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HYDRODYNAMICS OF THIN LIQUID FILMS. RATE OF THINNING OF EMULSION FILMS FROM PURE LIQUIDS

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Abstract—A hydrodynamic theory of the process of thinning of one-sided and symmetrical emulsion films is presented. The theory is essentially based on three assumptions: 1. the film is considered as being thin in the hydrodynamic sense; 2. the film surfaces are assumed to be plane-parallel, and 3. the dissipation of energy outside the film and the adjacent regions of the dispersion phase is neglected. The complete set of Navier–Stokes equations for the dispersion phase are solved. The case of non-steady flow is also considered. Some approximated equations valid for systems of practical importance are obtained.

1. INTRODUCTION

Many recent investigations have been dedicated to the study of the kinetics of thinning of emulsion films (MacKay & Mason 1963; Hartland 1967; Sonntag 1960; Platikanov & Manev 1964; Sheely & Leng 1971). In most, the experimental data have been interpreted by means of Reynolds equation, describing the thinning of a liquid film confined between two rigid parallel discs (Reynolds 1886). It has been shown however (Radoev, Dimitrov & Ivanov 1974) that in foam films, because of the mobility of the surfaces, the rate of thinning can be considerably greater than that calculated from Reynolds equation. Deviations from Reynolds equation for emulsion films can be even greater in cases where films are obtained in the absence of surfactant. This is pointed out in many studies (MacKay & Mason 1963; Hartland 1967; Platikanov & Manev 1964) but for lack of alternative governing equations, Reynolds equation is used.

The above considerations reveal that the correct interpretation of experimental results on the kinetic behavior of emulsion films requires the use of an equation for the rate of thinning which accounts for both the motion of the film surfaces and the motion of the liquid in the droplets. Murdoch & Leng (1971) have attacked this problem but have obtained a solution only for the film, while flow in the droplets has been accounted for by introducing some adjustable parameters, determined from the experiment. The present work is an attempt to give a complete hydrodynamic theory of the process of film thinning by solving Navier–Stokes equations both for the film and for the droplets. The rate of thinning is expressed only in terms of known experimental quantities. Similar theories are developed for the case of mutual approach of two non-deformable droplets (Wacholder & Weihs 1972; Reed & Morrison 1974; Haber, Hetsroni & Solan 1973). For cases where a plane-parallel film exists between droplets there is only one set of papers in which, as in ours, the motion of the liquid in the droplets is considered (Reed, Riolo & Hartland 1974 a,b). Unfortunately, the approach, the model and the approximations used by Reed *et al.* (1974) differ from ours, hindering any quantitative comparison of the two theories, though both lead to some identical qualitative results (see below).

2. FORMULATION OF THE PROBLEM

For simplicity, we consider the system shown in figure 1: the emulsion film of thickness h and radius R is formed in a tube of radius R_c by sucking out the liquid from a biconcave meniscus, II. The film and the meniscus form the dispersion medium. The tube, assumed infinitely long, is filled with liquid 1 forming the dispersion phase. The system does not contain any surfactant. The film

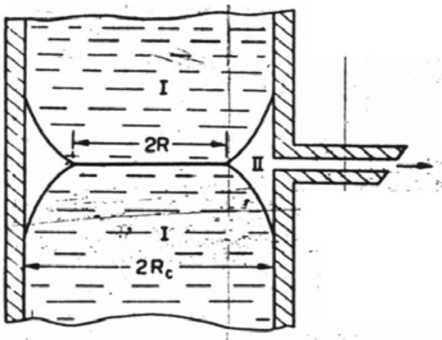

Figure 1. A model of emulsion film of radius R formed in a capillary of radius R_c. I—dispersion phase, II—dispersion medium.

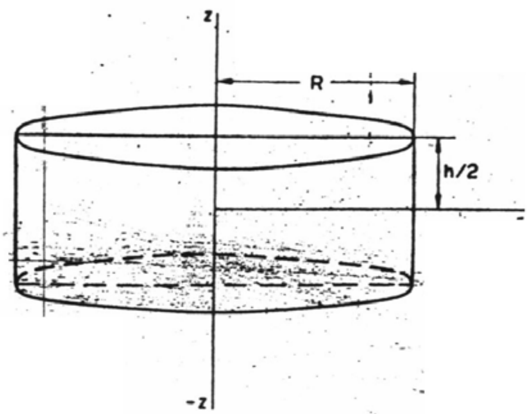

Figure 2. Scheme of a plane-parallel circular film of radius R and thickness h.

is plane-parallel† and sufficiently thin so that $h/R \ll 1$. Because of the natural symmetry of the system we use the cylindrical coordinates shown in figure 2, and all calculations are carried out only for $z > 0$. The flow in the film obeys the simplified Navier–Stokes equations (valid for $h/R \ll 1$) known from lubrication theory. Denoting all the quantities refering to the film by an asterisk we write these equations in the form (Kochin, Kibel & Roze 1965; Levich 1962)

$$\frac{\partial^2 v_r^*}{\partial z^2} = \frac{1}{\mu^*}\frac{\partial p^*}{\partial r}, \qquad [1a]$$

$$\frac{\partial p^*}{\partial z} = 0, \qquad [1b]$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r^*) + \frac{\partial v_z^*}{\partial z} = 0. \qquad [1c]$$

For the dispersion phase we solve the complete set of Navier–Stokes equations

$$\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial r} + v_z\frac{\partial v_r}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left[\frac{\partial^2 v_r}{\partial r^2} + \frac{\partial}{\partial r}\left(\frac{v_r}{r}\right) + \frac{\partial^2 v_r}{\partial z^2}\right] \qquad [2a]$$

$$\frac{\partial v_z}{\partial t} + v_r\frac{\partial v_z}{\partial r} + v_z\frac{\partial v_z}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left(\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r}\frac{\partial v_z}{\partial r} + \frac{\partial^2 v_z}{\partial z^2}\right), \qquad [2b]$$

$$\frac{1}{r}\frac{\partial}{\partial r}(r v_r) + \frac{\partial v_z}{\partial z} = 0, \qquad [2c]$$

where gravity has been neglected. In [1] and [2] v_r and v_z denote the velocity components in r- and z-directions, t time, p pressure, ρ density and μ and $\nu = \mu/\rho$ the dynamic and kinematic viscosities. To formulate the boundary conditions let us consider briefly the character of the liquid motion in the system. Since the outflow of the liquid from the film initiates motion of the liquid both in the dispersion phase and in the meniscus, the complete hydrodynamic description of the system under consideration is an extremely complicated task. Our intention is more modest: we only seek the correlation between the rate of film thinning and the driving force of this process. Investigations of the liquid flow in foam systems (films and bubbles) have shown that the dissipation of energy decreases sharply with increasing distance between the liquid interfaces, so that the energy is primarily dissipated in a narrow region situated immediately

†In fact the film is usually lens-shaped (the so called "dimple"). The problem of the film shape has been studied in many experimental and theoretical works (Hartland 1969; Frankel & Mysels 1962; Ivanov & Radoev 1970–71, 1972–73) and we do not discuss it here. For microscopic films of lesser diameter, however, the "dimple" is small and the film can be regarded as plane-parallel.

about the symmetry axis. This result allows us to assume that in the system considered here the predominant part of the energy is dissipated in the region $0 \leqq r \leqq R$, so that there is no need to consider liquid motion beyond this region.† This approach, however, restricts the scope of the solution for it does not allow the determination of the boundary conditions at $r = R$ with respect to v_r and v_z. Thus, when solving [1] and [2] the following boundary conditions can be employed

$$v_r^* = v_r = U(r) \quad [3a]$$

$$v_z^* = v_z = -V/2 \qquad \text{at} \quad z = h/2, \quad [3b]$$

$$\mu^* \frac{\partial v_r^*}{\partial z} = \mu \frac{\partial v_r}{\partial z} \quad [3c]$$

$$p^* = p_0^* \qquad \text{at} \quad r = R, \quad [3d]$$

$$\left.\begin{aligned} v_r &= 0 \\ p &= p_0 \end{aligned}\right\} \qquad \text{at} \quad z = \infty, \quad [3e] \; [3f]$$

$$\frac{\partial v_r^*}{\partial z} = 0 \qquad \text{at} \quad z = 0, \quad [3g]$$

where $V = -\mathrm{d}h/\mathrm{d}t$ is the rate of thinning of the film, $U(r)$ is the radial velocity on the interface, p_0 is the pressure in the dispersion phase far from the interface, and p_0^* is the pressure in a hypothetical equilibrium film of the same thickness. This pressure is related to the pressure p_m in the meniscus through the correlation

$$p_0^* = p_m + \Pi, \quad [4]$$

where Π is the disjoining pressure (see e.g. Sheludko 1966). All functions giving the solution of [1] and [2] must obviously be finite at $r = 0$.

The conditions [3a] and [3b] result from the very formulation of the problem, and [3c] is the continuity condition for the tangential component of the stress tensor on the interface. Equation [3d] follows from the assumption that the liquid in the meniscus is immobile and [3e] and [3f] account for the vanishing of the radial motion of the liquid in the dispersion phase at $z \to \infty$ (this does not apply to the velocity component v_z which, even at $z \to \infty$, has a finite value (see [13] and figure 3). Equation [3g] is the symmetry boundary condition.

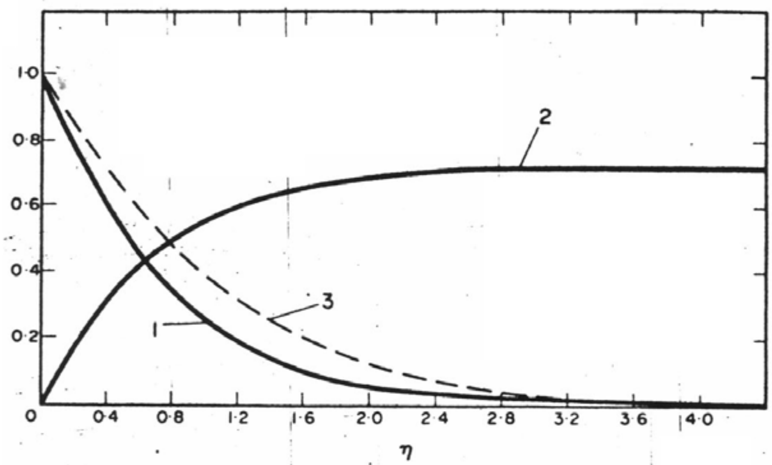

Figure 3. Plots of the solution of [16]: 1—dependence of the function f on the dimensionless coordinate η; 2—dependence of the function $\int_0^\eta f\,\mathrm{d}\eta$ on η; 3—dependence of the function f on η obtained in (Ivanov & Traykov 1971–72) by von Kàrmàn–Pohlhausen's method.

†This assumption leads to a certain similarity in both the approach as well as in the results of our theory and von Kàrmàn's solution for rotation of a disc in an infinite liquid (see e.g. Loytsianskyi 1962; Schlichting 1955).

The method of solution of [1] is given in detail by Radoev, Dimitrov & Ivanov (1974) and Ivanov & Traykov (1971–72) and we present only the final expressions for v_r^*, v_z^* and p^*:

$$v_r^* = \frac{3}{h^3}(2Uh - Vr)\left(z^2 - \frac{h^2}{4}\right) + U, \quad [5a]$$

$$v_z^* = -\frac{1}{r}\frac{\partial}{\partial r}\left[r(2Uh - Vr)\left(\frac{z^3}{h^3} - \frac{3}{4}\frac{z}{h}\right) + Urz\right] \quad [5b]$$

$$p^* = p_0^* + \frac{3\mu^* V}{h^3}(R^2 - r^2) - \frac{12\mu^*}{h^2}\int_r^R U\,\mathrm{d}r. \quad [5c]$$

The particular symmetry of the system implies the following form of the expression for v_r

$$v_r = U(r)f(\eta), \quad [6]$$

where the dimensionless coordinate

$$\eta = (z - h/2)\sqrt{(U/r\nu)}, \quad [7]$$

may, in principle, depend on r. The thus far unknown function $f(\eta)$ is determined later. Equations [3c], [5a] and [6] yield

$$\left(\frac{U}{r}\right)^{3/2} = \frac{3\mu^* \nu^{1/2}}{\mu h a_1}\left(2\frac{U}{r} - \frac{V}{h}\right) \quad [8]$$

where

$$a_1 = (\mathrm{d}f/\mathrm{d}\eta)_{\eta=0}. \quad [9]$$

Since [8] is an algebraic equation with respect to U/r, we can write

$$U = Ar, \quad [10]$$

where A (which does not depend on r and z) is one of the roots of [8]. Thus [6] acquires the form

$$v_r = Arf(\eta), \quad [11]$$

and η does not depend on r:

$$\eta = (z - h/2)\sqrt{\left(\frac{A}{\nu}\right)} \quad [12]$$

Integrating [2c] on z with the aid of [3b] and [11] we obtain

$$v_z = -2\sqrt{(A\nu)}\int_0^\eta f(\eta)\,\mathrm{d}\eta - V/2. \quad [13]$$

Taking into account [3f], [11] and [13], from [2b] we conclude that p does not also depend on r, i.e. the term $\partial p/\partial r$ in [2a] vanishes. Equations [11], [13] and the above considerations allow us to write [2] in a simpler form:

$$\frac{\partial v_r}{\partial t} + v_r\frac{\partial v_r}{\partial r} + v_z\frac{\partial v_r}{\partial z} = \nu\frac{\partial^2 v_r}{\partial z^2}, \quad [14a]$$

$$\frac{\partial v_z}{\partial t} + v_z \frac{\partial v_z}{\partial z} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu \frac{\partial^2 v_z}{\partial z^2}. \qquad [14b]$$

$$\frac{1}{r}\frac{\partial}{\partial r}(rv_r) + \frac{\partial v_z}{\partial z} = 0. \qquad [14c]$$

These equations are solved in the following sections.

No truly steady flow in the dispersion phase is possible (see section 6), but for the sake of simplicity in the next section we neglect the derivatives with respect to t in [14]. The case of a one-sided film (one surface bounding a liquid, the other a solid) is considered in section 4. In section 5 a solution for the case of non-steady flow is obtained. Some of the approximations used subsequently are analysed in appendix 1.

3. SYMMETRICAL FILM—STEADY FLOW

In this case the derivatives with respect to t in [14] disappear. In this manner from [14a] and [13], the relation [15] is obtained

$$f'' + 2f'\left(\int_0^\eta f\,d\eta + \frac{V}{4\sqrt{(A\nu)}}\right) - f^2 = 0, \qquad [15]$$

which after differentiation with respect to η is transformed into an ordinary differential equation

$$f'''f' - f''^2 + f''f^2 = 0. \qquad [16]$$

At $\eta = 0$, $f = 1$ (see [3a]) and $V/2\sqrt{(A\nu)} \ll 1$ (see [A.I.1]). In order for [15] to be valid, the condition $f''(0) = 1$ must be satisfied. Since f must go to zero when $\eta \to \infty$, we obtain the following boundary conditions for [16]

$$\left.\begin{matrix} f = 1 \\ f'' = 1 \end{matrix}\right\} \quad \text{at} \quad \eta = 0, \qquad \begin{matrix}[17a]\\ [17b]\end{matrix}$$

$$f = 0 \quad \text{at} \quad \eta = \infty. \qquad [17c]$$

Equations of the type of [16] appear in many hydrodynamics problem (see e.g. Schlichting 1955). Because of the previously noted similarity between our problem and von Kàrmàn's problem for rotation of a disc, it is convenient to solve [16] by the method of Cochran (Schlichting 1955), used in the solution of von Kàrmàn's problem (see also Levich 1962). We represent, therefore, the solution of [16] by the series

$$f_0 = \sum_{n=0}^{\infty} \frac{a_n \eta^n}{n!} \qquad [18]$$

for $0 \leqq \eta \ll 1$, and

$$f_\infty = \sum_{n=1}^{\infty} f_n\, e^{-n\beta\eta} \qquad [19]$$

for $\eta \gg 1$. The coefficients a_n, b_n and β are determined by substituting [18] and [19] in [16] and [17] and equating the values and the derivatives of f_0 and f_∞ at a point η_0. The numerical solution yields the following values: $\eta_0 = 1$; $\beta = 1.44$; $a_0 = 1$; $a_1 = -1.19$; $a_2 = 1$; $a_3 = 0$; $a_4 = -2$; $a_5 = 2.38$; ... $b_1 = 1.16$; $b_2 = -0.324$; $b_3 = 0.0905$; $b_4 = 0.0240$ etc. The functions f and $\int_0^\eta f\,d\eta$ calculated in this manner are shown in figure 3 (curves 1 and 2). They differ by no more than 2% from the computer solution of [16] carried out in the ACC of CLTOCT of BAN. In figure 4 the calculated streamlines are shown. Both figures reveal that at a given dimensionless distance

$\eta_t \approx 2.5$, the radial motion dies ($f(\eta_t) = 0.03$). This allows the quantity (see [12] and [23] at $\epsilon_2 \ll 1$)

$$\delta = 2.5\sqrt{\left(\frac{\nu}{A_2}\right)} \approx 3.5\sqrt{\left(\frac{h\nu}{V}\right)} \qquad [20]$$

to be considered as a thickness of the boundary layer, where the main part of the energy is dissipated.

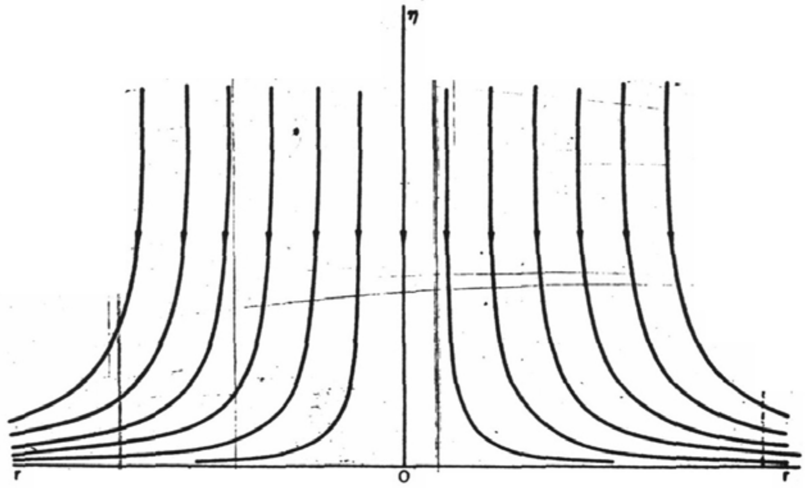

Figure 4. Streamlines in the dispersion phase at steady flow in a symmetrical emulsion film.

Equations [18] and [19] give the solution of Navier–Stokes equations [14] for the dispersion phase. The velocity v_z is easily calculated on this basis from [13]. The pressure p is obtained by integrating [14b] with the aid of the boundary condition [3f],

$$p = p_0 - 2\mu A\left[f + \left(\int_0^\eta f\, d\eta\right)^2 - \left(\int_0^\infty f\, d\eta\right)^2\right]. \qquad [21]$$

The velocity of thinning, V, can be found from the equation for the balance of forces acting upon the film surface,

$$\int_0^R p_{zz} r\, dr = \int_0^R p^*_{zz} r\, dr, \qquad [22]$$

where p_{zz} is the normal component of the stress tensor. Writing [8] in the form (see also [10])

$$U = A_2 r; \quad A_2 = \frac{V}{2h(1+\epsilon_2)}, \qquad [23]$$

where

$$\epsilon_2 = -\frac{a_1 \mu h}{6\mu^*}\sqrt{\left(\frac{A_2}{\nu}\right)}, \qquad [24]$$

and substituting in [5c] U from [23] we obtain

$$p^* = p^*_0 + \frac{3\mu^* V(R^2 - r^2)}{h^3}\frac{\epsilon_2}{(1+\epsilon_2)}. \qquad [25]$$

Thus from [12], [13] and [21], using [17a] we have, at $\eta = 0$,

$$p_{zz}(0) = -p(0) + 2\mu\left(\frac{\partial v_z}{\partial z}\right)_{\eta=0} = -p_0 + 3.04\mu A_2, \qquad [26a]$$

where the value of $\int_0^\infty f\,d\eta = 0.72$ is taken from figure 3. Similarly, from [5b], [23], and [25] we obtain

$$p^*_{zz} = -p^*_0 - \frac{3\mu^* V}{h^3}\frac{\epsilon_2}{(1+\epsilon_2)}(R^2 - r^2) - 4\mu^* A_2. \qquad [26b]$$

Equations [26a], [26b], and [4] yield

$$\frac{3\mu^* VR^2}{2h^3}\frac{\epsilon_2}{(1+\epsilon_2)} = \Delta P + (3.04\mu - 4\mu^*)A_2, \qquad [27]$$

where

$$\Delta P = P_c - \Pi \qquad [28]$$

is the driving force (per unit area) of the process ($P_c = p_0 - p_m$ is the capillary pressure). When the film is thinning under the action of an external force F, P_c must be replaced by $F/\pi R^2$. If $\Delta P \gg (3.04\mu - 4\mu^*)A_2$ (see [A.I.3]), [27] can be written as

$$\frac{V}{V_0} = 1 + \frac{1}{\epsilon_2}, \qquad [29]$$

where

$$V_0 = \frac{2h^3}{3\mu^* R^2}\Delta P \qquad [30]$$

is Reynolds' velocity of thinning of the film formed between two rigid parallel discs (Reynolds 1886). From [26] it is clear that the same result might be obtained by putting

$$p^*_{zz}(0) = -p^*, \qquad [31a]$$

and

$$p_{zz}(0) = -p(0) = -p_0. \qquad [31b]$$

The assumption $p(0) = p_0$ is equivalent to Prandtl's approximation $\partial p/\partial z = 0$ (see section 6).

4. ONE-SIDED FILM—STEADY FLOW

An expression for the rate of thinning of one-sided film can be obtained in a manner analogous to the above described. In this case the boundary conditions [3] are only valid for the upper surface, while for the lower surface they are replaced by

$$\left.\begin{aligned} v^*_z &= V/2 \\ v^*_r &= 0 \end{aligned}\right\} \quad \text{at} \quad z = -h/2. \qquad \begin{aligned}[32a]\\ [32b]\end{aligned}$$

Instead of [5], the solution of [1] now yields

$$v^*_r = \frac{3}{h^3}(Uh - Vr)(z^2 - h^2/4) + U\left(\frac{1}{2} + \frac{z}{h}\right), \qquad [33a]$$

$$v^*_z = \frac{V}{2} - \frac{1}{r}\frac{\partial}{\partial r}\left[r(Uh - Vr)\left(\frac{z^3}{h^3} - \frac{3z}{4h} - \frac{1}{4}\right) + \frac{Urh}{2}\left(\frac{z}{h} + \frac{z^2}{h^2} + \frac{1}{4}\right)\right], \qquad [33b]$$

$$p^* = p^*_0 + \frac{3\mu^* V}{h^3}(R^2 - r^2) - \frac{6\mu^*}{h^2}\int_r^R U\,dr \qquad [33c]$$

From [3c], [6], [7], and [33a] we obtain again an algebraic equation for U/r, similar to [8], whose solution can be written as

$$U = A_1 r; \quad A_1 = \frac{\beta V}{4h(1+\epsilon_1)}, \qquad [34]$$

with

$$\epsilon_1 = -\frac{a_1 h\mu}{4\mu^*}\sqrt{\left(\frac{A_1}{\nu}\right)}. \qquad [35]$$

When the film as a whole does not perform any translational motion, i.e. when the plane $z = 0$ is immobile, the forces acting upon its upper and lower surfaces must be equal. The balance of forces [22] can then be applied to the upper surface only. Since the boundary conditions at $z = h/2$ and $z = \infty$ are the same as in the previous section, p_{zz} at $\eta = 0$ is given by [26a] with A_1 replacing A_2. The value of p^*_{zz} at $\eta = 0$ is calculated from [33b], [33c] and [34].

$$p^*_{zz}(0) = -p^*_0 - \frac{3\mu^* V}{4h^3}\frac{(1+4\epsilon_1)}{(1+\epsilon_1)}(R^2 - r^2) - 4\mu^* A_1. \qquad [36]$$

Thus with [4], [28], and [22] we obtain

$$\frac{3\mu^* VR^2}{8h^3}\frac{(1+4\epsilon_1)}{(1+\epsilon_1)} = \Delta P + (3.04\mu - 4\mu^*)A_1. \qquad [37]$$

With $\Delta P \gg (3.04\mu - 4\mu^*)A_1$ (see [A.I.3]), and [30], [37] transforms into

$$\frac{V}{V_0} = 4\frac{1+\epsilon_1}{1+4\epsilon_1}. \qquad [38]$$

5. NON-STEADY FLOW IN THE DISPERSION PHASE

For a sufficiently thin plane-parallel film and constant external force (capillary pressure) the flow will be in fact, quasisteady. All time-dependent quantities depend on t only via h, e.g. $v_r = v_r[r, z, h(t)]$ and

$$(\partial v_r/\partial t) = (\partial v_r/\partial h)(\partial h/\partial t) = -V(\partial v_r/\partial h). \qquad [39]$$

This assumption is supported by the finding of Reed *et al.* (1974b) that in most cases their long-time assymptotic formula approximates reasonably well the exact solution for any time interval.

When deriving [23] (respectively [34]) we have not employed [14]. Therefore [23] can be used now, and from [23], [11], [12] and [39] we obtain

$$\frac{\partial v_r}{\partial t} = -V\left(f\frac{\partial A_2}{\partial h} + A_2 f'\frac{\partial \eta}{\partial h}\right)r = -\frac{Vr}{2}\left[(2f + \eta f')\frac{\partial A_2}{\partial h} - A_2\sqrt{\left(\frac{A_2}{\nu}\right)}f'\right]. \qquad [40]$$

From [23] we have $V(\partial A_2/\partial h) = -2A_2^2\kappa_2$ where

$$\kappa_2 = \left(1 - \frac{\partial \ln V}{\partial \ln h}\right)(1+\epsilon_2) + h\frac{\partial \epsilon_2}{\partial h}. \qquad [41]$$

Therefore,

$$\frac{\partial v_r}{\partial t} = \left[(2f + \eta f')\kappa_2 + \frac{V}{2A_2}\sqrt{\left(\frac{A_2}{\nu}\right)}f'\right]A_2^2 r. \qquad [42]$$

The other terms in [14a] are transformed as in the case of a steady flow, so that instead of [15] we obtain

$$f'' + 2f'\int_0^\eta f\,d\eta - f^2 - (2f + \eta f')\kappa_2 = 0, \qquad [43]$$

which after differentiation with respect to η transforms into

$$f'''f' - f''^2 + f''f^2 + (2ff'' - 3f'^2)\kappa_2 = 0. \qquad [44]$$

Substituting $\eta = 0$ in [43], we see that the boundary condition [17b] is replaced by

$$f'' = 1 + 2\kappa_2 \quad \text{at} \quad \eta = 0. \qquad [45]$$

The solution of [44] permits determination of the constant $a_1 = f'(0)$ which, for a non-steady flow, will depend on h through κ_2. In table 1, values of a_1 found by numerical solution of [44] for various values of the parameter κ_2 are presented.

The derivative $\partial v_z/\partial t$ in [14b] is calculated from [13] by using the same arguments as when deriving [42]. Thus we obtain

$$\frac{\partial p}{\partial \eta} = -2\mu A_2\left[f' + 2f\int_0^\eta f\,d\eta - \kappa_2\left(\eta f + \int_0^\eta f\,d\eta\right)\right]. \qquad [46]$$

In [46] we have neglected the term $(V/2)(\partial V/\partial h)$ which is of the order of $V/\sqrt{(A_2\nu)}$ with respect to the other terms. With $\eta \to \infty$, [46] yields $(\partial p/\partial \eta) \to 2\mu A_2\kappa_2 \int_0^\infty f\,d\eta$ = const (see figure 3) so that the boundary condition [3f] cannot be satisfied. The same difficulty arises in the exact non-steady solution of von Kàrmàn's problem for rotation of a disc (see e.g. Loytsianskyi 1962). In both cases this discrepancy is connected with a certain inconsistency of the model. The liquid having reached the film surface (respectively that of the rotating disc), is thrown out toward the periphery and its motion is no longer taken into account. Thus, in order to satisfy the continuity equation [2c] a flux along the axis z must arise which will compensate for the rejected liquid. With steady flow in the boundary layer, this flux is supported by the pressure gradient (see [21] or [46] with $\kappa_2 = 0$) $\partial p/\partial \eta = -2\mu A_2(f' + 2f\int_0^\eta f\,d\eta)$. According to [13], outside the boundary layer (at $\eta >> \eta_l$) the rate of this flux will be constant ($v_z = -2\sqrt{(A_2\nu)}\int_0^\infty f\,d\eta$) and the liquid there will move as a solid body without energy dissipation. Hence $\partial p/\partial \eta$ at $\eta > \eta_l$. For non-steady

Table 1. Dependence of the coefficients a_1 and B on κ_2 (see text)

κ	$-a_1$	B	κ	$-a_1$	B
−0.80	0.342	6.49	0.10	1.263	2.72
−0.70	0.486	5.07	0.20	1.341	2.62
−0.60	0.601	4.37	0.30	1.419	2.51
−0.50	0.703	4.02	0.40	1.481	2.44
−0.40	0.802	3.69	0.50	1.504	2.38
−0.30	0.900	3.42	0.60	1.598	2.32
−0.20	0.991	3.18	0.70	1.660	2.27
−0.10	1.082	2.98	0.80	1.722	2.22
0.00	1.189	2.82	0.90	1.771	2.17
			1.00	1.829	2.12
			1.20	1.930	2.07

flow, an additional term, $2\mu A$ $(\eta f + \int_0^\eta f\, d\eta)$, appears in $\partial p/\partial\eta = 0$ (see [46]). It accelerates the motion of the liquid along the axis z. Since at $\eta > \eta_l$ the liquid also alters its velocity with the time, in this case $\partial p/\partial\eta$ does not vanish beyond the boundary layer. In the real bounded system (such as the droplet) this effect can hardly play a significant role in the force balance. Moreover, even with non-steady flow, the liquid motion at $\eta > \eta_l$ does not result in energy dissipation. Therefore when integrating [46] we shall assume $\partial p/\partial\eta = 0$ at $\eta > \eta_l$. Thus from [46] and [3f] we obtain

$$p(0) \quad + 2\mu A_2\left[\left(\int^\infty \quad\right)^2 - \kappa_2\eta_l\int_0^\infty f\, d\eta - 1\right]. \qquad [47]$$

μ and $\int_0 f\, d\eta$ depend, naturally, on h, but for simplicity we shall use the values which are valid for steady flow. From [22], [26], [13], and [47] we obtain

$$\frac{3\mu^* VR^2}{\quad} = \Delta P + (3.0\ldots\ 3.60\kappa_2\mu - 4\mu^*)A_2. \qquad [48]$$

From this with $\mu A_2 \ll 1$ and $\mu^* A_2 \ll 1$ (note that ... 1) an equation is obtained which coincides in form with [28]. However, when calculating ... from [24], the dependence of a_1 on h must be taken into account.

As in the case of a steady flow, the transition from [48] to [29] is equivalent to using the approximation [A I.3]. From a logical viewpoint, rather than integrating [46] approximately, it might be better to substitute, following Prandtl, $\partial p/\partial z = 0$ for [14b] obtaining eventually the same result. We chose the former, less founded way, in order to get at least a rough estimate for the applicability of [29] at non-steady flow (see section 6).

The derivation for the one-sided film is carried out in the same way and [38] is again obtained. In this case

$$\kappa_1 = \frac{2}{3}\left(1 - \frac{\partial \ln V}{\partial \ln h}\right)(1 + \epsilon_1) + \frac{2}{3} h \frac{\partial \epsilon_1}{\partial h} \qquad [49]$$

must be substituted for κ_2 in [44] and [45].

6. DISCUSSION

For derivation of the formulae for the rate of thinning, [29] and [38], three main assumptions are made: 1. for $0 \leqq r \leqq R$ the approximation $h/R \gg 1$ (thin film) has been used, 2. the film has been assumed to be plane-parallel, and 3. the dissipation of the energy resulted by the liquid motion at $r > R$ has been disregarded.

Condition 1 is always well satisfied. In order that condition 2 be fulfilled, special measures must be taken, for the deviations from the plane-parallel form are usually substantial with emulsion films (see e.g. Hartland 1967, 1969). Condition 3 will be probably violated with films of very small radii when the magnitude of the transition region between the film and the meniscus is of the order of the film radius, or with very small droplets whose radii are comparable with the thickness of the boundary layer.

More convenient expressions for ϵ_2 and V can be derived from [23], [24], [29], and [30]:

$$\epsilon_2 = \frac{2}{3B}\left(\frac{\rho h^4 \Delta P}{R^2}\right)^{1/3} \cdot \frac{\mu^{1/3}}{\mu^*} = \epsilon_0 \frac{\mu^{1/3}}{\mu^*}. \qquad [50]$$

and

$$\frac{V}{V_0} = 1 + \frac{3B}{2}\left(\frac{\mu^{*3} R^2}{\mu\rho h^4 \Delta P}\right)^{1/3}, \qquad [51]$$

where

$$B(\kappa_2) = (-4\sqrt{2}\bar{a}_1)^{2/3}; \qquad [52]$$

and $\epsilon_0 = (2/3B)(\rho h^4 \Delta P/R^2)^{1/3}$ denote all factors in [50] which do not depend on the viscosities μ and μ^*. In experimental investigations of the thin liquid films, the values of the parameters determining ϵ_0 are of the order of magnitude of $\rho = 1\ \mathrm{g/cm^3}$, $h = 10^{-5}$ cm, $R = 10^{-2}$ cm and $\Delta P = 10^2\ \mathrm{dyn/cm^2}$. This yields $\epsilon_0 \approx 10^{-5}$ which ensures in practice the validity of the inequality $\epsilon_2 \ll 1$ for all systems. For a one-sided film, instead of [50] we obtain

$$\frac{\epsilon_1^{\,2}}{4+\epsilon_1} = \frac{27B^2}{8}\epsilon_0^{\,3}\frac{\mu}{\mu^{*3}}. \qquad [53]$$

In this case also $\epsilon_1 \ll 1$ for all systems of practical interest.

Because of the idealised model and the approximations used it is extremely difficult to indicate the exact limits of validity of the results obtained. However, it is quite sure that at $\mu \to \infty$ the applicability of [29] and [38] is not grounded, for then the approximations [A.I.1] and [A.I.3] employed when deriving these equations are not fulfilled. Nevertheless it is worth noting that with $\mu \to \infty$ both ϵ_1 and ϵ_2 (see [50] and [53]) tend to infinity so that [29] and [38] turn into Reynolds equation ($V = V_0$). With $\epsilon_1 \ll 1$, [38] turns into the equation $V = 4V_0$ for the velocity of thinning of a one-sided film verging on the upper surface with vacuum (Sheludko & Platikanov 1959–60), while with $\epsilon_2 \ll 1$ [29] and [50] yield

$$V = V_0/\epsilon_2 = B\left(\frac{h^5 \Delta P^2}{\rho\mu R^4}\right)^{1/3}, \qquad [54]$$

which follows also directly from [51]. A remarkable feature of this formula is the absence of the viscosity μ^* of the dispersion medium. This result is visualised by the calculation of energy dissipation. In appendix 2 it is shown that ϵ_2 is approximately equal to the ratio of the energies dissipated per unit film area and unit time respectively in the film and the drops. On the other hand from [24], [23] (with $\epsilon_2 \ll 1$) and [57] we have $\epsilon_2 \approx (\mu h/\mu^*)\sqrt{(V/h\nu)} \approx (\mu h/\mu^*\delta)$. This means that the energy dissipation is merely proportional to the thicknesses h and δ (i.e. the volumes) of the respective regions. Since according to [A.I.2], $h/\delta \ll 1$, with comparable viscosities μ and μ^* the predominant part of the energy will be dissipated in the drops. This effect will increase when h diminishes because $\delta \sim h^{-1/3}$ (see [54] and [57]).

Neglecting in [41] ϵ_2 and $h(\partial\epsilon_2/\partial h)$ (see [A.I.4]),

$$\kappa_2 = 1 + \partial \ln V/\partial \ln h. \qquad [55]$$

The latter equation allows the calculation of κ_2 (and hence of B) from the experimentally obtained function $V(h)$. The dependence of ΔP (i.e. of Π) on h can then be found from [51] and [52]. With the aid of [54], [55] can be written in the form

$$\kappa_2 = -\frac{2}{3}\left(1 + \frac{\partial \ln \Delta P}{\partial \ln h}\right) - \frac{\partial \ln B}{\partial \ln h}. \qquad [56]$$

Comparison of [16] and [44] reveals that the flow will be steady if $\kappa_2 = 0$. Since in the right hand side of [51] there are two quantities dependent on h in an entirely different manner, it is hardly probable that systems exist which obey the equations for steady flow at all thicknesses. The same conclusion was reached by Reed, Riolo & Hartland (1974b).

We have already mentioned that the solution of [14], represented graphically in figure 3, can be interpreted by means of the assumption that a boundary layer with thickness $\delta \approx 3.5\sqrt{(h\nu/V)}$

exists. Similar results are also obtained by the direct application of Prandtl's theory (see e.g Loytsianskyi 1962; Schlichting 1955) according to which

$$\delta = R/\sqrt{(Re)} = R/\sqrt{(U_0 R/\nu)} \approx \sqrt{(h\nu/V)}, \quad [57]$$

where Re is the Reynolds number and $U_0 = A_2 R \approx VR/2h$. The good agreement of the results obtained by the two approaches is illustrated by curve 3 in figure 3, which represents the function $f(\eta)$ calculated from the solution for steady flow on the basis of Prandtl's approximation (Ivanov & Traykov 1971–72). The formula for the velocity of thinning at $\epsilon_2 \ll 1$ derived in (Ivanov & Traykov 1971–72) for steady flow coincides with [49] but with $B = 2.98$ instead of the value 2.82 obtained in the present work.

The coincidence of some results obtained in the present paper with those obtained earlier (Ivanov & Traykov 1971–72) by von Kàrmàn–Pohlhausen's method does not mean that the validity of the present theory is restricted by the applicability of Prandtl's approximation $\delta/R \ll 1$. Indeed, when using Prandtl's approximation the terms $\partial^2 v_r/\partial r^2 + \partial(v_r/r)/\partial r$ in [2a] are neglected because they are small compared to $\partial^2 v_r/\partial z^2$ when $\delta/R \ll 1$. In the present theory, they are identically zero. This follows from [6] and [10], which are not at all related to Prandtl's approximation. The applicability of the above considerations to the case of non-steady flow is less certain because of the approximation made in deriving [47]. Nevertheless, we believe that despite the divergence of the expression for p at $\eta \to \infty$, the limits of validity of the theory are the same as in the case of steady flow.

In section 1, the theory of Murdoch & Leng (1971) is referenced. They describe the motion of the liquid in the dispersion phase through the adjustable parameter v_d, the radial velocity at a distance R_d from the film surface. These authors consider it possible to assume $v_d = 0$, which means that R_d must coincide with the thickness δ of the boundary layer. If we put $v_d = 0$ and $R_\delta = \delta$ in their equation [38] (see Murdoch & Leng 1971), using our result [20] we obtain again [54], but with $B = 5.8$ instead of $B = 2.82$, showing that the two theories are in qualitative agreement.

There are few experimental works where the thinning of emulsion films from pure (without surfactant) liquids has been investigated (Mackay & Mason 1963; Hartland 1967; Sheely & Leng 1971). Sheely and Leng (1971) report the only data for the symmetrical system of two identical drops treated in our theory. We use their data for Run No. 11, because only in this case were the film radius R and the driving force F (i.e. ΔP) constant during the film thinning. Although the calculations can be performed with variable B, for simplicity we assume that B does not depend on h. From [56] and table 1 we obtain $\kappa_2 = -2/3$ and $B = 4.98$. Integration of [54] yields

$$h_{cr}^{-2/3} - h_0^{-2/3} \approx 3.3\left(\frac{\Delta P^2}{R^4 \rho\mu}\right)^{1/3} \Delta t, \quad [58]$$

where h_0 is the initial thickness at which the film forms, h_{cr} the critical thickness of film rupture (Sheludko 1966) and Δt the time for thinning from h_0 to h_{cr}. According to Murdoch & Leng (1971) $h_0 \approx 10^{-4}$ cm. Using the experimental values $R \approx 5.5 \times 10^{-2}$ cm, $F = 5$ dyn ($\Delta P = F/\pi R^2 = 530$ dyn/cm^2), $\mu = 8.9 \times 10^{-3}$ P, $\rho = 0.995$ g/cm^3 and $\Delta t = 0.062$ sec, from [58] we obtain $h_{cr} \approx 6.3 \times 10^{-6}$ cm which is approximately equal to the measured critical thicknesses of foam films (see Sheludko 1966) and according Murdoch & Leng (1971), is a reasonable value.

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APPENDIX A

We discuss below some approximations used in our theory. The numerical calculations are carried out for steady flow ($B = 2.82$) in a typical system with $\rho = 1$ g/cm³, $h = 10^{-5}$ cm, $R = 10^{-2}$ cm and $\Delta P = 10^2$ dyn/cm². For brevity, only the case of symmetrical films is considered.

1. $V/\sqrt{(A_2\nu)} \ll 1$

From [23], [29] and [30], we have $V/\sqrt{(A_2\nu)} = (1+\epsilon_2)(2hV_0/\epsilon_2)^{1/2}$ which at $\epsilon_2 \ll 1$ gives

$$\frac{V}{\sqrt{(A_2\nu)}} \approx (2B)^{1/2}\left(\frac{\rho h^4 \Delta P}{R^2}\right)^{1/3} \cdot \mu^{-2/3} \approx 5.10^{-3}\mu^{-2/3}. \qquad [A.1.1]$$

With $\epsilon_2 \gg 1$ $(\mu \to \infty)$: $V/\sqrt{(A_2\nu)} \gg 1$, and this approximation is not correct. An alternative expression is obtained from [20] and [23]:

$$\frac{V}{\sqrt{(A_2\nu)}} \sim \sqrt{\left(\frac{Vh}{\nu}\right)} \sim \frac{h}{\delta}, \qquad [A.1.2]$$

which yields $h/\delta \ll 1$.

2. $\mu A_2/\Delta P \ll 1$ or $\mu^* A_2/\Delta P \ll 1$
Equations [23], [29], [30] and [50] yield

$$\frac{\mu A_2}{\Delta P} = \frac{\mu V_0}{2h\epsilon_2 \Delta P} = \frac{B}{2}\left(\frac{h^2}{R^4 \rho \Delta P}\right)^{1/3} \mu^{2/3} \approx 6.5 \times 10^{-2} \mu^{2/3}. \qquad [A.1.3]$$

With $\mu \approx 3P$ this ratio will be equal to 0.1, and the approximation will be invalidated. The same expression is obtained for $\mu^* A_2/\Delta P$ but in the final result $\mu^*/\mu^{1/3}$ must be substituted for $\mu^{2/3}$.

3. $h(\partial\epsilon_2/\partial h) \ll 1$
On the basis of [50] we have

$$h\frac{\partial \epsilon_2}{\partial h} \approx \epsilon_2 \ll 1 \qquad [A.1.4]$$

for all systems of practical interest.

APPENDIX B

We prove below that, at least in the case $\delta/R \ll 1$, the parameter ϵ_2 is proportional to the ratio of the energy dissipated in the film and in the drop. Since $(\partial v_r/\partial r)/(\partial v_r/\partial z) \approx (U_0/R)/(U_0/\delta) = (\delta/R) \ll 1$, by using [2c], [11] and [13], it is readily shown that the dissipative function w (Kochin, Kibel & Roze 1965) for the drop can be written as follows:

$$w = \mu\left(\frac{\partial v_r}{\partial z}\right)^2. \qquad [A.2.1]$$

In the thin film approximation the same expression will be true for the flow in the film. The total dissipation of energy per unit time will be $N = 2\pi \int_{r=0}^{R} \int_{z=-h/2}^{\infty} wr\, dr\, dz$ for the drop and $N^* = 2\pi \int_{r=0}^{R} \int_{z=-h/2}^{h/2} w^* r\, dr\, dz$ for the film. So from [A.2.1], [5a], [11], [23] and [24] we obtain

$$\frac{N^*}{N} = \frac{24\mu^*(\nu/A_2)^{1/2}\epsilon_2^2}{h\mu \int_0^\infty f'^2\, d\eta} = -\frac{4a_1}{\int_0^\infty f'^2\, d\eta}\epsilon_2 \approx \epsilon_2. \qquad [A.2.2]$$