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DYNAMIC EDGE ANGLES OF WETTING UPON SPREADING OF A DROP OVER A SOLID SURFACE

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The hydrodynamic free-boundary problem of the axisymmetric spreading of a viscous-fluid drop over the smooth surface of a solid under the action of capillary forces and under the conditions of weak gravitation is considered. For finite inclination angles of the free surface and small capillary numbers, the problem is reduced to the simpler hydrodynamic problem in a region with known boundary by the asymptotic method. An expression for the dynamic edge angle of the drop is obtained. It is shown that in addition to the local inclination angle of the boundary near the contact line of three phases, one drop has several dynamic edge angles. These angles are calculated for small Reynolds and Bond numbers.

1. The Problem of Drop Dynamics for Large Inclination Angles of the Free Boundary. We consider axisymmetric flows in a drop on a planar solid surface under the action of capillary forces which obey the equation of motion for an incompressible viscous fluid:

$$\rho d\mathbf{u}/dt = -\nabla p + \rho \mathbf{g} + \mu \Delta \mathbf{u}, \qquad \operatorname{div} \mathbf{u} = 0. \tag{1.1}$$

The problem is posed in an "external" region remote from the traveling contact line of three phases, which is possible if there is a large parameter $\ln(h_0/h_m) \gg 1$ (h_0 is the characteristic maximum height of the fluid–gas interface S_0 over the solid surface, and h_m is the minimum height of this interface near the contact line).

The base of the drop is a circle of unknown varied radius $r_0(t)$, and the height of the boundary is $h = 0$ along the circumference of the circle (the contact line) equal to zero in the macroscopic description on a large scale h_0.

We consider a planar cross section of the drop near the point $\mathbf{x}_0$ of the contact line. We put the arc $L_1(\mathbf{x}_e)$ of the circumference (Fig. 1), which is orthogonal to the tangent plane to S_0 at the point $\mathbf{x}_e$ and the planar surface of the solid, in correspondence with each point $\mathbf{x}_e$ of the free surface S_0 with coordinates r and $y = h$. In this manner, we separate the small fluid volume near the contact (wetting) line bounded from the remaining fluid by a surface of revolution with the generatrix $L_1(\mathbf{x}_e)$.

The characteristic height h_0 separates the external and internal regions used in the asymptotic description. In the internal region ($h \ll h_0$), the Reynolds numbers based on the distance h of the interface from the solid are small. For the case of a small capillary number Ca, the universal asymptotic behavior of the inclination angle of the interface $\alpha(h)$ [1–3] exhibits in the large-distance limit from the wetting line ($h/h_m \to \infty$):

$$\frac{1}{2}\int_{\alpha_m}^{\alpha} \frac{d\alpha}{Q(\alpha)} + \mathrm{Ca}\ln\frac{\sin\alpha}{\sin\alpha_*} = \mathrm{Ca}\ln\frac{h}{h'_m}, \quad \mathrm{Ca} = \frac{\mu v_0}{\sigma}, \quad |\mathrm{Ca}| \ll 1, \quad \ln(h/h'_m) \gg 1, \quad h \ll h_0. \tag{1.2}$$

Here $v_0 = dr_0/dt$ is the velocity of the wetting line and σ and μ are the coefficients of surface tension and dynamic viscosity. For the fluid–gas interface, we have $Q = \sin\alpha(\alpha - \sin\alpha\cos\alpha)^{-1}$. The quantities α_m, α_*,

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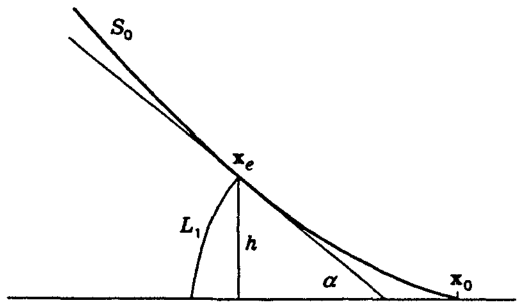

Fig. 1

and h'_m are given in [1–4], α_m is the macroscopic angle, and h'_m is the magnitude of the order of the minimal scale h_m of the distance of the free boundary from the solid surface within the framework of the macroscopic model used. The quantity h'_m can be of the order of the molecular size, which is supported by the analysis of the experiments in [1, 2] and by the conclusion of [3, 5, 6] that the precursory wetting film forms only at very small dynamic angles.

We note that Eq. (1.2) corresponds to the second-order theory with respect to Ca. The term linear in Ca on the left-hand side of (1.2) is similar, for example, to the term in the expression $f + \mathrm{Ca} f = \mathrm{Ca} + \ldots$, which takes into account the quadratic corrections to f for small Ca.

In the second approximation with respect to the small parameter Ca, the condition for the inclination angle of the boundary which corresponds to (1.2) can be set in the external problem [4]:

$$\alpha = \alpha_0 - 2\mathrm{Ca}\, Q_0 \ln(h_0/h) + \ldots, \quad h/h_0 \to 0, \quad Q_0 = Q(\alpha_0), \quad \ln(h_0/h) \ll \ln(h_0/h_m). \tag{1.3}$$

We note that $\alpha_0(h_0)$ is determined by (1.2), and the above inequality restricts the limiting transition in (1.3). The first-order approximation with respect to Ca for the interface in the external region corresponds to $O(1)$.

Excluding the small region near the contact line on the arc $L_1(\mathbf{x}_e)$, which bounds the region, from consideration, we set the velocity $\mathbf{u} = \mathbf{v}^{(0)} + \ldots$, $\mathbf{x} \in L_1(\mathbf{x}_e)$, $\mathbf{x}_e \to \mathbf{x}_0$, where $\mathbf{x}_0$ corresponds to the drop edge ($h = 0$) and $\mathbf{v}^{(0)}$ is the velocity of the creeping flow of a fluid inside the angle α with a moving side.

At the solid surface, the velocity equals zero:

$$\mathbf{u} = 0, \qquad y = 0.$$

Together with equations of motion, we use this condition only at great distances from the contact line.

At the fluid–gas interface S_0, the tangent stress p_τ equals zero, the normal fluid velocity coincides with the surface velocity w, and the mean curvature H corresponds to the normal-stress jump:

$$(\mathbf{un}) = w, \qquad p_\tau = 0, \qquad \mathbf{x} \in S_0; \tag{1.4}$$

$$2\sigma H = p_n + p_0, \qquad \mathbf{x} \in S_0. \tag{1.5}$$

Here p_0 is the gas pressure and p_n is the normal stress in the fluid.

As shown in [7], the allowance for the second-order terms with respect to Ca in the asymptotic behavior of the inclination angle of the free boundary provides better accuracy of the solution for the case $v_0 > 0$ if the angle α is smaller than the critical angle ($\alpha_k \approx 129°$). For $\alpha > \alpha_k$, only the main approximation with respect to Ca is justified.

2. Asymptotic Description of Drop Dynamics. It is known that, for a small capillary number Ca, there is a solution of the unsteady problem of drop spreading according to which the shape of the free surface of the drop is nearly spheroidal [1]. In the first approximation with respect to Ca, the free boundary in the external problem for (1.1) coincides with a segment of the sphere. In the second approximation, its shape can be determined by taking into account viscous stresses ($\mathrm{Ca} \neq 0$). We find the radius of the surface

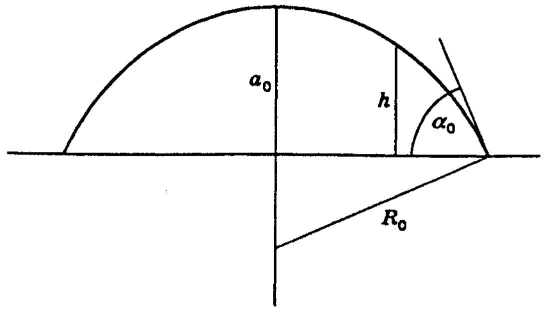

Fig. 2

in the polar coordinates R and θ:

$$R = R_0 + R_1(\theta) + \ldots, \qquad |R_1| \ll R_0. \tag{2.1}$$

Here θ is the polar angle, $\theta = 0$ is the axis of symmetry, and $y = a_0 - R_0$ is the center of the polar system. The time t can enter Eq. (2.1) as a parameter. For a sufficiently large time ($t \to \infty$), the smallness of the ratio R_1/R_0 is ensured by the small capillary number (Ca $\to 0$) and the predominant energy dissipation near the wetting line, which causes the dynamic wetting angle [1]. The details of the initial conditions ($t = 0$) are insignificant. Only the drop volume V and the initial radius $r_0(0)$ of the wetting line, which should be limited, are important.

We assume that a sphere of radius R_0 passes through the perimeter $[r = r_0(t)]$ of the drop base, so that

$$R_1(\theta) = 0, \qquad \theta = \theta_0. \tag{2.2}$$

The radius of the drop base is $r_0 = R_0 \sin\theta_0$. To determine the sphere, it is required to set the second condition in addition to (2.2). We consider three variants of this condition.

1. The radius of the sphere is equal to the radius of curvature of the drop surface at the axis of symmetry determined by the normal stress p_n in the fluid and the pressure p_0 in the gas:

$$p_n\Big|_{\theta=0} + p_0 = -2\frac{\sigma}{R_0}. \tag{2.3}$$

2. The height a_0 of the sphere segment is equal to the height of the drop (h at $\theta = 0$):

$$R_1 = 0, \qquad \theta = 0. \tag{2.4}$$

3. The volume V of the drop is equal to the volume of the sphere segment:

$$\frac{\pi}{2} a_0\left(r_0^2 + \frac{1}{3}a_0^2\right) = V. \tag{2.5}$$

If the shape of the drop is a segment of the sphere, the three spheroidal segments coincide.

It is required to solve the problem [1, 8] of a fluid flow inside the spheroidal segment of height $a_0 = R_0(1 - \cos\alpha_0)$ with varied wetting angle $\theta_0 = \alpha_0(t)$ on the solid surface (Fig. 2). According to (1.4), the tangent stress on the spheroidal segment equals zero, whereas the normal velocity u_R varies in proportion to the velocity of the segment edge v_0 and is proportional to h:

$$p_{R\theta} = 0, \quad u_R = \frac{2r_0 v_0}{r_0^2 + a_0^2}(a_0 - 2h) \ \text{ for } \ R = R_0, \ \ \theta < \theta_0, \ \ v_0 = \frac{dr_0}{dt}, \ \ h = R_0(\cos\theta - \cos\theta_0). \tag{2.6}$$

On the solid base of the segment, the velocity equals zero:

$$\mathrm{u} = 0 \quad \text{for} \quad R\cos\theta = R_0\cos\theta_0, \quad \theta < \theta_0. \tag{2.7}$$

The normal stress p_n on the sphere is found by solving the problem of viscous-fluid dynamics (1.1), (2.6), and (2.7) inside the spreading spheroidal segment (the equation of spreading is given below). In this problem, only the flows with small Reynolds numbers should be considered: $\mathrm{Re} = a_0 v_0/\nu \lesssim 1$ (in the case of small angles $\alpha\mathrm{Re} \lesssim 1$). For large Reynolds numbers ($\mathrm{Re} \gg 1$), the sphere approximation cannot be used, since appreciable deviations of the shape of the drop surface from a sphere are possible owing to the action of inertial forces despite the smallness of the capillary number Ca.

The normal stress on the sphere is of the form

$$p_n = p_{RR} = \frac{\mu}{R_0} v_0 P(\theta) + \mathrm{const}, \qquad P(\theta) = P(\theta, \alpha_0, \mathrm{Re}, t). \tag{2.8}$$

Generally, the dimensionless stress P in (2.8) depends on the angle α_0, the Reynolds number Re, and the time. For a finite Reynolds number, it is apparent that the prehistory of the nonstationary flow inside the spheroidal segment is of importance at each moment. For the case of a small Reynolds number ($\mathrm{Re} \ll 1$), the explicit $P(t)$ dependence is lacking.

To asymptotically match the outside solution and the inside asymptotics in the general form, it is sufficient to take into account only the dependence of P on θ, assuming the dependence on time. The perturbation of the radius R_1 can be determined from the Laplace condition (1.5) written in the following linearized form:

$$\frac{d}{d\theta} \sin\theta \frac{dR_1}{d\theta} + 2R_1 \sin\theta = \Big(\frac{p_n + p_0}{\sigma} + \frac{2}{R_0}\Big) R_0^2 \sin\theta = f(\theta). \tag{2.9}$$

The solution of Eq. (2.9), which is regular at the point $\theta = 0$, contains one arbitrary constant D:

$$R_1 = \cos\theta \Big\{ D + \int_0^\theta \frac{d\varphi}{\sin\varphi \cos^2\varphi} \int_0^\varphi f(\eta) \cos\eta \, d\eta \Big\}. \tag{2.10}$$

The function $f(\theta)$ includes a second arbitrary constant D':

$$f = \Big[D' + \Big(p_n - p_n\Big|_{\theta=0}\Big) R_0^2/\sigma\Big] \sin\theta. \tag{2.11}$$

We note that the perturbation of the radius is quite small ($R_1 \ll a_0$), and Eq. (2.9) is valid if the stress changes little in the central region of the drop compared to the capillary head σ/R_0 and the inclination angle of the free surface at the drop edge differs only slightly from the angle on the sphere:

$$|p_n(\theta) - p_n(0)| \ll \frac{\sigma}{R_0} \quad \text{for} \quad \theta_0 - \theta \sim \theta_0, \qquad |\alpha - \theta| \ll \alpha_0 \quad \text{for} \quad \theta_0 - \theta \ll \theta_0. \tag{2.12}$$

Condition (2.12) is violated in the limit $\theta \to \theta_0$, which is regarded as an intermediate angle restricted by small perturbations of the angle.

The perturbation of the inclination angle of the tangent near the drop edge, which enters the boundary condition (1.3), is of primary interest:

$$\alpha - \alpha_0 = -\frac{1}{R_0} \frac{dR_1}{d\theta} + \ldots, \qquad \theta \to \theta_0. \tag{2.13}$$

Determining the constants in (2.10) and (2.11) with allowance for (2.2) and (2.3)–(2.5), transforming the integrals in the expression for R_1, and using (2.13), we find the following formulas for the inclination angle α of the free boundary near the drop edge:

$$1. \quad \alpha - \alpha_0 = -\frac{R_0}{\sigma \sin\alpha_0} \int_0^\theta \frac{\cos\theta}{\cos\alpha_0} (p_n(\theta) - p_n(0)) \sin\theta \, d\theta + \ldots \quad (\theta \to \theta_0 = \alpha_0); \tag{2.14}$$

$$2. \quad \alpha - \alpha_0 = \frac{R_0}{\sin\alpha_0} \int_0^\theta \Big\{ \cos\theta - (1 + \cos\alpha_0)\Big[1 - \cos\theta \ln\Big(\cot\frac{\theta}{2} \tan\frac{\alpha_0}{2}\Big)\Big]\Big\} \frac{\Delta p_n}{\sigma} \sin\theta \, d\theta + \ldots$$
$$(\theta \to \theta_0), \qquad \Delta p_n = p_n(\theta) - p_n(0); \tag{2.15}$$

$$3.\quad \alpha - \alpha_0 = \frac{1}{\sin\alpha_0}\int\limits_h^{a_0}\left(2\frac{h}{a_0} - 1\right)\frac{\Delta p_n}{\sigma}\,dh + \dots \qquad (h \to 0). \tag{2.16}$$

For $\alpha_0 \to \pi/2$, the applicability of (2.14) is limited.

For the case of stresses determined by a viscous flow according to (2.8), the right-hand sides of (2.14)–(2.16) are proportional to the small number Ca.

We verify the effectiveness of the derived formulas by referring to the problem of the weak influence of gravity on drop spreading over a horizontal surface. In the gravitational field, we have $p_n = \rho g h + \text{const}$. Substituting p_n into (2.16), we find the wetting angle α_0' for a heavy drop:

$$\alpha_0' = \alpha_0 + \frac{\mathrm{B}}{6}\frac{\sin\alpha_0}{(1+\cos\alpha_0)^2}, \quad \mathrm{B} = \frac{\rho g r_0^2}{\sigma}.$$

This formula corresponds to the first term α_0' of the expansion with respect to the Bond number $\mathrm{B} = 0$, and one can use it to allow for the weak effect of gravity on drop spreading.

When the contact line moves along the solid, the asymptotics of the stress p_n as $\theta \to \theta_0$ $(h \to 0)$ is universal:

$$p_n = \frac{2}{h}\mu v_0 Q(\alpha)\sin\alpha + \dots .$$

The divergences in the integrals (1.14)–(2.16) correspond to this expression; separating them, we can write

$$\alpha - \alpha_0 = \mathrm{Ca}\, 2Q(\alpha_0)\Big\{-\ln\frac{a_0}{h} + C_1\Big\} + \dots . \tag{2.17}$$

For the three cases, we express the values of the constant C_1 in (2.17) in terms of the function Φ, which contains the dimensionless stress P (2.8):

$$\Phi(\theta) = \frac{P(\theta)}{2Q(\alpha_0)} - \frac{1}{h}R_0\sin\alpha_0.$$

Here

Case No. 1: $$C_1 = 1 - \frac{1}{\sin\alpha_0}\int\limits_0^{\alpha_0}\frac{\cos\theta}{\cos\alpha_0}\{\Phi(\theta) - \Phi(0)\}\sin\theta\,d\theta; \tag{2.18}$$

Case No. 2: $$C_1 = (1+\cos\alpha_0)\Big\{\tan^2\frac{\alpha_0}{2} - 2\ln\left(\cos\frac{\alpha_0}{2}\right) + \frac{\cos\alpha_0}{2}\Big[\zeta(2) + \int\limits_0^{\tan^2(\alpha_0/2)}\frac{\ln(1+x)}{x}\,dx\Big]\Big\}$$

$$+\frac{1}{\sin\alpha_0}\int\limits_0^{\alpha_0}\Big\{\cos\theta - (1+\cos\alpha_0)\Big[1 - \cos\theta\ln\left(\cot\frac{\theta}{2}\tan\frac{\alpha_0}{2}\right)\Big]\Big\}\Phi(\theta)\sin\theta\,d\theta; \tag{2.19}$$

Case No. 3: $$C_1 = 2 + \frac{1}{\sin\alpha_0}\int\limits_0^{a_0}\left(2\frac{h}{a_0} - 1\right)\Phi(h)\frac{dh}{R_0}. \tag{2.20}$$

In (2.19), $\zeta(z)$ is the Riemann zeta function; the first term in (2.19) equals 1.645 as $\alpha_0 \to 0$ and 1.693 for $\alpha_0 = \pi/2$, i.e., in practice it is independent of α_0.

Correlating (2.17) with the asymptotic condition (1.3) at the drop edge, we have

$$\alpha_0 = \alpha(h_0), \qquad h_0 = a_0\exp(-C_1), \tag{2.21}$$

where $\alpha(h_0)$ is the inclination angle of the boundary determined by the general asymptotics (1.2).

Although it is difficult to analytically find the stress $p_n(\theta)$ at arbitrary angles α_0 and Reynolds numbers, it can be readily calculated since the flow boundary is given. For small angles in the case of creeping motion, the asymptotically exact expression

$$p_n = p_n\Big|_{\theta=0} + 2\mu v_0 Q_0 \sin\alpha_0\left(\frac{1}{h} - \frac{1}{a_0}\right) \quad \left(Q_0 \sin\alpha_0 = \frac{3}{2\alpha_0}, \quad \alpha_0 \ll 1\right)$$

is known [1]. It follows from this expression and from (2.8) that all the integrals in (2.18)–(2.20) equal zero, and the following values of C_1 result from (2.21):

$$1)\ C_1 = 1; \qquad 2)\ C_1 = \zeta(2) \approx 1.645; \qquad 3)\ C_1 = 2. \tag{2.22}$$

Since $\ln(h_0/h_m) \gg 1$, the three dynamic wetting angles α_a, α_b, and α_c, which correspond to (2.22), differ slightly. For case No. 3, an even more exact solution is known [4]. The value of $C_1 = 1$ was reported in [1], and case No. 2 was considered in [8].

Among the three angles, the dynamic angle $\alpha_0 = \alpha_b$ is of primary importance. This angle is determined by the height a_0 and radius r_0 of the drop base: $a_0 = r_0 \tan(\alpha_0/2)$. It can be easily measured experimentally, which is a simpler procedure than the measurements of the local angle and can give more exact data on wetting processes.

The angle $\alpha_0 = \alpha_c$ can be determined via r_0 and the radius $R_{(e)}$ of a sphere of equivalent volume:

$$r_0 = 2R_{(e)} \cot\frac{\alpha_0}{2}\left(1 + 3\cot^2\frac{\alpha_0}{2}\right)^{-1/3}, \qquad R_{(e)} = \left(\frac{3V}{4\pi}\right)^{1/3}. \tag{2.23}$$

In combination with the dependence of the velocity v_0 on the angle α_0 and the parameter h_0, which is known from (2.21) and (1.2), differentiation of (2.23) with respect to time t yields the following equation of drop spreading [1]:

$$\frac{d\alpha_0}{dt} = -\frac{v_0}{R_{(e)}}\left[(2 + \cos\alpha_0)\sin\frac{\alpha_0}{2}\right]^{4/3}, \quad \alpha_0 \equiv \alpha_c, \quad v_0 = v_0(\alpha_0, h_0). \tag{2.24}$$

The solution of $\alpha_0(t)$ in this equation determines the dependence $r_0(t)$. Formula (2.24) holds true for creeping motion. For a finite Reynolds number, Eq. (2.24) should be solved together with the problem of a nonstationary flow inside a spheroidal segment. For a sufficiently large Reynolds number, the expression for v_0 depends not only on the instantaneous value of α_0, but also on the flow prehistory affecting the value of C_1, which contributes only slightly to the solution as long as the spheroidal approximation for the interface model is valid. This approximation is violated for a sufficiently large Reynolds number (Re $\gg 1$) or finite Bond numbers. As the drop spreads over the surface, the Reynolds number decreases: the drop "forgets" not only the initial conditions, but also the inertial forces.

Thus, based on the asymptotic matching method, the free-boundary hydrodynamic problem of drop spreading has been reduced to the simpler problem with known boundary.

Finally, the expediency of formulating the inverse problems of wetting dynamics, i.e., the problems of determination of the parameters h'_m and α_m of the asymptotics (1.2) from experimental data for various wetting rates, is worth noting. The above formulas can be used to gain refined information on the role of the flow on a microscale from experimental data.

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