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# Foam Microgeometry

G. B. Han[2], A. Dussaud[3], B. Prunet-Foch[1], A. V. Neimark[4], M. Vignes-Adler[1]
[1]Laboratoire de Physique de Matériaux Divisés et des Interfaces, Université de Marne-la-Vallée, Bâtiment Lavoisier, Cité Descartes, Marne-la-Vallée, France
[2]Xiamen University, Xiamen, Rep. of China
[3]Unilever Research US, Edgewater, NJ, U.S.A.
[4]TRI/Princeton, NJ, U.S.A.

Registration Number 886

## Abstract

We present an experimental study of the influence of long range molecular forces on the 2D-foam microgeometry. It is shown that the disjoining pressure effect cause the Plateau angles to deviate from 120°.

## 1. Introduction

Real foams and froths are random coarse dispersions of gas bubbles separated by thin films which meet at the so-called Plateau border. The extensive development of numerical modelling of foams requires a thorough analysis of the local geometrical arrangement of the contacting bubbles and liquid films, to provide a firm experimental basis for model assumptions.

Plateau provided the fundamental geometrical law describing foam microgeometry. He stated that in a two-dimensional equilibrium foam, liquid films constitute a polygonal network formed by three edges meeting at 120°. The Plateau law is based on the local mechanical equilibrium assuming that surface tension of all the interfaces and the film tension of all the connecting films are equal.

In a previous paper [1], this theoretical aspect was revisited. Plateau's consideration neglacts the effect of long range forces on the equilibrium thickness of thin liquid soap films. When the liquid film is so thin that surface forces – e.g., van der Waals, electrostatic, steric etc... forces – overlap, those give rise to the disjoining pressure which balances the normal component of the overpressure tensor acting on the film [2]. In a flat foam film, the disjoining pressure $\Pi$ is equal and opposite to the capillary pressure $P_c$ prevailing in the Plateau border and prevents the film from bursting if the thermodynamical conditions are favorable.

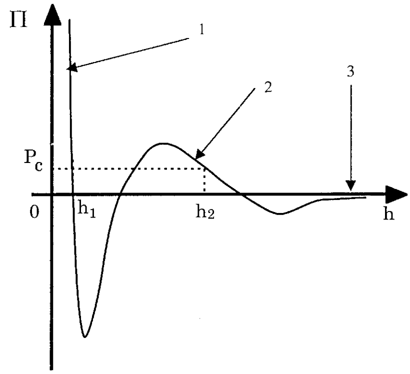


**Fig. 1.** Schematic sketch of a typical isotherm of disjoining pressure in soap films: 1 region of Newton black films; 2, region of common black films; 3, region of thick films.

For a given solution, the disjoining pressure Π depends on the film thickness $h$. Theoretical modelling of a single planar isolated soap film clearly shows that the behaviour of the disjoining pressure isotherms $\Pi(h)$ is non-monotonical (Fig. 1), and patches of various thicknesses – thick films (TF), common black films (CBF) and Newton black films (NBF) – can coexist in a film [3]. In a foam, one can therefore expect to get the films with different thicknesses for the same applied capillary pressure.

For a thick film,

$$\text{as } h \to \infty \quad \Pi(h) \to 0 \quad \text{and} \quad \gamma(h) \to \gamma_\infty \quad \text{with } \gamma_\infty = 2\sigma \tag{1}$$

where $\sigma$ is the usual surface tension of the bulk liquid.

For a thin film, the contribution of the disjoining pressure to the tension, $\gamma$, cannot be ignored. For a planar thin film, $\gamma$ is generally derived from the isotherm of disjoining pressure as

$$\gamma(h) = 2\sigma - \int_{\Pi(h)}^{0} h \mathrm{d}\Pi \tag{2}$$

The value of the integral in the RHS of (2) depends on the considered branch in the disjoining pressure isotherm (Fig. 1). The films, with same disjoining pressure but different thicknesses and film tensions, can therefore be in thermodynamic equilibrium as soon as

$$\Pi(h_1) = \Pi(h_2) \quad \text{with } h_1 \neq h_2 \quad \text{and} \quad \gamma(h_1) \neq \gamma(h_2) \tag{3}$$

Plateau's law for the inclination angles between contacting foam films requires that the film tensions of all films are equal to $\gamma$. Deviations in $\gamma$ caused by the differences in the disjoining pressure should lead to deviations in Plateau angles from 120° (eq. (2)),

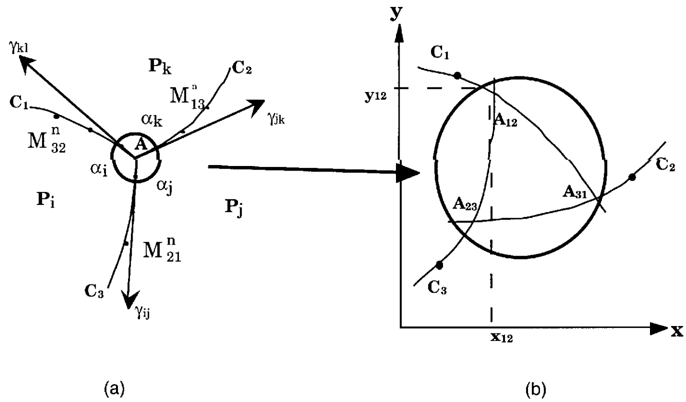


**Fig. 2.** (a) Normal cross section of a Plateau border formed by three bubbles $i$, $j$, and $k$ with different pressures $P_i \leq P_j \leq P_k$ ($\alpha_i, \alpha_j, \alpha_k$, are the Plateau angles, $\gamma_{ij}, \gamma_{jk}, \gamma_{ki}$ are the film tensions. (b) Angles measurement procedure.

[1]. Figure 2 presents a sketch of a normal cross section of a Plateau border formed by three bubbles. The film tension of the films between bubbles $i$ and $j$ can be written as

$$\gamma_{ij} = 2\sigma - \int_{\Pi(h)}^{0} h \mathrm{d}\Pi = \gamma_\infty + \Delta\gamma_{ij} \tag{4}$$

Denote as $\alpha_i$, $\alpha_j$, $\alpha_k$ the Plateau angles of the films of the bubbles $i, j$ and $k$ issued from the same vertex. From the conditions of mechanical equilibrium [1], it follows that

$$\alpha_i = \arccos\left[(\gamma_{jk}^2 - \gamma_{ij}^2 - \gamma_{ki}^2)/2\gamma_{ij}\gamma_{ki}\right] \tag{5}$$

Upon introduction of equations (4) in (5) and assuming that $\Delta\gamma_{ij}, \Delta\gamma_{jk}, \Delta\gamma_{ki}$ are small, equation (5) can be linearized and the following deviation in the Plateau angles, $\delta_i = \alpha_i - 120°$, holds

$$\delta_i = -(2\Delta\gamma_{jk} - \Delta\gamma_{ij} - \Delta\gamma_{ki})/\sqrt{3}\,\gamma_\infty. \tag{6}$$

The equations for $\alpha_j$ and $\alpha_k$ are obtained by circular permutation.

$$\delta_i \neq 0 \quad \text{if} \qquad 2\Delta\gamma_{jk} - \Delta\gamma_{ij} - \Delta\gamma_{ki} \neq 0. \tag{7}$$

The experimental analysis of this effect is the topic of the present paper.

## 2. Experimental

Two aqueous solutions of Sodium Bromide (NaBr) in which TetradecylTrimethyl-Amonium Bromide (TTAB) is dissolved were investigated. The concentrations and surface tensions of both solutions are reported in Table 1. Both solutions are micellar, the critical micellar concentration (cmc) changes with the salt concentration.

**Table 1.** Solutions properties: $\sigma$, bulk surface tension; $h_c$ and $\Pi_c$, thickness and film disjoining pressure at the TF→CB transition; $\gamma^{CB}$, $\gamma^{NB}$, average values of the CBF and NBF film tensions in the range of investigated disjoining pressures (Fig. 3).

| | $C_{TTAB}$ (mM) | $C_{NaBr}$ (mM) | cmc (mM) | $\sigma$ (mM/m) | $h_c$ (nm) | $\Pi_c$ (Pa) | $\gamma^{CB}$ (mN/m) | $\gamma^{NB}$ (mN/m) |
|---|---|---|---|---|---|---|---|---|
| Solution I | 0.57 | 0.1 | 0.36 | 34.63 | 10±0.2 | 206 | 69.25 | 68.21 |
| Solution II | 0.57 | 0.35 | 0.17 | 33.43 | 8±0.2 | 195 | 66.86 | 65.8 |

These solutions have been selected because it is known from [4] that both common and Newton black films can be obtained within the given range of salt and surfactant concentrations.

We have independently measured the disjoining pressure isotherm for single, isolated films formed from these solutions using the porous-plate technique, first developed by Mysels and Jones [5] and later refined by Exerowa and Sheludko [6] with a set-up which exists at (suppress) CRPP in Bordeaux (France). The principle is to measure interferometrically the film thickness under a microscope as a function of the liquid pressure in the Plateau border region. With the CRPP set-up, we were limited in the range of applied capillary pressures and it was only possible to measure the isotherm branch corresponding to the CB. The CBF→NBF transition was therefore not reachable. Results are plotted in Figure 3. The data can be fitted by the following empirical law

$$\Pi(h) = A \text{ csch } (Bh) + C/h \tag{8}$$

where $A$, $B$ and $C$ are empirical constants. The film thickness and disjoining pressure at the TF→CBF transition, the CBF and NBF tensions are reported in Table 1.

In NBF isolated foam, a contact angle $\theta$ between the central part of the film and its meniscus can be defined as [7]

$$\gamma = 2\sigma \cos\theta \tag{9}$$

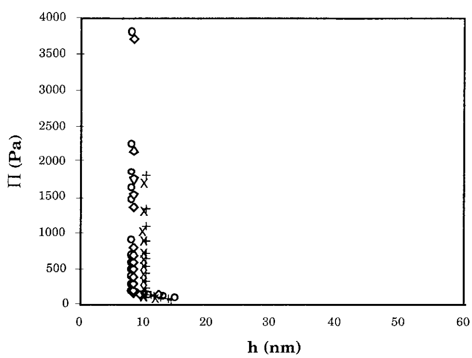


**Fig. 3.** Disjoining pressure of CBF formed from (a) solution I (A = 0.8697 × $10^{39}$ Pa, B = 8.3 Pa.m, C = 1.8 × $10^3$ Pa.m); (b) solution II ($A$ = 2.9326 × $10^{102}$ Pa, B = 28.68 Pa.m, C = 1.6 × $10^3$ Pa.m).

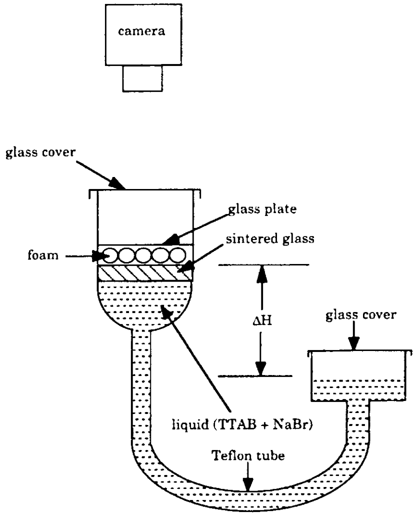


**Fig. 4.** Scheme of the experimental set-up.

Platikanov *et al.* [8] measured $\theta$ for 2%wt sodium dodecylsulfate (SDS) solutions in the presence of 0.32 mol of NaCl, which is very similar to the solutions employed here. They found $\theta = 10^\circ$. We have used this value to estimate the present NBF film tensions (Table 1).

An original set-up for measuring the Plateau angles has been built in which the capillary pressure applied to the foam is fully controlled. Basically, it consists of a glass funnel with a lower sintered glass plate which is connected to an outer reservoir by means of a teflon tube (Fig. 4). The foam cell itself is formed by the space between the sintered glass plate and an upper glass plate separated from the former by a 2 mm gap. The whole set-up is filled with a soapy solution and a two-dimensional foam is created by blowing filtered U-nitrogen at a constant flow rate. Before any experiment, all the glassware is washed with freshly made sulfochromic acid and the teflon pieces with boiling aqua regalia; then, they are profusely rinsed with milli-Q water to avoid foam killer contamination.

The capillary pressure is equilibrated by the weight of the solution column in the reservoir; it is adjusted by changing the column level $\Delta H$ from 0 to 40 cm in most cases. The intersections of the foam Plateau borders with the upper plate are photographed at several $\Delta H$. The duration of the experiment is as short as possible to diminish the coarsening process due to gas diffusion between bubbles.

The Plateau angles are measured directly on the photographs using the Bolton and Weaire decoration lemma [9]. It states that the 3 circular arcs which adjoin a triangular Plateau border may be continued with the same curvature to meet at a single point.

Since the angle deviations are expected to be of the order of one degree, an excellent precision is crucial. At each vertex, this is achieved by determining the equations of the three circles to which the circular arcs decorating the foam belong, and by calculating analytically the angles of intersections. Actually, three points $M_i^n$ $(n = 1, 2, 3)$ belonging to each decorating arc $i$ $(i = 1, 2, 3)$ (Fig. 2b) are pointed with a stylus connected to a motorized *X-Y* table, and the co-ordinates values read with a high precision (1 μm). The center and radius of each decorating circle, and the co-ordinates ($x_{ij}$ and $y_{ij}$) of their mutual intersections, $A_{12}, A_{23}$, and $A_{31}$ are analytically calculated. Each pair of circles intersects at two distinct points e.g. A and B usually one near and another one far from the vertex. Hence, to check the quality of the measurements, we calculate the quantity

$$Q = \sum_{i \neq j = 1,3} \left( \frac{|x_{ij} - x_0|}{x_0} + \frac{|y_{ij} - y_0|}{y_0} \right)$$

where $x_0 = \frac{1}{3}(x_{12} + x_{23} + x_{31})$ and $y_0 = \frac{1}{3}(y_{12} + y_{23} + y_{31})$, at the far meeting point. Measurement is rejected if $Q$ is larger than $5 \times 10^{-3}$; the error on the angle value is then estimated as $\delta = \arcsin Q$. Standard deviations of the errors are less than 0.1°. The three Plateau angles are then deduced by a straightforward calculation from independent measurements. Furthermore, we check that the sum is equal to 360°. Valuable measurements are extremely difficult to obtain especially when the radius of curvature of the circular arc is large; besides, the photographs must be very sharp.

## 3. Results

Three typical foams have been studied:

solution (I): foam with polydisperse bubbles (foam A)

solution (II): { foam with equal sized bubbles (foam B)
foam with polydisperse bubbles (foam C).

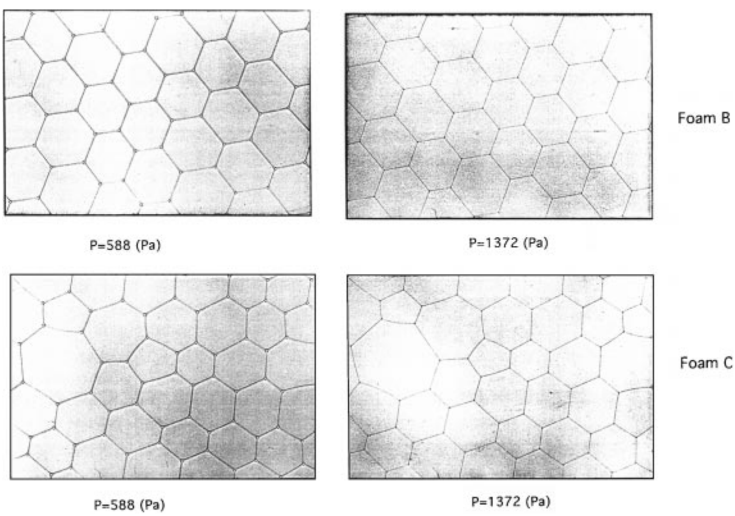


**Fig. 5.** Typical photographs of wet and dry foams.

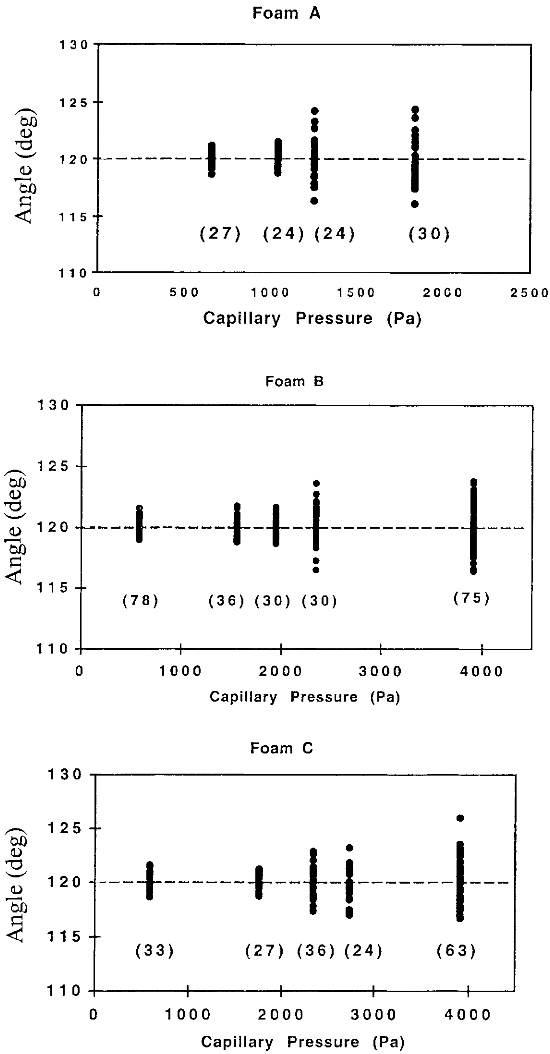


**Fig. 6.** Angles histograms.

As the applied capillary pressure $P$ is changed from about 600 Pa to 4000 Pa, the film thicknesses change because of capillary drainage and the foam films evolve from thick to thin (Fig. 5). All the measured angles are plotted versus $P$ in Figure 6. The number $N$ of data are reported in the figure. The mean angle value is $\alpha_m = 120 \pm 10^{-3}\,^{\circ}$ and the standard deviation of the angles, $\Sigma$, ranging from 0.6° to 1.88°. The higher standard deviations are one order of magnitude larger than the experimental error 0.1°. The measurements are therefore significant. We have also plotted the normalized standard deviation $\Sigma/\alpha_m$ vs $P$ in Figure 7. There is a critical value of the externally applied capillary pressure $P^*$ for which $\Sigma/\alpha_m$ abruptly changes from 0.5% to 1.5%. $P^* \approx 1150$ Pa for solution I and 2200 Pa for solution II.

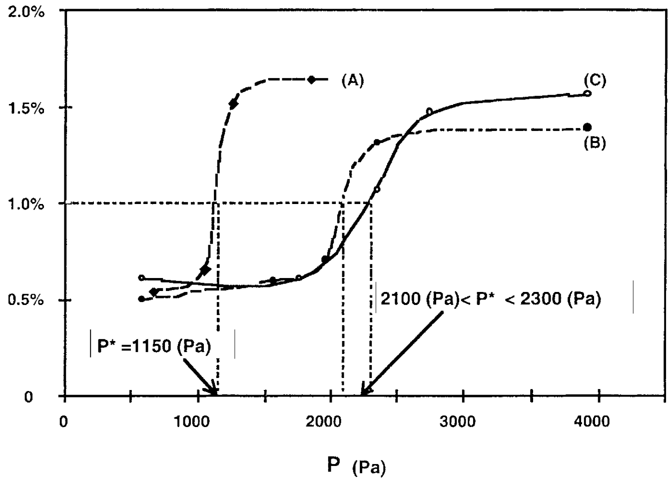


**Fig. 7.** Normalized standard deviation $\Sigma/\alpha$ vs capillary pressure *P*. (Lines are guides for eyes).

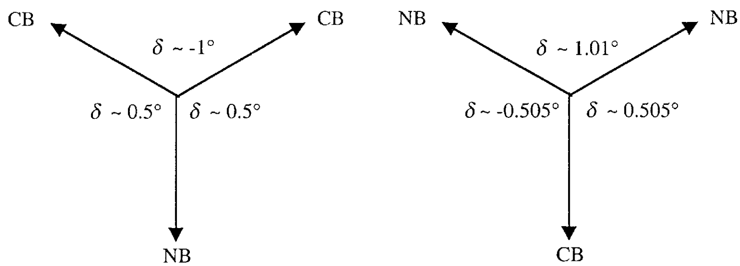


**Fig. 8.** Theoretical Plateau angles.

## 4. Discussion

The present experimental results confirm our earlier theoretical predictions [1] about the influence of surface forces on the foam microgeometry. Equation (7) shows that $\delta_i \equiv 0$ for junctions made of three thin films or three thick films. At the present working capillary pressures larger than the pressure transition TF $\rightarrow$ CBF, all the films in the foam can be common black. Deviations from 120° are expected for non-symetrical junctions made of two thick + one thin films or of one thick + two thin films (Fig. 8). When the pressure is reduced in the Plateau borders, NBF can nucleate at random in the foam. However, it takes a significant time to reach equilibrium, and non-symetrical junctions are expected to occur.

To analyze this point, we have calculated the expected deviation from the film tensions given in Table 1. The values are reported in Figure 8. We have also calculated the angle distribution function defined as

$$f_{\exp}(x) = \frac{1}{2} + \frac{1}{2} erf\left(\frac{x}{\sqrt{2}}\right) \quad \text{where} \quad x = \frac{\alpha - \alpha_m}{\Sigma}$$

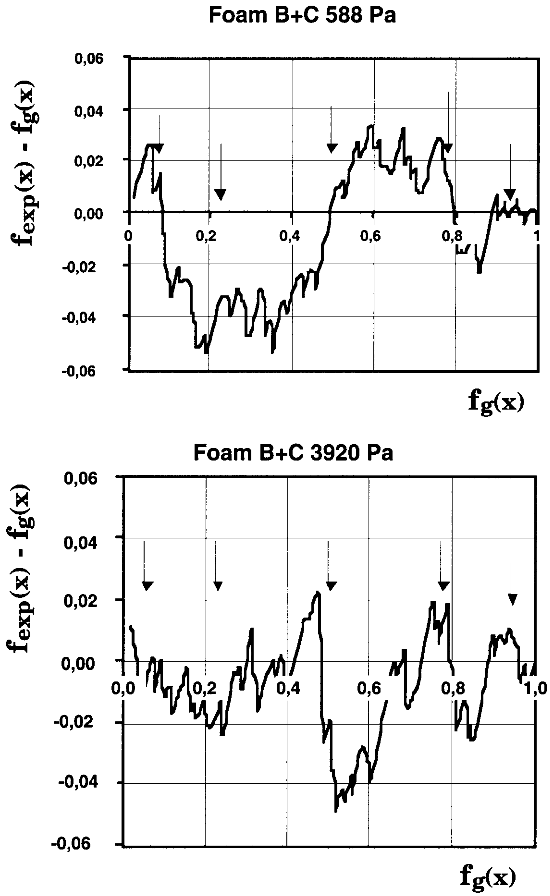


**Fig. 9.** Comparison between the experimental and the Gaussian distribution function.

and we have compared it to a Gaussian distribution $f_g(x)$ in Figure 9. The positive parts are the more significant since they are the one with many events. No peak would be observed with a Gaussian distribution. One observes peaks which are significantly separated remembering that the measuring error is very low. We have denoted by a straw the points corresponding to the theoretically expected angles. Comparison is quite good.

Our results are obtained for 2D foams and the equivalent measurements in 3D foams are presently out of our expertise. However, such effects are likely to occur in 3D since the basic physics is independent of boundary conditions. In the gravity field, a liquid foam column is usually drained and the film thicknesses are changing from the top to the bottom. It can also be exposed to a gradient of capillary pressure if the foam is created in a device similar to the present one. In both cases, it may exist a critical height beyond which the films are so thin that the disjoining pressure effect has to be taken into account and, therefore the assumption of the film tensions constancy is no longer true throughout the foam column.

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G. B. Han
Xiamen University
Xiamen
Republic of China

A. Dussaud
Unilever Research US
45 River Road
Edgewater, N.J. 07020
U.S.A.

A. V. Neimark
TRI/Princeton
601 Prospect Avenue
Princeton, N.J. 08542
U.S.A.

B. Prunet-Foch
M. Vignes-Adler[1)]
Laboratoire de Physique de
Matériaux Divisés et des Interfaces
Université de Marne-la-Vallée
Bâtiment Lavoisier, Cité Descartes
77454 Marne-la-Vallée, Cedex
France

[1)] Author to whom correspondence should be addressed.