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TWO-PHASE BOUNDARY DYNAMICS NEAR A MOVING CONTACT LINE OVER A SOLID

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Abstract—Consideration is given to the nonlinear problem on a shape of boundary between two viscous liquids, of which one displaces the other one from a solid surface, the Reynolds number being rather low. An asymptotic theory of wetting dynamics is developed that is of the second order with respect to small capillary numbers and valid for any ratio of viscosity coefficients of the media. A formula describing the dynamic contact angle (i.e. the inclination angle of the tangent to the interface) as a function of a distance to the solid is derived. Limitations on the angles for which the second-order theory is valid are shown. If the phase 2 viscosity is zero, the asymptotic second-order theory is valid for angles below 128.7°. A theory applicability domain depends on the ratio of viscosity coefficients. The applicability domain is not limited if the viscosity coefficients differ by a factor of less than four. Copyright © 1996 Elsevier Science Ltd.

Key Words: wetting, dynamic contact angle, hydrodynamics

1. INTRODUCTION

Two-phase boundary dynamics near a contact line is generally described by a notably nonlinear hydrodynamics problem since the boundary shape must be determined simultaneously with velocity fields for the phases.

Wetting hydrodynamics was considered in theoretical articles by Huh & Scriven (1971), Voinov (1976, 1977, 1978, 1988, 1995), Dussan (1979), Pismen & Nir (1982), Hervet & de Gennes (1984), de Gennes (1985), Cox (1986), Baiocchi & Pukhnachev (1990), Boender *et al.* (1991) and others.

Assuming small capillary number the boundary shape is described by an asymptotic relation for the dynamic boundary angle (that is, the inclination angle of a tangent to the interface) that varies slowly with distance to the solid (Voinov 1976). In (Voinov 1978) a relation with the second order of accuracy with respect to the capillary constant has been proposed for the case of a "liquid–gas" interface. A method for evaluating the constant in the boundary inclination angle asymptotic equation of the second order was demonstrated in (Voinov 1995).

Deriving a second-order asymptotic theory for the general case when viscosity coefficients of both liquids are not zero is obviously of interest. Within the second-order asymptotic theory the contribution of microprocesses near the contact line to the dynamic boundary angle may, in particular, be established at higher accuracy than the first-order theory provides.

Consider a creeping flow of two liquids over a flat solid surface. The boundary surface S_{12} between the liquids contacts the solid over a wetting line that moves at a velocity v along the normal to the wetting line (figure 1). A steady-state interface S_{12} near the three-phase contact line is described by a two-dimensional problem for Stokes equations:

$$-\nabla p + \mu \Delta \mathbf{u} = 0, \quad \operatorname{div} \mathbf{u} = 0$$

$$u_1 = -v, \quad u_2 = 0, \quad x_2 = 0;$$

$$(\mathbf{un})_1 = 0, \quad (\mathbf{u})_1 = (\mathbf{u})_2, \quad \mathbf{x} \in S_{12};$$

$$(p_\tau)_1 = (p_\tau)_2, \quad p_{\tau i} = p_{ik} n_k - p_n n_i, \quad \mathbf{x} \in S_{12}.$$

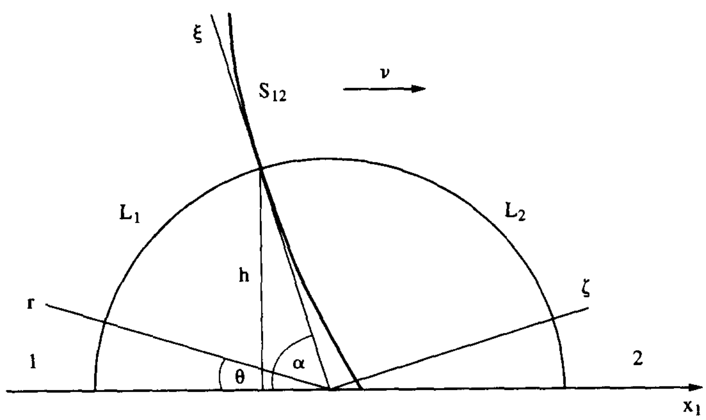

Figure 1. Interface motion schematic, notation.

$$p_{ik} = -p\delta_{ik} + \mu\left[\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right], \quad p_n = p_{ik}n_in_k;$$

$$(p_n)_1 - (p_n)_2 = q\sigma = -\frac{\mathrm{d}\cos\alpha}{\mathrm{d}h}\sigma, \quad \mathbf{x}\in S_{12}. \qquad [1]$$

Here, the subscript 1 or 2 at brackets denotes values for a medium 1 or 2, respectively; the repeating indices ($i, k = 1, 2$) are summation indices; x_1 and x_2 are Cartesian co-ordinates; n_i is a component of the normal; σ is the surface tension coefficient; q is the interface curvature; α is the inclination angle of a tangent to the interface; h is the distance from an interface point to the solid. The dynamic viscosity coefficient μ takes a value μ_j for a jth liquid ($j = 1, 2$). According to [1], the solid surface ($x_2 = 0$) and the interface S_{12} are domains to impose kinematic boundary conditions, the tangential stress p_τ is continuous across S_{12}, and the normal stress p_n undergoes a jump depending on capillary forces.

Assume that $Ca_j = \mu_j v/\sigma$ ($j = 1, 2$) is low ($Ca_j \to 0$). Below, we use $Ca = \mu_1 v/\sigma$ and assume that a viscosity ratio $\mu_* = \mu_2/\mu_1$ is finite. If $\mu_* = \infty$, the notation may easily be changed.

The distance h between the moving interface and the solid dictates a local characteristic value of liquid velocity variation along the x_2 axis. A minimum distance h_m between the interface and the solid must be much greater than a molecule size a for us to deal with the problem.

Symbolize with h_0 a characteristic maximum distance from the boundary S_{12} to the solid.

Let each interface point $\{x_2 = h\}$ be related to a semicircle that is normal both to the interface at that point and the solid surface. An arc $L_1(h)$ of such circle is assumed to be in the phase 1, and $L_2(h)$, in the phase 2. The flow area under consideration corresponds to h within the interval (h_m, h_0), and, in these terms, an arc L_j appears in positions from a minor arc $L_j(h_m)$ to a major arc $L_j(h_0)$ ($j = 1, 2$). At limiting arcs $L_j(h_m)$ and $L_j(h_0)$ the liquid velocity u components do not exceed the wetting velocity v, as to their order of magnitude.

It should also be assumed that the characteristic maximum (h_0) and minimum (h_m) values of the distance h from a point of the interface to the solid differ very much: $\ln(h_0/h_m) \gg 1$.

Of interest to us is a solution at a considerable distance from major arcs $L_j(H_0)$—specifically, over a domain $\{h \ll h_0\}$. The velocity field far from a major semicircle does not depend on the velocities that could be specified for the semicircle (for a particular boundary shape). Similarly, a velocity u over minor arcs $L_j(h_m)$ (over a minor semicircle) do not asymptotically affect the velocity field at a distance from these arcs $\{h \gg h_m\}$, given an interface S_{12} shape. This can be explained via the Saint–Venant principle for Stokes equations. When employing the Saint–Venant principle it suffices to take into account that the absolute value of the velocity u is on the order of magnitude of the wetting velocity v, so detail of the velocity field over the limiting arcs is of no importance.

The inequality $\ln(h_0/h_m) \gg 1$ enables adopting the following asymptotic boundary condition for the interface curvature q as a function of the distance to the solid, see (Voinov 1976, 1978):

$$q = -\frac{\mathrm{d}\cos\alpha}{\mathrm{d}h} \Rightarrow 0, \quad \frac{h}{h_m} \Rightarrow \infty. \qquad [2]$$

This is necessary for determining the dynamic boundary angle relation. Assume that [2] is valid for $\{h \ll h_0\}$. Asymptotic descriptions of the dynamic boundary angle usually show a slow variation of the angle α with the distance.

The problem is to establish dependence of the liquid interface inclination angle on the distance h in the second approximation with respect to a small capillary number Ca over an intermediate domain $\{h_m \ll h \ll h_0\}$.

The asymptotic solution defines the boundary inclination angle $\alpha(h)$ correct to a constant whose determination requires an extra condition to be posed. One knows that the first-order theory admits an angle at the minimum distance as the extra condition: $\alpha = \alpha_m$, $h = h_m$.

2. ASYMPTIOTIC SOLUTION TO THE INTERFACE DYNAMICS PROBLEM

2.1. *Successive approximations*

In the main approximation, see (Voinov 1976, 1978), the interface is locally close to its tangent at $h = h_1$. The tangent inclination angle β is equal to α at $h = h_1$, and a difference between these angles is only of importance in two limiting cases: $h \Rightarrow \infty$ and $h \Rightarrow 0$, if Ca is rather low.

The stream function ψ will be sought using the $\{r, \theta\}$ polar co-ordinate system whose center is at the point where the tangent (from $h = h_1$) intersects the solid. For each medium the function ψ is sought in successive steps, by writing

$$\psi_j = \psi_j^{(1)} + \psi_j^{(2)} + \cdots \qquad [3]$$

where $\psi_j^{(k)} \sim vr_1 Ca^{k-1}$, $k = 1, 2, \ldots$ For obtaining $\psi_j^{(1)}$, the interface (to be determined) is defined by the equation $\theta = \alpha$, and the theory for $\psi_j^{(2)}$ utilizes the small difference $\theta - \alpha$ $(\theta - \alpha \neq 0)$ derived from the first-order solution. The condition [1] for normal stresses should be satisfied by using successive approximations, and the condition at every approximation is a basis for the interface equation.

At the first approximation the normal stress p_n at $h = h_1$ is obtained from the problem on flow with a rectilinear interface (Voinov 1976, 1978). The stream function ψ (hereafter the index (1) is allowed to be omitted) in each of the two liquids satisfies the biharmonic equation

$$\nabla^4\psi = 0, \quad 0 < r < \infty, \quad 0 < \theta < \pi, \quad \theta \neq \alpha; \quad \psi = \psi_1, \quad \theta < \alpha; \quad \psi = \psi_2, \quad \theta > \alpha. \qquad [4]$$

Here, $\theta = \alpha$ is the interface over which the following conditions hold:

$$\theta = \alpha, \quad \psi_1 = \psi_2 = 0, \quad \frac{\partial\psi_1}{\partial\theta} = \frac{\partial\psi_2}{\partial\theta}, \quad \mu_1\left[\frac{1}{r^2}\frac{\partial^2\psi_1}{\partial\theta^2} - r\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi_1}{\partial r}\right)\right] = \mu_2\left[\frac{1}{r^2}\frac{\partial^2\psi_2}{\partial\theta^2} - \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial\psi_2}{\partial r}\right)\right]. \qquad [5]$$

Similarly, over the solid surface:

$$\theta = 0, \quad \psi^{(1)} = 0, \quad \frac{1}{r}\frac{\partial\psi_1^{(1)}}{\partial\theta} = v; \quad \theta = \pi, \quad \psi_2^{(1)} = 0, \quad \frac{1}{r}\frac{\partial\psi_2^{(1)}}{\partial\theta} = -v. \qquad [6]$$

Velocity components

$$u_\theta^{(1)} = -\frac{\partial\psi^{(1)}}{\partial r}, \quad u_r^{(1)} = \frac{1}{r}\frac{\partial\psi^{(1)}}{\partial\theta}$$

should naturally be limited. One could demonstrate that this requirement is sufficient for the solution $\psi_j^{(1)}$ to be unique over the domain [4].

By analogy with Taylor (1960), Moffatt (1964), Huh & Scriven (1971), Voinov (1976, 1988) the solutions of the biharmonic equation that satisfy [5] and [6] may be written as follows:

$$\psi_1^{(1)} = r[c_1\theta \sin\theta + d_1(\theta\cos\theta - \sin\theta) + v\sin\theta],$$

$$\psi_2^{(1)} = r[c_2\theta_2 \sin\theta_2 + d_2(\theta_2\cos\theta_2 - \sin\theta_2) + v\sin\theta_2], \quad \theta_2 = \pi - \theta;$$

$$c_1 = v\sin^2\alpha[(\mu_1 - \mu_2)(\sin^2\varphi - \varphi^2) - \mu_2\pi\varphi]\Delta^{-1}, \quad \varphi = \pi - \alpha,$$
$$c_2 = v\sin^2\alpha[(\mu_1 - \mu_2)(\alpha^2 - \sin^2\alpha) - \mu_1\pi\alpha]\Delta^{-1},$$

$$d_1 = -v\sin\alpha[(\mu_1 - \mu_2)(\varphi^2 - \sin^2\varphi)\cos\alpha + \mu_2\pi(\sin\varphi - \varphi\cos\varphi)]\Delta^{-1},$$

$$d_2 = -v\sin\alpha[(\mu_2 - \mu_1)(\alpha^2 - \sin^2\alpha)\cos\varphi + \mu_1\pi(\sin\alpha - \alpha\cos\alpha)]\Delta^{-1},$$

$$\Delta = \mu_1(\alpha - \sin\alpha\cos\alpha)(\varphi^2 - \sin^2\varphi) + \mu_2(\varphi - \sin\varphi\cos\varphi)(\alpha^2 - \sin^2\alpha). \quad [7]$$

Stresses at $h = h_1$ are derived with due account of the condition $\{p_{\theta\theta} \Rightarrow 0$ for $r \Rightarrow \infty$ over the line $\theta = \alpha\}$ that is a consequence from [2]. With this in mind, it should be concluded that $p \Rightarrow 0$ when $r \Rightarrow \infty$. In this case we have pressures in both media:

$$p_1^{(1)} = \frac{2\mu_1}{r}(c_1\sin\theta + d_1\cos\theta), \quad p_2^{(1)} = -\frac{2\mu_2}{r}(c_2\sin\theta_2 + d_2\cos\theta_2). \quad [8]$$

Making use of the expression

$$p_{\theta\theta} = -p - 2\mu\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial\psi}{\partial r},$$

we find the stress jump at $h = h_1$:

$$(p_{\theta\theta}^{(1)})_1 - (p_{\theta\theta}^{(1)})_2 = \frac{\sigma}{r}\epsilon, \quad \epsilon = Ca2Q(\alpha), \quad Ca = \frac{\mu_1 v}{\sigma},$$

$$Q = \frac{\sin\alpha}{\Delta\mu_1}((\mu_1\varphi + \mu_2\alpha)^2 - \sin^2\alpha(\mu_1 - \mu_2)^2), \quad \varphi = \pi - \alpha. \quad [9]$$

From the condition [1] for normal stresses and from [9], one can derive a relation for the curvature,

$$q = \frac{\epsilon}{r}, \quad r = \frac{h}{\sin\alpha} \quad [10]$$

and an equation for the angle α in the main approximation (if Ca is low).

$$\frac{d\alpha}{dh} = Ca\frac{2Q}{h}. \quad [11]$$

Integrating the latter, we obtain the function $\alpha(h)$, see (Voinov 1976, 1977, 1978, 1988).

2.2. *Approximate description of the interface in the vicinity of the tangent*

Let us use $\beta(h)$ to denote an interface inclination angle at an arbitrary point $\{h\}$, and α, at $h = h_1$. Introduce a Cartesian co-ordinate system $\{\xi, \zeta\}$ in which the ζ axis goes along the normal at the point $\{h = h_1\}$ and the origin is at the solid surface (figure 1); for this system we have the following transformation relations:

$$\mathrm{tg}(\theta - \alpha) = \zeta/\xi, \quad r^2 = \xi^2 + \zeta^2.$$

The curve corresponding to the function $\beta(h)$ may be rewritten in terms of $\zeta(\xi)$. Then from [10] the following simplified equations can be derived:

$$\frac{d^2\zeta}{d\xi^2} = \frac{\epsilon}{\xi} + \cdots \quad [12]$$

$$\frac{d\zeta}{d\xi} = \epsilon \ln \frac{\xi}{r_1}, \quad \zeta = \epsilon\left[\xi \ln \frac{\xi}{r_1} - \xi + r_1\right]. \qquad [13]$$

For it to be valid. $|\zeta|$ must be much less than $\xi \sin\alpha$.

It $\xi/r_1 \to 0$ then [13] holds when

$$\xi \gg |\epsilon| r_1 (\sin\alpha)^{-1} = r_*. \qquad [14]$$

From [13] and [14] it is clear that presenting the boundary as equation [12] is justified if the condition from (Voinov 1976, 1978, 1988) is met:

$$|Ca| Q \sin^{-1}\alpha \ll 1. \qquad [15]$$

The following formulas of an interface point vectorial angle θ and components of the normal are valid:

$$\theta = \alpha + \zeta/\xi + \cdots, \quad n_\theta = 1 + \cdots, \quad n_r = \frac{\zeta}{\xi} - \frac{d\zeta}{d\xi} + \cdots. \qquad [16]$$

Boundary conditions stated for the interface may rather accurately be rewritten for $\theta = \alpha$ by using (i) the first and second terms in the series expansion (in θ) of functions $f(r, \theta)$ present in the boundary conditions

$$f(r, \theta) = f(r, \alpha) + \frac{\partial f}{\partial \theta}(r, \alpha)(\theta - \alpha) + \cdots$$

and then (ii) the relation [16]. As a result, the kinematic conditions [1] at the interface will be of the following form at the line $\{\theta = \alpha\}$:

$$(u_\theta)_1 = (u_r^{(1)})_1 \frac{d\zeta}{d\xi}, \quad (u_\theta)_2 = (u_r^{(1)})_2 \frac{d\zeta}{d\xi}, \quad (u_r)_1 - (u_r)_2 = \left(\frac{\partial u_r^{(1)}}{\partial \theta}\right)_2 \frac{\zeta}{r} - \left(\frac{\partial u_r^{(1)}}{\partial \theta}\right)_1 \frac{\zeta}{r}. \qquad [17]$$

The requirement for continuity of tangential stresses at the interface in [1] provides an additional condition:

$$(p_{r\theta}^{(2)})_1 - (p_{r\theta}^{(2)})_2 = \left\{\left(\frac{\partial p_{r\theta}^{(1)}}{\partial \theta}\right)_2 - \left(\frac{\partial p_{r\theta}^{(1)}}{\partial \theta}\right)_1\right\} \frac{\zeta}{r}, \quad \theta = \alpha. \qquad [18]$$

A jump in normal stresses at the interface may be written by analogy with [17] and [18]. It is readily seen that at $r = r_1$ we have

$$(p_n)_1 - (p_n)_2 = (p_{\theta\theta}(r, \alpha))_1 - (p_{\theta\theta}(r, \alpha))_2 + \cdots. \qquad [19]$$

By using: (i) continuity of $p_r^{(1)}$ at $\theta = \alpha$; and (ii) equation [8], it is easy to demonstrate that [19] is also true for the case $r/r_1 \Rightarrow \infty$.

2.3. Boundary-value problem for stream function

Substitute in [17] and [18] the expressions for $u_r^{(1)}$, $p_{r\theta}^{(1)}$, and ζ as derived from [7] and [13]. This poses conditions for functions $\psi_j^{(2)}$:

$$\frac{\partial \psi_j^{(2)}}{\partial r} = -g_j \ln \frac{r}{r_1}, \quad \theta = \alpha \qquad [20]$$

$$\frac{1}{r}\frac{\partial \psi_1^{(2)}}{\partial \theta} - \frac{1}{r}\frac{\partial \psi_2^{(2)}}{\partial \theta} = g_3\left(\ln \frac{r}{r_1} - 1 + \frac{r_1}{r}\right) \qquad [21]$$

$$\mu_1\left[\frac{1}{r^2}\frac{\partial^2 \psi_1^{(2)}}{\partial \theta^2} - r\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial \psi_1^{(2)}}{\partial r}\right)\right] - \mu_2\left[\frac{1}{r^2}\frac{\partial^2 \psi_2^{(2)}}{\partial \theta^2} - r\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial \psi_2^{(2)}}{\partial r}\right)\right] = \frac{g_4}{r}\left(\ln \frac{r}{r_1} - 1 + \frac{r_1}{r}\right). \qquad [22]$$

The constants g_j, g_3, and g_4 are determined using

$$g_1 = g_2 = \epsilon \frac{v}{D} [(\varphi^2 - \sin^2\varphi)(\alpha\cos\alpha - \sin\alpha) - \mu_*(\alpha^2 - \sin^2\alpha)(\varphi\cos\varphi - \sin\varphi)], \quad \varphi = \pi - \alpha,$$

$$g_3 = \epsilon \frac{2v}{D} \sin^3\alpha(1-\mu_*)\pi, \quad g_4 = \epsilon\frac{2v}{D}\mu_1[\sin^2\alpha(1-\mu_*)^2 - (\varphi + \mu_*\alpha)^2]\sin\alpha \quad [23]$$

$$\epsilon = Ca\frac{2\sin\alpha}{D}[(\varphi+\mu_*\alpha)^2 - (1-\mu_*)^2\sin^2\alpha],$$

$$D = (\alpha - \cos\alpha\sin\alpha)(\varphi^2 - \sin^2\varphi) + \mu_*(\varphi - \cos\varphi\sin\varphi)(\alpha^2 - \sin^2\alpha). \quad [24]$$

Conditions at the solid become

$$\psi_1^{(2)} = 0, \quad \frac{\partial\psi_1^{(2)}}{\partial r} = 0 \quad \text{for} \quad \theta = 0 \quad [25]$$

$$\psi_2^{(2)} = 0, \quad \frac{\partial\psi_2^{(2)}}{\partial r} = 0 \quad \text{for} \quad \theta = \pi. \quad [26]$$

According to [21], the radial velocity disturbance $v_r^{(2)}$ is singular $(1/r)$ at $r = 0$. However, no mass sources/sinks are present in the close vicinity of that point (where $r \Rightarrow 0$). Therefore, [27] holds:

$$\psi_1(r_1, \alpha) = \psi_1(r_1, 0), \quad \psi_2(r_1, \alpha) = \psi_2(r_1, \pi). \quad [27]$$

These mean that there are no mass flows within media 1 and 2 through the above arcs of the circle (normal to both the interface and the solid surface.)

Additionally, it is required that singularity (for $r \Rightarrow 0$ and $r \Rightarrow \infty$) of the function $|\nabla\psi_j^{(2)}|$ in the second approximation be minimum. The "minimum singularity" is meant as follows: among the possible solutions the one is chosen which provides $|\nabla\psi_j^{(2)}|$ whose growth in going to a singular point is the slowest. From section 3 it is seen that this requirement is necessary for an asymptotic solution to be unique.

2.4. *Stream function and difference in normal stresses at interface*

Biharmonic functions that satisfy [20]–[27] and the "minimum singularity in velocity" principle are to be found by using the following superposition of solutions to the biharmonic equation

$$\psi_1^{(2)} = r\left(\ln\frac{r}{r_1} - 1\right)[a_1\theta\sin\theta + b_1(\theta\cos\theta - \sin\theta)]$$

$$+ f_1 r_1(\sin 2\theta - 2\theta) + l_1 r_1 \cos 2\theta,$$

$$\psi_2^{(2)} = r\left(\ln\frac{r}{r_1} - 1\right)[a_2\theta_2\sin\theta_2 + b_2(\theta_2\cos\theta_2 - \sin\theta_2)]$$

$$+ f_2 r_1(\sin 2\theta_2 - 2\theta_2) + l_2 r_1\cos 2\theta_2, \quad \theta_2 = \pi - \theta. \quad [28]$$

Here, a_j, b_j, f_j and l_j are constants $(j = 1, 2)$.

Singularities in $|\nabla\psi^{(2)}|$ (as described by [28]) at points $r = 0$ and $r = \infty$ are minimum because they correspond to singularities in boundary conditions [20] and [21]. The coefficients a_j and b_j are defined by the system of equations:

$$a_1\alpha\sin\alpha + b_1(\alpha\cos\alpha - \sin\alpha) = -g_1,$$

$$a_2\varphi\sin\varphi + b_2(\varphi\cos\varphi - \sin\varphi) = -g_1, \quad \varphi = \pi - \alpha,$$

$$a_1(\sin\alpha + \alpha\cos\alpha) - b_1\alpha\sin\alpha + a_2(\sin\varphi + \varphi\cos\varphi) - b_2\varphi\sin\varphi = g_3,$$

$$\mu_1(a_1\cos\alpha - b_1\sin\alpha) - \mu_2(a_2\cos\varphi - b_2\sin\varphi) = \tfrac{1}{2}g_4. \quad [29]$$

The coefficients f_j and l_j are defined by the system:

$$f_1(\cos 2\alpha - 1) - l_1 \sin 2\alpha + f_2(\cos 2\varphi - 1) - l_2 \sin 2\varphi = \tfrac{1}{2} g_3,$$
$$-\mu_1(f_1 \sin 2\alpha + l_1 \cos 2\alpha) + \mu_2(f_2 \sin 2\varphi + l_2 \cos 2\varphi) = \tfrac{1}{4} g_4,$$
$$f_1(\sin 2\alpha - 2\alpha) + l_1(\cos 2\alpha - 1) = -g_1,$$
$$f_2(\sin 2\varphi - 2\varphi) + l_2(\cos 2\varphi - 1) = -g_1, \quad \varphi = \pi - \alpha. \qquad [30]$$

The curvature variation condition [2] poses a requirement on normal stresses at a distance from the point $h = h_1$. According to [1], [2], and [19], it is necessary that disturbance $(p_{\theta\theta}^{(2)})_j$ to stresses over the line $\{\theta = \alpha\}$ tends to zero when $r \Rightarrow \infty$. Therefore, we should ensure that pressure p over the line $\{\theta = \alpha\}$ tends to zero in each of the liquids when $r \Rightarrow \infty$. Pressure p should be written for each of the stream functions in [28]; then corrections to the difference between normal stresses (at $r = r_1$) in the second approximation can be expressed:

$$(p_{\theta\theta}^{(2)})_1 - (p_{\theta\theta}^{(2)})_2 = -\frac{4}{r_1}(\mu_1 f_2 + \mu_2 f_2). \qquad [31]$$

Coefficients f_1 and f_2 are found from [30]:

$$f_1 = \frac{\sin\alpha}{4\Delta_*} g_3\mu_2(2\varphi\cos 2\varphi - \sin 2\varphi) - (\varphi\cos\varphi - \sin\varphi)[(\mu_2 - \mu_1)g_1\cos 2\alpha + \frac{g_4}{4}(\cos 2\alpha - 1)].$$

$$f_2 = \frac{\sin\alpha}{4\Delta_*} g_3\mu_1(2\alpha\cos 2\alpha - \sin 2\alpha) + (\alpha\cos\alpha - \sin\alpha)[(\mu_2 - \mu_1)g_1\cos 2\alpha + \frac{g_4}{4}(\cos 2\alpha - 1)].$$

$$\Delta_* = (\alpha\cos\alpha - \sin\alpha)(2\varphi\cos 2\varphi - \sin 2\varphi)\mu_2 + (\varphi\cos\varphi - \sin\varphi)(2\alpha\cos 2\alpha - \sin 2\alpha)\mu_1. \qquad [32]$$

Substituting [32] into [31], taking into account [23] and [24], and performing cumbersome transformation, we arrive at

$$(p_{\theta\theta}^{(2)})_1 - (p_{\theta\theta}^{(2)})_2 = -\frac{\sigma}{r_1}\epsilon^2 \operatorname{ctg}\alpha. \qquad [33]$$

2.5. Second-order asymptotic relation for boundary inclination angle

Substitution of [9] and [33] into [19] and then into the boundary condition for normal stresses leads us to a differential equation

$$\frac{d\alpha}{dh} = \frac{\epsilon}{h}(1 - \epsilon\, ctg\,\alpha), \quad \epsilon = \epsilon(\alpha). \qquad [34]$$

Taking into account that $\epsilon|\operatorname{ctg}\alpha| \ll 1$, rewrite [34].

$$\left(\frac{1}{\epsilon} + \operatorname{ctg}\alpha\right) d\alpha = \frac{dh}{h}, \quad \epsilon = 2CaQ, \quad Ca = \frac{\mu_1 v}{\sigma}. \qquad [35]$$

Integrating the latter generates the formula for the angle α:

$$\tfrac{1}{2}\int \frac{d\alpha}{Q(\alpha, \mu_*)} + Ca \ln\sin\alpha = Ca \ln h,$$

$$Q = \frac{\sin\alpha[(\varphi + \mu_*\alpha)^2 - (1 - \mu_*)^2 \sin^2\alpha]}{(\varphi^2 - \sin^2\varphi)(\alpha - \cos\alpha\sin\alpha) + \mu_*(\alpha^2 - \sin^2\alpha)(\varphi - \cos\varphi\sin\varphi)}, \varphi = \pi - \alpha. \qquad [36]$$

It is valid when Ca is low and h/h_m is very large (but $h \ll h_0$). The expression [36] describes slow angle variation with distance h if [15] is satisfied. The slow variation condition [15] may be violated around points $\alpha = 0$ and $\alpha = 180°$.

In the case of zero viscosity of the medium 2 ($\mu_* = 0$) the relation [36] correlates well with the similar second-order equation in (Voinov 1978) for "liquid–gas" interface and differs therefrom in the expression for Q only. Note that article by Voinov (1976) contains the main approximation equation for $\mu * = 0$; generalizing it to the case of $\mu_* \neq 0$ is an easy operation, see (Voinov 1988); however, deriving the second approximation is far from being simple.

The second addend at the left-hand side of [36] represents a contribution of the second approximation with respect to Ca. Unlike the first term (which is valid for any angle) the second one can be utilized over a restricted set of angles, see section 3.

The formula [36] contains an arbitrary constant that has been found in (Voinov 1976) for the main approximation. As for the second approximation, a determination method is outlined in (Voinov 1995). Proceeding as in the latter paper, rewrite [36]:

$$\frac{1}{2}\int_{\alpha_m}^{\alpha} \frac{d\alpha}{Q(\alpha, \mu_*)} + Ca \ln \frac{\sin \alpha}{\sin \alpha_*} = Ca \ln \frac{h}{h'_m},$$

$$\alpha_* = (9Ca)^{1/3} \quad \text{if} \quad \alpha_m^3 \leqslant 9Ca, \quad \alpha_* = \alpha_m \quad \text{if} \quad \alpha_m^3 \geqslant 9Ca. \quad [37]$$

Here, α_m is a static contact angle ($\alpha_m = 0$ in the case of perfect wetting) or a static wetting hysteresis angle (Voinov 1976). The angle α_m can also be determined with due account of nonequilibrium physicochemical processes (see Blake & Haynes 1971 for example) if these are of importance; that angle should not depend on energy dissipation due to viscosity in a liquid. The value h'_m must generally be obtained by experiments; it can be much less than the limiting (minimum) characteristic distance h_m that restricts validity of the macroscopic flow model adopted (which includes equations and boundary conditions). The main approximation and the experimental results were compared in (Voinov 1976, 1978); it has been shown that h'_m may be as low as a molecule size a, so there is every reason to write $h'_m = Ka$, where K is close to unity, see (Voinov 1995).

Other ways to establish the auxiliary parameter α_* in [37] are acceptable, provided that the order of magnitude thereof is maintained; note that h'_m depends on it. The difference in α_* for relatively low and high values of α_m in [37] is due to ln sin α tending to infinity when $\alpha \Rightarrow 0$ (and $\alpha \Rightarrow \pi$). For high angles α (comparable with π) an equation symmetric with respect to [37] can be written.

The present version of dependence of α_* on α_m and Ca is linked with the simplified relation valid at $\mu_* = 0$, see (Voinov 1976):

$$\alpha^3 = \alpha_m^3 + 9Ca \ln \frac{h}{h_m}. \quad [38]$$

It is effective for angles α less than 150°.

Difference of α_* from α_m in [37] may only be essential if $\alpha_m \ll 1$. Using the expansion of $Q(\alpha, \mu_*)$ with respect to the low variable α, it can be shown that establishing the angle α_* from [37] is justified if the viscosity ratio is rather low: $\mu_* < 6\pi/\alpha_m^3$.

Equation [37] (or its counterpart for $\alpha_m \simeq \pi$) may be employed to formulate external hydrodynamics problems, proceeding by analogy with the asymptotic theory in (Voinov 1995). In the external zone the interface can be nearly spherical, which simplifies treating the problem. The corresponding surface shape equation is presented in (Voinov 1995). Note that the relation for F in [34] of the latter reference should include a multiplier $R^2 \sin \theta$ (occasionally omitted).

3. VALIDITY DOMAIN OF ASYMPTOTIC RELATION FOR DYNAMIC CONTACT ANGLE

The solution for the stream function [28] with coefficients from [29] and [30] is unique under certain conditions. To establish these, consider a problem for [4] with homogeneous conditions. At the solid surface the velocity components are zero:

$$\theta = 0, \quad \psi_1 = 0, \quad \frac{\partial \psi_1}{\partial \theta} = 0; \quad \theta = \pi, \quad \psi_2 = 0, \quad \frac{\partial \psi_2}{\partial \theta} = 0. \quad [39]$$

Over the line $\{\theta = \alpha\}$ the conditions [5] are valid.

Consider a solution to the problem [4], [5], [39] in the following form:

$$\psi_j = r^{m+1} f_j(\theta), \quad j = 1, 2 \qquad [40]$$

$$f_j = a_j \cos(m+1)\theta_j + b_j \sin(m+1)\theta_j + c_j \cos(m-1)\theta_j + d_j \sin(m-1)\theta_j, \quad \theta_1 = \theta, \quad \theta_2 = \pi - \theta. \qquad [41]$$

This solution is similar to those of the problem formulated for the interior of a corner where use is made of the biharmonic equation with homogeneous conditions over corner sides, see Rayleigh (1920), Dean & Montagnon (1949), Moffatt (1964), Timoshenko & Goodier (1970).

Substitute [40] and [41] into [39] and [5]. This provides a homogeneous system of linear equations for eight coefficients in [41]. The solvability condition for the latter (i.e. a determinant being zero) leads us to the equation for the complex exponent m in [40]:

$$\mu_1(m \sin 2\alpha - \sin 2m\alpha)(m^2 \sin^2 \alpha_2 - \sin^2 m\alpha_2) + \mu_2(m \sin 2\alpha_2 - \sin 2m\alpha_2) \times (m^2 \sin^2 \alpha - \sin^2 m\alpha) = 0, \quad \alpha = \alpha_1, \quad \alpha_2 = \pi - \alpha. \qquad [42]$$

If a certain value m is a root of this equation then $-m$ is also a root. Therefore it suffices to analyse the case Re $m > 0$. Equation [42] has an unlimited set of roots at any μ_* ($\mu_* = \mu_2/\mu_1$) and α. Of major interest are roots with minimum positive real parts; these guarantee the slowest growth of $|\nabla\psi|$ when $r \Rightarrow \infty$ (or when $r \Rightarrow 0$ if $-m$ concerns). Hereafter, only such roots are dealt with.

At $\alpha = \pi/2$ the minimum Re m is provided by the (real) root $m = 2$ for any values of μ_*.

If $\alpha \Rightarrow \pi$, the root m tends to 1. Within a certain vicinity of the point $\alpha = \pi$ (with a radius of the vicinity depending on μ_*) Re m is minimal for a real root. For the case of α tending to π the root may be found analytically, by using two terms of Taylor series expansions with respect to α at the point $\alpha = \pi$ for each function in [42] (i.e. $\sin 2\alpha$, $\sin 2m\alpha$, etc.). This operation offers the derivative:

$$\frac{dm}{d\alpha} = -\frac{2}{\pi}\left(1 - \frac{\mu_1}{4\mu_2}\right) \quad \text{for } \alpha = \pi. \qquad [43]$$

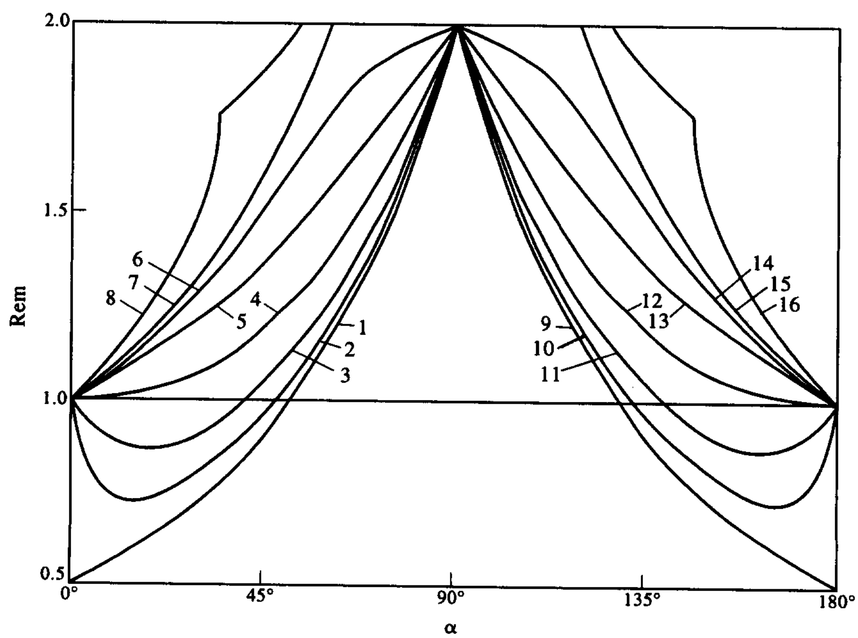

Figure 2. Minimum positive real part of exponent m: dependence on α. Curves 1–8: $\mu_* = \infty$, 30, 10, 4, 2, 1.25, 1, 0, respectively; curves 9–16: $\mu_* = 0$. 0.033, 0.1, 0.25, 0.5, 0.8, 1, ∞, respectively (inverse to the former set).

Table 1.

μ_*	0	0.106	0.171	0.215	0.241	0.25
α^+	128.7	140°	150°	160°	170°	180°

Thence it is clear that

(i) the function $m(\alpha)$ is equal to 1 at $\alpha = \pi$ and this value is its minimum for $\mu_1 < 4\mu_2$,

(ii) this value of the function is maximum for $\mu_1 > 4\mu_2$; in this case min Re $m < 1$.

Note that $m = 1$ formally satisfies [42] in the general case (at any α and μ_*). However, one should bear in mind that the root ($m = 1$) does only in particular situations (at certain values of α and μ_*) have relevance to the original problem—and should be rejected in other situations.

Results of computation of the root of [42] with a minimum Re m are depicted in figure 2 for various values of the angle α and viscosity ratio μ_*. The value α^+ at which m equals 1 grows with μ_* (from the minimum value, 128.7°, at $\mu_* = 0$ to π at $\mu_* = 1/4$). Similarly, for $\mu_* > 4$ there exists a (positive) point α^- at which $m = 1$.

In the important particular case with $\mu_* = 0$ (the medium 2 is inviscid as is with gases) the relation [42] breaks down into three equations, of which we should pay attention to one only:

$$m \sin 2\alpha = \sin 2m\alpha. \qquad [44]$$

The minimum positive value of Re m of a root of [44] decreases monotonically over the interval$(0, \pi)$. If μ_* is low (but non-zero), the function Re $m(\alpha)$ is not monotonic in a small-size vicinity of the point $\alpha = \pi$, see figure 2 and/or [43].

From the solution [28], the function $|\nabla\psi^{(2)}|$ varies at the singular points as follows:

$$|\nabla\psi^{(2)}| \sim 1/r, \quad r \Rightarrow 0 \qquad [45]$$

$$|\nabla\psi^{(2)}| \sim \ln r, \quad r \rightarrow \infty. \qquad [46]$$

For the solution $\psi^{(2)}$ to be unique it is sufficient that any solution ψ^* to a problem with homogeneous conditions ([4], [5], and [39]) ensures that the function $|\nabla\psi^{(2)}|$ at the zero point and/or at the infinitely remote point grows quicker than $|\nabla\psi^*|$:

$$r|\nabla\psi^*| \Rightarrow \infty, \quad r \Rightarrow 0 \qquad [47]$$

$$|\nabla\psi^*|(\ln r)^{-1} \Rightarrow \infty, \quad r \Rightarrow \infty. \qquad [48]$$

If conditions [47] or [48] are not met, then the solution is not unique since solutions of the homogeneous problem can be added to a solution, thus producing new ones. If [47] and [48] are met, then solutions of the homogeneous problem become eliminated due to the minimum singularity principle (section 2.4).

It is readily seen that [48] is met if [47] is. The condition [47] requires Re $m < -1$, therefore the equation [42] roots with Re $m > 0$ must be such that

$$\text{Re } m > 1. \qquad [49]$$

The latter is met if $\alpha < \alpha^+$ (μ_*) for $\mu_* < 1/4$ and if $\alpha > \alpha^-$ (μ_*) for $\mu_* > 4$. Critical values of α^+ and α^- are given in tables 1 and 2. If viscosity coefficients of the liquids differ by a factor of less than four ($1/4 < \mu_* < 4$), no restrictions are posed because [49] is met at any α. In the case of zero viscosity of the liquid 2 ($\mu_* = 0$) the critical angle α^+ is 128.7°. Increasing the viscosity ratio μ_* increases α^+, and at $\mu_* = 1/4$ the critical angle α^+ equals to π.

These conditions ensure uniqueness of the second-approximation solution. It may be demonstrated that if the condition [49] is not satisfied, then the velocity field essentially depends on the

Table 2.

μ_*	4	4.15	4.65	5.84	9.43	∞
α^-	0	10°	20°	30°	40°	51.3°

influence of a small vicinity of the point $r = 0$ (whose radius is r_*, see [14]) where the boundary notably differs from the tangent at $h = h_1$ and the asymptotic solution is not valid. If [49] is met, a contribution of this small vicinity to the velocity field at $r \simeq r_1$ is negligible.

4. CONCLUSION

The relation [36] for the tangent inclination angle describes the interface shape obtained from a nonlinear hydrodynamic problem. When deriving [36], the velocity field is determined taking into account a difference of the interface S_{12} from its tangent in the vicinity of the fixed point where this tangent is drawn. The relation [37] (or a similar relation for the case $\alpha_m \sim \pi$) may be a basis to formulate the external hydrodynamic problems (at a rather long distance from the contact line) as in (Voinov 1995). The parameter h_0 that outlines the internal domain ($h \ll h_0$) may be governed by various external flow conditions which could violate the assumptions underlying the asymptotic relation [36]. These conditions could include a nonstationary interface, nonzero interface curvature, and finite Reynolds number, etc.

The asymptotic second-order relation (valid at low capillary numbers) for the angle takes for the first time into account the effect of the viscosity ratio. It should be noted that the contribution of the second approximation to this relation coincides with a similar contribution in the case of liquid-gas interface (when one of the viscosity coefficients is zero) as shown in (Voinov 1978). The contribution of the second approximation to the asymptotic relation describing the interface is much simpler than the contribution of the first approximation.

Of importance is the conclusion that the second-order asymptotic theory is generally valid not for any value of the boundary inclination angle α. Unlike the first-order theory (that poses no restrictions with respect to α if Ca is low) the second-order theory may turn out to be bad for low or high angles. The range of validity (with respect to the angle) of the second-order asymptotic theory depends on the viscosity ratio μ_*. The range widens when the difference in viscosity coefficients diminishes. If $\mu_* \in (1/4, 4)$, the second approximation is valid regardless of the angle. If viscosity of the liquid 2 is zero ($\mu_* = 0$), the second approximation is valid for angles of no more than 128.7°.

According to the hydrodynamics theory, the dynamic contact angle exists over a limited range of the wetting velocity v (Voinov 1976, 1978, 1988). There can exist critical values of velocity v at which the angle is equal to 180° and 0. The second-approximation equation [37] may be used to refine the angle at velocities close to the maximum (critical) wetting velocity (but not equal thereto) if the viscosity coefficient of the second phase is rather high ($\mu_* > 0.25$). In the case of negative v a similar applicability condition ($\mu_* < 4$) of the second-approximation theory is valid for the entire possible negative v range.

This finer asymptotic theory for the interface dynamics may be useful in deriving reliable quantitative estimate of the microprocess influence on the dynamic contact angle in wetting dynamics experiments.

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