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Abstract

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THEORY OF FLUCTUATIONAL RUPTURE OF WETTING FILMS AND ITS APPLICATION TO THE KINETICS OF FLOTATION ADHESION

The adhesion of mineral particles to gas bubbles during the flotation concentration of useful minerals occurs as a result of rupture of the water film located between the particle and the bubble. In the present work we attempt to give a theory of this phenomenon. For the sake of simplification we shall assume that the liquid film is situated on an infinite plane substrate. In addition, we shall consider such films whose particles, upon rupture, move only in two dimensions parallel to the substrate and, consequently, preserve everywhere around the "hole" the initial constant thickness. Such two-dimensionality of the rupture process is most rigorously fulfilled for monomolecular films.

In considering the radial flow of a liquid layer around an expanding hole we shall use the conclusions of the work of D. M. Tolstoy (⁀1). In that work, when considering the flow of a viscous liquid over a solid substrate, the possibility was established of slip of the liquid at the boundary with the solid body, accompanied by friction against the substrate, which retards the motion of the liquid and is proportional to the velocity of its sliding,

$$f = -kv, \tag{1}$$

where v is the velocity of the liquid, and k is the coefficient of friction against the substrate. An estimate of the friction coefficient k (⁀1) led to the expression

$$k = \frac{\eta_0}{a} \frac{1}{e^{\frac{1}{6} S_{\mathrm{M}} \sigma_{12} (1-\cos\varphi)/\theta} - 1}, \tag{2}$$

where η_0 is the volume viscosity of the liquid; a is the mean distance between molecules; S_{M} is the area of the sphere bounding the microcavity, per one molecule ($S_{\mathrm{M}} \sim \pi a^2$); σ_{12} is the surface tension of the liquid at the boundary with vacuum; φ is the contact angle formed by it on the substrate; and θ is the absolute temperature multiplied by Boltzmann' s constant.

With such a formulation of the problem one can use the method of treating fluctuational rupture in work (^2), in which an expression was obtained for the mean lifetime of free thin films. The course of the calculation of the mean lifetime for the films considered here coincides with the course of the calculation for free films, and as a result a formula is obtained that is completely analogous to the formula for free films (see formula (19) in (^2)):

$$\alpha = \frac{\sqrt{\theta}\, e^{\pi\gamma^2/p_0\theta}}{2Dc_0\sqrt{p_0}} \left\{1 + A\left(\gamma\sqrt{\frac{\pi}{p_0\theta}}\right)\right\}, \tag{3}$$

where α is the mean lifetime; γ is the linear tension of the perimeter of the hole; c_0 is the number of holes of molecular radius per 1 cm^2 and per unit interval of radii; A is the error integral; D is a coefficient, in a certain formal sense analogous to the diffusion coefficient (for more detail see (^2)); and p_0 is the film tension at a large distance from the rupture site. For a monomolecular film

$$p_0 = \sigma'_{32} - \sigma_{32}, \tag{4a}$$

where σ_{32} is the surface tension of the clean solid substrate, σ'_{32} is the surface tension of the same substrate in the presence of a monomolecular film on it. In the case of a polymolecular film of thickness h, which still behaves upon rupture as a two-dimensional one,

$$p_0 = \sigma_{12}(1 - \cos\varphi) + \int_h^\infty P(h)\, dh, \tag{4 }$$

where $P(h)$ is the disjoining pressure of a film of thickness h.

To calculate the coefficient D, we, as in ([2]), use the Einstein relation, according to which

$$D = \theta\, \frac{V}{2\pi p_0 (R - R_c)}; \tag{5}$$

here R is the radius of the expanding hole; R_c is its critical radius; V is the rate of expansion ($V = dR/dt$). To determine the rate of expansion of the hole V, it is necessary to solve the equations of two-dimensional radial viscous flow of the liquid film, which, taking into account the frictional force against the substrate, have the form (in the acoustic approximation)

$$\frac{\partial p}{\partial t} + \rho_0 c^2 \left(\frac{\partial v}{\partial r} + \frac{v}{r}\right) = 0, \tag{6a}$$

$$\rho_0 \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial r} + \left(\zeta + \frac{4}{3}\eta\right)\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r}\frac{\partial v}{\partial r} - \frac{v}{r^2}\right) - kv. \tag{6 }$$

Here, as in ([2]), it is assumed that the velocity v depends only on the distance to the center of the hole r; ζ denotes the second two-dimensional viscosity of the liquid, manifested under uniform extension of the film in its plane; ρ_0 is the density of the liquid; c is the speed of sound ($c^2 = dp/d\rho$); p is the two-dimensional pressure of the film. In contrast to ([2]), where the quasi-stationary approximation was considered, here the term $\rho_0\, dv/dt$ is retained.

At the perimeter of the expanding hole the boundary condition is satisfied

$$\left[p - 2\eta\frac{\partial v}{\partial r} + \frac{\gamma}{R} + \left(\frac{2}{3}\eta - \zeta\right)\left(\frac{\partial v}{\partial r} + \frac{v}{r}\right)\right]_{r=R} = 0, \tag{7}$$

which follows from the two-dimensional analogue of the Laplace equation for the capillary pressure jump and from the expression for the component of the tensor of two-dimensional viscous stresses in the film.

We shall seek the solution of equations (6) in the form

$$v = V\,\frac{K_1(\varkappa r)}{K_1(\varkappa R)}, \tag{8}$$

where $\varkappa$ is a still unknown parameter having the dimension of inverse length, and K_1 is a Bessel function of imaginary argument, exponentially decreasing at large distances (Macdonald function). Substituting the expression for the velocity (8) into the continuity equation (6a) and differentiating with allowance for the recurrence formulas for Bessel functions,* we obtain

$$\frac{\partial p}{\partial t} = \rho_0 c^2 \varkappa\,\frac{V}{K_1(\varkappa R)} K_0(\varkappa r)$$

or, integrating and taking into account that as $r \to \infty$, $p = -p_0$,

$$p = -p_0 + \rho_0 c^2 \varkappa K_0(\varkappa r)\int_{R_c}^{R}\frac{dR}{K_1(\varkappa R)}. \tag{9}$$

* $\dfrac{1}{r}\dfrac{d}{dr}\left[rK_1(\varkappa r)\right] = -\varkappa K_0(\varkappa r).$

Let us now substitute the expressions for v and p into the Navier–Stokes equation (6b). Taking outside the brackets the spatial part, identical for all terms, we have

$$\left[\rho_0\frac{\partial V}{\partial R}\frac{V}{K_1(\chi R)} + \rho_0 V^2\frac{d}{dR}\left(\frac{1}{K_1(\chi R)}\right) - \rho_0 c^2\chi^2\int_{R_c}^{R}\frac{dR}{K_1(\chi R)} -\right.$$

$$-\left(\zeta+\frac{4}{3}\eta\right)\chi^2\frac{V}{K_1(\chi R)}+\frac{kV}{K_1(\chi R)}\Bigg]K_1(\chi r)=0. \tag{10}$$

We shall be interested in the dependence $V(R)$ only in the region of values R close to R_c. This will give us the coefficient D only at the point $R=R_c$. However, in view of the presence of the exponential factor in the formula for the mean lifetime

$$\alpha=\frac{1}{c_0}\int_0^\infty\frac{\exp(\Phi/kT)}{D}\,dR$$

(see (10) in ([2])), which rapidly decays for values of R sufficiently far from R_c, we may, without large error, replace $D(R)$ by the value D at the point R_c. With this in mind, let us expand all the quantities in the square bracket in (10) in powers of $(R-R_c)$ and retain only the linear terms.

Then, if we put $V=B(R-R_c)$ ($B=\text{const}$), we obtain the equation for the quantity B

$$\rho_0B^2-\rho_0c^2\chi^2-\left(\zeta+\frac{4}{3}\eta\right)\chi^2B+kB=0$$

or

$$B=\frac{\left(\zeta+\frac{4}{3}\eta\right)\chi^2-k+\sqrt{\left[\left(\zeta+\frac{4}{3}\eta\right)\chi^2-k\right]^2+4\rho_0^2c^2\chi^2}}{2\rho_0}. \tag{11a}$$

We are interested in values of B greater than zero. Therefore we have taken the plus sign before the root.

On the other hand, the expression for B can be obtained from the boundary condition (7):

$$B=\frac{p_0-\rho_0c^2\chi R_cK_0(\chi R_c)/K_1(\chi R_c)}{2\eta+\left(\zeta+\frac{4}{3}\eta\right)\chi R_cK_0(\chi R_c)/K_1(\chi R_c)}. \tag{11b}$$

Equating these two expressions, we obtain an equation for determining the quantity χ. To reduce it to dimensionless form, introduce the notations:

$$\frac{p_0}{\rho_0c^2}=\beta,\qquad\frac{2\eta}{\zeta+\frac{4}{3}\eta}=\delta,\qquad\chi R_c=x,$$

$$y=\frac{kR_c^2}{\eta+\frac{4}{3}\eta},\qquad\sigma=\frac{\rho_0cR_c}{\zeta+\frac{4}{3}\eta}.$$

Then the unknown quantity x is found from the equation:

$$\frac{x^2 - y + \sqrt{(x^2 - y)^2 + 4\sigma^2 x^2}}{2\sigma^2} = \frac{\beta - xK_0/K_1}{\delta + xK_0/K_1}. \tag{12}$$

Equation (12) must be solved numerically. After this the diffusion coefficient D is obtained from

$$D = \theta \frac{B}{2\pi\rho_0}.$$

Substituting here B from (11b), we obtain the diffusion coefficient D in the form

$$D = \frac{\theta M}{2\pi\left(\zeta + \frac{4}{3}\eta\right)}, \tag{13}$$

where

$$M = \frac{\beta - xK_0/K_1}{\delta + xK_0/K_1}.$$

The quantity x entering into the expression for M is the solution of equation (12). For fixed β, δ, σ, $M = M(y)$ is a function of y. In particular, for $\beta = 0.1$, $\delta = 1$, and $\sigma = 1.5$, $M(1) = 0.034$; $M(0.1) = 0.066$, $M(0.01) = 0.072$. If in all the preceding formulas we set $k = 0$, we obtain the case of free films.

Consideration of the problem in the quasistationary approximation was carried out in ([3]). The equation obtained there is simpler for numerical solution than (12). In the case considered here, in addition to the complication of the form of the equation (in comparison with the quasistationary case), a fourth parameter, σ, is also added.

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[3] B. V. Deryagin, Yu. V. Gutop, Proceedings of the Second Conference on Surface Forces, 1963.

Note: Figure translations are in progress. See original paper for figures.