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Variations from the Plateau law in foams

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In this paper we study microgeometry of real foam. We suggest an explanation of systematic variations from the classical Plateau law which may be observed in real froths and foams of random structure. We show that the variations in the inclination angles between liquid films forming Plateau borders are conditioned by the variations in disjoining pressure and surface tension in the films separating bubbles of different sizes. Equations for calculating the inclination angles from the isotherm of disjoining pressure are derived. For black foam films the deviations of the inclination angles from the ideal value of 120° are expected to amount up to several degrees.

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Real foams and froths are random coarse dispersions of gas bubbles separated by thin liquid films; for reviews see [1–6]. Many important problems connected with formation, stability, and rheology of foams require thorough analysis of microgeometry of bubbles and liquid films. The microgeometry of ideal equilibrium foam has been studied in detail by Josef-Antoine-Ferdinand Plateau over the course of a quarter century (1843–1869); for a modern description see [7].

The Plateau law can be formulated as follows. In three-dimensional (3D) equilibrium foam, the liquid films between coarsened bubbles constitute a polyhedral structure with two main geometrical features: (i) the edges, named Plateau borders, are formed by three liquid films equally inclined toward one another all along the edge, with mutual angles equal to 120°; (ii) the vertices are formed by four liquid films with the edges equally inclined toward one another in space at the Maraldi (tetrahedral) angle $\approx 109°28''16'$, whose cos is equal to $-\frac{1}{3}$. In two dimensions, liquid films in equilibrium constitute a polygonal network with vertices formed by three edges meeting at 120°.

The Plateau law is one of the most prominent physical laws in the natural sciences due to its simplicity and wide applicability to many cellular structures other than foams, such as biological tissues, polycrystals, and magnetic systems [1–6]. It is based on the clear supposition of local mechanical equilibrium with the only assumption that the surface tension of all interfaces is the same. The validity of the Plateau law has been reported for many various experimental systems [1–6]. Recently, Stavans and Glazier [8] have claimed that even in two-dimensional (2D) froth the angles between the liquid edges do not always meet at 120° angles. These departures from Plateau's law have been reported for a random froth structure with a significant distribution of bubble sizes. The authors [8] have found that the average internal angle in small bubbles having a number of sides less than 6 is smaller than 120°, and in big bubbles having a number of sides more than 6 it is larger than 120°. Moreover, similar deviations from the Plateau law have been observed by Stine *et al.* [9] in cellular patterns formed in lipid (PDA) monolayers on a water surface.

To the best of our knowledge the only attempt to explain the observed deviations from the Plateau law [8] has been made by Bolton and Weaire [10]. They addressed the deviations in inclination angles between liquid films from 120° to the particular procedure of measuring these angles used in [8], which leads in the case of thick Plateau borders to an apparent increase of the inclination angles in large bubbles and to an apparent decrease of the inclination angles in small bubbles. Bolton and Weaire have shown that the Plateau law should be valid even in the case of thick Plateau borders provided that the angles are measured between the extensions of curved bubble edges meeting at a point at the center of the border. It is worth noting that afterwards the authors of [8] agreed with the arguments of Bolton and Weaire [6,11] and in recent experiments with dry foam [11] deviations from the Plateau law have not been observed. After the appearance of these papers, discussion on possible violations of the Plateau law was implicitly closed.

In this paper we are revisiting this problem. The major purpose is to theoretically predict the inevitable deviations from the Plateau law in any random foam made of unequal bubbles. The range of these deviations depends on the film's nature and on the conditions of mechanical equilibrium. These deviations may be negligibly small or sufficiently large depending on the foaming and antifoaming agents employed in foam preparation. The largest deviations are expected in a foam where different films coexist: thick films, common black films, and Newton black films. The coexistence of different films is typical for soap foams and the corresponding observations date back to Isaac Newton (1704).

Recent special experiments with dry 2D foam [12] prepared by nitrogen injection in an octaethylene glycol monodecyl ether (OGME) solution (concentration $c = 0.1$ mol/m^3) give strong evidence of essential deviations from 120°. A typical example is presented in Fig. 1. The devi-

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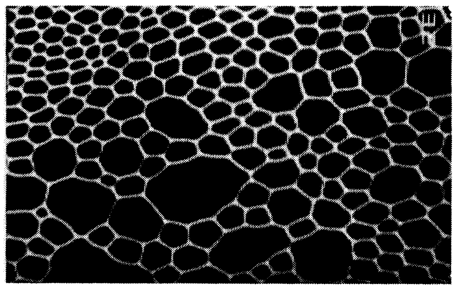

FIG. 1. A pattern of dry 2D foam of a OGME solution. Positive deviations in the inclination angles in large bubbles and negative deviations in small bubbles are easily seen.

ations from the conventional value of 120° are easily seen and may hardly be regarded as experimental errors. Although the angles could not be calculated exactly because of the insufficient quality of the obtained pictures, we believe that this is clearly a violation of the Plateau law. We are aware of the pitfalls facing the authors [8] in the case of wet foam, and the method of Bolton and Weaire [10] is unable to explain the deviations from 120° in the pattern of dry 2D foam presented in Fig. 1. One of us (M. V.-A.) is currently taking precise measurements, which is planned to be communicated elsewhere. We are not now in a position to discuss in detail the experimental data presented in Fig. 1, but these experiments have stimulated us to develop a theory presented below that explains the possible violations of the Plateau law in real films.

The problem—whether the deviations from the Plateau law are typical for all random froths and foams or whether the above-mentioned data are the exceptions confirming a general rule—is of great practical value in connection with the repeated attempts to produce adequate structure models for real cellular systems [13–15]. The fulfillment of the Plateau law is one of the main regular requirements for the theoretical and computer models of foams and other cellular systems of random structure. Conventional laws of foam evolution such as the famous von Neumann law [16] for two-dimensional froth are based on the Plateau law. When the deviations from the Plateau law are essential, these models of foam microgeometry and the dynamic laws based on them require modifications [8,10,17].

It is worth noticing that the Plateau law as well as the Bolton and Weaire theory imply the equality of surface tension for all liquid films independent of their curvature and of bubble sizes, and therefore may be considered for thick films only. Experimentally, thick films are usually thermodynamically unstable unless the Gibbs-Marangoni effect is acting and they turn spontaneously into thin black films [18]. The extensive experimental and theoretical studies of black films have been carried out in the 1960s [19–22]; for a review of numerous papers of researchers see [3]. Two modifications of black films are well known, the so-called common and Newton black films. They differ in thickness and in thermodynamic properties, in particular in surface tension. The difference in surface tension causes a nonzero contact angle between a thin film and a bulk liquid that has been observed in a number of experiments, in particular with foam films (for an extended review, see, e.g., [3], and references therein). The contact angles observed in these experiments amount up to 10° and even more [23,24], which corresponds to a surface tension difference of about 1 mN/m [23]. In real foam with films of different thickness and curvature, similar effects may cause the deviations in the inclination angles from the equilibrium value of 120°, as required by the Plateau law. To our knowledge, experimental evidence of these effects in real 3D foam is lacking.

Any foam is a nonequilibrium thermodynamic system that evolves in time. This process is mostly conditioned by gas diffusion from the smaller bubbles to the bigger ones due to the pressure difference between the bubbles. Despite these inevitable changes, the instantaneous foam configuration may be regarded as an equilibrium configuration in a current field of pressure since the characteristic time of the establishment of local mechanical equilibrium between the bubbles and films is much smaller than the characteristic time of pressure changes due to mass transfer. This has led us, together with other researchers [1–6], to believe that these processes can be separated in time while modeling the microgeometry of foam. By microgeometry we mean the local configuration of contacting bubbles and films. With this hypothesis in mind we suppose that the foam microgeometry is determined by the current pressure in the bubbles P_i (i is the number of the bubble) and by the external pressure P_0 (actually, P_0 is the pressure in the bulk liquid in thermodynamic equilibrium with the film liquid). Isothermal conditions and the inefficiency of gravity on the scale of 1–2 bubbles are supposed also.

First, let use consider a liquid film between two bubbles of different size (Fig. 2). This problem was studied in detail earlier by Churaev and Starov [25] by taking into account the transition zone between the interlayer and the bulk liquid. To analyze the equilibrium configuration in this system, we apply the Derjaguin equation [26] for the equilibrium of thin liquid films on curved solid surfaces:

$$P_g + 2\sigma / R_c = \Pi(h) + P_0 \, , \tag{1}$$

where P_g is the gas pressure, σ is the surface tension on the liquid-gas interface, R_c is the mean radius of curvature of the liquid-gas interface supposed equal to the mean radius of curvature of the solid substrate provided film thickness h is much less than R_c, $\Pi(h)$ is the disjoining pressure in the liquid film of thickness h, and P_0 is the external pressure in bulk liquid that is in equilibrium with

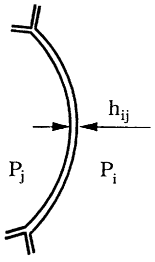

FIG. 2. Thin film bubbles two bubbles i and j with different pressures $P_i < P_j$.

the film. The Derjaguin equation implies that the contributions of capillary and surface forces are additive and that the latter do not depend on the film curvature.

Application of the Derjaguin equation (1) to the liquid film between the bubbles is based on the fact that the equilibrium configuration of the film does not change when one of the bubbles would be replaced (mentally) by a solid of the same form. This procedure applied to the bubble leads to the equilibrium equation for the interface between liquid film and bubble i,

$$P_i + 2\sigma / R_{ij} = \Pi(h_{ij}) + P_0 \ , \tag{2a}$$

where h_{ij} is the film thickness and R_{ij} is the mean radius of curvature of this interface. It is assumed that $P_i < P_j$. For the interface between the liquid film and the bubble j, the symmetric equation holds,

$$P_j - 2\sigma / R_{ji} = \Pi(h_{ij}) + P_0 \ . \tag{2b}$$

The thickness of real foam films is considerably less than their radius of curvature; $h_{ij} \ll R_{ij}$ and therefore the values R_{ij} and R_{ji} in Eqs. (2a) and (2b) can be regarded as being equal.

From Eqs. (2a) and (2b) it follows that (i) the mean radius of film curvature is calculated from the ordinary Laplace equation for a thick film between two phases,

$$R_{ij} = (P_j - P_i)/4\sigma \ ; \tag{3}$$

and (ii) the film thickness is calculated from the isotherm of disjoining pressure $\Pi(h)$,

$$\Pi(h_{ij}) = (\Delta P_j + \Delta P_i)/2 = \bar{P}_{ij} \ . \tag{4}$$

Here, $\Delta P_i = (P_j - P_0)$ is the capillary overpressure in bubble i. It is worth noting that Eq. (4) is in fact a particular case of a general equation [27],

$$\Pi(h_{ij}) = (\sigma_i \Delta P_j + \sigma_j \Delta P_i)/(\sigma_i + \sigma_j) \ , \tag{5}$$

valid for the disjoining pressure in a curved film between two phases with the different surface tension on the interface with the liquid film. In the present case, $\sigma_i = \sigma_j = \sigma$, and Eq. (5) is turned into Eq. (4).

Equation (4) states that the disjoining pressure and thickness of a liquid film between two bubbles are the same as those of a liquid film pressed onto an inert solid substrate with the pressure $\bar{P}_{ij}$ equal to the arithmetical average pressure in the bubbles. Equation (4) makes it possible to predict the film thickness provided that the isotherm of disjoining pressure is known.

In foam films the isotherms of disjoining pressure are governed by an interplay between dispersion and electrostatic forces. They may have a rather complicated shape with the negative and positive regions, maxima and minima [3,18]. A typical sketch of the disjoining pressure isotherm for a soap film is presented in Fig. 3. Nonmonotonic behavior of the isotherm causes the existence of several metastable states with the same disjoining pressure, i.e., with the same chemical potential, e.g., common and Newton black films.

The surface tension of a film may depend on its thickness and curvature [26]. For real foam films, the latter factor is hardly essential but the former should be considered while analyzing the foam microgeometry. The surface tension of thin liquid film is calculated from the isotherm of disjoining pressure [3,18,26,28]:

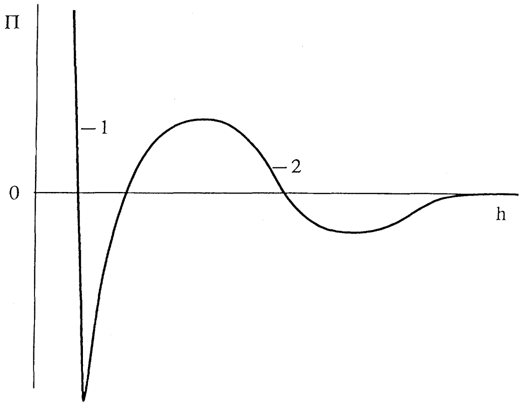

FIG. 3. Schematic sketch of typical isotherm of disjoining pressure $\Pi(h)$ in soap films 1, region of Newton black films; 2, region of common black films.

$$\sigma(h) = 2\sigma + \int_h^\infty \Pi \, dh + \Pi(h) h = 2\sigma - \int_{\Pi(h)}^0 h \, d\Pi \ . \tag{6}$$

For thick films, $h \to \infty$ and $\Pi(h) \to 0$; Eq. (6) gives the trivial relation for a thick film,

$$\sigma_\infty = 2\sigma \ . \tag{7}$$

The difference between the surface tension of a thin film and of a thick film,

$$\Delta\sigma(h) = \int_h^\infty \Pi \, dh + \Pi(h) h = -\int_{\Pi(h)}^0 d \, d\Pi \ , \tag{8}$$

may amount for soap films to several percent [26], which yields a perceptible nonzero contact angle between thin films and bulk liquid.

Recall that the Plateau law for the inclination angles between contacting foam films is based on the supposition that the surface tension of all films is equal to σ_∞ (7). The deviations in surface tension conditioned by the difference in disjoining pressure due to Eq. (8) should lead to the deviations in inclination angles from the ideal value of 120°.

Figure 4 presents a sketch of a normal cross section of a Plateau border formed by three bubbles with different pressure $P_i \geq P_j \geq P_k$. The disjoining pressure in the films between bubbles is determined by Eq. (4) and the surface tension is determined by Eq. (6):

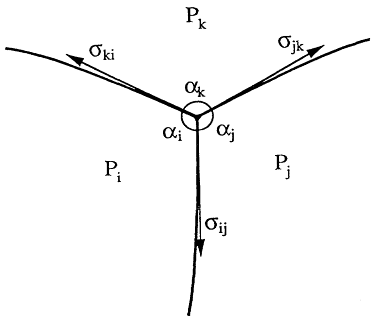

FIG. 4. Normal cross section of a Plateau border formed by three bubbles i, j, and k with different pressures $P_i \geq P_j \geq P_k$ (α_i, α_j, and α_k: the inclination angles; σ_{ij}, σ_{jk}, and σ_{ik}: the surface tension of liquid films).

$$\sigma_{ij}=2\sigma-\int_{\Pi(h)}^{0} h\,d\Pi=\sigma_{\infty}+\Delta\sigma_{ij}\ . \tag{9}$$

Denote as α_i the inclination angle between the films coarsening the bubble *i*. Then, the usual conditions of mechanical equilibrium are written as

$$\sigma_{ij}=\sigma_{ki}\cos(\pi-\alpha_i)+\sigma_{jk}\cos(\pi-\alpha_j)\ , \tag{10}$$

$$\sigma_{ki}\sin(\pi-\alpha_i)=\sigma_{jk}\sin(\pi-\alpha_j)\ . \tag{11}$$

From Eqs. (10) and (11) it follows that

$$\alpha_i=\arccos[(\sigma_{jk}^2-\sigma_{ij}^2-\sigma_{ki}^2)/2\sigma_{ij}\sigma_{ki}]\ . \tag{12}$$

The equations for α_j and α_k are obtained by circle permutations of subscripts $i\rightarrow j$, $j\rightarrow k$, and $k\rightarrow i$.

This simple relation together with Eqs. (4) and (9) enables us to calculate the inclination angles at given bubbles pressures. Only when the bubble pressures are equal are the inclination angles equal to 120°. The pressure difference inevitably causes the deviations from this classical value, which can be predicted when the disjoining pressure isotherm is known.

If the deviations of surface tension $\Delta\sigma_{ij}$, $\Delta\sigma_{jk}$, $\Delta\sigma_{ij}$ are small, Eq. (12) can be linearized and the following relation for the deviations in the inclination angles, $\delta_i=\alpha_i-120°$, holds:

$$\begin{aligned}\delta_i&=-(2\sigma_{jk}-\sigma_{ij}-\sigma_{ki})/\sqrt{3}\sigma_{\infty}\\&=-(2\Delta\sigma_{jk}-\Delta\sigma_{ij}-\Delta\sigma_{ki})/\sqrt{3}\sigma_{\infty}\ .\end{aligned} \tag{13}$$

Because the overpressure ΔP_i is greater in smaller bubbles, positive deviations should be observed for the angles between the films in the bigger bubbles and negative ones between the films in the smaller bubbles.

Let considered two typical simple situations: (i) two large bubbles *j* and *k* in contact with a small bubble *i* ($P_i>P_j\approx P_k$) and (ii) two small bubbles *j* and *k* in contact with a large bubble *i* ($P_i<P_j\approx P_k$). In case (i), $\sigma_{jk}=\sigma_{ll}>\sigma_{ij}\approx\sigma_{ij}=\sigma_{ls}$ and $\delta_i=-2(\Delta\sigma_{ll}-\Delta\sigma_{ls})/\sqrt{3}\sigma_{\infty}<0$; $\delta_j=\delta_k=-\frac{1}{2}\delta_i$. In case (ii), $\sigma_{jk}=\sigma_{ss}<\sigma_{ij}\approx\sigma_{ij}=\sigma_{ls}$ and $\delta_i=-2(\Delta\sigma_{ss}-\Delta\sigma_{ls})/\sqrt{3}\sigma_{\infty}>0$; $\delta_j=\delta_k=-\frac{1}{2}\delta_i$.

The fact that the angle deviations are positive in large bubbles and negative in small bubbles was observed in [12]. The pattern in Fig. 1 confirms this conclusion qualitatively.

Referring to the above-mentioned experiments with black soap films [3,23,24], we can estimate crudely the deviations in the inclination angles. Actually, in these experiments the differences in surface tensions of black and thick films, $\Delta\sigma(h)$ [see Eq. (8)], have been measured. For example, in black films obtained from the solution of natrium dodecylsulfate, $\Delta\sigma$, with the increase of the electrolyte (NaCl) concentration from 0.3 to 0.5 mol/l, increases from a negligible value to 1.4 mM/m [23]. Such a difference in surface tensions leads to contact angles between black and thick films of up to 10°, which is observed in the experiments with free films [3,23]. If we suppose that in foams the differences $|\Delta\sigma_{ll}-\Delta\sigma_{ls}|$ and $|\Delta\sigma_{ss}-\Delta\sigma_{ls}|$ may be of order 0.3–3 mN/m and $\sigma_{\infty}\approx 70$ mN/m, we would predict from Eq. (13) that the inclination angles between the bubbles with black and thick films increased up to $\delta_i\approx\pm(0.3-3°)$. The quantitative estimations based on the experimental isotherms of disjoining pressure $\Pi(h)$ as well as more precise experimental measurements of the inclination angles in 2D froths will be presented elsewhere.

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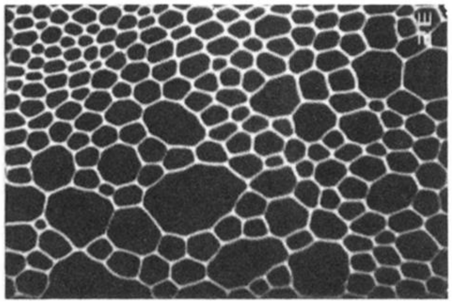

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