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On cusped interfaces

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An asymptotic analysis of two-dimensional free-surface cusps associated with flows at low Reynolds numbers is presented on the basis of a model which, in agreement with direct experimental observations, considers this phenomenon as a particular case of an interface formation–disappearance process. The model was derived from first principles and earlier applied to another similar process: the moving contact-line problem. As is shown, the capillary force acting on a cusp from the free surface, which in the classical approach can be balanced by viscous stresses only if the associated rate of dissipation of energy is infinite, in the present theory is always balanced by the force from the surface-tension-relaxation 'tail', which stretches from the cusp towards the interior of the fluid. The flow field near the cusp is shown to be regular, and the surface-tension gradient in the vicinity of the cusp, caused and maintained by the external flow, induces and is balanced by the shear stress. Existing approaches to the free-surface cusp description and some relevant experimental aspects of the problem are discussed.

1. Introduction

Experiments originally reported by Joseph *et al.* (1991) and since then repeated by many authors show that at finite values of the capillary number, different for different fluids, convergent flow near a free surface produces a cusped two-dimensional interface so that 'no rounding can be detected, at least on a visible lengthscale' (Joseph *et al.* 1991). Another essential point is that as soon as the cusp appears, the stagnation line, which exists on the rounded free surface at relatively low capillary numbers, is no longer present so that 'if powder is sprinkled on the free surface, this powder is immediately swept through the cusp into the interior of the fluid' thus suggesting that 'fluid particles on the free surface are similarly advected through the cusp into the interior' (Jeong & Moffatt 1992).

The principal theoretical results in modelling of free-surface interfaces with line singularities of curvature are as follows. Richardson (1968) presented an analysis of deformation of two-dimensional bubbles in Stokes flow and proved that in the framework of the classical fluid-mechanical approach the only possible line singularity of the interface between a Newtonian viscous liquid and an inviscid gas is a genuine cusp. Then to balance the capillary force 2σ per unit length of the cusp acting on the liquid, the flow field has to be singular at the cusp so that for a cusp that opens on the negative x-axis (figure 1) the leading contribution to the stream function, expressed in polar coordinates (r, θ), is given by

$$\psi = \frac{\sigma}{2\pi\mu} r \log r \sin\theta, \tag{1.1}$$

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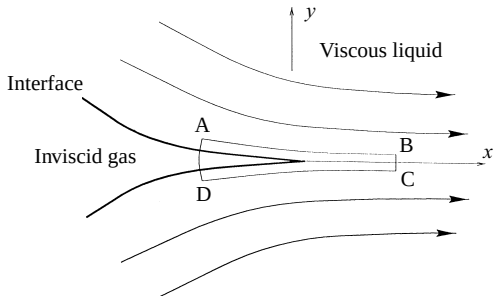


FIGURE 1. A definition sketch for a flow near a cusp.

where σ and μ are the surface tension and viscosity, respectively, and the deviation of the free interface from a flat surface in the leading term is neglected. As should be expected, since the capillary force is a concentrated force (i.e. produces a finite total force, σ per unit length, while acting on a line), it can be balanced by a viscous stress, which is a distributed force (and, if integrable, gives a finite total force acting on an area) only if the viscous stress density has a non-integrable singularity at the cusp, and the associated rate of dissipation of energy is infinite. Obviously, from a physical point of view such a singularity cannot be accepted.

Joseph *et al.* (1991) presented an asymptotic analysis of the flow near the cusp tip for the case of zero surface tension (where no concentrated capillary force acts on the liquid) and found that at leading order the free surface shape is given by

$$y = \pm c|x|^{3/2} \quad (x < 0), \tag{1.2}$$

where c is a constant determined by the external flow. This asymptotics implies infinite curvature of the free surface at the origin. Inclusion of a finite surface tension in the analysis changes the power in (1.2), so that $\frac{3}{2}$ becomes the limit as the capillary number Ca tends to infinity but, however, does not make the asymptotics applicable up to the cusp, where in this case (i) the concentrated capillary force is present thus invoking all associated difficulties, and (ii) since the curvature of the free surface goes to infinity as the cusp is approached, the model describing the interfaces as geometrical surfaces of zero thickness with a constant surface tension becomes inapplicable.

Jeong & Moffatt (1992) presented an exact analytical solution for a symmetrical creeping flow near a free surface which, in the corresponding experiment, leads to the cusp formation. The solution confirms (1.2) as the true asymptotics at high capillary numbers, Ca, not close to the tip and determines the value of c. The free surface is described as smooth at finite capillary numbers with an exponentially decreasing radius of curvature on the line of symmetry on the free surface as Ca increases so that, strictly speaking, the cusp appears when $Ca = \infty$. However, for typical values of the flow parameters corresponding to cusp formation in experiments the exact solution predicts the radius of curvature at the tip to be comparable with the molecular size, thus clearly indicating that the solution, being self-consistent, falls outside the limits of applicability of the model, where interfaces are treated as geometrical surfaces of zero thickness thus implying the radius of curvature to be large compared with the interfacial layer thickness. Thus, if the problem is considered on a macroscopic (i.e. hydrodynamic) length scale, then a genuine cusp has to be introduced at a finite capillary number, and one has to balance the capillary force by the viscous stress and will inevitably arrive at (1.1). Besides this, in the exact solution the line of symmetry

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on the free surface at finite capillary numbers is always a stagnation line so that the interface always consists of the same material particles. This is in conflict with the experimental observations cited above, which suggest that the cusp formation corresponds to a qualitative change in the flow kinematics.

In other words, at finite capillary numbers in the conventional model there is either no cusp or a cusp together with the singular flow field associated with an infinite rate of dissipation of energy.

The above-mentioned difficulties were, of course, well-understood and pointed out by the authors of the cited works. Thus, the results obtained highlight, from different points of view, the fact that the Navier–Stokes equations together with the classical boundary conditions on the free surface provide an adequate description of the flow and evolution of the free surface until the radius of curvature becomes so small that the solution approaches the limit of applicability of the model. Then (in a real fluid) some additional physical mechanisms, not taken into account in the classical model, come into action, making possible the existence of a genuine cusp (on a macroscopic length scale) and (also macroscopic) advection of fluid particles initially belonging to the free surface through the cusp into the interior.

The necessity of incorporating 'extra' physical mechanisms follows also from the fact that for different fluids the transition to a cuspidal regime corresponds to considerably different values of the only similarity parameter associated with the classical model (the capillary number) so that one should expect the implicit presence of other similarity parameters and hence 'extra' physical mechanisms.

It should be emphasized that the inapplicability of the Navier–Stokes equations together with the classical boundary conditions on the free surface to the description of the flows with steady two-dimensional cusps does not at all mean the breakdown of the continuum approximation itself: to describe the macroscopically observed cusp on the macroscopic (hydrodynamic) length scale one should include in the corresponding mathematical model the macroscopic 'outcome' of those physical mechanisms which become important when a rounded free surface transforms into a cusp. (Since the geometrical indication of the cusp formation sometimes brings speculations about 'apparent cusps' or 'almost cusps', the kinematic definition associated with the disappearance of the stagnation line on the free surface seems more relevant from a physical point of view, implying that it corresponds to a fully developed cusp.)

In other words, we may say that, remaining on the macroscopic level of description, one should expect that in the end intermolecular forces, which are often assumed to be responsible for the cusp formation, or other (micro- or macroscopic) physical mechanisms will manifest themselves acroscopically (as additional macroscopic forces, changes in the transport coefficients, etc.) to allow for the existence of a macroscopic cusp. More specifically, one should expect the appearance of a concentrated non-hydrodynamic force borne and maintained by the external flow, which will balance the capillary force acting on the cusp, thus allowing the hydrodynamic flow field to be regular (or at least less singular) near it.

The key idea of the present study is very simple. Since experiments show that on a macroscopic length scale there is advection of liquid particles through the cusp into the interior, we may consider cusping as a particular case of a more general physical phenomenon, namely the process of interface formation or disappearance. Other particular examples of such a process are the moving-contact-line problem (see Dussan V. 1979 and Shikhmurzaev 1997, §9 for reviews), the sliding plate problem (Batchelor 1967, p. 224; Koplik & Banavar 1995), the oscillating jet phenomenon (Bohr 1909) to mention a few. Thus, we may apply a model, which was derived

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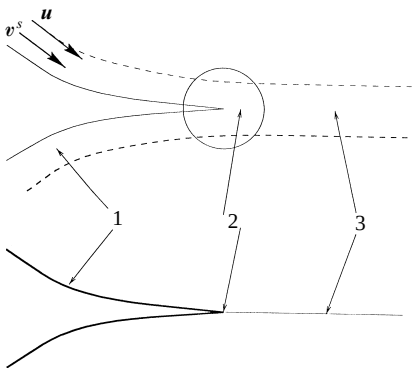


FIGURE 2. Schematic illustration of the physical picture of the flow near a cusp. On the macroscopic (hydrodynamic) length scale the liquid–gas interfacial layer (1) can be modelled as a geometrical surface of zero thickness, the transition zone (2) is seen a cusp line, and the surface-tension-relaxation 'tail' (3) becomes a gradually disappearing 'internal interface'.

from first principles to incorporate this process and originally used for the analysis of the moving-contact-line problem (Shikhmurzaev 1993*a*, *b*, 1994, 1996, 1997), without making any *ad hoc* changes adjusting the model to the cusp problem.

Then the physical picture of flow with a free-surface cusp is as follows. Fluid particles which initially belong to the free surface and, being under the non-symmetrical influence of intermolecular forces from the bulk phases, possess some surface properties (such as and first of all, the surface tension) pass through the cusp into the bulk (figure 2) so that their surface properties have to gradually disappear, and they eventually become ordinary 'bulk particles'. Hence there must be a relaxation 'tail' which stretches from the cusp towards the interior and where the surface tension and other 'surface' parameters gradually vanish. The surface tension changes continuously across the cusp, and hence the capillary force acting on the cusp from the free surface is always balanced by that from the surface-tension-relaxation 'tail'. The external flow, which forces the particles on the free surface to pass through the cusp, thus causes the surface-tension gradient in the vicinity of it, and this gradient has a reverse influence upon the flow and induces shear stress (an example of the flow-induced Marangoni effect). Since in the present model the viscous stresses have to balance not the capillary force, which is already compensated by the force from the relaxation 'tail', but only the surface-tension gradient near the cusp, the flow field appears to be regular at the cusp.

The goal of the paper is to consider the fundamental difficulty brought by a cusp and present a local asymptotic analysis of the flow near it, which can be incorporated as an element in different global solutions. In §2, the mathematical formulation of the problem is given, and §3 deals with a local analysis of the flow near a genuine cusp. In §4, the main points of the model and some relevant questions are discussed, and a possible way of experimental verification (or otherwise) of the present work is proposed.

2. Problem formulation

Consider a symmetrical cusp formed by an interface between an incompressible Newtonian liquid and an inviscid gas (i.e. physically a vacuum) which opens on the negative x-axis of the Cartesian coordinate frame (x, y) with the origin coincident

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with the cusp (figure 1). Owing to the symmetry of the problem we may consider the region $y \geqslant 0$ and in what follows will assume that the flow is steady and the associated Reynolds number is small so that the inertial terms may be neglected. In the bulk in the absence of mass forces one has

$$\nabla \cdot \boldsymbol{u} = 0, \quad \nabla \cdot \boldsymbol{P} = 0, \tag{2.1}$$

where $\boldsymbol{u}$ is the fluid velocity and $\boldsymbol{P} = -p\boldsymbol{I} + \mu[\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^{\mathrm{T}}]$ is the stress tensor (p and μ are the pressure and viscosity, respectively; $\boldsymbol{I}$ is the metric tensor).

According to experiments (Jeong & Moffatt 1992), liquid particles on the free surface are swept through the cusp, and one has to expect that they form a relaxation 'tail' stretching towards the interior of the liquid, where their surface properties gradually disappear (figure 2). Since in the symmetrical case the tangential force on the plane of symmetry is absent, one may use the following equations both on the free surface and the semiaxis $x \geqslant 0$ (Shikhmurzaev 1993*a*, 1994):

$$\boldsymbol{u} \cdot \boldsymbol{n} = 0, \tag{2.2}$$

$$(\boldsymbol{I} - \boldsymbol{nn}) \cdot \boldsymbol{P} \cdot \boldsymbol{n} - \nabla p^s = 0, \tag{2.3}$$

$$p^s = \gamma(\rho^s - \rho_0^s), \tag{2.4}$$

$$\nabla \cdot (\rho^s \boldsymbol{v}^s) = -\frac{\rho^s - \rho_e^s}{\tau}, \tag{2.5}$$

$$(1 + 4\alpha\beta)\nabla p^s = 4\beta(\boldsymbol{u} - \boldsymbol{v}^s) \cdot (\boldsymbol{I} - \boldsymbol{nn}), \tag{2.6}$$

and the change in the environment for a fluid particle as it comes from the free surface to the bulk is given by

$$\rho_e^s = \begin{cases} \rho_{1e}^s, & x < 0 \\ \rho_0^s, & x \geqslant 0. \end{cases} \tag{2.7}$$

Here n is a unit inward normal to the interface; p^s and ρ^s are the 'surface' pressure, defined as the negative surface tension, and the surface density, respectively; v^s is the velocity associated with the mass flux along the interface ($v^s \cdot n = 0$), and α, β, γ, τ, ρ_0^s and $\rho_{1e}^s (< \rho_0^s)$ are phenomenological constants.

The free-surface shape is determined by

$$\boldsymbol{n} \cdot \boldsymbol{P} \cdot \boldsymbol{n} + p_g + p^s \kappa = 0, \tag{2.8}$$

where p_g is the (constant) pressure in the gas, and κ is the curvature of the free surface.

Some comments on the boundary conditions seem relevant. Equations (2.2) and (2.8) are the usual kinematic and normal-stress boundary conditions, and (2.3) generalizes the usual zero tangential stress condition to account for the surface pressure gradient† – this equation is used as the basis for the studies of the Marangoni flows. To incorporate the interface formation–disappearance process in the frame of the general fluid-mechanical approach, one has to introduce the surface equation of state and some equations describing the process of relaxation of the surface parameters, which characterize the current state of the interface. The simplest set of the corresponding equations is given by (2.4)–(2.6), where we use a linear equation of state (2.4), which relates the surface pressure to the surface density, and a linear term in (2.5) describing

† Note a misprint in the sign of the surface pressure gradient in equations (6) in Shikhmurzaev (1996). The subsequent formulae in that paper are correct.

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relaxation of the surface density to its equilibrium value ρ^s_e. The constant ρ^s_0 is the surface density corresponding to zero surface pressure; ρ^s_{1e} in (2.7) is the equilibrium surface density for the gas–liquid interface ($\rho^s_{1e} < \rho^s_0$ so that $\sigma = -p^s(\rho^s_{1e}) > 0$ is the equilibrium surface tension), and τ is the relaxation time. Coefficients α, β describe the influence of the surface and bulk forces on the velocity difference across the interface (these coefficients appear in a combination here, whereas in the case of a liquid–solid interface, where the corresponding set of equations are slightly different, the coefficients appear separately). Details of the model can be found elsewhere (Shikhmurzaev 1993*a*, 1994). Some aspects are also discussed in §4 of the present paper.

Obviously, for most hydrodynamic flows, where the characteristic time scale is much larger than τ and the length scale is large compared with $U\tau$, where U is the characteristic value of the fluid velocity, equations (2.2)–(2.6), (2.8) reduce to the classical boundary conditions on the free surface.

The distributions of the surface parameters along the free surface (Σ) and the relaxation 'tail' (S) are linked by the surface mass and momentum balance conditions at the cusp ($r = r_0$):

$$(\rho^s v^s)_{|r\to r_0,\ r\in\Sigma} = (\rho^s v^s)_{|r\to r_0,\ r\in S}, \qquad p^s|_{r\to r_0,\ r\in\Sigma} = p^s|_{r\to r_0,\ r\in S}. \tag{2.9}$$

Taking account of (2.4), conditions (2.9) require simply continuity of the surface parameters at the cusp point.

To complete the problem formulation one has to prescribe the values of $\rho^s\,(=\rho^s_{1e})$ and $v^s\,(=u)$ far away from the cusp and specify the boundary conditions for the outer flow which give rise to the cusp formation.

3. Analysis

We shall analyse the asymptotics of the solution near the origin, where the classical hydrodynamic approach faces the difficulty of principle briefly described in §1. If U is the characteristic value of the flow velocity, then one may use the following scales for lengths, velocities, the pressure difference $p - p_g$ (which will be used instead of p), surface pressures and densities:

$$U\tau,\ U,\ \frac{\mu}{\tau},\ \sigma,\ \rho^s_0$$

to make the equations and boundary conditions non-dimensional. Using the notation $\theta = \pi - g(r)$ for the position of the free surface located above the cusp in the plane polar coordinates (r, θ) and eliminating p^s with the help of (2.4), one can rewrite (2.2), (2.3), (2.5)–(2.6) as

$$\boldsymbol{u}\cdot\boldsymbol{n} = 0, \tag{3.1}$$

$$Ca(\boldsymbol{I} - \boldsymbol{nn})\cdot\boldsymbol{P}\cdot\boldsymbol{n} = \lambda\nabla\rho^s, \tag{3.2}$$

$$\nabla\cdot(\rho^s\boldsymbol{v}^s) = -(\rho^s - \rho^s_e(\theta)), \tag{3.3}$$

$$\nabla\rho^s = 4V^2(\boldsymbol{u} - \boldsymbol{v}^s)\cdot(\boldsymbol{I} - \boldsymbol{nn}), \tag{3.4}$$

where

$$Ca = \frac{\mu U}{\sigma}, \quad \lambda = \frac{1}{1-\rho^s_{1e}}, \quad V^2 = \frac{\tau\beta U^2}{(1+4\alpha\beta)\sigma\lambda}, \quad \rho^s_e(\theta) = \begin{cases} \rho^s_{1e}, & \theta = \pi - g(r) \\ 1, & \theta = 0 \end{cases}$$

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and (2.8) takes the form

$$\boldsymbol{n}\cdot\boldsymbol{P}\cdot\boldsymbol{n} = \frac{\lambda(\rho^s - 1)}{Ca}\left[\frac{rg'' + 2g' + r^2g'^3}{(1 + r^2g'^2)^{3/2}}\right]. \tag{3.5}$$

We will look for a solution for the flow field near the cusp as a perturbation of uniform flow in the positive x-direction and the free surface as a perturbation of the negative x-semiaxis. If ρ_c^s and v_c^s denote respectively the values of the surface density and the x-component of the surface velocity at the origin, then one can immediately find from (3.3) and (3.4) that the leading terms of an asymptotic expansion of ρ^s and v^s, which is a projection of v^s on the tangent to the interface directed along the flow (hence v^s is positive both on the free surface and in the bulk), about the origin are given by

$$\left.\begin{aligned}\rho^s &= \rho_c^s - ar + \dots\\ v^s &= v_c^s + b_1 r + \dots\end{aligned}\right\}\ (\theta = \pi - g(r)), \tag{3.6}$$

and

$$\left.\begin{aligned}\rho^s &= \rho_c^s + ar + \dots\\ v^s &= v_c^s + b_2 r + \dots\end{aligned}\right\}\ (\theta = 0), \tag{3.7}$$

where

$$v_c^s = 1 - \frac{a}{4V^2}, \quad \rho_c^s = \frac{av_c^s - \rho_{1e}^s}{b_1 - 1}, \quad b_2 = \frac{1}{\rho_c^s}(1 - \rho_c^s - av_c^s),$$

and a and b_1 are determined externally. It is noteworthy that the surface density gradient (and hence, due to (2.4), the surface pressure gradient) is continuous at the cusp since, as is clear from (3.4), the second terms on the right-hand sides of (3.6) and (3.7) depend on the leading terms of the expansions of u and v^s, which are continuous at the origin.

We will introduce a stream function ψ by

$$u_r = \frac{1}{r}\frac{\partial\psi}{\partial\theta}, \qquad u_\theta = -\frac{\partial\psi}{\partial r}$$

and look for the leading terms of an asymptotic series

$$\psi = \psi_1(r,\theta) + \sum_q \psi_q(r,\theta) \equiv r\sin\theta + \sum_q r^q F_q(\theta), \tag{3.8}$$

where ψ_q are solutions of the biharmonic equation.

Substituting (3.8) in (3.1), (3.2), (3.5) and using (3.6) and (3.7), we get after straightforward calculations that the second term in (3.8) is associated with a shear flow

$$\psi_2(r,\theta) = \frac{\lambda a}{2Ca}r^2\sin^2\theta, \tag{3.9}$$

whilst the third one, which corresponds to

$$q > 2, \tag{3.10}$$

is a solution of an eigenvalue problem, provided that

$$q < 3, \tag{3.11}$$

and hence the contribution from the third terms on the right-hand sides of (3.6) and (3.7) to the right-hand side of (3.2) does not appear when the terms of order r^{q-2} are considered.

In other words, conditions (3.10), (3.11) correspond to the situation where the flow-induced Marangoni effect, which is a consequence of the physical mechanism

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put at the basis of the explanation of the free-surface cusps existence, has already come into play ($q > 2$), and at the same time only the leading terms associated with this effect are taken into account ($q < 3$).

The second term of (3.8) provided by (3.9) does not give us the leading term of the free-surface shape expansion about the origin. The cusp 'opens' only when we arrive at the third term of (3.8).

The function F_q satisfies

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}\theta^2} + q^2\right)\left(\frac{\mathrm{d}^2}{\mathrm{d}\theta^2} + (q-2)^2\right) F_q = 0, \tag{3.12}$$

and, using that from (3.1) on the free surface

$$g(r) = -r^{q-1}F_q(\pi),$$

one can rewrite (3.1), (3.2) on $\theta = 0$ and (3.2), (3.5) on the free surface as

$$F_q(0) = 0, \tag{3.13}$$

$$F_q''(0) = 0, \tag{3.14}$$

$$F_q''(\pi) - q(q-2)F_q(\pi) = 0, \tag{3.15}$$

$$F_q'''(\pi) + (3q^2 - 6q + 4)F_q'(\pi) + \frac{\lambda}{Ca}[(1-\rho_c^s)q + 2a](q-1)(q-2)F_q(\pi) = 0. \tag{3.16}$$

Equation (3.12) together with (3.13)–(3.16) provide the eigenvalue problem mentioned above.

The solution of (3.12), which satisfies (3.13) and (3.14), has the form

$$\psi_q(r,\theta) = r^q[C_1\sin(q\theta) + C_2\sin((q-2)\theta)], \tag{3.17}$$

where C_1 and C_2 are non-zero if q satisfies an equation

$$\tan(q\pi) = -\frac{2qCa}{\lambda[(1-\rho_c^s)q + 2a]}, \tag{3.18}$$

which can be obtained after substituting (3.17) in (3.15), (3.16) and making the determinant of the corresponding set of linear algebraical equations equal to zero. Conditions (3.10), (3.11) provide the selection of a unique root of (3.18). In particular, if $a = b_1 = 0$, then (3.18) reduces to the corresponding equation of classical hydrodynamics†, $\tan(q\pi) = -2Ca$. In this equation, Ca is the only similarity parameter while (3.18) includes other dimensionless parameters characterizing the fluid and outer flow.

In Cartesian coordinates the free surface is described by

$$y = \mp|x|^q(C_1 + C_2)\sin(q\pi) \qquad (x < 0).$$

Constants C_1 and C_2 are related through

$$C_1 q + C_2(q-2) = 0$$

imposed by (3.15) so that there is only one degree of freedom which has to be determined from the external conditions.

Condition (3.10) implies that the free-surface curvature tends to zero as the cusp is

† Note a misprint in the sign of curvature in Joseph *et al.* (1991) which led to the corresponding misprint in their equation (11). The same misprint in the same equation occurred earlier in Benney & Timson (1980) – see Ngan & Dussan V. (1984) for details.

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approached, and (3.8), (3.9), (3.17) show that the flow field near the cusp is regular. At the cusp point the angle of the interface has a jump of 2π, but the concentrated capillary force, which appears because of this jump, is balanced by that from the surface-tension relaxation 'tail' stretching from the cusp towards the interior of the liquid and does not require any non-integrable (or even integrable) singularities in the flow field. Equation (3.6) together with (2.4) show that, in general, the surface tension begins to disappear before the particles belonging to the interface reach the cusp, and (3.6), (3.7) give that both the surface tension and its gradient are continuous across the cusp point.

4. Discussion

In this section, we will discuss the physical background of the present work and the process of cusping from the point of view of existing mathematical models of this phenomenon.

4.1. *Relaxation time*

The key idea of the present work is to use experimental evidence which indicates that cusping is a particular case of the interface formation–disappearance process. This implies that the fluid particles which initially belonged to the free surface, being swept through the cusp into the interior of the fluid, will form the surface-tension-relaxation 'tail', which will balance the concentrated force acting on the cusp due to the surface tension of the free surface. This also suggests that a mathematical model derived earlier to incorporate the interface formation–disappearance process and originally applied to another similar problem will be applicable without any *ad hoc* assumptions. To be qualitatively correct, this idea requires only a non-zero time of surface tension relaxation. This is, of course, true. However, application of the present model brings more restrictive conditions.

The model is macroscopic in the sense that it considers flows on a characteristic length scale large compared with the thickness of the interfacial layer so that one may deal with interfacial surfaces instead of interfacial layers, the surface tension instead of a three-dimensional stress tensor in the interfacial layer, a surface density instead of a distribution of the actual density inside this layer, etc. This implies that the interfacial layer thickness h is small compared both (i) with the radius of curvature of the free surface and (ii) with the length of the surface-tension-relaxation 'tail'. Condition (i) is satisfied since according to results of §3 the curvature of the free surface tends to zero as the cusp is approached. Condition (ii) implies that

$$h \ll U\tau. \tag{4.1}$$

The limitation imposed by this inequality on the value of τ is not very restrictive. Indeed, even for low velocities corresponding to the onset of cusping, experiments (Joseph *et al.* 1991) show that the critical velocity U_c varies from 3.6 cm s^{-1} (silicone oil – 5000 cS) to 21.06 cm s^{-1} (castor oil). Thus, for $h \sim 10^{-7}$–10^{-6} cm one has $\tau \gg 5 \times 10^{-9}$–$3 \times 10^{-7}$ s. As U goes up from U_c, inequality (4.1) imposes less and less restrictive limitations on τ.

Although the required relaxation time is quite macroscopic, its experimental determination is a formidable problem. The difficulties come from the requirement to measure mechanical parameters with high spatial or/and temporal resolution and especially from the necessity to interpret the results by analysing usually unsteady and at least two-dimensional flows theoretically. At present, one of the most

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reliable is the oscillating jet method originally proposed by Bohr (1909) for the determination of the equilibrium surface tension of a newly formed water-air interface. In this method, a jet of liquid coming out of an elliptic orifice produces a wave pattern which can be analysed to calculate the surface tension. Interesting results have been reported by Rusanov and co-workers (Kochurova, Shvechenkov & Rusanov 1974; Kochurova & Rusanov 1981*a*, *b*, 1995), who used the oscillating jet method to determine the dynamic surface tension of water. The authors had improved the method by taking into account the non-uniform velocity profile across the jet (Kochurova, Noskov & Rusanov 1974*b*)†, which, as shown by Bohr (1910), can lead to a variation in the observed wavelength on the free surface thus affecting the result. It has been found that for water $\tau \sim 10^{-4}$–10^{-3} s (Kochurova *et al.* 1974*a*; Kochurova & Rusanov 1981*a*, *b*, 1995). By approximating the data with the relaxation equation, one obtains $\tau \approx 6 \times 10^{-4}$ s (Kochurova & Rusanov 1981*a*). This surprisingly big value, however, is in agreement with early measurements by other authors (see in Kochurova & Rusanov 1981*a*, figure 1) and coincides in order of magnitude with the relaxation time of the surface potential (Kochurova & Rusanov 1981*a*, figure 3) so that a serious experimental error seems unlikely. It should be pointed out also that in non-polar liquids the relaxation time is much shorter and no systematic deviation of the surface tension from its equilibrium value has been detected in the submillisecond range (Kochurova & Rusanov 1981*b*).

4.2. *Relaxation mechanism*

The macroscopic surface-tension-relaxation time expected in the cusp phenomenon and measured in experiments poses a question about the corresponding relaxation mechanism. The straightforward way of attacking this problem would be to consider the structure of the interfacial layer and the process of its formation explicitly, and then to find the corresponding macroscopic parameters by averaging the microscopic ones across this layer. The fundamental difficulty of this way is associated with a very small thickness of the interfacial layer. As is known, constitutive equations for micromechanical systems may be not the same as for macroscopic ones. Besides this, one would face the problem of representing intermolecular forces macroscopically as forces between 'material particles' or, if a non-continuum approach is used, has to deal with well-known fundamental difficulties of the kinetic theory of fluids. Anisotropy of the system will also contribute to the difficulties. (For example, one may expect elastic behaviour of the interfacial layer in the normal direction combined with viscous behaviour along it.)

The present model was derived (Shikhmurzaev 1993*a*, *b*) using a 'structureless' approach (Bedeaux, Albano & Mazur 1976), where from the very beginning the interfacial layer is represented as an already averaged and therefore two-dimensional 'surface phase' with its specific 'surface' properties. Now the problem is to determine fluxes of mass, momentum and energy between the bulk and the surface phases and to formulate the constitutive equations. This problem was resolved by methods of irreversible thermodynamics, thus implying mechanisms of mass, momentum and energy exchange associated with diffusion expressed in its most general form in terms of thermodynamic 'forces' and 'fluxes'. This can also be interpreted as a 'chemical reaction' of adsorption/desorption of molecules to/from the 'surface phase'.

† This correction undermines an early result by Vandegrift (1967) – see Kochurova & Rusanov (1981*b*).

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The relaxation time is given by (Shikhmurzaev 1993*a*)

$$\tau = \frac{1}{k_\rho(\mathrm{d}\mu^s/\mathrm{d}\rho^s)(\rho^s_{1e})}, \tag{4.2}$$

where k_ρ is the Onsager coefficient associated with the mass transfer between the bulk and the surface phase, μ^s is the chemical potential of the surface phase. An important feature of the 'structureless' approach is that it does not imply that the interfacial structure can be described in the frame of continuum mechanics in a closed form, i.e. without involving intermolecular interactions.

It should be noted that a diffusion mechanism of the interface formation and the possibility of elastic behaviour of the interfacial layer are not incompatible since they refer to kinematic and dynamic properties, respectively.

It is worth mentioning that a mechanism of relaxation similar to the one used in the present model would also follow from consideration of the structure of the interfacial layer (see, for example, Brenner 1979), though, of course, the assumptions made for this 'structural' way are neither weaker nor more evident than those used in the 'structureless' approach.

4.3. *On the surface density*

To formulate an equation of state for the 'surface' phase, one has to choose parameters which will characterize a current state of the interface. In the simplest variant of the present model, a current state of an interface in isothermal (or, more generally, 'surface barotropic') processes is characterized by one parameter, i.e. the surface density ρ^s. This parameter was used in different forms in a number of works (for example, Kovac 1977; Albano, Bedeaux & Vlieger 1979; Napolitano 1979; Ronis & Oppenheim 1983; dell'Isola & Kosiński 1993. See also Defay, Prigogine & Sanfeld 1977 for a review of earlier works and Gibbs 1928, p. 224 as the starting point).

The physical meaning of ρ^s is quite clear. Indeed, molecules in the interfacial layer experience non-symmetrical action from intermolecular forces of the 'bulk' molecules, which is the physical reason for the surface tension and leads to a non-trivial structure of the interface. In particular, the distribution of the actual density in the interfacial layer does not change abruptly as we cross the layer. In macroscopic fluid mechanics, when a diffuse interface is replaced by a geometrical surface of zero thickness, the actual density ρ averaged across the interfacial layer gives a 'surface' density ρ^s. In equilibrium, this parameter has a certain equilibrium value ρ^s_{1e} determined by the structure of intermolecular forces from the bulk phases, which are responsible for the surface tension. If two free surfaces are brought in contact so that the interface disappears, the 'surface' density, which is now simply the averaged density of the same layer in a symmetrical field of intermolecular forces, will change to the value ρ^s_0 corresponding to zero surface tension. Thus, ρ^s may be used as a macroscopic characteristic of a current state of the interface. Evidently the surface tension is a function of the 'excess' surface density, i.e. the difference $\rho^s - \rho^s_0$. In this paper, we use the simplest linear surface equation of state (2.4), which reflects only the tendency of the surface-tension variation with the surface density. A method of determining the actual surface equation of state from experiments is described in Shikhmurzaev (1996).

4.4. *Cusping*

Let us consider the physical picture of cusping as it is given by existing mathematical models. The solution to the problem found in the framework of classical fluid mechanics (Jeong & Moffatt 1992) is mathematically self-consistent and has no

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internal limitations. It can be obtained also as the result of the corresponding transient flow (Pozrikidis 1997).

However, as was pointed out in §1, a limitation comes from outside and is associated with a physical parameter – the thickness of the interfacial layer h – neglected in the classical hydrodynamics. Indeed, as the radius of curvature of the free surface R becomes comparable with h, the classical model falls outside its limits of applicability since the interface can no longer be modelled as a geometrical surface with a constant surface tension along it. Physically, $R \sim h$ corresponds to the beginning of transition from a flow regime with a stagnation line on a (rounded) free surface to that with a cusp, where (macroscopically) no stagnation line is present. In a continuum-mechanical modelling, the genuine cusp means that macroscopically a concentrated capillary force is acting on the cusp line, and hence it must be balanced by another concentrated force of a non-hydrodynamic origin, which is borne and maintained by the outer flow. Experiments suggest that this is the force from the surface-tension-relaxation 'tail', and the present paper provides a mathematical description of its mechanical properties when it is long compared with h. If the critical velocity U_c satisfies inequality (4.1), then the present model is applicable from the start of formation of the cusp, otherwise it will be applicable for higher flow rates (a fully developed cusp), when the length of this 'tail' becomes long enough. In an intermediate regime when $h \sim U\tau$, one has to consider the structure of the ('short') relaxation tail and the free surfaces in the vicinity of the cusp in more detail taking into account their finite thickness. From the macroscopic point of view, the dimensions of such a tail may be neglected, and its presence will manifest itself as a concentrated (non-hydrodynamic) force acting on the free surface and balancing that from the surface tension of contacting free surfaces.

Pictorially, we may say that the process of cusp formation starts when R becomes comparable with h, and the external flow becomes able to 'sweep' the liquid-facing side of the interfacial layer into the interior. As the flow rate increases so does the proportion of the interfacial layer swept into the bulk. Finally the whole interfacial layer is swept into the interior of the fluid, so that the stagnation line on the free surface disappears, and the liquid particles moved from the interface into the bulk form the surface-tension-relaxation 'tail'. This situation corresponds to a fully developed cusp, which, according to the 'kinematic definition' of cusping, is associated with a qualitative change in the flow kinematics.

In other words, on the macroscopic length scale the cusp formation is a transition from a regime where the Laplacian capillary pressure due to a rounded free surface is balanced by the bulk stress to a regime where the concentrated capillary force is balanced by that from the surface-tension-relaxation tail.

4.5. *Intermolecular forces*

It is necessary to make a special remark concerning intermolecular forces and their place in the present model. As is clear from the physical picture described above, in the intermediate regime corresponding to the transition from a rounded interface to that with a fully developed cusp, the interfaces cannot be regarded as geometrical surfaces, and their diffuse nature must be taken into account. Thus, this regime is the subject of microhydrodynamics, which includes intermolecular forces explicitly and considers the interfacial layers as the 'bulk'.

The regime of a fully developed cusp, where (4.1) is satisfied, can again be described macroscopically with neglect of h. In the present model, intermolecular forces manifest themselves implicitly through the transport coefficient, relaxation times and

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parameters of the constitutive equations, as they always do in macroscopic fluid mechanics.

A simplifying assumption was made about the change of the equilibrium surface parameters, which is assumed to occur in the cusp region (see figure 2 and (2.7)). Although this simplification prescribes an abrupt change in ρ_e^s, the resulting distribution of the surface parameters is continuous and the change in the surface pressure is smooth. One may develop the present (macroscopic) approach further by using a smooth function ρ_e^s instead of (2.7) and/or generalizing the model itself, say, along the lines discussed in Shikhmurzaev (1994). This programme, which seems rather straightforward but may require some additional and very non-trivial assumptions, remains beyond the scope of the present paper.

If we take a closer look at the cusp region, a contribution from intermolecular forces may also appear as an additional bulk force acting between interfaces in the vicinity of the cusp. This force may become an additional factor influencing the free-surface shape near the cusp, but it cannot be responsible for the existence of the cusp itself. Indeed, the first reason for this is that according to experiments the cusp is borne and maintained by external hydrodynamical flow, while this force is essentially non-hydrodynamic in origin and would be present even if the external flow were absent. Then one should have a cusp in a liquid at rest where the free surfaces are 'sealed' together by intermolecular forces. However, experiments show that in these conditions the cusp disappears. The second reason is that this force will be normal to the interfaces, while the capillary force acting on the cusp is tangential to them and should be balanced by another force directed along the contacting free surfaces.

Finally we will illustrate the role of intermolecular forces and the hydrodynamic aspect of the problem qualitatively with the help of integral considerations. Let us look at a control volume ABCD (figure 1), which comprises the cusp and has sides AB and CD lying just outside the range of influence of intermolecular forces while AD and BC are at a finite distance from the cusp, so that all the boundaries are located in the bulk where only the physical mechanisms incorporated in the classical hydrodynamics are important. In this case, the intermolecular forces, being internal with respect to volume ABCD, cannot balance those from the surface tension acting on AD. The latter can be compensated by the normal stress applied to BC or/and by the tangential stress acting on AB and CD. The classical boundary conditions on the free surface and along the plane of symmetry in the bulk imply zero tangential stress so that the tangential forces on AB and CD are negligible, and the only possibility is that the capillary forces are balanced by the normal stress imposed on BC. If one neglects the length scale associated with intermolecular forces compared to the characteristic length scale of the flow (the hydrodynamic limit), then the capillary forces (the surface tension) acting on AD remain finite while the size of BC becomes infinitesimal and, for the total force acting on BC to remain finite, the normal stress distribution should have a non-integrable singularity. Hence one arrives at Richardson's solution (1.1), which assumes a genuine cusp at finite capillary numbers and therefore has to produce a finite total force as a result of the action of viscous stress on a line. On the other hand, the present model gives the mechanism of generating tangential stress (3.9) along AB and CD, which still have a finite length in the hydrodynamic limit, and hence allows for balancing the capillary forces without giving rise to singularities.

4.6. *Gas viscosity*

In the present study, the displaced fluid, a gas, is assumed to be inviscid and therefore dynamically passive. In the literature, one can find two mutually contradictory points

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of view on how the displaced fluid viscosity affects the evolution of the free-surface associated with a convergent flow.

Koplik & Banavar (1994) have considered the situation of two immiscible fluids of equal viscosity driven by counter-rotating solid rollers on a microscopic length scale in the framework of molecular dynamics simulations. They found that the curvature of the separating interface increases with rotation rate but 'high curvature interfaces do not reach a steady state': instead 'drops of the fluid above the free surface are detached' so that 'in no case does a true cusp form'. This is in qualitative agreement with experiments by Joseph *et al.* (1991), where for two liquids no cusps were detected.

Pozrikidis (1997) has considered the same system numerically in the framework of the conventional fluid mechanical model and found that 'a cusp that is even sharper than the one developing on a free surface is seen to form'. The author attributes Koplik & Banavar's result to instability of the flow around the cusp on the grounds that similar droplets to those obtained by Koplik & Banavar appear in the conventional fluid mechanical treatment of the evolution of a two-dimensional bubble placed at the centre of the 4-roller Taylor's mill. It should be noted, however, that in the conventional fluid-mechanical formulation one may speak only about the tendency in the free-surface evolution but not about the cusp itself since the model is not applicable (and the computational method breaks down) as the radius of curvature of the free surface becomes sufficiently small.

As is known from experiments, the cusps do exist, and at the same time the gas viscosity is, of course, non-zero. Let us look at how these two facts meet in a mathematical model. If one assumes that (*a*) a genuine cusp does exist on a macroscopic length scale, (*b*) the viscous fluid model is valid for the displaced gas up to the cusp point and (*c*) the difficulties associated with application of the conventional model to the liquid are resolved (say, by the generalization of the model used in the present paper), then it becomes evident that these assumptions are incompatible. Indeed, since the gas experiences tangential forces from the liquid on the free surfaces directed towards the cusp, pressure in the gas should increase as the cusp is being approached to be able to push the gas from the cusp along the plane of symmetry thus maintaining the steady flow. At the same time, the shape of the free surface implies that, because of the Laplacian pressure, the gas pressure at the cusp is at least not higher than that in the liquid. Thus we arrive at the contradiction, and hence a steady cusp cannot exist.

A possible qualitative explanation for this apparent paradox is as follows. If one has a genuine cusp, then the gap between the free surfaces goes to zero faster than the distance from the point, where the gap is measured, to the cusp: this is actually a geometrical definition of the cusp. Therefore the average intermolecular distance in the gas phase becomes comparable with the gap size long before the cusp is reached. This means that Knudsen's effects become important at a finite distance from the cusp, and the conventional model should be abandoned. In macroscopic terms, this implies that the gas viscosity, as it is felt by the liquid, goes to zero as the cusp is being approached, and the asymptotics obtained in the present paper can be used to describe a real gas–liquid system. In the case of two liquids, continuum-mechanics models would break down simultaneously for both phases, the arguments mentioned above become inapplicable, and one has the situation described by Koplik & Banavar (1994).

4.7. *Possible experiments*

Experimental investigation of the processes associated with the cusp formation and development, which could directly confirm or invalidate the present theory, is a difficult

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and challenging problem. One route is to study the physics at the basis of the theory and look into the fine structure of the surface-tension-relaxation 'tail'. The existence of such a tail implies that after the fluid particles belonging to the free surface traverse the cusp, they still have the properties of those on the free surface which might be detected. Another measurable local characteristic is the fluid velocity profile near the cusp, which, according to the theory, should have a component corresponding to the shear flow (3.9). The difficulty is that, because the relaxation time τ is very small, especially for non-polar liquids, and hence the relaxation tail is very short, the measurements of local characteristics will require a very high spatial resolution.

An indirect method of testing the theory is to compare a global solution obtained in the framework of the present theory (for which §3 will provide the local asymptotics) and that found in the framework of the conventional model, for which the local asymptotics could be extracted from Jeong & Moffatt's result, with experimental data. In particular, one might expect that since the cusp 'resistance' to the outer flow is associated with different mechanisms in the two models (the surface tension gradient and the Laplacian pressure, respectively), the free-surface shape and especially the cusp position as a function of the flow rate will be informative and could indicate the dominant physical process.

Experiments with free-surface cusps are also interesting from another point of view. If the cusp phenomenon is viewed as a particular case of the interface formation–disappearance process, then, used as a method of measuring the characteristics of such processes, this flow has several advantages over those considered in traditional techniques. Indeed, in a flow with the cusp, (i) liquid–solid and gas–solid interfaces do not affect the region of interest, (ii) the process is steady, and (iii) the flow conditions can be well-defined. Besides that, one could extract information from the behaviour of different parameters simultaneously to be able to cross-check the results. In particular, the distribution of the surface parameters along the relaxation 'tail' could give information about the surface-tension-relaxation time τ, and the conditions for the onset of cusping could be used to investigate the fine structure of interfaces.

5. Summary

The paper suggests a physical mechanism which allows for the existence of genuine cusps on a free surface. The mechanism is associated with the surface-tension-relaxation process occurring as the fluid particles belonging to the free surface are swept into the interior of the fluid. It explains the origin of a non-hydrodynamic concentrated force which balances that from the surface tension of the free surface thus making possible a regular flow field in the vicinity of the cusp. In the case of a long surface-tension-relaxation tail, a local asymptotical analysis of the distribution of surface parameters near the cusp is presented.

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REFERENCES

Albano, A. M., Bedeaux, D. & Vlieger, J. 1979 On the description of interfacial properties using singular densities and currents at a dividing surface. *Physica* A **99**, 293–304.

Batchelor, G. K. 1967 *An Introduction to Fluid Dynamics*. Cambridge University Press.

Bedeaux, D., Albano, A. M. & Mazur, P. 1976 Boundary conditions and non-equilibrium thermodynamics *Physica* A **82**, 438–462.

https://doi.org/10.1017/S0022112098008532 Published online by Cambridge University Press

Benney, D. J. & Timson, W. J. 1980 The rolling motion of a viscous fluid on and off a rigid surface. *Stud. Appl. Maths* **63**, 93–98.

Bohr, N. 1909 Determination of the surface-tension of water by the method of jet vibration. *Phil. Trans. R. Soc. Lond.* A **209**, 281–317.

Bohr, N. 1910 Determination of the tension of a recently formed water-surface *Proc. R. Soc. Lond.* A **84**, 395–403.

Brenner, H. 1979 A micromechanical derivation of the differential equation of interfacial statics. *J. Colloid Interface Sci.* **68**, 422–439.

Defay, R., Prigogine, I. & Sanfeld, A. 1977 Surface thermodynamics. *J. Colloid Interface Sci.* **58**, 498–510.

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

Gibbs, J. W. 1928 *The Scientific Papers of J. Willard Gibbs.* Yale University Press.

dell'Isola, F. & Kosiński, W. 1993 Deduction of thermodynamic balance laws for bidimensional nonmaterial directed continua modelling interface layers. *Arch. Mech.* **45**, 333–359.

Jeong, J.-T. & Moffatt, H. K. 1992 Free-surface cusps associated with flow at low Reynolds number. *J. Fluid Mech.* **241**, 1–22.

Joseph, D. D., Nelson, J., Renardy, M. & Renardy, Y. 1991 Two-dimensional cusped interfaces. *J. Fluid Mech.* **223**, 383–409.

Kochurova, N. N., Noskov, B. A. & Rusanov, A. I. 1974*a* Taking account of the velocity profile in determining surface tension by the method of an oscillating jet. *Colloid J.* (*USSR*) **36**, 559–561.

Kochurova, N. N. & Rusanov, A. I. 1981*a* Dynamic surface properties of water: surface tension and surface potential. *J. Colloid Interface Sci.* **81**, 297–303.

Kochurova, N. N. & Rusanov, A. I. 1981*b* Properties of the nonequilibrium surface of water and aqueous solutions. *Colloid J.* (*USSR*) **43**, 36–42.

Kochurova, N. N. & Rusanov, A. I. 1995 Special properties of freshly formed surfaces of water and aqueous solutions. *Colloid J.* (*USSR*) **57**, 571–573.

Kochurova, N. N., Shvechenkov, Yu. A. & Rusanov, A. I. 1974 Determination of the surface tension of water by the oscillation jet method. *Colloid J.* (*USSR*) **36**, 785–788.

Koplik, J. & Banavar, J. R. 1994 Fluid cusps at the molecular scale. *Phys. Fluids* **6**, 480–488.

Koplik, J. & Banavar, J. R. 1995 Corner flow in the sliding plate problem. *Phys. Fluids* **7**, 3118–3125.

Kovac, J. 1977 Non-equilibrium thermodynamics of interfacial systems. *Physica* A **86**, 1–24.

Napolitano, L. G. 1979 Thermodynamics and dynamics of surface phases. *Acta Astronautica* **6**, 1093–1112.

Ngan, C. G. & Dussan V., E. B. 1984 The moving contact line with a 180° degree advancing contact angle. *Phys. Fluids* **27**, 2785–2587.

Pozrikidis, C. 1997 Numerical studies of singularity formation at free surfaces and fluid interfaces in two-dimensional Stokes flow. *J. Fluid Mech.* **331**, 145–167.

Richardson, S. 1968 Two-dimensional bubbles in slow viscous flows. *J. Fluid Mech.* **33**, 476–493.

Ronis, D. & Oppenheim, I. 1983 On the derivation of dynamical equations for a system with an interface: II. The gas-liquid interface. *Physica* A **117**, 317–354.

Shikhmurzaev, Y. D. 1993*a* The moving contact line on a smooth solid surface. *Intl J. Multiphase Flow* **19**, 589–610.

Shikhmurzaev, Y. D. 1993*b* A two-layer model of an interface between immiscible fluids. *Physica* A **192**, 47–62.

Shikhmurzaev, Y. D. 1994 Mathematical modeling of wetting hydrodynamics. *Fluid Dyn. Res.* **13**, 45–64.

Shikhmurzaev, Y. D. 1996 Dynamic contact angles in gas/liquid/solid systems and flow in vicinity of moving contact line. *AIChE J.* **42**, 601–612.

Shikhmurzaev, Y. D. 1997 Moving contact lines in liquid/liquid/solid systems. *J. Fluid Mech.* **334**, 211–249.

Vandegrift, A. E. 1967 Experimental evidence that water has no dynamic surface tension. *J. Colloid Interface Sci.* **23**, 43–45.

https://doi.org/10.1017/S0022112098008532 Published online by Cambridge University Press