DRAINING OF LIQUID FROM THIN AXIALLY SYMMETRIC FILMS

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The problem of the movement of liquid in a thin film under the effect of forces of capillary pressure when one or both film surfaces are retarded is analyzed by the iteration method. The results obtained allow one to trace the evolution of the film, i.e., to construct its profiles at different times and to find the law of its thinning. A comparison is made with experimental data.

The draining of liquid from thin films separating different phases determines in considerable measure the kinetics of the processes of coalescence or coagulation of emulsions and the stability of foams and colloids and is of interest in a number of technological applications (flotation, heterogeneous boiling, the movement of gas–liquid mixtures), which has caused intensive experimental study of the kinetics of the thinning and separation of films [1]. However, in numerous theoretical works it has been possible to construct only very rough models of the thinning based on a considerable idealization of the draining process. The latter is connected with the variety of physical factors which affect this process (capillary forces, molecular interaction of the film surfaces, mass transfer of surface-active substances, etc.), for which a comparative analysis was presented in [2-4], and with the complexity of the mathematical problems which arise.

The modelling of a real film by plane-parallel liquid layers with free or retarded surfaces in the presence of both capillary and molecular forces has become the most widespread. The effect of the diffusion of surface-active substances on the velocity of the liquid near partially retarded surfaces has also been analyzed within the framework of this model [5, 6]. It is clear that such a model is internally inconsistent, since the capillary pressure gradient, which is the main cause of the draining of liquid from the film, should be entirely absent in a plane-parallel layer. A more realistic model of a film of nonuniform thickness, based on a simplified formulation of the mathematical problem, was analyzed by Frankel and Mysels [7], who took into account only the capillary forces.

Finally, a self-similar mode of drainage was studied in [4] with neglect of the molecular forces and the diffusion of surface-active substances. A generalization of the results of [4] to the situation where the surface diffusion of an undissolved substance plays the main role and the van der Waals forces of attraction of the opposite surfaces of the film are important is contained in [8]. An analysis shows that the self-similar modes of [4, 8] can be realized in the case where the total pressure drop between the center and the periphery of the film varies in a special way. In the more general case the nonlinear equations for the film thickness have been studied only by numerical methods (see [9], for example).

1. Let us consider the evolution of the film between a drop (bubble) and a flat solid wall. We shall consider the film as axially symmetric and introduce a cylindrical coordinate system with its center at the point of intersection of the axis of symmetry with the wall. In accordance with experimental data we assume that the thickness h(t, r) of the film varies significantly only over distances considerably exceeding h(t, r) and is not too small (not less than ~1000 Å), so that one can neglect the effect of molecular forces on the drainage process. Since the boundary of the film with the wall is always retarded we will consider only the limiting cases when its boundary with the drop is either completely retarded or is free. Then there is no need to study the transfer of surface-active substances in the system.

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Equations describing the variation in the thickness of the film and the flow of liquid in it were obtained in [4] in the approximation of a thin liquid layer:

$$\sigma\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right]=-\frac{\partial p}{\partial r}=\frac{3n^2\mu}{h^3}Q; \tag{1.1}$$

$$\frac{\partial h}{\partial t}=-\frac{1}{r}\frac{\partial}{\partial r}(rQ),$$

where μ is the viscosity of the liquid in the film; σ is the surface tension at the boundary with the drop; Q(t, r) is the radial flow of liquid in a calculation per unit length of a circle of radius r; p is the pressure; n=1, 2 is the number of retarded surfaces of the film. We note that the flow in the film is assumed to be slow and quasistationary and the shear stress at the boundary with the drop is equal to zero. The latter assumption can be violated in a number of cases and it is necessary to allow for the circulation of liquid within the drop induced by the movement in the film [10]. It is easy to eliminate Q(t, r) from (1.1) and obtain a nonlinear equation in fourth-order partial derivatives for the thickness h(t, r).

The solution of this equation at present can only be obtained numerically, with its form essentially depending on the initial profile h(0, r) of the film, which is not known in advance. Therefore, it is advisable to consider only an approximate solution of the problem, which would have the required degree of universality.

For this purpose let us introduce the following iteration procedure for the construction of the solution. Suppose the i-th iteration $h^{(i)}(t, r)$ for the thickness of the film is known. The corresponding values of the flow and the pressure can be calculated from (1.1) with the condition that the flow is reduced to zero at r=0:

$$Q^{(i)}(t,r)=-\frac{1}{r}\int_0^r \xi\frac{\partial h^{(i)}}{\partial t}\Big|_{r=\xi}d\xi; \tag{1.2}$$

$$p^{(i)}(t,r)=-3n^2\mu\int_0^r\frac{Q^{(i)}}{h^{(i)3}}\Big|_{r=\xi}d\xi$$

(the pressure is reckoned from its value at r=0). The next (i+1)-th iteration $h^{(i+1)}(t, r)$ is then calculated from the equation

$$h^{(i+1)3}\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h^{(i+1)}}{\partial r}\right)\right]=\frac{3n^2\mu}{\sigma}Q^{(i)}, \tag{1.3}$$

which follows from (1.1), in the right side of which the i-th iteration of the flow from (1.2) figures.

Obviously, the conditions of symmetry relative to the axis r=0 lead to the requirements that

$$\frac{\partial h^{(i+1)}}{\partial r}=\frac{\partial^3 h^{(i+1)}}{\partial r^3}=0,\quad r=0. \tag{1.4}$$

In addition, the width of the film (the value $r=a_*$ which determines its outer boundary) and the pressure drop

$$\int_0^{a_*}\frac{\partial p^{(i+1)}}{\partial r}dr=\Delta p=-\frac{2\sigma}{a} \tag{1.5}$$

must be taken as known (given) values, since they are both determined by the geometry of the system and the condition of balance of the forces acting on the drop and hardly depend on the processes in the film. In the general case a_* and a, which represent the average radius of curvature of the drop near the wall, depend on the time. Here for simplicity we will take them as constant, which corresponds to a drop which is in equilibrium [4].

As the zeroth iteration let us examine the function $h^{(0)}(t, r)=H(t)$, where H(t) is the thickness of the film at its center (r=0). From (1.2) we have

$$Q^{(0)}(t,r)=-\frac{1}{2}\frac{dH}{dt}r;\quad \frac{1}{H^3(t)}\frac{dH}{dt}=-\frac{8\sigma}{3n^2\mu a a_*^2}. \tag{1.6}$$

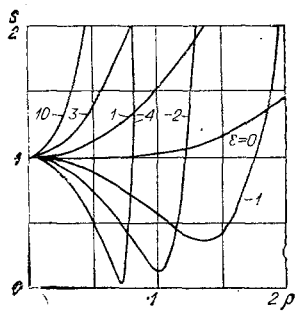

Fig. 1

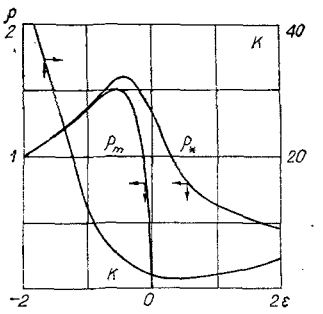

Fig. 2

If one is limited to only this very rough iteration then the second equation in (1.6), which coincides with the well-known equation of Scheludko's model [1], can be considered as the equation determining the law of thinning of the film. For the first iteration we obtain from (1.3) and (1.6)

$$h^3\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right]=\frac{3n^2\mu}{\sigma}Ar;\quad A=-\frac{1}{2}\frac{dH}{dt} \tag{1.7}$$

[the index (1) is omitted for simplicity]. It is convenient to introduce the dimensionless variables s and ρ through the equations

$$h(t,r)=H(t)\,s(t,\rho);\quad r=R\rho;\quad R=H\left(\frac{\sigma}{3n^2\mu A}\right)^{1/4}. \tag{1.8}$$

From (1.4), (1.7), and (1.8) we obtain the problem

$$\frac{\partial}{\partial\rho}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial s}{\partial\rho}\right)\right]-\frac{\rho}{s^3}=0;\quad s=1;\quad \frac{\partial s}{\partial\rho}=0;\quad \frac{\partial^2 s}{\partial\rho^2}=\varepsilon\,(\rho=0). \tag{1.9}$$

Here ε is some unknown parameter, which can be determined in principle using (1.5). Assuming in accordance with experimental data that ε is much smaller than the limiting curvature s = s(t, ρ) of the surface as $\rho\to\infty$, taking the upper limit of integration in the condition (1.5) to infinity, and allowing for (1.1) and (1.8), we obtain from (1.5) the following condition for the determination of ε:

$$\frac{1}{H}\left(\frac{3n^2\mu a^2}{\sigma}A\right)^{1/2}=\frac{2}{K(\varepsilon)};\quad K(\varepsilon)=\lim_{\rho\to\infty}\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial s}{\partial\rho}\right). \tag{1.10}$$

The dimensionless width $\rho=\rho_*$ of the film must be determined from the condition that the pressure (or curvature) gradient is maximal at $\rho=\rho_*$ [11]. Using Eq. (1.9), for ρ_* we have the equation

$$\frac{1}{s^2(\rho_*)}\left(1-\frac{3\rho}{s}\frac{ds}{d\rho}\right)_{\rho=\rho_*}=0;\quad \rho_*=\frac{a_*}{R}. \tag{1.11}$$

Characteristic film profiles $s(\rho;\varepsilon)$ corresponding to different ε are shown in Fig. 1 (the calculations were made for $-7\le\varepsilon\le10$). For $\varepsilon\ge0$ the function $s(\rho;\varepsilon)$ has a minimum at $\rho=0$ and increases monotonically with ρ, the faster, the larger ε. When $\varepsilon<0$ the $s(\rho;\varepsilon)$ curves have a minimum at $\rho=\rho_m(\varepsilon)$, which usually lies very close to the outer film boundary $\rho=\rho_*(\varepsilon)$. Films of just this shape are most often observed experimentally [9, 12].

The dependences of the dimensionless curvature $K(\varepsilon)$ from (1.10) and the values ρ_* and ρ_m on ε are presented in Fig. 2. The function $K(\varepsilon)$ has a minimum at $\varepsilon=0.2$, while $\rho_*(\varepsilon)$ and $\rho_m(\varepsilon)$ have maxima at $\varepsilon=-0.5$.

The dependences of the value $K(\varepsilon)-K(\rho;\varepsilon)$, where $K(\rho;\varepsilon)$ is the dimensionless curvature of the surface $s(\rho;\varepsilon)$ in the region of $\rho<\infty$, on ρ for different ε are plotted in Fig. 3. Actually, this value represents the excess capillary pressure in the film, to which it is proportional. For negative ε the curves of Fig. 3 differ considerably from the parabolic pressure distribution which is realized in a plane-parallel liquid layer (dashed line in Fig. 3) and which follows, for example, from (1.6), and are very close to the pressure profiles observed experimentally [11]. With an increase in ε the pressure profile in the film approaches ever closer to the parabolic profile. Note that the curves in Fig. 3 corresponding to different ε intersect at values of ρ close to the corresponding $\rho_*(\varepsilon)$, which is also observed experimentally [11].

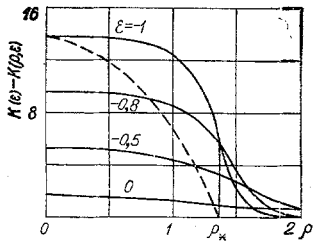

Fig. 3

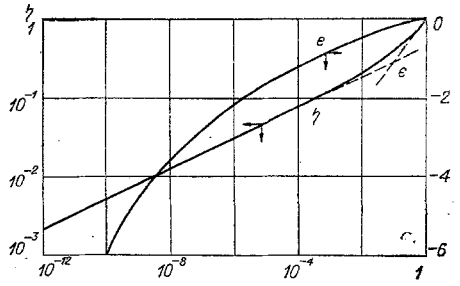

Fig. 4

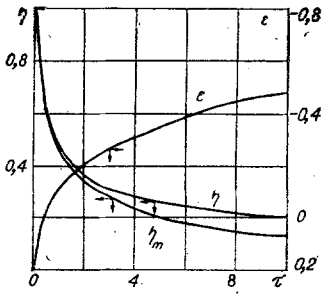

Fig. 5

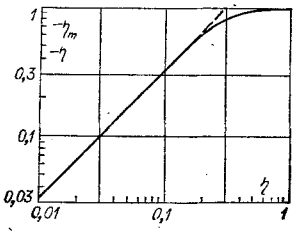

Fig. 6

The next iteration for the film thickness h(t, r) could also be examined in principle. However, a comparison of the results which follow from the analysis of the first iteration with the experimental data (see below) shows that these results are accurate enough not only in a qualitative but also in a quantitative respect. We should emphasize that Eq. (1.7) can be considered as the same as that obtained from (1.11) under the simplifying assumption that Q(t, r) = A(t)r. Such an assumption was actually made in [7], but the equation for h(t, r) was written in an incorrect form.

2. The results of Sec. 1 allow one to construct film profiles corresponding to different ε, but the connection between ε, which in general represents a function of time, and the thickness H(t) of the central part of the film remains unknown. For its determination we use an expression for the dimensional film radius a_* and the dimensional curvature $2/a$ from (1.5)

$$a_* = R\rho_*(\varepsilon);\ 2a^{-1} = HR^{-2}K(\varepsilon), \tag{2.1}$$

where the values of R, K, and ρ_* are determined, respectively, in (1.8), (1.10), and (1.11).

Let us introduce the dimensionless film thickness η at the center and the dimensionless time τ through the equations

$$\eta = H/\varkappa a_*;\ \tau = \varkappa^3\sigma/3n^2\mu a_*;\ \varkappa = a_*/a. \tag{2.2}$$

From (2.1) and (2.2) we have the equations

$$-\frac{d\eta}{d\tau} = \rho_*^4(\varepsilon)\eta^4;\ -\frac{d\eta}{d\tau} = \frac{4}{K^2(\varepsilon)}\eta^2. \tag{2.3}$$

Using the results presented in Fig. 2 to eliminate ε, we obtain the dependence

$$-d\eta/d\tau = f(\eta), \tag{2.4}$$

which is illustrated in Fig. 4. This dependence makes it possible to calculate $\eta = \eta(\tau)$ for an arbitrary initial condition, where the corresponding function $\varepsilon = \varepsilon(\tau)$ is determined from the equation

$$\eta^2(\tau) = 4\rho_*^{-4}(\varepsilon)K^{-2}(\varepsilon), \tag{2.5}$$

which follows from (2.3). This function and the value $\eta = \eta(\tau)$ obtained by numerical integration of Eq. (2.4) are shown in Fig. 5. The condition $\eta(0) = 1$ is used as the initial condition, although the curve $\eta(\tau)$ in Fig. 5 in the region of $\tau - \tau_0 > 0$ can be considered to be just like that corresponding to any initial condition $\eta(\tau_0) < \eta(0)$ when $\tau = \tau_0$.

Thus, the behavior of a thinning film is universal in the sense that the law of thinning is described by a single curve $\eta(\tau)$, the function $\varepsilon(\tau)$ is uniquely determined by the function $\eta(\tau)$ (the dependence of ε on η is illustrated by the corresponding curve in Fig. 4), and the profiles of different films, when reduced to the dimensionless coordinates s and ρ, depend only on ε. As the film becomes thinner the value ε which characterizes its shape decreases monotonically. If $\varepsilon(\tau_0) > 0$ at the initial moment then the shape of the film at first approximates the shape of a plane-parallel layer until the value $\varepsilon = 0$ is reached (see the corresponding profile in Fig. 1). Henceforth ε becomes negative and the minimum of the film thickness approaches ever closer to its periphery, with the relative variation in thickness becoming stronger. These conclusions concerning the general nature of the evolution of a film profile are fully confirmed by experiments in [9, 12]. There is a clear dependence of the film profile on the ratio between its radius a_* and the value a which determines the excess capillary pressure. If $a_* \sim a$, which occurs locally, for example, for films between a drop and a solid wall, then η is small and the film is characterized by a maximum thickness at the center. If $a_* \ll a$, which is often satisfied for films which form a foam, η may be on the order of unity or greater and the minimum thickness is reached in the central part of the film.

Its minimum thickness $H_m(t)$ serves as an important characteristic of a film. Obviously, $H_m(t) = H(t)$ when $\varepsilon > 0$ and $H_m(t) < H(t)$ when $\varepsilon < 0$. The dependence of the value

$$\eta_m = \frac{H_m(t)}{\varkappa a_*} = \frac{H(t)s(\rho_m)}{\varkappa a_*}$$

on τ is also shown in Fig. 5. The intensification of the variation in the film thickness as it becomes thinner is conveniently characterized by the ratio η_m/η, whose dependence on η is illustrated in Fig. 6.

In the region of $\eta \leqslant 0.1$ the function $f(\eta)$ from (2.4) is approximated well by the power function (see the dashed line in Fig. 4)

$$f(\eta) \approx 10\sqrt{2}\eta^5 \approx 26\eta^5. \tag{2.6}$$

In the same region one can assume with high accuracy (see the dashed line in Fig. 6) that

$$\eta_m/\eta \approx 3.33\eta. \tag{2.7}$$

Using (2.6) and (2.7) and considering that $\eta(\tau) \ll \eta(\tau_0)$, in this region we have

$$\eta \approx 0{,}31(\tau - \tau_0)^{-1/4}, \quad \eta_m \approx 0.32(\tau - \tau_0)^{-1/2}. \tag{2.8}$$

In dimensionless form these equations are written as

$$H \approx 0.41\left(\frac{n^2\mu a_*^6}{\sigma a t}\right)^{1/4}; \qquad H_m \approx 0.57\left(\frac{n^2\mu a a_*^2}{\sigma t}\right)^{1/2} \tag{2.9}$$

(for simplicity we took $t_0 = 0$).

These equations, which are valid for small η, have the same structure as the fundamental equations obtained in [7] but differ from them in the numerical coefficients. The latter is evidently connected with the use in [7] of a less exact expression for the curvature of the film surface than that which figures in Eq. (1.7). We note that the approximation (2.7) is rather good down to values of $\eta \sim 10^{-3}$-10^{-4}, although the approximation (2.7) is violated for $\eta < 10^{-3}$, i.e., for sufficiently small η the ratio η_m/η falls off more slowly with time than follows from (2.7). This very fact may explain the deviations of the actual value of η_m/η from the linear function in (2.7) which have been observed experimentally for thin films [12]. One must keep in mind, however, that for thin films the effect of molecular forces on the draining process becomes important. The latter lead either to an acceleration of the thinning (if attraction of the opposite film surfaces occurs) or to the formation of a stationary profile (if a positive disjoining pressure arises in the film).

In the region of $\eta > 0.1$ the thinning of the film occurs faster than according to the law (2.8) and is characterized by the curve in Fig. 5. For $\eta \sim 1$, when the central part of the film differs little from a plane-parallel layer, the following approximation is valid:

$$f(\eta) \approx 1.75\eta^3. \tag{2.10}$$

The use of (2.10) leads to a law of thinning of the same form as follows from (1.6).

Equations of the type of (2.9), which are valid for relatively thin films, are in accordance with the data in [9, 12] where the dependences $H \sim t^{-1/4}$ and $H_m \sim t^{-1/2}$ were obtained experimentally for the final stage of thinning just before the rupture of the film (the duration of this stage was 10^{-2}-10^{-3} for the films

studied in [9, 12]). A comparison between the limiting values of H^4t and H_m^2t obtained in [9, 12] and those estimated on the basis of (2.9) indicates a satisfactory description of the final stage of thinning on the basis of the proposed theory.

According to the experimental data in [9, 12], in the initial stage of thinning the values of H^4t and H_m^2t increase monotonically from zero to the indicated limiting values. A similar conclusion also follows from the theory, which allows one to construct the dependence of these values on t using the curves in Figs. 5 and 6.

In conclusion, we note that the law of thinning $H \sim t^{-1/4}$ is also valid for thin films formed during the penetration of a solid sphere or a drop through the boundary of separation of two liquids (see the experimental results in [3], for example).

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