

The meniscus depression of a porous spherical particle at the three phase contact line

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Abstract

The description of the processes at the three phase contact line is very important for the study of elementary steps in flotation. When a hydrophobic particle is attached to a gas-liquid interface, it is influenced by a number of forces, including surface tension, capillary and buoyancy forces on one hand and the particle weight on the other. In the case of porous particles, capillary forces acting in the porous surface must also be considered. The meniscus depression at the three-phase contact line is determined by the resultant force. The meniscus depression of the floating particle was studied using the image analysis method. The depression was studied for spherical polystyrene particles of diameters from 0.5 to 3mm. We compared the experimental values of meniscus depression with the data calculated using theoretical and semi-empirical models. The theoretical description of forces acting on the floating spherical porous particle is also given. We found that the existence of pores and surface inequalities has a significant influence on particle behaviour on the phase interface.

Keywords: floating particle, meniscus depression, porous surface, capillarity.

1 Introduction

The analysis of forces on the particle attached to the bubble surface has been the focus of the study of flotation processes since the early days of its industrial utilization. When a hydrophobic particle is attached to a gas-liquid interface, it is influenced by a number of forces, including the surface tension and buoyancy forces on the one hand and the particle weight on the other [1,2]. It is customary



to sum the forces, which are a function of the position of the three-phase contact and to describe them jointly as the adhesive forces. The other forces, which are independent of the position of the three-phase contact, such as the particle weight less its buoyancy and the inertial forces, are jointly termed the detaching force.

One of the most important forces is the capillary force F_c . Due to the rotational symmetry along the vertical axis, the horizontal component of this force vanishes and only the vertical component remains.

$$F_c = 2\pi r_p \sigma \sin \alpha \sin(\theta - \alpha) \quad (1)$$

The next force, which supports the particle suspension at the interface, is the buoyancy F_b of the particle immersed in the liquid phase. This force can be described by the following equation

$$F_b = \frac{\pi r_p^3 \rho_l g}{3} (2 + 3 \cos \alpha - \cos^3 \alpha) \quad (2)$$

The pressure force F_p , which stabilizes the particle suspension, results from the hydrostatic pressure, which acts over an effective area πr_{tpc}^2 enclosed by the three-phase contact line.

$$F_p = \pi r_p^2 H \rho_l g \sin^2 \alpha \quad (3)$$

Another important force acting on the particle is the particle weight F_g , which tends to pull the attached particle into the liquid phase.

$$F_g = -\frac{4\pi r_p^3 \rho_p g}{3} \quad (4)$$

Here H is the meniscus depression at the three-phase contact, r_p is the particle radius, r_{tpc} is the radius of the three phase contact line, σ is the surface tension, g is the acceleration due to gravity, and ρ_p , ρ_l and ρ_g are the densities of the particle, liquid and gas, respectively. θ is the contact angle and α is the central angle. The model behaviour of a solid particle is depicted on figure 1.

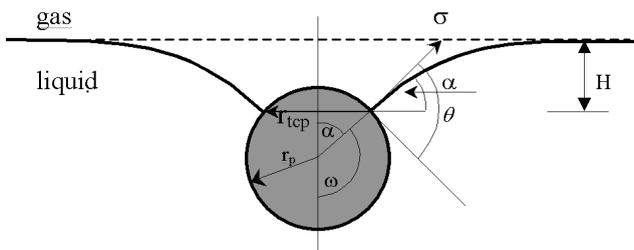


Figure 1: A model of solid spherical particle attached to planar gas-liquid surface.

In summary, there are four static forces acting on the smooth and spherical non-porous particle attached to a free water surface [1,2,3]. Equilibrium is attained if

$$F_c + F_b + F_p + F_w = 0 \quad (5)$$

and consequently

$$\left\{ \frac{H}{r_p} \sin^2 \alpha + \frac{2 + 3 \cos \alpha - \cos^3 \alpha}{3} \right\} (\rho_l - \rho_g) g \pi r_p^3 + \quad (6)$$

$$2 \pi r_p \sigma \sin \alpha \sin (\theta - \alpha) - g (\rho_p - \rho_g) 4 \pi r_p^3 / 3 = 0$$

Let's consider about a slightly porous particle. The capillary force for one pore [4] is given as

$$F_c = 2 \pi R_p \sigma \sin \gamma \quad (7)$$

Here R_p is the pore radius and γ is the contact angle inside the pore. When we consider the capillary force for all pores around the three-phase contact line and the force equilibrium, it is possible to re-write equation 5:

$$F_c + F_b + F_p + F_w + \sum_i 2 \pi R_{pi} \sigma \sin \gamma_i = 0 \quad (8)$$

This equation should be a general relationship to express the meniscus depression for a slightly porous particle.

In a flotation process, empirical equations are used often also. For three-phase contact line with small radius, the fundamental equation (6) can be solved by employing the method of matched asymptotic perturbation [5]. The final result for the meniscus depression is described by the Derjaguin equation:

$$H = r_{tpc} \sin \beta \left(\ln \frac{4L / r_{tpc}}{1 + \cos \beta} - \gamma \right), \quad (9)$$

where $\gamma = 0.577$ and it is the Euler constant, r_{tpc} is the radius of three-phase contact line and due geometric symmetry $\beta = \theta - \alpha$ [2]. The capillary length L is defined by the following equation

$$L = \sqrt{\frac{\sigma}{(\rho_l - \rho_g)g}}. \quad (10)$$

Comparison of this equation to the numerical results of the Young-Laplace equation² indicates, that the Derjaguin equation is accurate for $r_{tcp} / L \leq 0.2$.

For three-phase contact with large radius the approximate solution of the equation (6) can be derived also. For the meniscus depression the modification yields

$$\frac{H}{L} = \sin (\beta / 2) \frac{2}{\sqrt{1 + (L / r_{tpc})}} \quad (11)$$

This simple equation derived in the limit of the large radius compares with the numerical results surprisingly well, down to $r_{tcp} / L \geq 2$. For three-phase contacts with the radius in the range of $2.0 \geq r_{tcp} / L \geq 0.2$ no analytical solutions for the meniscus depression are available. The explicit dependence of the meniscus depression on the three-phase contact radius and the meniscus angular inclination can be obtained only empirically. Nguyen [3] describes this solution based on the asymptotic analytical results and the numerical



computational results of solution to the Young-Laplace equation. According to this method one can obtain

$$\frac{H}{L} = a \sin (b \beta), \quad (12)$$

where a and b are empirical parameters. It is assumed, that b is independent of β and is a function of r_{tcp} / L only. It has two asymptotes, $b = 0.5$ and 1 for very small and very large values of r_{tcp} / L , respectively. For the range of $2 \geq r_{tcp} / L \geq 0.1$, fitting to the exact numerical data gives:

$$b = 0.5 + 0.332 \exp(-2.122 r_{tpc} / L) \quad \text{and} \quad a = \frac{2.186}{1 + 0.649(L / r_{tpc})} \quad (13)$$

The aim of this research was the experimental study of the meniscus depression at the three-phase contact of the floating plastic particle using image analysis method. Plastic materials are characteristic for their polymeric structure with long chains. Therefore for these compounds it is possible to assume the occurrence of surface inequality from a microscopic point of view and also the appearance of pores. The depression was studied for polystyrene particles of different diameters (0.1 – 3mm). All experiments were performed in a small apparatus monitored by a high-speed CCD camera with a macro-objective. The obtained data were processed using an image analysis software LUCIA. The experimental data were compared with the theoretical models.

2 Experimental materials and methods

The model spherical particles of expandable polystyrene EPS (originating from Kaucuk Kralupy, Czech. Rep.) were used for the experiments. We used 70 particles with diameters from 0.5 mm to 2.6 mm and the density of these balls was 1.03 g.cm^{-3} . The value of the contact angle for this type of polystyrene in distilled water was 79.2° [6]. The contact angles were measured by direct method, monitoring the drop profile on smooth flat surface, represented by a foil made from polystyrene balls. For all the measurements the distilled and de-ionised water was used. Here, pH was 6.13 and conductivity $1,6 \mu\text{S/cm}$.

For interpretation of obtained data the program LUCIA was used. LUCIA is a software program evaluated for capturing, analysing and saving images. This program works with an A/D converter on the graphical chip in computer, the graphical chip converts the analogue signal to the digital signal. The program uses dimensional analysis and with a calibrated picture it is possible to obtain the precise size of particles. The program enables automatic detection of boundaries, measurement of angles and automatic calculation of the count of objects with help of attributes of objects. The system of image analysis consists of three parts: a microscope, CCD camera and PC with LUCIA software for analysis of captured images. Resulting images from the experiment are adjusted by the software (brightness, contrast and detection of objects) and mathematically evaluated.



3 Results and discussions

For polymeric compounds it is possible to assume the occurrence of surface inequality from a microscopic point of view and also the appearance of pores. As an experimental material we used expandable polystyrene, which contains pentane as an expanding component. This gas vanishes after a short time, but in the interior structure small bubbles or holes remain. Their diameter is 6 μm and this value was measured using the electronic microscope. If the bubble is in the near vicinity of the surface, it can happen that the smooth structure is damaged and a pore is originated. On the figure 2 are illustrated details of the surface with a big enlargement. Here some pores and surface inequalities are visible. From the image analysis we know that the pore radii lie between 6 to 15 μm . Unfortunately, it was not possible to measure pore diameters for all particles separately. According to our measurements we expect that the number of pores could not exceed the value of 5 pores per 1 mm on the contact line.



Figure 2: The detail of a surface.

The images of floating particles were the basis of all experimental data. The software LUCIA uses dimensional analysis and using calibrated images the particle diameters were determined with an accuracy 0,001 mm. The obtained data (r_p) were utilized for the assessment of the radius of the three-phase contact r_{tpc} and meniscus depression H . On the figure 3 (left) is an original image of a floating particle. The scanned image was processed using the software LUCIA. On a figure 3 (right) is plotted a spherical particle shape and results of a size analysis are also marked.

All used experimental particles have the same density and the value of a contact angle. Therefore, it is possible to presume, that the radius of three-phase contact r_{tpc} should be proportional to the particle radius r_p . This dependence was confirmed and the results are depicted on the figure 4. We found, that the radius of three-phase contact can be calculated for the polystyrene balls using the equation

$$r_{tpc} = 0,8835 r_p \quad (14)$$

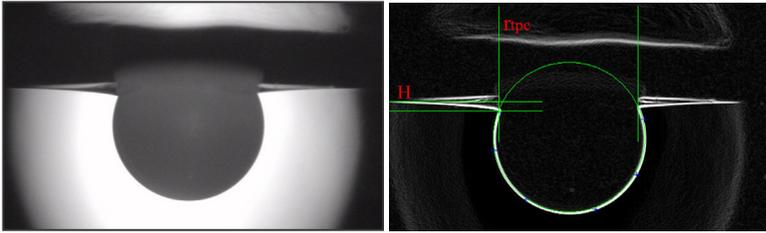


Figure 3: Detail of the floating particle (left) and the image analysis using the software LUCIA (right).

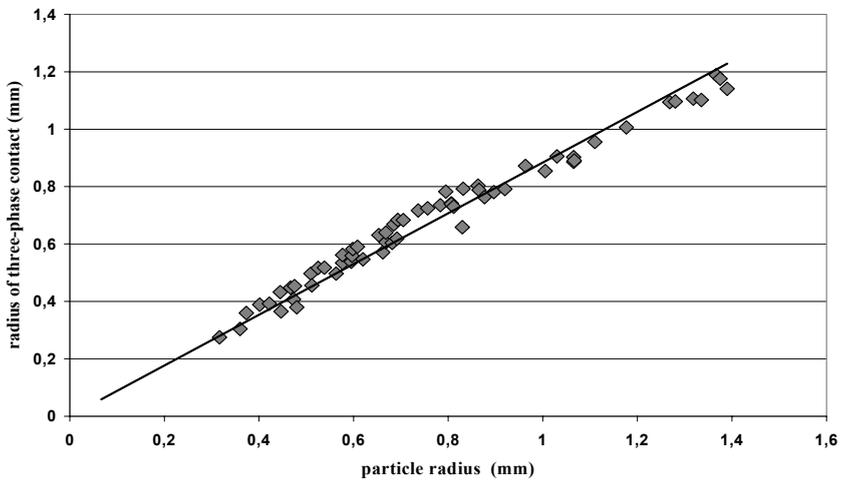


Figure 4: The dependence of the radius of the three-phase contact r_{tpc} on the particle radius r_p .

The angle α was measured experimentally and the angle β (see Fig.1) was calculated according to the relation $\beta = \theta - \alpha$ [2]. For the calculation of meniscus depression H three equations were used. In the literature [2,3], it is recommended to calculate meniscus depression with regard to the value of r_{tpc} / L . For three-phase contact with small radius ($r_{tpc} / L \leq 0.2$) the Derjaguin equation (9) is suggested. The data, calculated using this equation, are denoted as H_{small} . For three-phase contacts with the radius in the range of $2.0 \geq r_{tpc} / L \geq 0.2$ the semi-theoretical equations (12-13) were used. The calculated values are denoted as H_{middle} . Finally the fundamental theoretical equation (6) was applied. The calculated data are denoted as H_{theor} . On figure 5 are demonstrated experimental data and calculated dependences of meniscus depression on the radius of three-phase contact.

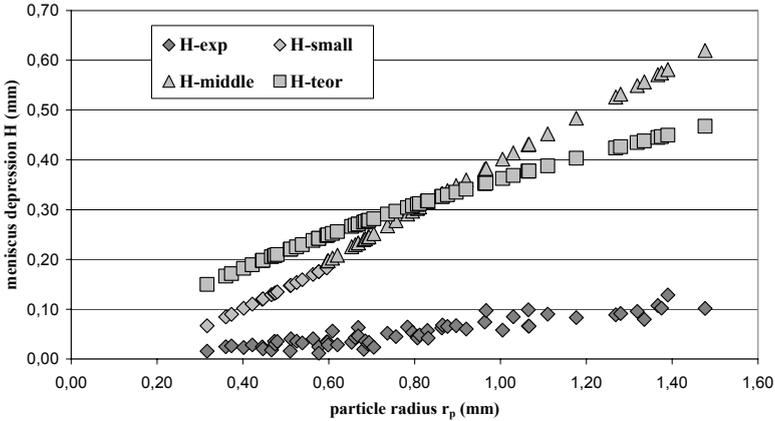


Figure 5: The dependence of the meniscus depression on the radius of three-phase contact line – experimental and calculated data.

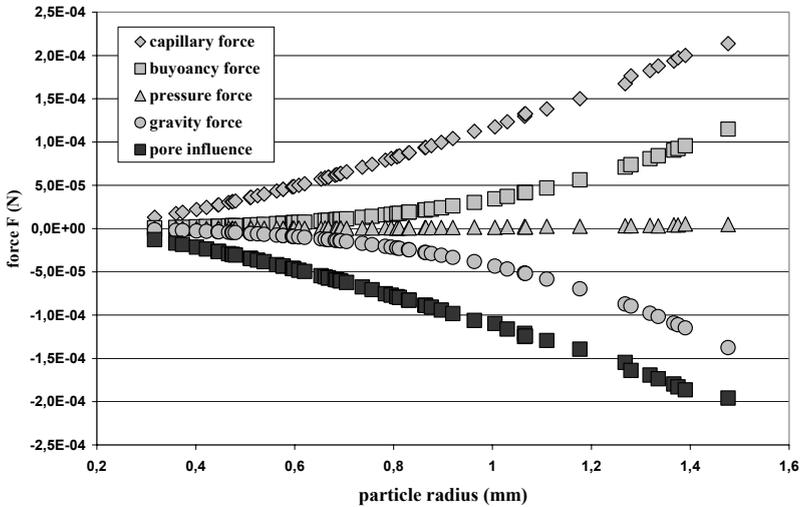


Figure 6: The calculated values of capillary force F_c , buoyancy F_b , pressure force F_p , particle weight F_g and capillary force of pores F_c and their dependence on the particle radius.

A substantial inconsistency of experimental and calculated data is obvious from these results. All used theoretical relationships (equations 6, 9 and 12 – 13) were derived for smooth and non-porous spherical particles and therefore do not reflect the pore existence. It is obvious from experimental measurements that the influence of surface roughness and pores is remarkable. The value of meniscus depression is even several times lower. Thus for even slightly porous particles



the usage of theoretical relationships is not suitable for calculations in flotation, e.g. for the estimation of maximum size of a floating particle.

On figure 6 are plotted the calculated values of capillary force F_c , buoyancy F_b , pressure force F_p and particle weight F_g as a dependence on the particle radius. Also the force reflecting the pore influence was calculated according to eqn. (8). Here the force balance at equilibrium should be equal to zero. The most significant forces are the capillary force acting on the whole particle and the force influenced by the pore existence. This result is not surprising if we consider all aspects of the law of capillary rise [4]. On figure 7 is given one example of the estimation of pore number. Here the pore radius $15\mu\text{m}$ was used and the calculation was done for several values of the contact angle. We could expect that the contact angles in pores have the same or lower value than the contact angles on a flat surface.

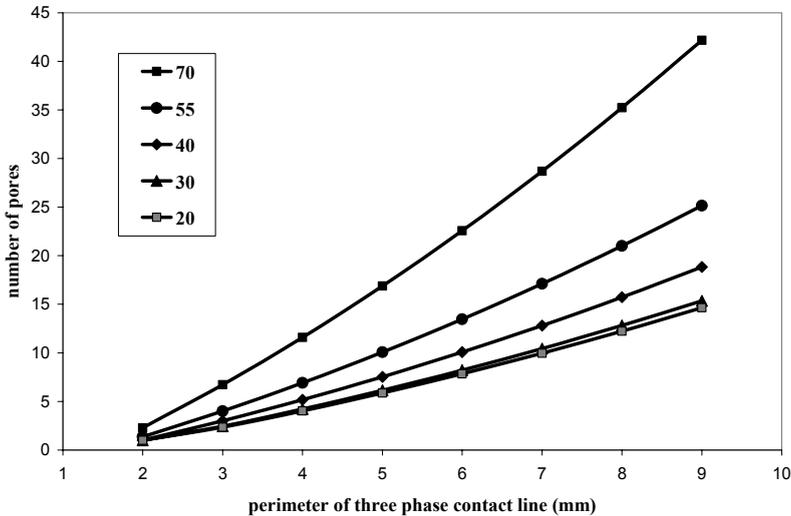


Figure 7: The estimated number of pores as a dependence on the perimeter of the three phase contact line for contact angles from 20° to 70° and pore radius $15\mu\text{m}$.

4 Conclusions

The meniscus depression H at the three-phase contact line of the floating slightly porous particle was studied using the image analysis method (software LUCIA). We compared the experimental values of meniscus depression with the data calculated using theoretical and semi-empirical models derived for the non-porous particles. We found out a big difference between experimental and theoretical values. It is obvious from experimental measurements that the influence of surface roughness and pores is remarkable. The value of meniscus

depression is even several times lower. Thus for even slightly porous particles the usage of theoretical relationships is not suitable for calculations in flotation, e.g. for the estimation of maximum size of a floating particle. The existence of pores and surface inequalities has a really significant influence on the particle behavior on the phase interface.

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