Line tension and capillary pressure in foams

Valery V. Krotov and Anatoly I. Rusanov*

Department of Chemistry, St. Petersburg State University, 199034 St. Petersburg, Russian Federation. Fax: +7 812 428 6939; e-mail: rusanov@rus.usr.pu.ru

The line tension of Plateau borders is introduced and a general equation for the capillary pressure in a foam is derived, allowing for line tension and including the case of thin films typical of polyhedral foams and emulsions.

Films and Plateau borders are the principal elements of polyhedral foams and concentrated emulsions. Introducing a unique dividing surface for each film and a dividing line for each Plateau border, one can consider a foam as a network of geometrical surfaces possessing film tension γ^f and lines possessing line tension κ. The description of a foam in these terms and the derivation of a general equation for the foam-cell capillary pressure are the goals of this work.

A rectilinear Plateau border is of the shape of a triangular column with concave surfaces. Assuming the foam films to be very thin, and neglecting the contact angle at the junction of the Plateau border and film surfaces, one can approximate a Plateau border as the space, filled with a liquid (phase α), between three touching cylinders of phase β of radius r, whose cross-section is shown in Figure 1. In this model, the cross-sectional area A_b of a Plateau border is

$$A_b = r^2(3^{0.5} - \pi/2) \cong 0.1612r^2 \qquad (1)$$

If each film of a foam is depicted by a single dividing surface (the lines marked with γ^f in Figure 1), their meeting place (point O in Figure 1) should be a line, and a corresponding line tension can be derived. To do this, we first calculate the total force, f_b, acting through the cross-section of a Plateau border. Such a force is the combination of surface and bulk contributions. The surface part is clearly $\pi r\gamma$ since the perimeter of the circular triangle (Figure 1) is πr. According to the Laplace equation, the stress inside the Plateau border is $-p^\alpha = -p^\beta + \gamma/r$ (p is pressure and γ is surface tension) and the corresponding force is $(-p^\beta + \gamma/r)A_b$. So, the total force is

$$f_b = \pi r\gamma + (-p^\beta + \gamma/r)A_b = -p^\beta A_b + (3^{0.5} + \pi/2)\gamma r \qquad (2)$$

where equation (1) has been used. Introducing the Plateau-border line tension as an excess quantity, we have to compare the above force (acting across the left part of Figure 1) with the force acting across the right part of Figure 1 and equal, evidently, to $-p^\beta A_b + 3\gamma^f l_b$ where $l_b = r/3^{0.5}$ is the length of the bisector of the circular triangle calculated from its centre (Figure 1). Subtracting this force from equation (2), we obtain the Plateau-border line tension κ as

$$\kappa = (\pi/4 - 3^{0.5}/2)\gamma^f r \cong -0.0806\gamma^f r \qquad (3)$$

Since the surface tension of liquids is always positive, equation (3) predicts a negative value for the Plateau-border line tension. It is of note that the latter has nothing to do with ordinary interfacial line tension (which we neglected in the above calculation) and is by several orders of magnitude larger in value: *e.g.* equation (3) yields $\kappa = -8\times10^{-7}$ N at $\gamma = 50$ mN m^{-1} and $r = 0.1$ mm.

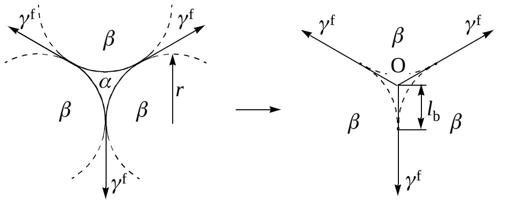

Figure 1 The cross-section of a Plateau border and passing to its linear image.

Generally, the Laplace equation gives the pressure difference in neighbouring phases or cells, speaking about a foam (then the surface tension is replaced by film tension), *i.e.* it defines the capillary pressure of a foam cell with respect to the pressure in the neighbouring cell. The latter, however, is not under control in the experiment, so it is convenient to introduce a more general definition of the capillary pressure of a foam cell, p_c, as the difference between the pressure inside the cell and the outer (say, atmospheric) pressure. Derjaguin[1] was the first to suggest an expression for such a capillary pressure of the foam cell as

$$p_c = 2\gamma s/3 \qquad (4)$$

where s is the specific surface area of a foam. However, equation (4) is inexact in two respects. Firstly, it refers to thick films, whereas the presence of thin films is typical for polyhedral foams. Thin films possess a disjoining pressure and their tension is not 2γ as is implied in equation (4). Secondly, equation (4) does not take into account linear phenomena in foams. Although the influence of line tension can be small, it should be represented in a rigorous relationship.

To derive a more general expression for the foam-cell capillary pressure, let us consider the variation of the volume of a polyhedral monodisperse foam which is represented as part of a space compactly filled with polyhedrons. If λ is a certain linear parameter of a single polyhedron, the total length of its edges (Plateau borders) L_p, the polyhedron surface area A_p and the polyhedron volume v are related to λ by the relationships

$$L_p = k_1\lambda,\ A_p = k_2\lambda^2,\ v = k_3\lambda^3 \qquad (5)$$

where k_1, k_2 and k_3 are proportionality coefficients. Then, we have from equation (5)

$$\mathrm{d}\ln L/\mathrm{d}\ln v = 1/3,\ \mathrm{d}\ln A^f/\mathrm{d}\ln v = 2/3 \qquad (6)$$

At a fixed temperature and amounts of all components, the fundamental thermodynamic equation for the free energy F of the system, including the polyhedral foam and a surrounding medium, is

$$\mathrm{d}F = -p'\mathrm{d}V' - p\mathrm{d}V + \gamma^f\mathrm{d}A + \kappa\mathrm{d}L \qquad (7)$$

where p' is the outer pressure acting on the foam, V' is the volume of the surrounding medium, p is the pressure inside the foam polyhedrons, V is the foam volume (equal to the sum of the volumes of all polyhedrons), A is the total surface area of the polyhedral network and L is the total line length of the network.

The Gibbs equilibrium principle is formulated in this case as

$$\mathrm{d}F_{V+V'} = 0 \qquad (8)$$

Putting equation (7) in (8), we arrive at the mechanical equilibrium condition

$$p - p' = \gamma^f\mathrm{d}A + \kappa\mathrm{d}L = \gamma^f a\frac{\mathrm{d}\ln A}{\mathrm{d}\ln V} + \kappa l\frac{\mathrm{d}\ln A}{\mathrm{d}\ln V} \qquad (9)$$

where $a \equiv A/V$ and $l \equiv L/V$ are the surface area and the line length per unit volume, respectively. Let us calculate the derivatives on the right-hand side of equation (9). If the number of polyhedrons is n, the foam volume is $V = nv$ where v is the volume of a single polyhedron. Since each polyhedron's face, except the outer faces, belongs simultaneously to two adjacent polyhedrons, the total surface area of the network is $A = (n/2)A_p$ where A_p is the surface area of a single polyhedron. Similarly, since each line (except the outer lines) belongs simultaneously to three polyhedrons according to the Plateau rule, $L = (n/3)L_p$ where L_p is the total length of edges of a single polyhedron (n is suggested to be large enough to neglect the outer foam cells). Therefore, for variations not influencing the number of polyhedrons, we have

$$\mathrm{dln}V = \mathrm{dln}v,\ \mathrm{dln}A = \mathrm{dln}A_p,\ \mathrm{dln}L = \mathrm{dln}L_p \tag{10}$$

Then, according to equation (5), we have

$$\frac{\mathrm{dln}A}{\mathrm{dln}V} = \frac{\mathrm{dln}A_p}{\mathrm{dln}v} = \frac{2}{3},\quad \frac{\mathrm{dln}L}{\mathrm{dln}V} = \frac{\mathrm{dln}L_p}{\mathrm{dln}v} = \frac{1}{3} \tag{11}$$

Now putting equation (11) in (9), we obtain

$$p_c \equiv p - p' = 2\gamma^f a/3 + \kappa l/3 \tag{12}$$

Equation (12) is a general expression for the capillary pressure of the foam cell. Let us consider some particular and approximate forms of equation (12). Roughly regarding the films of a polyhedral cell as thick films, and setting $\gamma^f \approx 2\gamma$, equation (12) becomes

$$p_c \approx 4\gamma a/3 + \kappa l/3 \approx 4\gamma a/3 - 0.054\gamma lr \tag{13}$$

where r is the curvature radius of the Plateau-border surface and the last term has been estimated with the aid of equation (3). Since typically $lr < a$ in a polyhedral foam, the last term in equation (13) plays the role of a small correction.

Passing to real polyhedral foams, a is approximately the specific film area in a foam. The corresponding specific surface area of a foam s is twice as much as a (since each film has two sides), so equation (13) can also be written, neglecting the last term, in the form of equation (4). As seen from equation (13), a more exact form of Derjaguin's equation is

$$p_c \approx 2\gamma^f a/3 \approx \gamma^f s/3 \tag{14}$$

It is of note that the above derivation of equation (12) is valid at an arbitrary outer phase surrounding the foam. The outer phase can be the same gas as inside the foam bubbles or another gas (say, the air) or a liquid phase including the case when the outer phase coincides with the continuous phase of the foam (a foam in the bulk of a solution). The concept of capillary pressure expressed in equation (12) is also applicable to polyhedral concentrated emulsions.

References

1 B. V. Derjaguin, *Zh. Fiz. Khim.*, 1931, **2**, 745 (in Russian).

Received: Moscow, 15th June 1998
Cambridge, 17th July 1998; Com. 8/05508D