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DYNAMIC CONTACT ANGLE FOR WETTING OF A SURFACE BY A VAN DER WAALS FLUID

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We consider the creeping motion of a thin layer of a nonvolatile viscous fluid spreading due to capillary forces over a rigid surface covered by a thin homogeneous film (microfilm). The influence of van der Waals forces on the asymptotic slope of the free boundary of the layer is studied in the region of large thickness, where capillary forces dominate. A solution of the problem of the slope angle is obtained for the entire possible range of the microfilm thickness. In the limit of small thickness of the microfilm, this solution is in agreement with the well-known solution of the problem of the dynamics of wetting of a dry surface in the presence of a precursory film and van der Waals forces. The role of the condition at the end of the precursory film is studied.

1. Basic Equations. In a small neighborhood of a relatively large mass of a fluid spreading over a rigid surface, small-scale flow can be nearly steady. In this case, the outer length scale of this large mass of the fluid can be considered infinite. We shall determine the inner asymptotic form of the free surface, which is necessary for solving various outer problems of the dynamics of wetting. We consider the free surface of a thin layer of a viscous fluid on a flat rigid surface in creeping motion when the layer passes to the relatively large mass of the fluid at one end and, at the other end, it becomes a thin homogeneous film (microfilm) of small thickness (Fig. 1), which is rather large relative to the molecule's size. Motion of the fluid layer under van der Waals and capillary forces is governed by the equation [1]

$$\sigma \frac{d^3h}{dx^3} - \frac{A'}{2\pi h^4}\frac{dh}{dx} - \frac{3\mu v}{h^3}(h - h_+) = 0. \tag{1.1}$$

Here h is the layer thickness ($|dh/dx| \ll 1$), v is the velocity, h_+ is the microfilm thickness, σ is the surface-tension coefficient, μ is the dynamic viscosity, and A' is Hamaker's constant [2] (we assume that $A' > 0$). The microfilm thickness must not exceed 10^{-7} m in order that the contribution of van der Waals forces to the effective pressure inside the film equals $-A'/(6\pi h^3)$. The thin-layer approximation requires that the capillary number ($\mathrm{Ca} = \mu v/\sigma$) be sufficiently small.

One needs to find a solution of Eq. (1.1) that is unbounded ($h \to \infty$) as $x \to -\infty$ and satisfies the boundary conditions

$$\frac{d^2h}{dx^2} \to 0, \qquad x \to -\infty, \qquad h \to h_+, \qquad x \to +\infty. \tag{1.2}$$

The form of the fluid layer in the region of large thickness ($h \to \infty$) is of primary interest. In this region, in the case of zero static contact angle, the angle α of the free-boundary slope (local dynamic contact angle) has the well-known asymptotic form [1, 3]

$$\alpha^3 = \Big(-\frac{dh}{dx}\Big)^3 = 9\,\mathrm{Ca}\Big(\ln\frac{h}{h'_m} - \frac{1}{3}\ln\ln\frac{h}{h'_m}\Big), \quad \ln\frac{h}{h'_m} \gg 1. \tag{1.3}$$

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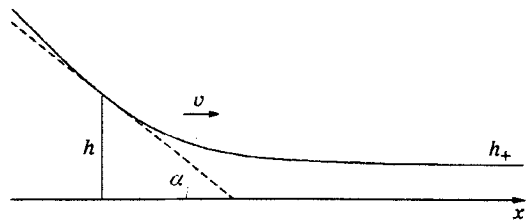

Fig. 1

The problem is to determine the unknown parameter of the asymptotic form h'_m.

We introduce the dimensionless variables [1]

$$\zeta = xh_m^{-1}(3\,\mathrm{Ca})^{1/3}, \quad y = h/h_m, \quad h_m = (A'/(2\pi\sigma))^{1/2}(3\,\mathrm{Ca})^{-1/3}. \tag{1.4}$$

Then, problem (1.1) and (1.2) becomes

$$y''' - \frac{y'}{y^4} - \frac{y - y_+}{y^3} = 0, \quad y_+ = \frac{h_+}{h_m}, \qquad y'' \to 0, \quad \zeta \to -\infty, \quad y' \to 0, \quad \zeta \to +\infty. \tag{1.5}$$

The last condition is equivalent to the conditions $y \to y_+$ and $\zeta \to +\infty$.

The asymptotic form (1.3) corresponds to

$$\Big(-\frac{dy}{d\zeta}\Big)^3 = 3\ln\frac{y}{C} - \ln\ln\frac{y}{C} + \ldots; \tag{1.6}$$

$$h'_m = Ch_m, \qquad C = C(y_+). \tag{1.7}$$

The unknown dimensionless parameter C can be found from the solution of the boundary-value problem (1.5). According to (1.6) [or (1.3) and (1.7)], this parameter determines the effect of the microfilm on the slope of the free surface which varies slowly with distance from the rigid body.

2. Method of Solution. To solve the boundary-value problem, we use calculations of the problems with initial conditions taken for the asymptotic form for large h.

We note that, according to (1.6), for a specified value $z = \ln(y/C) \gg 1$, the error of calculation of the constant C is much higher ($3z$ times) than the error of calculation of the angle α. Therefore, if one takes account of two terms in the asymptotic relation (1.6), it is necessary to use large values of $h/h'_m = y/C \sim 10^5$–10^6 for reasonable accuracy of calculation of C.

In order that the asymptotic solution can be used for much smaller values of y/C (of the order of 10^3–10^4), it is necessary to use high-order terms of the expansion of $\alpha(z)$ for $z = \ln(h/h'_m) \gg 1$ in calculations. This expansion is obtained from the equation

$$y''' = 1/y^2.$$

A rigorous substantiation of the asymptotic solution was given in [1], where this equation was reduced to the first-order equation

$$\frac{dY}{du} = \frac{1}{Y} - u,$$

where $Y = u\,\dfrac{du}{dS}$, $\dfrac{dy}{d\zeta} = u(S)$, $S = \ln\Big(\dfrac{C}{y}\Big)$, and $C = \mathrm{const}$.

Using the variables

$$\Phi(z) = \frac{1}{3}\Big(-\frac{dy}{d\zeta}\Big)^3, \qquad z = \ln\frac{h}{h'_m}, \tag{2.1}$$

following [1], for Φ we write

$$\Phi' = 1 + \Phi'' - \Phi'^2/(3\Phi). \tag{2.2}$$

With allowance for the first boundary condition (1.5), this equation for $z \gg 1$, as the equation in [1], is solved by the iteration method. As a result, we have

$$\Phi = z - \frac{1}{3}q + \sum_{n=1}^{N}(a_{0n}q^n + a_{1n}q^{n-1} + \ldots + a_{nn})z^{-n} + \ldots,$$
$$q = \ln z, \qquad N \geqslant 1. \tag{2.3}$$

The coefficients a_{in} $(i = 0, 1, \ldots, n)$ in (2.3) are calculated for $N = 5$:

$$\Phi = z - \frac{1}{3}q + \frac{q-4}{9z} + \frac{(q-5)^2+18}{54z^2} + \frac{2q^3 - 15q^2 + 300q - 1101}{486\,z^3} + \ldots . \tag{2.4}$$

The first three terms in (2.4) correspond to the similar solution for $u(z) = -y'$ obtained in [1]. Using the first-order equation for $Y(u)$, we obtain an expansion of $S(u)$ as $u \to -\infty$ that is equivalent to (2.4):

$$\ln\left(\frac{C}{y}\right) = \frac{1}{3}u^3 - \ln\frac{|u|}{3^{1/3}} + \frac{4}{3u^3} + \frac{35}{6u^6} + \frac{440}{9u^9} + \frac{7007}{12u^{12}} + \frac{8337\cdot 16}{15u^{15}} + \ldots .$$

The asymptotic solution (2.4) for Φ (2.1) (or the last expansion) ensures that the condition $y'' \to 0$ as $z \to \infty$ holds. To satisfy the second boundary condition in (1.5), we used the shooting method in calculations with the initial data for large y obtained from (2.4). To calculate the constant C with an accuracy of the order of 10^{-3} for $z \geqslant 10$, it suffices to take into account four terms in (2.4).

3. Effect of the Microfilm Thickness (h_+) on the Parameter h'_m of the Asymptotic Slope Angle α. Let us obtain expansions of $C(y_+)$ for small and large y_+. For small y_+, we can write

$$C = C_0 + ay_+ + py_+^2 + \ldots \qquad (y_+ \ll 1), \tag{3.1}$$

where a and p are constants. For large y_+, we rewrite Eq. (1.5) in terms of the variables

$$f = y/y_+, \quad \zeta_1 = \zeta/y_+, \quad f^3 f''' - f'(fy_+^2)^{-1} - f + 1 = 0.$$

Here $y_+^{-2} \ll 1$ and, therefore,

$$C_1 = C/y_+ = b + d/(y_+^2 + g) + O(y_+^{-6}) \qquad (y_+ \gg 1), \tag{3.2}$$

where b, d, and g are constants.

Numerical calculations of problem (1.5) using (1.6) yield the following formulas corresponding to (3.1) and (3.2):

$$C = 1.085 + y_+ + 0.29y_+^2, \qquad y_+ = h_+/h_m < 1; \tag{3.3}$$

$$C = C_1 y_+, \quad C_1 = 1.891 + 0.57/(y_+^2 + 0.18), \quad y_+ > 1, \quad h'_m = C_1 h_+. \tag{3.4}$$

Figure 2 shows results of calculation of the function $C(y_+)$. Plots of functions (3.3) and (3.4) coincide with the curve in Fig. 2.

The slope angle of the free boundary depends on the parameter $h'_m = Ch_m = C_1 h_+$. The role of van der Waals forces is significant for $h_+ \lesssim h_m$. It is important that in the limit $y_+ \to 0$ $(h_+ \ll h_m)$, the solution is in agreement with the solution of the problem of wetting of a dry surface [1]. The value $C = 1.085$ is close to the value $C = 1$ [1]. For small h_+/h_m, we have $h'_m \approx h_m + h_+$.

In the case of $y_+ \gg 1$ $(h_+ \gg h_m)$, where the layer dynamics is determined by capillary forces rather than van der Waals forces, the constant $C_1 = 1.891$ is close to the value 1.84 obtained in [1].

The solution obtained is bounded by fairly small values of the slope angle ($\alpha \ll 1$), for which h_m is large in comparison with the molecule's size [1].

We note that for $h \sim h_+$, the flow in the microfilm region ($h_+ \ll h_m$) does not affect the solution in the region $h \gg h_+$, which is the same as for the wetting of a dry surface. Therefore, the end of the precursory film has no effect on the relatively thick part of the film. It is of interest to compare this result with the case

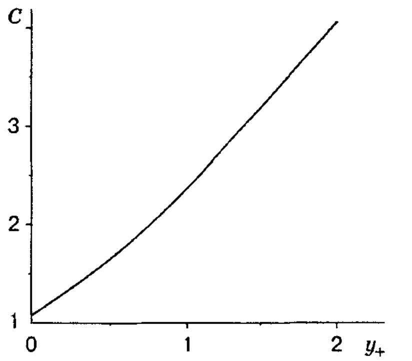

Fig. 2

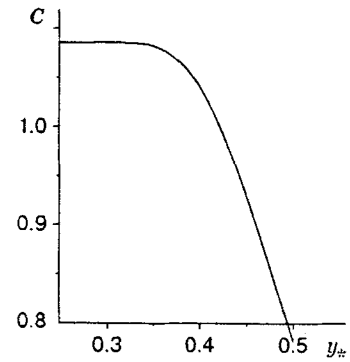

Fig. 3

of perfect wetting where the thickness of an equilibrium film is minimal [4, 5], i.e., the film ends abruptly at $h \approx h_*$.

We carried out calculations of the end effect taking account of the minimum thickness h_* for a dry surface. The minimum thickness h_* was determined using the asymptotic solution for $h \to 0$ when $|dh/dx| \to \infty$ in accordance with the following equation (see, e.g., [6]):

$$\left(\frac{\partial h}{\partial x}\right)^2 = \frac{\lambda^2}{3h^2} - \frac{\lambda^2}{h_*^2} + \ldots, \quad h \to 0, \quad \lambda^2 = \frac{A'}{2\pi\sigma}.$$

The constant C, which, according to (1.4) and (1.7), defines the constant h'_m of the asymptotic slope of the free-boundary (1.3) versus the parameter $y_* = h_*/h_m$, is shown in Fig. 3. For $h_* < 0.45h_m$, the constant C differs from 1 by less than 0.1 ($C > 0.93$), i.e., it is almost independent of the minimum thickness h_*. In this case, there exists a region of the precursory film where $h \approx \text{const}/(x - x_0)$. If $h_* \sim h_m$, the precursory film does not exist. Therefore, the closeness of the constant C to unity ($h_* < 0.45h_m$) is, at the same time, the condition for the existence of the precursory film. The conclusion of [1] that $C \approx 1$ is valid as long as a precursory film exists, irrespective of the minimum thickness h_*. The minimum thickness h_* (as well as the microfilm thickness) does not affect the magnitude of the dynamic contact angle in flows with a precursory film. Therefore, the model of [1] for the transition from a precursory film to a layer moving under capillary forces is valid independently of the end effect, i.e., the model is general.

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