Pergamon

Int. J. Multiphase Flow Vol. 21, No. 5, pp. 801–816, 1995
Elsevier Science Ltd. Printed in Great Britain
0301-9322(94)00073-5

MOTION OF LINE OF CONTACT OF THREE PHASES ON A SOLID: THERMODYNAMICS AND ASYMPTOTIC THEORY†

O. V. VOINOV
Institute of Mechanics of Multiphase Systems, Tyumen 625000, Russia

(Received 20 February 1994; in revised form 11 October 1994)

Abstract—A thermodynamics approach to the description of the dynamic boundary angle is proposed. An energy equation for the moving line of contact of three media is derived taking into account viscous flow. The energy equation is used to substantiate the boundary condition of the asymptotic theory for the free boundary slope angle at a small distance from the solid.

Second-order asymptotic relations of the dynamic wetting theory are developed assuming a low capillary constant. Boundary conditions for Navier–Stokes equations over a moving three-phase contact line for a general flow of viscous liquid are derived. A solution procedure for the case of low Reynolds numbers is considered. Assuming a stationary movement of the interface in a capillary, a method for establishing the second-order terms is proposed. Exact asymptotic solutions are obtained. Symmetry of theasymptotic relation for the dynamic boundary angle in the principal approximation is described.

Key Words: wetting, dynamic contact angle, hydrodynamics

1. INTRODUCTION

Theoretical studies on shock waves in continua are known to give much attention to integral conservation laws for the moving discontinuity surfaces. When a solid body is wetted with a liquid the liquid–gas contact line is moving at a much lesser speed. The interface surfaces intercept one another on the moving contact line for the three phases, i.e. on the wetting line. In a small-size vicinity of the line the conservation laws must also hold. Such an approach (Voinov 1976) is of interest in connection with the problem of substantiating within the wetting hydrodynamics the boundary condition for a small-size area; numerous discussions are currently undertaken, and various models [the contributions by Dussan (1979) and Baiocchi & Pukhnachev (1990)] are proposed in order to eliminate the sigularity in stresses near the contact line and for the flow within the corner; the singularity has been revealed by Moffat (1964) and Huh & Scriven (1971).

In the contributions by Hansen & Toong (1971), Voinov (1976, 1977) and Boender *et al.* (1991), the liquid–gas boundary slope angle is taken to be equal to the equilibrium boundary angle at a certain small distance from the solid surface.

Of course, mechanisms of dependence of the capillarity angle on the wetting velocity can well differ from hydrodynamic ones. The angle is known to depend on kinetic processes near the wetting line (Blake & Haynes 1969).

We consider the influence of viscous flow on the boundary angle, and address the thermodynamics in the validation of the boundary condition around the wetting line (see section 2).

A non-linear flow pattern, in the caseof a free boundary in the vicinity of a moving contact line on a smooth solid surface, has been established asymptotically in two approximations, with respect to the capillary constant, Ca (Voinov 1976, 1977, 1978), introducing one arbitrary constant. This arbitrary constant reflects the influence of a microscopic flow on the interface shape if the second iteration is dealt with. This is the major challenge in closing the theory in the next iterations with respect to the low constant, Ca. It is only in the first iteration that the effects of microscopic flow are insignificant. In the case of a general velocity field, the above arbitrary constant is known for the first iteration. There are only two flow modes with low dynamic boundary angles for which the closed-form solutions have been derived in the second iteration (Voinov 1977):

†Due to circumstances beyond the Publisher's control, this paper appears in print without author corrections.

—wetting of a surface covered with a thin liquid film
—slow wetting of a dry surface under the effects of Van der Waals forces.

Other analytical approaches (Boender *et al.* 1991) to solving the problem of wetting a capillary with low-Reynolds-number flows correspond, in the accuracy achieved, to the first iteration.

There arises a natural desire to find a method for closing the asymptotic theory of flows in the vicinity of the moving contact line at the second iteration with respect to the capillary constant; the result will be a reliable basis in large characteristic distance, h_0, between the free boundary and the solid surface. In this domain the flow of a viscous incompressible liquid subjected to body forces is described by the following equations:

$$\rho \frac{\mathrm{d}u}{\mathrm{d}t} = -\nabla P + \rho g + \mu \Delta u, \operatorname{div} u = 0. \qquad [1]$$

At the solid surface (assumed smooth) we impose a normal condition$u = u_s (u_s$ is the speed of the solid). Over the liquid–gas interface, S_{12}, the normal velocity component of the liquid (u_n) is equal to the normal velocity component ω of the surface point; no tangential stress P_τ exists here; and a normal stress P_n is described by the Laplacian relation in terms of the mean curvature of the interface

$$P_n = -\mathrm{P}_0 + \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad [2]$$

where R_1 and R_2 are the principle curvature radii, P_0 is the gas pressure and σ is the surface tension.

In the analytical theory for the dynamic boundary angle, the boundary condition [2] is satisfied in the course of iterations. These utilize the fact that the contribution of viscous stresses to [2] is relatively small.

The asymptotic theory of wetting dynamics is based on two perturbations:

$$|\mathrm{Ca}| = \frac{\mu |v|}{\sigma} \ll 1, \quad \ln^{-1}\frac{h_0}{h_m} \ll 1 \qquad [3]$$

where h_0 and h_m are the maximum and minimum characteristic distances, respectively, from the free boundary to the solid. The macroscopic description of liquid flow is limited by a minimum distance, h_m of the free boundary from the solid; this value is conventionally on the order of a few molecular sizes a. In going to very low dynamic angles the minimum length may turn out to be very large $h_m \gg a$, is the motion equations do not explicitly take into account of Van der Waals forces (Voinov 1977).

2. ENERGY EQUATION FOR THE VICINITY OF THE MOVING CONTACT LINE

Let the surface, S_{12}, of contact between a liquid (the index "1") and a gas (the index "2") move along a flat surface of a solid body at a constat velocity, v.

Within this two-dimensional problem we outline a small cylindrical volume V_0 that includes the wetting line and a fixed set of particles of the three continua (figure 1). At a time, t, we can, without loss of generality, assume that the surface, S_0, of this volume is normal to the boundary, S_{12}, along the intersection line. The line, L_1, along which S_0 intercepts the first medium, is allowed to be modeled with a circle are at the present time t. The entirety of the flat section of the control surface S_0 can be modeled with a circumference if the wetting line is within it. When the dynamic boundary angle is very small, the wetting line may turn out to be beyond such a circumference. In this case the control surface S_0 must obviously be prolonged in the motion direction (i.e. along the x_1 axis). the x_3 of the Cartesian system $\{x_1, x_2, x_3\}$ runs along the wetting line, the value $x_2 < 0$ corresponding to the solid.

The distance h from the solid surface to the point of intersection of the free boundary S_{12} with the contour L_1 of the surface S_0 must be a macroscopic parameter large enough to enable the continuum mechanics approach to be employed.

We should take into account the energy preservation law: in the case of slow motion of substances (with very low kinetic energy), both the external work per unit time, W_Σ, and the variation rate of free energy, F, correspond to the total dissipation of energy, E_Σ, per unit time within the control surface S_0:

$$-\frac{\mathrm{d}F}{\mathrm{d}t} + W_\Sigma = E_\Sigma. \qquad [4]$$

The quantities involved refer to a unit length of the wetting line. It is usual in hydrodynamics to assume that the heat power due to viscosity is rather low, so the process may be considered isothermal.

The variation rate of free energy F is governed by a rate of variation of a total free surface energy on the interface within S_0:

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \sigma\frac{\mathrm{d}l^{12}}{\mathrm{d}t} + (\sigma_1 - \sigma_2)v \qquad [5]$$

when σ_1 and σ_2 are the surface densities of free energy on the boundaries between the solid and the first and second phases, respectively; σ is the same as for the interface S_{12} of the two phases. The speed of variation of the length l_{12} of the contour of the surfaces S_{12} within S_0 may be found with due account for stability of the shape of the surface S_{12}:

$$\frac{\mathrm{d}l_{12}}{\mathrm{d}t} = u_\tau + v\cos\alpha. \qquad [6]$$

Here α is the angle of the slope of the tangent to S_{12} at the point $x_2 = h$ of intersection with S_0; u_2 is the tangential speed component at that point. The external work within S_0 is that of the surface forces

$$W_\Sigma = \sigma u_\tau + W,$$

$$W = \int_{L_1 \cup L_2} p_{ij}n_ju_i\,\mathrm{d}l \int_{L_1} (P_{ij}n_j + P_0n_i)u_i\,\mathrm{d}l, \qquad [7]$$

where curves L_1 and L_2 are on S_0(figure 1); P_{ij} is a stress tensor; n_j is a normal vector; u_i is a velocity in the co-ordinate system of the immovable solid; the repeating indices $i,j = 1, 2$ are summation indices.

From [4]–[7] we obtain the main energy equation (Voinov 1976) for the vicinity of the interface of three phases

$$-\sigma v\cos\alpha + (\sigma_2 - \sigma_1)v + W = E_\Sigma \qquad [8]$$

where W is the work of distributed surface forces per unit time [7]; E_Σ is the total dissipated energy per unit time within the surface S_0.

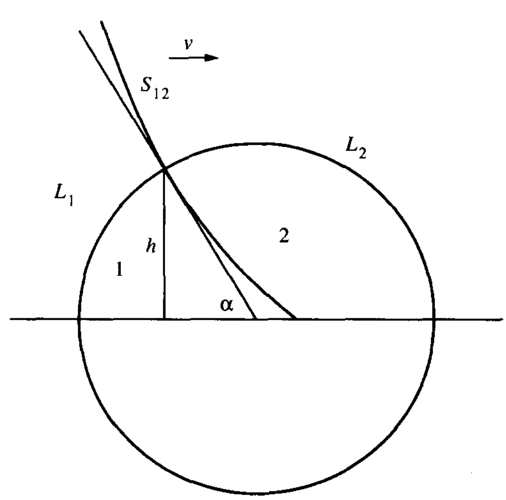

Figure 1.

Let S_l be a flat section of a liquid volume inside S_0, this domain being outlined by the arc L_l that is related to h. The dissipated energy E_Σ may be represented in a similar way to that in Voinov (1976): as a sum of the viscous dissipation E in the liquid volume and dissipation E_m on the wetting line (inside the domain S_m, which coincides with the domain S_l at $h = h_m$),

$$E_\Sigma = E + E_m, \quad E_m = G|v| = \tilde{E}_m + \tilde{G}|v|. \qquad [9]$$

Here, $\tilde{E}_m$ is the viscous dissipation in the domain S_m. Note that the coefficient $\tilde{G} \geqslant 0$ can depend on the velocity v. The domain S_l, with the domain S_m eliminated, is rather far from the wetting line, therefore the viscous dissipation within S_l/S_m is estimated on the basis of an invariant of the strain rate tensor ϵ_{ij}

$$E = 2\mu \int_{S_l \setminus S_m} \epsilon_{ij}\, \mathrm{d}S \qquad [10]$$

where μ is the dynamic viscosity.

2.1. Boundary condition in a small-size domain

Assuming that the wetting angle determined from [8] and [9], without accounting for viscous dissipation ($\tilde{E}_m = 0$ and $W = 0$), is not zero,

$$\cos \alpha_m = (\sigma_2 - \sigma_1 - \tilde{G} \sin v)/\sigma < 1. \qquad [11]$$

If $\tilde{G} = 0$, then the angle σ_m is equal to the static boundary angle σ_S.

Let us assume that the wetting speed V is slow enough that the angle σ varies insignificantly with the distance from the solid surface; with this, liquid flow is close to flow in a corner. The above assumptions become valid if the capillary constant satisfies the criterion below:

$$3|\mathrm{Ca}| \ll \sigma^3. \qquad [12]$$

The viscous energy dissipation $E + \tilde{E}_m$ in the liquid takes place mainly in a flow with macroscopic characteristic lengths and vanishes at scales as small as the size of a molecule, a. Therefore, energy dissipation may be estimated within the hydrodynamic theory by regularizing the dissipation in a small domain, with a length

$$h_\epsilon = ka \qquad [13]$$

written using a constant $k = 2 - 3$.

When determining the velocity field u from the Stokes equations, we impose the usual conditions (see section 1). On the interface S_{12}:

$$P_n + P_0 = -\sigma \frac{\mathrm{d} \cos \sigma}{\mathrm{d}h} \quad \frac{\mathrm{d} \cos \sigma}{\mathrm{d}h} \to 0, \quad \frac{h}{h_m} \to \infty. \qquad [14]$$

The radial density of dissipation of energy, E (introduced in [10]), for a corner flow is described by

$$E_z = \frac{\mathrm{d}E}{\mathrm{d}z} = 2\mu \frac{v^2}{z} Q \sin \alpha \qquad [15]$$

$$Q(\sigma) = \frac{\sin \alpha}{\alpha - \sin \alpha \cos \alpha}. \qquad [16]$$

We now address the difference between the total viscous dissipation $E + \tilde{E}_m$ and the result of the estimation by the hydrodynamics relations [15] and [16] for $z > z_\epsilon$ where z_ϵ is a regularization radius ($h_\epsilon = z_\epsilon \sin \alpha$)

$$E + \tilde{E}_m - \int_{z_\epsilon}^{z} E_z\, \mathrm{d}z = 0(1) z E_z = 0(1) \mu v^2 Q \sin \alpha. \qquad [17]$$

The coefficient 0(1) in [17] accounts for an error of calculation employing the viscous dissipation equation for the microscopic scale when $\mathrm{Ca} \to 0$.

To calculate the work of the surface forces, W (see [7]), we use the expression of the jump in normal stresses over the boundary of phases 1 and 2 (Voinov 1976)

$$P_n + P_0 = 2\mu v Q \frac{\sin\alpha}{h}. \qquad [18]$$

This equation is valid when condition [14] is satisfied.

After transformations, from [7], [16] and [18] we obtain

$$WA = -2\mu v^2 Q \sin\alpha. \qquad [19]$$

From the energy equation [8] and the formulae [15], [17] and [19] for small capillarity numbers ($\mathrm{Ca} \to 0$) and macroscopic distances h, we can derive

$$\alpha - \alpha_m = 2\,\mathrm{Ca}\,Q(\alpha_m)\left[\ln\frac{h}{h_c} + 0(1)\right], \quad h = z\sin\alpha. \qquad [20]$$

The latter relation can be compared to the asymptotic representation for the angle α (Voinov 1976; Pismen & Nir 1982)

$$\int_0^\alpha \frac{d\beta}{Q(\beta)} = 2\,\mathrm{Ca}\ln h + \text{const}. \qquad [21]$$

Linearizing the relation [21] at $\alpha \sim \alpha_m$ leads to

$$\alpha = \alpha_m + 2\,\mathrm{Ca}\,Q(\alpha_m)\ln\frac{h}{h'_m}. \qquad [22]$$

From [20] and [22], the boundary condition for [21] is derived in the following form:

$$\alpha = \alpha_m \quad \text{for} \quad h = h'_m = h_c\exp(0(1)). \qquad [23]$$

Here the difference between h'_m and h_c does not exceed the error in the determination of h_c from [13]. Therefore, if the distance from the solid surface is large ($\ln h/h_m \to \infty$), the constant for [21] under the boundary condition [21] should be evaluated assuming $h'_m = h_c$ in the principle approximation with respect to the large parameter $\ln h/h_m$. A condition such as [23] is suitable in the first approximation with respect to $\mathrm{Ca} \ll 1$ (Voinov 1976, 1977).

It is important to note that condition [23] has been derived without continuing the macroscopic theory equations to the microscopic length range—though [23] incorporates the small parameter h'_m.

The derivation of [23] is limited to condition [12] of the slow variation of the angle α with the distance k. The angle α varies rapidly with h over a small distance range if $3\,\mathrm{Ca} \sim \alpha_m^3$; but this does not invalidate the above estimates of the viscous energy dissipation, and [23] is effective as a certain approximation.

In the case of a statistically complete wetting, when $\alpha_m = 0$, we should the relation $\sigma_2 - \sigma_1 \geqslant \sigma$ in [8]. Note that, in these circumstances, the difference in free energies, $\sigma_2 - \sigma_1 - \sigma$, insignificantly influences the viscous flow in the volume since the minimum value of the microscopic angle in [23] is σ_m. Therefore the energy difference above should be equated to the coefficient G (in [9]) of the energy dissipation over the wetting line.

The limiting case of extremely low angles ($\alpha \ll 1$) introduces its own features, since Van der Waals forces can show themselves in macroscopic phenomena. It is important that condition [23] holds, except for the fact that the characteristic length h'_m can significantly exceed the molecular size due to Van der Waals forces (Voinov 1977).

3. BOUNDARY CONDITIONS FOR NAVIER–STOKES EQUATIONS OVER A MOVING THREE-PHASE CONTACT LINE

3.1. Internal asymptotic solution in the second iteration

Consider a flow in a domain where the free boundary is at a short distance ($h \ll h_0$) from the solid, but this distance is large in comparison with the minimum characteristic length ($k \gg k_m$).

The asymptotic solution to the creeping flow problem with a free boundary in the internal region was established utilizing the assumption of slow variation of the boundary slope angle α as a function of the distance h (Voinov 1976)

$$\frac{h}{\alpha}\left|\frac{d\alpha}{dh}\right| \ll 1.$$

To satisfy this strong inequality, we not only require a small capillary number, but we also need to ensure that $\ln h/h_m \gg 1$. This is possible due to [3].

The asymptotics in the second approximation with respect to Ca for arbitrary α angles may be written as in Voinov (1978):

$$\frac{1}{2}\int_0^{\alpha}\frac{d\alpha}{Q(\alpha)} + \text{Ca}\ln\sin\alpha = \text{Ca}\ln h + \text{const.} \quad [24]$$

Here the constant does not depend on h and Q is defined in [16]. The asymptotic solution [24] was obtained taking into account the fact that the interface differs from a straight line; this is utilized when calculating shear stresses at each point of the free boundary on the basis of the corresponding boundary value problem for Stokes equations.

If the α angles are low, the relation [24] is transformed by iterations into the boundary slope angle equation derived in Voinov (1977) from the thin layer motion equation:

$$\alpha^3 = g\,\text{Ca}(S - \tfrac{1}{3}\ln|S|),$$

$$S = \ln\frac{h}{h_m} + C|S| \gg 1, \quad [25]$$

where C does not depend on h. The constants present in [24] and [25] can be determined under the condition that, as the distance $h \to h_m$ becomes less, the angle α must be matched with its value from the energy equation [8].

From the first iteration [21] the dissipated energy amount E is a diverging function for large values of $k \to \infty$, $E \to \infty$. This divergence becomes the basis for closing the theory in the first iteration; such considerations should be taken into account when closing the theory in higher iterations. The divergence provides a positive consequence: variation of the dissipated energy amount within the short length h_m is comparatively small. Therefore the α_m estimates of the angle α for $h \sim h_m$, which are obtained from [8] by neglecting both W and the viscous energy dissipation rate within the characteristic length $h_m(h \sim h_m)$, are valid:

$$\alpha(h_m) \approx \alpha_m = \alpha_S, \quad \cos\alpha = \frac{\sigma_2 - \sigma_1}{\sigma} \quad \text{for} \quad \sigma_2 - \sigma_1 < \sigma$$

$$\alpha_m = 0 \quad \text{for} \quad \sigma_2 - \sigma_1 \geq \sigma. \quad [26]$$

The relation [26] offers a lower estimate for the case $v > 0$ and an upper estimate if $v < 0$. In the first approximation, with respect to the perturbation Ca, we have $\alpha(h_m) = \alpha_m$. If the additional dissipation over the wetting line is essential [as in the case in Blake & Haynes (1969)], then the characteristic value of $\alpha(h_m)$ can notably differ from the value of α_m in [26].

The theory in the second approximation is closed by the following asymptotic formula for the free boundary slope angle α while allowing for the limit $h/h'_m \to \infty$:

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

$$\alpha_* = \alpha_m \quad \text{for} \quad \alpha_m \geq (g\,\text{Ca})^{1/3}, \quad \alpha_* = (g\,\text{Ca})^{1/3} \quad \text{for} \quad \alpha_m \leq (g\,\text{Ca})^{1/3}. \quad [27]$$

Note that the characteristic length $h'_m = Ka$ where a is the liquid molecule dimension and the constant K is determined by identifying the theory on the basis of the experiments. The asymptotic solution [27] depends on a single constant to be evaluated from parameters α_m and h'_m. These new parameters, in opposition to the prior constant, are physically meaningful and ensure matching with the thermodynamics.

When writing [27], use was made of the fact that, in the first iteration with $\alpha_m = 0$, we have $\alpha \sim Ca^{1/3}$ which is valid even for large values of $\alpha = 150°$ (Voinov 1976, 1978). Note that other definitions of α_* in [27] are possible if the order of α_* in them corresponds to [27]. A value of h'_m in this case will differ by a multiplier on the order of unity. In the first approximation (Voinov 1976) it was presumed that $K = 2 - 3$. Experiments confirmed that, as regards the orders of magnitude, we have $K = 1$, if the dynamic wetting angle is not too low (Voinov 1976, 1978).

When the angles are low ($\alpha < 1$), the formula [27] can be transformed in a relation corresponding to [25]. Then, the constant C in [25] is determined by

$$C = \lambda \quad \text{for} \quad \lambda \leqslant 1, \quad C = \lambda + \tfrac{1}{3}\ln\lambda \quad \text{for} \quad \lambda \geqslant 1$$
$$\lambda = \alpha_m^3/g\,\text{Ca}. \tag{28}$$

If the flow velocity is very slow (and the angle $\alpha \ll 1$) and the van der Waals forces are of importance, then $K \gg 1$. For complete wetting, we have, after Voinov (1977),

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

and the coefficient of this equation satisfactorily corresponds to the second approximation; see Voinov (1988); the constant A' is equal to the difference in the Hamaker constants for molecular interaction of a unit volume of liquid with unit volumes of a solid and the same liquid.

3.2. Asymptotic boundary conditions for Navier–Stokes equations

To formulate the hydrodynamic problem for domains at large distances from the wetting line, we replace the internal variable h/h_m with the external variable h/h_0. Let us outline the external region by the inequality

$$\ln(h_0/h) \ll \ln(h_0/h_m). \tag{29}$$

Let L_0 be the solid surface line over which the external variable $h/h_0 = 0$. L_0 is a contact line in "external description." The normal speed of the point L_0 is symbolized by v. The value of v generally varies along the line L_0.The external contact line L_0 is determined in the external domain at $h/h_0 \to 0$, but $h \gg h_m$. the wetting line L_0 can differ from the real line L_* when the dynamic α_0 angles are very small ($\alpha_0 \to 0$) and the influence of Van der Waals forces is considerable. The difference between lines L_0 and L_* in this case is related to the fact that the line L_0 is preceded by the motion of an anomalous thin fim ($h < h'_m$) under Van der Waals forces. The stationary theory of motion of such fims has been considered in Huh & Scriven (1971), Voinov (1977) and Hervet & DeGennes (1984).

To impose restrictions on the wetting line L_0, we consider a plane section S_N in the liquid volume, this section being normal to L_0 at a point x_0. In S_N, for a point x_e of the free boundary L_{12} we may point out a circular arc L_1 passing through this point, the arc being normal to L_{22} at x_e and normal to the solid surface at the intersection point (figure 1). We can formulate the problem on creeping flow beyond the small size domain near L_0, this domain being outlined by the arc L_1 that is related to x_e. Boundary conditions for the line in the external domain can be written taking into account both the internal limit $h/h_0 \to 0$ of the external variable h/h_0 and the necessity to match the "external" boundary angle with [27] in respect of the parameter $\ln h/h_0$:

$$\text{for} \quad x_e \to x_0 \quad \alpha \to \alpha_0(\text{Ca}, h_0) - 2\,\text{Ca}\,Q(\alpha_0)\ln\frac{h_0}{h},$$
$$(u - u_S)\,|\,L_1 \to v^{(0)}; \quad x_e \in S_{12}, \quad x_0 \in L_0. \tag{30}$$

Here the function $\alpha_0(\text{Ca}, h_0)$ is specified by [27], u_S is the speed of the solid at $x = x_0$, the velocity $V^{(0)}$ corresponds to a two-dimensional flow in a corner α that is governed by the stream function

$$\psi^{(0)} = vQ(\cos\alpha\sin\theta - \theta\cos(\alpha - \theta))z,$$
$$Q^{-1} = \frac{\alpha}{h'_n\alpha} - \cos\alpha; \quad v_2^{(0)} = z^{-1}\frac{\partial\psi^{(0)}}{\partial\theta}, \quad v_\theta^{(0)} = -\frac{\partial\psi^{(0)}}{\partial z}. \tag{31}$$

The asymptotic boundary conditions [30] for Navier–Stokes equations notably simplify the derivation of the hydrodynamics problems with free boundary—due to the fact that a domain with a short characteristic length for the distances h is eliminated (from the analysis). We are allowed to search for a small correction, with respect to Ca, to the free boundary shape in the external solution.

3.3. Scheme of external solution for low Reynolds numbers

If the characteristic speed v of the wetting line L_0 is simultaneously a characteristic speed of the flow in the external domain (with a large characteristic length) and Reynolds numbers are low, then the solution procedure can be simplified on the basis of the successive approximation method. Within the first approximation the Stokes equation is transformed into hydrostatics equations, and the free boundary S_{12} is described by

$$\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=P_{\mathrm{n}}^{(1)}+P_0=\mathrm{const}+\rho U \qquad [32]$$

where U is the potential of the external body-forces and R_1 and R_2 are the first and second radii of curvature of S_{12}. Within the second approximation, we

- —solve the problem for Stokes equations with the interface line known and the normal velocity profile specified;
- —derive a jump in normal stresses with due account for viscous flow. The surface $S_{12}^{(2)}$ is determined from the equation

$$\frac{1}{R_1}+\frac{1}{R_2}=\frac{P_{\mathrm{n}}^{(2)}+P_0}{\sigma}=\frac{P_{\mathrm{n}}^{(1)}+P_0}{\sigma}+\mathrm{O(Ca)}. \qquad [33]$$

The left-hand side of [33] is written approximately (assuming that deviations of $S_{12}^{(2)}$ from $S_{12}^{(1)}$ are low) through the corresponding differential operator over the known surface $S_{12}^{(1)}$ for which the right-hand side of [33] has been found. In each iteration, S_{12} is determined using the boundary conditions [30]. The method is appropriate for small and moderate Bond numbers $\mathrm{Bo}=\rho g l^2 \sigma$ where l is the characteristic length of the flow.

A similar approach was used in Voinov (1976), including estimation of the influence of gravity on the spreading of drops.

When the effects of body forces are insignificant, the surface S_{12} is a segment of a sphere with a radius R_0. In the second approximation, with respect to Ca, the perturbation of the radius, $\bar{R}$, is established from the problem

$$(\bar{R}'\sin\theta)'+2\bar{R}\sin\theta=\frac{P_{\mathrm{n}}^{(2)}+P_0}{\sigma}-\frac{2}{R_0}=F(\theta), \quad \bar{R}-R-R_0$$

where θ is the vectorial angle; $\theta=0$ corresponds to the symmetry axis. A solution to this problem can be written up to a constant:

$$\bar{R}=\cos\theta\int\frac{\mathrm{d}\theta}{\sin\theta\cos^2\theta}\int_0^{\theta}F(\theta_1)\cos\theta_1\,\mathrm{d}\theta_1. \qquad [34]$$

4. ASYMPTOTIC SOLUTION OF THE DYNAMIC PROBLEM OF WETTING A CAPILLARY IN THE CASE OF LOW ANGLES

4.1. Perturbation of the meniscus. External solution

If a free boundary slope is shallow, the flow can be described within the thin layer assumption; so, for the steady-state flow, we have

$$\frac{\mathrm{d}^3h}{\mathrm{d}x^3}=\frac{3\,\mathrm{Ca}}{h^2}. \qquad [35]$$

At a distance from the external line of wetting ($x=0$) the layer shape is close to a meniscus, i.e. constant curvature surface with a radius R

$$h-h_{(1)}=\mathrm{O}(1), \quad x/R|a_1|\to-\infty$$

$$h_{(1)}=a_0x^2+a_1\mathrm{x}, \quad a_0=1/2R, \quad a_1<0 \qquad [36]$$

In going to the wetting line the layer thickness h becomes less:

$$\frac{h}{h_0} \to 0, \quad x \to -0; \quad \ln\frac{h_0}{h} \ll \ln\frac{h_0}{h_m}. \qquad [37]$$

The lower limit for h in [37] corresponds to the definition of the external domain.

The problem [35]–[37] can be solved in the vicinity of the meniscus

$$h = h_{(1)} + h_{(2)}, \quad |h_{(2)}| \ll h_{(1)}. \qquad [38]$$

For $h_{(2)}$ we have the problem

$$h_2''' = 3\,\mathrm{Ca}/h_{(1)}^2 \quad h_2 = 0, \quad x = 0$$

$$h'_{(2)} \to 0, \quad h''_{(2)} \to 0 \quad \text{for} \quad x \to -\infty. \qquad [39]$$

After three integrations in [39], we obtain

$$h_{(2)} = -\frac{3\,\mathrm{Ca}}{a_1^2 \beta}\left(\frac{x - 2\beta}{2}\ln\frac{x - 2\beta}{2} + \beta\right)x, \quad \beta = R\,|a_1|. \qquad [40]$$

In accordance with [36], [38] and [40] the following relation is valid for a region far from the wetting line:

$$\frac{x}{R\,|a_1|} \to -\infty, \quad h - h_{(1)} \to a_2 = -\frac{3\,\mathrm{Ca}\,R}{|a_1|}. \qquad [41]$$

In the close vicinity of the wetting line, we have

$$x \to -0, \quad h = a_1 z + \frac{3\,\mathrm{Ca}}{a_1 2} x\left(\ln\frac{2\beta}{|x|} - 1\right) + \ldots,$$

$$h' = a_1 + \frac{3\,\mathrm{Ca}}{a_1 2}\left(\ln\frac{2\beta}{|x|} - 1\right) + \ldots, \qquad [42]$$

According to [42], the boundary slope angle for $h/h_0 \to 0$ is described by

$$\alpha = -h' = \alpha_0 - \frac{3\,\mathrm{Ca}}{\alpha_0^2}\left(\ln\frac{2R\alpha_0^2}{h} - 2\right) + \ldots,$$

$$\alpha_0 = -a_1 \qquad [43]$$

4.2. Matching the disturbed meniscus with the asymptotics of the dynamic boundary angle (with the internal solution)

The angle α_0 is established by using the common relations [30] for matching. From [25] and [43] it follows that

$$\alpha_0 = \alpha(h_0), \quad h_0 = \frac{2}{e^2}\alpha_0^2 R \qquad [44]$$

where $\alpha(h)$ is governed by the asymptotic solution for small angles [25] and [28] and R is the meniscus curvature radius. The transcendental equation [44] (taking into account [25] and [28]) for α_0 can easily be solved by iteration, since the right-hand side in [44] is almost constant with respect to h_0 and α_0.

The form of the function $h_0 = c\alpha_0^2 R$ is known. The coefficient $C = 0.5$ (Voinov 1976, 1977) and a refined estimate $c = 0.5\,e^{-0.376} = 0.343$ (Voinov 1988) are close to the exact value $2e^{-2} = 0.2706\ldots$ [44], because the angle α_0 only slightly depends on the coefficient c.

4.3. equation for contact angle measured when liquid wets capillary

Consider the angle between the meniscus and the solid surface α_a as obtained from the equation of the meniscus for $h \gg h_0$; here, the meniscus is assumed to be insignificantly disturbed by viscous stresses. After [41], we can write

$$\frac{x}{\alpha_0 R} \to -\infty, \quad h - a_0(x - x_0)^2 + \alpha(x - x_0) \to 0$$

$$\alpha_a = \alpha_0 - \frac{x_0}{R} \qquad [45]$$

where x_0 is a minimum root of the quadratic equation

$$a_0 x_0^2 - \alpha_0 x_0 + a_2 = 0. \qquad [46]$$

We should take into account the strong inequality $3\,\mathrm{Ca} \ll \alpha_0^3$ and consider relations [41], [45] and [46] to derive the following principle approximation with respect to $\ln^{-1}(h_0/h_{\mathrm{m}})$:

$$x_0 = -\frac{3\,\mathrm{Ca}}{\alpha_0^2} R, \quad \alpha_a = \alpha_0 + \frac{3\,\mathrm{Ca}}{\alpha_0^2}. \qquad [47]$$

The angle described by [45] corresponds to modelling the free boundary by a sphere which touches the boundary at the axis of the capillary tube and intersects the solid surface at an angle α_a. Let H_a designate the height of the spherical segment thus obtained. Measuring the value H_a is a challenging task for experimenters. It is usual to measure, instead, the distance (along the capillary axis) between locations at which points of the free boundary are on the capillary axis and the wetting line; thereafter the angle α_b is calculated by utilizing a segment of sphere to model the boundary from the capillary axis to the wetting line. In so doing,

$$H = x|_{h=0} - x|_{h=h_K}$$

$$\frac{H}{h_K} = \frac{1 - \sin\alpha_b}{\cos\alpha_b} \qquad [48]$$

(h_K is the capillary radius). These heights differ (due to translation) by the value x_0 described in [46] and [47]

$$H_a = H(\alpha_b) + x_0. \qquad [49]$$

Writing the right-hand side of [48] in the limiting case of low α angles:

$$\frac{1 - \sin\alpha}{\cos\alpha} = 1 - \alpha + \frac{\alpha^2}{2} + \ldots,$$

we have, from [47]–[49]:

$$\alpha_b = \alpha_0\left(1 + \frac{x_0}{R}\right) = \alpha_0\left(1 - \frac{3\,\mathrm{Ca}}{\alpha_0^2}\right). \qquad [50]$$

It is important that, in contrast to [45], the small correction to α_0 in [50] is on the order $\alpha_0 x_0/R$ rather than x_0/R. This allows α_b to be determined with a noticeably higher accuracy than α_a is determined on the basis of (i) the same value of a_2 in [41] and (ii) the corresponding increment x_0.

The relation for the measured contact angle (defined by [48]) is derived by substituting [50] into [44] with allowance of asymptotics [25]:

$$\alpha_b^3 = \alpha_{\mathrm{m}}^3 + g\,\mathrm{Ca}\left(\ln\frac{h_0}{h'_{\mathrm{m}}} - \alpha_b - \frac{1}{3}\ln\frac{\alpha_b}{\alpha*}\right)$$

$$h_0 = \frac{2}{e^2}\alpha_0^2 h_K. \qquad [51]$$

The latter expression differs from [44] (and [25]) by the second term in the brackets to the right. If we go to very low angles of α_b, the difference between α_0 and α_b vanishes.

5. ASYMPTOTIC THEORY OF WETTING OF A CAPILLARY: ARBITRARY DYNAMIC BOUNDARY ANGLES

5.1. Solution procedure for the external hydrodynamics problem

The boundary condition over S_{12} in the axisymmetric problem

$$-\frac{\mathrm{d}\cos\alpha}{\mathrm{d}h}+\frac{\cos\alpha}{h_K-h}=\frac{P_n+P_0}{\sigma}$$

can be rewritten through integrals after resolving it with respect to $\cos\alpha$:

$$\cos\alpha=\frac{1}{h_K-h}\int_h^{h_K}(h_K-h)\frac{P_n+P_0}{\sigma}\,\mathrm{d}h. \qquad [52]$$

If the capillary constant is small, the function $\alpha(h)$ is close to the function $\alpha_1(h)$ for a sphere in the external domain [29]

$$\alpha(h)=\alpha_1(h)+\alpha_2(h), \quad |\alpha_2|\ll\alpha_1$$

$$\cos\alpha_1=\cos\alpha_0\left(1-\frac{h}{h_K}\right). \qquad [53]$$

We can assume that a sphere touches S_{12} at the capillary axis, the sphere radius R_0 satisfying the equality

$$\frac{2\sigma}{R_0}=P_n|_{h=h_K}+P_0.$$

It is convenient to resort to a non-dimensional function G that characterizes an increment of normal stresses

$$P_n=P_n|_{h_K}+\frac{2\mu v}{h}Q(\alpha_0)\sin\alpha_0 G\left(\frac{h}{h_K},\alpha_0\right) \qquad (54)$$

where $\alpha_0=\alpha_a$ is the angle which the sphere makes at the intersection with the solid, a formula for the small term $\alpha_2(h)$ in [53] will result from expanding the left-hand side of [52] into a series at $\alpha=\alpha_1$:

$$\alpha_2(h)=-2\,\mathrm{Ca}\frac{Q(\alpha_0)\sin\alpha_0}{\sin\alpha_1(h)(h_K-h)}\int_h^{h_K}\frac{h_k-h}{h}G\,\mathrm{d}h. \qquad [55]$$

Substituting [55] into [53] and going to the limit $h/h_K\to 0$ in the external solution makes it possible to write

$$\alpha\to\alpha_0-2\,\mathrm{Ca}\,Q(\alpha_0)\ln\frac{h_0}{h} \qquad [56]$$

$$h_0=h_K\exp(-\tilde{C}_1), \quad \tilde{C}_1=\int_0^{h_K}\left[1-\left(\frac{h}{h_K}\right)G\right]\frac{\mathrm{d}h}{h}. \qquad [57]$$

Validity of the relation [56] is limited by the inequality [29]. From [56] and the common boundary conditions [30] it follows that

$$\alpha_a=\alpha(h_0), \quad h_0=h_K\exp(-\tilde{C}_1) \qquad [58]$$

where $\alpha(h)$ is the asymptotic expression for [27].

In a two-dimensional problem we have the relation [59] that is similar to [57]:

$$\tilde{C}_1=\int_0^{h_K}(1-G)\frac{\mathrm{d}h}{h} \qquad [59]$$

5.2. Equation for dynamic contact angles measured in experiments

The axial distance H between the locations where $h = 0$ and $h = h_K$ differs (due to α_2) from H_a for a sphere:

$$H - H_a = \Delta H = \Delta \int_0^{h_K} \frac{\mathrm{d}h}{\operatorname{tg}\alpha(h)} = -\frac{h_K}{\cos\alpha_0}\int_{\alpha_0}^{\tau_{1/2}} \frac{\alpha_2}{\sin\alpha_1}\,\mathrm{d}\alpha_1. \quad [60]$$

We can determine the measured angle α_b on the basis of H and [48] and write

$$\frac{\Delta H}{h_K} = \frac{\sin\alpha_a - 1}{\cos^2\alpha_a}(\alpha_b - \alpha_a), \quad |\alpha_b - \alpha_a| \ll \alpha_s. \quad [61]$$

From [60] and [61] the measured angle is related to α_2:

$$\alpha_b = \alpha_a + \frac{\cos\alpha_0}{1-\sin\alpha_0}\int_{\alpha_0}^{\tau_{1/2}} \frac{\alpha_2\,\mathrm{d}\alpha_1}{\sin\alpha_1}. \quad [62]$$

Substitution into [62] of the expression $\alpha_2(h)$ from [55] provides the description of the measured angle:

$$\alpha_b = \alpha_a - 2\,\mathrm{Ca}\frac{Q\sin\alpha_0\cos^2\alpha_0}{1-\sin\alpha_0}\int_{\alpha_0}^{\tau_{1/2}} \frac{\mathrm{d}\alpha_1}{\sin^2\alpha_1\cos\alpha_1}\int_{h(\alpha_1)}^{h_K}\left(1-\frac{h}{h_K}\right)G\frac{\mathrm{d}h}{h}. \quad [63]$$

Here the angle α_1 is an angle of slope of the tangent to the sphere. The double integral can easily be transformed into a single one (using the integration in part). Substituting [58] into [63], we find the constant C_1 for determination of the angle α_b from the general asymptotic relation:

$$\alpha_B = \alpha(h_0), \quad h_0 = h_K\exp(-C_1) \quad [64]$$

$$C_1 = \tilde{C}_1 + \frac{\sin\alpha_0\cos_2\alpha_0}{1-\sin\alpha_0}\left[(1-\tilde{C}_1)f(\alpha_0) - \int_0^1 \frac{\ln\zeta + (1-\zeta}{\sin^2\alpha_1\cos\alpha_1}\mathrm{d}\zeta - \int_0^1 f(\alpha_1)(1-\zeta)(G-1)\frac{\mathrm{d}\zeta}{\zeta}\right] \quad [65]$$

$$\zeta = \frac{h}{h_K}, \quad f(\alpha) = \frac{1}{\sin\alpha} + \frac{1}{2}\ln\frac{1-\sin\alpha}{1+\sin\alpha}, \quad \cos\alpha_1 = \cos\alpha_0(1-\zeta).$$

Here, $\tilde{C}_1$ is from [57] and corresponds to the angle α_a [58].

In the two-dimensional problem (where a capillary is formed by parallel planes) the expression [65] should be replaced by

$$C_1 = \tilde{C}_1 + \frac{\sin\alpha_0\cos^2\alpha_0}{1-\sin\alpha_0}\left[-\frac{\tilde{C}_1}{\sin\alpha_0} - \int_0^1 \frac{\ln\zeta}{\sin^3\alpha_1}\mathrm{d}\zeta - \int_0^1 \frac{1-\zeta}{\zeta\sin\alpha_1}(G-1)\,\mathrm{d}\zeta\right]. \quad [66]$$

We analyse [65] and [66] in the case of shallow slopes; for this case section 3 provides a reference solution. When $\alpha_0 \ll 1$, we find from the thin layer motion equation [35]:

$$P_n = P_n\Big|_{h_K} + 3\mu v\int_h^{h_K}\frac{\mathrm{d}h}{\alpha_1 h^2} \quad [67]$$

The latter is only valid where the distance h is short; but its error for $h \sim h_K$ is insignificant because the major contribution to C_1 is from the region $h \sim h_0$. The relation [67], in connection with [55], corresponds to

$$G = \alpha_0 h\int_h^{h_K}\frac{\mathrm{d}h}{\alpha_1 h^2} \approx h\int_h^{h_K}\frac{\mathrm{d}h}{h^2(1+2h/\alpha_0^2 h_K)^{1/2}}. \quad [68]$$

Substituting [68] into [59] and [65] and deriving the asymptotics of the integrals for $\alpha_0 \to 0$ allow us to write

$$C_1 = -\ln(2\alpha_0^2) + 2 + \alpha_0. \quad [69]$$

This is in line with the solution [51] which has been found for the case of shallow slopes. Note that poor information about viscous stresses for $h \sim h_K$ does not degrade the small-value second term in [18]. The possibility of taking into account the terms on the order of α in C_1 exists only for the measured angles of α_b determined from [48] (see comment to [50]).

The pair [57] and [65] (or the pair [59] and [66]) make it possible, in the general case, to exactly calculate the term of the second approximation if we additionally solve the creeping flow problem with a prescribed interface S_{12} in the shape of a segment of a sphere (a circular cylinder) with a boundary angle α_0 and if we use the increments of normal stress in [54] to obtain the function $G(h/h_K, \alpha_0)$. With this, the problem becomes notably simplified. First, instead of the problem with a free boundary we have a much more simple problem with a fixed boundary. Second, the wetting line stress singularity, which complicated the numerical solution of the problem, is eliminated due to the boundary conditions posed for the external solution.

5.3. An approximate analytical solution for finite boundary angles

Let us try to solve completely the problem in the second approximation. The search for simple approximations for calculating the coefficient C_1 is meaningful, in particular, because this coefficient very significantly affects the contact angle and a poor accuracy will satisfy us.

Note that the normal stress increment

$$\Delta P_n = P_n - P_n|_{h=h_K}$$

must fulfil two conditions on the capillary axis:

$$\Delta P_n = 0 \quad \text{and} \quad \frac{\partial}{\partial h}\Delta P_n = 0 \quad \text{at} \quad h = h_K \qquad [70]$$

The second condition allows for symmetry in the problem. In addition, we are aware of the form of stress increment for $h \longrightarrow 0$:

$$\Delta P_n = 2\mu v \frac{Q(\alpha_1)\sin\alpha_1}{h} \qquad [71]$$

It is seen that ΔP_n is restrained by numerous conditions. One could reveal that a smooth function with numerous conditions imposed can be approximately written without solving the boundary value problem. This is evidenced by the experience in the boundary layer theory of fluid mechanics. Therefore, by analogy with Voinov (1976), we can adopt the following approximation:

$$\Delta P_n = \frac{2\mu v}{h} Q(\alpha_1)\sin\alpha_1\left(1 - \frac{h}{h_K}\right)^2 \qquad [72]$$

According to [72], the function G is

$$G = \frac{Q(\alpha_1)\sin\alpha_1}{Q(\alpha_0)\sin\alpha_0}\left(1 - \frac{h}{h_K}\right)^2 \qquad [73]$$

The results of the calculation of $C_1(\alpha_0)$ in accordance with {[57], [65]} or {[59], [66]} (for circular and flat capillaries) and [73] are represented in figure 2. Values of C_1 from the reference equation for low angles $\alpha_0 \longrightarrow 0$ [69] are given for the sake of comparison. Note that all three curves in figure 2 are close to one another where $\alpha_0 = 30$–$60°$; this validates the approximation [72]. As regards features of the picture, a plateau of the curve $C_1(\alpha_0)$ for $\alpha_0 \sim 90°$ should be mentioned. At $\alpha \sim 90°$ the values of C_1 are 2.4 and 2.1666 for the circular and flat capillaries, respectively. These exceed the previously known values of 1.83 and 1.5 (Voinov 1976), that were computed for the angle α_a rather than α_b which is now dealt with. Note that in typical experimentation conditions this difference between the angles α_0 and α_b is small, only 2%, although these are defined in different ways.

6. ON THE SYMMETRY OF THE ASYMPTOTIC RELATION OF THE DYNAMIC WETTING ANGLE

Within the first approximation the slope angle α of the tangent to the liquid–gas interface can be asymptotically described (according to [16] and [21]) for small capillary numbers

$$\int_0^\alpha \left(\frac{\beta}{\sin\beta} - \cos\beta\right) d\beta = 2\,\mathrm{Ca}\ln h + \text{const} \qquad [74]$$

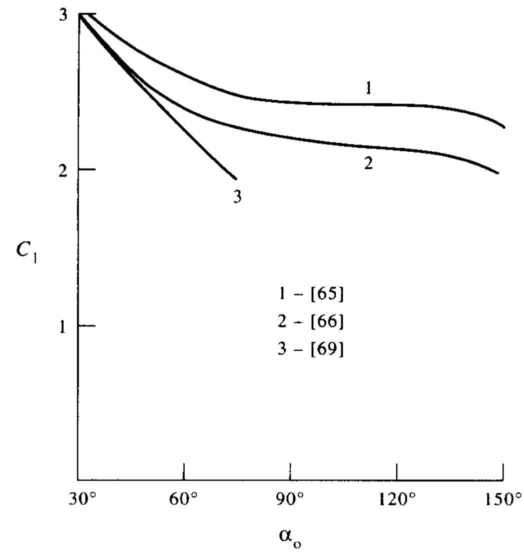

Figure 2.

In Boender *et al.* (1991), for a similar equation the left-hand side integral [which is symbolized by $2P(\alpha)$] is proposed to be approximated on the basis of the conventional relation from Bronstein & Semendyaev (1973):

$$P(\alpha)=\frac{\alpha-\sin\alpha}{2}+\frac{\alpha}{2}\ln\frac{\tan\alpha/2}{\alpha/2}-\sum_{n=1}^{\infty}2^{2n}\frac{(2^{2n-1}-1)}{(2n+1)!n}\,\mathrm{Bn}\left(\frac{\alpha}{2}\right)^{2n+1} \qquad [75]$$

where Bn is the Bernoulli number. The equation is cumbersome and slowly converges when $\alpha\sim\pi$ (as in $1/n$). Moreover, it fails to show why the approximation $P\approx\alpha/g$ (Voinov 1976) is successful.

Note that the simple approximation (when $\alpha\sim\pi$) in Voinov (1976, 1978) has an exact sense. To prove this, it is enough to subdivid the integral [74] into two integrals over intervals $(0,\pi/2$ and $(\pi/2,\alpha)$ and to use the substitution $\beta\rightarrow\pi-\beta$ for the latter interval. Then transformations provide

$$P(\alpha)=P(\pi-\alpha)+\frac{\pi}{2}\ln\tan\frac{\alpha}{2} \qquad [76]$$

Equation [76], unlike [75], exactly sets apart the non-analytical feature of $P(\alpha)$ at $\alpha=\pi$. The additional summand that is the difference between the values of $P(\alpha)$ for $\alpha>\pi/2$ and elsewhere, is extremely simple, so we can conclude a special symmetry of [74].

The symmetry formula [76] reduces the problem of approximation over $(0,\pi)$ to that for the interval $\{0,\pi/2\}$. If $\alpha<\pi/2$ (i.e. is far enough from the singular point $\alpha=\pi$ where $P=\infty$) various approximation concepts are suitable. For example, the expression to be integrated may well be expanded as a series in β to give

$$P(\alpha)=\frac{\alpha^3}{g}\left(1-\frac{1}{50}\alpha^2+\frac{13}{5880}\alpha^4+\cdots\right)$$

This clearly demonstrates the cause of the effectiveness of the approximation $P\approx\alpha^3/g$ for rather large values of α, not only for $\alpha\rightarrow 0$.

The symmetry enables the approximation suggested in Voinov (1976):

$$P=\frac{\alpha^3}{g},\quad d<\frac{3}{4}\pi;\qquad P=\frac{1}{g}(\pi-\alpha)^3+\frac{\pi}{2}\ln\tan\frac{\alpha}{2},\quad \alpha>\frac{3\pi}{4}$$

So the special symmetry equation [76] offers the most effective approach to the approximation of the dependence of the dynamic wetting angle on speed.

7. CONCLUSION

The basic results can be summarized as follows.

(1) It becomes clear that the therymodynamics approach notably simplifies the solution of the problem of stress singularity near a moving line of contact of three phases with due account of viscous flow. The energy conservation equation [8] offers an exact expression of the dynamic boundary angle α at a macroscopic distance h from the solid surface. The problem of the dynamic boundary angle has been transformed into the problem of energy dissipation E_Σ and the power W of external forces distributed over a surface of a small control volume. The integral formula [8] for the dynamic boundary angle made it possible to substantiate (without special assumptions) the boundary condition [23] for points a small distance from the solid. It should be mentioned that the derivation does not consider details of flow in microscopic lengths—unlike the set of previous contributions. The boundary condition for a domain with a small characteristic length is a consequence of analysis of macroscopic values at a notable distance from the contact line.

(2) The most important result is the method for evaluating the constant of the exact internal asymptotics of the interface slope angle in the second approximation with respect to he small capillary number [27]; the method is based on matching the values to the thermodynamic equation over a small-size vicinity of the contact line.

(3) We obtain common boundary conditions over the three-phase line for the external problem for Navier–Stokes equations that deal with the flow far enough from the wetting line. These boundary conditions notably simplify the solution procedure for non-linear problems in interface dynamics.

(4) A rigorous method has been developed through which the dynamics of the interface of a low Reynolds number flow in a capillary is analysed asymptotically in the second approximation with respect to the capillary constant. The principle of the method applies to other problems with creeping flow.

(5) A reference solution to the problem of wetting a capillary with shallow slopes has been obtained.

(6) An approximate relation for deriving the second approximation valid for angles $\alpha_0 = 30$–$150°$ has been found.

The theory corresponds to experiments with capillaries [the contributions by Zheleznyi (1972, 1974) and Hoffman (1975)] and spreading drops because good convergence with the test results has already been achieved in the first approximation (Voinov 1976, 1978). To refine the slight effects of the microscopic processes on the dynamic boundary angle measured, more accurate experiments are a necessity. Non-equilibrium processes within a microscopically narrow domain near the wetting line (Blake & Hanes 1969) can influence the dynamic boundary angle in accordance with the thermodynamics equation, due to extra dissipation of energy. Where the "approximate" use of an equilibrium angle within the region with a minimum characteristic length provides good agreement between the hydrodynamic theory and the tests, the additional non-hydrodynamic mechanisms in the variation of the dynamic boundary are of no importance.

REFERENCES

Baiocchi, C. & Puknachev, V. V. 1990 Problem with one-sided limitations for Navier–Stokes equations and the dynamic contact angle problem. *J. Appl. Mech. Technol. Phys. USSR* **2,** 27–40.

Blake, T. D. & Haynes, J. M. 1969 Kinetics of liquid/liquid displacement. *J. Colloid Interface Sci.* **30,** 421–423.

Boender, W., Chesters, A. K. & van der Zanden, A. J. J. 1991 An approximate analytical solution of the hydrodynamic problem associated with an advancing liquid–gas contact line. *Int. J. Multiphase Flow* **17,** 661–676.

Bronstein, I. N. & Semendyayev, K. A. 1973 *A Guid Book to Mathematics.* Harri Deutsch/Springer, Berlin.

Dussan, V. E. B. 1979 On the spreading of liquids on solid surfaces: static and dynamic contact lines. *A. Rev. Fluid Mech.* **11,** 371–400.

Hansen, R. J. & Toong, T. Y. 1971 Dynamic contact angle and its relationship to forces of hydrodynamic origin. *J. Colloid Interface Sci* **37,** 196–207.

Hervet, H. & de Gennes, P. G. 1984 The dynamics of wetting of "dry" solid. *C. R. Acad. Sci. Paris Ser. II* **299,** 400–503.

Hoffman, R. L. 1975 A study of the advancing interface. I. Interface shape in liquid–gas systems. *J. Colloid Interface Sci.* **50,** 228–241.

Huh, C. & Scriven, L. E. 1971 Hydrodynamic model of steady movement of a solid/liquid/fluid contact line. *J. Colloid Interface Sci* **35,** 85–101.

Moffat, H. K. 1964 Viscous and resistive eddies near a sharp corner. *J. Fluid Mech.* **18,** 1–18.

Pismen, L. M. & Nir, A. 1982 Motion of a contact line. *Phys. Fluids* **25,** 3–7.

Voinov, O. V. 1976 Hydrodynamics of wetting. *Fluid Dynam.* **11,** 714–721.

Voinov, O. V. 1977 On the interface inclination in moving liquid layers. *J. Appl. Mech. Technol. Phys. USSR* **2,** 92–99.

Voinov, O. V. 1978 Asymptote to the free surface of a viscous liquid creeping on a surface and the velocity dependence of the angle of contact. *Sov. Phys. Dokl.* **23,** 891–893.

Voinov, O. V. 1988 Hydrodynamics wetting theory. Preprint of the Institute of Thermophysics (SO AN SSSR), No. 179, pp. 1–31.

Zheleznyi, B. V. 1972 Experimental study of the contact angle dynamic hysteresis. *Dokl. Akad. Nauk. SSSR* **207,** 647–650.

Zheleznyi, B. V. 1974 To the hydrodynamics of an advancing meniscus. *Dokl. Akad. Nauk. SSSR* **219,** 130–133.