Physicochemical Hydrodynamics

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The shear stress exerted on the liquid film is given by

$$F=\mu\frac{1}{r}\left(\frac{\partial u}{\partial\varphi}\right)=$$
$$=\frac{r}{2}\cdot\frac{\partial p}{\partial x}\operatorname{tg}2\alpha+\frac{R}{2}\frac{\partial p}{\partial x}\frac{4}{\alpha}+\sum_{n=0}^{\infty}(-1)^{n+1}\frac{1}{\left[(2n+1)\frac{\pi}{2\alpha}\right]^{2}-4}\left(\frac{r}{R}\right)^{\frac{(2n+1)\pi}{2\alpha}-1} \quad (132.8)$$

The shear stress becomes zero at r = 0 and at r = R.

For small angles of the sector the sum of the series is small compared to the first term on the right, and

$$F\approx\frac{r}{2}\left(\frac{\partial p}{\partial x}\right)\operatorname{tg}2\alpha. \quad (132.9)$$

Under the action of the stress F a film of thickness h is set into motion with a velocity v given by

$$\mu_{\text{liq}}\frac{v}{h}=F. \quad (132.10)$$

In practice, the thickness h and velocity v are measured with an interferometer. The first is measured directly, while the second is measured by the rate of displacement of the interference bands during the blow-off process.

Thus, using equation (132.10), the liquid viscosity can be determined as a function of the shear stress from a single experiment. In the case of normal liquids, this function is a straight line that passes through the origin. At the same time, the blow-off method can be used to determine the thickness of a moving liquid layer. In other words, interferometric measurements can be used to determine that distance from the solid surface at which the liquid particles can undergo displacement relative to the wall.

According to experimental measurements, this distance does not exceed $5\cdot10^{-7}$ cm. This should be considered as the most accurate value for the minimum distance from a solid surface at which a liquid retains its mobility.

The blow-off method and its modifications are widely used in the study of hydrodynamic properties of liquids [4].

133. THICKNESS OF FILM REMAINING ON THE SURFACE OF A SOLID WITHDRAWN FROM A QUIESCENT LIQUID

As a typical example of steady-state motion of a liquid film where capillary forces play an important part, we examine a solid withdrawn from a quiescent liquid [5]. A thin film of liquid remains on the surface when the solid is withdrawn. The film thickness is of interest from many practical standpoints, for example, that of coating of solids with a layer of a solute. When the solid object is withdrawn from a solution at a constant speed, its surface remains covered by a layer of solution which is of uniform thickness. As the solvent evaporates, a thin layer of the solute remains on the solid surface. It is interesting to determine the dependence of the thickness of the layer on the withdrawal rate and the effect of the physicochemical properties of the solution.

Another important example is the migration of petroleum in earth strata. When such migration occurs in the presence of water and gas, a portion of the petroleum is retained in the pores of the strata. It is of interest to determine the factors that govern the thickness of the petroleum layer retained on the pore surface of petroliferous strata.

The thickness of a liquid film remaining on the surface of a solid body is of great importance in accurate handling of chemical solutions. The walls of vessels, when emptied, retain a layer of the liquid solution which constitutes a source of error in accurate measurement of liquid volumes. The presence of liquid on the walls must be considered in the quantitative analysis of chemical solutions, in the use of capillary viscometers for absolute measurements of viscosity, and other cases where the "emptying error" is one of the principal inaccuracies of the method.

At the same time, determination of the film thickness can serve as a method for measuring liquid viscosity.

In view of the great practical significance of this problem, much published material has been devoted to it. In an official review from the General Electric Company [6], a summary of the research in this field was presented. Later, experimental and theoretical studies on the determination of the thickness of a liquid layer were published [7]. In theoretical studies by Jeffreys [8], the thickness of the liquid layer was determined from the balance between gravitational and viscous stresses developed in the film, but without considering capillary forces.

We show below that in the most important case met in practice, that of slow withdrawal of a solid from a liquid, capillary forces play a basic role and disregarding them leads to completely inaccurate results. Equally erroneous were the computations by Couger and Ward, presented in the review from the General Electric Company mentioned above. In studying the flow of a film the authors not only disregarded capillary forces, but also employed the wrong boundary conditions.

On the basis of certain simplifying assumptions we examine the thickness of the liquid layer remaining on the surface of a solid withdrawn from a liquid. We assume that the curvature of the solid surface is very small compared to the thickness of the film remaining on the surface. In this manner we can consider the body as an infinite plane and the film as a closely adhering parallel liquid layer. We also assume that the vessel containing the liquid is relatively large, so that we may disregard the wall effect on the meniscus in the vicinity of the solid. We limit our analysis to the withdrawal of a plate at a constant, low velocity v_0. The significance of the low velocity is explained later.

Let us assume that the solid is being withdrawn vertically upward [9]. The liquid far from the plate is at rest, and its surface is horizontal. We take this surface as the plane $y = 0$. We direct the y axis in a direction perpendicular to the plate, and the x axis along the plate.

The liquid that wets the surface of the solid forms a meniscus in the vicinity of the plate. The shape of a meniscus near a moving plate differs substantially from that of a meniscus near a stationary plate, the case examined in Section 65.

In the vicinity of a moving plate the liquid is entrained and set into motion behind the plate. This motion is due to the following: 1) transfer of a certain momentum from the plate to the viscous liquid (the liquid particles on the surface of the plate are fully entrained by the latter); 2) the effect of gravity, which causes the liquid to flow down the plate. In addition, capillary pressure acts at the surface of the liquid, producing a meniscus near the plate.

It is evident that the thickness h of the liquid layer that remains on the plate must be a function of the velocity of withdrawal v_0, of the liquid viscosity μ, of the product ρg and of the surface tension σ. It varies, of course, with the height along the plate, and

$$h = h(x).$$

At a sufficient height above the liquid surface, the thickness of the entrained film is extremely small and the motion of the liquid is almost rectilinear. On the other hand, far from the plate, the shape of the meniscus remains virtually undistorted by the motion of the plate.

Thus, the liquid surface may be subdivided into two regions, one in which the liquid is directly entrained by the motion of the plate, and another region where the meniscus is static. The liquid in the first region moves almost parallel to the surface of the plate. In the second region, the liquid is almost motionless. The quantitative considerations given below define accurately the dimensions of these two regions. A separate solution of the hydrodynamic equations must be obtained for each region, and then a smooth matching of the two solutions is required. We begin by analyzing the static meniscus region.

The equation for the shape of a liquid surface with a static meniscus was derived in Section 65. In the case of a plate, this equation is

$$\frac{\frac{d^2h}{dx^2}}{\left[1+\left(\frac{dh}{dx}\right)^2\right]^{3/2}} = \frac{\rho g x}{\sigma}. \tag{133.1}$$

The integral of equation (133.1) that satisfies the condition requiring the liquid surface far from the plate to be a horizontal surface is

$$\frac{\frac{dh}{dx}}{\left[1+\left(\frac{dh}{dx}\right)^2\right]^{1/2}} = \frac{\rho g x^2}{2\sigma} - 1. \qquad (133.2)$$

For a moving plate equation (133.2) is valid only far from the plate, where the thickness of the liquid layer is large and its height x is small.

At large x and small h, the entrainment of the liquid cannot be disregarded. A low value of the film thickness in equation (133.2) corresponds to a transition from the static to the entrainment region. In this case, the liquid film is almost vertical and parallel to the plane y = 0. When the derivative $\frac{dh}{dx} = 0$, the film is in a vertical position. Therefore, the transition to the entrainment region occurs as $\frac{dh}{dx} \to 0$. Equation (133.2) shows that $\frac{dh}{dx} \to 0$ as $x \to \sqrt{2}\left(\frac{\sigma}{\rho g}\right)^{1/2}$. Also, equation (133.1) shows that

$$\frac{d^2h}{dx^2} \to \sqrt{2}\left(\frac{\rho g}{\sigma}\right)^{1/2}.$$

Thus, the solution of the equation for the static meniscus region becomes also the solution for the entrainment region when the following conditions are fulfilled simultaneously:

$$h \to 0, \qquad (133.3)$$

$$\frac{dh}{dx} \to 0, \qquad (133.4)$$

$$x \to \sqrt{2}\left(\frac{\sigma}{\rho g}\right)^{1/2}, \qquad (133.5)$$

$$\frac{d^2h}{dx^2} \to \sqrt{2}\left(\frac{\rho g}{\sigma}\right)^{1/2}. \qquad (133.6)$$

Conditions (133.3) to (133.6) must be satisfied by the function h(x) at the boundary of the static meniscus region. The function h(x) over the entire region can be obtained from a solution for the entrainment region that can be matched with the solution of the static surface equation at the boundary between the two regions. These matching conditions are given by (133.3) to (133.6).

We now turn to the analysis of a liquid film on the plate in the entrainment region.

Here, the liquid motion can be considered to be almost vertical. In the entrainment region the vertical velocity component v_x, which is parallel to the plate, is very large compared to the horizontal component v_y. We examined this type of motion in Section 131.

In slow steady-state motion, the quadratic terms in equation (131.11) may be omitted and, with the body force per unit denoted by g, this equation can be rewritten as

$$\frac{\sigma}{\rho}\frac{d^3h}{dx^3}+\nu\frac{\partial^2 v_x}{\partial y^2}+g=0. \tag{133.7}$$

The boundary conditions here give the entrainment of the film by the rising plate

$$v_x=v_0 \quad \text{at} \quad y=0. \tag{133.8}$$

and

$$\mu\frac{\partial v_x}{\partial y}=0 \quad \text{at} \quad y=h(x). \tag{133.9}$$

Integrating equation (133.7) with respect to y and considering conditions (133.8) and (133.9), we obtain the velocity distribution across the film

$$v_x=v_0-\left(\frac{\rho g}{\mu}+\frac{\sigma}{\mu}\cdot\frac{d^3h}{dx^3}\right)\left(\frac{y^2}{2}-hy\right). \tag{133.10}$$

We introduce the so-called "liquid consumption rate" which represents the liquid flow in the film

$$Q=\int_0^{h(x)} v_x\,dy=\text{const}. \tag{133.11}$$

Substituting v_x from (133.10) into (133.11), we get

$$Q=v_0h+\left(\rho g+\sigma\frac{d^3h}{dx^3}\right)\frac{h^3}{3\mu}. \tag{133.12}$$

Equation (133.12) determines the film thickness h(x) in terms of the given quantities v_0, ρ, g, σ and μ. It is a third-order differential equation. When integrated, three constants appear in the expression for h. In addition, another unknown constant enters equation (133.12), namely, the liquid flow Q. We therefore require four conditions to determine all the constants.

These are the four boundary conditions that must be satisfied by a solution of equation (133.12).

Before turning to a formulation of these conditions, we rewrite (133.12) in dimensionless form.

We introduce a new dimensionless coordinate λ, defined by

$$\lambda=\left(\frac{3\mu}{\sigma}\right)^{1/3}\frac{v_0^{4/3}}{Q}x, \tag{133.13}$$

and a dimensionless liquid film thickness

$$L=\frac{v_0 h(\lambda)}{Q}. \tag{133.14}$$

Introducing λ and L into (133.12), we get

$$\frac{d^3L}{d\lambda^3}-\frac{1-L}{L^3}+\frac{\rho g Q^2}{3\mu v_0^3}=0. \tag{133.15}$$

Now, the boundary conditions that must be satisfied by a solution of (133.15) can be formulated.

At a considerable height above the liquid surface the film must have a constant limiting thickness, and its surface must be parallel to the plate. The limiting thickness h_0 is

$$h_0=\frac{Q}{v_0}.$$

The limiting value of film thickness is obtained at a very high value of x. We may assume with sufficient accuracy that

$$h\to h_0 \quad \text{as} \quad x\to\infty,$$

or

$$L\to 1 \quad \text{as} \quad \lambda\to\infty. \tag{133.16}$$

The condition for the verticality of the liquid surface is

$$\frac{dL}{d\lambda}\to 0 \quad \text{as} \quad \lambda\to\infty. \tag{133.17}$$

Since the surface must be planar, its curvature is zero. This gives

$$\frac{d^2L}{d\lambda^2}\to 0 \quad \text{as} \quad \lambda\to\infty. \tag{133.18}$$

The fourth condition is derived from the matching conditions of the solution of equation (133.15) and the static meniscus equation (133.1). To find the matching conditions we first simplify equation (133.15) on the assumption that its last term is small and may be omitted. This assumption is valid when the flow Q is proportional to the plate velocity v_0 to a power $n>\frac{2}{3}$ and v_0 is sufficiently small.

The computations below show that $Q \approx v_0^{5/3}$ and thus the last term is actually proportional to $v_0^{1/3}$. For a sufficiently low v_0, it is therefore small compared to unity. The other terms of equation (133.15) are dimensionless and of the order of unity. We may therefore write

$$\frac{d^3L}{d\lambda^3} - \frac{1-L}{L^3} = 0. \tag{133.19}$$

Since no dimensional quantities enter equation (133.19), its numerical solution is considerably simplified. Moreover, an important conclusion regarding the fourth boundary condition can be reached. Matching of the solutions of equations (133.1) and (133.19) must occur within a range of film thicknesses that is very large compared to the limiting thickness h_0 (the dimensionless thickness $L = 1$), but at the same time, small compared to the film thickness in the static meniscus region. As shown by (133.5) the region of small meniscus thicknesses corresponds to a definite value of x and to a constant but small value of the surface curvature (as a reminder — with small curvature, the surface is given by $\frac{d^2h}{dx^2}$). The matching condition, therefore, requires a constant curvature of the liquid surface in the matching region. More exactly, it is required that the surface curvature found from the static solution as $h \to 0$ be equal to the curvature of the entrained film as $h \to \infty$. The matching condition in dimensionless form is

$$\left(\frac{d^2L}{d\lambda^2}\right)_{L\to 0}^{\text{stat}} = \left(\frac{d^2L}{d\lambda^2}\right)_{L\to\infty}^{\text{entr}}, \tag{133.20}$$

where $\left(\frac{d^2L}{d\lambda^2}\right)_{L\to 0}^{\text{stat}}$ is the dimensionless static meniscus curvature for small film thicknesses, and $\left(\frac{d^2L}{d\lambda^2}\right)_{L\to 0}^{\text{entr}}$ is the same for the entrained film in a zone of large film thicknesses. Since no dimensional quantities enter equation (133.19), we have

$$\left(\frac{d^2L}{d\lambda^2}\right)_{L\to\infty}^{\text{entr}} = \alpha, \tag{133.21}$$

where α is an unknown constant. Its value may be found from a numerical solution of equation (133.19). Thus, owing to the fact that equation (133.12) could be transformed into a dimensionless equation (133.19), the matching condition can be greatly simplified by using $\left(\frac{d^2L}{d\lambda^2}\right)_{L\to\infty}^{\text{entr}}$ from the simple relation (133.21).

The value of $\left(\frac{d^2L}{d\lambda^2}\right)_{L\to 0}^{\text{stat}}$ is computed easily from (133.6) and from the definition of L and λ given by (133.13) and (133.14), respectively. A simple calculation gives

$$\left(\frac{d^2L}{d\lambda^2}\right)^{\text{stat}}_{L\to 0} \to \sqrt{2}\left(\frac{\rho g}{\sigma}\right)^{1/2}\frac{Q}{v_0^{5/3}}\left(\frac{\sigma}{3\mu}\right)^{2/3}. \quad (133.22)$$

The boundary condition (133.20) can now be rewritten as

$$Q=\frac{\alpha}{\sqrt{2}}\frac{v_0^{5/3}(3\mu)^{2/3}}{\sigma^{1/6}(\rho g)^{1/2}}. \quad (133.23)$$

Numerical integration of (133.19) gives

$$\alpha=0.63. \quad (133.24)$$

Then the liquid flow through one linear centimeter of film breadth is

$$Q=0.93\,\frac{v^{5/3}\mu^{2/3}}{\sigma^{1/6}(\rho g)^{1/2}}. \quad (133.25)$$

The limiting thickness of the liquid layer entrained by the plate is given by [5]

$$h_0=\frac{Q}{v_0}=0.93\,\frac{(\mu v)^{2/3}}{\sigma^{1/6}(\rho g)^{1/2}}. \quad (133.26)$$

Equation (133.26) shows that the limiting thickness of the entrained film is proportional to the withdrawal velocity of the solid and to the liquid viscosity to the 2/3 power. The thickness is but a weak function, however, of the liquid density and surface tension. The very weak dependence of the thickness on surface tension indicates that surface-active agents should have little effect.

The thickness of a pure water film ($\sigma = 72$, $\mu = 10^{-2}$, $\rho = 1$) entrained by the solid is, according to (133.26),

$$h_0\approx 8\cdot 10^{-3}v_0^{2/3}.$$

In deriving equation (133.26), or more exactly, in deriving (133.19) from (133.15), we have neglected $\frac{\rho g Q^2}{3\mu v_0^3}$ as small compared with unity.

Substitution of Q from (133.25) shows that this procedure is valid, provided the following inequality holds

$$v_0\ll\frac{\sigma}{\mu}. \quad (133.27)$$

For pure water, this inequality gives $v_0 \ll 7\cdot 10^3$ cm/sec; for glycerine we obtain $v_0 \ll 40$ cm/sec, etc. Although the above solution is valid in principle only at low velocities, it is always valid for withdrawal velocities encountered in practice with low-viscosity liquids.

For high velocities of withdrawal an expression for h_0 may be derived by dimensional analysis: the thickness of the film remaining on the solid at high withdrawal velocities cannot depend on the nature of the static liquid meniscus. In other words, h_0 is no longer a function of surface tension and is determined exclusively by the quantities g, ρ, μ and v_0. The only combination with the dimension of length that may be constructed of these quantities is the expression $\left(\frac{\mu v_0}{\rho g}\right)^{1/2}$.

Therefore, at $v_0 \gg \frac{\sigma}{\mu}$, we have

$$h_0 = A\left(\frac{\mu v_0}{\rho g}\right)^{1/2}, \tag{133.28}$$

where A is an undetermined constant. It was evaluated by B. V. Deryagin [10] by integrating equation (133.15) and was found to be equal to unity.

In the general case of an arbitrary withdrawal velocity of the plate, we get

$$h_0 = \left(\frac{\mu v_0}{\rho g}\right)^{1/2} f\left(\frac{\mu v}{\sigma}\right), \tag{133.29}$$

where the function $f\left(\frac{\mu v_0}{\sigma}\right)$ takes the form

$$f\left(\frac{\mu v_0}{\sigma}\right) \approx 0.93\left(\frac{\mu v_0}{\sigma}\right)^{1/6} \quad \text{for} \quad \frac{\mu v_0}{\sigma} \ll 1, \tag{133.30}$$

$$f\left(\frac{\mu v_0}{\sigma}\right) \approx 1 \quad \text{for} \quad \frac{\mu v_0}{\sigma} \gg 1. \tag{133.31}$$

Equation (133.29) has been carefully verified in the experiments of B. V. Deryagin and A. S. Titiyevskaya [11] over a wide range of withdrawal velocities.

Figure 109 gives a comparison between the theoretical (solid and broken curves) and measured (circles) values of film thickness.

It is evident that agreement between the theory and experimental data is quite satisfactory. The differences between the computed and the measured thicknesses lie within the range of the experimental error.*

Equation (133.29) may be used to estimate the thickness of the liquid film on a solid of any shape, provided its radius of curvature is extremely large in comparison to the capillary constant $\left(\frac{\sigma}{\rho g}\right)^{1/2}$.

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*The study by B. V. Deryagin and A. S. Titiyevskaya [11] mentions a discrepancy between the experimental values for h_0 and those computed by L. D. Landau and the author. This is based on a misunderstanding. The original article by Landau and Levich contained a serious and obvious typographical error in the substitution of numerical values into equations (133.23) and (133.25); instead of $0.63\frac{\sqrt[3]{9}}{\sqrt{2}} = 0.93$, the text shows = 2.29.

An important experimental verification of the above theory was made by M. M. Kusakov [12]. If some object — a thread, for example — is placed at a certain distance (of the order of the capillary constant) from the plate being withdrawn from the liquid, that object has a significant effect on the film thickness. The object's "shadow" is discovered in interferometric measurements of the film thickness; within the "shadow" the film thickness is less than it is over the balance of the surface of the plate. Introducing the object alters the meniscus, but apparently cannot directly affect the film that remains on the solid. M. M. Kusakov's study clearly demonstrated the role of the meniscus. A change in the meniscus affects the matching conditions, and this, in turn, is reflected in the thickness of the film. Entrainment of liquid by a thin thread ($R < h$)

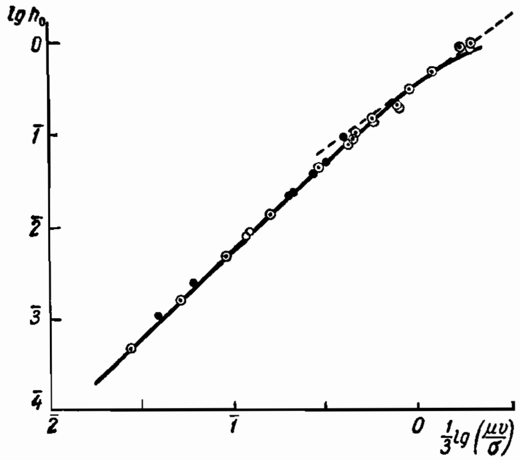

Figure 109. Entrained film thickness h_0 as a function of the dimensionless group $\mu v/\sigma$.

and liquid flow down the thread were theoretically examined by B. V. Deryagin [9] and experimentally verified by V. S. Bondarenko [13]. These studies established that capillary waves appear on the liquid surface film. The importance of surface tension during flow of the film at a large height above the meniscus has thus been established. The development of such capillary waves with time results in break-up of the cylindrical layer into a series of large and small drops that succeed one another at regular intervals. The shape of the drops depends in large measure on the contact angle.

134. WAVE MOTION IN THIN LIQUID LAYERS

As indicated above, the strictly laminar gravity flow down a plate is superseded by a wave regime at Reynolds numbers in excess of