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The drainage of free liquid films

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Abstract

A review is presented of the present theoretical understanding of the thinning of free liquid films by marginal regeneration. The theory of this phenomenon, introduced by Mysels et al. (K.J. Mysels, K. Shinoda and S. Frankel, Soap Films, Studies of their Thinning and a Bibliography, Pergamon, New York, 1959) is modified so as to understand its direction dependence, i.e. the difference between marginal regeneration phenomena at the top, bottom and vertical side Plateau borders in a vertical film. A central role is played by squeezing-mode surface waves; this leads also to an understanding of the thinning of horizontal films. The thinning rate of a film is shown to be related to the bulk viscosity of the liquid phase involved.

Keywords: Drainage; free liquid films; marginal regeneration.

1. Introduction

Free liquid films, i.e. thin liquid films limited on both sides by an interface which is deformable either perpendicular to the surface or parallel to the surface, or both, are encountered in such diverse systems as foams, blisters in coatings, and emulsions. These systems have a common characteristic in that they are inherently unstable owing to the presence of relatively large interfaces which make a positive contribution to their Gibbs free energy. Such systems occur in many practical situations; in most cases, they are considered to be a nuisance and the aim of people encountering them is primarily to destroy them as rapidly as possible. However, there are also situations in which foams or emulsions are desired, at least temporarily. Thus foams are employed in flotation operations and in the manufacture of foamed concrete or polystyrene, and emulsions may be employed in liquid/liquid extractions and in oil recovery. In such cases the fact that the stability of foams or emulsions is only limited may be a problem rather than a bonus, although in most cases the foams or emulsions should finally be destroyed.

For handling such situations rationally, an understanding of the effects leading to the temporary stability and final destruction of the systems concerned is important.

Thin liquid films have, in fact, drawn man's attention for quite a long time. Early authors such as Boyle [1] and Newton [2] devoted passages in their work to thin liquid films. However our modern understanding of them can perhaps be stated to have originated with the work of Derjaguin and Kussakov in 1939 [3], with the important insight that the properties of thin films are different from those of the bulk phases. These workers introduced the parameter "disjoining pressure" for characterizing the difference between thermodynamic properties of matter in the film and in the bulk phases respectively.

In foam or emulsion destruction, two processes can in general be discerned: the thinning of liquid films and their fracture. Modern theories of film rupture [4-6] imply that the rupturing process

proper starts only after film thinning has reduced the film thickness to a "critical thickness" h_c , which is reported to vary between 24 and 110 nm [7-9]. The present paper is concerned with the thinning process. Among the previous review papers on this subject, the most important appears to be that of Mysels et al. [10] which presents important data on the thinning of vertical films. Many workers, however, have studied horizontal films. Although in this case some simplification of a complicated situation is achieved because the influence of gravity is eliminated, it will appear shortly that this implies quite an important modification of the film-thinning mechanism. This paper considers first the ideas regarding the thinning of horizontal films: the thinning of vertical films is then treated in Section 3.

2. The thinning of horizontal films

Experimentally, such films have been studied with regard to their thinning rate by a large number of workers (see, for example, Refs [10, 11-23]).

Theoretically, the starting point used to be the Reynolds equation, based on the Navier-Stokes equation under the conditions pertaining to thin liquid films:

$$-\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{2h^3}{3\eta R^2} \Delta P \tag{1}$$

where h is the film thickness, t is time, η is the bulk viscosity, R is the film radius (horizontal films formed with the usual technique are, at a good approximation, circular), and ΔP is the force per unit film surface area causing the drainage. This pressure, ΔP , consists of the capillary pressure in the surrounding Plateau border and the disjoining pressure in the film, caused by the London-van der Waals and electrostatic interactions between the film surfaces.

While former studies regarded the agreement of experimental thinning rates with the Reynolds equation to be "reasonable" (see, for example, Ref. [23]), at present this agreement is considered to be far from satisfactory (see, for example, Refs [7,9,24,25]). Good agreement between thinning rates and the Reynolds equation has been found only for very small films, e.g. with $R < 50 \, \mu m$. For larger films, increasing deviations between experimental and theoretical values for the film rate have been reported [7,9].

Equation (1) rests on boundary conditions such as zero flow rates at the interfaces, which cannot in general be relied upon as being satisfied at mobile interfaces (such as liquid/gas (L/G) interfaces). At mobile interfaces the requirement mentioned is satisfied only under special conditions, e.g. if a shear stress exerted on the surface is balanced by a surface tension gradient. However, the introduction of the boundary condition of zero flow rate at the interface is probably not of importance in the context of the present discussion; it has been argued that the flow at the interface itself cannot explain the disagreement between experiment and theoretical prediction by the Reynolds equation (Eqn (1)), since theoretical treatments incorporating such mobile (but still plane-parallel) interfaces [10,26] all lead to a proportionality between thinning rate and the inverse second power of the film radius, in agreement with Eqn (1). Experimentally, however, a much lower dependence on R is reported, e.g. a proportionality to $R^{-0.8}$ [7].

A preliminary solution to this dilemma has been proposed by Sharma and Ruckenstein [9,24,27]. These workers hold surface inhomogeneities to be responsible for the deviation between experiment and theory. Such surface inhomogeneities are caused by the outward flow, and they induce surface waves which have a "pumping action", transporting liquid from the film centre towards its rim.

The quantitative description of such a pumping action, as far as it goes at present, is perhaps best presented in Ref. [28]. The film thickness H is thought to be made up of an average thickness h (corresponding to a plane-parallel film) and a surface inhomogeneity η_s . The thinning rate of a

film, $V = -\partial h/\partial t$, is regarded as being made up of a superposition of the Reynolds thinning rate according to Eqn (1) (V_0) and a thinning rate due to the presence of the surface inhomogeneities. These workers indeed succeed in deriving an equation for the latter effect, based on the following ideas:

- (a) Surface inhomogeneities are, under the influence of tangential pressure gradients, continuously convected towards the film peripheries. Such inhomogeneities have indeed been observed experimentally [7], although their motion was not directly observed.
- (b) The growth coefficient of these surface inhomogeneities contains a real and an imaginary part. The real part represents the stabilizing influence of film drainage on surface wave growth (e.g. by dissipation and by surface tension), and the destabilization of perturbations due to van der Waals dispersion interactions. The imaginary part of the growth coefficient determines the temporal oscillations and convection of thickness inhomogeneities.

If, in spite of the considerable mathematical constructed Sharma apparatus by Ruckenstein, their analysis fails to be completely convincing, this is due to the complication that a net transport from the film centre to its peripheries can only result if, for the surface inhomogeneities, periodic functions are assumed which have, on average, positive slopes $\partial \eta_s/\partial r$ (where r is the direction from the centre of the circular film towards its rim). There appears to be no a priori reason for this hypothesis; it is not shown, for example, by Fourier components such as sine or cosine functions. It is shown by other periodic functions such as saw-tooth waves and was supposed to be found in "peacock-tail" waves. The latter have indeed been observed near the edge of thin liquid films, but only in the case of vertical films (in which gravity-induced surface tension gradients play an important role; see Section 3). In films that are predominantly horizontal (for example, see Ref. [10], plate III), it is necessary to

introduce deviations from the plane shape in order to obtain them.

3. Drainage of films in a gravitational field directed along the LG surface

Films subject to a gravitational field acting so as to influence film drainage are, of course, very important from a practical point of view. That the drainage of thin liquid films is influenced greatly by the presence of a gravitational field is shown in a qualitative sense by the appearance of a draining vertical film being totally different from that of a horizontal film, when investigated through interference of light waves reflected at front and back surfaces respectively: the film/Plateau border transition is, with horizontal films, much more smooth than with vertical films. Horizontal films do not show the typical "peacock-tail" phenomena, mentioned in Section 2, which are found with vertical films. Such phenomena are caused by an exchange of film elements with volume elements from the surrounding Plateau border [10], and have been named "marginal regeneration".

In addition, vertical films show in their central regions at some distance from the border/film boundaries a very regular interference pattern, indicating a regular change in film thickness over the height of the film. This is to be contrasted with the "dimples" formed frequently in horizontal films.

For vertical mobile films it has been known for quite a long time that film drainage is much more rapid than can be accounted for by the Reynolds equation (Eqn (1)). This is shown in Fig. 1 [29] where the thinning rate of films supported by frames of different widths, b, is plotted against the reciprocal frame width for some values of the film thickness. It is seen that the thinning rate increases linearly, at a given film thickness, with increasing values of the reciprocal film width 1/b; apparently most of the transport of liquid from the film occurs towards the vertical Plateau borders. For $b \to \infty$ (i.e. for $1/b \to 0$) the drainage rate is quite small. Even the small values obtained on linear extrapola-

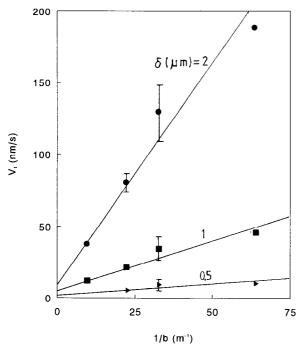


Fig. 1. Thinning rate in a direction perpendicular to the film surface vs reciprocal supporting frame width 1/b in 0.02 M CTAB solution [29] for various film thicknesses: \blacktriangleright , $0.5 \mu m$; \blacksquare , $1 \mu m$; \blacksquare , $2 \mu m$.

tion to 1/b = 0, as drawn in Fig. 1, are still an order of magnitude larger than those predicted by the Reynolds equation for a liquid between rigid surfaces.

Mysels et al. [10] present arguments that the phenomenon of marginal regeneration is decisive for the rapid drainage of vertical films. Their view is that accidental thickness fluctuations in the film lead to a replacement of thicker film volume elements by volume elements from the Plateau border, which on introduction into the film become thinner than the original film volume elements; the pressure difference between film and Plateau border exerts a greater force on the thicker than on the thinner parts of the film.

The "marginal regeneration" concept as introduced by Mysels et al. explains a large amount of experimental data. Nevertheless, on applying it to experimental observations of thin liquid film behaviour there remain some unresolved puzzles.

Thus the marginal regeneration as presented by Mysels et al. should be independent of direction. The reason why the typical "peacock-feather" view of film margins is only seen in vertical films but not in horizontal films, therefore remains unexplained. Even in vertical films it is not found near all film margins; it is not found in the film margin at the top of the film but is found near the vertical margins and the bottom margin only. However, it is not understood why the marginal regeneration phenomenon is responsible for the rapid drainage of vertical films, in view of the fact that the horizontal drainage predominates as strongly as is shown in Fig. 1, since marginal regeneration is found both at the vertical margins and near the bottom margin of the film.

A possible answer to this objection against the theory of Mysels et al. could be the following. At the bottom and vertical side Plateau borders, thin films are produced which can move upwards because there is room to do so, and because they are lighter than the surrounding film. At the top Plateau border, however, thin film parts cannot move downwards because this would imply that they replace a thicker film which should be pushed upwards when there is marginal regeneration at this Plateau border. However, there is nothing in the mechanism of Mysels et al. which precludes such a motion, and to a certain extent this indeed occurs at the vertical sides. We will return to this point later. From a more detailed look at the profile of the inflow regions it will appear (see the discussion of Fig. 2) that inflow regions are, in the intermediate stages of film drainage, frequently thicker than the average film thickness at the height concerned. Such an inflow would not be precluded by the argument that a thinner film element should always move upwards; nevertheless it does not occur at the top film/Plateau border transition.

In addition, there are difficulties in the quantitative treatment of the drainage, as introduced by Frankel [30]. Frankel treated the flow as a superposition of a flow due to entrainment of liquid in the border by a surface flow and a flow caused by

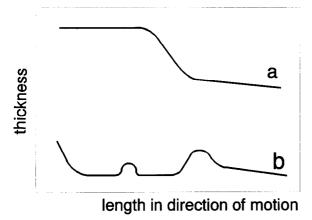


Fig. 2. Typical thickness patterns of inflow regions of marginal regeneration (direction of flow is from left to right): curve a, intermediate stages (see Fig. 3(a)) (film thickness at right, about 1.14 μ m; in the inflow region (left), 1.30 μ m); curve b, later stages (see Fig. 3(b)) (film thickness at right, about 0.55 μ m; in the inflow region, about 0.45 μ m).

the pressure gradient:

$$q = 2hv_{\rm s} - \frac{h^3 dp}{12\eta dx} \tag{2}$$

where q is the net volume flow into the film from the border per unit length along the border (therefore to be expressed in square metres per second), p is the pressure in the film, $v_{\rm s}$ is the surface flow velocity (m s⁻¹), η is the viscosity of the solution in the film and x is the length in the horizontal direction from the Plateau border into the film, taken as increasing in this direction; q and $v_{\rm s}$ are also taken as positive in this direction.

Frankel arrived at an approximate numerical solution of this equation on the basis of the assumption that q and v_s are constant, i.e. independent of the value of x, in the film and Plateau border at a given height above the bulk meniscus. The numerical solution obtained by Frankel was, however, not consistent with experimental data: a "neck" of minimum thickness between border and film was predicted, which is not found experimentally. Moreover, the theoretically predicted thickness ratio of the films falling into the border, and being drawn out of the border, respectively, does not agree with experiments.

A more fundamental reason for doubting the validity of the Mysels-Frankel theoretical treatment is that they neglected one effect which will appear to be of great importance for the thinning of liquid films subject to a gravitational field: the increase in surface tension in the film with increasing height in the film.

That such an increase must occur has been remarked already by Gibbs [31] (see also Lucassen [32]); in essence, it is caused by the necessity of mechanically supporting an increasing amount of liquid in the film, with increasing height. In the Plateau border this is accomplished by an increasing curvature of the L/G interface with increasing height, corresponding to an increasing pressure difference between the liquid and the surrounding gas. This cannot be realized in the film, however, because of the virtual absence of surface curvature in the film; therefore the surface tension must increase with increasing height.

The existence of such a surface tension increase towards the top of the film is apparent from pronounced flows in the Plateau border, when film volume elements in the process of marginal regeneration enter the Plateau border and cause an increasing surface tension with increasing height in that part of the Plateau border adjacent to the film [29]. The complicated pattern of such flows (upwards near the film, downwards in parts of the Plateau border that are more remote from the film) appears to contradict the assumption of Mysels et al. of the constancy of the quantities q and v_s from Eqn (2) in the film and adjoining Plateau border, at a given height. Such flows indeed cause a greater curvature (smaller radius of curvature) at low heights above the bulk liquid than corresponds with hydrostatic equilibrium [33,34]. A theoretical calculation shows that the surface tension gradients involved may indeed be significant enough to lead to observable pressure differences in the border [35].

In the context of the present paper, the significance of this result lies in its predicting inward and outward flow, from the border into the film and in the opposite direction, respectively, as soon as there are slight deviations from the equilibrium film thickness. At any height there is a certain film thickness, which in combination with a given surface tension in the film and a given hydrostatic pressure in the Plateau border, makes q in Eqn (2) equal to zero. This thickness is indicated here as the "local equilibrium" film thickness. However, a film slightly thicker than that with the local equilibrium thickness will, with the same values of hydrostatic pressure in the border and surface tension in the film, lead to outflow from the film into the border. Similarly, a slightly thinner film will lead to inflow from the border into the film.

This has been shown by numerically integrating Eqn (2), on the basis of the following assumptions.

- (a) The pressure in the border far away from the film is equal to the hydrostatic equilibrium pressure at the height concerned.
- (b) The surface tension in the border is equal to the bulk surface tension of the surfactant solution concerned, but it changes on going from the border into the film, in agreement with the Gibbs-Lucassen effect.
- (c) The horizontal flows q and v_s in Eqn (2) decrease exponentially on going from the film into the border, but both flows are constant in the film, and equal to their value at the film/border transition.

In these calculations, no "disjoining pressure" effects [3] have been taken into account. In the context of the present paper, the calculations refer to films of thickness 1500 nm, which is too large for either London-van der Waals forces or electrostatic repulsion forces to be significant. Hydrophobic hydration forces may have a larger range of action than London-van der Waals forces [36-38], but are characterized by decay lengths of the order of 12 nm even for completely hydrophobized (silanized) solid-liquid (SL) surfaces [37]; this value is still two orders of magnitude smaller than our film thickness. In addition, in a cetyltrimethylammonium bromide (CTAB) solution of concentration higher than the CMC, incomplete hydrophobization of the interfaces is expected in view of the contact-angle characteristics on SL surfaces [38]; although solid/aqueous solution interfaces are not completely comparable to LG surfaces, an even less pronounced hydrophobization on CTAB adsorption is expected for the latter since there the hydrophilic tetraalkylammonium groups are directed towards the aqueous phase even at low concentrations. Hydrophilic interaction forces do not extend beyond about 0.75 nm [38]. The neglect of surface forces for LG films of thickness greater than 1 µm in solutions of ionic surfactants is in agreement with the calculations by de Feijter and Vrij [39] for sodium dodecyl sulphate (SDS) solutions.

The details of the calculation have been reported in Ref. [35] and will not be repeated here, but the effect of a film thinner than the "local equilibrium" film leading to inflow, and the effect of a thicker film leading to outflow can be seen from the form of Eqn (2): the first surface flow term on the right-hand side of this equation (corresponding with inflow) is proportional to h, and the second term (corresponding to outflow due to a pressure gradient) is proportional to h^3 .

The primary cause of marginal regeneration, according to this mechanism, is thickness fluctuations in the film along the border/film transition, in a situation where a plane film inflow due to the surface tension gradient and an outflow due to the pressure gradient just balance. Such thickness fluctuations may be caused, for example, by "squeezing-mode" surface waves [4,5]. Once formed, the primary thinner parts of the film lead to inflow into the film, while the adjacent thicker parts lead to outflow into the border. The new film elements, coming from the border, have a lower surface tension than the surrounding film, and therefore they expand, pushing aside old film elements which in the course of this process become thicker (the film is too thin to make the mixing of new and old film elements important).

This then is an example of a thin film element pushing aside and slightly upwards a thicker film. This stimulates outflow from the thicker parts, and this in turn will stimulate the inflow in the inflow region. The spreading of an inflow region in the

film is limited by a pressure gradient counteracting the surface tension gradient causing the inflow. The pressure gradient in the region surrounding the inflow region is caused by local deviations from the plane character of the film surfaces (see later), and stimulated outflow from nearby regions may be expected to decrease the corresponding surface curvatures, consequently reducing the pressure gradient opposing the spreading of the inflow region and thus stimulating the inflow. Thus the inflow/outflow effect is self-reinforcing until it is slowed down by dissipative effects, e.g. those connected with viscosity. Recent work [40,41] has shown that the bulk viscosity is in this respect more important than the surface rheological characteristics, at least in the case of the surfactants investigated in the study concerned.

This mechanism, which is only summarized here, can be compared with experiments in the following respects.

- (a) According to this mechanism, old film elements between newly entered elements should be thicker than the film at the same height far away from the border. This is confirmed by the upwards bending of the interference fringes between new film elements (see Fig. 3).
- (b) The mechanism can be used to calculate the dependence of drainage rate on film thickness. Thus, if the net flow out of the film, $q_{\rm net}$, is described by a power-law dependence on the film thickness t

$$q_{\text{net}} = kh^n \tag{3}$$

then the exponent n can be evaluated numerically from the proposed mechanism. This agrees with experimental values of this exponent $\lceil 29 \rceil$.

(c) The mechanism explains one of the unsolved problems of the Mysels mechanism of marginal regeneration: its direction dependence [42]. Thus no typical marginal regeneration phenomena are found near the top border/film transition, in spite of the fact that near this boundary there are differences between the properties of film and border which are at least as pronounced as those at the other boundaries: there is a pressure differ-

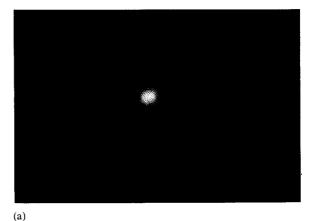


Fig. 3. Photographs of interference patterns on which Fig. 2 is based: (a) 0.02 M cetyltrimethylammonium bromide (CTAB) solution after 46 s; (b) 0.02 M CTAB solution after 97 s.

(b)

ence between film and border, and a surface tension difference similar to those found at the bottom and vertical border/film transitions. However, the surface tension gradient is, at the top border/film boundary, directed so that any flow from the border into the film would be an anti-Marangoni flow and therefore can only occur if there are other driving forces dominating the surface tension gradient. Indeed, no marginal regeneration phenomena are seen at the top border/film transition. At the bottom border/film transition, the surface tension increases on going into the film in a direction perpendicular to the border/film boundary. Outflow from the border into the film is therefore possible because it is in the direction of increasing

surface tension. However, it is directed perpendicular to the boundary; the pushing-aside of old film volume elements occurs predominantly far away from the border/film transition, and therefore no stimulation of outflow is expected. Therefore at this boundary, typical marginal regeneration turbulences are found, but they are not very active with regard to drainage; this appears from Fig. 1, where the intercept of the lines with the vertical axis indicates the thinning rate of the film due to the outflow at the bottom border/film transition (because this corresponds to the case of the film width tending to infinity). Near the vertical film boundaries, however, the inflows from the border are directed along the boundary. Therefore the newly formed film elements expand in this direction; a pushing-aside of old film elements occurs in the vicinity of this transition, and outflow along these boundaries predominates.

The mechanism presented here may also explain the thinning rate of horizontal films referred to in Section 2. A connection with surface waves was suggested by Sharma and Ruckenstein, which, however, required that the slopes of the surface waves be asymmetric $(\partial \eta_s/\partial r \ge 0$ on average). As already stated, there is no a priori evidence for that; Sharma and Ruckenstein refer to the profiles of peacock-tail waves observed in liquid films in which gravity is important. On a closer look at the profiles of typical marginal regeneration inflow regions, it appears that such profiles change character. In the early and intermediate stages of film flow, the character of a profile along the inflow region is predominantly as shown in Fig. 2 (curve a) (for a typical photograph, see Fig. 3(a)). However, in later stages, when the film has become thin so as to lead to only small surface tension differences between border and film, the character of a profile is shown as in Fig. 2 (curve b). In the midst of the inflow region, a small spot is seen of about the thickness of the film at this height, far away from the Plateau border. It is surrounded by a broad rim of smaller thickness, and this in turn is surrounded by a narrow rim of thickness larger than the normal film thickness at the height concerned (for a typical photograph at that stage, see Fig. 3(b), especially the two inflow regions in the upper left-hand corner). The early type of profile cannot easily be reconciled with Sharma and Ruckenstein's requirement that $\partial \eta_s/\partial r > 0$, on average (where r is the direction of expansion of the inflow region), and the transition from one type of profile to the other can best be explained by expansion through surface tension differences.

The profiles shown in Fig. 2 indicate schematically the deviations from the plane shape responsible for the pressure gradients counteracting inflow, which have been referred to earlier in this paper.

It appears to the present author that it is not necessary to introduce any postulate regarding $\partial \eta_s/\partial r$ for explaining the thinning of horizontal films. If there are surface waves with film thicknesses alternatively larger and smaller than the average film thickness (i.e. of the squeezing-mode type [4,5]), then a local temporarily larger thickness than the average thickness will correspond to outflow, and a temporarily smaller than average thickness will lead to inflow. However, the outflow will predominate because again it is proportional to the third power of the film thickness, while the inflow is only proportional to the first power of the film thickness. This would, as a net effect, lead to a thinner film near the film/border boundary than in the centre of the film, but such thickness differences at a particular level in the film are straightened out by flows induced by the requirement of thickness and surface tension equality at one level in the film (i.e. the same requirements that lead to the setting up of a vertical thickness profile of the film).

4. Influence of surfactant solution characteristics on thinning of liquid films

From a practical point of view, it is important to establish what influence differences in viscosity, surface tension, surface viscosity and elasticity etc. have on the thinning of liquid films. The viscosity, especially, appears to be an important property in view of the expectation that the inflow/outflow

effect will be self-reinforcing until it is slowed down by some dissipative effect. Some preliminary experimental data on this subject are given below; it should be obvious, however, that our present knowledge is not yet exhaustive and that in particular, the influence of surface rheology is not yet known for certain.

An increase in bulk viscosity of the surfactant solution decreases the thinning rate. This has been stated already by Mysels et al. [10], but without extensive reference to experimental evidence. New evidence in this respect is based upon experiments with surfactant solutions with increasing amounts of glycerol [41]. The thinning rate is found to be inversely proportional to the viscosity.

It is surprising that the *bulk* viscosity of the surfactant solution is the determining factor; at first sight, a connection with the *surface* rheology of the surfactant solution might be sought.

The experiments referred to in the preceding paragraph do not exclude the possibility that it is in reality the surface viscosity which determines the film thinning rate, since in the case of homogeneous solutions, the bulk and surface viscosity may be connected. However, the connection with the bulk viscosity is confirmed by experiments in which the viscosity of the surfactant solutions is altered by the presence of solid particles (polystyrene): in this case again a thinning rate inversely proportional to the viscosity of the polystyrene suspension has been found [40], although no direct influence of such solid particles on the surface rheology is expected.

5. Conclusion

The occurrence of squeezing-mode surface waves can be regarded as triggering the marginal regeneration phenomenon. Expansion of inflow regions by surface tension gradient-induced flows leads to self-reinforcement of the inflow at the vertical film/border boundaries until dissipative processes connected with the bulk viscosity become important.

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