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SPREADING OF A DROP OF VISCOUS LIQUID OVER A SURFACE UNDER THE ACTION OF CAPILLARY FORCES†

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The capillary dynamics of a thin layer of viscous liquid which wets a smooth solid surface is considered. To formulate the problems of wetting dynamics the method of matched asymptotic expansions is used. A general method of closing the asymptotic theory of the dynamic wetting angle which was previously known in the first approximation of a small capillary number is described [1]. For the arbitrary external problem of thin-layer hydrodynamics, which describes the flow outside a small neighbourhood of a moving wetting line, asymptotic boundary conditions are formulated on the wetting line in the third approximation. The transient problem of the spontaneous spreading of a drop of viscous liquid over a solid surface, for which the first-approximation theory is known [2], is solved. The dynamics of the drop is determined for long times. The shape of the drop is obtained in three approximations in the capillary number. The effect of the gravity force on the shape of the spreading drop is determined. The limits of applicability of the model of the quasi-uniform shape of a drop with a dynamic wetting angle which depends on the velocity of the edge of the drop are found.

1. THE BOUNDARY CONDITIONS ON A MOVING WETTING LINE WHEN A THIN LAYER OF LIQUID SPREADS

We will consider the flows of a thin layer of a viscous incompressible liquid over a solid surface when there is no tangential stress on the free surface of the layer and the normal stress is determined by the capillary pressure $p_n = -p_0 + \sigma(R_1^{-1} + R_2^{-1})$ (p_0 is the pressure in the gas, R_1 and R_2 are the principal radii of curvature and σ is the surface tension). The no-slip condition is satisfied on the solid surface.

When the surface is wet, Reynolds number Re falls as one approaches the contact line between the three phases due to the decrease in the layer thickness h, and in a fairly small neighbourhood of this line Re < 1. We will assume that the characteristic maximum thickness h_0 and the characteristic minimum thickness h_m of the layer in creeping flow differ considerably: $s_0 = \ln (h_0/h_m) \gg 1$.

In problems of the wetting of a smooth solid surface, h_m is the minimum thickness of the layer for which a macroscopic description of its flow is appropriate. The value of h_m is usually equal to several molecular dimensions a. For very small dynamic contact angles ($\alpha_0 \ll 1$) relatively large values of h_m ($h_m \gg a$) are possible if the van der Waals forces are ignored in the equations of motion.

The non-linear structure of the creeping flow of a layer in the region of the contact (wetting) line, as we know [1–3], has a universal form. Using the asymptotic solution of the third approximation [1], when $h \gg h_m$ we can write the following relation for the slope α of the tangent to the surface of the layer

$$\alpha^3 = 9\,\mathrm{Ca}\left(s - \frac{1}{3}\ln s + \frac{\ln s - 4}{s} + \ldots\right), \quad \alpha = |\nabla h| \tag{1.1}$$

$$s = \ln(h/h'_m) + C, \quad |s| \gg 1, \quad |\mathrm{Ca}| \ll 1$$

Here ∇ is calculated in coordinates on the solid surface $h'_m \sim h_m$, and the capillary number

$$\mathrm{Ca} = \mu \upsilon_0 / \sigma, \quad \upsilon_0 = (\mathbf{n}\,\partial \mathbf{x}_0 / \partial t)$$

(μ is the dynamic viscosity and n is the normal to the contact line L_0 at the point x_0 directed into the dry surface).

Relation (1.1) holds in a small neighbourhood of the wetting line and corresponds to the condition for the curvature to decrease

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$$d\cos\alpha/dh \to 0, \quad h/h_m \to \infty$$

Note that the terms of the expansion in the large parameter s in (1.1) correspond to successive approximations with respect to Ca, which eliminate the residual in the boundary condition for the normal stress [2, 3].

The parameter $C - \ln h'_m$ of the asymptotic form (1.1) is generally known for the first approximation [1, 2]. We will describe a general method of determining it for the higher approximations. Estimating the angle $\alpha(h_m)$ from the energy equation in the region of the wetting line [2], which holds by virtue of the thermodynamics of irreversible processes, we can write

$$C = \alpha_m^3/(9\,\mathrm{Ca}), \quad \lambda = \alpha_m^3/(9\,\mathrm{Ca}) < 1 \tag{1.2}$$

$$C = \lambda + \tfrac{1}{3}\ln\lambda, \quad \lambda > 1; \quad h'_m = Ka$$

Here a is the size of the molecule of liquid, which determines the lower limit (with respect to the layer thickness) of the region of energy dissipation, and $\alpha_m = \alpha_s$ (α_s is the equilibrium wetting angle and $\alpha_m = 0$ in the case of complete wetting), if we can neglect the non-viscous component of the energy dissipation on the wetting line (for example, dissipation due to kinetic effects [4]). If the dissipation at the microscopic level in the region of the wetting line is considerable, it must be included in the determination of the angle α_m from the energy equation [2].

The coefficient K in (1.5) must, in general, be determined using experimental data, since its accurate value depends on the energy dissipation at the microscopic scale of the flow, where the macroscopic equations are unsuitable. If the dynamic wetting angle is finite or, for small h, the van der Waals forces are not appreciable, we have $K \sim 1$. This is confirmed by a comparison of the first-approximation theory [2, 3], in which $K = 2$, with experiments. For the second and third approximations with respect to s a more vigorous knowledge of the coefficient is necessary.

For very small dynamic wetting angles $\alpha_0 \to 0$ and when the van der Waals forces have a considerable effect, large values of $K \gg 1$ are possible, and for complete wetting ($\alpha_m = 0$) [1]

$$h'_m = (3\,\mathrm{Ca})^{-1/3}(A'/(2\pi\sigma))^{1/2} \tag{1.3}$$

where A' is the difference in the Hamaker constants, which characterize the liquid–solid and liquid–liquid interaction [5]. The coefficient in (1.3) corresponds quite well to the second approximation in (1.1).†

Suppose h_0 is the maximum scale of the layer thickness in the inner region, where the dynamic wetting angle described by (1.2) exists. This definition applies, generally speaking, to the region in the section of the liquid layer orthogonal to the wetting line at the point x_0, and the scale h_0 may change considerably along the line L_0.

In the inner region of relatively great thicknesses ($h \gg h_0$) the line of contact between three phases (the inner line) corresponds to taking the limit as $h/h_0 \to 0$, $\mathbf{x} \to \mathbf{x}_0 \in L_0$. The outer contact line L_0 may not coincide with the microscopic wetting line L_* for very small values of α_0 and when the van der Waals forces have a considerable effect, if in the region of the wetting line an anomalously thin film is moving [1, 6, 7].

The boundary-value problem for determining the transient dynamics of the wetting line L_* was formulated in [8]. This problem will be formulated after the law of motion of L_0 is obtained.

We will simplify the formulation of the hydrodynamic problem using the large parameter s_0. We will limit the outer region by the strong inequality

$$\ln(h_0/h) \ll s_0 \tag{1.4}$$

If the ratio h/h_0 satisfies (1.4), the right-hand side of (1.1) can be represented in the form of a series in powers of $\ln(h/h_0)$. Confining ourselves to two terms of the expansion, we can rewrite (1.1) in a small neighbourhood of the line L_0 in the following form

$$\alpha^3 = \alpha_{(0)}^3(h_0) + 9\,\mathrm{Ca}\left(1 - \frac{1}{3s_0}\right)\ln\frac{h}{h_0} + \ldots, \quad \mathbf{x} \to \mathbf{x}_0 \tag{1.5}$$

†VOINOV O. V. The hydrodynamic theory of wetting. Preprint No. 179-88. Inst. Teplofiz. Sibirsk. Otd. Acad. Nauk SSSR, 1988.

The angle $\alpha_{(0)}$ is found from the asymptotic form (1.1) when $h = h_0$.

The parameter h_0 enables the solution procedure to be refined. Note the linearity with respect to $\ln(h/h_0)$ of the third-approximation relation (1.5). The term with $\ln^2(h/h_0)$ appears in (1.5) only in the fourth approximation with respect to s in (1.1).

Because of condition (1.4) when formulating external problems of the dynamics of a liquid layer a small neighbourhood of the wetting line $L_{(0)}$ is excluded from the region in which $h(\mathbf{x}, t)$ is defined. The non-linear asymptotic form (1.1) or its linearized version (1.5) (with the constraint (1.4)) can be considered as the boundary condition on the wetting line.

2. DYNAMICS OF A SPREADING DROP

The spreading of a drop of viscous liquid over a plane solid surface under the action of capillary forces for small values of the slope of the free boundary α and low Reynolds numbers is described by the evolution equation [9]

$$\frac{\partial h}{\partial t} = -\frac{\sigma}{3\mu}\operatorname{div}(h^3 \operatorname{grad} \Delta h)$$

which has the following form in the axisymmetric case

$$\frac{\partial h}{\partial t} = -\frac{\sigma}{3\mu}\frac{1}{r}\frac{\partial}{\partial r}h^3 r\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial h}{\partial r} \tag{2.1}$$

(r is the radius). At the edge of the drop ($r = r_0$)

$$h/h_0 \to 0 \quad \text{as} \quad r \to r_0 \tag{2.2}$$

The passage to the limit (2.2) is limited by condition (1.4), which is valid by virtue of the fact that $s_0 \gg 1$.

The conditions for the solution to be regular at the drop centre

$$\frac{\partial}{\partial r}\Delta h = 0, \quad \frac{\partial h}{\partial r} = 0 \quad \text{when} \quad r = 0 \tag{2.3}$$

must also be satisfied.

The evolution of the drop shape depends on the initial conditions and, generally speaking, the shape of the surface $h(r, t)$ must be specified at a certain t_0. However, as $t \to \infty$ the solution depends only slightly on the conditions when $t = t_0$ if, in the region of the edge of the drop, the asymptotic form (1.1) or the boundary condition (1.5) holds. Hence, the limit solution, to which the solutions with specified initial conditions are close at long times, is of the greatest interest.

It is necessary to obtain the asymptotic solution of Eq. (2.1) with conditions (1.5), (2.2) and (2.3) as $t \to \infty$. A solution was obtained in [2] in the first approximation. According to this solution the radius of the base of the drop $r_0 \sim t^{1/10}$ as $t \to \infty$.

The left-hand side of (2.1) in the outer region is relatively small at long times. Hence, the solution of Eq. (2.1) can be sought in the form of a series in powers of $\mathrm{Ca} = \mu \upsilon_0/\sigma$ ($\upsilon_0 = \dot{r}_0$) with coefficients which depend on time

$$h = f_0 + f_1 + f_2 + \ldots, \qquad f_n \sim \mathrm{Ca}^n, \quad f_0 = a_0(1 - r^2/r_0^2) \tag{2.4}$$

We obtain the equations for f_n after substituting (2.4) into (2.1) and equating the sums of terms with like powers of Ca.

We will refine the conditions for determining f_n. We will assume, without loss of generality, that the parabolic profile (see Fig. 1) of the zeroth approximation $h = f_0$ defines the volume of the drop V, where the corrections f_n ($n \geq 1$) do not perturb this volume

$$a_0 r_0^2 = \frac{2}{\pi}V; \qquad \int_0^{r_0} r f_n \, dr = 0, \quad n \geq 1 \tag{2.5}$$

By (2.2) we have at the edge of the drop

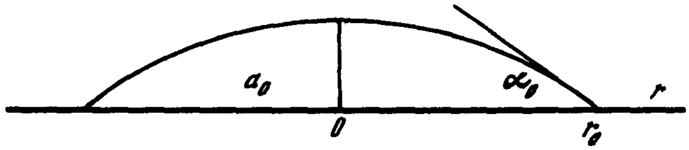

Fig. 1.

$$f_n = 0, \qquad r = r_0 \tag{2.6}$$

In the first approximation, this method gives (in agreement with [2])

$$\alpha_0^3 = (2a_0 / r_0)^3 = \alpha_m^3 + 9\,\mathrm{Ca}\, s_0, \quad h_0 = a_0 \tag{2.7}$$

Note that in [2] a more accurate expression for α_0^3 is given which differs from (2.7) in that it has the additional term $-9\mathrm{Ca}$.

To construct a solution in higher approximation we will represent (2.1), taking (2.3) and (2.4) into account, in equivalent integral form, by introducing the variable z instead of the radius

$$\frac{3\mu r_0^4}{16\sigma h^3}\int_z^1 \frac{\partial' h}{\partial t}\,dz = (1-z)\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial h}{\partial z}, \quad z = 1 - \frac{r^2}{r_0^2} \tag{2.8}$$

$$\frac{\partial'}{\partial t} = \frac{\partial}{\partial t} + 2(1-z)\frac{\upsilon_0}{r_0}\frac{\partial}{\partial z}, \quad \upsilon_0 = \dot{r_0}$$

Hence we obtain equations for the small perturbations f_1 and f_2 in (2.4)

$$(1-z)\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial f_1}{\partial z} = \frac{3\mu r_0^4}{16\sigma f_0^3}\int_z^1 \frac{\partial' f_0}{\partial t}\,dz \tag{2.9}$$

$$(1-z)\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial f_2}{\partial z} = \frac{3\mu r_0^4}{16\sigma f_0^3}\left(\int_z^1 \frac{\partial' f_1}{\partial t}\,dz - \frac{3f_1}{f_0}\int_z^1 \frac{\partial' f_0}{\partial t}\,dz\right) \tag{2.10}$$

The equations of the higher approximations can be written similarly. When determining $f_1, f_2, \ldots$ from (2.5), (2.6) and (2.8) the following problem arises

$$\frac{d^2}{dz^2}(1-z)\frac{d\psi_n}{dz} = \Phi_n(z); \quad n = 1, 2, \ldots \tag{2.11}$$

$$\int_0^1 \psi_n dz = 0; \quad \psi_n = 0,\ z = 0; \quad (1-z)\frac{d\psi_n}{dz} = 0,\ z = 1$$

Specific expressions for Φ_1 and Φ_2 are defined by (2.9) and (2.10).

By calculating the right-hand of (2.9) and integrating (2.11) we obtain, in the second approximation

$$f_1 = \frac{\beta}{a_0^2}\psi_1, \quad \beta = \frac{3}{8}r_0^3\,\mathrm{Ca}, \quad \Phi_1 = -\frac{1}{z^2} \tag{2.12}$$

$$\psi_1 = 2z + \int_0^z \frac{\ln z}{1-z}\,dz$$

Boundary condition (1.5) can be satisfied for solutions of the second and third approximations simultaneously.

3. THE OUTER SOLUTION $h(r, t)$ IN THE THIRD APPROXIMATION

We will consider the most interesting case of complete wetting ($\alpha_m = 0$). The following relations hold for the coefficient β in (2.12) by (2.7)

$$\frac{\beta}{a_0^2} = \frac{a_0}{3s_0} + \ldots, \quad \left(\frac{\beta}{a_0^2}\right)^{\cdot} = \frac{\dot{a}_0}{3s_0} + \ldots \tag{3.1}$$

Using (2.5), (2.7), (2.12) and (3.1) we obtain from (2.10)

$$\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial f_2}{\partial z} = \frac{\beta^2}{a_0^5}\Phi_2 + \ldots, \quad \Phi_2 = \frac{2\psi_1}{z^3} \tag{3.2}$$

Integrating problem (2.11) corresponding to (3.2) we obtain

$$f_2 = \frac{\beta^2}{a_0^5}\psi_2, \quad \psi_2 = (\ln z - z - 4)\int_0^z \frac{\ln z}{1-z}dz - \frac{3}{2}\int_0^z \frac{\ln^2 z}{1-z}dz - 9z - \frac{z}{2}\ln^2 z + 2Iz \tag{3.3}$$

$$I = \int_0^1 \frac{\ln^2 z}{1-z}dz = 2\zeta(3) = 2{,}4041\ldots$$

($\zeta(x)$ is the Riemann zeta-function).

We take the limit as $z \to 0$ in the expression for the slope α for solution (2.4), (2.12) and (3.3)

$$\alpha = \frac{2}{r_0}\frac{\partial h}{\partial z} = \frac{2}{r_0}\left(a_0 + \frac{\beta}{a_0^2}\psi_1' + \frac{\beta^2}{a_0^5}\psi_2'\right) \tag{3.4}$$

$$\psi_1' = 2 + \ln z + \ldots, \quad \psi_2' = 2I - 6 - (2 + \ln z)^2 + \ldots$$

Using (3.1) we obtain from (3.4)

$$\alpha^3 = \alpha_0^3 + 9\mathrm{Ca}(2 + \ln z + (2I - 6)/3s_0), \quad z \to 0 \tag{3.5}$$

$$\alpha_0 = 2a_0 / r_0$$

We express $\ln(h/h_0)$ for $h_0 = a_0$ in (1.3) in terms of $\ln z$ using (2.4) and (3.1) and bearing in mind the inequality $f_0 \gg f_1$. We obtain

$$\ln(h/a_0) = \ln z + (1 + \ln z)/(3s_0) + \ldots, \quad z \to 0$$

As a result, boundary condition (1.5) takes the form

$$\alpha^3 = \alpha_{(0)}^3(a_0) + 9\mathrm{Ca}(\ln z + 1/(3s_0)) + \ldots, \quad z \to 0 \tag{3.6}$$

($\alpha_{(0)}$ is given by (1.1) with $h = a_0$). By requiring that (3.5) and (3.6) should be identical we obtain the dynamic wetting angle α_0 of a spherical segment of equivalent volume

$$\alpha_0^3 = 9\mathrm{Ca}\left(s_0 - 2 - \frac{\ln s_0}{3} + \frac{\ln s_0 + c_0}{9s_0}\right), \quad s_0 = \ln\frac{a_0}{h_m'}$$

$$\alpha_0 = 2a_0 / r_0, \quad c_0 = 17 - 12\zeta(3) = 2{,}575\ldots \tag{3.7}$$

The relatively small value of the contribution of the last term in (3.7), corresponding to the third approximation (the second makes a considerable contribution) indicates the effectiveness of the method of solution. Thus, for $s_0 = 10$, which is typical for macroscopic drops, the term of the second approximation is 28% of s_0, which is a relatively large value, while the term of the third approximation is only 0.5%.

Formula (3.7) can be represented in the equivalent form

$$\alpha_0^3 = \alpha_{(0)}^3(h_0) + 0{,}575\ldots\mathrm{Ca}/\,s(h_0) \tag{3.8}$$

$$s = \ln(h\,/\,h'_m), \quad h_0 = a_0 e^{-2}$$

(the quantity $\alpha_{(0)}(h)$ is defined by (1.1)). The quantity h_0 in (3.8) corresponds better to the upper limit of the inner region than the height of the spherical segment a_0, and hence (3.8) should be more accurate than (3.7).

The solution for $\alpha_m = 0$ is an intermediate asymptotic form as $t \to \infty$, since because $\mathrm{Ca} \to 0$, by (1.3) the parameter s_0 decreases and the fundamental condition $s_0 \gg 1$ should break down for sufficiently large values of t.

For incomplete wetting ($\alpha_m > 0$), relaxation of the angle $\alpha_0 \to \alpha_m$ occurs. In the second approximation, using (1.2) we obtain for $\lambda > 1$

$$\alpha_0^3 = \alpha_m^3 + 9\,\mathrm{Ca}[s_0 - 2 - \tfrac{1}{3}\ln(1 + s_0\,/\,\lambda)], \quad s_0 = \ln(a_0\,/\,h'_m) \tag{3.9}$$

Unlike (3.7) there is no term with $\ln s_0$ in (3.9) for long times since $\lambda \to \infty$.

The formulae for the wetting angle (3.7), (3.8) or (3.9) give complete information on the limit dynamics of the edge of the spreading drop. Taking into account the fact that $v_0 = \dot{r}_0$ we obtain an ordinary first-order differential equation (as in [2]), which is easily integrated.

4. THE EFFECT OF THE GRAVITY FORCE ON THE SPREADING OF THE DROP

The axisymmetric spreading of a viscous drop over a horizontal solid surface taking capillary forces and the ponderability of the liquid into account for small angles is described by the equation

$$\frac{\partial h}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{h^3}{3\mu}r\frac{\partial}{\partial r}\left(\rho g h - \frac{\sigma}{r}\frac{\partial}{\partial r}r\frac{\partial h}{\partial r}\right)\right) \tag{4.1}$$

(ρ is the density of the liquid and g is the acceleration due to gravity). A solution of (4.1) will be sought as $t \to \infty$ with conditions (1.5), (2.2) and (2.3).

The spreading of a drop can be described in the first approximation using the model of the equilibrium shape of a free surface in a gravitational field with a dynamic wetting angle which depends on velocity. The weak effect of the gravity force on the spreading of a drop was estimated in [2] using this model. This effect leads, in particular, to a relative slowing of the decrease in the wetting angle, although the spreading is accelerated. It is interesting to obtain the limits of applicability of the equilibrium model with respect to the Bond number

$$B = \rho g r_0^2\,/\,\sigma \tag{4.2}$$

The solution $h(r, t)$ will be sought in the form of a series in powers of Ca and B with coefficients $\varphi_{nm}(r, t)$. Here we take into account the most important terms with the lowest powers

$$h = \sum_{m=0}^{M} B^m \varphi_{0m} + \mathrm{Ca}\sum_{m=0}^{2} B^m \varphi_{1m} + \mathrm{Ca}^2\,\varphi_{20} + \ldots \tag{4.3}$$

$$\varphi_{nm}\,\mathrm{Ca}^n B^m = f_{nm}; \quad f_{n0} \equiv f_n, \quad f_0 = a_0 z; \quad M \geqslant 2$$

The quantities f_n are known from (2.4), (2.12) and (3.3) with $B = 0$.

Terms of the form $\mathrm{Ca}^2 B^m$, $m \geqslant 1$ are not considered in view of the smallness of the term f_{20} that is quadratic in Ca. In view of the fact that the second term in (4.3) is small compared with the first, a quadratic approximation in B, while simultaneously taking into account a large number of terms in the first sum (4.3), is reasonable. To determine the coefficients f_{nm} in (4.3) it is convenient to integrate Eq. (4.1), bearing (2.3) in mind. We obtain

$$\frac{3\mu r_0^4}{16\sigma h^3}\int_z^1 \frac{\partial' h}{\partial t}dz=(1-z)\left[-\frac{B}{4}\frac{\partial h}{\partial z}+\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial h}{\partial z}\right] \tag{4.4}$$

The derivative $\partial'/\partial t$ is defined in (2.8). The conditions for finding the coefficients f_{nm} when $n + m > 0$ follow from (2.3), (2.5) and (2.6)

$$f_{nm}=0,\ z=0;\quad (1-z)\frac{\partial f_{nm}}{\partial z}=0,\ z=1;\quad \int_0^1 f_{nm}dz=0 \tag{4.5}$$

Substituting (4.3) into (4.4) we obtain

$$f_{01}=\frac{1}{48}Ba_0(2z-3z^2) \tag{4.6}$$

To obtain the coefficients in (4.3) it is sufficient to represent the quantities on the left-hand side of (4.4) in the following form

$$h=f_0+f_{01}+f_{02}+f_{10}+\ldots$$

$$f_0^3/h^3=1-3(f_{10}+f_{01}+f_{02})/f_0+6f_{01}^2/f_0^2+\ldots$$

Evaluating the integrals

$$\int_z^1 \frac{\partial' f_0}{\partial t}dz=-\frac{2a_0\upsilon}{r_0}z(1-z),\quad \int_z^1 \frac{\partial' f_{01}}{\partial t}dz=-\frac{a_0\upsilon B}{12r_0}z(1-z)^2$$

we obtain, after substituting (4.3) into (4.4), and equation for f_{11}

$$\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial f_{11}}{\partial z}-\frac{B}{4}\frac{\partial f_{10}}{\partial z}=\frac{\beta B}{48a_0^2}\left(\frac{4}{z^2}-\frac{7}{z}\right)$$

Hence, taking into account the expression for f_{10} using (2.12) and conditions (4.5) we obtain

$$f_{11}=\frac{\beta B}{48a_0^2}\left(\frac{13}{2}z-6z^2-17z\ln z+(13-12z)\int_0^z\frac{\ln z}{1-z}dz\right) \tag{4.7}$$

The term in (4.3) that is quadratic in B, which is independent of Ca, is found from (4.4) with the left-hand side equal to zero. We obtain

$$f_{02}=\frac{1}{1152}B^2a_0(-z+2z^3) \tag{4.8}$$

Using (2.12), (4.6) and (4.8) we obtain from (4.4) an equation for f_{12}

$$\frac{\partial^2}{\partial z^2}(1-z)\frac{\partial f_{12}}{\partial z}-\frac{B}{4}\frac{\partial f_{11}}{\partial z}=\frac{\beta B^2}{1152a_0^2}\left(-\frac{8}{z^2}+\frac{22}{z}-13\right) \tag{4.9}$$

The solution of (4.9) on the basis of expression (4.7) for f_{11} and conditions (4.5)

$$f_{12}=\frac{\beta B^2}{1152a_0^2}\left[\frac{127}{3}z-\frac{79}{2}z^2+4z^3+(-19z+\frac{87}{2}z^2)\ln z+6\left(3z^2-7z+\frac{9}{2}\right)\int_0^z\frac{\ln z}{1-z}dz\right]$$

enables us to obtain, as $z\to 0$

$$\partial f_{12}/\partial z=(1/1152)\beta B^2a_0^{-2}(8\ln z+70/3) \tag{4.10}$$

The other terms in (4.3) give as $z \to 0$

$$\frac{\partial f_{01}}{\partial z} = \frac{Ba_0}{24}, \quad \frac{\partial f_{10}}{\partial z} = \frac{\beta}{a_0^2}(2 + \ln z) \tag{4.11}$$
$$\frac{\partial f_{02}}{\partial z} = -\frac{1}{1152} a_0 B^2, \quad \frac{\partial f_{11}}{\partial z} = -\frac{\beta B}{a_0^2}\left(\frac{7}{32} + \frac{1}{12} \ln z\right)$$

where $\beta = {}^3\!/_8 r_0^3$ Ca from the solution of the first approximation in Ca.

As $r \to r_0$ it follows from (4.10) and (4.11) that

$$\alpha^3 = \alpha_0^3(B) + 9\,\text{Ca}\left[2 + \ln z - \frac{5}{4}\frac{B}{24} + \frac{7}{6}\left(\frac{B}{24}\right)^2 + \ldots\right] \tag{4.12}$$
$$\alpha = \frac{2}{r_0}\frac{\partial h}{\partial z} + \ldots, \quad \alpha_0(B) = \frac{2a_0}{r_0}\left(1 + \frac{B}{24} - \frac{1}{2}\left(\frac{B}{24}\right)^2 + \ldots\right)$$

The fact that there is no contribution from B and B^2 in the coefficient in front of $\ln z$ in (4.12) confirms the correctness of (4.10) and (4.11). The corresponding terms occur in (4.10) and (4.11), but they compensate one another when calculating α^3.

By requiring that (4.12) and (1.5) (or (3.6)) should be identical we obtain

$$\alpha_0^3(B) = 9\,\text{Ca}\left[s_0 - 2 + \frac{5}{4}\frac{B}{24} - \frac{7}{6}\left(\frac{B}{24}\right)^2 - \frac{1}{3}\ln s_0\right], \quad s_0 = \ln\frac{a_0}{h'_m} \tag{4.13}$$

The quadratic perturbation with respect to Ca is identical with the corresponding term in (3.7) and hence is not written in (4.13) for brevity.

The expansions in powers of B which occur in (4.13) lose their significance when $B = 24$. This can be seen if we continue the expansion of $\alpha_0(B)$

$$\alpha_0 = \frac{2a_0}{r_0}\left(1 + b - \frac{1}{2}b^2 + \frac{2}{5}b^3 - \frac{7}{20}b^4 + \frac{11}{35}b^5 - \frac{797}{2800}b^6 + \ldots\right), \quad b = \frac{B}{24} \tag{4.14}$$

Here the coefficients of b^n hardly change with n for $n \gg 1$, and the radius of convergence $b_0 \approx 1$ ($B_0 \approx 24$). We can determine the function $\alpha_0(B)$ in exact form instead of using expansion (4.14), which diverges when $B = B_0$. With a perturbation on the right-hand side of (4.13), which depends on B, the situation becomes more complex, since then the whole series in B becomes difficult to construct.

Note that the quadratic perturbation in B in (4.13) is approximately the same as the linear perturbation for $B = 24$. At this point all the higher terms of the expansion $\sim \text{Ca}B^m$ are obviously important. The sign of the term with B^2 on the right-hand side of (4.13) and the analogy with (4.14) indicate that the exact value of the perturbation in B on the right-hand side of (4.13) should not exceed the first term $(5/96)B$ in order of magnitude. Hence, in view of the fact that $s_0 \gg 1$ formula (4.13) may be approximately true when $B \sim 24$ provided $\alpha_0(B)$ is calculated in exact form. When $B > 24$ the model of the equilibrium shape of the drop loses its meaning.

The equilibrium solution (Ca = 0) of Eq. (4.1) can be written in terms of a modified Bessel function of the first kind of zero order

$$h = \frac{a_0}{2}\left[I_0(\sqrt{B}) - I_0\left(\frac{r}{r_0}\sqrt{B}\right)\right]\Omega(B)$$
$$\Omega^{-1} = I_0(\sqrt{B}) - 2\int_0^1 I_0(\zeta\sqrt{B})\zeta\, d\zeta \tag{4.15}$$

where a_0 is given by (2.4). By (4.15)

$$\alpha_0(B) = -\frac{\partial h}{\partial r}\bigg|_{r=r_0} = \frac{2a_0}{r_0} k(B) \tag{4.16}$$

$$k(B) = \frac{1}{4}\sqrt{B}\, I_0'(\sqrt{B})\Omega(B)$$

The root of the equation $(B\Omega(B))^{-1} = 0$, which has the least modulus, defines the accurate value of the radius of convergence B_0 of the expansion of $\alpha_0(B)$. Calculation gives $B_0 = 26.37$, which confirms the estimate $B_0 \approx 24$ obtained from (4.14).

Hence, the formula for the wetting angle (4.13) is suitable up to relatively high values of the Bond number $B \sim 24$ if $\alpha_0(B)$ is found from (4.16). When $B \leqslant 12$, Eq. (4.13) gives an accuracy in calculating α_0^3 not worse than 1% for $s_0 \sim 10$.

By combining (2.5), (4.2) and the equality $v_0 = r_0^{\cdot}$ with (4.13) and (4.16) we can write a differential equation for the change in the drop radius r_0 for the equation of the change in the wetting angle α_0, which refines the analogous equation of the first approximation [2].

For incomplete wetting ($\alpha_m > 0$) the formula for the dynamic wetting angle α_0, taking the values of B into account for large T, is written in the same way as (3.9).

REFERENCES

1. VOINOV O. V., The slopes of the boundary in moving liquid layers. *Zh. Prikl. Mekh. Tekh. Fiz.* **2**, 92–99, 1977.
2. VOINOV O. V., The hydrodynamics of wetting. *Izv. Akad. Nauk SSSR. MZhG* **5**, 76–84, 1976.
3. VOINOV O. V., The asymptotic form of the free surface of a viscous liquid in creeping motion and the dependence of the wetting angle on velocity. *Dokl. Akad. Nauk SSSR* **243**, 6, 1422–1425, 1978.
4. BLAKE T. D. and HAYNES J. M., Kinetics of liquid/liquid displacement. *J. Coll. Interface Sci.* **30**, 3, 421–423, 1969.
5. BARASH Yu. S., *Van der Waals Forces*. Nauka, Moscow, 1988.
6. HUH C. and SCRIVEN L. E., Hydrodynamics model of steady movement of a solid/liquid/fluid contact line. *J. Coll. Interface Sci.* **35**, 1, 85–101, 1971.
7. HERVET H., de GENNES P. G., Dinamique du mouillage: films precurseurs sur solide "sec". *C. R. Acad. Sci. Paris. Ser. II* **299**, 9, 499–503, 1984.
8. VOINOV O. V., A dynamic theory of the wetting of a solid by a viscous liquid under the action of van der Waals forces. *Zh. Prikl. Mekh. Tekh. Fiz.* **6**, 69–85, 1994.
9. VOINOV O. V., Relaxation of a liquid layer under the action of capillary forces. *Zh. Prikl. Mekh. Fiz.* **1**, 73–77, 1970.

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