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Flows with quasi-equilibrium free boundaries in the dynamics of wetting of solids☆

O.V. Voinov

Tyumen

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Abstract

Slow flows of a viscous fluid with free boundary over the solid surface when there is the moving three-phase contact line are considered. The second-order asymptotic theory, which describes the regularities of free boundary variations under the action of capillary forces, is developed.

The approximate power-like dependencies of the contact angle on the dimensionless velocity in the case of wetting the boundary as well as on the dimensionless time in the case of spreading a drop over the wall are well-known[1–3]; these dependencies were proposed to consider[4] as similarity laws in the wetting dynamics. However, due to the effect of scale factor[1,2] these dependencies can be treated as similarity laws only in some narrow sense.

The appearance of a dynamical (visible) contact angle is a consequence of multiscale properties of viscous flow described by general asymptotic forms.[1] The large parameter in the theory is the width of the scale range in logarithmic scale. The second-order theory describes the scale effect of the wetting dynamics on the basis of a large parameter or a small parameter being reverse to that. The second-order asymptotic solutions of the problems of wetting dynamics are well-known in the case of small contact angles.[2] The flows considered below at finite dynamical contact angles (in the case of wetting a tube or spontaneous spreading a drop over a wall) have a common property of quasi-equilibrium state of free boundaries at the macroscale, namely, at maximal scale in the multiscale flow near the moving contact line.

The foundations of the theory of wetting statics were laid by Young[5] and Gauss[6] (see, also the works by Gibbs[7]). In the wetting theory a direct relation between the statics and dynamics exists in the form of energy equation on the moving contact line.[1] This equation enables one to describe the experimental dependencies[8] of the contact angle on the wetting rate that are due to the processes at molecular level.

In the dynamics of wetting of dry surface the slow macroscopic flow with free boundary depends on the flow at molecular (microscopic) scale near the wetting line. It is well known that at complete wetting and at low wetting rate the asymptotic form of the slope of free boundary involves the microscale defined by the van der Waals long-range molecular forces.[2] The shape of the film on the free surface is specified by its viscous flow under the action of van der Waals forces.[9,2,4]

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E-mail address: o.v.voinov@mtu-net.ru.

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It is well known that near contact line in leading approximation the asymptotic forms of normal stress on the free surface at microscale involves a logarithmic singularity in addition to Taylor's singular term, and this is useful to keep in mind in numerical calculations. In the theory of finite angles the asymptotic matching of expansions is carried out on the basis of the statics at microscale to an accuracy of the order of the quantity of small parameter. Unlike the analytical theory at small contact angles, numerical calculations of the stress on the free boundary are necessary when constructing the second-order theory at finite contact angles.

The fluid spreading over absolutely unwetted surface,[14] when the stress singularity on the contact line is integrable, differs essentially from the spreading over wetted surface; this case corresponds to the homogeneous Rayleigh's problem of the flow in a corner.[15]

1. Relations on the moving contact line

When setting the problems of the dynamics of wetting the solids it is necessary to keep in mind that there are the mechanisms of the wetting dynamics which act beyond the scope of fluid dynamics, namely, at the molecular (microscopic) scale. These mechanisms are described by the energy equation on the moving contact line[1]

$$\cos\alpha_m = (\sigma_2 - \sigma_1 - G\,\mathrm{sign}(v))/\sigma \tag{1.1}$$

Here v is the velocity of the contact line motion over the solid surface, $G = G(v)$ is the coefficient of energy dissipation $E_m = |v|G(v) \geq 0$ in the contact line per unit length and in a unit time, σ_1 and σ_2 are the densities of free surface energies on the interfaces "solid body – liquid" and "solid body – gas" correspondingly, σ is the surface tension coefficient of the liquid, and α_m (v) is the microscopic wetting angle. If the microdissipation vanish, $E_m = 0$, we get a static contact angle; in this case energy Eq. (1.1) is in agreement with the Young equation[5] and corresponds to the variational setting the problem of capillary equilibrium of a liquid in contact with the solid proposed by Gauss.[6] Eq. (1.1) is one of basic equations in the theory of wetting the solids nevertheless the review by de Gennes[4] does not include this equation. Using the energy equation a description of the following important effects in the wetting dynamics was obtained.

1°. If at incomplete wetting $G \to const > 0$ as $v \to 0$, Eq. (1.1) describes the effect of dependence of the contact angle on the sign of small velocity v (the hysteresis of the static contact angle of wetting).

In the case of increasing velocity, relation (1.1) at $G = const$ also describes another effect, namely, a constancy of the angle with increasing the velocity (Ablett's effect[8]), which manifests itself in certain systems and low-viscosity fluids under incomplete wetting. This effect is used in computer modelling of the flows at impact of fluid drops on the wall.[16–18] Eq. (1.1) is valid for arbitrary motion of the contact line independently of Reynolds number. Hence, it becomes clear why the results of Abletts' experiments carried out at low Reynolds numbers can be used in flow modelling at high Reynolds numbers. The experiments on wetting dynamics at velocities much higher than those in Abletts' experiments are of interest, but such experimental data are only available for some special cases at velocities of order 1 m/s.[17]

In the case of energy difference $\Delta\,\sigma = \sigma_2 - \sigma_1 - \sigma < 0$, Eq. (1.1) with variable coefficients of the energy microdissipation C describes the dependence α_m (v) that manifests itself in Abletts' experiments at sufficiently small velocity v.

2°. In the case of complete wetting ($\Delta\,\sigma > 0$), the fluid fully spreads over the surface. At low rate of spreading the hyperthin creeping (precursor) film can appear ahead of the wetting front.[2] In this case, the energy balance at microscale obeys the energy equation[1] when $G = \Delta\,\sigma$ and $\alpha_m = 0$. The increase in the surface energy difference $\Delta\,\sigma > 0$ due to replacing one solid body to another does not accelerate the fluid spreading since the contact angle α_m is minimal and the equation $G = \Delta\,\sigma$ for the coefficient of energy dissipation inside the film is true. The energy balance on the basis of Eq. (1.1) is more general than the energy balance for the precursor film flow given in Ref. 4 on the basis of the special model of viscous flow of the film under the action of van der Waals forces.[2,4]

3°. To the well-known case $\Delta\,\sigma > 0$ and $G - \Delta\,\sigma > 0$[1] it is assigned the negative contact angle α_m and this means the effect of appearance of the contact angle at complete wetting due to the energy microdissipation E_m. Such contact angle is possible in experiments with low-viscosity liquids and that came to be observable fairly not long ago.[19]

We will consider the viscous energy dissipation per unit length E in the flow near the moving contact line assuming that the flow is multiscale one. If the dissipation E is high, the visible contact angle α_0 can essentially differ from the microscopic angle α_m.[1]

We restrict ourselves to the case of incomplete wetting $\Delta\sigma < 0$ and compare the dissipation E with the microdissipation E_m. If $E \gg E_m$, the dependence of α_m on $\mathbf{v}$ for the values of the visible angle α_0 is inessential.

We will write the estimate of viscous dissipation[1] at small values of angles $\alpha_0 \approx \alpha_m$

$$E \approx 3\mu\upsilon^2\alpha_0^{-1}s; \quad s = \ln(r_0/r_m) \gg 1 \tag{1.2}$$

here μ is the dynamic viscosity of the liquid, r_0 is the macroscale of the distance from the contact line and r_m is the microscale[1] to which it is assigned the microscale of the distance from the free boundary to the wall h_m, the arcs of radii r_0 and r_m are the parts of the boundary of the flow domain considered. We will write, according to relations (1.1) and (1.2), the ratio of two dissipations in the form

$$\frac{E}{E_m} \approx \frac{3s}{\alpha_0}\frac{\mu\upsilon}{G(\upsilon)} \tag{1.3}$$

If the value $G \sim |\Delta\sigma|$ is not small and the macrodissipation E is essential, ratio (1.3) is small due to Eq. (1.1) at the same condition at which the contribution from the viscosity in the approximate expression for the angle $\alpha_0^3 = \alpha_m^3 + 9s\mu\upsilon/\sigma$ is small.[1,2] In this case the small viscosity has no effect on the visible contact angle, which is close to the microangle: $\alpha_0 \approx \alpha_m$. Note that the viscous dissipation E can be negligibly small both in the case $E_m = 0$ and at low Reynolds number of the flow.

Further we will consider the case of liquids with high viscosity when the role of viscosity is important.

2. Second-order asymptotic theory of wetting dynamics

When the values of Bond and Reynolds numbers and the capillary number $\mathrm{Ca} = \mu\upsilon/\sigma$. are low, we will consider two problems in the dynamics of nonvolatile liquid: on steady fulling a circular tube and on non-steady spreading of a drop over the plate wall. We use a smallness of Bond number when solving the problems at microscale.

In the first problem the fluid moves in the circular tube at a constant mean consumption and the "liquid-gas" interface crossing the tube wall differs from the static capillary meniscus due to the action of normal viscous stresses in the fluid. We want to find the free boundary shape.

The second problem concerning the spontaneous spreading of a drop over the wall, unlike the first problem, is time-dependent and the free boundary of the fluid varies with time as well as the contact line radius. Generally speaking, this is an initial value problem, and hence it is necessary to specify the initial shape of the drop. We consider transient solutions that are close to quasi-steady ones at every instant of time. A possibility of such an approach is justified by the fact that in the transient problem of drop spreading the main energy dissipation proceeds near the contact line, and in every instant of time the drop shape has a time to relax to the equilibrium state due to a small velocity of the drop edge motion.

The system is macroscopic one, and for the scales essentially greater then a certain small scale the flow is described by the Stokes equations. On the solid surface the velocity vanish, $\mathbf{u} = 0$. On the free boundary S the shear stress also vanish, $P_\tau = 0$, and the jump of normal stress is equal to the Laplace capillary pressure $2\sigma H = P_n + p_0$ (P_n is the normal stress in the fluid, p_0 is the pressure in the gas and H is the mean curvature); the normal fluid velocity on S is equal to normal velocity of the surface w: $\mathbf{u}\cdot\mathbf{n} = w$.

Near the moving contact line it is valid the universal asymptotic form for the slope α to the free surface[1–3]

$$\frac{1}{2}\int_{\alpha_m}^{\alpha}\left(\frac{\alpha}{\sin\alpha} - \cos\alpha\right)d\alpha + \mathrm{Ca}\ln\frac{\sin\alpha}{\sin\alpha_*} = \mathrm{Ca}\ln\frac{h}{h_m}, \quad h \gg h_m \tag{2.1}$$

The microangle α_m corresponds to Eq. (1.1); $\alpha_* = \alpha_m$ at $\alpha_m \geq |9\mathrm{Ca}|^{1/3}$ and $\alpha_* = (9\mathrm{Ca}^{1/3})$ in opposite case; such a definition of the constant α_* provides the well-known[3] agreement of asymptotic form (2.1) with the asymptotic theory for small values of contact angle at complete wetting ($\alpha_m = 0$).[2] Asymptotic form (2.1) in the flow at finite Reynolds number is valid at low local Reynolds number $hv/\nu \ll 1$ (ν is the kinematic viscosity), and in the unsteady flow with the specific time τ this asymptotic form is valid at low $h/v \ll \tau$. Asymptotic form (2.1) is true at $h_m \ll h \ll h_0$; the upper boundary (macroscale) of the distance between the free surface and the wall h_0 can be found by the method of matching of asymptotic expansions or be estimated in the order of magnitude. The value h_0 enables one to calculate the dynamical contact angle $\alpha_0 = \alpha\ (h_0)$ using asymptotic form (2.1).

According to relation (2.1), the free boundary is close to its tangent, that is, the angle α slowly varies along the boundary: $d\ln\alpha/d\ln h \ll 1$,[1] and this is true due to the high value of the parameter $\ln(h_0/h_m) \gg 1$. We put

$$\varepsilon = 1/\ln(h_0/h_m) \quad (2.2)$$

The second small term in the left-hand side of relation (2.1) is of the order Ca $\ln\varepsilon$.

If there is a precursor film moving under the action of van der Waals forces,[2,4,9] the microscale equals its maximal thickness[2]

$$h_m = (A'/(2\pi\sigma))^{1/2}(3\mathrm{Ca})^{-1/3} \quad (2.3)$$

(A is Hamaker's constant). The maximal thickness of the precursor film has been also considered by de Gennes.[4] The similar formula for the parameter of the asymptotic form has been written by de Gennes and Hervet[4] by numerical solving the problem. And the coefficient in Eq. (2.3) had been found with the essentially high accuracy as compared to that in similar formula,[4] as one can see from.[20]

The precursor film can appear only at small contact angles, and at finite angles the microscale h_m can have the order of the size of fluid molecules[1,2,4] in agreement with the fact that in the case of non-Newtonian fluid the length of wall-adjacent sliding can have the order of the size of molecule.

If the surface is preliminary covered by the microscopic film of the thickness h_∞, the microscale $h_m = 1.84h_\infty$.[2] The parameter h_m is also known in the case when the thickness of the covering film is microscopic one.[21]

In the case of small angles $h_0 \gg h_m$ the condition $\alpha_0 \ll 1$, which restricts an applicability of the theory, can be written explicitly as the condition of availability of small parameter a_1 in the problem of wetting dynamics under the motion of capillary meniscus.[2] The limit of applicability of the wetting asymptotic theory under the meniscus motion in the special case of prewetted solid[2] equals

$$a_1 = 1.77h_\infty R_0^{-1}\mathrm{Ca}^{-2/3} = 1$$

(R_0 is the meniscus radius).

Alongside with the formulae of microscale, it is known a number of approximate formulae for macroscale.[1,2]

In the flow with finite Reynolds number the upper boundary h_0 of the area of applicabilty of the asymptotic form (2.1) can be approximately defined by the condition of smallness of local Reynolds number[a]: $hv/\nu < 1; h_0 = \nu/v$. In this case the scale factor includes low Reynolds number defined in terms of microscale: $\ln(h_0/h_m) = |\ln(h_m v/\nu)|$. For small angles the more exact condition $\alpha_0\ hv/\nu < 1$ should be used. In addition, in the case of capillary meniscus it is necessary to take into account another condition that approximately define h_0 as the boundary of the domain of values h for which the contour of the free surface is close to its tangent: $h < \alpha_0^2\ R_0/2$.[1,2] The quantity h_0 is equal to the least of two boundaries presented.

In asymptotic form (2.1) one can use the distance to contact line $r = h/\sin\alpha$ and the parameter $r_m = h_m/\sin\alpha_*$ instead of the distance h and the parameter h_m.[1] However, in the important case of prewetted surface when the surface is covered by a thin macroscopic film, the parameter r_m varies many times over when varying the wetting rate (the number Ca) whereas the microscale h_m does not depend of the rate. Hence, the distance to the wall h rather than the distance to the contact line r is used as an independent variable.

We will consider the domain of microscale, where the distances from the contact line are relatively large, namely, have the order of the system size, and the distance of the free surface from the wall is $h \sim h_k$ in the case of filling the tube of radius h_k or $h \sim h(0)$ in the case of drop spreading ($h(0)$ is the height of the drop).

We will seek for the solution by formal perturbations in the number Ca. At the macroscale the free surface S is close to the quasi-static one, since near the contact line the angle α varies slowly with the distance according to relation (2.1), and at fixed angle α_0 the wetting rate is low: $v \sim \epsilon$. Setting the static surface S_1 be close to S, we find the increment of

[a] Voinov O.V. Thermodynamics and the asymptotic theory of the contact line motion of three phases under wetting of solid bodies. Deposited in VINITI. 1994. No 2136-B94.

normal stress on the surface S_1 to its value on the axis of symmetry $P_n - P(0)$ from the problem of the viscous fluid flow. Using this, we find the small perturbation of the surface S_1 from the boundary Laplace's condition[1] and define the small perturbation of the slope near the contact line. The matching of asymptotical expansions for the slope with respect to the boundary α at the microscale and the general asymptotic form (2.1) near the contact line enables one to find the formulae for contact angle of the surface S_1 that ininvlves the parameter h_0 in the form of functional of the stress P_n on the boundary.[1,11b]

Further we will numerically find the parametric dependence of the minimal scale $h_0 = h_0(\alpha_0)$ that specifies the contact angle from asymptotic form (2.1) in the form of $\alpha_0 = \alpha_{as}$ (ln h_0). As the result we obtain the solution of the problem of wetting dynamics with the accuracy of the second order.

The analytical theory of the second order is known for the case of small angles.[2] This theory and the asymptotic forms of stress near the contact line at large scale[10] can be used for checking the solutions obtained at combining asymptotic and numerical approaches.

3. Free boundary at microscale and the matching of asymptotic expansions

We will write the equation for the slope of the surface S

$$\frac{\sigma}{x}\frac{d}{dx}(x\cos\alpha) = P_n + p_0 \tag{3.1}$$

Here x is the distance from the axis of the system symmetry, α is the angle between the tangent to S and the solid wall. In the case of the drop on the surface one has to change $\alpha + \pi/2$ for α.

The surface of the first approximation, namely, the segment of sphere S_1 passes through the contact line and has the curvature

$$R^{-1} = (P_n(0) + p_0 - c)/(2\sigma)$$

where c is a small arbitrary constant. We will seek the radius of perturbed surface in the form

$$r' = |R + \bar{R}(\theta)|, \quad \bar{R} \ll R_0 = |R|$$

(the axis $\theta = 0$) is directed along the axis of symmetry of the system. On the axis of symmetry and on the contact line the following conditions are true

$$d\bar{R}/d\theta = 0 \text{ when } \theta = 0, \quad \bar{R} = 0 \text{ when } \theta = \theta_0 \tag{3.2}$$

The ordinary differential equation for perturbation of the radius includes a small arbitrary constant:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d\bar{R}}{d\theta} + 2\bar{R} = \frac{R^2}{\sigma}(P_n(\theta) - P_n(0) + c); \quad P_n - P_n(0),\ c \ll 2\frac{\sigma}{R_0} \tag{3.3}$$

We will consider the versions of specifying the static surface, namely, the segment of sphere passing through the contact line: (a) the sphere curvature is equal to the mean curvature of the surface S on the axis $R^{-1} = H(0)$ (the constant c vanishes; (b) the sphere is tangent to the surface S at the point on the axis of symmetry of the system having the coordinate x_2 ($\bar{R}(0) = 0$), $A_0 = x_2$ is the segment height (the contact line is situated on the plane $x_2 = 0$), for the case of a drop $a_0 = h(0)$. The height a_0 of spherical segment is related to the contact angle a_b and the radius of the base by elementary formula.

The perturbation of the tangent slope α on the contour of the sphere is

$$\alpha - \alpha_1(\theta) = R_0^{-1}d\bar{R}(\theta)/d\theta$$

[b] See also: Voinov O.V. On spreading of a viscous fluid drop over horizontal surface. Deposited in VINITI. 1995. No 3495-V95.

From this and Eq.(3.1), the Eq. (3.3) follows. Integrating Eq. (3.3) with taking into account conditions (3.2), we find a behavior of the surface slope at the edge, $\theta \to \theta_0$. We obtain

$$\alpha - \alpha_1 = \int_0^{\theta} \frac{P_n(\theta') - P_n(0)}{\sigma} \Lambda(\theta_0, \theta') R_0 d\theta' + \dots \quad (3.4)$$

Here $\alpha_1 \approx \alpha_0$, the angle $\theta_0 = |\pi/2 - \alpha|$ in the case of a tube and $\theta_0 = \alpha_0$ in the case of a drop; the function $\Lambda(\theta_0, \theta)$ for the case (a) and (b) is correspondingly equal to

$$\Lambda_a(\theta_0, \theta) = -\frac{\sin 2\theta}{\sin 2\theta_0} \quad (3.5)$$

$$\Lambda_b(\theta_0, \theta) = \left[\cos\theta - (1 + \cos\theta_0)\left(1 + \cos\theta \ln\left(\operatorname{ctg}\frac{\theta_0}{2}\operatorname{tg}\frac{\theta}{2}\right)\right)\right]\frac{\sin\theta}{\sin\theta_0} \quad (3.6)$$

We will normalize the stress on the contour of the sphere segment to its first term of the asymptotic form near the contact line (to the stress of the flow in the corner)

$$P_n - P_n(0) = 2\mu\upsilon Q(\alpha_0)\sin\alpha_0 G h^{-1}, \quad Q = \sin\alpha/(\alpha - \sin\alpha\cos\alpha) \quad (3.7)$$

If $h \to 0$, we have $G \to 1$ according to the solution of the problem of a flow in the corner.

The matching of asymptotical expansions with the accuracy $O(\epsilon^2)$ is well known for the case of small contact angles in the problem of wetting under the meniscus motion.[2] For finite contact angles we can write the Taylor series expansion for the asymptotic form of the slope of free surface (2.1) at the point $z_0 = \ln(h_0)$

$$\alpha = \alpha_0 + \varphi(\alpha_0)(z - z_0) + \dots, \quad \alpha_0 = \alpha_{as}(z_0), \quad \varphi = \alpha'_{as}(z_0) = 2Q\mathrm{Ca} \quad (3.8)$$

This expansion is valid when $h \ll h_0 z_0 - z \ll \ln(h_0/h_m) \gg 1$; formula (3.8) holds under replacing h by the distance from contact line r. Relation (3.8) can be written in the form

$$\alpha = \alpha_0\left(1 + \frac{h}{\alpha}\frac{d\alpha}{dh}(z - z_0) + \dots\right)\left(\frac{r}{\alpha}\frac{d\alpha}{dr} \approx \frac{h}{\alpha}\frac{d\alpha}{dh} \approx \varepsilon\frac{\alpha^3 - \alpha_m^3}{3\alpha^3} \ll 1\right)$$

The small effect of the meniscus curvature at $h \ll h_0$ is accounted for by the formula

$$\alpha = \alpha_1(z) + \varphi(\alpha_0)(z - z_0); \quad \alpha_1 = \alpha_0 + h/(R\sin\alpha_0) + \dots = \alpha_0 + r/R + \dots$$

which gives the profile of the slope of the boundary near the moving contact line at macroscale; this formula can be used in experimental investigations of free surface.

Above one could take the distance from the contact line r as an independent variable instead of h by substituting $\ln r$ for z without changing (3.8). Advantages of using the variable h in description the free boundary instead of using the variable r were pointed out in Section 2.

4. Solving the problem of steady filling a tube

Matching expansions (3.4) and (3.8) at $h < h_0$ ($\theta \to \theta_0$) in the case of the flow in the tube of radius h_k and using equalities (3.7), we can write

$$\alpha_0 = \alpha_{as}(\ln h_0), \quad h_0 = h_k \exp(-C_0) \quad (4.1)$$

$$C_0 = \lim_{\theta \to \theta_0}\left\{\sin\alpha_0 \int_0^{\theta} \Lambda(\theta_0, \theta') R_0 \frac{G(\theta')}{h} d\theta' + \ln\frac{h_k}{h}\right\} \quad (4.2)$$

Using the relation $R_0 \sin\theta = h_k - h$ for the sphere, from relations (4.2), (3.5) and (3.6) we obtain for the above-mentioned variants of specifying the static phase interface

$$C_{0a} = 1 - \int_0^{h_k}\left(1 - \frac{h}{h_k}\right)\frac{G-1}{h}dh \tag{4.3}$$

$$C_{0b} = \operatorname{ctg}\theta_0 \int_0^{\theta_0}\left\{\Lambda_b(\theta_0, \theta)G(\theta) + \frac{\cos\theta}{\cos\theta_0}\right\}\frac{h_k}{h}d\theta \tag{4.4}$$

Note that, in contrast to the singular stress P_n, the function $(G-1)/h$ has a weak singularity when the angle α_0 is less than 129°.[10]

Parameters of the solutions for variants (a) and (b) are connected by the relations

$$\alpha_a - \alpha_b = 2\mathrm{Ca}Q(\alpha_b)\ln\frac{h_{0a}}{h_{0b}} = 2\mathrm{Ca}Q(\alpha_b)(C_b - C_a) = \left(\frac{1}{R_a} - \frac{1}{R_b}\right)\frac{h_k}{\sin\alpha_b}$$

The stress P_n on the segment S of the sphere was calculated for the flow in the tube; in the tube section at the distance H from the contact line the velocity profile of the Poiseuille flow had been specified. The problem for Stokes equations was solved under boundary conditions on S: the normal velocity $u_n = 0$, the shear stress $P_\tau = 0$; on the rigid wall at $x_1 = 1$; $u_1 = 0$, $u_2 = -1$; in the section $x_2 = -H$: $u_1 = 0$, $u_2 = 1 - 2x_1^2$.

Here x_1 is the distance from the tube axis, x_2 is the distance along the axis. The equation for contact line has the form $x_2 = 0$ and $x_1 = 1$.

In calculations at $H > 3.5R$ the stress on the surface S is practically independent of H.

The calculations were carried out under the restriction $\alpha_0 \leq 160°$, since at $\alpha_0 = \pi$ the problem of a flow in the corner is degenerate one ($Q = 0$). Among the tests it has been used the asymptotic form of stress near the contact line in the problem at microscale,[10] which contains the term with logarithmic singularity (in addition to the singular term).

Numerical solution of the problem for the Stokes equations has been found using a new method of boundary integral equation (IE). The velocity components and the pressure of axially symmetric flow were expressed in terms of two harmonic functions by several procedures including an application of Oberbeck's formula.[22] To find them, it has been used the modified IE, in which the harmonic function $\Phi(x')$ in the integrand was modified in such a way that the double layer density vanished at a certain value $\mathbf{x}' = \mathbf{x}$[23]

$$4\pi K\Phi(\mathbf{x}) = \iint_{S_L}\left\{\frac{1}{r}\frac{\partial\Phi}{\partial n}(\mathbf{x}') - (\Phi(\mathbf{x}') - \Phi(\mathbf{x}))\frac{\partial}{\partial n}\frac{1}{r}\right\}dS, \quad \mathbf{x}, \mathbf{x}' \in S_L; \quad r = |\mathbf{x} - \mathbf{x}'|$$

S_L is the liquid boundary, the coefficient K depends of geometry of the problem. For unbounded domain, which is external with respect to the boundary S_L, the value $K = 1$.[23] In the case when the part of the surface in unbounded and at infinity is close to a plane, the value $K = 1/2$. For the problem in the closed surface S_L the coefficient $K = 0$. The modification of IE leads to increasing the accuracy of its discrete approximation. To provide a high accuracy, the special quadrature formula had been used.[23]

Numerical solutions of the problems of dynamics of ideal fluid with free boundaries[23,24] demonstrates the efficiency of this approach and its advantage over the approach of later papers where IE without modification were used.

The results of calculating the parameter $C_0 = C_0(\alpha_0)$ in formula (4.1) for contact angle α_0 are presented in Fig. 1. Continuous curves (a) and (b) are the results of calculating contact angles of sphere segments for variants (a) and (b) (see, Section 3) according formulae (4.3) and (4.4). Dash lines correspond to the formulae for C_0 from the analytical theory of small angles[2,11]:

$$a)\ C_0 = 1 - \ln(2\alpha_0^2), \quad b)\ C_0 = 2 - \ln(2\alpha_0^2) \tag{4.5}$$

The first equality (4.5) asymptotically corresponds to the explicit solution[2] and means that either $h_0 \sim \alpha_0^2 R$ or $r_0 \sim \alpha_0 R$.[1,2] The dash curves are close to those calculated at small value of α_0. Increasing the parameter C_0 with decreasing the contact angle of meniscus is due to decreasing the size of the macrodomain where the angle α slightly differs from the angle α_0. The conjecture $r_0 \sim R$ does not reflect this important point (see, Refs. 25,4).

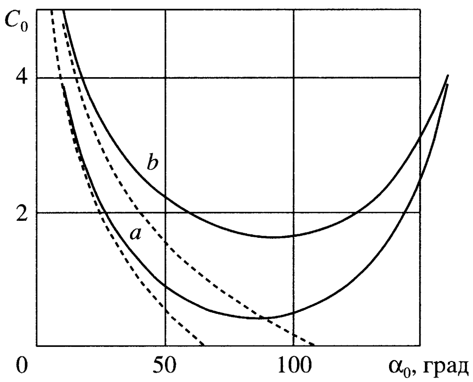

Fig. 1.

In combination with asymptotic form (2.1) the curves obtained give the dependence of the dynamic contact angle on the velocity $\alpha_0 = \alpha_0$ (Ca) in the parametric form. The value $C_{0b}(\pi/2) = 1.64$ is in agreement with the value of similar constant $c_1 = 1.834$[1] at finite contact angles. Note the well-known agreement[1,3] between the theory[1] and experimental data.[26–28] The existence of minimum of the parameter C_0 in continuous curves presented in Fig. 1 and its increasing at $\alpha_0 > 15°$ in the domain of small $\pi - \alpha_0$ is in agreement with the estimate $h_0 \sim (\pi - \alpha_0)^2 R_0$, which is symmetric to the estimate of h_0 at small α_0.

In the case of using the variable r, the curves in Fig. 1 allow a simple recalculation: instead of $h_0 = h_k \exp(-C_0)$ we have $r_0 = h_k \exp(-C_0)/\sin\alpha_0$.

5. Non-steady flow of a drop on the wall

The axisymmetric flow of a liquid drop on the plane surface is described by the general quasi-equilibrium model with the parameters h_m and α_m.[1,2] If $\alpha_m = 0$, in the case of a thin drop it can arise a quasi-steady precursor film,[2] the theory of non-steady film moving near the edge of spreading drop under the action of van der Waals forces is also known.[29] At the microscale the drop surface is close to the segment of the sphere with radius $R_0(t)$ and contact angle α_0 (t). In addition to two variants of specifying static interface (a) and (b), we will consider the third variant, namely, the sphere segment with the volume being equal to the drop volume: $V_0 = V$ (variant (c)). The contact angle α_0 is connected with the radius of the drop base x_0 and the equivalent radius R_e by the relation

$$x_0 = 2R_e \cos\frac{\alpha_0}{2}(2+\cos\alpha_0)^{-1/3}\left(\sin\frac{\alpha_0}{2}\right)^{-1/3}, \quad R_e = (3V/(4\pi))^{1/3} \tag{5.1}$$

The function in the formula for perturbation (3.4) has the form

$$\Lambda(\theta_0, \theta) = \left(1 - 2\frac{h}{a_0}\right)\frac{\sin\theta}{\sin\theta_0}, \quad h = R_0(\cos\theta - \cos\theta_0) \tag{5.2}$$

The matching of asymptotical expansions (3.4) and (3.8) with replacing the radius h_k by the drop height a_0 in formula (4.1) gives again formula (4.2) where one has to replace h_k by a_0; for different variants of surfaces of the first approximation, namely, the sphere segments, and taking into account relations (3.5), (3.6) and (5.2), we have

$$C_{0a} = \int_0^{a_0}\left(1 - \frac{\cos\theta}{\cos\theta_0}G\right)\frac{dh}{h}, \quad \theta_0 < \frac{\pi}{2} \tag{5.3}$$

$$C_{0b} = \int_0^{\theta_0}\{\sin\theta + \sin\theta_0\Lambda_b(\theta_0, \theta)G(\theta)\}\frac{R_0}{h}d\theta \tag{5.4}$$

$$C_{0c} = 2 + \int_0^{a_0}\left(2\frac{h}{a_0} - 1\right)\frac{G-1}{h}dh \tag{5.5}$$

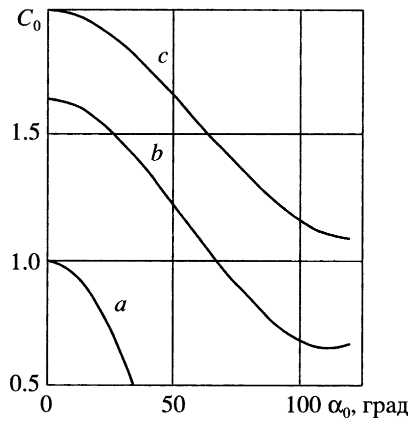

Fig. 2.

The normal stress P_n on the surface S of the deforming segment of the sphere was found from the solution of the problem for Stokes equation provided with following boundary conditions:

on S: $u_n = v \sin \alpha_0 (1 - 2h/a_0)$ is the normal velocity, $P_\tau = 0$ is the shear stress and $v = 1$ is the velocity of the drop edge;
on the wall ($x_2 = 0$): $u_1 = 0$ and $u_2 = 0$ (x_2 is the coordinate along the axis of symmetry).

The calculations have been carried out in the range $10° \le \alpha_0 \le 120°$. According to formulae (5.3)–(5.5) the dependencies $C_0(\alpha_0)$ have been found for variants (a), (b) and (c) and are presented in Fig. 2. At small angle α_0 in the case (a) the parameter $C_{0a} \approx 1$; for the case (b) and (c) at small angles $C_{0b} \approx 1.64$ and $C_{0c} \approx 2$ in agreement with analytical theory.[12,13] The value $C_{0c}(\pi/2) = 1.23$ is close to similar constant[1] being equal to unit. Three dynamical contact angles of different types give the more complete description of the shape of flowing drop than the single angle. Different contact angles take close values. Parameter of the contact angle α_b enables one to take into account a small distinction of the drop height $h(0)$ from the height of sphere segment a_0 in the case (c).

6. Model of drop dynamics at finite contact angles

The equation for contact angle of the drop follows from the relation $\dot{x}_0 = v$ for the segment of the sphere[1]:

$$\dot{\alpha}_0 = -\frac{\upsilon}{R_e}\left[(2+\cos\alpha_0)\sin\frac{\alpha_0}{2}\right]^{4/3} \tag{6.1}$$

$$\upsilon = \frac{\sigma}{\mu}\left\{\ln\frac{h_0}{h_m} - \ln\frac{\sin\alpha_0}{\sin\alpha_*}\right\}^{-1}\frac{1}{2}\int_{\alpha_m}^{\alpha_0}\frac{d\alpha}{Q(\alpha)}, \quad h_0 = a_0\exp(-C_0(\alpha_0)) \tag{6.2}$$

$a_0 = x_0 \mathrm{tg}(\alpha_0/2)$ is the height of the segment.

The dependence $C_{0c}(\alpha_0)$ is shown in Fig. 2.

Adding the expressions for microparameters h_m and α_m (in one of special cases) to relations (6.1) and (6.2), we obtain a closed model of the drop dynamics on the wall. The second term in the braces in expression (6.2) is always small since $\ln(h_0/h_m) \gg 1$.

The equations for contact angle of spreading drop (6.1) and (6.2) are close to similar equation[1] where the integral in asymptotic form (2.1) is approximated by the angle to the third power. This approximation is an approximation of the integral at small angles and turns out to be also efficient at finite angles up to 150°.

The model enables one to describe the flow in the drop with an accuracy $O(\epsilon^2)$. The parameters h_m and α_m are common for the problems of fluid dynamics at the microscale and are suitable for the drops of arbitrary volume. At long times the details of initial conditions of the problem are of no importance.

The ordinary differential equation of the model is easily integrated analytically if the microangle α_m does not depend of the velocity $v(\alpha_m = \alpha_s)$. Really, the expression in braces in relation (6.2) is a slow function of time due to availability of the logarithm of large quantity. In the leading approximation, under integrating one has to take this quantity as constant and to take into account its slow variation in the formula obtained. The corrections can be found by iteration. By this method from Eqs. (6.1) and (6.2) at small α_0 and complete wetting it can be obtained the approximate solution $\alpha_0 \sim t^{-3/10}$ and $x_0 \sim t^{1/10}$ valid [1,2] at different expressions for microscale h_m (including the flow of precursor film). This is supported by many experiments, part of which is pointed out in the review by de Gennes.[4]

In conclusion we note that at Reynolds number of order unity the wetting theory based on the Stokes equations can be suitable with the accuracy of $O(\epsilon)$.

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