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Masahiro WATANABE*, Przemyslaw B. KOWALCZUK **, Jan DRZYMALA **

ANALYTICAL SOLUTION OF EQUATION RELATING MAXIMUM SIZE OF FLOATING PARTICLE AND ITS HYDROPHOBICITY

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An analytical form of the equation relating particle hydrophobicity, expressed as the so-called contact angle, and the maximum size of spherical particle able to float with a bubble is presented. The starting equation, which is based on the balance of forces operating at the moment of particle detachment from a bubble, can be solved only numerically. In this paper the third-degree polynomial equation is transformed into an analytical trigonometric function. Although there are several roots of the equation, practically only one is valid for the detachment contact angle calculation.

keywords: flotation, flotometry, contact angle, particle size, cubic equation

1. INTRODUCTION

Well designed flotation experiments can be used for determination or estimation of different properties of the system. One of them is the so-called contact angle which reflects the hydrophobicity of particles. The procedure of contact angle determination is based on measuring the maximum size of floating particles and using equations, which result from a balance of forces at the moment of particle-bubble rupture. It was applied in the particle levitation technique (Li et al., 1993), bubble-capture-by-particles method (Hanning and Rutter, 1989) and Hallimond cell flotation experiments (Drzymala, 1994). The method, also called flotometry (Konovalov and Tikhonov, 1982; Drzymala and Lekki, 1989), provides a detachment contact angle being

* 4-28-1 Minami-Sakasai, Kashiwa-shi, Chiba 277-0043, Japan, mwsqp@yahoo.co.jp

** Wrocław University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland, przemyslaw.kowalczuk@pwr.wroc.pl, jan.drzymala@pwr.wroc.pl

equivalent to the advancing contact angle, which can be simply recalculated into the equilibrium (Young's) contact angle.

The derivation of the equation relating the maximum size of floating spherical particle and hydrophobicity of the particle starts with the balance of forces involved in the process. Assuming that the main adhesive force is the capillary force F_{σ} and that the detachment occurs when the capillary force reaches maximum $F_{\sigma(\max)}$ (Scheludko et al. 1976, Drzymala, 1994), the balance (Fig. 1) is:

$$F_{\sigma(\max)} - F_{\mathrm{w}} - F_{\mathrm{e}} - F_{\mathrm{a}} = 0 \tag{1}$$

where F_{w} is the weight of particle partially immersed (due to attachment to the bubble) in a liquid, F_{e} denotes the excess force, and F_{a} stands for different forces generated during movement of bubbles with the attached particles, both immersed in the liquid medium.

Another assumption regarding the adhesive forces in the balance was proposed by Nguyen (2003, 2004). Since it is based on non-existing forces such as the weight of a completely immersed particle, this approach does not seem to be correct.

The maximum capillary force at the moment of particle detachment from the bubble, $F_{\sigma(\max)}$, is expressed by the equation:

$$F_{\sigma(\max)} = \pi r_{\max}\sigma(1-\cos\theta_{\mathrm{d}}), \tag{2}$$

where σ is liquid surface tension, $r_{\max}$ maximum radius of floating spherical particle, θ_{d} angle of detachment of particles from bubble (equivalent to the advancing contact angle) and π is 3.14.

The weight of the particle partially immersed in water F_{w} is in fact equal to $F_{\mathrm{g}} - F_{\mathrm{b}}$, where F_{g} is the gravity force and F_{b} is the buoyancy:

$$F_{\mathrm{w}} = \tfrac{4}{3}\pi r_{\max}^{3}\rho_{\mathrm{p}}g - \pi r_{\max}^{3}\rho_{\mathrm{w}}g\left[\tfrac{2}{3} + \cos(\theta_{\mathrm{d}}/2) - \tfrac{1}{3}\cos^{3}(\theta_{\mathrm{d}}/2)\right], \tag{3}$$

where ρ_{w} is density of liquid, ρ_{p} density of particle, g acceleration due to gravity while $r_{\max} \leq R$.

The excess force F_{e} is defined as ($F_{\mathrm{p}} - F_{\mathrm{h}}$), where F_{p} is an additional pressure inside the bubble and F_{h} stands for the hydrostatic pressure and is given by:

$$F_{\mathrm{e}} = F_{\mathrm{p}} - F_{\mathrm{h}} = \pi r_{\max}^{2}(1-\cos\theta_{\mathrm{d}})(\sigma/R - R\rho_{\mathrm{w}}g), \tag{4}$$

where R is bubble radius.

There are also hydrodynamic forces in the system. Their list includes inertia, drag, diffusive, and other forces (Morris and Matthesius, 1988). For practical purpose it was proposed by Schulze (1993), and later by Ralston (Gontijo et al., 2007), to combine the hydrodynamic forces into one effective acceleration force, F_{a}. The mathematical formula for the effective acceleration force is not well established. Gontijo et al.

(2007) used:

$$F_{\mathrm{a}} = \frac{4}{3}\pi r^3 \rho_{\mathrm{p}} a \tag{5}$$

where a is the acceleration of particle in the external flow field. Another expression in which $\rho_{\mathrm{p}}-\rho_{\mathrm{w}}$ instead of ρ_{p} in Eq. (5) was used by Mitrofanov et al. (1970) while Koch and Noworyta (1992) used $\rho_{\mathrm{p}}+f\rho_{\mathrm{w}}$ instead of ρ_{p} in Eq. (5) (where f is a constant). Since the acceleration force does not depend on contact angle, the inversion of the numerical equation into the analytical form does not require, during the derivation, the knowledge of the detailed expression for F_{a}.

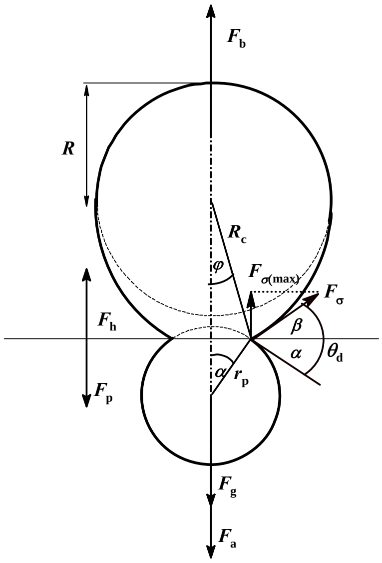

Fig. 1. Particle-bubble aggregate at the moment of particle detachment when the contact angle becomes detachment angle θ_{d}. F_σ denotes capillary force, α central angle, β angular inclination of meniscus at the three-phase contact, φ central angle at the bubble center, R_{c} bubble curvature, $r_{\mathrm{p}}=r_{\mathrm{max}}$. Other symbols are explained in the text

Taking into account expressions for appropriate forces one gets the following equation:

$$\begin{aligned}&\pi r_{\max}\sigma(1-\cos\theta_{\mathrm{d}}) - \left\{\frac{4}{3}\pi r_{\max}^3\rho_{\mathrm{p}}g - \pi r_{\max}^3\rho_{\mathrm{w}}g\left[\frac{2}{3}+\cos(\theta_{\mathrm{d}}/2)-\frac{1}{3}\cos^3(\theta_{\mathrm{d}}/2)\right]\right\}\\&-\pi r_{\max}^2(1-\cos\theta_{\mathrm{d}})(\sigma/R-R\rho_{\mathrm{w}}g)-F_a=0.\end{aligned} \tag{6}$$

Analytical solution of Eq. (6) for $r_{\max}$ can be easily obtained since it becomes a quadratic equation of $r_{\max}$ after division by $r_{\max}$. On the other hand is it much more difficult to solve Eq. (6) for θ_{d} because it assumes a cubic form. The solution of Eq. (6) is presented in this paper.

2. SOLUTION

In Eq. (6) the detachment angle occurs as θ_d and $\theta_d/2$. Therefore, we have to use the double-angle formula for cosine, $\cos\theta_d = 2\cos^2(\theta_d/2) - 1$. Substituting this into Eq. (6), we obtain a cubic equation:

$$X^3 + 3AX^2 - 3X - 3A + 2B = 0\,, \tag{7}$$

where

$$X = \cos(\theta_d/2) \qquad (0 < X < 1), \tag{8}$$

$$A = \frac{2\sigma(1 - r_{max}/R)}{r_{max}^2 \rho_w g} + \frac{2R}{r_{max}} \qquad (2 \le A), \tag{9}$$

$$B = 1 + 2\cdot\frac{\rho_p - \rho_w}{\rho_w} + \frac{3F_a}{2\pi r_{max}^3 \rho_w g} \qquad (1 < B). \tag{10}$$

The ranges of X, A and B are due to $0^\circ < \theta_d < 180^\circ$, $r_{max} \le R$ and $\rho_w < \rho_p$, respectively. Analytical solutions of cubic equations are known, therefore we are able to solve Eq. (7) for X and then calculate θ_d, because $\theta_d = 2\arccos X$.

To eliminate the second-degree term in Eq. (7), we put

$$X = Y - A\,, \tag{11}$$

and next we get a reduced cubic equation:

$$Y^3 - 3(A^2 + 1)Y + 2(A^3 + B) = 0\,. \tag{12}$$

To solve Eq. (12) one can use either algebraic or trigonometric solution. Since both provide the same results, only the algebraic path is presented in this paper.

Equation (12) can be solved by a well-known cubic formula (Bewersdorff, 2006; Cox, 2004; Dickson, 1914; King, 1996; Rotman, 2000; Rotman, 2007; Uspensky, 1948):

$$Y = \sqrt[3]{-(A^3 + B) + \sqrt{D}}\cdot\left(-\frac{1}{2} + \frac{\sqrt{3}}{2}i\right)^{j-1} + \sqrt[3]{-(A^3 + B) - \sqrt{D}}\cdot\left(-\frac{1}{2} - \frac{\sqrt{3}}{2}i\right)^{j-1} \tag{13}$$

where j=1, 2, 3, and D denotes the discriminant, in our case defined as:

$$D = (A^3 + B)^2 - (A^2 + 1)^3\,, \tag{14}$$

which can be either zero or positive, or even negative. Using Eq. (13), taking into account the signs of D, we have 3·3, that is 9, solutions.

For $D = 0$ or $B = (A^2+1)^{3/2} - A^3$, it is known that there are three real roots of a reduced cubic equation and at least two of them are equal. The roots of Eq. (7) are given by:

$$X_{\mathrm{Z1}} = -2\sqrt{A^2+1} - A\,, \tag{15}$$

$$X_{\mathrm{Z2}} = X_{\mathrm{Z3}} = \sqrt{A^2+1} - A\,, \tag{16}$$

where Z denotes that D is zero. X_{Z1} is negative while X_{Z2} and X_{Z3} are within the range of $0<X<1$ (Fig. 2).

For $D > 0$ or $B > (A^2+1)^{3/2}-A^3$, a reduced cubic equation has one real root and two imaginary roots. The real root of Eq. (7), in which we are interested, is given by:

$$X_{\mathrm{P1}} = -\sqrt[3]{A^3+B-\sqrt{\left(A^3+B\right)^2-\left(A^2+1\right)^3}} - \sqrt[3]{A^3+B+\sqrt{\left(A^3+B\right)^2-\left(A^2+1\right)^3}} - A \tag{17}$$

where P denotes that D is positive. The expression for X_{P1} clearly indicates that X_{P1} is negative and should be rejected. Discussion on the imaginary roots X_{P2} and X_{P3} is omitted.

For $D < 0$ (called the *casus irreducibilis*) or $B < (A^2+1)^{3/2}-A^3$, there are three distinct real roots and Eq. (13) leads to the following equation (Bewersdorff, 2006; Dickson, 1914; King, 1996; Uspensky, 1948):

$$Y_{\mathrm{N}j} = 2\sqrt{A^2+1}\,\cos\left[\frac{\phi}{3}+\frac{2(j-1)\pi}{3}\right]\ (j = 1, 2, 3), \tag{18}$$

where N denotes that D is negative, and ϕ is defined as:

$$\phi = \arccos\left[-\frac{A^3+B}{\left(A^2+1\right)^{3/2}}\right]\quad (\phi < \pi)\,. \tag{19}$$

As ϕ is in the second quadrant, it can be shown that X_{N2}:

$$X_{\mathrm{N2}} = 2\sqrt{A^2+1}\,\cos\left(\frac{\phi}{3}+\frac{2\pi}{3}\right) - A\,, \tag{20}$$

is outside the range of $0<X<1$. X_{N1} and X_{N3} are:

$$X_{\mathrm{N1}} = 2\sqrt{A^2+1}\,\cos\frac{\phi}{3} - A\,, \tag{21}$$

$$X_{\mathrm{N3}} = 2\sqrt{A^2+1}\,\cos\left(\frac{\phi}{3}+\frac{4\pi}{3}\right) - A\,, \tag{22}$$

and their boundary is X_{Z2} or X_{Z3}. X_{N1} is always in the range of $0 < X < 1$ and provides detachment angles between 0° and 180°. On the other hand X_{N3} yields different values from X_{N1} for a given set of A and B, and may be in the range of $0 < X < 1$, or $X < 5^{1/2}-2$ precisely, providing detachment angles greater than 152.69°. Such a large contact angle does not occur in normal situations (e.g. Chau, 2009). Therefore X_{N3} should be excluded and only equation for X_{N1} taken into consideration.

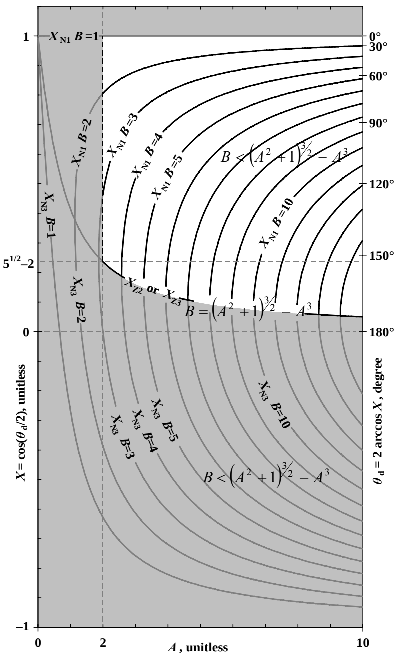

Fig. 2. Relationship between real roots X of the considered cubic equation and parameters A and B. The arccosine scale on the right-hand side indicates how X corresponds to θ_d. For clarity the graph was truncated at A=10, though in practical applications A can reach 20,000 and more

A final solution of the cubic equation (Eq. (7)) was obtained by including Eq. (16) into Eq. (21) combined with Eq. (19):

$$X = 2\sqrt{A^2+1}\,\cos\left\{\frac{1}{3}\arccos\left[-\frac{A^3+B}{\left(A^2+1\right)^{3/2}}\right]\right\} - A\,,\ (B \le \left(A^2+1\right)^{3/2} - A^3), \tag{23}$$

where X, A and B are defined by Eqs. (8–10), respectively. The third term on the right-hand side of Eq. (10) is neglected in the case of "static" flotation.

For the particle size and hydrophobicity encountered in flotation parameter B is usually smaller than $(A^2+1)^{3/2}-A^3$ and thus the analytical form of the flotometric equation for spherical particles is practically given only by Eq. (23).

Besides the cubic formula, there is a trigonometric solution of the cubic equation (Bewersdorff, 2006; Birkhoff and Mac Lane, 1965; Cox, 2004; Dickson, 1914; Rotman, 2000; Rotman, 2007; Tignol, 1988). It provides identical results and therefore is not included in this paper.

3. CONCLUSION

The flotometric equation delineates flotation and relates the maximum size of floating particle with its hydrophobicity expressed as detachment contact angle. The flotometric equation is based on the balance of forces involved in flotation and can be utilized after solving it by iterative methods. In this work the flotometric equation, being a third-degree polynomial of $\cos(\theta_d/2)$, was transformed into analytical form which is much easier to handle. For the particle size and hydrophobicity encountered in flotation parameter B is usually smaller than $(A^2+1)^{3/2}-A^3$ and thus the final form of the equation relating detachment contact angle and the maximum size of floating particle is given by the equation being a combination of Eqs (23) and (8–10)

$$\theta_d = 2\arccos\left\{\begin{array}{l} 2\left[\sqrt{\left(\frac{2\sigma(1-r_{max}/R)}{r_{max}^2\rho_w g}+\frac{2R}{r_{max}}\right)^2+1}\right]\cdot \\ \cos\left\{\frac{1}{3}\arccos\left[-\frac{\left(\frac{2\sigma(1-r_{max}/R)}{r_{max}^2\rho_w g}+\frac{2R}{r_{max}}\right)^3+1+2\cdot\frac{\rho_p-\rho_w}{\rho_w}+\frac{3F_a}{2\pi r_{max}^3\rho_w g}}{\left(\left(\frac{2\sigma(1-r_{max}/R)}{r_{max}^2\rho_w g}+\frac{2R}{r_{max}}\right)^2+1\right)^{3/2}}\right]\right\} \\ -\left(\frac{2\sigma(1-r_{max}/R)}{r_{max}^2\rho_w g}+\frac{2R}{r_{max}}\right) \end{array}\right\}$$

This analytical equation can be used for many further applications, especially involving derivations.

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W pracy została przedstawiona analityczna forma równania wiążącego maksymalny rozmiar flotującego ziarna i jego hydrofobowość, wyrażoną jako kąt zwilżania. Równanie to, zwane fotometrycznym, oparte jest na bilansie sił działających w układzie ziarno-pęcherzyk powietrza-ciecz w momencie zerwania ziarna i do tej pory rozwiązywane było tylko numerycznie. Rozpatrywane równanie fotometryczne, posiadające postać wielomianu trzeciego stopnia, zostało przedstawione jako funkcja trygonometryczna, dla której istnieje tylko jedno rozwiązane.

słowa kluczowe: flotacja, flotometria, kąt zwilżania, ziarno grube, wielomian, równanie kubiczne