THE FLOTATION LIMIT OF FINE PARTICLES
BASED ON CONTACT ANGLE MEASUREMENTS

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Abstract. The flotation limit of fine particles has been re-examined based on the effect of bubble size on contact angle, and a new surface chemistry-limited relationship describing the minimum particle size which can be floated is proposed. In this analysis the critical value of bubble-solid contact radius ($r_c$) for which there is no effective attachment between particle and bubble has to be determined. The values of $r_c$ determined by extrapolation of our experimental data for contact angle versus bubble-solid contact diameter permit the prediction of the flotation limit of methylated quartz particles, with fractional coverage of trimethylsilyl groups from 0.07 to 0.51. The limit of fine particle flotation as determined by this theoretical approach agrees well with experimental data reported in the literature.

Introduction

Highly-mechanized mining techniques and advanced grinding methods needed for liberation of low grade mineral resources leads to the generation of large quantities of fine particles. In many cases these fine mineral particles have been discarded resulting in ineffective use of our mineral resources and causing environmental problems. A decline in the quality of our mineral resources, economic-related need for selective separation, and environmental restrictions have pushed industry to deal with the processing, separation, and recovery of fine particles. In this regard, the particle size limit for the flotation of small particles has important practical significance in separation technology. Considerable experimental and theoretical research results have been reported in order to evaluate the optimum particle size which can be floated effectively. Only the upper limit for the flotation of coarse particles can be successively predicted using several theoretical analyses (Schulz et al., 1976; Schulz, 1977; 1984), whereas the flotation limit of fine particles is still unpredictable.

A theoretical treatment of the problem for the flotation limit of fine particles was undertaken by Scheludko et al. (1976). They considered the flotation process as the formation of a wetting perimeter, the three-phase contact line, on the basis of the capillarity theory and the kinetic energy of the particles. The minimum particle diameter which can be floated was found to be:

$$D_{\text{min}} = 2 \left[ \frac{3 \gamma_{LV}^2}{\Delta \rho \ k^2 \ \gamma_{LV} (1 - \cos \theta)} \right]^{1/3}$$

(1)

where $\gamma_{LV}$ is the line tension defined thermodynamically as the free energy change for the three-phase system, $\delta F$, caused by the change in the three-phase contact line length, $\delta L$, at constant temperature, $T$, volume, $V$, and interfacial area, $A$. Thus, $\gamma_{LV} = (\delta F/\delta L)_{N/A}$. Also, $\gamma_{LV}$ is the surface tension of aqueous phase; $\Delta \rho$ is the density difference between the particle and the liquid; $u$ is the bubble ascent velocity; $\theta$ is the contact angle for gas bubble attached to the particle measured through the aqueous phase.

Ralsdon and co-workers (Blake and Ralsdon, 1985; Crawford and Ralsdon, 1988) presented experimental data for the flotation limit of fine hydrophobized quartz particles. The results did not correlate at all with the theoretical values calculated using Eqn (1), when an order of magnitude estimate of line tension of $10^{-20}$ N, as suggested for such systems by Scheludko et al. (1976), was used. The theoretical values for the flotation limit of methylated quartz particles were found to be at least an order of magnitude smaller than those determined experimentally. The reasons responsible for such significant discrepancy between theory and experiment are discussed in this contribution and the Scheludko-Tochev-Bojadjiev capillary theory of flotation is reexamined and modified. A new surface chemistry-limited relationship describing the minimum particle size which can be floated is proposed and is supported experimentally. The new surface-chemistry limited relationship allows for the prediction of the flotation limit of fine methylated quartz particles.

Scheludko-Tochev-Bojadjiev Flotation Limit of Fine Particles

Scheludko et al. (1976) analysed the process of formation of a wetting perimeter when a spherical particle touches a planar liquid surface, such as shown in Figure 1. They derived a relationship for the elementary work of expansion of the three-phase contact line as follows:

$$dW = 2 \pi r \left[ \frac{\gamma_{SLV}}{r} - \gamma_{LV} (1 - \cos \theta) \right] \, dr$$

(2)

where $W$ is the work of expansion of the three-phase contact line; $r$ is the radius of the perimeter of the three-phase contact line for the liquid/spherical particle interface (see Figure 1); other nomenclature is the same as used in the equation (1).

After integration of Eqn (2) for the limits of $r = 0$ and $r = r_c$, they obtained the relationship for the work which should be overcome in order for attachment to occur:

$$W_C = \pi r_c \gamma_s L = \frac{\pi \gamma_{SLV}^2}{\gamma_{LV} (1 - \cos \theta)}$$

(3)

Figure 1. Small spherical particle at the fluid interface.
where \( r_c \) is the critical radius of the perimeter of the three-phase contact line below which there is no effective attachment between mineral particle and gas bubble.

Further, they assumed that the mean kinetic energy for collisions of mineral particles with gas bubble during flotation process is equal to the half of the kinetic energy for central collision:

\[
U_m = \frac{U}{2} = \frac{m u^2}{4} = \frac{\pi D^3 \Delta \rho u^2}{24}
\]

(4)

where \( m \) is the mass of the solid particle in liquid; \( D \) is the solid particle diameter.

They concluded that the mean kinetic energy for collision should be at least equal to the work of the formation of the three-phase contact line for attachment between mineral particle and gas bubble to occur, \( U_m = W_c \), and on this basis they derived the expression, Eqn (1), for the minimum diameter of spherical particle which can be floated:

\[
D_{\text{min}} = \left( \frac{3 \gamma_{FL}^2}{\Delta \rho u^2 \gamma_{LV} (1 - \cos \theta)} \right)^{\frac{1}{3}}
\]

(1)

Skeludko et al. (1976) considered a simple model of a spherical solid particle at the liquid surface which surface is homogeneous and smooth. For such system the modified Young equation which include the line-tension term is as follows (Skeludko et al., 1976):

\[
\gamma_{SV} - \gamma_{SE} = \gamma_{LV} \cos \theta - \frac{\gamma_{SL} \cos \alpha}{r}
\]

(5)

which can be expressed in another form:

\[
\cos \theta = \cos \theta_m + \frac{\gamma_{SL} \cos \alpha}{\gamma_{LV}}
\]

(6)

where \( \gamma_{SV} \) and \( \gamma_{SE} \) are the solid-vapor and solid-liquid interfacial free energies, respectively; and \( \alpha \) is the angle between the solid surface and the plane containing the wetting perimeter (see Figure 1).

Equation (6) describes the changes in contact angle for a spherical solid particle at the planar water surface with respect to the effect of the excess energy at the three-phase contact line. At the time of formulation of the capillary theory of flotation by Scheludko et al. (1976), the effect of solid surface imperfections, heterogeneity and roughness, on contact angle/bubble (drop) size relationship was not recognized. The shape of the most mineral particles which are separated during flotation is irregular and their surface is heterogeneous due to incomplete liberation of minerals, anisotropy of mineral phases, and nonuniform distribution of adsorbed collectors, surfactants, impurities etc. In this regard, more rigorous treatment of the thermodynamic conditions at the three-phase contact line is required.

The Effect of Surface Heterogeneity and Roughness on Contact Angle

Surface Heterogeneity: For some time it was generally accepted that the equilibrium contact angle for composite surfaces can be predicted from the Cassie equation which is as follows (Cassie, 1948):

\[
\cos \theta = \sum f_i \cos \theta_i
\]

(7)

where \( f_i \) is the fractional area of the surface with a contact angle of \( \theta_i \).

At a time when Cassie considered the equilibrium three-phase contact angle for heterogeneous solids, a little was known on the excess energy associated with the contact line common to all three phases. Consequently, he could not predict that the heterogeneity of a solid surface may cause corrugation of the three-phase contact line due to variation of the local contact angle. A hypothetical model of a spherical solid particle with a smooth heterogeneous surface composed of two types of material differing in surface free energy is shown in Figure 2. A similarly composed, but planar, solid surface was considered in previous contributions (Drewich and Miller, 1992a; 1993), and the Cassie equation was modified to include the line-tension term. For a smooth two-component heterogeneous and spherical solid particle, such as shown in Figure 2, the modified Cassie equation is as follows:

\[
\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 + \left( \frac{\cos \alpha}{\gamma_{LV}} \right) \left( \frac{f_1 \gamma_{SL} - f_2 \gamma_{SL}}{r_1} \right)
\]

(8)

or expressed in another form:

\[
\cos \theta = \cos \theta_m + \frac{\cos \alpha}{\gamma_{LV}} \left( \frac{f_1 \gamma_{SL} - f_2 \gamma_{SL}}{r_1} \right)
\]

(9)

![Figure 2. Small spherical particle with heterogeneous surface at the fluid interface.](image-url)
where \( r_1 \) and \( r_2 \) are the radii of local curvatures as shown in Figure 2; \( \gamma_{LV}, \gamma_{SV}, \) and \( \gamma_{LS} \) are the line tensions for two different regions of solid surface.

The modified Young equation for such a system is:

\[
\gamma_{SV} - \gamma_{SE} = \gamma_{LV} \cos \theta - \left( f_1 \frac{\gamma_{LV}}{r_1} - f_2 \frac{\gamma_{LV}}{r_2} \right) \cos \alpha
\]

Eqn (10) shows that the line-tension term in the description of heterogeneous surface is much more complex than the line-tension term in the modified Young equation (5) for an ideal spherical solid particle with a smooth and homogeneous surface.

**Surface Roughness:** Modification of the Young equation for a rough solid surface was proposed by Wenzel (1936) as shown below:

\[
x(\gamma_{SV} - \gamma_{SE}) = \gamma_{LV} \cos \theta
\]

\[x = \frac{da}{dt} \geq 1 \tag{11a}\]

with \( x \) as the actual interfacial area, and \( A \) as the "apparent" area of the "geometrical" interface.

Similar to the case considered by Cassie, Wenzel did not predict a contribution of the three-phase contact line in the description of the equilibrium contact angle for liquid at a rough solid surface. The Wenzel equation, Eqn (11), was corrected for the line tension effect in previous contributions (Drellich and Miller, 1992a; Drellich, 1993). For the flotation system under consideration, a simple model for a rough solid particle with a regular roughness pattern is considered and presented in Figure 3. The Young equation must be modified for such a system to include the roughness factor and the line-tension term, and such modification leads to the following equation:

\[
x(\gamma_{SV} - \gamma_{SE}) = \gamma_{LV} \cos \theta - x \frac{\gamma_{LV}}{r} \cos \alpha
\]

or

\[
\cos \theta_r = x \left( \cos \theta_s + \frac{\gamma_{LV}}{r} \cos \alpha \right)
\]

where subscripts \( r \) and \( s \) correspond to rough and smooth surface, respectively.

**Surface Heterogeneity and Roughness:** Most mineral particle surfaces are heterogeneous and rough. Imperfections at solid surface make the system even more complicated than has been discussed so far. For such complex systems, the modified Cassie-Wenzel equation was derived and presented in another contribution (Drellich, 1993). For the simplified case of a spherical solid particle with a surface composed of two types of material with different energetic properties, as in Figure 2, and also regularly roughened, as in Figure 3, the relationship for equilibrium contact angle was derived from the general formula (Drellich, 1993) and found to be:

\[
\cos \theta_r = x \left( f_1 \cos \theta_1 + f_2 \cos \theta_2 + \frac{\gamma_{LV}}{r_1} - \frac{\gamma_{LV}}{r_2} \right) \cos \alpha
\]

where superscript "het" indicates heterogeneous surface, and other subscripts are the same as used in the equations presented in the previous sections.

This short theoretical background indicates the complexity of such an analysis of heterogeneous surfaces when the line-tension term is taken into consideration (additional discussion on this problem is presented in the following references: Drellich and Miller, 1992a; 1992b; Drellich et al., 1993; Drellich, 1993). It is evident that Scheludko et al. (1976) considered only the simplest ideal model of spherical solid particle with a smooth and homogeneous surface. Such systems can be described by Eqn (6) which predicts a linear relationship between \( \cos \theta \) and \( 1/r \) (Figure 4). Deviation of the solid surface from ideality, chemical heterogeneity and/or roughness, may make the \( \cos \theta \) vs. \( 1/r \) relationship nonlinear according to the complications which arise from the line-tension term (see Eqns (8), (13), (14)). Already this concept was demonstrated experimentally for several imperfect surfaces (Drellich and Miller, 1992a; 1992b; Drellich et al., 1993; Drellich, 1993) and generally for such systems a nonlinear \( \cos \theta \) vs. \( 1/r \) relationship, as presented in Figure 4, was observed. These results allowed us to conclude that the elementary work of expansion of the three-phase contact line derived by Scheludko et al. (1976), Eqn (2), can not be used for real, heterogeneous and rough, solid particles. In this regard, the theoretical model of Scheludko et al. (1976) was modified (Drellich and Miller, 1992b) to take into consideration the effect of surface imperfections on the work of expansion of the three-phase contact line and how such an effect would alter the equation describing the flotation limit of fine particles.

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**Figure 3.** A hypothetical model of a small spherical particle with uniformly corrugated surface at the fluid interface.

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**Portion of the model particle surface:**

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The Flotation Limit of Fine Particles

**Modified Theoretical Relationship:** The elementary work of expansion of the three-phase contact line for imperfect systems, heterogeneous and/or rough, may be expressed as follows:

\[
dW = k(\eta) \left[ \frac{\gamma_{LV}}{r} - \gamma_{LV} (1 - \cos \theta) \right] dr
\]

where \(l(\eta)\) is the length of the three-phase contact line; \(\gamma_{LV}\) is the pseudo-line tension.

Because of the complexity of equilibrium conditions at heterogeneous and/or rough solid surfaces including the line-tension term for describing such surfaces, the pseudo-line tension was proposed in the literature (Good and Koo, 1979; Drellich and Miller, 1992a; 1992b; Drellich et al., 1993; Drellich, 1993) to replace the line-tension term. The difference between line tension and pseudo-line tension can be visualized by the following expressions, which describe the relationship between the pseudo-line tension and line-tension terms for simple model surfaces such as presented in the previous section (Drellich and Miller, 1992; Drellich, 1993):

- for heterogeneous surface:
  \[ \frac{\gamma_{LV}}{r} = \sum \left( f_i \frac{\gamma_{LV}}{r_i} \right) \]

- for rough surface:
  \[ \frac{\gamma_{LV}}{r} = 2 \frac{\gamma_{LV}}{r} \]

- for heterogeneous and rough surface:
  \[ \frac{\gamma_{LV}}{r} = \sum \left( x_i f_i \frac{\gamma_{LV}}{r_i} \right) \]

The pseudo-line tension may be determined experimentally for each system from the \(\cos \theta\) vs. \(1/r\) relationship, since the shape of the local curvatures \((c)\) and the line tensions \((\gamma_{LV})\) themselves are most difficult to determine for microscopic regions of real solid surfaces (see the following references for further discussion: Drellich and Miller, 1992a; 1992b; Drellich et al., 1993; Drellich, 1993).

An expression for the pseudo-line tension can be derived from Eqn (15) for equilibrium conditions, \(dW = 0\), and is:

\[ \gamma_{LV} = \gamma_{LV} (1 - \cos \theta) r_c \]

Also, the integration of Eqn (15) for the limits of \(r = 0\) and \(r = r_c\) \((r_c\) is the critical radius of the perimeter of the three-phase contact line below which there is no effective attachment between mineral particle and gas bubble, as used in previous equations) leads to an expression similar to Eqn (3) for the work of expansion of the three-phase contact line:

\[ W_C = \frac{\pi^2 \gamma_{LV}^2}{\gamma_{LV} (1 - \cos \theta)} \]

Next, following the assumption suggested by Scheludko et al. (1976) that the work of expansion of the three-phase contact line must be at least equal to the mean kinetic energy for collision between gas bubble and solid particle for attachment to occur, \(W_m = W_C\), the flotation limit of fine particles, Eqn (1), is modified as follows:

\[ D_{\text{min}} = 2 \left[ \frac{3\gamma_{LV}^2}{\Delta \rho u^2 \gamma_{LV} (1 - \cos \theta)} \right]^{\frac{1}{3}} \]

As was found in previous studies (Drellich and Miller, 1992a; 1992b; Drellich et al., 1993), the pseudo-line tension changes with change in bubble (drop) size for most nonideal systems. This inconsistency in the pseudo-line tension value over a wide range of bubble size may complicate the determination of the minimum particle size from Eqn (18). Fortunately, the pseudo-line tension may be eliminated in Eqn (18).
by substituting Eqn (16). When such a mathematical operation is performed, the expression for the flotation limit of fine particles is of the following form (Drellich and Miller, 1992b):

\[
D_{mb} = 2 \left[ \frac{3 \gamma_{LS} (1 - \cos \theta)}{\Delta \rho \, a^2} \right]^{1/3} \tag{19}
\]

Neither the line tension nor the pseudo-line tension are required in Eqn (19). The value that needs to be determined from contact angle measurements is the critical radius for the bubble base below which there is no attachment between the solid surface and gas bubble.

Experimental Verification: Several quartz plates, each with a different degree of hydrophobization, were used to examine the contact angle/bubble size relationship and determine the critical radius of the bubble size for which \( \theta = 0 \) (Drellich and Miller, 1992b; Drellich, 1993). Examples of experimental data are presented in Figure 5. Linear regression extrapolation analysis of experimental data of contact angle versus bubble base radius for small bubbles (bubble base radius of \( r < 0.1 \) mm) was used to determine the value of \( r_c \) for \( \theta = 0 \).

On this basis the flotation limit of fine particles was calculated using Eqn (19) with the following values, \( \gamma_{LS} = 72.4 \) mN/m, \( \Delta \rho = 1650 \) kg/m³, and \( V = 0.2 \) and 0.3 m/s, as specified for the flotation experiments reported by Blake and Ralston (1985), and Crawford and Ralston (1988). The contact angles (\( \theta \) in Eqn (19)) for water drops placed at the methyalted quartz surfaces were measured and used in the calculations of \( D_{mb} \) values.

Calculated average values of \( D_{mb} \) based on contact angle measurements, are presented in Figure 6 together with the data for the flotation limit of methyalted quartz particles (Blake and Ralston, 1985; Crawford and Ralston, 1988). Additionally, minimum particle sizes of methyalted quartz which can be floated were calculated from the theory of Scheludko et al. (1976), Eqn (1), using the extreme values of the line tension of \( 2.8 \times 10^{-10} \) N and \( 5.6 \times 10^{-9} \) N (values of line tension estimated for this system by Scheludko et al., 1976), and are presented in Figure 6.

There is a good agreement between the experimental values taken from the literature (Blake and Ralston, 1985; Crawford and Ralston, 1988) and average values calculated from proposed surface chemistry-limited relationship, Eqn (19), except for the sample with \( \theta = 17^\circ \). Some differences between the experimental \( D_{mb} \) values of Ralston et al. (Blake and Ralston, 1985; Crawford and Ralston, 1988) and those calculated from contact angle data may be expected since the fine particles examined in the flotation experiments probably differed in roughness from quartz plates used in the contact angle measurements. Also, it might be expected that the distribution of adsorbed trimethylsilyl groups could differ slightly. This uncertainty may be included in the confidence intervals associated with the determination of \( D_{mb} \) values.

Contact angle measurements were limited to bubbles with a base diameter larger than 0.06 mm, which leads to some uncertainty in the determination of \( r_c \) (Drellich and Miller, 1992b; Drellich, 1993). The confidence intervals for the flotation limit of fine methyalted quartz particles were calculated from Eqn (19) using contact angle data and are also marked in Figure 6. Even taking into consideration the uncertainty in the calculated values of minimum particle size it is clear that this analysis gives a much better explanation of the experimental values of Ralston and co-workers than the analysis using the Scheludko-Toshev-Bojadjiev equation, Eqn (1) (see Figure 6). Nevertheless, there is still some uncertainty with respect to the hydrodynamic conditions of the flotation experiments of Ralston et al. (Blake and Ralston, 1985; Crawford and Ralston, 1988), which were not considered when the critical radius of bubble base, \( r_c \), was determined.

Correction for Hydrodynamic Conditions: A new surface chemistry-limited relationship describing the minimum particle size which can be floated, Eqn (19), requires experimental determination of the critical bubble radius, \( r_c \), for which there

![Figure 5](image)

**Figure 5.** The effect of bubble size on contact angle for methyalted quartz plates; \( f \) is the fractional area of the quartz surface with adsorbed trimethylsilyl groups; \( \theta \) is the contact angle; \( r \) is the radius of the bubble size (Drellich and Miller, 1992b; Drellich, 1993).
is no effective attachment between solid surface and gas bubble. In the determination of the flotation limit of methylated quartz particles this critical value was obtained after extrapolation of the contact angle/bubble size relationship to the value of bubble size for which $\theta = 0$. In other words such a procedure assumes that the energy of particle detachment from the gas bubble surface follows only from wetting properties of solid surface. The experimental data from such a procedure for methylated quartz were compared with the flotation limit of fine particles reported by Ralston et al. (Blake and Ralston, 1985; Crawford and Ralston, 1988), as obtained in the Hallimond tube (Figure 6). It can be expected that our average values are overestimated due to the fact that hydrodynamic conditions in the flotation cell used by Ralston et al. were not taken into consideration. In real flotation experiments, it can be expected that turbulent conditions in flotation cell can cause particle detachment from the bubble even if there is a weak adhesion between phases, $20 > \theta > 0$, as analysed by Schulze (1977, 1984). In this regard the hydrodynamic conditions in the flotation cell should always be considered in the analysis of the flotation limit of fine particles, and the critical bubble radius for which there is no effective attachment between solid particle and gas bubble needs to be considered in more detail. According to the kinetic theory of Schulze (1977, 1984) it can be expected that any stresses in the turbulent field and liquid flow around bubble will cause particle/bubble detachment for a situation when the contact angle is from 5° to 20°, depending of course on the turbulent field in the flotation cell, the hydrophobic properties of the mineral particles, the distribution and size of heterogeneities, and the physico-chemical properties of system. Whereas the hydrodynamic conditions may not be as important in the analysis the flotation limit for strongly hydrophobic minerals, say $\theta > 40°$, they can be an important correction factor in the determination of the flotation limit of slightly hydrophobic particles, $\theta < 20-30°$.

**Conclusions**

The flotation limit of fine particles has been re-examined based on the effect of bubble size on contact angle, and a new surface chemistry-limited relationship describing the minimum particle size which can be floated was derived:

$$D_{\text{min}} = 2 \left[ \frac{3 \, r_c^2 \, \gamma_{LV} \,(1 - \cos \theta)}{\Delta \rho \, u^2} \right]^{1/3}$$

This new relationship was derived based on a more realistic model of heterogeneous and rough solid particle than the idealized homogeneous and smooth model of a spherical particle considered by Scheludko et al. (1976). The analysis requires that the critical value of the bubble-solid contact radius ($r_c$) for which there is no effective attachment between solid particle and gas bubble be determined. In this regard, the value of $r_c$ for which the contact angles are zero were determined by extrapolation from the experimental data of contact angle versus bubble-solid contact radius for methylated quartz plates. From this analysis a more accurate prediction of the surface-chemistry limited flotation size of methylated quartz particles was possible. The utility of this analysis requires the evaluation of hydrodynamic conditions in the flotation cell, and these phenomena are now being taken into consideration.

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