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The effect of surface contamination on thermocapillary flow in a two-dimensional slot

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We consider the effect of insoluble surfactants on the steady thermocapillary flow in a differentially heated slot treated previously by Sen & Davis (1982). The equation of state for interfacial tension is taken to be linear in both temperature and surfactant concentration. We treat the problem in the limit of shallow slots and low thermal Marangoni numbers so that the effect of surfactants is described by only two parameters: a surface Péclet number *Pe* and an elasticity parameter denoted by E, the ratio of the compositional elasticity to the tension difference due to the imposed temperature difference. Using lubrication theory and matched asymptotic expansions, we reduce the problem to a single nonlinear integral–algebraic equation (for the outer core variables), which we solve both numerically and in various asymptotic limits by perturbation theory. It is shown that the general effect of surfactants is to retard the strength of the motion, but that this retardation is not necessarily uniform in space. Surprisingly, there are only extreme cases in which condensed surfactant layers will form, these being $E \ll 1$, $Pe \gg 1$. Sharp gradients in surfactant concentrations will not form in the general case of $E = O(1)$. This behaviour is due to the strong coupling between the flow and the interfacial stress, and is contrasted with certain well-known forced-convection problems.

1. Introduction

Thermocapillary convection refers to flows that are driven by the coupling between temperature gradients which may exist on the interface between two fluids and the tangential stress which results as a consequence of the dependence of the surface or interfacial tension on temperature. This general class of flows has been the subject of review articles by Levich & Krylov (1969), Kenning (1968) and Ostrach (1977, 1982). There has been renewed interest in both analytical and experimental studies of such flows in recent years due in part to the effects such flows may have on systems of macroscopic dimension in the low-gravity environment of space (Ostrach 1982). Nonetheless, our understanding of such flows is still at a primitive stage of development, due in part to the fact that an interface is present and the problems thus involve the location of an unknown boundary. Most of the existing analyses are for rectilinear or nearly rectilinear flows (see e.g. Yih 1968, 1969; Adler & Sowerby 1970). Recently, Sen & Davis (1982) have analysed steady thermocapillary convection in a bounded two-dimensional slot. Their work forms the basis of the problem we consider, so it is discussed in detail in §3 below. Chang & Wilcox (1976) (with corrections by Clark & Wilcox 1980) have numerically solved for thermocapillary convection in a cylindrical geometry subject to thermal boundary conditions of interest in crystal-growth applications.

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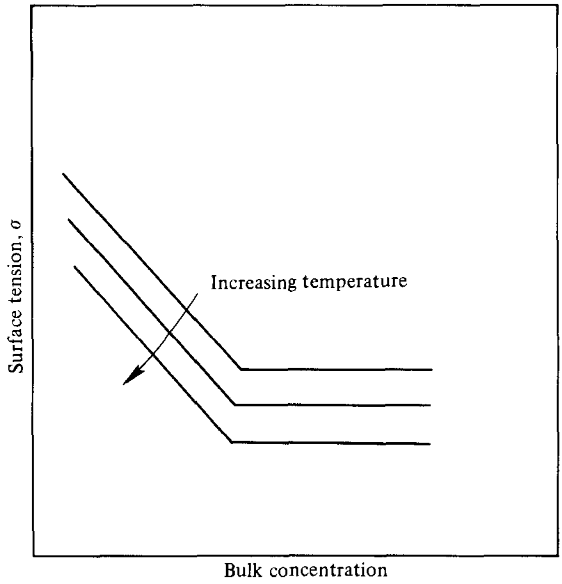

FIGURE 1. Idealized relationship between σ and bulk concentration.

We shall be interested in this paper in the effect of surfactants on the nature and strength of such thermocapillary flows. It is well known that surfactants can exert a profound influence on interfacial flows. This influence is due to both the dependence of interfacial tension on surface concentration and the surface phase behaviour. Interfacial tension generally decreases with increasing surface concentration. Such effects give rise to forces within the interface which have been termed 'compositional elasticity', as such forces are proportional to surface displacement. These effects are responsible for the stabilization of convective instabilities (Berg & Acrivos 1965), the apparent stabilization of viscous film flows (Whitaker 1964), and the relative stabilization of foams and thin films during coalescence processes.

In addition, one or more phase changes may occur as the surface species become more concentrated. Surface monolayers may also reach saturation above a certain concentration, and any attempt to increase the local concentration results in monolayer collapse, solubilization of the surfactant into the bulk, or both. Figure 1 shows an idealization of the behaviour of interfacial tension with bulk concentration for the simple case of adsorption followed by the formation of a single condensed phase at saturation. Such models have been used with good success to study the effect of surfactants on the rise velocity of small bubbles (Horton, Fritsch & Kintner 1965; Davis & Acrivos 1966), and monolayer formation at a stagnation point (Merson & Quinn 1964). Figure 2 shows a schematic of the behaviour in these latter problems, in which a unidirectional convective flow toward a stagnation point causes the buildup of a condensed film whose dynamic effect is to render that portion of the interface immobile.

A key feature of situations such as those sketched in figure 2 is that the velocity is externally imposed, and as such these may be considered as forced-convection problems as far as the surface mass balance is concerned. It will develop below that there is a fundamental difference in behaviour between such problems and those under consideration in this paper, in which the flow is driven solely by stresses due to gradients of either temperature or concentration within the interface. This latter class

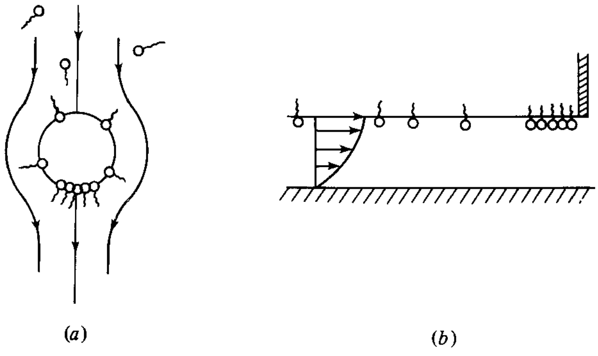

FIGURE 2. Formation of condensed films at stagnation points: (a) droplet flow; (b) channel flow.

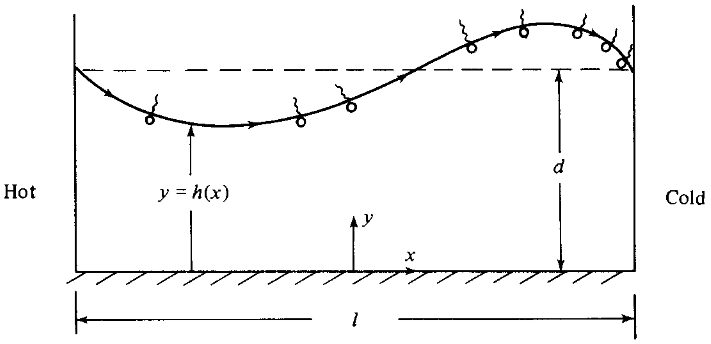

FIGURE 3. Schematic of thermocapillary flow with an adsorbed surfactant.

of problems may be considered to be akin to natural convection problems. This difference is discussed in detail in §6.

Consider now the situation sketched in figure 3. A fluid is contained between two horizontal walls held at different temperatures. A temperature gradient will exist along the free surface, causing thermocapillary flow to occur. If the surface has an insoluble surfactant adsorbed on it, the surfactant will be convected by the flow and in general there will occur a gradient in surface concentration, with possible surface phase change and/or resolubilization of surface species. This in turn causes a gradient in interfacial tension, which will couple the surfactant concentration to the flow field, causing a moderation of the flow driven by thermocapillarity alone. In this paper we will seek to analytically describe the effect of such insoluble surfactants on the thermocapillary flow treated by Sen & Davis (1982, hereinafter referred to as SD).

2. Formulation

Consider a two-dimensional channel of height h and length l as sketched in figure 3, heated differentially from the side, with a free surface on which an insoluble surface species is adsorbed. The coordinate system is as shown, and the horizontal and vertical velocity components are u and v respectively. We consider the vertical boundaries to be isothermal and impenetrable and the lower horizontal boundary to be insulated and similarly impenetrable. The interfacial tension of the liquid is taken to depend upon both temperature and local surface composition of the surfactant: thus

$$\sigma = \sigma_0 - \gamma_T(T' - T_0) - \gamma_c(c' - c_0)), \tag{2.1}$$

where σ_0 is the mean tension at temperature T_0 and surface concentration c_0 (which is in general lower than that for $c_0 = 0$). The reference temperature T_0 is taken as the average of the vertical wall temperatures, and c_0 is the average surface concentration. γ_T and γ_c are the usual (constant) rates of change of σ with respect to temperature and concentration. Owing to variations in T' and c', there will be a tangential stress in the interface which is balanced by a viscous stress due to motion in the bulk. Our problem is to solve for this motion as a function of the parameters of the problem. In writing such an equation of state for the surface, we are neglecting any surface phase transitions, and are thus limiting our analysis to 'gaseous' surface species (see Gaines 1966).

In order to render the equations dimensionless, it is necessary to choose characteristic scales. We follow Ostrach (1977) and SD in choosing the following:

$$x^* \sim l, \quad y^* \sim d, \quad u^* \sim \frac{\gamma_T(T_{\mathrm{H}} - T_{\mathrm{C}})}{\mu}\frac{d}{l}, \quad v^* \sim \frac{\gamma_T(T_{\mathrm{H}} - T_{\mathrm{C}})}{\mu}\left(\frac{d}{l}\right)^2,$$

$$p^* \sim \frac{\mu u^* l}{d^2}, \quad T^* \sim T_{\mathrm{H}} - T_{\mathrm{C}} \equiv \Delta T, \quad c^* \sim c_0.$$

The scale u^* arises from the primary balance between the thermocapillary and viscous stresses; that for v^* is consistent with the continuity equation. The viscous scale for P^* anticipates a lubrication-theory analysis. The location of the free surface $y = h(x)$ is scaled with the depth d.

The equations governing the velocity, temperature and pressure fields in the bulk are the steady Navier–Stokes equations and the energy equation, which read (SD)

$$u_x + v_y = 0, \tag{2.2a}$$

$$RA(uu_x + vu_y) = -P_x + u_{yy} + A^2 u_{xx}, \tag{2.2b}$$

$$RA^3(uv_x + vv_y) = -P_y + A^2(v_{yy} + A^2 v_{xx}), \tag{2.2c}$$

$$MA(uT_x + vT_y) = T_{yy} + A^2 T_{xx}. \tag{2.2d}$$

The parameters appearing in these equations are

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

$$R = \frac{u^* d}{\nu} = A\frac{\gamma_T \Delta T d}{\mu\nu} \quad \text{(Reynolds number)},$$

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

The boundary conditions on the solid walls may be written directly:

$$u = v = T_y = 0 \quad (y = 0), \tag{2.3a}$$

$$u = v = (T \mp \tfrac{1}{2}) = 0 \quad (x = \pm\tfrac{1}{2}). \tag{2.3b}$$

In addition to the bulk equations and the above boundary conditions, we also have conditions which must hold on the free boundary $y = h(x)$. These arise from the usual boundary conditions on the flow variables and from a surface-continuity equation for the surfactant. Thus

$$v = uh_x, \tag{2.3c}$$

$$-P + \frac{2A^2}{N^2}[v_y - h_x u_y + A^2 h_x(-v_x + h_x u_x)] = \frac{A^2}{C}\frac{h_{xx}}{N^3}(1 - CT - EC(c-1)), \tag{2.3d}$$

$$(1 - A^2 h_x^2)(u_y + A^2 v_x) + 2A^2 h_x(v_y - u_x) = -N(T_x + h_x T_y + Ec_x], \tag{2.3e}$$

$$\frac{T_y - A^2 h_x T_x}{N} + L(T + x) = 0, \tag{2.3f}$$

$$\frac{\mathrm{d}^2 c}{\mathrm{d}x^2} - A^2 \frac{\mathrm{d}c}{\mathrm{d}x}\frac{h_x h_{xx}}{N^2} = Pe\, N^2 \left[\frac{\mathrm{d}}{\mathrm{d}x}(uc) + \frac{A^2 uch_x h_{xx}}{N^2}\right], \tag{2.3g}$$

where for convenience we have written

$$N^2 = 1 + A^2 h_x^2. \tag{2.3h}$$

Note that we have assumed that, in addition to surface convection, surfactant can diffuse in the surface. We shall be interested in the consequences of this model. These equations are the kinematic condition, the normal and tangential stress balances, the thermal condition and the species continuity equation, all of which hold on the free boundary $y = h(x)$.

Note that in (2.3f) we have modelled the thermal conditions of the top surface in terms of a constant dimensionless heat-transfer coefficient (a Biot number) L. As it will develop, our solutions will be conduction-dominated, and therefore the precise form of this condition will be immaterial to the main conclusions of the analysis. Equation (2.3g) must be solved subject to the conditions

$$\frac{\mathrm{d}c}{\mathrm{d}x} = 0 \quad (x = \pm\tfrac{1}{2}). \tag{2.3i}$$

Equation (2.3d) is to be solved subject to conditions which hold at the contact line. The behaviour of the contact line must therefore be modelled. Here we take a fixed contact line, which implies

$$h = 1 \quad (x = \pm\tfrac{1}{2}). \tag{2.3j}$$

Such a condition may be approximated experimentally by the use of a knife-edge in the plane of the undistorted interface. Other boundary conditions may be treated in a similar fashion, as discussed by SD. The major conclusions of this work are independent of the exact form of the boundary condition on the contact line. The additional parameters occurring in these equations are

$$C = \frac{\gamma_T \Delta T}{\sigma_0} \quad \text{(capillary number)},$$

$$L = \frac{hd}{k} \quad \text{(Biot number)},$$

$$E = \frac{c_0 \gamma_c}{\Delta T \gamma_T} \quad \text{(elasticity number)},$$

$$Pe = \frac{u^* l}{D} = \frac{\gamma_T \Delta T d}{D} \quad \text{(surface Péclet number)}.$$

The derivation of the surface balance, (2.3g), is given in Appendix A.

A few comments regarding the surface equations are in order. The thermal condition is that of SD. Note that we have defined the capillary number in a slightly different manner than SD. As defined here, $C \sim \Delta\sigma/\sigma_0$, which is in general a small quantity. Thus we will treat the limit $C \ll 1$. For small capillary number, the deflection of the interface due to normal stresses generated by the flow is in general small, as can be seen by examining (2.3*d*), and thus the free-boundary location may be obtained as a perturbation about the rest state of capillary statics. In this context, this takes the form of treating the distinguished limit $C = \bar{C}A^3$ as $A \rightarrow 0$; for a further discussion see SD.

The primary coupling between the fields arises from the tangential stress balance (2.3*e*). The relative magnitude of the stress due to temperature and surfactant is given by the parameter E. E may be interpreted as the ratio of the change in interfacial tension due to the addition of a uniform surfactant concentration of c_0 to that due to the imposition of a temperature difference ΔT. However, since in our problem the only *applied* gradient is that of temperature, it is more compelling to interpret E as the ratio of the compositional elasticity $c_0(\partial\sigma/\partial c)_{c_0}$ to the change in tension $\Delta\sigma = \Delta T(\partial\sigma/\partial T)_{T_0}$. As we shall see, this compositional elasticity will oppose the motion due to the thermocapillary stress, as a result of concentration gradients produced by convection of the surfactant in the thermocapillary flow field.

Values of the compositional elasticity $c_0(\partial\sigma/\partial c)_{c_0}$ can vary from zero to quite large numbers, e.g. 1 N/m for hexonic acid solutions (Pierson & Whitaker 1978). Values for γ_T usually are small, 10^{-4} N/mK for a silicone oil. Thus E can vary from a very small to a quite large number, strongly depending on the mean concentration c_0 and the temperature difference ΔT.

The value of Pe depends upon both fluid properties and the geometry of the box. If we consider a fluid with typical data, taking the surface diffusion coefficient to have the same order of magnitude as bulk diffusivities,

$$\gamma_T = 1\times10^{-4}\,\mathrm{N/mK},\quad D = 1\times10^{-9}\,\mathrm{m/s^2},\quad \mu = 1\times10^{-3}\,\mathrm{kg/m\,s},$$

we obtain

$$Pe = \frac{\gamma_T \Delta T d}{d\mu} = 1\times10^{3}\,\Delta T[\mathrm{K}]\,d[\mathrm{m}].$$

Thus for $\Delta T = 1$ K, $d = 1$ cm we would get $Pe = 10^6$. We can conclude that Pe can vary from arbitrarily small values (corresponding to small ΔT) to quite large values.

The problem is thus to solve the field equations subject to the boundary conditions and the following integral constraints,

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} h(x)\,\mathrm{d}x = 1, \tag{2.4a}$$

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} c(x)\,\mathrm{d}x = 1, \tag{2.4b}$$

expressing conservation of total liquid volume and total surfactant respectively.

3. The shallow cavity with no surfactant

Sen & Davis (1982) have analysed the problem of thermocapillary convection with no surfactant, which corresponds to the problem posed in §2 with $c \equiv 0$. Because our analysis follows closely from theirs, we briefly highlight the features of the solution technique. The interest is in analytical descriptions of these flows which may be obtained for shallow slots $A \to 0$. In this case, the lubrication equations apply in the central regions of the cavity. Furthermore, it is desirable to perturb about the case of an initially flat interface, which may be obtained by neglecting the normal stress due to the flow and either fixing the contact line, or choosing the contact angle close to $\frac{1}{2}\pi$. This corresponds to the case $C \ll A^2$, cf. (2.3*d*). In order to obtain the first corrections to the case of a flat interface at lowest order in an asymptotic expansion in A, the distinguished limit $C = \bar{C}A^3$ is taken. Thus, in the central regions of the cavity, SD found that

$$\left.\begin{aligned} h &= 1 + Ah_1(x) + A^2h_2(x), \\ p &= p_0(x) + Ap_1(x,y) + \ldots, \\ u &= u_0(y) + Au_1(x,y) + \ldots, \\ T &= T_0(x) + AT_1(x,y) + \ldots . \end{aligned}\right\} \tag{3.1}$$

It is further found that the temperature field is conductive to lowest order. The parallel flow $u_0(y)$ and its associated pressure field are then determined as solutions to the lubrication equations with a constant thermocapillary stress applied at the interface $y = 1$. These fields are not uniformly valid, as they do not satisfy the conditions at the vertical boundaries of the cavity. It is necessary to analyse the problem in boundary layers within $O(A)$ of the ends of the cavity in which the flow turns to return fluid to the interior, and where local adjustments to temperature and pressure fields and to interfacial position may also be present.

The stress associated with $p_0(x)$ is then known in the central regions and the corresponding deflection $h_1(x)$ may be determined. Taking the additional distinguished limits

$$R = \bar{R}A, \quad M = \bar{M}A \tag{3.2}$$

allowed SD to analyse the problem in a conduction-dominated situation, so that interfacial deflections due to a constant thermocapillary stress could be analytically described to the relatively high order of $O(A^2)$. The results which are relevant here are for the case of fixed contact line, for which

$$h = 1 - \tfrac{1}{4}A\bar{C}(x)\,(x^2 - \tfrac{1}{4}) + O(A^2), \tag{3.3a}$$

$$u = \tfrac{1}{4}(3y^2 - 2y) + \tfrac{3}{16}A\bar{C}x(x^2 - \tfrac{1}{4})\,y^2 + O(A^2). \tag{3.3b}$$

These expressions are subject to boundary-layer corrections within $O(A)$ of $x = \pm\frac{1}{2}$ which are given in detail by SD. Note that in the core the deflections from the flat interface are negative in the left half and positive in the right half of the cavity. To leading order, the fluid surface velocity is constant with a value of $\frac{1}{4}$, and the corrections indicate that the fluid is slightly accelerated and decelerated out of phase with the surface deflections.

We shall be interested in the effects of surfactants on this behaviour.

4. Lubrication theory for the contaminated interface

We wish to treat shallow cavities in the limit $A \to 0$, $C = \bar{C}A^3$, Pe, $E \sim$ arbitrary. We anticipate the following behaviour: since the thermocapillary stress results in a nearly uniform surface velocity, there will be convection of surfactant from the left (hot) boundary to the right (cold) boundary. This convection will be resisted by surface diffusion, the dimensionless strength of the convection relative to diffusion being given by Pe. This will cause a positive concentration gradient to develop which, through (2.1), will cause a stress *opposite* to the thermocapillary stress to develop, thus retarding the motion near the right (cold) boundary. The strength of this opposing stress due to compositional elasticity relative to the thermocapillary stress is simply the elasticity number E. Thus one can foresee strong coupling between the surfactant distribution and the motion if either Pe or E is large, and weak coupling if they are small. We seek an analytical description of this coupling.

We begin with the field equations in the central portions of the cavity, which we shall call the core region. We assume the expansions

$$\left.\begin{aligned} u &= u_0 + Au_1 + \dots, \\ v &= v_0 + Av_1 + \dots, \\ h &= h_0 + Ah_1 + \dots . \end{aligned}\right\} \tag{4.1}$$

At lowest order we have

$$u_{0x} + v_{0y} = 0, \quad u_{0yy} = p_{0x}, \tag{4.2a, b}$$

$$p_{0y} = 0, \quad T_{0yy} = 0. \tag{4.2c, d}$$

These are to be solved subject to the conditions

$$u_0 = v_0 = T_{0y} = 0 \quad (y = 0), \tag{4.3a}$$

$$\left.\begin{aligned} v_0 = u_0 h_{0x}, \quad h_{0xx} = 0, \\ u_{0y} = -(T_{0x} + h_{0x} T_{0y} + Ec_{0x}), \quad T_{0y} + L(T_0 + x) = 0 \end{aligned}\right\} \quad (y = h(x)), \qquad (4.3b, c) \quad (4.3d, e)$$

$$h_0(\pm\tfrac{1}{2}) = 1. \tag{4.3f}$$

Equation (4.3*f*) cannot be justified without a detailed analysis of the boundary-layer regime: see SD and Appendix B.

It is advantageous to treat the surface-continuity equation in some generality. Accurate to $O(A)$, it becomes

$$\frac{\mathrm{d}^2 c}{\mathrm{d}x} = Pe \frac{\mathrm{d}}{\mathrm{d}x}(u_s c), \tag{4.4a}$$

where we have written the surface velocity as $u_s(x) = u(y = h(x), x)$. Thus $u_s(x)$ includes boundary-layer corrections to the core flow. The conditions on (4.3*a*) are

$$\frac{\mathrm{d}c}{\mathrm{d}x} = 0 \quad (x = \pm\tfrac{1}{2}), \tag{4.4b}$$

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} c(x)\,\mathrm{d}x = 1, \tag{4.4c}$$

and thus the general solution is

$$c(x) = k \exp\left[Pe \int_{-\frac{1}{2}}^{x} u_s(t)\,\mathrm{d}t\right], \tag{4.5a}$$

$$k^{-1} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \exp\left(Pe \int_{-\frac{1}{2}}^{x} u_s(t)\,\mathrm{d}t\right)\mathrm{d}x, \tag{4.5b}$$

where we have used the fact that the contact lines are stagnation points, and thus $u_s(\pm\frac{1}{2}) = 0$. It is clear that the boundary-layer corrections to $u_s(x)$ cannot affect the value of k, being exponentially small, and so an approximation to $c(x)$ *in the core*, accurate to $O(A)$, is

$$c_0(x) = k_0 \exp\left\{Pe \int_{-\frac{1}{2}}^{x} u_{0s}(t)\,\mathrm{d}t\right\}, \tag{4.6a}$$

$$k_0^{-1} = \int_{-\frac{1}{2}}^{\frac{1}{2}} \exp\left\{Pe \int_{-\frac{1}{2}}^{x} u_{0s}(t)\,\mathrm{d}t\right\}\mathrm{d}x, \tag{4.6b}$$

where we have set

$$u_s(x) \approx u_{0s}(x). \tag{4.6c}$$

This solution is not uniformly valid and must be corrected in the end boundary layers, which are discussed in Appendix B. It is clear from this solution and the above discussion that the concentration profile may develop a boundary layer of thickness $O(1/Pe)$ near the right-hand boundary as the Péclet number gets large. Thus the approximate equations (4.5) will be valid only when this concentration boundary layer, if it exists, lies *outside* the flow boundary layer: otherwise the true surface velocity $u_s(x)$ and the exact solution (4.4) must be used. Thus we are formally limited in this analysis to $Pe = o(1/A)$. We shall see below that this restriction does not always hold.

The solution of equations (4.2*a–d*) subject to (4.3*a–c*, *e*) may be easily found as

$$h_0 = 1, \quad T_0 = -x, \tag{4.7a, b}$$

$$u_0 = a(x)\,[3y^2 - 2y], \quad P_{0x} = 6a(x). \tag{4.7c, d}$$

The equation for the unknown surface speed $a(x)$ is obtained by combining the tangential stress balance (4.3*d*) with (4.7*a*, *b*) and (4.6*a*). It reads

$$a(x)\left[1 + \tfrac{1}{4}E\,Pe\,k_0[a(x)]\exp\left\{Pe\int_{-\frac{1}{2}}^{\frac{1}{2}} a(t)\,\mathrm{d}t\right\}\right] = \tfrac{1}{4}. \tag{4.8a}$$

We have indicated that the constant k is a functional of $a(x)$, viz

$$k_0^{-1}[a(x)] = \int_{-\frac{1}{2}}^{\frac{1}{2}} \exp\left\{Pe\int_{-\frac{1}{2}}^{x} a(t)\,\mathrm{d}t\right\}\mathrm{d}x. \tag{4.8b}$$

The solution of (4.8) is formidable, but if obtained may be used to determine the first-order correction to the surface deflection in a manner analogous to SD. We consider the $O(A)$ equations; in particular, from (2.3*d*) we have

$$h_{1xx} = -\bar{C}P_0(x). \tag{4.9}$$

Combining (4.9) with (4.7*d*) we find

$$h_1 = \bar{C}\left[-6\int^{x}\int^{x_3}\int^{x_2} a(x_1)\,\mathrm{d}x_1\,\mathrm{d}x_1\,\mathrm{d}x_2 + K_1x^2 + K_2x + K_3\right]. \tag{4.10}$$

From a consideration of the boundary layers (see Appendix B) we find that $h_1(x)$ must satisfy

$$h_1(\pm\tfrac{1}{2}) = 0, \tag{4.11}$$

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} h_1(x)\,\mathrm{d}x = 0. \tag{4.12}$$

These conditions in turn determine the constants K_1, K_2 and K_3 in (4.10), as discussed by SD.

5. Solution

The analytical solution to (4.8) is complicated, so we seek both numerical and asymptotic solutions.

5.1. *Small Péclet number*

For small Péclet number, we expect the surface concentration to be nearly uniform. The solution for the surface speed may be expanded for small Pe as

$$a(x) = a_0(x) + Pe\, a_1(x) + Pe^2 a_2(x) + \dots . \tag{5.1}$$

Straightforward analysis of (4.8) then gives

$$a(x) = \tfrac{1}{4} - \tfrac{1}{16} Pe\, E + \tfrac{1}{64} Pe^2\, E\,(E - x) + O(Pe^3). \tag{5.2}$$

Note that, at leading order, we recover the result of SD for uniform concentration, namely $a(x) = \frac{1}{4}$. The first-order effects of surface convection are to decrease the surface speed *uniformly* by the factor $1 - \frac{1}{4} Pe\, E$. The reason for this behaviour is clear, as weak surface convection will produce a core concentration profile linear in x, with a corresponding *constant* compositional stress $\sim Pe\, E$ which opposes the uniform thermocapillary stress. The non-uniform retardation of the surface velocity is given at $O(Pe^2)$, and indicates a relative increase in speed near $x = -\frac{1}{2}$ and decrease near $x = \frac{1}{2}$, in accord with our general expectations discussed above.

The corresponding surface elevations may be obtained, through $O(Pe^2)$, as

$$\begin{aligned} h = 1 + A\overline{C}\{\tfrac{1}{4}x(\tfrac{1}{4} - x^2)[1 - \tfrac{1}{4} Pe\, E + \tfrac{1}{16} Pe^2\, E^2] \\ + \tfrac{1}{64}\tfrac{1}{320} Pe^2\, E\,(80x^2 - 4)\,(x^2 - \tfrac{1}{4})\} + O(A^2) + O(Pe^3). \end{aligned} \tag{5.3}$$

Note that we recover the result of SD, (3.3*a*), as $Pe \rightarrow 0$. As Pe increases, the deflection is nearly uniformly *decreased* relative to the uncontaminated case. Since to leading order the deflection is due to the pressure gradient associated with a uniform surface velocity, and since that velocity is uniformly retarded, this result follows immediately. The $O(Pe^2 E)$ terms indicate a slight increase in the deflection near the hot boundary and a correspondingly slight decrease in the elevation near the cold boundary, but these are secondary effects.

5.2. *Small elasticity*

We set

$$a(x) = a_0(x) + E a_1(x) + O(E^2), \tag{5.4}$$

and obtain in a straightforward but tedious manner

$$a(x) = \tfrac{1}{4}\left[1 - \frac{E\, Pe^2\, \mathrm{e}^{\frac{1}{4}Pe\, x}}{32 \sinh \frac{1}{8}Pe}\right] + O(E^2). \tag{5.5}$$

In this case we see the developing boundary-layer character of the concentration gradient as Pe increases, with the corresponding non-uniform retardation of the surface velocity.

An equally tedious calculation gives, for the surface displacement, correct to $O(E)$,

$$h = 1 + A\overline{C}\left\{\tfrac{1}{4}x(\tfrac{1}{4} - x^2) + \frac{3E}{Pe}\left[\frac{\mathrm{e}^{\frac{1}{4}Pe\, x}}{\sinh \frac{1}{8}Pe} + \frac{12}{Pe}(4x^2 - 1) + \tfrac{1}{2}\coth \tfrac{1}{8}Pe\,(1 - 12x^2) - 2x\right]\right\}. \tag{5.6}$$

Shown in figure 4 is the $O(E)$ correction to the surface deflection, with Pe as a

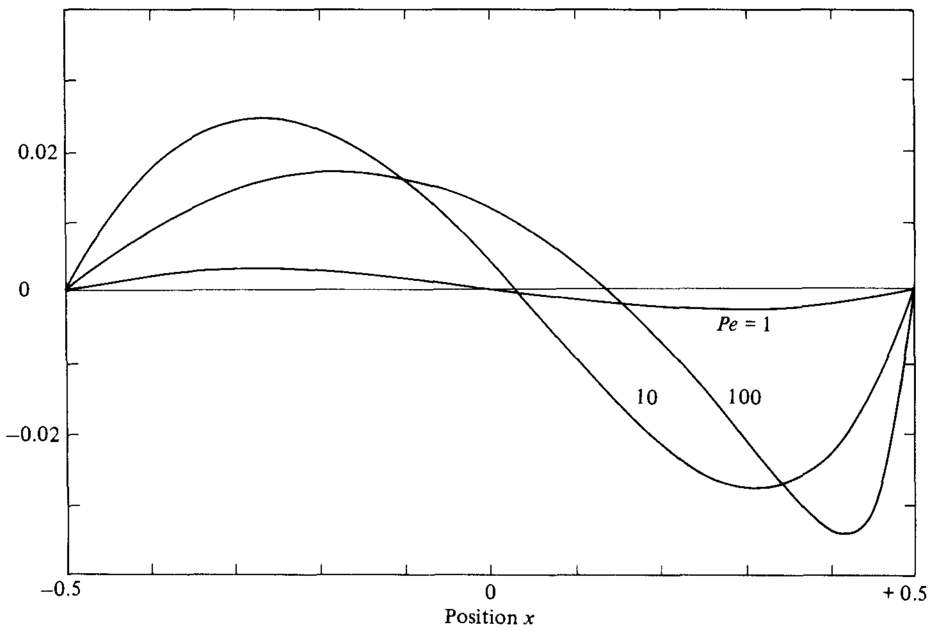

FIGURE 4. The $O(E)$ correction to the surface velocity with surface Péclet number as a parameter.

parameter. For small Pe, the surface concentration is again nearly uniform, resulting in no change from the uncontaminated case. As Pe increases, there is first a contribution to the surface displacement which is antisymmetric in x and opposite in sign to the SD result, in agreement with the results of the previous sub-section. However, as Pe increases further, the surface deflections become markedly nonsymmetric and begin to decrease near the hot boundary, indicating the development of a concentration boundary layer near the stagnation point at the cold boundary.

5.3. *Numerical solution*

The equations (4.8) were solved numerically where the solution was obtained by iterating in the following way:

$$a_{i+1}(x_j) = \cfrac{1}{4 + Pe\,E\,\dfrac{\exp\left\{Pe\displaystyle\int_{-\frac{1}{2}}^{\frac{1}{2}} a_i(t)\,\mathrm{d}t\right\}}{\displaystyle\int_{-\frac{1}{2}}^{\frac{1}{2}} \exp\left\{Pe\displaystyle\int_{-\frac{1}{2}}^{x_j} a_i(t)\,\mathrm{d}t\right\}\mathrm{d}x}} \quad (i = 1, 2, \ldots). \tag{5.7}$$

The domain $-\frac{1}{2} < x < \frac{1}{2}$ was divided up into 100 intervals, and all integrals were evaluated by the trapezoidal rule. Typical results for $E = 1$ are given in figure 2 with Pe as a parameter.

We see that for E fixed the average surface velocity decreases with increasing Pe. The reason for this may be seen as follows. For small Pe we have a homogeneous distribution of the surfactant, so that nothing is changed except that the mean surface tension is decreased by the addition of the surfactant. As Pe increases, the concentration gradients cause a stress opposite in sign to that due to the temperature gradient, causing a retardation of the motion.

What is not expected is the behaviour for large Pe, for which the surface velocity is nearly *uniformly* retarded, indicating that the tangential stress is also nearly constant. The reason for this may be seen as follows. Assume a fixed $O(1)$ surface velocity: as the Péclet number increases one would expect a boundary layer in surface concentration to develop near the (right) stagnation point near the cold wall. For $E = O(1)$, such a boundary layer, if it existed, would lead to large compositional stresses since concentration gradients would be high. These stresses would *oppose* and overwhelm the thermocapillary stress driving the motion. If this were to occur, it would in turn lead to a flow reversal and a *destruction* of the concentration boundary layer, leading to a contradiction. Thus the assumption that $u_s(x) = O(1)$ as Péclet number becomes large is incorrect, and the correct behaviour is a nearly uniform retardation of the surface speed with increasing Pe.

Detailed calculations of the interfacial deflection may be made, since the surface speed is known. These were not undertaken, since the smooth variation of $u_s(x)$ for $E = O(1)$ implies that the surface deflection will be very nearly that given by (3.3*a*), but with a diminished magnitude, representing the decrease of the pressure gradient relative to the uncontaminated case.

5.4. *High Péclet number, $E = O(1)$*

The numerical results of §5.3 indicate that as Pe increases the surface velocity is smoothly retarded and as a result no concentration boundary layers are formed. It is possible to obtain an analytical solution to (4.8) valid asymptotically as $Pe \rightarrow \infty$ as follows.

We begin with the observation that there are no concentration boundary layers. From the solution (4.6) for $c_0(x)$ this in turn implies that

$$u_s(x) \sim \frac{\hat{u}(x)}{Pe} \quad \text{as} \quad Pe \rightarrow \infty, \tag{5.8}$$

where $\hat{u}(x)$ is an $O(1)$ function to be determined. Inserting (5.8) into (4.8) and taking the limit as $Pe \rightarrow \infty$, we find that $\hat{u}(x)$ must satisfy

$$\hat{u}(x)\, E \exp\left\{\int_{-\frac{1}{2}}^{\frac{1}{2}} \hat{u}(s)\, \mathrm{d}s\right\} \Big/ \int_{-\frac{1}{2}}^{\frac{1}{2}} \exp\left\{\int^{x} \hat{u}(s)\, \mathrm{d}s\right\} \mathrm{d}x = 1. \tag{5.9}$$

It is possible to solve (5.9) by first differentiating with respect to x and using (5.9) to obtain

$$\hat{u}'/\hat{u}^2 = -1, \tag{5.10}$$

and thus

$$\hat{u} = \frac{1}{x+\beta}. \tag{5.11}$$

The constant of integration β may be obtained by requiring that (5.11) satisfy (5.9); we find

$$\beta = E, \tag{5.12a}$$

$$\hat{u} = \frac{1}{x+E}, \tag{5.12b}$$

and thus

$$u_s(x) = \frac{1}{Pe\,(x+E)} \quad \text{as} \quad Pe \rightarrow \infty. \tag{5.13}$$

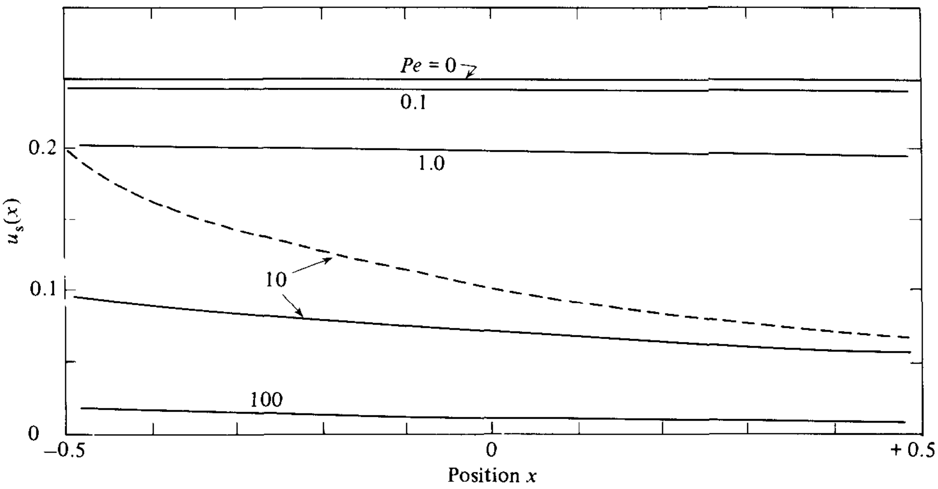

FIGURE 5. The surface velocity as a function of Péclet number for $E = 1$: ——, numerical solution; ----, asymptotic solution for $Pe \gg 1$; (5.13). The two results for $Pe = 100$ are indistinguishable.

This relation is also plotted in figure 5 as dashed curves with $E = 1$, and, as can be seen, provides an excellent representation of the solution for $Pe > 100$. This solution appears to be valid for $E > \frac{1}{2}$, thus avoiding the existence of a singularity of (5.13) on $-\frac{1}{2} \leqslant x \leqslant \frac{1}{2}$.

6. Summary and discussion

We have analysed the effect of insoluble surfactants on the thermocapillary flow in a shallow cavity. We find that, in addition to the parameters that govern the uncontaminated case, two additional parameters characterize the solution. These are the elasticity number E and the surface Péclet number Pe. Using lubrication theory for shallow cavities, and analysing the turning-flow regions by matched asymptotic expansions, it is possible to pivot a solution about the limiting case of conduction-dominated fields and a flat interface, and to derive a single integral–algebraic equation governing the variables in the interior of the cavity, (4.8). We than solve (4.8) by perturbation theory for small E, small Pe, numerically for arbitrary (E, Pe), and asymptotically for large Pe.

The main results of analysis are as follows: for small elasticity, the surface velocity is nearly constant, with the result that, for small Pe (large surface diffusion), the surface concentration is nearly uniform while, for large Pe, it develops a boundary layer near the stagnation point at the cold wall, resulting in high local surface concentrations, possibly leading to a surface phase change, monolayer collapse, and/or resolubilization of the surface species. While these latter effects have little effect on the main flow, since they are small, of order E, they may have profound effects at the liquid–solid interface, or the three-phase line. For example, in the case of crystal growth, all surface impurities would be convectively swept to the freezing boundary, and, if resolubilization were to occur, would be incorporated into the bulk and perhaps the solid crystal. The condition for the formation of such concentration boundary layers is small elasticity and large Péclet number. In terms of the dynamics, these conditions imply that the surface species have little effect on the flow, and as nearly non-diffusing species are passively convected in a unidirectional flow field.

In the opposite extreme, that of small Pe, $E = O(1)$, we find that the surface concentration is nearly uniform, and that the small uniform gradient produces a uniform reduction in surface velocity and interfacial displacement. This behaviour persists as Pe increases, with a rapid decrease in the magnitude of the surface velocity.

Finally in the limit of large Pe, we show that $u_s \sim (1/Pe)(x+E)$ as $P \to \infty$, with the somewhat surprising result that, the less mobile a surface species, the larger is its effect on the surface speed. It is of interest to examine the dimensional form of our limiting results. These are

$$u' = \frac{\gamma_T(\Delta T)\,d}{4\mu l} \quad (Pe \ll 1), \tag{6.1}$$

$$u' = D\left(\frac{\Delta T \gamma_T}{x'\Delta T \gamma_T + l c_0 \gamma_c}\right) \quad (Pe \gg 1). \tag{6.2}$$

Thus we find vastly different dependences of the strength of the convection on physical parameters in these limits.

Finally we make a comparison between the present problem and the other general class of problems discussed in §1. The main difference relates to the formation of concentration boundary layers. In the present problem, the flow is generated by the relationship between the temperature and concentration gradients and the stress they produce. Thus these fields are tightly coupled and, as we have seen, any tendency to form sharp gradients in surface concentration results in a large compositional stress which *always* acts to oppose the motion driven by the temperature gradient, leading to a nearly uniform retardation of the flow strength and not to the formation of concentration boundary layers, condensed or collapsed surface phases, or resolubilization. On the other hand, the class of problems treated heretofore are ones in which the convective velocity is *externally imposed*, and, although the coupling between fields certainly exists, it is not strong enough to eliminate the production of clean surface and thus surfactant boundary layers. This broad distinction would seem to apply to similar problems in different geometries as well.

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Appendix A. Derivation of surface continuity equation

As a starting point, we define the unit normal and tangent to the surface $y = h(x)$:

$$\boldsymbol{n} = (-Ah_x, 1)/N, \tag{A 1a}$$

$$\boldsymbol{t} = (1, Ah_x)/N, \tag{A 1b}$$

$$N = (1+A^2h_x^2)^{\frac{1}{2}}. \tag{A 1c}$$

Now the dimensionless surface continuity equation is

$$Pe\frac{\mathrm{d}(\boldsymbol{u}\cdot\boldsymbol{t}c)}{\mathrm{d}s} = \frac{\mathrm{d}^2c}{\mathrm{d}s^2},$$

where $c = c'/c_0$, $\boldsymbol{u} = (u, Av)$, and s is the arclength, made dimensionless with respect to l. Using the facts that

$$\mathrm{d}s = N\,\mathrm{d}x, \tag{A 2}$$

$$\boldsymbol{u}\cdot\boldsymbol{t} = \frac{u + A^2 h_x v}{N}, \tag{A 3}$$

$$v = h_x u, \tag{A 4}$$

we have

$$Pe \frac{\mathrm{d}}{\mathrm{d}x}(ucN) = \frac{\mathrm{d}}{\mathrm{d}x}\left(N^{-1}\frac{\mathrm{d}c}{\mathrm{d}x}\right), \tag{A 5}$$

which in expanded form may be written

$$\frac{\mathrm{d}^2 c}{\mathrm{d}x^2} - A^2 \frac{\mathrm{d}c}{\mathrm{d}x}\frac{h_x h_{xx}}{N^2} = Pe\, N^2 \left[\frac{\mathrm{d}}{\mathrm{d}x}(uc) + \frac{A^2 uch_x h_{xx}}{N^2}\right], \tag{A 6}$$

which is (2.3*g*).

Appendix B. The boundary layers

We wish to discuss the solutions near $x = \pm\frac{1}{2}$ necessary to render the core solutions compatible with the endwall boundary conditions, to verify that for a fixed contact line the conditions

$$h(\pm\tfrac{1}{2}) = 0, \tag{B 1}$$

$$\int_{-\frac{1}{2}}^{\frac{1}{2}} h(x)\,\mathrm{d}x = 1 \tag{B 2}$$

may be applied to the core solutions, and to show that (4.6) is a uniformly valid approximation to $c(x)$.

The starting point is the full set of equations, written in terms of a stream function, $u = \psi_y$, $v = \psi_x$,

$$\psi_{yyyy} + 2A^2\psi_{xx}\psi_{yy} + A^2\psi_{xxxx} = RA(\psi_y(\psi_{yy} + A^2\psi_{xx})_x - \psi_x(\psi_{yy} + A^2\psi_{xx})_y), \tag{B 3}$$

$$MA(\psi_y T_x - \psi_x T_y) = T_{yy} + A^2 T_{xx}, \tag{B 4}$$

with boundary conditions

$$\psi_x = \psi_y = T_y = 0 \quad (y = 0), \tag{B 5}$$

$$\psi_x = \psi_y = (T \mp \tfrac{1}{2}) = 0 \quad (x = \pm\tfrac{1}{2}), \tag{B 6}$$

$$h(\pm\tfrac{1}{2}) = 1, \quad c_x(\pm\tfrac{1}{2}) = 0, \tag{B 7a, b}$$

$$\left.\begin{aligned}
&-P + \frac{2A^2}{N}[-(\psi_{xy} + h_x\psi_{yy}) + A^2 h_x(\psi_{xx} + h_x\psi_{yx})] \\
&\qquad = \frac{A^4 C^{-1} h_{xx}}{N^3}[1 - CT - EC(c-1)], && \text{(B 8)} \\
&(1 - A^2 h_x^2)(\psi_{yy} - A^2\psi_{yy}) - 4A^2 h_x\psi_{xy} = -N[T_x + h_x T_y + Ec_x], && \text{(B 9)} \\
&\psi_x + h_x\psi_y = 0, && \text{(B 10)} \\
&N^{-1}(T_y - A^2 h_x T_x) + L(T + x) = 0, && \text{(B 11)} \\
&\frac{\mathrm{d}^2 c}{\mathrm{d}x^2} = A^2\frac{\mathrm{d}c}{\mathrm{d}x}\frac{h_x h_{xx}}{N^2} = Pe\, N^2\left[\frac{\mathrm{d}(\psi_y c)}{\mathrm{d}x} + \psi_y c\frac{A^2 h_x h_{xx}}{N}\right] && \text{(B 12)}
\end{aligned}\right\} \quad (y = h(x)).$$

Now consider the boundary layer near $x = -\frac{1}{2}$. It is appropriate to define a boundary-layer coordinate $\xi = (x+\frac{1}{2})/A$, and to assume the expansions

$$\left.\begin{aligned} \tilde{\psi}(\xi, y) &= \tilde{\psi}_0(\xi, y) + A\tilde{\psi}_1(\xi, y) + \dots, \\ \tilde{T}_0 &= \tilde{T} + A\tilde{T}_1 + \dots, \quad \tilde{c} = \tilde{c}_0 + 1 + \dots, \\ \tilde{P} = \tilde{P}_0 + A\tilde{P}_1 + \dots, &\quad \tilde{h} = \tilde{h}_0 + A\tilde{h}_1 + \dots, \quad \tilde{N} = \tilde{N}_0 + \dots. \end{aligned}\right\} \tag{B 13}$$

To lowest order we have

$$\tilde{\nabla}^4\tilde{\psi}_0 = \left(\frac{\partial}{\partial\xi^2} + \frac{\partial^2}{\partial y^2}\right)^2 \tilde{\psi}_0 = 0, \tag{B 14}$$

$$\tilde{\nabla}^2\tilde{T}_0 = 0, \tag{B 15}$$

$$\tilde{\psi}_{0\xi} = \tilde{\psi}_{0y} = \tilde{T}_{0y} = 0 \quad (y = 0), \tag{B 16}$$

$$\tilde{\psi}_{0\xi} = \tilde{\psi}_{0y} = (\tilde{T}_0 + \tfrac{1}{2}) = \tilde{h}_0 - 1 = \tilde{c}_{0\xi} = 0 \quad (\xi = 0), \tag{B 17}$$

$$\left.\begin{aligned} \tilde{h}_{0\xi\xi} = 0, \quad \tilde{h}_{0\xi}\tilde{T}_{0y} + \tilde{T}_{0\xi} + E\tilde{c}_{0\xi} = 0, \quad \tilde{\psi}_{0\xi} + h_{0\xi}\tilde{\psi}_{0y} = 0, \\ \tilde{N}^{-1}(\tilde{T}_{0y} - \tilde{h}_{0\xi}\tilde{T}_{0\xi}) + L(\tilde{T}_0 - \tfrac{1}{2}) = 0, \quad \tilde{c}_{0\xi\xi} = 0. \end{aligned}\right\} \; (y = h_0(x)) \quad \begin{aligned} &(\text{B } 18, \text{B } 19, \text{B } 20) \\ &(\text{B } 21, \text{B } 22) \end{aligned}$$

Solutions to these equations must match with core solutions; this matching requirement eliminates (to this order) terms linear in ξ. Thus we have

$$\left.\begin{aligned} \tilde{T}_0 &= +\tfrac{1}{2}, \\ \tilde{c}_0(\xi) &= \tilde{c}^0, \\ \tilde{h}_0 &= 1. \end{aligned}\right\} \tag{B 23}$$

As shown by SD, it is necessary to compute $\tilde{T}_1$ in order to complete the boundary condition for $\tilde{\psi}_0$. In the distinguished limit treated by them, i.e. $M = \bar{M}A$, $R = \bar{R}A$, the final condition is found to be

$$\tilde{\psi}_{0yy} = 1. \tag{B 24}$$

Thus (B 14), subject to (B 16*a*, *b*, B 17*a*, *b*, B 20, B 24), and matching conditions are sufficient to determine $\tilde{\psi}_0$.

We shall need the normal-stress condition to $O(A)$, which reads

$$\tilde{h}_{1\xi\xi} = 0, \quad \tilde{h}_1(0) = 0, \tag{B 25a, b}$$

with solution

$$\tilde{h}_1 = \tilde{h}^1\xi. \tag{B 25c}$$

The concentration and deflections must be matched to the core solutions. We find simply that

$$\lim_{\xi\to\infty} \tilde{c}(\xi) = \tilde{c}^0 = \lim_{x\to-\frac{1}{2}} c_0(x) = c_0(-\tfrac{1}{2}). \tag{B 26}$$

Similar considerations hold for the opposite boundary layer near $x = \frac{1}{2}$. The boundary layer in $\tilde{c}$ at higher order in A then allows the satisfaction of the true boundary condition (B 7*b*). Thus the concentration differs from $c_0(x)$ by an $O(A)$ quantity only within the boundary layers, justifying the use of the solution of §4, (4.6), as a uniformly valid solution for $c(x)$ (but not the flux c_x).

For the deflections, we find to $O(A)$

$$\lim_{\xi\to\infty} 1 + A\tilde{h}^1\xi = \lim_{\xi\to\infty} (h_0 + Ah_1(x) + \dots), \tag{B 27}$$

where the limits are interpreted in terms of matching:

$$\begin{aligned}\lim_{x\to-\frac{1}{2}} (h_0+Ah_1(x))+O(A^2) &\approx h_0+Ah_1(-\tfrac{1}{2})+Ah_1'(-\tfrac{1}{2})\,(x+\tfrac{1}{2}) \\ &\approx h_0+Ah_1(-\tfrac{1}{2})+h_1'(-\tfrac{1}{2})\,\xi A^2 \\ &\approx h_0+Ah_1(-\tfrac{1}{2})+O(A^2). \qquad \text{(B 28)}\end{aligned}$$

Matching terms in (B 27) gives

$$h_0 = 1, \quad h_1(-\tfrac{1}{2}) = 0, \quad \tilde{h}^1 = 0. \qquad \text{(B 29)}$$

Thus the outer solution satisfies the boundary condition

$$h(-\tfrac{1}{2}) = 0$$

at least to $O(A^2)$.

Similar considerations hold for the boundary layer near $x = \frac{1}{2}$.

Thus we have shown that the conditions

$$\left.\begin{aligned}\int_{-\frac{1}{2}}^{\frac{1}{2}} c_0(x)\,\mathrm{d}x = \int_{-\frac{1}{2}}^{\frac{1}{2}} h(x)\,\mathrm{d}x = 0,\\ h(\pm\tfrac{1}{2}) = 1\end{aligned}\right\} \qquad \text{(B 30)}$$

may be applied to $O(A^2)$ to the core solutions.

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