V}$  cos  $\theta$ . It counteracts the formation of the tplc in Scheludko's theory which neglects thin film drainage and other hydrodynamic effects. Experimental data for hydrophobic, angular quartz particles between about 10 and  $35 \mu m$ in average diameter follow a general trend that is predicted by eqn [15], although quantitative agreement is poor. If a pseudo-line tension, embracing surface heterogeneities, replaces  $\kappa$  in eqn [15], then this in turn enables  $D_{\min}$  in eqn [15] to be reexpressed in terms of a critical bubble radius below which attachment does not occur. Reconciliation between theory and experiment is then achieved although the concept of pseudo-line tension needs to be placed on a firmer experimental foundation.

# **The Future**

In terms of our fundamental understanding, there is no entirely adequate collision model that can correctly account for particle size and inertial effects in the presence and absence of soluble surfactants. Thin film drainage is poorly understood when one of the interfaces is both physically and chemically heterogeneous, and the other is deformable. The nature of the hydrophobic interaction between a particle and a bubble requires both experimental and theoretical verification. There is no reliable model at present to describe the movement of a three-phase contact line over a physically and chemically heterogeneous surface. Thus major research challenges exist that, if they are to be successfully overcome, must embrace systems where surfactants are both present and absent.

From a separation technology point of view, froth flotation will continue to be one of the principal means by which ores are successfully beneficiated for many years to come. Increasingly the technique is also being used in the deinking of paper, soil remediation, plastics recycling and heavy metal ion decontamination, to name but a few examples. Both research and practice are expected to accelerate strongly over the next decades as new techniques and theoretical approaches are used.

# **Further Reading**

- Anfruns JF and Kitchener JA (1977) Rate of capture of small particles in flotation. *Transactions of the Institution of Mining and Metallurgy, Section C 86: C9-C15.*
- Blake TD and Kitchener JA (1972) Stability of aqueous films on hydrophobic methylated silica. *Journal of the Chemical Society*, *Faraday Transactions I* 68: 1435-1442.
- Blake TD (1993) Dynamic contact angles and wetting kinetics. In: Berg JC (ed.), ch. 5. *Wettability*. New York: Marcel Dekker.
- Collins GL and Jameson GJ (1976) Experiments on the flotation of fine particles: the influence of particle size and charge. *Chemical Engineering Science* 31: 985-991.
- Crawford R and Ralston J (1988) The influence of particle size and contact angle in mineral flotation. *International Journal of Minerals Processing* 23: 1-24.
- Dai Z, Dukhin SS, Fornasiero D and Ralston J (1998) The inertial hydrodynamic interaction of particles and rising bubbles with mobile surfaces. *Journal of Colloid and Interface Science* 197: 275-292.
- Derjaguin BV and Dukhin SS (1960-61) Theory of flotation of small and medium-size particles. *Transactions of the Institute of Mining and Metallurgy* 70:  $221 - 246.$
- Diggins D, Fokkink LGJ and Ralston J (1990) The wetting of angular quartz particles. *Colloids and Surfaces* 44: 299-313.
- Drelich J and Miller JD (1992) The effect of surface heterogeneity on pseudo-line tension and the flotation limit of fine particles. Colloids and Surfaces 69:  $35 - 43$
- Fielden ML, Hayes RA and Ralston J (1996) Surface and capillary forces affecting air bubble-particle interactions in aqueous electrolyte. *Langmuir* 12: 3721}3727.
- Hewitt D, Fornasiero D, Ralston J and Fisher LR (1993) Aqueous film drainage at the quartz-water interface. *Journal of the Chemical Society*, *Faraday Transactions* 89: 817-822.
- Hewitt D, Fornasiero D and Ralston J (1995) Bubble particle attachment. *Journal of the Chemical Society*, *Fara*day Transactions 91: 1997-2001.
- Israelachvili JH (1991) *Intermolecular and Surface Forces*, 2nd edn. London: Academic Press.
- Laskowski JS and Ralston J (1992) *Developments in Mineral Processing*. *Colloid Chemistry in Mineral Processing*. Amsterdam: Elsevier.
- Lynch AJ, Johnson NW, Manlapig EV and Thorne CG (1981) *Mineral and Coal Flotation Circuits*: *Their Simulation and Control*. Amsterdam: Elsevier.
- Miklavcic SJ, Horn RG and Bachmann (1995) Colloidal interaction between a rigid solid and a fluid drop. *Journal of Physical Chemistry* 99: 16357-16364.
- Ralston J (1992) The influence of particle size and contact angle in flotation. In: Colloid Chemistry in Mineral *Processing*, ch. 6. Amsterdam: Elsevier.
- Scheludko A, Toshev BV and Bojadjiev DT (1976) Attachment of particle to a liquid surface (capillary theory of flotation). *Journal of the Chemical Society*, *Faraday Transactions* 72: 2815-2828.
- Schulze HJ (1983) *Physico-chemical Elementary Processes in Flotation*: *An Analysis from the Point of View of Colloid Science Including Process Engineering Considerations*. Amsterdam: Elsevier.
- Sutherland KL (1948) Kinetics of the flotation process. *Journal of Physical Chemistry* 52: 394–425.
- Sutherland KL and Wark IW (1955) *Principles of Flotation*. Melbourne: Australasian Institute of Mining and Metallurgy.
- Ye Y and Miller JD (1989) The significance of bubble-particle contact time during collision in the analysis of flotation phenomena. *International Journal of Mineral Processing* 25: 199-219.

# **Column Cells**

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## **Introduction**

### **History**

The first pneumatic flotation cell, which used air sparging through a porous bottom and horizontal slurry flow, was patented in 1914 by Callow. The first countercurrent column flotation device was designed and tested by Town and Flynn in 1919. Cross-current pneumatic flotation machines were widely used in industry in the 1920s and 1930s, but were later replaced by the impeller-type flotation devices in mineral-processing plants. Dissolved-air flotation became the main type of flotation for water treatment applications. These substitutions were the result of the absence of effective and reliable air spargers for fine bubble generation and the lack of automatic control systems on the early columns. During this period, both the poor flotation selectivity and entrainment of slimes characteristic of impeller-type cells were offset by the use of complex flow sheets using large numbers of cleaner stages and recycle lines. Column flotation devices were reintroduced