The effect of surface contamination on thermocapillary flow in a two-dimensional slot. Part 2. Partially contaminated interfaces

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We consider the flow driven by a thermally induced surface stress in a fluid held in a shallow two-dimensional slot, and show that, for low Maragoni number, the extent of surface stagnation due to the presence of a non-diffusing surfactant depends on a single parameter E, the elasticity number defined in Part 1 of this analysis (Homsy & Meiburg 1984). For situations in which the adsorbed species are insufficient to result in a fully covered surface, we find that the interface is either clean and subject to constant stress, or contaminated and no-slip. There is a region in which one type of surface is replaced by the other. The Wiener–Hopf technique is used to obtain an analytic expression for the stream function in the vicinity of the leading edge of the stagnant surface in the limit of creeping flow. This result shows that the flow dies off under the stagnant surface at a distance of the order of the depth of the fluid, in a series of vortices of exponentially decreasing magnitude.

1. Introduction

The temperature dependence of the tension in an interface between two bulk fluids causes a surface stress when the interface is subject to tangential thermal gradients. Viscous balancing of this stress results in bulk fluid flow, a phenomenon termed thermocapillary convection. Flows driven by thermodynamically induced surface stress have been reviewed by Kenning (1968) and by Levich & Krylov (1969). In general, the flow driven by arbitrary thermal conditions in a fluid domain possessing free surfaces will be due to a combination of buoyancy and thermocapillary effects, but thermocapillary forces will be dominant when gravity is negligible, as in problems of small scale or in microgravity environments. Ostrach (1982) has discussed the importance of thermocapillary convection in the microgravity environment of space, and its role in projected space-based material-processing applications. Because the character of convection within the melt largely determines the quality of crystals grown from melts (an issue reviewed in detail by Hurle 1983, principally in reference to Czochralski crystal growth), an understanding of thermocapillary flow is essential in assessing the potential of crystal growth in a microgravity environment.

Advances in the understanding of the basic states and stability characteristics of thermocapillary flows have been slow because the physical phenomenon is complex, involving coupled flow and temperature fields in what is often a mathematically inconvenient domain determined in part by a free surface. These difficulties tax analytical methods, which have required the introduction of several simplifications. Flows of vanishing depth allow the approximations of lubrication theory, as in Yih (1969). For flows of small but finite depth, the lubrication approximations are valid

except in boundary layers near the end walls, where the streamlines close. Sen & Davis (1982) have used this approach to examine the flow driven by a constant temperature difference imposed between the endwalls of a shallow, two-dimensional channel. They obtain additional simplification by neglecting convective terms in the momentum and energy equations and by assuming the scale of surface deflection, the capillary number, to be very small. More complex problems evidently must be solved numerically (see for example Clark & Wilcox 1980; Strani, Piva & Graziani 1983; Zebib, Homsy & Meiburg 1984).

An important aspect of thermocapillary convection in problems of practical interest is the presence of surface-active species, whereby thermally induced stresses may be modified by concentration gradients determined by a mass-transport problem coupled with the temperature and velocity fields. This is a difficult analysis in the general case, involving interphase mass transfer and the possible precipitation of new, distinct phases where convection creates critical surfactant concentrations. Homsy & Meiburg (1984) (hereinafter referred to as HM) extended the analysis of Sen & Davis to consider the presence of a fixed quantity of surfactant, simplifying the mass-transport problem by assuming the surfactant to be insoluble in the bulk-fluid phases. This might reasonably be expected in crystal-growth problems, where bulk-phase impurities are in very low concentration. They define two dimensionless parameters which determine the influence of an insoluble surfactant on thermocapillary convection: the reciprocal dimensionless diffusivity, a surface Péclet number; and an elasticity number E scaling the relative dependence of surface tension on compositional and thermal variations. They then solve for the flow in the 'core' region, where lubrication theory may be applied, of a shallow, bounded two-dimensional channel, asymptotically and numerically for a range of values of the parameters E and Pe. Their method of solution combines the surfactant continuity equation and an expression for the surface tangential stress balance valid in the core region, forming an integral equation for the surface speed. This approach gives a solution of some generality, but requires that the lubrication approximation remains valid away from the endwalls of the channel, and cannot be used to solve problems when lubrication theory breaks down in the central region of the channel. The breakdown is anticipated when the surfactant distribution forms a region of stagnant surface extending into the channel, forcing streamlines to turn in the central region of the channel. As convection must dominate the surfactant continuity equation in order that this strong non-uniformity of surfactant distribution be maintained, the formation of stagnant surface regions is evidently a large-Péclet-number phenomenon.

The numerical calculations of HM covered a limited range of parameters, and led to the conclusion that separate regions of clean surface and surfactant-contaminated stagnant surface would not form for this class of flows. However, we shall show here that this conclusion is misleading, as it requires that sufficient surfactant be present to form a concentration gradient counteracting the thermally induced stress over the entire interface. If this is not the case then the separate regions *will* form. One of the objectives of the present paper is to examine more closely the formation of stagnant surface regions in surfactant-contaminated thermocapillary flow. We consider the case of infinite surface Péclet number and determine the range of values of the elasticity number for which mixed boundary conditions of stagnant and mobile surface are obtained, and present an analytic solution to the resulting thermocapillary problem for an asymptotically shallow channel. The mixed boundary case is of particular interest as it offers a thermocapillary analogy to the well-studied problem of flow past surfactant-contaminated drops, where the anticipated formation of a
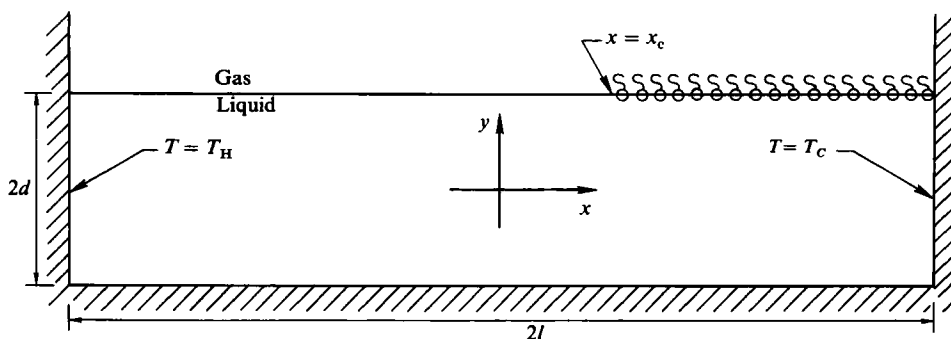
FIGURE 1. Thermocapillary flow driven in a two-dimensional channel by an imposed temperature gradient. The horizontal boundaries are insulated. The point $x = x_c$ marks the transition from mobile to stagnant surface.

stagnant cap of surfactant on the surface of the drop at high Péclet number has been confirmed by the success of the mixed boundary model in predicting the rise velocities of these drops (Davis & Acrivos 1966).

2. Formulation

The system we will consider is that of HM, as sketched in figure 1. Across a two-dimensional channel of depth $2d$ and length $2l$, containing a Newtonian liquid with constant physical properties (viscosity μ, density ρ, thermal conductivity k, and thermal diffusivity α), a temperature gradient is maintained by the fixed temperatures T_H and T_C of the solid vertical boundaries of the channel. The lower boundary is a solid insulating surface. The fluid above the channel is a gas of negligible viscosity and conductivity and therefore will not influence the flow and temperature fields in the liquid, as neither heat nor momentum can be transferred across the upper surface.

It remains to characterize the gas–liquid surface. We assume the surfactant to exist on the surface as an ideal film, with the following equation of state describing the dependence of surface tension σ on temperature T and concentration c:

$$\sigma = \sigma_m - \gamma_T (T - T_m) - RcT. \tag{2.1}$$

The constants appearing here are: R, a gas constant; T_m, equal to $\frac{1}{2}(T_C + T_H)$; γ_T, the coefficient in the linear relation between the tension of the clean surface and the temperature, obtainable from an expression like the Ramsay–Shields correlation (Adamson 1982); and σ_m, the tension of the clean surface at temperature T_m. This choice of an equation of state is one of many possible, and the equation is of course only approximately valid over any interval of temperature and concentration. See Gaines (1966) for a discussion of equations of state for surface films.

We will impose restrictions on parameters appearing in the *dimensionless* equation of state. This equation is:

$$\sigma = 1 - CT - CR^*\left(T + \frac{T_m}{\Delta T}\right)c. \tag{2.2}$$

Here $\Delta T = T_H - T_C$ is the imposed temperature difference, $C = \gamma_T \Delta T / \sigma_m$ is the capillary number, and $R^* = Rc_m / \gamma_T$ is a dimensionless gas constant. R^* is in general a small number, as can be seen from an examination of typical values: $R \approx 10$ N m/K mol, $c_m \approx 10^{-7}$ mol/m^2, $\gamma_T \approx 10^{-4}$ N/mK, so $R^* \sim 10^{-2}$. When we make the reasonable assumption that the mean absolute temperature is much larger

than the imposed difference, we obtain $R^*(T+T_m/\Delta T) \simeq R^*T_m/\Delta T \equiv E$, the elasticity number of HM. The dimensionless equation of state we obtain for small R^* and large $T_m/\Delta T$ is therefore

$$\sigma = 1 - CT - Ec. \tag{2.3}$$

The material behaviour embodied by (2.3) may of course also be used for non-gaseous surface films which admit a local linearization of the $\sigma(c, T)$ relationship.

As in HM, we refer the dimensional variables in our problem to the following characteristic scales:

$$x^* \sim l, \quad y^* \sim d, \quad c^* \sim c_m, \quad T^* - T_m \sim \Delta T,$$

$$u^* \sim \frac{\gamma_T \Delta T}{\mu} \frac{d}{l}, \quad v^* \sim \frac{\gamma_T \Delta T}{\mu} \frac{d^2}{l^2}, \quad p^* \sim \frac{\gamma_T \Delta T}{d}.$$

We define c_m as the mean surfactant concentration.

Introduction of this lubrication-type scaling gives the dimensionless continuity, momentum and energy equations, in the absence of gravity, and neglecting viscous heat generation:

$$u_x + v_y = 0; \tag{2.4}$$

$$RA(uu_x + vv_y) = -p_x + A^2 u_{xx} + u_{yy}; \tag{2.5a}$$

$$RA^3(uv_x + vv_y) = -p_y + A^2(A^2 v_{xx} + v_{yy}); \tag{2.5b}$$

$$MA(uT_x + vT_y) = A^2 T_{xx} + T_{yy}. \tag{2.6}$$

The parameters appearing here are:

$$R = \frac{\gamma_T A \Delta T d\rho}{\mu^2} \quad \text{(Reynolds number)};$$

$$M = \frac{\gamma_T A \Delta T d}{\mu\alpha} \quad \text{(Marangoni number)};$$

$$A = \frac{d}{l} \quad \text{(aspect ratio)}.$$

We will neglect convective terms of these equations everywhere in our analysis; to the order of approximation we will consider, this requires $R, M \sim O(A)$.

The free-surface boundary conditions take on a complex form with the deformable surface, but for small aspect ratio and very small capillary number considerable simplification is possible. For our purposes, the following set will suffice for the conditions applied at surface $y = 1$:

$$u_y = -T_x - Ec_x; \quad T_y = 0; \tag{2.7a, b}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}(uc) = 0; \quad \int_{-1}^{1} c(x)\,\mathrm{d}x = 2; \quad v = 0. \tag{2.7c, d, e}$$

These equations are the surface tangential-stress balance, the surface heat balance (neglecting the contribution of surface work), the continuity equation for a non-diffusing surfactant, a conservation requirement on the surfactant, and a kinematic condition. Derivation of the free-surface boundary conditions is given in full detail by Sen & Davis and HM.

The remaining boundary conditions are straightforward:

$$u = v = 0, \quad T = \mp 1 \quad (x = \pm 1); \tag{2.8a, b}$$

$$u = v = 0 \quad T_y = 0 \quad (y = -1). \tag{2.8c, d}$$

Our problem is to solve (2.4)–(2.6) subject to the boundary conditions (2.7 a–c), (2.8a–d), for small aspect ratio. We will find that the lubrication-scaled problem admits a uniformly valid solution at leading order for the temperature, but fails to yield a uniformly valid solution for the flow field. We will then examine the boundary layer associated with the formation of a stagnant surface region, and find a solution valid throughout the central region of the channel.

3. Core solutions

The flow field is more conveniently found by introducing the conventional stream function ψ, where $u = \psi_y$ and $v = -\psi_x$. We seek solutions for the unknowns $\psi(x, y)$, $T(x, y)$ and $c(x)$ in the form of expansions in powers of A:

$$\psi = \psi_0 + O(A); \quad T = T_0 + O(A); \quad c = c_0 + O(A).$$

The leading-order problem is:

$$\psi_{0yyyy} = 0, \quad T_{0yy} = 0; \tag{3.1a, b}$$

$$\psi_0 = \psi_{0x} = 0; \quad T_0 = \mp 1 \quad (x = \pm 1); \tag{3.2a, b}$$

$$\psi_0 = \psi_{0y} = 0; \quad T_{0y} = 0 \quad (y = -1); \tag{3.3a, b}$$

$$\psi_{0yy} + T_{0x} + Ec_{0x} = 0 \tag{3.4a}$$

$$T_{0y} = 0 \tag{3.4b}$$

$$\left. \begin{array}{l} \end{array} \right\} \quad (y = 1);$$

$$\frac{\mathrm{d}}{\mathrm{d}x}(\psi_{0y} c_0) = 0 \tag{3.4c}$$

$$\psi_0 = 0 \tag{3.4d}$$

$$\int_{-1}^{1} c_0 \, \mathrm{d}x = 2. \tag{3.4e}$$

The solution for T_0 is $T_0 = -x$, as in Sen & Davis. This solution satisfies all the appropriate boundary conditions and hence is uniformly valid in the channel.

The surfactant-continuity equation (3.4c) may be written as

$$\psi_{0y} c_0 = 0 \quad (y = 1) \tag{3.5}$$

because there is no flux of surfactant through the channel. This expression requires that either ψ_{0y} or c_0 be equal to zero at all points on the surface; both cannot equal zero over any finite length without contradicting the tangential-stress balance, (3.4a). Equation (3.5) evidently requires that all the surfactant exist on a stagnant surface region. This region must be continuous, for, if separate stagnant regions existed, the surface motion between them would pull them together. We therefore require that the surfactant exist in a stagnant region between the cold endwall at $x = 1$ and a point as yet unknown, $x = x_c$; refer to figure 1. The tangential-stress balance (3.4a)

and the surfactant-continuity equation (3.5) may now be combined into conditions applicable on distinct regions on the surface, substituting $T_0 = -x$:

$$\psi_{0yy} - 1 = 0; \quad c_0 = 0 \quad (x < x_c); \tag{3.6a, b}$$

$$\psi_{0yy} - 1 + E c_{0x} = 0; \quad \psi_{0y} = 0 \quad (x > x_c). \tag{3.6c, d}$$

We assume that $x = x_c$ is far from the endwalls of the channel. We must locate $x = x_c$ by solving the problems posed by (3.1a), (3.2a, b), (3.3a, b), (3.4d, e), (3.6a–d) and matching the results with boundary-layer solutions valid near $x = x_c$. The fact that $c_0 = 0$ for $x < x_c$ has the consequence that far from the influence of the stagnant surface, i.e. for $-1 \leqslant x \ll x_c$, we recover the problem of Sen & Davis, and we may appeal to their solution of the boundary-layer problem near $x = -1$ without duplicating their numerical solution.

A solution for ψ_0 satisfying (3.1a), (3.2a, b), (3.3a, b), (3.4d), (3.6d) is $\psi \equiv \psi_R \equiv 0$. This solution for ψ_0 is valid in the region $x_c \ll x \leqslant 1$, the region covered by stagnant surface, away from the leading edge. Note that, since the fluid is stagnant under the surfactant-covered surface, no boundary layer associated with a turning flow exists near the cold wall. In the stagnant region, the tangential-stress balance gives

$$c_0(x) - c_b = \frac{1}{E} [T_0(x_c) - T_0(x)]. \tag{3.7}$$

The constant c_b is the correction to c_0 arising from non-zero viscous stress in the boundary layer. We will show in the next section that this correction is an $O(A)$ quantity.

The other core solution for ψ_0 is the Sen & Davis core solution,

$$\psi_0 \equiv \psi_L = \tfrac{1}{8}(y+1)(y^2-1),$$

which satisfies the boundary conditions on the clean interface. This solution must be matched to solutions for the boundary-layer regions of turning flow near the hot endwall and near the leading edge of the stagnant surface. The details of the flow structure near the hot endwall are not important to our present purpose, and we refer the reader to Sen & Davis for this analysis.

4. Solution near $x = x_c$

We introduce the rescaled coordinates $\xi = (x - x_c)/A$, $\eta = y$ in order to analyse the flow near $x = x_c$. We require that the boundary-layer solutions be consistent with the outer solutions of the previous section, in the appropriate limits, and therefore seek our solutions in the form of expansions in powers of A:

$$\hat{\psi}(\xi, \eta) = \hat{\psi}_0 + O(A); \quad \hat{T}(\xi, \eta) = \hat{T}_0 + A\hat{T}_1 + O(A^2); \quad \hat{c}(\xi, \eta) = \hat{c}_0 + A\hat{c}_1 + O(A^2).$$

The uniformly valid solution $T_0 = -x$, obtained in the previous section, in local coordinates becomes $\hat{T} = -x_c - A\xi$. Our system for the unknowns $\hat{\psi}_0$ and $\hat{c}_0$ is:

$$\nabla^4 \hat{\psi}_0 = 0; \tag{4.1}$$

$$\hat{\psi}_0(\xi, -1) = \hat{\psi}_0(\xi, 1) = \hat{\psi}_{0\eta}(\xi, -1) = 0; \tag{4.2a, b, c}$$

$$\left. \begin{aligned} \hat{c}_{0\xi} &= -\hat{T}_{0\xi} = 0 \\ \hat{\psi}_{0\eta\eta} &= 1 - E\hat{c}_{1\xi} \\ \hat{\psi}_{0\eta}\hat{c} &= 0 \end{aligned} \right\} \quad (y = 1); \qquad \begin{aligned} &(4.3a) \\ &(4.3b) \\ &(4.3c) \end{aligned}$$

$$\lim_{\xi \to -\infty} \hat{c}_0 = 0, \quad \lim_{\xi \to \infty} \hat{c}_0 = c_{\mathrm{b}}, \qquad (4.4a,b)$$

$$\lim_{\xi \to -\infty} \hat{\psi}_0 = \psi_{\mathrm{L}}, \quad \lim_{\xi \to \infty} \hat{\psi}_0 = \psi_{\mathrm{R}}. \qquad (4.5a,b)$$

Again, the reader is referred to HM for the development of these equations. Equation $(4.3a)$ is simply the leading-order tangential-stress balance; the balance at the next order, $(4.3b)$, provides the required condition on $\hat{\psi}_0$.

The solution for $\hat{c}_0$ is $\hat{c}_0 = c_{\mathrm{b}} \equiv 0$. At the next order, $\hat{c}_1$ is determined by $(4.3b,c)$, with the solution

$$\hat{c}_1 = 0 \quad (\xi < 0), \qquad (4.6a)$$

$$\hat{c}_1 = \frac{1}{E} \int_0^\xi (1 - \hat{\psi}_{0\eta\eta}(\xi', 1)) \, \mathrm{d}\xi' \quad (\xi > 0). \qquad (4.6b)$$

This solution requires $\hat{c}_{0\eta} = 0$ for $\xi > 0$. The boundary conditions on $\hat{\psi}_0$ from the tangential-stress balance and surfactant continuity are now

$$\hat{\psi}_{0\eta\eta} = 1 \quad (\xi < 0), \qquad (4.7a)$$

$$\hat{\psi}_{0\eta} = 0 \quad (\xi > 0). \qquad (4.7b)$$

The complete problem for $\hat{\psi}_0$ is given by (4.1), $(4.2a,b,c)$, $(4.5a,b)$ and the two above conditions.

We solve for $\hat{\psi}_0$ with the Wiener–Hopf technique in an analysis similar to that of Richardson (1970) for the stick–slip problem of a plane jet at low Reynolds number with large surface tension. Our result is an analytic solution in the form of two eigenfunction expansions, one valid for $\xi < 0$, the other for $\xi > 0$.

$(\xi < 0)$

$$\hat{\psi}_0(\xi, \eta) = \tfrac{1}{8}(\eta^3 + \eta^2 - \eta - 1) + \sum_{n=1}^\infty \frac{e^{-ip_n\xi}}{B_+(p_n) p_n^2 (2 \cosh p_n - 2)}$$
$$\times \left[\begin{array}{l} (2p_n + 2 \sinh p_n) \, [\eta \sinh p_n \cosh (p_n \eta) - \cosh p_n \sinh (p_n \eta)] \\ + (2p - 2 \sinh p_n) \, [\sinh p_n \cosh (p_n \eta) - (\eta \cosh p_n \sinh (p_n \eta)] \end{array} \right]. \quad (4.8a)$$

$(\xi > 0)$

$$\hat{\psi}_0(\xi, \eta) = \frac{1}{2} \sum_{n=1}^\infty \frac{e^{-ir_n\xi}}{r_n B_-(r_n)} \left[\frac{\sinh r_n \cosh (r_n \eta) - \eta \cosh r_n \sinh (r_n \eta)}{1 + \cosh 2r_n} \right]$$
$$+ \frac{1}{2} \sum_{n=1}^\infty \frac{e^{-iq_n\xi}}{q_n B_-(q_n)} \left[\frac{\eta \sinh q_n \cosh (q_n \eta) - \cosh q_n \sinh (q_n \eta)}{1 - \cosh 2q_n} \right]. \quad (4.8b)$$

In these expressions we define two product functions:

$$B_+(z) = \frac{\displaystyle\prod_{n=1}^\infty \left(1 + \frac{4z}{\beta_n}\right)\left(1 - \frac{4z}{\bar{\beta}_n}\right)}{\displaystyle\prod_{n=1}^\infty \left(1 + \frac{4z}{\alpha_n}\right)\left(1 - \frac{4z}{\bar{\alpha}_n}\right)}; \quad B_-(z) = \frac{2 \displaystyle\prod_{n=1}^\infty \left(1 - \frac{4z}{\alpha_n}\right)\left(1 + \frac{4z}{\bar{\alpha}_n}\right)}{\displaystyle\prod_{n=1}^\infty \left(1 - \frac{4z}{\beta_n}\right)\left(1 + \frac{4z}{\bar{\beta}_n}\right)}; \quad (4.9b)$$

where $\alpha_1, \alpha_2, \ldots$ are the ordered roots of the equation $\alpha - \sinh \alpha = 0$ in the upper right quadrant of the complex plane, and $\beta_1, \beta_2, \ldots$ are the ordered roots of $\tfrac{1}{2}\beta^2 + 1 - \cosh \beta = 0$ in the upper right quadrant.

The eigenvalues p_n, q_n, and r_n have the following definitions:

$$p_n = \tfrac{1}{4}\bar{\alpha}_n, -\tfrac{1}{4}\bar{\alpha}_n; \quad q_n = -\tfrac{1}{2}\alpha_n, \tfrac{1}{2}\bar{\alpha}_n; \quad r_n = -\tfrac{1}{2}\gamma_n, \tfrac{1}{2}\bar{\gamma}_n.$$

n	α_n	γ_n
1	$2.77 + 7.50i$	$2.25 + 4.21i$
2	$3.35 + 13.9i$	$3.10 + 10.7i$
3	$3.72 + 20.2i$	$3.55 + 17.1i$
4	$3.98 + 20.6i$	$3.86 + 23.4i$
5	$4.19 + 32.9i$	$4.09 + 29.7i$
6	$4.37 + 39.2i$	$4.28 + 36.0i$
7	$4.51 + 45.4i$	$4.44 + 42.3i$
8	$4.64 + 51.7i$	$4.58 + 48.6i$
9	$4.76 + 58.0i$	$4.70 + 54.4i$
10	$4.86 + 64.3i$	$4.81 + 61.2i$

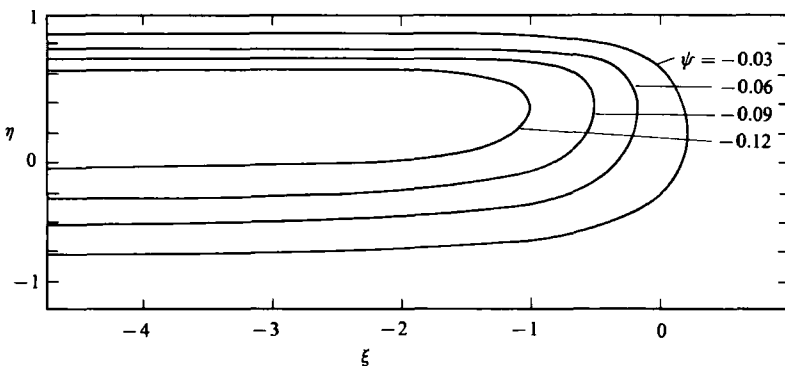TABLE 1. Numerical values of the first ten eigenvalues

FIGURE 2. First-order streamlines in the region near the leading edge of the stagnant surface.

Here γ_1, γ_2, ... are the ordered roots of $\gamma + \sinh \gamma = 0$ in the upper right quadrant. The first ten roots of a $\alpha - \sinh \alpha = 0$ and of $\gamma + \sinh \gamma = 0$ are given in table 1. The roots of a $\alpha - \sinh \alpha = 0$ agree with the values reported by Hillman & Salzer (1943). We are unaware of any published values for the roots of $\gamma + \sinh \gamma = 0$. Following Hardy (1902), the asymptotic forms for α_n and γ_n are easily shown to be

$$\mathrm{Re}\,(\alpha_n) \sim \log_e (4n+1)\,\pi, \quad \mathrm{Im}(\alpha_n) \sim (2n+\tfrac{1}{2})\,\pi,$$

$$\mathrm{Re}\,(\gamma_n) \sim \log_e (4n-1)\,\pi, \quad \mathrm{Im}(\gamma_n) \sim (2n-\tfrac{1}{2})\,\pi.$$

In order to compute numerical values of the stream function, we truncate the expansion at a finite number of terms, chosen so that the remaining terms are numerically insignificant. The product functions $B_+(\cdot)$ and $B_-(\cdot)$ are evaluated using the first 200 terms, and the expansions for ψ_0 are evaluated to a maximum of 50 terms. The stream function near $x = x_c$ computed in this way is plotted in figure 2. We see in this figure that the solution does satisfy the required matching conditions, approaching the Sen & Davis core-region solution as $\xi \to -\infty$, and approaching $\psi_{0R} \equiv 0$ for $\xi \to \infty$. An interesting feature of the solution is the appearance of a series of vortices under the stagnant surface, shown in logarithmic scale in figure 3.

We note that these vortices are in accord with (4.8b) and the occurrence of complex eigenvalues, the smallest of which has a real part which is $O(1)$. Thus the strength of the circulation under the stagnant surface falls of exponentially with x, with characteristic scale A, indicating that the turning flow takes place in a distance of the order of the depth of the layer.
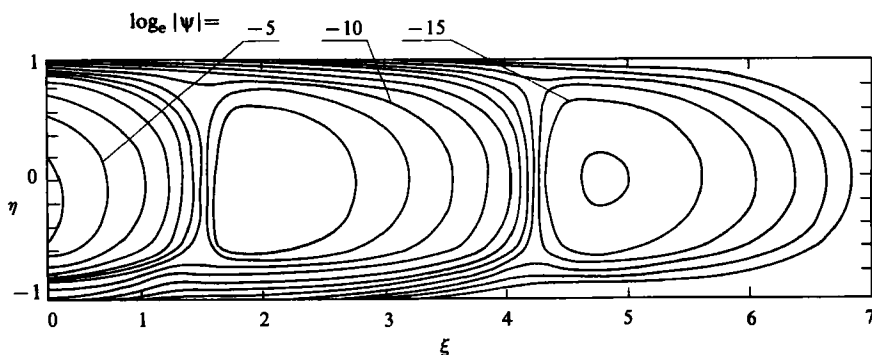
FIGURE 3. Exponentially decreasing vortices (shown in log scale) under the stagnant surface, near the edge of the stagnant surface.
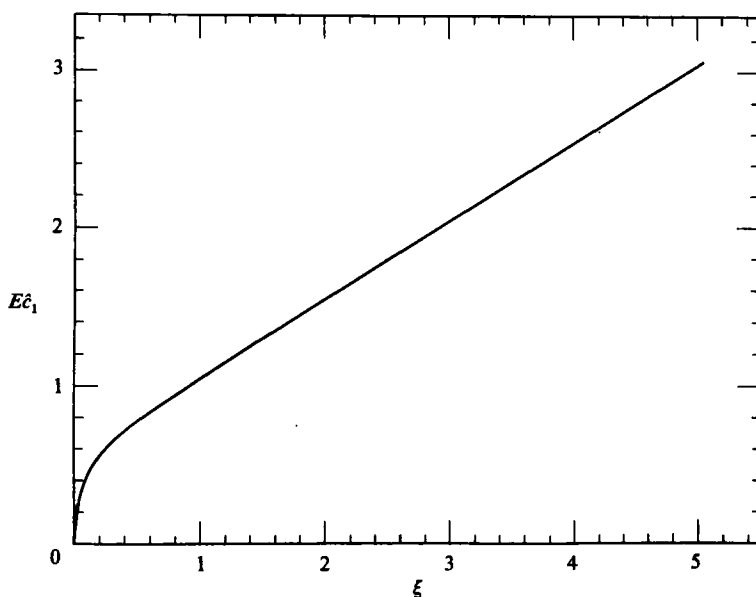

FIGURE 4. Surface concentration of the non-diffusing surfactant, near the edge of the stagnant surface.

With the solution for $\hat{\psi}_0$ we can use (4.6 b) to calculate $\hat{c}_1$. The integral of the viscous stress is evaluated analytically termwise with a maximum of 100 terms in each series. The surfactant surface concentration near $x = x_c$ is plotted in figure 4. The viscous contribution to the surfactant gradient dies off rapidly from the leading edge, and represents only an $O(A)$ correction to the uniform solution for the surfactant concentration, $c_{0u} = (1/E) A\xi = (x - x_c)/E$. We now may determine x_c by integrating from $x = x_c$ to $x = 1$, using the surfactant-conservation condition (3.4 e) to obtain

$$x_c = 1 - 2E^{\frac{1}{2}}. \qquad (4.10)$$

We see that, for $E > 1$, no solution exists within the range of x. This case corresponds to a situation in which the total surfactant present is sufficient to form a gradient balancing a given thermal gradient over the full length of the channel, stagnating the entire surface. For values of E in the range $0 < E < 1$, this expression gives values of x_c within the range of x, indicating the formation of stagnant regions on the free

interface. This simple dependence of the extent of the stagnant region upon the elasticity number is due to the fact that, in the conduction-dominated problem, the temperature gradient along the stagnant surface is fixed, independent of the value of x_c.

5. Discussion

This work examines the influence of a non-diffusing, insoluble surfactant on thermocapillary flow. The influence of a surfactant is determined in general by its transport behaviour, characterized by a surface Péclet number Pe and by its effect on the local surface tension as described by some equation of state for the surface. With the simplifying assumptions that the surfactant exists as an ideal gaseous film, and that the temperature variation is small, this effect can be characterized by a single parameter, E, the elasticity number. Thus when Pe is fixed at infinity, as in our analysis, the transport problem is set in the sense that the surfactant must exist in a stagnant surface region. The role of E, or of the multiple parameters that might describe the compositional dependence of surface tension in a more complicated model, is to determine the extent of the stagnant-surface region. In this work we assume the temperature field to be conduction dominated, with the result that the stagnant surface grows simply as $E^{\frac{1}{2}}$ until for $E = 1$ the entire surface becomes stagnant. Our analysis complements the result of HM, who found in the limit $Pe \to \infty$ an expression for the speed of the free surface

$$u_s = \frac{1}{Pe}\left(\frac{1}{x+E}\right), \qquad (5.1)$$

which gives uniform stagnation as $Pe \to \infty$ unless E is in the range of x, where the expression is singular for some $x = E$. We see that a value of E in the range of x is the condition for the existence of a stagnant surface of partial extent, for which our analysis applies. The unlikely case of $E < 0$ will arise for a surfactant which increases surface tension; in this case the stagnant surface will be found against the hot boundary of the channel. Thus some region of partial stagnation can be found for all cases in which the HM solution is singular, except for the senseless $E = 0$ case corresponding to zero total surfactant.

The solution for the stream function in the low-Reynolds-number limit, obtained by the Wiener–Hopf technique, shows that viscous stress contributes only $O(A)$ terms to the surfactant concentration, and that the flow under the stagnant interface dies off in an $O(A)$ distance from the leading edge of the stagnant interface in a series of vortices of exponentially decreasing magnitude. The result (4.10) for the location of the leading edge of the stagnant surface in the thin channel is independent, at leading order, of the flow field, hence valid for $R \sim O(1)$, and does not require the $R \sim O(A)$ assumption made in the solution of the leading-order flow field. The extent of surface stagnation to leading order does depend on the Marangoni number, because the introduction of convective terms into the energy equation changes the temperature field in the channel (Zebib *et al.* 1984). Since the extent of surface stagnation is essentially determined by the balance of thermal and compositional contributions to the surface stress, for large Marangoni number the extent of stagnation and the temperature field will be coupled problems: the extent of stagnation influences the role of convection in the thermal problem, and convection in the thermal problem changes the temperature gradient on the stagnant surface. However, as the extent of stagnant surface approaches the full length of the channel, the temperature

gradient in the stagnant region clearly approaches the gradient of the low-Marangoni-number solution, and the condition $E \geqslant 1$ will give uniform surface stagnation for arbitrary Marangoni or Reynolds numbers. Of course, in this case the Marangoni and Reynolds numbers lose their relevance as transport scales, because the characteristic velocity used in their definitions is no longer appropriate.

In this analysis we have assumed the surfactant to have zero diffusivity. The results we obtained for the mobile- and stagnant-core regions correspond to the leading terms in double expansions of the solutions of the large-Péclet-number problem for these two regions, in powers of the aspect ratio and inverse powers of the Péclet number. The $O(1/Pe)$ correction to the stream function in the stagnant-core region may be obtained by inserting the leading-order surfactant solution into the surfactant continuity equation, which reads

$$\frac{1}{Pe}\frac{dc}{dx} = \psi_y c \quad (y = 1),$$ (6.2)

and using the resulting expression as the additional boundary condition on ψ, giving

$$\psi \sim \frac{1}{4Pe(x - x_c)}(y^2 - 1)(y + 1),$$ (6.3)

in the stagnant core region. The $O(1/Pe)$ correction to the surfactant solution in the mobile-core region, determined in a similar manner, is identically zero.

Additional boundary layers appear in the finite-Péclet-number problem, as no-flux boundary conditions must be satisfied by the surfactant solution, and surfactant diffusion must be balanced by convection at leading order in an $O(1/Pe)$ boundary layer near $x = x_c$. For sufficiently large Péclet number (i.e. for $1/Pe \ll A$) the boundary layers in the surfactant solution can be shown to have a simple exponential form, but away from this limit the surfactant boundary layers couple with the flow field near the regions of turning flow, and a more complex structure may be anticipated.

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