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Profile of the Plateau Border in a Vertical Free Liquid Film

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Profiles of the Plateau border at a vertical film in a 0.02 *M* cetyltrimethylammonium bromide solution are measured by optical interference, in the part of the border near the film, at two heights above the bulk liquid surface. The Laplace pressure in the border, calculated from these profiles, appears to be lower than the hydrostatic equilibrium pressure at a height close to the bulk liquid meniscus (6.2 mm); at a greater altitude (11.3 mm) the pressures are equal. An upward flow in the border close to the film is observed, while a downward flow takes place in the periphery of the border. Both effects can be explained by Marangoni flows. © 1990 Academic Press, Inc.

INTRODUCTION

In the course of an investigation on the stability of foams in suspensions we came across the problem that for mobile films the first stages of foam history, viz, drainage, are not completely understood, in spite of the fundamental work by Mysels and collaborators on this subject (1). These authors found that in a film drawn vertically in a foam, drainage to the Plateau border predominates over the vertical drainage directly to the bulk liquid. They started from the following assumptions:

(i) In the Plateau border, the pressure is equal to, or slightly larger than, the hydrostatic equilibrium pressure at the height concerned.

(ii) If a film is drawn from a border, the surface tension in the film must surpass that in the border.

On the basis of these assumptions, Mysels *et al.* (1) predicted a dip in film thickness just before the junction with the border. This, however, was not found experimentally in mobile films. In addition, a limit was derived for the thickness of the film which can be drawn out of a border with energy supplied by the falling in of film of a given thickness,

but this prediction was contradicted by experiments.

Later studies of film thinning concentrated in most cases on contact angles at the transition film/Plateau border (2–17) and on the influence of surface waves on film drainage (18–23). Thus, the paradoxes mentioned in the previous paragraph remained, to the knowledge of the present authors, unsolved. This lack of understanding of mobile film behavior is to be regretted, since many foams formed either intentionally or unintentionally consist of mobile films.

We therefore thought it profitable to learn more about pressure and flows in Plateau borders, by extending the optical interference method developed by Scheludko *et al.* (2–5) and Haydon *et al.* (9,10) for measuring contact angles in horizontal films, to vertical films, and to larger distances from the film into the Plateau border.

EXPERIMENTAL

Materials

CTAB (cetyltrimethylammonium bromide, Sigma Chemical Co.). The surface tension vs concentration graph had a distinct break near the cmc ($=9 \cdot 10^{-4}$ *M* (24)) and was without

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a minimum; no further purification was applied. All experiments refer to 0.02 *M* CTAB solutions at 25°C. In this solution, the surface tension measured by the Wilhelmy plate method at 25°C, was 37 mN/m. In this concentration range, there is only a slight concentration dependence. A 0.25 *M* solution at 25°C (supersaturated) had a surface tension of 33 mN/m.

Glass (Louwers Glass, Hapert, The Netherlands). The glass consisted of spherical particles with diameters < 10 μm . The sample was divided into fractions with narrower size distributions by sedimentation in deionized water. Particle size distributions were measured with a Coulter counter; standard deviations amounted from 0.2 μm for the fraction with the smallest particles (< 1 μm) to 2.7 μm for the fraction with the largest particles (> 5 μm). Before fractionation by sedimentation the density of the glass particles was determined with a Quantachrome stereopyknometer to be 2.47 g/cm³.

Water. The water employed in the Plateau border experiments was twice distilled.

Apparatus

A film was drawn in a vertical glass frame, which was held at a fixed position. The frame consisted of a 2-mm-thick, 10 × 21-mm glass plate with a rectangular, 4 × 10-mm cutout at one of the short ends; the two legs thus formed had rectangular cross sections. The observation point was fixed at 1.2 mm below the upper edge of the cutout; its height above the bulk liquid could be varied by changing the sample amount in the glass vessel below the frame.

This height was determined by measuring the conductance of the liquid between two platinum wire ends connected parallel to and 4 mm in front of the frame legs (Fig. 1), which hung in the liquid. Care was taken not to create a film between the two wires or between a wire and a frame leg. The conductance of a 0.02 *M* CTAB solution varied linearly with the depth in the liquid of the two wires, and thus

FIG. 1. Schematic representation of the two wire ends, via an insulator block attached to the glass frame, used for obtaining the depth in the liquid through resistance measurements.

with the measuring height, by an amount of 42.94 $\mu\text{mho/mm}$.

For the calibration line the height of the bulk liquid meniscus with respect to the observation height was changed manually and measured with a kathetometer. Because the bulk liquid surface in the small glass vessel (inner diameter, 16.5 mm) containing the surfactant solution was disturbed by the frame legs and the wire ends, we measured the height of the bulk liquid in a larger, external beaker connected with the sample vessel by a very thin, sample-filled hose.

Before an experiment the frame was surrounded by the sample vessel. The frame and the glass vessel were contained in a double-walled stainless steel vessel of 30-mm inner diameter. Samples were left in this closed sample chamber at 25°C for several hours before the experiments. A film was drawn by lowering the vessel pneumatically in less than 1 s at the start of an experiment.

The films were observed through a Leitz Metalloplan microscope placed on its backside in order to permit direct observation of a vertical film without the intervention of mirrors. A 10-mm-working-distance, 20× objective with a numerical aperture of 0.4 was inserted

in the sample chamber and together with a $12.5\times$ ocular resulted in a $250\times$ magnification.

A 50-W super pressure mercury lamp (Osram HBO 50-W) was used as the light source; the principal wavelengths of the light (*in vacuo*) were 440 and 554 nm. The microscope images of the transition region between film and Plateau border were photographed at predetermined times by a Minolta X-700 camera equipped with an autowinder and a multi-function back. We used Agfacolor 1000 ASA films. These photographs were converted into half film thickness vs distance graphs, with Fizeau's formulas for plane parallel films (correction of curvature not necessary; see Appendix); distances were measured between the blue or, with the use of a 546-nm interference filter, the black lines. In both cases these are subsequent interference orders of the 554-nm wavelength's minima.

The interference order p was determined by a comparison of the photographs of one series starting from the last one, in which the Plateau border adjoins the black film: the first blue or black line is of order $p = 1$, the second of order $p = 2$, etc. For these lines the local Plateau border thickness δ_f is then calculated from the wavelength $\lambda = 554$ nm in air and the index of refraction $n = 1.3342$ (25) according to Fizeau's equation for interference minima (26, 27),

$$\delta_f = \frac{p\lambda}{2n}. \quad [1]$$

The calibration scale for the horizontal distance was determined with an object micrometer. The origin of this distance was taken arbitrarily, but remained fixed during a series of experiments with one film.

For experiments with glass particles a magnetic stirrer was used to keep these particles in suspension; during an experiment stirring was ceased in order to minimize vibrations. Movements of the glass particles in the Plateau border were recorded with a Sony video camera and recorder.

The contact angle of the sample solution at the glass frame Θ_g was measured by photo-

graphing a droplet of the surfactant solution on the glass surface in a closed chamber and manually fitting a circle section to the droplet surface on the photograph near its base. To match the conditions during an experiment, the hydrophobic monolayer of CTAB on the glass was not removed, and the receding contact angle was determined by sucking away part of the liquid in the droplet after its deposition on the glass plate.

Surface tension measurements were performed with a Krüss Digital Tensiometer K10T, using a Wilhelmy plate.

RESULTS

A typical series of experimental data is shown in Fig 2. In this graph, the film is at the left side, and one frame leg is off the right side at a distance of about $460\text{ }\mu\text{m}$. In this figure, the Plateau border profiles at times $t = 169$ and 192 s start from a black film, while the thickness at the utmost left points of the curves at $t = 31, 49$, and 109 s is calculated for $p = 1$ and at $t = 7$ s for $p = 4$ [1], as determined from the photographs. The experiments are restricted to the part of the Plateau border near the film, since the optical arrangement did not permit the reception of light rays reflected in the region of the Plateau border near the frame

FIG. 2. Profiles of the film-near region of the vertical Plateau border in a vertical free liquid film, drawn out of a 0.02 M CTAB solution as a function of time t after film formation (horizontal cross section). The x -axis, in the direction away from the film, is the symmetry axis of the profiles; y -axis perpendicular to the film, $y = 0$ in the mid of the film, origin otherwise arbitrary.

(see Appendix). Here typical marginal regeneration phenomena analogous to those reported by Mysels *et al.* (1, 28) are observed. The turbulences gradually decrease in time and marginal regeneration is practically finished when a black film is formed.

The obvious feature of Fig. 2 is the contraction of the Plateau border toward the leg of the frame (or, put differently, the ability of the film to expand) with increasing time. No dip in film thickness, at the transition to the border is seen, in agreement with the observations of Mysels *et al.* (1).

We have developed two methods for analyzing the data for surface curvature at the moment each set of data was obtained; the first one permits the detection of changes in the radius of curvature of the Plateau border in a horizontal section, but requires smoothing of the data. The second one starts from the assumption of a constant radius of curvature in a horizontal section in that part of the border in which measurements are possible, but no smoothing of data is required.

First Method of Calculating the Radius of Curvature of a Horizontal Section through the Border

If we want to check whether the radius of curvature changes along the measured profile of the transition region between the film and the Plateau border, we must be able to calculate these radii at any arbitrary point P on the curve. For this, the relation for the radius of curvature

$$r_P = \frac{-\left[1 + \left(\frac{dy_b}{dx}\right)^2\right]^{3/2}}{\frac{d^2y_b}{dx^2}} \quad [2]$$

is applied to the experimental data. The first and second derivatives have to be obtained from the experimental data.

Taking first and second derivatives of adjoining points causes large instabilities even when the scattering of the measured points is small. Therefore, a smoothed curve through

these points is calculated by performing a polynomial fit of maximum power 2 in each point using all points. Deviations of the measured points from the curve were within the measuring error. On this fitted curve 105 points at the most are taken for calculating the radii of curvature.

Through linear interpolation a limited number of equidistant points are obtained for calculating the first and second derivatives using Lagrange's five-point interpolation formulas (29). The radii of curvature are calculated for different numbers of interpolated points.

As a test for this calculation we calculated the radius of curvature for (i) points of a geometrical circle of radius $500\ \mu\text{m}$, and (ii) the curve derived from the interference pattern calculated for such a circle by the method described in the Appendix, in which the influence of the border curvature is taken into account. The results are shown in Fig. 3. Except for the first and last points of the curve, where numeric instability still causes large deviations, the radii of curvature for both curves are fairly constant. The profile-derived sub (i) has a slightly smaller radius ($488.0 \pm 2.3\ \mu\text{m}$) than the profile from the geometrical circle ($500.3 \pm 2.2\ \mu\text{m}$). This can be seen in Fig. 3, because one profile has a slightly larger radius than the

FIG. 3. Radii of curvature, calculated according to the first method (■), for a circular profile (●) and radii of curvature (□) for a profile calculated according to the computed interference pattern for this circular profile (○). Five to ten interpolated values for double numeric differentiation. Also drawn are the two profiles of Fig. 11, together with the smoothed curve of the proper circle (—). See Appendix.

other. These radii, as well as those for the experimental data, are calculated as the mean of the radii for 5 to 15 interpolated points, omitting extreme values on the edges, which results in about 100 of 110 values. The fact that the radius of the derived curve deviates $12.3\ \mu\text{m}$ or 2.5% from the circle radius is somewhat surprising, since the deviation in the x -values of the profiles amounts to only about 1%.

This indicates that small deviations in the x -values have a large effect on the radius of curvature. Furthermore, both radius curves show a slight ascending tendency, which is ascribed to the method of calculation. We conclude that for curves smoothed by the described procedure this method works reasonably well.

A typical example is shown in Fig. 4 for experimental data. The smoothed curve follows the measured points quite well. The radii of curvature calculated from these smoothed curves are always constant with a standard deviation of $2.5\ \mu\text{m}$ at the most. The radius increases slightly with the distance from the film, as already described for the circle; this is taken into account in the standard deviation.

In Fig. 5 the results of all the calculations according to the first method are plotted as a function of time from film formation for three experiments, two at a height of $6.2 \pm 0.1\ \text{mm}$ and one at a height of $11.3 \pm 0.1\ \text{mm}$ above the meniscus. In the case of the 11.3-mm altitude, the frame legs, having a length of 10

FIG. 4. Measured (●) and smoothed (◻) Plateau border profile and calculated local radii of curvature (◻). Measuring height, 6.2 mm; 192 s after film formation; 5 to 10 interpolated values for double numeric differentiation. See first method under Results.

FIG. 5. Calculated radii of curvature vs time after film formation for two measuring heights (●, ▴, 6.2 mm; ○, 11.3 mm). Also drawn are the (time independent) radii of curvature for these heights, when the Laplace pressure equals the hydrostatic equilibrium pressure according to [3].

mm, are completely above the bulk liquid surface, but connected with it by a 1.3-mm-high meniscus. This is clearly less than the maximum meniscus height, which for this aqueous solution with surface tension $\gamma = 37\ \text{mN/m}$ and glass contact angle $\theta = 10^\circ$ (see below) amounts to 3.87 mm (30, 31), i.e., when the large glass plate is horizontal and above the level of liquid. It is also less than the meniscus height for this solution against a vertical glass plate, which amounts to 2.50 mm (1, 30, 31).

Also shown are two dashed lines representing the radii at the heights concerned according to hydrostatic equilibrium, when the Laplace pressure equals the hydrostatic pressure,

$$\Delta\rho g z = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \approx \frac{\gamma}{r}, \quad [3]$$

where $\Delta\rho$ is the difference in density between the solution and the surrounding air, g is the gravity acceleration, z is the height of the observation point above the bulk liquid meniscus, γ is the surface tension of the bulk solution (37 mN/m), and R_1 and R_2 are the principal radii of curvature (see Discussion, part b); if one of the radii becomes infinite, then the other radius approaches r , the Plateau border radius at hydrostatic equilibrium. We see that the experimental radii do not show a distinct trend with time; except for two points at the height of 6.2 mm, the values cluster

around a level. For the height of 6.2 mm this level amounts to $434 \pm 11 \mu\text{m}$, for the 11.3-mm height the values oscillate around an average value of $297 \pm 12 \mu\text{m}$, being less well-defined than the former level.

Except for one value 6.2-mm height at short time, all experimental radii are smaller than the radius for hydrostatic equilibrium at this height. For the high observation point range of 11.3 mm the calculated hydrostatic radius equals the level of the experimental points.

Second Method of Analyzing Horizontal Section Data for Surface Curvature

This is based on the result of the first method, that the surface curvature is constant over the interval measured. Compared with the first method, it has the advantage that smoothing of experimental data, which might introduce systematic errors, is avoided. It is based on the assumption that at a certain height above the bulk liquid meniscus, pressure and surface tension are constant (but not necessarily equal to the hydrostatic equilibrium pressure at that height and the surface tension of the bulk solution, respectively).

In addition it is assumed that the surface curvature agrees with the Laplace equation,

$$\frac{1}{r} = \frac{\Delta p_L}{\gamma}, \quad [4]$$

with Δp_L as the pressure difference according to the Laplace equation and again,

$$\frac{1}{R_1} + \frac{1}{R_2} \approx \frac{1}{r}. \quad [5]$$

This equation implies that only one of the radii of curvature of the surface of the Plateau border is important for determining the pressure.

Deviations from the Laplace equation are improbable, because they imply a disturbance of force equilibrium, which would result in accelerated motion of the surfaces concerned to be expected, especially because of the pronounced mobility of the surface.

The surface curvature at the observation

heights concerned is found from the experimental data as follows:

We calculate a $y_b(x)$ -curve (with x = distance in horizontal direction away from the film into the border; y_b = half-thickness of the Plateau border) starting from the experimental point lying farthest away from the film, (i.e., most border-inward). We assume a slope dy_b/dx at that point and a value for the surface curvature $1/r$ and calculate $y_b(x)$ numerically by a large number of step calculations:

$$\left(\frac{d^2 y_b}{dx^2} \right)_{k+1} = \frac{\left[1 + \left(\frac{dy_b}{dx} \right)^2 \right]^{3/2}}{r} \quad [6]$$

$$\left(\frac{dy_b}{dx} \right)_{k+1} = \left(\frac{dy_b}{dx} \right)_k + \left(\frac{d^2 y_b}{dx^2} \right)_{k+1} dx \quad [7]$$

$$(y_b)_{k+1} = (y_b)_k + \left(\frac{dy_b}{dx} \right)_{k+1} dx. \quad [8]$$

Equation [6] is derived from Eq. [2].

In the calculations, a step value $dx = 0.03 \mu\text{m}$ was taken, much smaller than the distance between experimental points. The initial slope $(dy_b/dx)_{k=1}$ and the curvature $1/r$ were then fitted by a least-squares method. Alternatively, only the initial slope was fitted while the curvature was assumed to be consistent with the hydrostatic equilibrium pressure and the surface tension of the bulk solution.

Figure 6 compares the deviations from experimental values for a curve calculated with both surface curvature and initial slope fitted, with those for a curve calculated with only initial slope fitted. It is seen not only that the deviations in the latter case are larger than those in the former (which is to be expected, since there is only one parameter fitted in the latter case), but also that there are systematic deviations of the curve calculated with only the slope fitted from the experimental data; the calculated values are in this case systematically too low near the film and too high at the other end of the border.

The deviations are consistent with a radius of curvature that is smaller for the experi-

FIG. 6. Deviations from experimental values $\Delta[\text{Thickness}]$ for a curve, calculated with both surface curvature and initial slope fitted (●) and with only initial slope fitted (○). Measuring height, 6.2 mm; 192 s after film formation. See second method under Results.

mental points than for the values calculated on the basis of $p = p_{\text{hydrostatic equilibrium}}$ and $\gamma = \gamma_{\text{bulk solution}}$. The radii of curvature as calculated according to this second method, where both slope and curvature are fitted, are roughly the same as those resulting from the first method, as expected.

Flow Visualization

Flow visualization in the border was effected by the addition of glass particles. Two distinct regions could be clearly discerned: in the region near the film, an upward flow was observed, while near the frame, a downward flow was seen. In between, the glass particles showed little movement, in most cases circulating movements (downward when closer to the frame, upward when closer to the film).

DISCUSSION

According to Fig. 5 the radius of curvature of the vertical Plateau border close to the bulk liquid meniscus is smaller than the radius calculated on the basis of hydrostatic equilibrium, while this discrepancy vanishes at greater heights. This means that at the lower height investigated the local underpressure in relation with the outside pressure is larger than one would expect from the hydrostatic equilibrium pressure. Since this is quite unexpected (1), we must check whether this result is really a

physical phenomenon. For this, three questions need to be answered carefully:

(a) Is the radius of curvature constant at a certain height? The experiments show that the radius of curvature of the Plateau border close to the transition region between the film and the border varies only slightly over the first $30 \pm 10 \mu\text{m}$ in a horizontal direction. The total distance film/glass frame, i.e., the breadth of the Plateau border, at the heights concerned was taken from separate photographs of the glass frame with the film as a whole. The Plateau border was found to be $460 \pm 25 \mu\text{m}$ in width at the height of 6.2 mm above the bulk meniscus and about $300 \mu\text{m}$ at 11.3 mm. This means we have established that the radius is constant over 6, 10% of the Plateau border width.

The contact angle with the glass Θ_g was separately measured to be 10° . If we assume a constant radius of curvature in the horizontal plane, then with the aid of this contact angle Θ_g and the experimental radii of curvature in the transition region r the width of the Plateau border x_b is calculated according to

$$x_b = r \cos \Theta_g. \quad [9]$$

As a result we found $x_b = 427 \pm 11 \mu\text{m}$ for the height of 6.2 mm and $x_b = 292 \pm 12 \mu\text{m}$ for the 11.3-mm altitude. These values appear to be lower than the directly measured widths mentioned above, but the differences are within the standard deviations. We conclude that the radius of curvature may slightly increase in the direction toward the frame; however, this increase should be small.

(b) Is the radius of curvature in the vertical direction large enough to allow us to neglect its reciprocal value? Until now we have neglected other than horizontal curvatures. The macroscopic photographs, however, show that in a film in a glass frame as small as that used in our experiments vertical curvatures may be significant; e.g., the actual thin film in the rectangular frame is not really rectangular, but its periphery shows an appreciable curvature because of a meniscus between the two frame

legs and a decreasing Plateau border width in the upward direction, as illustrated in Fig. 7. The meniscus between the legs, i.e., the transition between the film and the bottom Plateau border (H in Fig. 7), is pulled up about 2.5 mm by the film, compared with the situation in the absence of the film (K in Fig. 7). This fluid bridge shows strong vertical curvatures not only in a plane parallel to the film, but also in a plane perpendicular to it.

Let us consider a pending drop or a bowl with a vertically oriented axis of rotation. Twice the mean surface curvature J at a certain point $P(r_P, z_P)$ on the outer and inner surfaces of these objects is defined as (31)

$$J = \frac{1}{R_1} + \frac{1}{R_2}, \quad [10]$$

where R_1 is the meridional (pertaining to the plane through the axis of an object with rotational symmetry and a point P on its surface) radius of curvature and R_2 is the azimuthal (pertaining to the plane through P normal to the surface and to the meridian) radius of curvature; the circles with these radii osculating

to the surface at P lie in these planes. Therefore, R_1 can be derived from the equation describing the meridional circle by double differentiation,

$$R_1 = \frac{\left[1 + \left(\frac{dz}{dr}\right)^2\right]^{3/2}}{\frac{d^2z}{dr^2}}, \quad [11]$$

and R_2 , being the distance between P and the rotation axis perpendicular to the tangent plane, can be calculated by

$$R_2 = \frac{r_P \left[1 + \left(\frac{dz}{dr}\right)^2\right]^{1/2}}{\frac{dr}{dz}}. \quad [12]$$

In these equations the z -axis is the rotation axis and the r -axis runs horizontally, perpendicular to the z -axis; r_P is the horizontal distance from P to the z -axis.

Application of these equations to our Plateau border is restricted to the first quadrant of the ground plane ($=xy$ -plane; $r^2 = x^2 + y^2$) and is justified only if a vertical rotation axis is present. However, the measured horizontal radius of curvature decreases with increasing height z , while dz/dr remains positive. This means that the center of the circles describing the border gradually moves toward the border while ascending along the z -axis, which destroys the symmetry. If, however, we consider only small increases in height (dz), we may regard the border as rotation symmetrical and we may apply the above equations to height fractions dz . In this way the Plateau border surface can be regarded as being built up by cylinder segments in the first quadrant of height dz , each one with its axis shifted along the bisector of the x - and the y -axis toward the border in such a way that it leans slightly over its lower neighbor (Fig. 8).

The question is whether the meridional curvature of the Plateau border $1/R_1$ is sufficiently strong at greater heights above the bulk liquid meniscus for J to differ considerably

FIG. 7. Macroscopic drawing of the glass frame with the liquid film suspended in it. Because of the curved Plateau borders, the film deviates substantially from a rectangle. P.B., Plateau border; L, bulk liquid meniscus. See the text for the remaining symbols.

FIG. 8. Schematic representation of the Plateau border, built up of cylinder segments with radius r_p and height dz .

from the azimuthal curvature $1/R_2$. The macroscopic photographs tell us that the strongest curvature of the periphery appears just above the meniscus, although this is not one of the principal radii of curvature: the radius of this curvature is in the order of 1 mm (H in Fig. 7), while at larger altitudes the radius increases very rapidly. At the heights concerned the meridional curvature is negligible and J approaches the azimuthal curvature $1/R_2$, which in turn approaches the measured horizontal curvature $1/r_p$ for dz/dr approaching infinity.

(c) Does the surface tension in the Plateau border differ from the bulk liquid value? Another possibility is that the deviation of the experimental radii of curvature from the theoretical ones at hydrostatic equilibrium at the height of 6.2 mm is caused by a strong decrease in surface tension, which, e.g., might be effected by evaporation. This is highly improbable for three reasons:

(i) The solution was left in the metal vessel long enough to saturate the environment.

(ii) The bulk liquid's surface tension in a 0.02 M CTAB solution was measured to be 37 mN/m, while for a supersaturated solution of 0.25 M CTAB, the surface tension did not reach a value lower than 33 mN/m. This decrease is not sharp enough, since for the experimental radii to agree with the hydrostatic equilibrium, the surface tension should be 26.4 mN/m [3].

(iii) This mechanism does not explain why the difference between the radius observed ex-

perimentally and that agreeing with the hydrostatic equilibrium value vanishes at a greater height.

On the other hand, both the anomalous radius of curvature of the border at low heights and the complex flow patterns can be explained by a systematic variation of surface tension in the border in the direction

$$\gamma < \gamma_A < \gamma_B < \gamma_C = \gamma_D = \gamma_E = \gamma_F \quad [13]$$

(for the meaning of the letters A, B, C, etc., see Fig. 7).

Proposed Mechanism for Flows and Radii of Curvature Observed in the Border

The simultaneity of the gradual vanishing of the flows in the border and the marginal regeneration suggests a connection between both phenomena:

In the film there exists a surface tension gradient in the vertical direction, because the weight of liquid in the film up to a certain level B must be supported by the surface tension along BG (Fig. 7) (32).

During film drainage there is an exchange of film volume elements with accompanying surfaces against Plateau border volume elements, in the process of marginal regeneration (1). A film volume element, after being exchanged with a border volume element, occupies a position with a slightly larger thickness compared with its original film thickness, and consequently its surface in the border is smaller than in its original position. Part of the surface of the original film volume element migrates to the bulk, when it arrives at the border. This causes a local surfactant concentration that is higher than that of the surrounding border bulk, while the surface tension at that instant is not changed compared with the film surface tension. Diffusion of surfactant molecules to the surface will lower this surface tension, until complete equilibrium has been established. In addition, the surfactant concentration at the surface may change because of expansion or contraction of the surface during the film/border element ex-

change. In view of the incompressibility of the liquid, this also involves transport of water from the surface to the bulk. However, if molecular transport is assumed to be slow compared with the marginal regeneration exchange, then the new border element is expected to retain its original surface tension (i.e., that of the film at the height concerned) and thus to have a larger surface tension than the surrounding border.

Thus, marginal regeneration leads to a surface tension gradient $\gamma_A < \gamma_B < \gamma_C$ along the film/border transition region, if equal amounts of surface exchange take place at all heights. However, drainage is less pronounced for thinner films than for thicker ones (1, 33). This effect reduces the surface tension gradient expected; it is assumed here that the latter is not quite suppressed.

This surface tension gradient causes a Marangoni flow. Initially, surface tension differences may be leveled off by a horizontal flow (e.g., at level B in Fig. 7, by a flow from E to B). However, this will lead to a slightly increased surface tension at this level (compared with the surface tension of the bulk solution), because at E there is only a finite amount of liquid available for surface renewal.

At A, however, bulk liquid can be sucked up, and the amount of liquid available for surface renewal is much larger. This increases the driving force for a flow from A to C, viz, the surface tension difference between A and C, and makes the upward flow from A to C self-reinforcing. This self-reinforcement lets the flow along the border/film transition establish itself rather than flow in a horizontal direction. A similar self-reinforcement is assumed in the establishment of Marangoni instabilities due to temperature gradients (34).

The Marangoni flow becomes stationary when it is counteracted sufficiently by a pressure gradient and a viscous drag. The latter is not very pronounced (see below), and the pressure gradient that corresponds to the Plateau border at C is too bulky, and at A is too thin (as observed experimentally). The excess liquid at C is leveled off horizontally to D and

removed downward along E and F to the bulk liquid. This flow is then no longer a Marangoni flow. Thus, the experimentally observed flow pattern can be accounted for.

Liquid moving from C through D to E and F entrains a surface with a relatively large surface tension. This explains the absence of horizontal flow, e.g., from E to B, once the vertical upward flow from A to C has been established. The excess pressure at E (compared with the hydrostatic equilibrium pressure), which is shown by the downward flow there, cannot level off the overly low pressure at B, which is evidenced by the radius of curvature, because a flow from E to B would be anti-Marangoni.

Thus, at F a surface tension difference with the bulk liquid is generated which counteracts (but does not completely suppress) the transport of liquid from the border to the bulk liquid. This is evidenced by the gradual thinning of the border (Fig. 2).

The horizontal surface tension differences, between, e.g., E and B, should only be small in view of the observed constancy of the radius of curvature both in the direct observation range (Fig. 4) and calculated from the contact angle and the total breadth of the Plateau border.

At first, this process might seem unlikely, because of a large hydrodynamic resistance expected for the flow bulk $\rightarrow$ A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ D $\rightarrow$ E $\rightarrow$ F $\rightarrow$ bulk, especially since the thinness of the border would make pronounced contributions to the hydrodynamic resistance, which are connected with velocity differences in the direction perpendicular to the midfilm plane. However, both the front and the back surfaces of the border are expected to have the same velocity. Consequently, there is no large velocity gradient in the direction concerned. All hydrodynamic resistance experienced by this flow is then connected with the border/film transition, the upward/downward flow transition, and the border/glass frame boundary. Nevertheless, the hydrodynamic resistance of the observed flows is expected to be larger than that experienced by horizontal flows such as E $\rightarrow$ B. The reason for the es-

establishment of the experimentally observed flows (in preference to the horizontal flows) therefore should be found in the larger driving force of the bulk $\rightarrow A \rightarrow B \rightarrow C \rightarrow D \rightarrow E \rightarrow F \rightarrow$ bulk flows rather than in their low resistance. This larger driving force is generated by their self-reinforcing character.

This mechanism is a tentative one, since the most important hypothesis on which it is based, viz, the surface tension differences in the Plateau border, cannot be checked independently. However, it can account for the experimental data.

CONCLUSIONS

In a foam film drawn from a surfactant solution by means of a glass frame with square legs, there exists a pressure lower than that in the hydrostatic equilibrium, shortly above the bulk meniscus. At greater heights (≈ 10 mm) above the meniscus, the hydrostatic equilibrium pressure is observed.

The phenomena may be explained by a Marangoni flow caused by surface tension gradients in the border induced by surface tension differences in the film.

SUMMARY

The measured deviation of the local pressure in the vertical Plateau border from the hydrostatic equilibrium pressure near the film base, which vanishes at higher altitudes, indicates an extra suction in the lower part of the border. Flows in opposite directions in the border are observed: an upward flow near the transition region with the film, and a downward flow at some distance from the film. Both effects are explained by flows due to surface tension gradients.

APPENDIX

INTERFERENCE PATTERN OF LIGHT REFLECTED FROM FRONT AND BACK SURFACES OF A PLATEAU BORDER VIEWED IN A MICROSCOPE

Consider the microscope to be focused in the front surface of the film (to be distinguished from the front surface of the Plateau

FIG. 9. (a) Example of two rays reflected and refracted by a circular Plateau border, whereby the rays leaving the condensed phase coincide. (b) Detail of Fig. 9a showing the construction of points A and J on the focussing plane.

border, see Fig. 9a). The image seen in the microscope then corresponds to a real object as far as the film is concerned; in the Plateau border the object is a virtual one. Thus, in the image of a point like A (Fig. 9b) a number of rays such as GFEDC (reflected at the back surface of the border) and HDC (reflected at the front surface) are combined, which do not really pass through A.

For brevity, rays reflected at the front surface are indicated as "primary" rays, and rays

reflected at the back surface are called "secondary" rays. A minimum light intensity will be observed apparently coming from a point A in the focusing plane, when the majority of rays like HD and GFED interfere destructively at D.

The fact that interference is observed implies that primary and secondary rays, having the same phase, when being generated at the light source, are within one coherence length, when interfering at D. This in turn implies that they have the same phase when arriving at the focusing plane, when the border is absent; differences in the geometrical path length between the light source and the focusing plane are partially compensated by differences in the lengths of paths through various media (air, different types of glass) so as to make the optical paths lengths, in terms of wavelengths, equal.

The phase difference between a primary and a secondary ray, interfering at a point like D (Fig. 9a), can then be calculated for a cylindrical Plateau border with radius r as follows:

(i) Consider a secondary ray (DC), leaving the border while making an angle τ_2 with the normal to the focusing plane. It makes an angle $\tau = \tau_2 - \alpha_3$ with the normal to the front surface of the border at D (where $\alpha_3 = \arctg(dy_3/dx)$; $y_3 = r - \sqrt{(r^2 - x^2)}$ in the coordinate system described in Fig. 9a).

This secondary ray has traversed the Plateau border, after having been reflected at the back surface, along line ED. Line ED makes an angle $\beta_2 = \arcsin(\sin \tau/n)$ with the normal to the front surface, and an angle $u_2 = \beta_2 + \alpha_3$ with the normal to the focusing plane.

Thus, once point A and angle τ_2 are chosen, line AC is fixed and the coordinates of its intersection point D with the Plateau front surface can be calculated. With the angles mentioned in the preceding paragraph, line DE is known, and the coordinates of its intersection point E with the Plateau back surface ($y_2 = -r - \delta_f + \sqrt{(r^2 - x^2)}$) can be calculated, as can the angle which line DE makes with the normal to the Plateau back surface

($u_2 - \alpha_2$, with $\alpha_2 = \arctan(dy_2/dx)$ at E, $\alpha_2 < 0$).

Then the angle which the secondary ray makes, before reflection at the back surface, with the normal to the back surface at E is $u_1 = -u_2 + \alpha_2$. Thus, the angle which FE makes with the normal to the focusing plane is known ($-u_2 + 2\alpha_2$), and, therefore, the coordinates of point F, where the secondary ray enters the Plateau border are also known. Then the angle between the normal to the front surface at F and the normal to the focusing plane is known ($\alpha_1 = \arctan(dy_1/dx)$ at F); the angle which the secondary ray makes with the normal to the front surface then is $\beta = u_1 + \alpha_2 - \alpha_1$; the angle which it makes with the normal to the front surface, before it enters the border, is $\arcsin(n \sin \beta)$; and, therefore, the angle which it makes with the normal to the focusing plane is

$$\delta = \arcsin\{n \sin(u_1 + \alpha_2 - \alpha_1)\} - \alpha_1. \quad [14]$$

(ii) The course of the primary ray is calculated straightforwardly from the condition that it must, after reflection at point D, coincide with the secondary ray considered. Thus, its angle with the normal to the focusing plane after reflection is τ_2 , and its angle with the normal to the focusing plane before reflection is $-\tau_2 + 2\alpha_3$.

(iii) Let the phase which the secondary ray GF would have, when arriving in the absence of liquid, at point I in the focusing plane be ϕ_0 . Its phase when arriving at F is

$$\phi_{2F} = \phi_0 - (FI)2\pi/\lambda. \quad [15]$$

Therefore, its phase when arriving at D is

$$\begin{aligned} \phi_{2D} = \phi_0 - (FI)2\pi/\lambda \\ + (FE + ED)2\pi n/\lambda. \end{aligned} \quad [16]$$

Similarly, the phase of the primary ray when arriving at D is

$$\phi_{1D} = \phi_0 - (DJ)2\pi/\lambda, \quad [17]$$

which becomes after reflection,

$$\phi_{1D} = \phi_0 - (DJ)2\pi/\lambda - \pi/2. \quad [18]$$

The phase difference between the rays is

$$\Delta\phi = \phi_{2D} - \phi_{1D} = \{DJ - FI + n(FE + ED)\}2\pi/\lambda + \pi/2. \quad [19]$$

The coordinates of the points I and J can be calculated from the coordinates of D and F and the angles τ_2 and δ . With these coordinates and those of point E, $\Delta\phi$ can be calculated for any ray which appears to originate at point A and makes an angle τ_2 with the normal to the focusing plane.

(iv) The intensity of the light emerging at a time t at point D, making an angle τ_2 with the normal to the focusing plane, is then given by

$$\text{Int} = \{A_1 \sin(Kct) + A_2 \sin(Kct - \Delta\phi)\}^2. \quad [20]$$

A_1 and A_2 are the amplitudes of the electric field vector for the primary and secondary rays, respectively, $K = 2\pi/\lambda$, and c is the velocity of light *in vacuo*. The average intensity reflected over one period from point D in the direction concerned is obtained by summing Eq. [20] for various values (usually 100) of $t(t_0 < t < t_0 + T)$, and the total intensity appearing to originate from point A is obtained by summing the values of the intensity thus obtained for different values of τ_2 .

The summations were performed by means of a program (INSIDE.PAS) written in Pascal, which can be run on any IBM compatible PC. In the calculations A_1 and A_2 have been taken to be equal. Any additional intensity due to, e.g., the primary ray being more pronounced than the secondary one, would be superimposed on the interference pattern, but does not shift the latter's minima.

In the calculations, the restriction was imposed that both incoming and outgoing primary and secondary rays had to be within the numerical aperture (NA) of the objective employed.

The result of such a calculation is shown in Fig. 10 for a Plateau border radius of $500 \mu\text{m}$ and a film thickness of $0.1 \mu\text{m}$; the step size

FIG. 10. Computed interference pattern for the transition from a film, $0.1 \mu\text{m}$ thick, to a circular Plateau border with radius of curvature $500 \mu\text{m}$. $x = 0$ at the start of the border. The computation is performed for 50 rays in a two-dimensional cone of light, transmitted by an objective with $\text{NA} = 0.4$. The stepwise decreasing number of angles is due to the increasing number of emitted rays, which do not reach the objective after reflection/refraction while approaching the steeper part of the border.

amounts to $0.05 \mu\text{m}$, which means that after each calculation the observation point D moves $0.05 \mu\text{m}$ in the x -direction. This theoretical interference pattern shows several discontinuities due to the fact that for each point a summation is performed for 50 different values of τ_2 , which obey the condition

$$\tau_2 \leq \arcsin(\text{NA}). \quad [21]$$

where NA is the numerical aperture of the objective used; in this case $\text{NA} = 0.4$. Also, the angles $-\tau_2 + 2\alpha_3$ and δ of the primary and secondary incoming rays, respectively, must satisfy this condition. If one of them does not, there will be no interference, and the other ray will be added to the background light; if they both do not, then the outgoing ray with the τ_2 concerned cannot originate from any ray coming out of the objective. In both cases the outgoing ray is omitted in the summation.

While approaching the steeper part of the Plateau border surface (the positive x -direction in Fig. 10) less and less rays participate in the summation. Since the number of rays is limited (50), each time an outgoing ray is omitted, the intensity of the interference light decreases abruptly. In Fig. 10, the steps in the number of rays used in the calculation correspond to the discontinuities in the interfer-

ence curve. Although an integration over the angles, if possible, would make these discontinuities disappear and thus would result in a more accurate interference pattern, this would not change the locations of the minima.

After determination of the x -values of the minima, these data are treated the same way as experimental data, which means that every x -value is provided with the proper thickness. These thicknesses are obtained by employing Fizeau's equation of interference minima [1] for which a plane parallel film is assumed. The order of interference is determined by the film thickness: the thickness for the first interference minimum should be calculated for the smallest p , for which δ_b is larger than the film thickness.

In this case, $p = 1$ and $\delta_b = 0.20775 \mu\text{m}$. The other thicknesses are calculated with successive p -values. Also, the original circular Plateau border profile, for which the interference pattern is computed, is calculated according to the proper circle equation with the thicknesses of the interference minima,

$$x_c^2 + (y_b - y_f - r)^2 = r^2, \quad [22]$$

where x_c is the x -value for the circle, y_b and y_f are the half-thicknesses of the Plateau border and the film, respectively, measured from the film's parallel symmetry plane, and r is the radius of the circular Plateau border.

Figure 11 shows a plot of this circular profile (closed circles) and the profile, according to the calculated interference pattern (open circles). It is clear that the deviation of the latter from the circle is small: it varies from $0.09 \mu\text{m}$ for the 1st minimum to $0.39 \mu\text{m}$ for the 25th minimum, or in percentages, from 1.2 to 0.7%. Considering the accuracy with which the minima are measured on the photographs, this deviation is negligibly small. To see what effect this deviation has on the radius of curvature, the reader is referred to the first method under Results.

We realize that this is only a two-dimensional analysis, while in reality we are dealing with a three-dimensional cone of light. However, rays out of the horizontal plane and re-

FIG. 11. Profiles of a circular Plateau border (●, film thickness = $0.1 \mu\text{m}$; radius of curvature = $500 \mu\text{m}$) and a border calculated according to the interference pattern in Fig. 10 (○), (·) Smoothed curve, computed for the circular profile. The utmost left point is calculated only for the circle, but is not derived from the interference pattern.

flected/refracted by a circular Plateau border encounter an ellipsoidal border upon refraction, which makes a computation rather complicated. Furthermore, three-dimensional calculations for a wedge-shaped border were compared with analogous two-dimensional ones, showing no large deviations. Therefore, one may apply the assumption that for determination of the local thickness of a Plateau border, measured interferometrically with a microscope with conical illumination, the surfaces are considered plane parallel; in other words, Fizeau's equations for maxima and minima are valid and Fig. 3 does not need to be corrected.

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