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DYNAMICS OF A DIVERGING LIQUID MENISCUS IN A CAPILLARY, TAKING INTO ACCOUNT THE SPECIFIC PROPERTIES OF THIN FILMS

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The theory of the diverging meniscus of a Newtonian liquid for capillary flow conditions at low meniscus velocities,in which the thermodynamic and rheological features of thin wetting films appear, is set forth. Two cases are considered: thermodynamically stable wetting film with high viscosity in the boundary layer on a completely wetted solid surface and a thermodynamically unstable film on a conditionally wetted solid surface exhibiting a liquid slip effect.

The relation between the thickness h* of the film left on the walls of the cylindrical capillary behind a diverging liquid meniscus and the rate v at which the meniscus travels is determined when studying the properties of wetting films in the capillary method [1]. Extrapolation of h_* (v) to zero velocity makes it possible to find the thickness of equilibrium films with a meniscus in capillaries of various radii R and to thereby determine the basic thermodynamic characteristic of equilibrium wetting films – the wedging pressure isotherm. Moreover, h_* (v) provides information about the rheological properties of wetting films. A theory of the diverging meniscus that would take into account the specific properties of thin films is necessary in order to interpret this information and to correctly extrapolate h_* (v) to zero velocity.

The dynamics of the diverging meniscus of a wetting liquid has been previously considered under the assumption that the film deposited on a solid film surface exhibits the properties of a bulk liquid phase (the viscosity coefficient η_0 and coefficient of surface tension σ are given by tables) [2-4]. Various methods have yielded the equation

$$\sigma d^3h/dl^3 = 3\eta_0 v(1/h^2 - h_*/h^3), \tag{1}$$

which describes steady flow in one direction in a flat film of a Newtonian liquid on a plane (or circular cylindrical) solid surface if flow occurs only due to capillary forces (capillary flow regime). In Eq. (1) h_* is the

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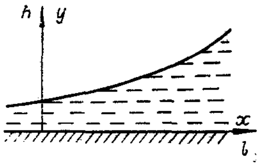

Fig. 1

finite thickness of the wetting surface deposited on the solid surface behind the meniscus, and h is the current thickness of the film for the current coordinate l, counted off along the solid surface in the direction in which the meniscus travels; the coordinate system is bound to the meniscus, i.e., the center of the meniscus is assumed fixed and the solid surface is assumed to travel in the negative direction of the l axis with velocity $|v|$.

Equation (1) expresses the relation between a motive flow force (capillary pressure gradient) and steady flow through a given cross section of a flat film. We will demonstrate that this is so by deriving an analogous equation to take into account the specific properties of thin films. Let us consider flow in the direction x in a flat wetting film on a plane surface (Fig. 1). Suppose the film has constant thickness in the z direction perpendicular to the plane of the figure; the film "profile," i.e., the curve h(x), is invariant over time and in space, while the solid surface moves at a velocity v. Such a steady state is realized near a liquid meniscus moving at a constant velocity in a capillary if the system is considered in the coordinate system given above.

Suppose the motive flow force is a bulk force G (pressure gradient) and that no tangential stress is present on the free surface of the film. If the declivity condition

$$dh/dl \ll 1 \tag{2}$$

holds, the flow velocity component in the direction of the y axis perpendicular to the solid surface can be disregarded and flow can be considered as unidirectional. If the liquid in the film has constant viscosity coefficient and the wall attachment condition is valid, solution of the Navier–Stokes equation for this case leads to the equation

$$q = Gh^3/3\eta_0 - vh,$$

where q is total flow per unit length in the z direction, $Gh^3/3\eta_0$ is the flow component due to the force G, and $-vh$ is the flow component due only to the choice of the moving coordinate system. If G is determined solely by capillary forces, at the distance from the meniscus at which the film acquires a constant thickness h_*, $G = 0$ and $q = vh_*$, i.e., the film travels as a whole together with the wall with a velocity $-v$. Since flow q is identical in the steady state, we have for an arbitrary cross section

$$Gh^3/3\eta_0 = v(h - h_*). \tag{3}$$

In the case of a flat film, the usual capillary forces satisfy the equation [2]

$$G = -dp/dl \approx \sigma d^3h/dl^3, \tag{4}$$

where p is capillary pressure, negative for a concave (to the gas phase) meniscus. Substituting Eq. (4) in Eq. (3), we arrive at Eq. (1).

In order to extend the theory to the case of thin films it is necessary to take into account how the thermodynamic and rheological properties of such films may vary. The thermodynamic features of thin films manifest themselves in the appearance of a wedging pressure P in addition to the usual capillary pressure. The way in which this pressure can be taken into account in the equations of motion of thin films has been set forth in [5]. This method has now become widespread [6, 7] and will be adopted here without any changes. According to [5], the effect of the wedging pressure on flow in a flat film is formally identified with the effect of an external pressure equal to it in magnitude but oppositely directed, i.e., with the effect of an additional force of the same nature as the usual capillary pressure. Here it is assumed that the local value of the wedging pressure in a given cross section of a flat film is a function solely of thickness $[P = P(h)]$, as in the case of a flat film, but is independent of the shape of the surface bounding the film in neighborhoods of the cross section. Thus, Eq. (4) may be replaced by the equation

$$G = -d(p - P)/dl. \tag{5}$$

The equation for G can also include such bulk forces as gravity, though whenever the specific properties of thin films manifest themselves, these forces are usually inessential, and so will be disregarded.

In order to use Eq. (5) in interpreting Eq. (3) it is necessary to have the relation P(h), called the wedging pressure isotherm. In many cases it is expressed by a power law of the form

$$P = -A/6\pi h^n, \tag{6}$$

where A is a constant and $n = \text{const} > 1$. When $n = 3$, Eq. (6) expresses the well-known Gamaker law for nonretarding disperse interaction, and in this case A is called the Gamaker constant (the numerical factor 6π occurs precisely in the Gamaker equation, and is retained here for generality in the case of arbitrary n). We will use Eq. (6) as P(h) for $n = 3$ and 2. These two values of n correspond to experimentally discovered isotherms P(h) for wetting films of low-polar and high-polar liquids [1].

The sign of A is determined by the nature of the energy interaction between the liquid and the solid surface. Negative A corresponds to strong interaction and is realized in the case of a lyophilic (completely wetted) solid surface and corresponds to thermodynamically stable polymolecular liquid films. Positive A corresponds to weak interaction and is realized for a lyophobic (conditionally wetted) solid surface characterized by a strongly nonzero balanced wetting angle. Polymolecular liquid films are thermodynamically unstable on such a surface.

The rheological properties of thin films are taken into account using two rheological models corresponding to the different types of the energy interaction between the liquid and the solid surface. In the case of thermodynamically stable films (lyophilic solid surface) an attachment model will be used in which it is assumed that there is no liquid slip along the surface and that the local viscosity coefficient in the boundary layer is not a single-valued function of the distance to the solid surface.

A slip model, in which it is assumed that the liquid slips as it moves along the solid surface, and where the rate of slip is proportional to the tangential stress on the solid surface, while the viscosity coefficient of the liquid within the film (coefficient of viscous friction) is constant and equal to η_0, will be used for the case of thermodynamically unstable films (lyophobic surface). In both models proportionality between the motive force and the flow under steady-state conditions is retained; in particular, Eq. (3) can be used by replacing η_0 by the effective viscosity coefficient η_e of the film, which is a function of the thickness h of the latter. We may assume that for sufficiently large h, $\eta_e(h)$ in the attachment model is described by the equation

$$\eta_e = \eta_0(1 + k/h), \tag{7}$$

and that

$$\eta_e = \eta_0(1 + k/h)^{-1}, \tag{8}$$

where $k = \text{const} \geq 0$, is valid for all h in the slip model; the coefficients k in Eqs. (7) and (8) are determined by the actual physical properties of the system.

Previously obtained [8] experimental results can be used as a basis for selecting the rheological attachment model, while results given in [9] can be used for selecting the slip model. A more detailed presentation of the effective viscosity coefficient of a thin film (layer) will be given in a future report.

It should be noted that no equilibrium polymolecular ("liquid") film with a meniscus can exist on a lyophobic surface [10]. Only if a diverging meniscus moves fast enough behind it can a film that is uniform in thickness be deposited over a restricted section of the surface. This film will be thermodynamically unstable and before long decomposes into separate drops of liquid. However, if such a film that is uniform in thickness exists for at least a brief time at some distance from the meniscus, the process by which this film decomposes can be disregarded in studying the meniscus dynamics, since in this case it will not affect the shape of the meniscus nor the value of h_* (after the film decomposes h_* will characterize the total mass of the liquid that has been deposited in the form of separate drops on the lyophobic surface). The slip model corresponds to flow conditions precisely in such a "short-lived" wetting film.

If we assume that Eqs. (6)-(8) are valid over the entire range of film thicknesses ($h \geq h_*$) being studied, we find from Eqs. (3) and (5)-(7) for the case of a lyophilic solid surface that

$$\sigma d^3h/dl^3 + nA/6\pi h^{n+1} \cdot dh/dl = (3\eta_0 v/h^3)(1 + k/h)(h - h_*), \tag{9}$$

where $A < 0$. In the case of a lyophobic solid surface Eqs. (3), (5), (6), and (8) imply that

$$\sigma d^3h/dl^3 + nA/6\pi h^{n+1} \cdot dh/dl = (3\eta_0 v/h^3)(h - h_*)/(1 + k/h), \tag{10}$$

where $A > 0$.

TABLE 1

β \ α	0	0,1	0,3	1	3	10	30
0	0,6430	0,6740	0,7392	0,9945	1,8524	5,2073	15,1213
0,1	0,6643	0,6956	0,7611	1,0165	1,8713	5,2195	15,1286
0,3	0.7060	0,7378	0.8039	1,0594	1,9084	5.2437	15,1430
1	0,8439	0,8767	0,9443	1,1998	2.0329	5,3273	15,1936
3	1,1897	1,2237	1,2930	1,5479	2,3542	5,5587	15.3369
10	2,1399	2,1748	2,2453	2,4985	3,2695	6,2984	15.8267
30	4,1222	4,1575	4,2284	4,4799	5,2247	8,0645	17,1418

TABLE 2

β \ α	0	0,1	0,3	1	3	10	30
0	0,6430	0,6604	0,6971	0,8453	1,3738	3,5561	10,1307
0,1	0,6643	0,6818	0,7189	0,8675	1.3931	3,5688	10.1384
0,3	0.7060	0,7239	0,7615	0,9101	1,4311	3,5941	10,1536
1	0.8439	0,8625	0,9013	1,0502	1,5580	3,6815	10.2068
3	1,1897	1,2092	1,2493	1.3982	1,8842	3.9923	10,3574
10	2.1399	2,1601	2,2011	2,3491	2,8073	4.6860	10.8707
30	4,1222	4,1427	4,1840	4,3308	4,7694	6,4871	12,2395

TABLE 3

β \ α	0	0,1	0,3	1	3	10	30
0	0,6430	0.6265	0,5955	0,5097	0,3841	0,2499	0,1578
0,1	0,6227	0,6064	0,5760	0,4933	0,3741	0.2455	0,1560
0,3	0,5874	0,5715	0,5423	0,4648	0,3562	0,2375	0,1527
1	0,4999	0,4851	0,4588	0,3944	0,3098	0,2147	0,1426
3	0,3733	0,3602	0,3385	0,2929	0,2375	0,1737	0,1219
10	0,2286	0,2176	0,2026	0,1769	0,1481	0,1151	0.08666
30	0,1298	0,1210	0,1117	0,09223	0,08374	0,06777	0,05387

The film model described by Eq. (9) is said to be a "stable" film, while the model described by Eq. (10) is called an "unstable" film. Note that the terms "stable" and "unstable" used to denote these models differ from the analogous thermodynamic concepts. From the standpoint of equilibrium thermodynamics, film stability is determined only by the sign of the derivative $\partial P/\partial h$; a plane film is stable if $\partial P/\partial h < 0$; and is unstable if $\partial P/\partial h > 0$ [11]. The models used here describe not the equilibrium state, but the flow process of a thin film and presuppose, first, the actual form of the isotherm P(h) and, second, a particular type of rheological properties of the film.

Equations (9) and (10) are analogs to Eq. (1) for the case of stable and unstable thin wetting films, respectively. A film that exhibits the usual properties of the bulk liquid phase, i.e., such that $A = 0$ and $k = 0$, is called ideal. Equations (9) and (10) degenerate into Eq. (1) in the case of an ideal film.

The final purpose of the theory is to determine $h_*(v, R)$. For this purpose we must integrate Eqs. (9) and (10) in order to find the profile of a diverging meniscus in the slippage region and to relate this part of the profile with the profile of the central part of the meniscus in which condition (2) breaks down and Eqs. (9) and (10) become inapplicable.

The way in which Eqs. (9) and (10) are integrated is analogous to the way in which Eq. (1) is integrated [2]. Introduction of the dimensionless variables $y = h/h_*$, $x = (3v\eta_0/\sigma)^{1/3} l/h_*$ and parameters

$$\alpha = -\frac{nA}{6\ \pi\sigma N h_*^{n-1}}; \tag{11}$$

$$\beta = k/h_*, \tag{12}$$

where $N = (3v\eta_0/\sigma)^{2/3}$, makes it possible to represent Eqs. (9) and (10) in dimensionless form:

$$d^3y/dx^3 = \alpha/y^{n+1} \cdot dy/dx + (1 + \beta/y)(1/y^2 - 1/y^3); \tag{13}$$

$$y''' = \alpha y'/y^{n+1} + [1/(y + \beta)](1/y - 1/y^2). \tag{14}$$

The initial conditions of integration for Eqs. (13) and (14) correspond to a smooth transition from the flat part of a meniscus to a film of constant thickness,

$$y \to 1,\ y' \to 0,\ y'' \to 0 \quad \text{as} \quad x \to -\infty. \tag{15}$$

Equations (13) and (14) were numerically integrated under the conditions (15) using the M-222 and BÉSM-4 computers. Analytic solutions of the linear equations

$$z''' = \alpha z' + (1+\beta)z; \tag{16}$$

$$z''' = \alpha z' + z/(1+\beta), \tag{17}$$

into which Eqs. (13) and (14) are transformed as $y \to 1$ under the substitution $z = y - 1$, are used as the initial segments of the integral curves $y(x)$. The particular solution of Eqs. (16) and (17) under the conditions (15) has the form

$$z = C \exp(\varepsilon x),$$

where ε is the real root of the corresponding characteristic equation and C is the constant of integration, which is determined by the choice of the origin of the x axis. Since the origin can be arbitrarily chosen in this problem, C may be assigned any nonzero value that does not affect the final result.

It is clear from the form of the Eqs. (13) and (14) that $y''' \to 0$ as $y \to \infty$ when $n > 1$. Therefore, the integral curve for any particular solution of these equations (corresponding to the actual values of α and β) approaches without limit some limiting parabola described by the equation $y'' = C(\alpha, \beta) = \text{const}$ as $y \to \infty$. This limiting value of the second derivative is used to combine the profiles of the flat and central parts of the meniscus. A method for "combining" both parts of the profile was given a general formulation in [12]. In the cases being considered here $h_* \ll R$ and the radius of curvature of the central part of the meniscus in the xy plane is nearly equal to the radius of the cylindrical capillary R or to half the width of the plane capillary. In this case we have [12]

$$h_* = C(\alpha, \beta) RN, \tag{18}$$

where the coefficient $C(\alpha, \beta)$ is a function of the parameters α and β. If $C(\alpha, \beta)$ is known, the system of equations (11), (12), and (18) provide parametric dependence of h_* on v and R.

In Table 1 can be found values of $C(\alpha, \beta)$ obtained as a result of numerical integration of Eq. (13) for different values of α and β in the case $n = 2$, while Table 2 is constructed for $n = 3$, and Table 3 provides analogous results of integrating Eq. (14) for $n = 3$. When $\alpha = 0$ and $\beta = 0$, $C(\alpha, \beta) \equiv C_0 \equiv 0.643$ and Eq. (18) describes the well-known relation $h_*(v, R)$ for an ideal film [2, 3]

$$h_* = 0.643 RN. \tag{19}$$

The case $\alpha = 0$, $\beta \neq 0$ corresponds to a film with viscosity different from that of an ideal film, but identical to it in terms of thermodynamic properties ($P \equiv 0$). In this case $C(\alpha, \beta) \equiv C(\beta)$ (second column of Tables 1-3) and $h_*(v, R)$ is given by the equation

$$1/\beta = C(\beta)\,(R/k) N, \tag{20}$$

which follows from Eqs. (12) and (18).

The relation $h_*(N, R)$ for this case can be found in Fig. 2, in which curve 1 corresponds to an ideal film, curve 2 to the attachment model of Eq. (7), and curve 3 to the slip model of Eq. (8). Note that all three curves pass through the origin.

As $\beta \to 0$ ($h_* \to \infty$) $C(\beta)$ is expressed by the equation

$$C(\beta) = C_0 \pm (C_0/3)\beta, \tag{21}$$

where the sign of the last term is determined by the selected rheological model. Equations (20) and (21) imply that $h_*(N, R)$ in this case ($P \equiv 0$) approaches asymptote parallel to the line corresponding to a linear dependence ($h_*/k = 1.93RN/k$) for an ideal film and k/3 units from it along the y axis as $N \to \infty$ (Fig. 2, curves 4 and 5). Note that these asymptotes correspond to values of $h_*(N, R)$ for an ideal film if the origin of the h axis (cf. Fig. 1) is shifted $\pm k/3$ units from the solid surface. That is, for large enough h (i.e., small deviations of η_e from η_0), variation of the film viscosity can be formally represented as the result of a decrease (in the attachment model) or an increase (in the slip model) of the effective thickness of the film by k/3 units if the film has normal viscosity (η_0). A similar result can be obtained from the theory for the relation $\eta_e(h)$.

By Eq. (11), if $A \neq 0$, $|\alpha| \to \infty$ as $N \to 0$. If follows from Tables 1 and 2 that $C(\alpha, \beta) \to \alpha/n$ as $\alpha \to \infty$ in the case of stable films, which together with Eqs. (11) and (18) yields the equation

$$h_* \to h_0 = |AR/6\pi\sigma|^{1/n} \quad \text{as} \quad v \to 0. \tag{22}$$

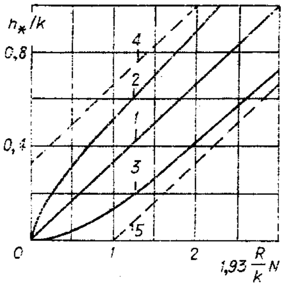

Fig. 2

The quantity h_0 obtained from the hydrodynamic equation as the limiting thickness of a stable film as $v \to 0$ is equal to the thickness of a thermodynamically equilibrium film with a meniscus. It can also be obtained in a purely thermodynamically fashion, which demonstrates that our approach is theoretically correct.

The system of equations (11), (12), and (18) can be transformed by means of h_0 to a more suitable form for practical use. We introduce the variable $N_0 = h_0/C_0R$, where C_0 is a constant and let $H = h_*/h_0$; and $W = N/N_0$; $\gamma = k/h_0$. The coefficient 0.643 occurring in Eq. (19) should be chosen as C_0. Equations (11), (12), and (18) now imply that

$$H = [nC(\alpha,\ \beta)/\alpha]^{1/n}; \tag{23}$$

$$W = [C_0/C(\alpha,\beta)]H = [0.643/C(\alpha,\ \beta)]H; \tag{24}$$

$$\gamma = \beta H = \beta[nC(\alpha,\ \beta)/\alpha]^{1/n}. \tag{25}$$

The system of equations (23)-(25) is equivalent to the system (11), (12), and (18). The variable γ is assumed given. The values of the coefficients $C(\alpha, \beta)$ occurring in Eqs. (23) and (24) are found by solving Eq. (25) for given γ and α using a suitable coefficient table.

The system (23)-(25) makes it possible to construct universal dependences $H(W, \gamma)$. In particular, when $\gamma = 0$ (the rheological properties of a thin film are identical to the properties of an ideal film) isotherms of the type of Eq. (6) have a unique $H(W)$ for given n that is invariant relative to the radius of the capillary and the constants σ, η, A.

Figure 3 depicts the family of curves $H(W, \gamma)$ for stable films when $n = 3$ and $\gamma = 0$, 1, 3, and 10 (curves 2-5, respectively). As $W \to 0$, all the curves other than curve 1, which corresponds to an ideal film, converge at the point ($H = 1$) corresponding to an equilibrium film. Note that this occurs independently of the degree to which the rheological properties of the film vary. When $\gamma = 0$, the curve $H(W)$ asymptotically approaches the line $H = W$ as $W \to \infty$; this line corresponds to an ideal film. When $H = W$, the curves $\gamma \neq 0$, the curve $H(W)$ approaches asymptotes parallel to this line and $\gamma/3$ units along the y axis from it as $W \to \infty$, i.e., the curves approach the same asymptotes as in the case considered above of a film that is thermodynamically identical to an ideal film (the asymptotes of the curves 3-5 are represented by the broken lines 6-8, respectively).

Thus, h_* becomes a function of the isotherms $P(h)$ for sufficiently thick films (correspondingly, sufficiently fast menisci), but the effect of a variation in the viscosity in the boundary layer remains the same for all thicknesses. However, since $h_*/h_i \to 1$ as $v \to \infty$ (h_i is the thickness of an ideal film for given velocities and capillary radii), neither can a variation in viscosity practically be discovered at great film thicknesses. For thin films (slow menisci), on the other hand, the thermodynamic features of thin films exert a more substantial effect than do the rheological features, which leads to a qualitatively new result. Stable films will have an equilibrium thickness, while unstable films will have a critical wetting velocity.

As $\alpha \to \infty$ ($W \to 0$, $H \to 1$), $C(\alpha, \beta)$ for stable films can be expressed by the equation

$$C(\alpha,\ \beta) = \alpha/n + (C_1 + C_2\beta)/\sqrt{\alpha},$$

where C_1 and C_2 are constants that weakly depend on n. We apply this relation to Eqs. (23)-(25), obtaining for $H(W)$ near $W = 0$ the equation

$$H = 1 + (C + C_*\gamma)V, \tag{26}$$

where C and C_* are constants that determine the size of n and $V = W^{3/2} = v/v_i$ (v_i is the meniscus velocity at which the value of h_* for an ideal film is equal to h_0). When $n = 3$, $C = 0.271$ and $C_* = 0.157$, while when $n = 2$, $C = 0.465$ and $C_* = 0.274$.

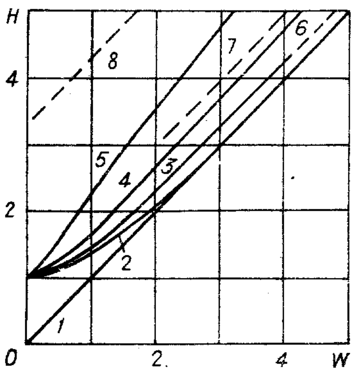

Fig. 3

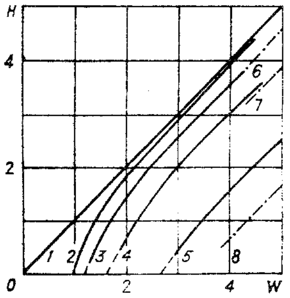

Fig. 4

By Eq. (26), h_* (v) is linear at low velocities, which is of significance if we are to extrapolate experimental h_* (v) to zero velocity in order to find h_0. Moreover, the angle of inclination of the line H(V) at low velocities can be used to find γ, i.e., determine the degree of variation of the rheological properties of a film.

Curves H(W) for unstable films constructed by means of Table 3 are presented in Fig. 4, where curves 1-8 represent the same situations as in Fig. 3. In this case h_0 is only of mathematical importance, since there is no equilibrium wetting film with a meniscus. However, the value of h_0 that can be determined from Eq. (22) makes it possible to also use the system (23)-(25) to construct universal curves for H(W). These curves, as in the case of stable films, approach asymptotes parallel to the line H=W and $\gamma/3$ units along the y axis from it as $W \to \infty$. Every curve intersects the x axis for some critical $W = W_0$ depending on γ. In general, no wetting film is deposited on a lyophilic surface if the meniscus travels slowly.

Near W_0, i.e., as $\alpha \to -\infty$ and $\beta \to \infty$, the solution of Eq. (14) becomes unstable, so that w_0 cannot be determined very accurately. Clearly, there exists a single-valued $W_0(\gamma)$. This dependence can be established by analyzing the function $C(\alpha, \beta)$ as β and $|\alpha|$ tend to infinity in the light of the following considerations. As $W \to W_0$, i.e., as $h_* \to 0$, $C(\alpha, \beta)$ will be such that, according to Eq. (18), after α and β have been replaced by the corresponding expressions from Eqs. (11) and (12), the result can be expressed by the equation

$$C(\alpha,\ \beta)=h_* f(\omega, k), \tag{27}$$

where $\omega = A/\sigma W_0$; and $f(\omega, k)$ is a function of the variables ω and k and is independent of h_*. Moreover, the corresponding values of α and β near W_0 for each point of the curve H(W) (for the given γ) are connected by the equation

$$\alpha/\beta^{n-1}=0.643n/\gamma^{n-1}W_0, \tag{28}$$

which follows from Eqs. (11) and (12).

Equations (27) and (28) make it possible to establish $W_0(\gamma)$ for unstable films. It is clear from Table 3 that at high γ, $C(\alpha, \beta)$ apparently obeys the relation

$$C(\alpha,\ \beta) \approx C/\alpha^s\beta^t, \tag{29}$$

where C, s, and t are constants, as $|\alpha|$ and β tend to infinity. By Eqs. (27) and (28), the exponents of α and β in Eq. (29) will be connected by the relation $s(n-1)+t=1$. Based on the values of the coefficients in the lower right corner of Table 3, we may set $s=0.2$, $t=0.6$, and $C=0.8$. Using these values, for large γ, Eqs. (18) and (29) result in

$$W_0 \approx 0.93\sqrt{\gamma}.$$

When $\gamma=0$ (no slip), $C(\alpha, \beta) \equiv C(\alpha)$ for an unstable film is expressed by the row of Table 3 corresponding to $\beta=0$. By Eq. (27), as $\alpha \to -\infty$ this relation will be expressed by the equation $C(\alpha)=C/\sqrt{\alpha}$, where C is a constant. By analyzing Table 3, we can establish the more exact equation

$$C(\alpha)=0.98/(\sqrt{\alpha}+0.72). \tag{30}$$

Near W_0, Eqs. (18) and (30) imply that when $\gamma=0$, H(W) is given by

$$H=2.17(V-V_0), \tag{31}$$

where $V_0=W_0^{3/2}=0.912$.

By Eq. (31), H(W) is weakly convex to the W axis near W_0, whereas at higher W, the curve for H(W) is weakly concave to this axis, as can be seen in Fig. 4. Thus, there is an inflection point near W_0, and H(W) in this region is generally linear. There are grounds for supposing that H(W) is of the same nature also for nonzero γ. This makes it possible to linearly extrapolate H(W) until the point at which it intersects the x axis in the region of low film thicknesses; in this region it is difficult to determine the exact form of H(W) in view of the instability of the solution of Eq. (14) mentioned above. Segments of the curves for H(W) constructed in this way are depicted in Fig. 4 by dashed–dot lines.

The instability of the solution of Eq. (14) as $|\alpha| \to \infty$ and $\beta \to \infty$ reflects the fact that the process by which film deposited on a lyophobic surface decomposes starts even near the diverging meniscus as the critical wetting velocity $V_0(\gamma)$ is approached (i.e., as $H \to 0$). An investigation of this phenomenon is beyond the scope of the present report.

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