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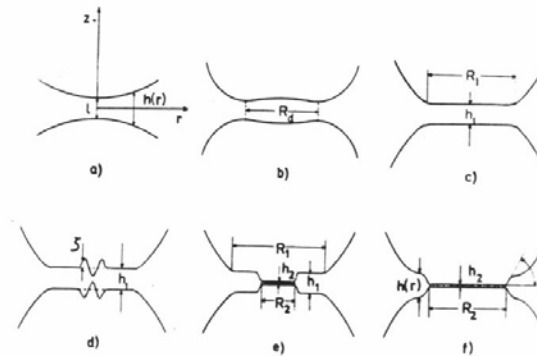


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HYDRODYNAMICS OF FOAM AND EMULSION FILMS

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The main stages of formation and evolution of a thin liquid film originated between two foam bubbles are (fig. 1 a - f):



a) mutual approaching of two slightly deformed bubbles under the action of an external driving force  $F$ ; b) at a given value  $l_1$  of the distance  $l=h(0)$  the curvature at  $r=0$  changes its sign and a cupped-shaped formation (dimple) of radius  $R_d$  arises; c) the dimple height initially increases then decreases and eventually a quasiplane parallel first film of

From here, for the radius  $R_d$  of the dimple and for the thickness  $l_1$  at which it forms we have

$$a) R_d^2 = R_1^2(1 - l/l_1) ; \quad b) l_1 = F/4\pi\bar{\sigma} \quad (5)$$

$$\text{where } R_1^2 = F\bar{R}/2\pi\bar{\sigma} \quad (6)$$

is the radius of the equilibrium film which would appear between the two bubbles (at  $l \ll l_1$ ) in the presence of long range (electrostatic) disjoining pressure. With various limiting values of  $\bar{R}$  and  $\bar{\sigma}$  equation (6) gives as particular cases all the known expressions for the radius of the equilibrium film: a) bubble-solid surface ( $R_a = \infty, \sigma_a = \infty$  - Derjaguin and Kussakov), b) solid sphere-plane liquid surface ( $R_a = \infty, \sigma_b = \infty$  - Allan, Charles and Mason), c) two identical bubbles ( $R_a = R_b = R, \sigma_a = \sigma_b = \sigma$  - Princen; Lee and Hodgson) and d) bubble-plane liquid surface ( $R_a = \infty, \sigma_a = \sigma_b = \sigma$  - Chappellear). Eqs. (4)-(6) are in qualitative and semi-quantitative agreement with the experimental results of Roberts and of McKay and Mason.

The method of matching of the coordinate expansions<sup>5</sup> was also applied at  $l \ll l_1$ . At that the deformation of the bubbles has been taken into account in a general form without assuming the presence of a thin film of definite radius. In the final results only, the radius of the equilibrium film  $R_1$  has been introduced through (6). The numerical analysis of the obtained equation for the surface of the bubbles shows that at  $0 \leq r \leq R_1$  the thickness  $h$  does not depend practically on  $r$ , i.e. a film of almost uniform thickness forms. This thickness diminishes at the rate  $V = h_1^3 F / 2\pi \mu R_1^4$ . This expression differs from Reynolds' equation (3b) very little (by the numerical coefficient only) which justifies the application of eq.(3b) for calculating the rate of thinning of plane parallel foam films (stage c).

The shape of the film surface corrugated by thermal fluctuations (stage d) can be represented as a result of the superposition of waves, one of which, with wave number  $k$  and equation  $\zeta(r, h)$  (we assume cylindrical symmetry) is determinant for the rupture of the film. For the velocity of deepening

of this wave  $v_\zeta^0 = \partial \zeta / \partial t$  from (1) (in the right hand side of (1b) in this case a term  $-2(d\bar{\Pi}/dh_1)(d\zeta/dr)$  must be added) we obtain  $v_\zeta^0 = -(k^2/24\mu)(\bar{\sigma}k^2 - 2d\bar{\Pi}/dh_1)h_1^3\zeta$ . Since  $v_\zeta^0 = d\zeta/dt = (d\zeta/dh)(dh/dt)$ , the wave amplitude  $\zeta$  and respectively the critical thickness of film rupture  $h_{cr}$ , will depend on the ratio  $v_\zeta^0/v_{Re}$ :

$$\zeta = \text{const} \exp\left[-\int \frac{v_\zeta^0}{v_{Re}} dh_1\right] \quad (7)$$

Hence the final expression for  $h_{cr}$  depends<sup>6,13</sup> on  $F, \bar{\Pi}$  and  $\bar{\sigma}$  but not on  $\mu$ .

In the analysis of the stage e) the black spot is considered as a piston expanding in radial direction with velocity  $V_r$ . The velocity of thinning  $V$  of the first film is also allowed for. Complicated expressions have been obtained for  $V_r$  and  $V$  which give<sup>8</sup>  $V_r = h_1(\Delta_1 - \Delta_2)/12\mu R_2 \ln(R_1/R_2)$  in the particular case of  $V=0$ . This result is in agreement with the established by Kolarov, Scheludko and Exerowa proportionality between  $V_r$  and  $\Delta_1 - \Delta_2$ . The problem for the expansion of a second film (stage f) has been solved by the method of parametric expansion<sup>9</sup>. The expression obtained for the velocity of expansion of the film  $V_r = \bar{\sigma}^2 F [\delta \pi \eta \mu R_2 \ln(R\bar{\sigma}^2/12, 2h_2)]^{-1}$  ( $n=1$  for a film on a substratum and  $n=4$  for a symmetrical film) satisfactory agrees with the experimental results of Tchalyovska and Kolarov in the cases when the second film is thick enough to assume that the viscosity has its bulk value.

In fact, never are the interfaces in foam and emulsion systems immobile. The velocities of tangential motion  $U_a = U_b = U$  (for identical droplets or bubbles) are determined by the balance of forces acting tangentially on the interface:

$$\mu(\partial v_r / \partial z) = \mu^*(\partial v_r^* / \partial z) + (\partial \bar{\sigma} / \partial r) + \mu_s \partial (v_r v_r) / \partial r \quad (8)$$

where  $v_r$  is the radial component of the velocity,  $\nabla_r$  is the radial part of the surface gradient and  $\mu_s$  is surface viscosity. The asterisk denotes that the respective quantities refer to the droplet. The local value of the surface tension is expressed as a sum of the equilibrium value  $\bar{\sigma}$  and

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where  $v_r$  is the radial component of the velocity,  $\nabla_r$  is the radial part of the surface gradient and  $\mu_s$  is surface viscosity. The asterisk denotes that the respective quantities refer to the droplet. The local value of the surface tension is expressed as a sum of the equilibrium value  $\bar{\sigma}$  and

the small perturbation  $\tilde{c}$ . Analogous approximations are also used for the bulk and the surface surfactant concentrations  $c$  and  $\Gamma$ . The velocity  $v_r$  is found by solving Navier-Stokes' equations for the drop and  $\tilde{c}$  is found from the adsorption isotherm, the diffusion equation (which for the dispersion medium has the form  $\partial^2 \tilde{c} / \partial z^2 + \Delta_r \tilde{c} = 0$ ) and the condition of conservation of the surfactant:

$$\Gamma v_r U - D_s \Delta_r \tilde{\Gamma} = -D(\partial \tilde{c} / \partial z) + D'(\partial \tilde{c}' / \partial z)$$

Here  $D$  and  $D_s$  are the bulk and surface diffusion coefficients respectively.

The application of the above presented method (with  $\mu_s = 0$ ) to the stages a)-d) of the film evolution<sup>2,3,6,10,11</sup> led to the equations

$$V/V_{\text{immob}} = v_c/v_c^0 = 1 + \alpha; \quad \alpha = -\left(1 + \frac{2D_s}{D} \frac{d\Gamma}{h_1 dc} \right) \frac{3D\mu}{\Gamma(\partial \tilde{c} / \partial z)} \quad (9)$$

where  $V_{\text{immob}}$  is  $V_T$  for the stages a) and b) and  $V_{Re}$  for the stage c). Equation (9) has been experimentally confirmed by measuring the velocity of thinning of films of aqueous solutions of three fatty acids<sup>12</sup>. The value of  $D_s$  thus obtained is of the order of magnitude  $10^{-4}$  cm/s. The amplitude  $\tilde{c}$  of the fluctuational waves and the critical thickness of rupture in this case depend on  $v_c/V$  and according to (7) and (9) must have the same values as with immobile surfaces i.e.  $h_{cr}$  should not depend on the surfactant concentration<sup>6</sup>. The term allowing for the effect of  $\mu_s$  on the velocity of thinning  $V$  (stage c) is proportional to  $h_1/R^2$  and on  $v_c$  (stage d) to  $h_1 k^2/6$ . Since  $kR_1 \approx 10$ , it is possible that<sup>13</sup>, with  $\mu_s \approx 10^{-3}$  s.p., the effect of  $\mu_s$  on  $V$  to be negligibly small, being, at the same time, so great with respect to  $v_c$  that  $v_c = v_c^0$ . Then  $h_{cr}$  will depend not on  $v_c^0/V_{Re}$  but on  $v_c^0/V$  and its value will be smaller than that with immobile surfaces (or with  $\mu_s = 0$ ). At sufficiently low surfactant concentrations the surface viscosity  $\mu_s$  vanishes and the velocity of wave motion becomes equal to  $v_c = v_c^0(1 + \alpha)$  which results in increasing of  $h_{cr}$ . This is a possible explanation for the

experimentally observed increase of  $h_{cr}$  when  $c$  diminishes<sup>6</sup>.

The case of mutual approaching of two identical emulsion non-deformable droplets of radius  $R$  in the absence of surfactant (stage a) was also considered<sup>14</sup>. From the obtained general equation, analogous to the equation derived by Haber, Hetsroni and Golan the following more important limiting cases result: 1) at  $1/R \gg 1$  one obtains

$$F = 6\pi\mu R \frac{2\beta + \mu/\mu}{1 + \mu/\mu} \left[ 1 + \frac{1 + 11(\mu/\mu) + 45(\mu^2/2\mu)^2}{15(2/3 + \mu/\mu)(1 + \mu/\mu)} \right] \quad (10)$$

which is a generalization of the well-known formulae of Stokes, Ryzczynski-Hadamard and Lorentz; 2) at  $1/R \ll 1$  we have

$$F = (3\pi^2/8\sqrt{2}) \mu^* V R \sqrt{R/\ell} \quad (11)$$

Note that in (11) and (13) (see below)  $F$  does not depend on the viscosity  $\mu$  of the dispersion phase; 3) at  $1/R \ll 1$  and  $\mu^* = 0$  (non-deformable bubbles)  $F = 2\pi\mu V R \ln(R/l)$ .

When the distance between the emulsion droplets is sufficiently small a plane parallel film appears between them (stage c). In the case of soluble only in the dispersion medium surfactant and  $\mu_s = 0$ , the velocity of thinning of the film<sup>15</sup> is

$$V/V_{Re} = 1 + \alpha/(1 + \alpha\epsilon); \quad \epsilon = \frac{2}{3B} \left( \frac{\rho^* \mu^* h_1^4 F}{\pi \mu^3 R_1^4} \right)^{1/3} \quad (12)$$

where  $\rho^*$  is density and  $B \approx 3$  is dimensionless quantity depending very little on  $h_1$ . For systems of practical interest  $\epsilon \ll 1$  and (12) turns into (9) i.e.  $V$  is chiefly determined by the effect of the surfactant. In this case the velocity  $V$  is greater but still of the order of magnitude of Reynolds' velocity  $V_{Re}$ . In the case, when only soluble in the dispersion phase, the surfactant is evenly distributed over the film surface ( $\partial \tilde{c} / \partial r = 0$  in (8)) and the system behaves as in the absence of surfactant. Then (put  $\alpha \rightarrow \infty$ )

$$V = V_{Re} (1 + 1/\epsilon) \approx B (h_1^5 F^2 / \pi^2 \rho^* \mu^* R_1^8)^{1/3} \quad (13)$$

so that  $V \gg V_{Re}$  (note that  $\xi \ll 1$ )<sup>16,17</sup>. These results show that the droplets formed by the liquid in which the surfactant is soluble will coalesce much faster than those formed by the other liquid and, according to Bancroft's rule, this emulsion will be stable in which the surfactant is soluble in the dispersion medium. On the other hand, these results indicate that the disregard of the hydrodynamic factor in Davies' theory of HLB is not grounded, at least in the case of low stable emulsions<sup>15</sup>.

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