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The hydrodynamics of the spreading of one liquid on the surface of another

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The mechanisms involved in the spreading of one liquid on the surface of another are considered for the case of a positive spreading coefficient. Taking into account the effects of gravity, capillary pressure and the spreading coefficient, the general equations determining the spreading are derived. These are then solved for the situation where the spreading liquid is introduced onto the surface of a uniformly flowing substratum at a position upstream of a barrier on the substratum surface. In this manner a steady-state situation is achieved for which the variation of spreading-liquid thickness with position is obtained as a function of the deposited volume of spreading liquid and the velocity of the substratum.

1. Introduction

When a volume of liquid (phase 1) is deposited on the horizontal surface of another immiscible liquid (phase 2) which is denser than phase 1, it spreads out on the surface owing to gravity and surface-tension forces (Fay 1969). As the layer of phase 1 thins, gravity becomes a less effective driving force and whether it continues to spread depends on the sign of the Harkins (1952, p. 42) spreading coefficient, which is defined as

$$S \equiv \sigma_{23} - \sigma_{13} - \sigma_{12}, \tag{1.1}$$

where the void or air space is conveniently termed phase 3 and σ_{ij} is the tension of the i,j interface. If $S < 0$, phase 1 (designated as 'oil' for convenience) spreads on phase 2 (designated as 'water') only until it forms a liquid lens from the balance of capillary and gravity forces (Pujado & Scriven 1972). However, if $S > 0$, the oil spreads until the available water surface is completely covered, usually in the form of a monomolecular layer. It is only this latter situation ($S > 0$) that will be considered in this paper.

Although the above requirement ($S > 0$) for the continued spreading of the oil to form a thin film is well known, the relation between gravity, capillary pressure and the value of S as the contributing forces for spreading is not well understood. Neither is exactly how the oil spreads for $S > 0$ well understood since it is not possible for the interfacial tension forces to balance at a line of three-phase contact between the liquids.

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Spreading experiments described in the literature are mainly concerned with how the spreading distance l changes with time t, the spreading rate being usually expressed in the form

$$l = kt^n. \tag{1.2}$$

The values of n reported vary from experiment to experiment: Landt & Volmer (1926), von Guttenberg (1941) and Burgers, Greup & Korvezee (1950) reported $n = \frac{3}{4}$, $\frac{2}{3}$ and $\frac{1}{2}$ respectively for the radial spreading of a fatty-acid monolayer on water, while Lugton & Vines (1960) gave $n = \frac{1}{2}$ for cetyl alcohol on water and Marwedel & Jebsen-Marwedel (1961) $n = \frac{1}{4}$ for lacquer spreading on another lacquer. For unidirectional spreading of polydimethyl siloxane monolayers, the value $n = \frac{1}{2}$ was reported by Banks (1957) and Ahmad & Hansen (1972). However, Langmuir (1936) and Mercer (1939) observed that the velocity of spreading of several fatty acids initially increased exponentially with time but then showed a decay. The effects on spreading of the viscosities of the oil and water, of gravity, of the interfacial tensions and of the value of S also show apparent conflict between experiments. Recent interest in the control of oil spills (Hoult 1972; Buckmaster 1973; Wicks 1969; Garrett & Barger 1970) produced attempts to understand the dynamics of spreading. Fay (1969), Hoult & Suchon (1970) and Hoult (1972) showed from theoretical and experimental studies that, when gravity was the dominant driving force, $n = \frac{3}{8}$ and $\frac{1}{4}$ for unidirectional and radial spreading respectively while, when the effect of the spreading coefficient became dominant, a value of $n = \frac{3}{4}$ was obtained for both cases. Still unknown are (i) the exact manner in which the spreading coefficient S affects the motion, (ii) the role played by capillary pressure and (iii) the combined effect of gravity, the spreading coefficient and capillary pressure.

In many spreading systems for which $S > 0$, the oil forms an advance band of small thickness at the contact line distinct from the bulk liquid (Mercer 1939; Zisman 1941). This band consists of either a monolayer or a layer of submicron thickness (Mar & Mason 1968). It is well known (Sheludko 1966) that the phenomenological behaviour of such thin films is different from that of the bulk phase, and we suggest the possibility that, owing to a surface-density variation of the monolayer (Adamson 1967) (or equivalently its thickness variation), the composite interfacial tension σ of the oil-covered interface in this advance band varies from the value σ_{23} for the water–air interface at the leading edge to the value $\sigma_{12}+\sigma_{13}$ for a thick oil layer (where there is no molecular interaction between the oil–water and oil–air interfaces) at the inner boundary between the band and the bulk of the oil. In this manner the force difference S is thus distributed across the band (and thus avoids the difficulty in having a force S per unit length acting along a three-phase contact line, where it would produce an infinite velocity). The surface concentration of oil in the band is assumed to adjust itself such that the net force (due to the composite surface-tension variation) on any surface element exactly balances the hydrodynamic drag on the lower surface of the element. While the band (which we shall for convenience refer to as the monolayer) is considered as a two-dimensional surface (being so thin that the continuum hydrodynamic equations are not applicable within the oil there), we do consider the bulk of the oil (which we shall refer to as the bulk layer) as a three-dimensional continuum permitting the use of the Navier–Stokes equations there and the inclusion of the effects of gravity and capillary pressure. The thickness of the oil in the bulk layer at the boundary with the monolayer is thus taken to be zero. The angle formed by the

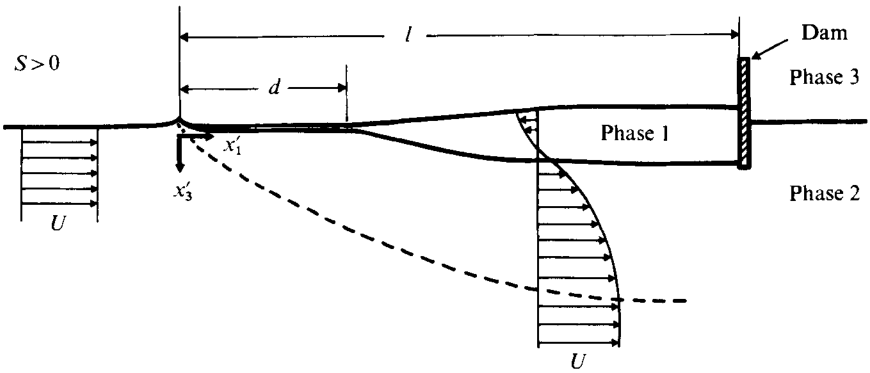

FIGURE 1. Schematic diagram showing the steady-state situation of an oil (with $S > 0$) spreading against a uniform flow.

oil–water and oil–air surfaces at this boundary must also be zero since we have assumed that $\sigma = \sigma_{23} - S = \sigma_{12} + \sigma_{13}$ there.

We describe in this paper how the equations which determine spreading in both the monolayer and the bulk layer may be obtained. These equations are, however, difficult to solve in general, particularly for those spreading processes which are time dependent. Thus the particularly simple steady-state situation is considered in which oil with volume V per unit width is introduced onto the surface of water (with a free surface at $x_3' = 0$) flowing with velocity U along a channel, the oil being held in place by a vertical barrier projecting below the water surface (figure 1). Forward spreading of the oil is restrained by the substratum flow, and a steady, unidirectional spreading situation is established with the leading edge of the oil at a fixed position which may be taken to be $x_1' = 0$, the barrier being at $x_1' = l$, where l is the total length of the oil layer. The oil is assumed to have negligible evaporation and dissolution with the contact angles between the barrier and both the oil–water and the oil–air interface being 90°. The feasibility of obtaining this steady-state spreading situation has been demonstrated by Sellin (1968) and McCutchen (1970; see also McDowell & McCutchen 1971). In terms of the oil volume V and water velocity U, the variation of the oil thickness with position and the lengths of the monolayer and bulk layer are obtained. This example represents a suitable model for an oil containment boom and the results obtained may be used to estimate the volume V of oil which may be contained by a boom employed across a river which is flowing with velocity U (or by a boom towed with a velocity U at sea).

2. Monolayer spreading

The equations governing the spreading of the oil in the monolayer region are now obtained. Since, in this region, the oil thickness is so small compared with the thickness of the boundary layer in the water immediately under the oil layer, the velocity $\mathbf{u}'$ may be assumed to be constant across the oil layer. Thus the conservation of mass for the oil requires that

$$\partial H'/\partial t' + \nabla' . (H' \mathbf{u}') = 0, \tag{2.1}$$

where ∇' is the surface (two-dimensional) gradient operator, t' is the time and H'

the thickness of the oil layer, which, since it may be of molecular thickness, should more properly be considered as the surface concentration (i.e. the volume per unit area).

The surface tension σ of the monolayer-covered substratum varies from a value of $\sigma_{12}+\sigma_{13}$ at the boundary between the thick oil layer (the bulk layer) and the monolayer to σ_{23} at the leading edge of the monolayer, where there is an oil-free air–water interface. The resulting surface-tension gradient along the monolayer must be balanced by the shear stress $\boldsymbol{\tau}'$ exerted by the substratum flow on the oil (see Scriven 1960). Thus

$$\nabla'\sigma+\boldsymbol{\tau} = 0. \tag{2.2}$$

The value of σ at any point is given by the monolayer equation of state (see Adamson 1967; or Sheludko 1966), which, assuming that there are no hysteresis or time-dependent effects, relates σ to the surface concentration H'. This constitutive relation is, for certain spreading liquids, available from experiment or, in certain limiting situations, from approximate theoretical calculations (Sheludko 1966; Adamson 1967). Thus

$$\sigma = \sigma(H'), \tag{2.3}$$

which when substituted into (2.2) yields

$$(d\sigma/dH')\nabla' H'+\boldsymbol{\tau}' = 0. \tag{2.4}$$

Equations (2.1) and (2.4), together with a relationship between $\mathbf{u}'$ and $\boldsymbol{\tau}'$ obtained from solving the boundary-layer equations in the water, may thus be solved for $\mathbf{u}'$, $\boldsymbol{\tau}'$ and H'.

Should the water–air interface on which this oil layer is situated be disturbed from the horizontal owing either to the presence of a flow in the water or to the existence of the bulk layer, (2.1) and (2.4) would still be valid. However, the pressure difference across the monolayer from the water to the air must be equal to the local value of σ times the surface curvature. Thus, taking a rectangular Cartesian set of axes (x_1', x_2', x_3') with the x_3' axis vertically downwards, the elevation of the monolayer-covered water–air surface $x_3' = h_{23}'$ must satisfy

$$P'|_{\text{wat}} = \sigma(1/R_1+1/R_2), \tag{2.5}$$

where $P'|_{\text{wat}}$ is the dimensional pressure P' in the water (phase 2) and where R_1 and R_2 are the principal radii of curvature of the surface. For convenience the pressure in the air has been taken to be zero. If the slope of the surface is small then (2.5) may be approximated by

$$P'|_{\text{wat}} = \sigma\nabla'^2 h_{23}', \tag{2.6}$$

where ∇'^2 is the two-dimensional surface Laplacian $\partial/\partial x_1'^2+\partial/\partial x_2'^2$. In the regions where the water–air surface is occupied by the monolayer, σ is a function of x_1' and x_2' (and is determined by (2.1), (2.4) and the solution within the boundary layer), while, in the monolayer-free regions, σ takes the constant value σ_{23}.

For the particular situation where the undisturbed flow velocity $\hat{U}'$ of the water (in the absence of the monolayer) is irrotational and steady, the pressure $P'|_{\text{wat}}$ in (2.6) must satisfy Bernoulli's equation

$$P'|_{\text{wat}}+\tfrac{1}{2}\rho_2\hat{U}'^2-\rho_2 g h_{23}' = \text{constant} \quad (\equiv G) \tag{2.7}$$

since there can be no pressure variation (to the lowest order) across the boundary layer in the water beneath the monolayer. The quantity $\hat{U}'$ appearing in (2.7) is the magnitude $|\hat{\mathbf{U}}'|$ of the velocity evaluated immediately below the boundary layer. Choosing the origin of the co-ordinate system such that with $\hat{\mathbf{U}}' = 0$ the water–air interface is the horizontal surface $x_3' = h_{23}' = 0$, it is seen that the constant G appearing in (2.7) is zero. Thus from (2.6) and (2.7)

$$\sigma\nabla'^2 h_{23}' + \tfrac{1}{2}\rho_2 \hat{U}'^2 - \rho_2 g h_{23}' = 0. \tag{2.8}$$

3. Gravity–viscous spreading: expansion procedure

By means of a type of lubrication theory, the equations governing the spreading of a thick layer of oil (the bulk layer) are now obtained for the situation where the effects of gravity and surface tension are both important. It is assumed that the oil-layer thickness is such that (i) the oil may be regarded as a continuum and (ii) the oil–water and oil–air interfaces have well-defined constant interfacial tensions of values σ_{12} and σ_{13} respectively [i.e. the disjoining pressure (see Sheludko 1966) is negligible].

Letting the oil–air and oil–water interfaces be $x_3' = h_{13}'$ and $x_3' = h_{12}'$ respectively, the thickness H' of the oil layer is

$$H' = h_{12}' - h_{13}', \tag{3.1}$$

where h_{12}', h_{13}' and H' are functions of x_1', x_2' and t'. The basic assumption is made (as in lubrication theory) that the oil-layer thickness is small with respect to the horizontal dimensions of the oil. Thus, denoting by h the characteristic value of the oil thickness H' and by B the typical horizontal dimension of the bulk layer of oil, we define

$$\epsilon = h/B \tag{3.2}$$

as the small parameter in terms of which expansions of the fluid velocities will be made.

We denote by P' the hydrodynamic pressure in either the oil or the water and by p' the excess pressure above hydrostatic, i.e.:

$$p' = P' - \rho_1 g x_3' \tag{3.3}$$

for the oil and

$$p' = P' - \rho_2 g x_3' \tag{3.4}$$

for the water.

For the purposes of this analysis we neglect the viscosity and density of the air in comparison with those of the oil and water. It will also be assumed for generality that there is a flow in the water (which would exist even without the oil layer) with a velocity of $\hat{\mathbf{U}}'$ and with a pressure excess above hydrostatic of $\hat{p}'$.

In the oil (phase 1), the fluid velocity $\mathbf{u}'$ satisfies the Navier–Stokes and continuity equations, which may be written in tensor† form as

$$\rho_1 \frac{\partial u_\beta'}{\partial t'} + \rho_1 u_\alpha' \frac{\partial u_\beta'}{\partial x_\alpha'} = -\frac{\partial p'}{\partial x_\beta'} + \mu_1 \frac{\partial^2 u_\beta'}{\partial x_\alpha' \partial x_\alpha'}, \tag{3.5}$$

$$\partial u_\alpha'/\partial x_\alpha' = 0. \tag{3.6}$$

† The summation convention is used throughout, the Latin indices taking the values 1 and 2 and Greek indices the values 1, 2 and 3.

To compare the magnitudes of the various terms in the Navier–Stokes equations (3.5) it is convenient to define dimensionless quantities x_1, x_2, x_3, P, h_{12}, h_{13}, u_1, u_2, u_3 and t in terms of μ_1 (the oil viscosity), U (a characteristic velocity of the oil) and either h or B as

$$\left.\begin{aligned} x_i &= B^{-1}x_i', \quad p = (h^2/\mu_1 BU)p', \quad & u_i &= U^{-1}u_i', \\ x_3 &= h^{-1}x_3', \quad P = (h^2/\mu_1 BU)P', \quad & u_3 &= (\epsilon U)^{-1}u_3', \\ t &= UB^{-1}t', & h_{1i} &= h^{-1}h_{1i}' \end{aligned}\right\} \quad (i = 2, 3). \tag{3.7}$$

The co-ordinates (x_1, x_2, x_3) so defined are stretched in the vertical direction to make the variations of x_3 of order unity across the layer.

If we also define a Reynolds number for the flow as

$$Re \equiv \rho_1 BU/\mu_1, \tag{3.8}$$

then the horizontal components of (3.5) may be written in non-dimensional form using (3.7) as

$$\frac{\partial p}{\partial x_k} = \frac{\partial^2 u_k}{\partial x_3^2} + \epsilon^2 \frac{\partial^2 u_k}{\partial x_i \partial x_i} - \epsilon^4 Re\left(\frac{\partial u_k}{\partial t} + u_\alpha \frac{\partial u_k}{\partial x_\alpha}\right), \tag{3.9}$$

while from the vertical component of (3.5)

$$\frac{\partial p}{\partial x_3} = \epsilon^2 \frac{\partial^2 u_3}{\partial x_3^2} + \epsilon^4 \frac{\partial^2 u_3}{\partial x_i \partial x_i} - \epsilon^4 Re\left(\frac{\partial u_3}{\partial t} + u_\alpha \frac{\partial u_3}{\partial x_\alpha}\right) \tag{3.10}$$

and from the continuity equation (3.6)

$$\partial u_\alpha / \partial x_\alpha = 0. \tag{3.11}$$

We suppose that the velocity and pressure fields can be expanded in power series in the small parameter ϵ as

$$\mathbf{u} = \mathbf{u}_0 + \epsilon \mathbf{u}_1 + o(\epsilon), \tag{3.12}$$

$$p = p_0 + \epsilon p_1 + o(\epsilon). \tag{3.13}$$

Substituting these expansions into (3.9), (3.10) and (3.11) and assuming that

$$\epsilon^2 Re \ll 1 \tag{3.14}$$

so that the effects of fluid inertia are negligible, we have to lowest order in ϵ that

$$\partial p_0/\partial x_k = \partial^2 (u_0)_k/\partial x_3^2, \quad \partial p_0/\partial x_3 = 0, \qquad (3.15), (3.16)$$

$$\partial (u_0)_\alpha/\partial x_\alpha = 0, \tag{3.17}$$

where $(u_0)_k$ represents the kth component of the lowest-order (or zeroth-order) approximation $\mathbf{u}_0$ for the fluid velocity. Equations for higher-order terms may be obtained in a similar manner.

4. Gravity–viscous spreading: boundary conditions

The oil–air and oil–water interfaces are fluid–fluid interfaces across which the following boundary conditions must be met:

(i) the continuity of tangential stress,

(ii) that the difference in the normal components of the stresses be balanced by interfacial-tension forces,

(iii) the continuity of the tangential velocity components,

(iv) the kinematic free-surface condition.

4.1. *Tangential-stress boundary conditions*

Expressing the unit normals $\mathbf{n}_{13}$ and $\mathbf{n}_{12}$ to the oil–air and oil–water interfaces (directed away from the oil) in dimensionless form and expanding in powers of ϵ, we obtain

$$\mathbf{n}_{13} = \left(\epsilon\frac{\partial h_{13}}{\partial x_1}+O(\epsilon^3), \epsilon\frac{\partial h_{13}}{\partial x_2}+O(\epsilon^3), -1+\tfrac{1}{2}\epsilon^2\left[\left(\frac{\partial h_{13}}{\partial x_1}\right)^2+\left(\frac{\partial h_{13}}{\partial x_2}\right)^2\right]+O(\epsilon^4)\right) \quad (4.1)$$

and

$$\mathbf{n}_{12} = \left(\epsilon\frac{\partial h_{12}}{\partial x_1}+O(\epsilon^3), \epsilon\frac{\partial h_{12}}{\partial x_2}+O(\epsilon^3), +1+\tfrac{1}{2}\epsilon^2\left[\left(\frac{\partial h_{12}}{\partial x_1}\right)^2+\left(\frac{\partial h_{12}}{\partial x_2}\right)^2\right]+O(\epsilon^4)\right). \quad (4.2)$$

Since the motion induced in the air by the spreading of the oil is of little interest and since the viscosity of the air is assumed negligible, we shall take the tangential stress at the oil–air interface to be zero and omit the continuity of tangential velocity there.

If the stress tensor in the oil is denoted by $p'_{\alpha\beta}$ so that

$$p'_{\alpha\beta} = -P'\delta_{\alpha\beta}+\mu_1(u'_{\alpha,\beta}+u'_{\beta,\alpha}), \quad (4.3)$$

where P' is the hydrodynamic pressure [see (3.3)], $\delta_{\alpha\beta}$ is the Kronecker delta and the comma in the subscripts denotes differentiation, then the condition that the tangential stress be zero at the oil–air interface may be written as

$$p'_{i\alpha}n_\alpha-(n_\beta p'_{\beta\gamma}n_\gamma)n_i = 0 \quad \text{at} \quad x'_3 = h'_{13}, \quad (4.4)$$

where n_α is the αth component of the unit normal $\mathbf{n}_{13}$.

Similarly, at the oil–water interface the continuity of tangential stress gives

$$[p'_{i\alpha}n_\alpha-(n_\beta p'_{\beta\gamma}n_\gamma)n_i]^{\text{oil}}_{\text{wat}} = 0 \quad \text{at} \quad x'_3 = h'_{12}, \quad (4.5)$$

where n_α is here the αth component of the unit normal $\mathbf{n}_{12}$ at the oil–water interface.

Expressing (4.4) and (4.5) in dimensionless variables and using the expansions (3.12) and (3.13) for $\mathbf{u}$ and p and (4.1) and (4.2) for the unit normals, we obtain to the lowest order in ϵ

$$\partial(u_0)_i/\partial x_3 = 0 \quad \text{at} \quad x_3 = h_{13} \quad (4.6)$$

and

$$\mu_2[\partial(u_0)_i/\partial x_3]_{\text{wat}} = \mu_1[\partial(u_0)_i/\partial x_3]_{\text{oil}} \quad \text{at} \quad x_3 = h_{12}. \quad (4.7)$$

4.2. *Normal-stress boundary conditions*

The normal-stress difference across the fluid interfaces must be equal to the interfacial tension times the sum $1/R'_1+1/R'_2$ of the principal curvatures of the interface. Thus

$$n_\alpha p'_{\alpha\beta}n_\beta|^{\text{oil}}_{\text{air}} = -\sigma_{13}(1/R'_1+1/R'_2) \quad \text{at} \quad x'_3 = h'_{13}$$

and

$$n_\alpha p'_{\alpha\beta}n_\beta|^{\text{oil}}_{\text{wat}} = -\sigma_{12}(1/R'_1+1/R'_2) \quad \text{at} \quad x'_3 = h'_{12},$$

where the principal radii of curvatures are taken positive if the corresponding centres of curvature lie on the oil side of the interface.

Again, expressing these relations in dimensionless form and expanding in powers of ϵ, we obtain at lowest order

$$p_0\,|_{\text{oil}}+\frac{\rho_1 g h^3}{\mu_1 B U}h_{13}=\frac{\sigma_{13}h^3}{\mu_1 B^3 U}\left(\frac{\partial^2 h_{13}}{\partial x_1^2}+\frac{\partial^2 h_{13}}{\partial x_2^2}\right)\quad\text{at}\quad x_3=h_{13} \tag{4.8}$$

and

$$\frac{(\rho_2-\rho_1)gh^3}{\mu_1 BU}h_{12}+p_0\,|_{\text{wat}}-p_0\,|_{\text{oil}}=\frac{\sigma_{12}h^3}{\mu_1 B^3 U}\left(\frac{\partial^2 h_{12}}{\partial x_1^2}+\frac{\partial^2 h_{12}}{\partial x_2^2}\right)\quad\text{at}\quad x_3=h_{12}. \tag{4.9}$$

In obtaining (4.8), the ambient atmospheric pressure was taken as zero.

4.3. *Tangential-velocity boundary condition*

When expressed in dimensionless form and expanded in powers of ϵ, the continuity of the tangential velocity at the oil–water interface, i.e.

$$[u_i'-(u_\alpha' n_\alpha)n_i]_{\text{oil}}^{\text{wat}}=0,$$

becomes at lowest order

$$(u_0)_i\,|_{\text{oil}}^{\text{wat}}=0\quad\text{at}\quad x_3=h_{12}. \tag{4.10}$$

4.4. *Kinematic free-surface conditions*

The kinematic free-surface boundary conditions are

$$d(x_3'-h_{13}')/dt'=0\quad\text{at}\quad x_3'=h_{13}'$$

and

$$d(x_3'-h_{12}')/dt'=0\quad\text{at}\quad x_3'=h_{12}',$$

where x_3' represents the x_3' co-ordinate of a fluid particle on the fluid–fluid interface and d/dt' is the material-derivative operator, which measures the time rate of change following the fluid particle. To the lowest order in ϵ these give

$$(u_0)_3=\partial h_{13}/\partial t+(u_0)_i\,\partial h_{13}/\partial x_i\quad\text{at}\quad x_3=h_{13} \tag{4.11}$$

and

$$(u_0)_3=\partial h_{12}/\partial t+(u_0)_i\,\partial h_{12}/\partial x_i\quad\text{at}\quad x_3=h_{12}. \tag{4.12}$$

5. Equations governing gravity–viscous spreading

The lowest-order equations (3.15)–(3.17) for the velocity and pressure fields in the oil are now solved with the lowest-order boundary conditions (4.6)–(4.12). Thus from (3.16)

$$p_0=p_0(x_1,x_2), \tag{5.1}$$

so that by integrating (3.15) twice with respect to x_3 and by making use of the boundary condition (4.6), it is seen that the horizontal components of the velocity are

$$(u_0)_i=\tfrac{1}{2}(\partial p_0/\partial x_i)(x_3-h_{12})(x_3+h_{12}-2h_{13})+U_i\,|_{\text{wat}}, \tag{5.2}$$

where $U_i\,|_{\text{wat}}$ is the horizontal component of the velocity at the oil–water interface made dimensionless by the characteristic velocity U.

Since p_0 is constant across the oil layer [see (5.1)], the value of p_0 within the oil at $x_3 = h_{13}$ given by (4.8) must be the same as the value of p_0 within the oil at $x_3 = h_{12}$ given by (4.9). Thus

$$\nabla^2(\sigma_{12}h_{12}+\sigma_{13}h_{13})-gB^2\{(\rho_2-\rho_1)h_{12}+\rho_1 h_{13}\} = (\mu_1 B^3 U/h^3)p_0|_{\text{wat}}, \tag{5.3}$$

where $p_0|_{\text{wat}}$ is the pressure excess over hydrostatic in the water at the oil–water interface. Since, to lowest order, there is no pressure difference across the boundary layer in the water below the oil, $p_0|_{\text{wat}}$ may be interpreted as the pressure excess over hydrostatic immediately below the boundary layer.

Substituting the horizontal velocity components given by (5.2) into the continuity equation (3.17), we obtain

$$\frac{\partial u_3}{\partial x_3} = -\frac{1}{2}\left(\frac{\partial^2 p_0}{\partial x_1^2}+\frac{\partial^2 p_0}{\partial x_2^2}+\frac{\partial p_0}{\partial x_1}\frac{\partial}{\partial x_1}+\frac{\partial p_0}{\partial x_2}\frac{\partial}{\partial x_2}\right)[x_3^2-2h_{13}+2h_{13}h_{12}-h_{12}^2]-\left.\frac{\partial U_i}{\partial x_i}\right|_{\text{wat}}, \tag{5.4}$$

which when integrated across the oil layer using the kinematic free-surface conditions (4.11) and (4.12) yields

$$\partial H/\partial t+\nabla.(H\mathbf{U}|_{\text{wat}})-\tfrac{1}{3}\nabla.(H^3\nabla p_0) = 0, \tag{5.5}$$

where $H = H'/h$ is the dimensionless oil-layer thickness and where the operators ∇ and $\nabla.$ signify the two-dimensional surface gradient and divergence respectively. The substitution of the value of $p_0(x_1, x_2)$ obtained from (4.8) into (5.5) yields

$$\frac{\partial H}{\partial t}+\nabla.(H\mathbf{U}|_{\text{wat}})-\tfrac{1}{3}\nabla.\left\{H^3\left[-\frac{\rho_1 g h^3}{\mu_1 BU}\nabla h_{13}+\frac{\sigma_{13}h^3}{\mu_1 B^3 U}\nabla\nabla^2 h_{13}\right]\right\} = 0 \tag{5.6a}$$

while, in a similar manner, the value of $p_0(x_1, x_2)$ obtained from (4.9) yields the alternative equation

$$\frac{\partial H}{\partial t}+\nabla.(H\mathbf{U}|_{\text{wat}})-\tfrac{1}{3}\nabla.\left\{H^3\left[\frac{(\rho_2-\rho_1)gh^3}{\mu_1 BU}\nabla h_{12}-\frac{\sigma_{12}h^3}{\mu_1 B^3 U}\nabla\nabla^2 h_{12}+\nabla p_0|_{\text{wat}}\right]\right\} = 0. \tag{5.6b}$$

Since, to lowest order in ϵ, the dimensional tengential stress $\boldsymbol{\tau}'$ exerted by the water on the oil at the oil–water interface is given by

$$\tau_k' = \mu_2[\partial(u_0')_k/\partial x_3']_{\text{wat}} \tag{5.7}$$

evaluated at $x_3' = h_{12}'$, the dimensionless stress $\boldsymbol{\tau} = h\boldsymbol{\tau}'/\mu_2 U$ is

$$\tau_k = [\partial(u_0)_k/\partial x_3]_{\text{wat}}. \tag{5.8}$$

Now by integrating (3.15) across the oil layer once and making use of (4.6), we obtain

$$H\,\partial p_0/\partial x_k = [\partial(u_0)_k/\partial x_3]_{\text{oil}} \quad \text{at} \quad x_3 = h_{12}, \tag{5.9}$$

which by the tangential-stress boundary condition (4.7) gives

$$H\frac{\partial p_0}{\partial x_k} = \frac{\mu_2}{\mu_1}\left.\frac{\partial(u_0)_k}{\partial x_3}\right|_{\text{wat}} \quad \text{at} \quad x_3 = h_{12}. \tag{5.10}$$

Hence

$$\boldsymbol{\tau} = (\mu_1/\mu_2)H\nabla p_0, \tag{5.11}$$

which upon substitution of the value of p_0 given by (4.8) yields

$$\boldsymbol{\tau} = H\left[-\frac{\rho_1 g h^3}{\mu_2 BU}\nabla h_{13}+\frac{\sigma_{13}h^3}{\mu_2 B^3 U}\nabla\nabla^2 h_{13}\right]. \tag{5.12a}$$

In a similar manner, by making use of the value of p_0 given by (4.9), $\boldsymbol{\tau}$ may alternatively be expressed as

$$\boldsymbol{\tau} = H\left[\frac{(\rho_2-\rho_1)gh^3}{\mu_2 BU}\nabla h_{12} - \frac{\sigma_{12}h^3}{\mu_2 B^3 U}\nabla\nabla^2 h_{12} + \frac{\mu_1}{\mu_2}\nabla p_0|_{\text{wat}}\right]. \tag{5.12b}$$

Equations (5.3), (5.6*a*) [or (5.6*b*)] and (5.12*a*) [or (5.12*b*)] together with the relation

$$H = h_{12} - h_{13} \tag{5.13}$$

represent five *scalar* relations between the seven *scalar* quantities H, h_{12}, h_{13}, U_i and τ_i ($i = 1, 2$). The two further relationships necessary in order to solve for these quantities are obtained by solving for the flow in the boundary layer in the water under the boundary conditions that

$$u_i|_{\text{wat}} = U_i|_{\text{wat}} \quad (i = 1, 2) \tag{5.14}$$

on the oil–water interface $x_3 = h_{12}$ and

$$u_i|_{\text{wat}} \to \hat{U}_i \quad \text{as} \quad x_3 \to \infty, \tag{5.15}$$

where $\hat{\mathbf{U}} = \hat{\mathbf{U}}'/U$ is the dimensionless undisturbed flow velocity in the water. The value of $\boldsymbol{\tau}$ is then given by

$$\tau_i = [\partial u_i/\partial x_3]_{\text{wat}} \tag{5.16}$$

evaluated at the oil–water interface $x_3 = h_{12}$. From the definitions (3.7) of the dimensionless quantities, it is seen that in dimensional form (5.3) may be written as

$$\nabla'^2(\sigma_{12}h'_{12} + \sigma_{13}h'_{13}) - g[(\rho_2-\rho_1)h'_{12} + \rho_1 h'_{13}] = p'_0|_{\text{wat}} \tag{5.17a}$$

while, similarly, the dimensional forms of (5.6*a*) and (5.12*a*) are

$$\frac{\partial H'}{\partial t'} + \nabla'.(H'\mathbf{U}') - \tfrac{1}{3}\nabla'.\left\{H'^3\left[-\frac{\rho_1 g}{\mu_1}\nabla' h'_{13} + \frac{\sigma_{13}}{\mu_1}\nabla'\nabla'^2 h'_{13}\right]\right. = 0 \tag{5.18a}$$

and

$$\boldsymbol{\tau}' = H'[-\rho_1 g\nabla' h'_{13} + \sigma_{13}\nabla'\nabla'^2 h'_{13}], \tag{5.19a}$$

where $\mathbf{U}'$ is the velocity at the oil–water interface. Alternative forms of (5.18*a*) and (5.19*a*) obtained from (5.6*b*) and (5.12*b*) are respectively

$$\frac{\partial H'}{\partial t'} + \nabla'.(H'\mathbf{U}') - \tfrac{1}{3}\nabla'.\left\{H'^3\left[\frac{(\rho_2-\rho_1)g}{\mu_1}\nabla' h'_{12} - \frac{\sigma_{12}}{\mu_1}\nabla'\nabla'^2 h'_{12} + \frac{1}{\mu_1}\nabla' p'_0|_{\text{wat}}\right]\right\} = 0 \tag{5.18b}$$

and

$$\boldsymbol{\tau} = H'[(\rho_2-\rho_1)g\nabla' h'_{12} - \sigma_{12}\nabla'\nabla'^2 h'_{12} + \nabla' p'_0|_{\text{wat}}]. \tag{5.19b}$$

Since the pressure excess $p'_0|_{\text{wat}}$ over hydrostatic appearing in (5.17*a*), (5.18*b*) and (5.19*b*) may be evaluated below the boundary layer in the water, where the flow is inviscid, it is seen that $p'_0|_{\text{wat}}$ satisfies

$$\nabla p'_0|_{\text{wat}} = -\rho_2(\hat{\mathbf{U}}'.\nabla'\hat{\mathbf{U}}' + \partial\mathbf{U}'/\partial t'), \tag{5.20}$$

so that (5.18*b*) and (5.19*b*) may be rewritten as

$$\frac{\partial H'}{\partial t'} + \nabla'.(H'\mathbf{U}') - \tfrac{1}{3}\nabla'.\left\{H'^3\left[\frac{(\rho_2-\rho_1)g}{\mu_1}\nabla' h'_{12} - \frac{\sigma_{12}}{\mu_1}\nabla'\nabla'^2 h'_{12} - \frac{\rho_2}{\mu_1}\left(\hat{\mathbf{U}}'.\nabla'\hat{\mathbf{U}}' + \frac{\partial\hat{\mathbf{U}}'}{\partial t'}\right)\right]\right\} = 0 \tag{5.18c}$$

and

$$\boldsymbol{\tau}' = H'[(\rho_2-\rho_1)g\nabla' h'_{12} - \sigma_{12}\nabla'\nabla'^2 h'_{12} - \rho_2(\hat{\mathbf{U}}'.\nabla'\hat{\mathbf{U}}' + \partial\hat{\mathbf{U}}'/\partial t')]. \tag{5.19c}$$

For the particular case of steady irrotational flow in the water, the pressure $p'_0|_{\text{wat}}$ appearing in (5.17*a*), (5.18*b*) and (5.19*b*) is, by Bernoulli's equation,

$$p'_0|_{\text{wat}} = -\tfrac{1}{2}\rho_2 \hat{U}'^2, \tag{5.21}$$

so that for this case

$$\nabla'^2(\sigma_{12}h'_{12}+\sigma_{13}h'_{13}) - g[(\rho_2-\rho_1)h'_{12}+\rho_1 h'_{13}] + \tfrac{1}{2}\rho_2\hat{U}'^2 = 0, \tag{5.17b}$$

$$\frac{\partial H'}{\partial t'} + \nabla'.(H'\mathbf{U}') - \tfrac{1}{3}\nabla'.\left\{H'^3\left[\frac{(\rho_2-\rho_1)g}{\mu_1}\nabla' h'_{12} - \frac{\sigma_{12}}{\mu_1}\nabla'\nabla'^2 h'_{12} - \frac{\rho_2}{\mu_1}\hat{U}'\nabla'\hat{U}'\right]\right\} = 0, \tag{5.18d}$$

$$\boldsymbol{\tau}' = H'[(\rho_2-\rho_1)g\nabla' h'_{12} - \sigma_{12}\nabla'\nabla'^2 h'_{12} - \rho_2\hat{U}'\nabla'\hat{U}']. \tag{5.19d}$$

At the 'contact line' separating the bulk layer (where the motion is determined by (3.1), (5.17*a*), (5.18*a*), (5.19*a*) and the solution of the boundary-layer equations in the water) from the monolayer (where the motion is determined by (2.1), (2.4), (2.8) and the solution of the boundary-layer equations in the water) the surfaces must be continuous, so that

$$h'_{12} = h'_{13} = h'_{23}. \tag{5.22}$$

Furthermore, for the surface-tension forces to balance there, the slopes of the surfaces in the direction normal to the contact line must be equal, so that

$$\hat{\mathbf{n}}.\nabla' h'_{12} = \hat{\mathbf{n}}.\nabla' h'_{13} = \hat{\mathbf{n}}.\nabla' h'_{23}, \tag{5.23}$$

where $\hat{\mathbf{n}}$ is a unit vector normal to the contact line lying in the horizontal plane. From (5.22) and (5.23) it is seen that the oil thickness H' in the bulk layer satisfies

$$H' = 0, \quad \hat{\mathbf{n}}.\nabla' H' = 0 \tag{5.24}$$

at the contact line.

6. Steady unidirectional spreading

As an example of the use of the theory described in §§ 2–5, we consider water flowing with a constant velocity U in the x'_1 direction while a constant volume V per unit width of oil is held in a steady configuration against the flow by means of a barrier placed perpendicular to the flow and projecting below the water surface a sufficient distance to prevent the oil from seeping under the barrier (see figure 1). Taking the origin of the axes at the leading edge of the monolayer and letting $x'_1 = d$ at the contact line separating the monolayer from the bulk layer, it is seen that for the monolayer $(0 \leqslant x'_1 \leqslant d)$ the equations reduce to

$$\frac{\partial}{\partial x'_1}(H'u'_1) = 0, \quad \frac{d\sigma}{dH'}\frac{\partial H'}{\partial x'_1} + \tau'_1 = 0, \tag{6.1),(6.2}$$

$$\sigma\,\partial^2 h'_{23}/\partial x'^2_1 - \rho_2 g h'_{23} = 0 \tag{6.3}$$

if the plane $x'_3 = 0$ is taken to be the undisturbed surface of the water flowing with velocity U. From (6.1), it is observed that $H'u'_1$, the flux of oil in the monolayer, is a constant. However, since this flux is zero at the leading edge (with $H' = 0$ there) it follows that it is zero everywhere. Thus

$$u'_1 = 0 \quad \text{for} \quad 0 \leqslant x'_1 \leqslant d \tag{6.4}$$

at the oil. Hence the boundary layer in the water below the monolayer must be a Blasius boundary layer (see Schlichting 1968, p. 128), so that the stress τ_1' is

$$\tau_1' = \alpha(\mu_2 \rho_2 U^3)^{\frac{1}{2}} (x_1')^{-\frac{1}{2}}, \quad \text{where} \quad \alpha = 0{\cdot}33206. \tag{6.5}$$

Since $\sigma = \sigma_{23}$ at the leading edge $x_1' = 0$, it follows from (6.2) that

$$\sigma = \sigma_{23} - 2\alpha(\mu_2 \rho_2 U^3 x_1')^{\frac{1}{2}}. \tag{6.6}$$

At the contact line $x_1' = d$, σ must equal $\sigma_{12} + \sigma_{13}$, so that

$$d = S^2/4\alpha^2 U^3 \mu_2 \rho_2, \tag{6.7}$$

where $S = \sigma_{23} - (\sigma_{12} + \sigma_{13})$ is the spreading coefficient.

For the bulk layer from $x_1' = d$ to the barrier (at $x_1' = l$ say), the equations describing the motion reduce to

$$\partial^2(\sigma_{12} h_{12}' + \sigma_{13} h_{13}')/\partial x_1'^2 - g[(\rho_2 - \rho_1) h_{12}' + \rho_1 h_{13}'] = 0, \tag{6.8}$$

$$\frac{\partial}{\partial x_1'}\left[H' U_1' - \tfrac{1}{3} H'^3 \left\{ -\frac{\rho_1 g}{\mu_1}\frac{\partial h_{13}'}{\partial x_1'} + \frac{\sigma_{13}}{\mu_1}\frac{\partial^3 h_{13}'}{\partial x_1'^3}\right\}\right] = 0, \tag{6.9}$$

$$\tau_1' = H' \left\{ -\rho_1 g \frac{\partial h_{13}'}{\partial x_1'} + \sigma_{13} \frac{\partial^3 h_{13}'}{\partial x_1'^3}\right\}, \tag{6.10}$$

where

$$H' = h_{12}' - h_{13}'. \tag{6.11}$$

Noting that H' is essentially zero at $x_1' = d$, it is observed that integrating (6.9) gives

$$U_1' = +(3\mu_1)^{-1} H'^2 \, \partial f/\partial x_1', \tag{6.12}$$

where

$$f = \sigma_{13} \frac{\partial^2}{\partial x_1'^2} h_{13}' - \rho_1 g h_{13}' = (\rho_2 - \rho_1) g h_{12}' - \sigma_{12} \frac{\partial^2}{\partial x_1'^2} h_{12}' \tag{6.13}$$

is the pressure excess over hydrostatic within the oil layer. Equation (6.10) may therefore be written as

$$\tau_1' = H' \, \partial f/\partial x_1'. \tag{6.14}$$

Differentiating (6.13) and making use of (6.11) to eliminate h_{12}' and h_{13}', we obtain

$$(\sigma_{12} + \sigma_{13}) \frac{\partial^2 f}{\partial x_1'^2} - \rho_2 g f = -\sigma_{12}\sigma_{13} \frac{\partial^4 H'}{\partial x_1'^4} + [\rho_1 g \sigma_{12} + (\rho_2 - \rho_1) g \sigma_{13}] \frac{\partial^2 H'}{\partial x_1'^2} - \rho_1(\rho_2 - \rho_1) g^2 H'. \tag{6.15}$$

From (6.12) and (6.14)

$$U_1' = (3\mu_1)^{-1} H' \tau_1'. \tag{6.16}$$

However, since the magnitude of τ_1' is

$$\tau_1' \sim (\mu_2/\delta)(U - U_1'), \tag{6.17}$$

where δ is the local boundary-layer thickness, it follows that

$$U_1' \sim \frac{\mu_2}{\mu_1} \frac{H'}{\delta} (U - U_1'). \tag{6.18}$$

In order to simplify the numerical computation of the solution of (6.8)–(6.11) [with the boundary-layer equations in the water] the following assumptions are made:

$$\text{(i)} \quad \frac{\mu_2}{\mu_1}\frac{H}{\delta} \ll 1 \tag{6.19}$$

and

$$\text{(ii)} \quad (\rho_2/\rho_1 - 1) \ll 1, \quad \sigma_{12}/\sigma_{13} \ll 1. \tag{6.20}$$

From (6.18), it is seen that assumption (i) implies that

$$U_1' \ll U, \tag{6.21}$$

so that the velocity U_1' at the oil–water interface is very small, the boundary layer in the water being therefore approximately that of Blasius. Hence the stress τ_1' is given by (6.5). While assumption (i) is obviously satisfied for the bulk layer close to the contact line [where $H \simeq 0$ with δ of order $(\nu d/U)^{\frac{1}{2}}$], its validity for the entire region $d \leqslant x_1' \leqslant l$ must be checked once the solution has been obtained.

Writing (6.8) in the form

$$\sigma_{13}\frac{\partial^2}{\partial x_1'^2}\left\{h_{13}' + \frac{\sigma_{12}}{\sigma_{13}}h_{12}'\right\} - g\rho_1\left\{\left(\frac{\rho_2-\rho_1}{\rho_1}\right)h_{12}' + h_{13}'\right\} = 0$$

we see that assumption (ii) implies that

$$\sigma_{13}\partial^2 h_{13}'/\partial x_1'^2 - g\rho_1 h_{13}' \simeq 0 \quad \text{for} \quad x_1' \geqslant d.$$

Since $h_{12}' = h_{23}'$ and $\partial h_{12}'/\partial x_1' = \partial h_{23}'/\partial x_1'$ at $x_1' = d$ with h_{23}' satisfying (6.3) for $x_1' \leqslant d$, it follows that h_{13}' and h_{23}' must be very small, so that

$$H' \simeq h_{12}', \tag{6.22}$$

the oil–air interface of the bulk layer being almost flat. Thus from (6.13),

$$f = (\rho_2 - \rho_1)gH' - \sigma_{12}\partial^2 H'/\partial x_1'^2,$$

which when substituted into (6.14) with the value of τ_1' given by (6.5) yields

$$(\rho_2-\rho_1)gH'\,\partial H'/\partial x_1' - \sigma_{12}H'\,\partial^3 H'/\partial x_1'^3 = \alpha(\mu_2\rho_2 U^3)^{\frac{1}{2}}x_1'^{-\frac{1}{2}}. \tag{6.23}$$

Defining new dimensionless variables as

$$\left.\begin{aligned} \bar{H} &= (H'/D)(2S/\sigma_{12})^{\frac{1}{2}}, \quad \bar{x}_1 = x_1'/D, \quad \bar{d} = d/D, \quad \bar{l} = l/D, \quad \bar{y}_1 = \bar{x}_1 - \bar{d}, \\ \bar{V} &= (V/D^2)(2S/\sigma_{12})^{\frac{1}{2}}, \quad \lambda = \alpha(\mu_2\rho_2 U^3 D)^{\frac{1}{2}}/2S, \end{aligned}\right\} \tag{6.24a}$$

where

$$D = (\sigma_{12}/(\rho_2-\rho_1)g)^{\frac{1}{2}} \tag{6.24b}$$

is the capillary length scale for the water–oil interface, (6.23) may be written as

$$\bar{H}(\partial\bar{H}/\partial\bar{x}_1 - \partial^3\bar{H}/\partial\bar{x}_1^3) = \lambda\bar{x}_1^{-\frac{1}{2}}. \tag{6.25}$$

The dimensionless quantity λ may by (6.7) be written as

$$\lambda = \tfrac{1}{4}(D/d)^{\frac{1}{2}} = \tfrac{1}{4}\bar{d}^{-\frac{1}{2}} \tag{6.26}$$

and is thus related to the ratio of the capillary length scale D to the length of the monolayer d. In terms of the dimensionless distance $\bar{y}_1$ measured from the contact line,

$$\bar{H}\left(\frac{d\bar{H}}{d\bar{y}_1} - \frac{d^3\bar{H}}{d\bar{y}_1^3}\right) = \frac{4\lambda^2}{(1+16\lambda^2\bar{y}_1)^{\frac{1}{2}}} \tag{6.27}$$

with the boundary conditions [from (5.24)]

$$\bar{H} = d\bar{H}/d\bar{y}_1 = 0 \quad \text{on} \quad \bar{y}_1 = 0. \tag{6.28a}$$

Also

$$d\bar{H}/d\bar{y}_1 = 0 \quad \text{on} \quad \bar{y}_1 = \bar{l} - \bar{d} \tag{6.28b}$$

if it is assumed that the contact angles of the oil–air and water–oil interfaces with the barrier at $x = l$ are 90°. The dimensionless volume per unit width of the oil (neglecting that of the monolayer) is

$$\bar{V} = \int_0^{\bar{l}-\bar{d}} \bar{H}\, d\bar{y}_1. \tag{6.29}$$

It is to be noted that in the absence of any flow in the water, so that $\lambda = 0$, (6.27) and (6.28) have $\bar{H} = 0$ as a solution. This indicates that under these circumstances the oil will continue to spread indefinitely.

To integrate (6.27) numerically with the boundary conditions (6.28), we employ the Runge–Kutta method. As stepwise integration is not possible at $\bar{y}_1 = 0$ (where $\bar{H} = 0$), we use the asymptotic expansion of $\bar{H}$ for $\bar{y}_1 \to 0$, which may be obtained (see appendix) as

$$\bar{H} \sim (\tfrac{32}{3})^{\frac{1}{2}} \lambda \bar{y}_1^{\frac{3}{2}} + c\bar{y}_1^{\frac{1}{4}(5+\sqrt{13})}. \tag{6.30}$$

This provides values of $\bar{H}$, $\partial\bar{H}/\partial\bar{y}_1$ and $\partial^2\bar{H}/\partial\bar{y}_1^2$ at $\bar{y}_1 = \bar{\delta}\ (\bar{\delta} \ll \bar{l} - \bar{d})$ for the start of the integration in $\bar{\delta} < \bar{y}_1 < \bar{l} - \bar{d}$. Thus for different values of c, (6.27) may be integrated until the point where $\partial\bar{H}/\partial\bar{y}_1 = 0$ is attained. From the value of $\bar{l}$ so obtained, $\bar{H}$ at the barrier $\bar{y}_1 = \bar{l} - \bar{d}$ (which we shall denote by $\bar{H}^*$) and $\bar{V}$ [calculated from (6.29)] are calculated. By varying the value of c, we can thus obtain $\bar{H}^*$ and $\bar{l}$ as functions of $\bar{V}$ and λ.

7. Numerical results and discussion

The dimensionless profile of the oil film (i.e. $\bar{H}$ as a function of $\bar{l} - \bar{x}_1$) as calculated in the manner described in §6 is shown in figure 2 for $\lambda = 1$ for various values of the dimensionless oil volume $\bar{V}$. It is seen that, although $d\bar{H}/d\bar{x}_1$ is zero at $\bar{x}_1 = \bar{d}$, the oil film does increase in thickness rapidly in the bulk layer close to the contact line. Figures 3(*a*), (*b*) and (*c*) show for $\bar{V} = 5$, 1 and 0·1 respectively the oil-film profile in the bulk layer for different values of λ. For a fixed $\bar{V}$, the profiles obtained for decreasing values of λ may be considered [see (6.24)] as those for a fixed volume of oil for which the water velocity U is decreased. It is noted the bluntness of the profile near the contact line decreases as the value of λ is decreased. In figures 2 and 3 the values of the dimensionless monolayer length $\bar{d} = 1/16\lambda^2$ have been indicated. From figure 3 it is seen that the length $\bar{l} - \bar{d}$ of the bulk layer increases and the depth $\bar{H}^*$ of the oil at the barrier decreases as the value of λ is decreased. The length of the bulk layer (and also that of the monolayer) increases without limit as $\lambda \to 0$. Figure 4 summarizes the results by showing the calculated values of $\bar{l}$ and $\bar{H}^*$ as functions of $\bar{V}$ and λ. It may be noted from figure 3 that when the oil volume is large the oil thickness profile near the contact line approaches a limit for each value of λ. The value of this limiting profile (i.e. the value of $\bar{H}$ for $\bar{V} \to \infty$) is shown in figure 5. It may be noted that figure 4(*b*) (showing the values of $\bar{H}^*$ as a function of λ and $\bar{V}$) may be used to estimate the volume V per unit width that may be held by a containment boom of depth H^*

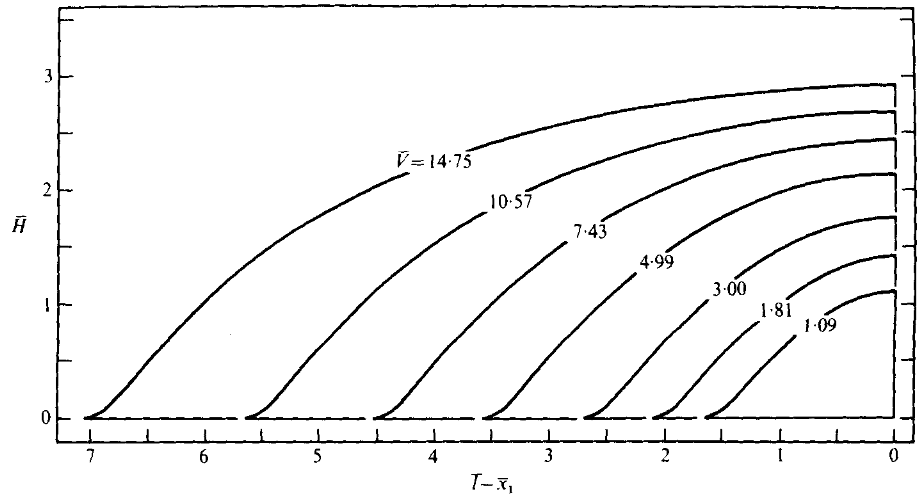

FIGURE 2. $\bar{H}$ as a function of $l-\bar{x}_1$ for $\lambda = 1$ with different values of $\bar{V}$. The value of $\bar{d}$ is 0·0625; $S > 0$.

placed across a river flowing with velocity U, the dimensional quantities V, H^* and U being given by

$$V = \bar{V}\left(\frac{2S\sigma_{12}}{(\rho_2-\rho_1)^2 g^2}\right)^{\frac{1}{2}}, \quad H^* = \bar{H}^*\left(\frac{2S}{(\rho_2-\rho_1)g}\right)^{\frac{1}{2}}, \quad U = \left(\frac{4}{\alpha^2}\right)^{\frac{1}{3}}\left(\frac{\lambda^4 S^4(\rho_2-\rho_1)g}{\sigma_{12}\mu_2^2\rho_2^2}\right)^{\frac{1}{6}}.$$

Further discussion concerning the form of figure 4(*b*) for larger values of $\bar{H}^*$ and $\bar{V}$ will be given in a subsequent paper.

As a specific example, the properties of a spreading fluid with positive spreading coefficient, namely the Dow-Corning Silicone fluid used by Huh, Inoue & Mason (1975), have been listed in table 1 together with the dimensional values of V, U, H' and x_1' which correspond respectively to specific values of $\bar{V}$, λ, $\bar{H}$ and $\bar{x}_1$.

The conditions for the validity of the various assumptions made in the theory are now examined. First, for the lubrication theory to apply

$$\epsilon = h/B \ll 1, \tag{7.1}$$

where locally one may take the characteristic value of h/B to be dH'/dx_1', so that the condition

$$dH'/dx_1' \ll 1 \tag{7.2}$$

must be satisfied everywhere. From (6.24), this implies

$$\left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}}\left(\frac{d\bar{H}}{d\bar{x}_1}\right)_{\max} \ll 1, \tag{7.3}$$

where $(d\bar{H}/d\bar{x}_1)_{\max}$, the maximum value of $d\bar{H}/d\bar{x}_1$, tends to zero (see figures 2 and 3) as $\lambda \to 0$. Thus the condition (7.1) is satisfied if *either*

$$S \ll \sigma_{12} \quad \text{with} \quad \lambda \quad \text{of order unity} \tag{7.4a}$$

or

$$\lambda \ll 1 \quad \text{with} \quad S/\sigma_{12} \quad \text{of order unity.} \tag{7.4b}$$

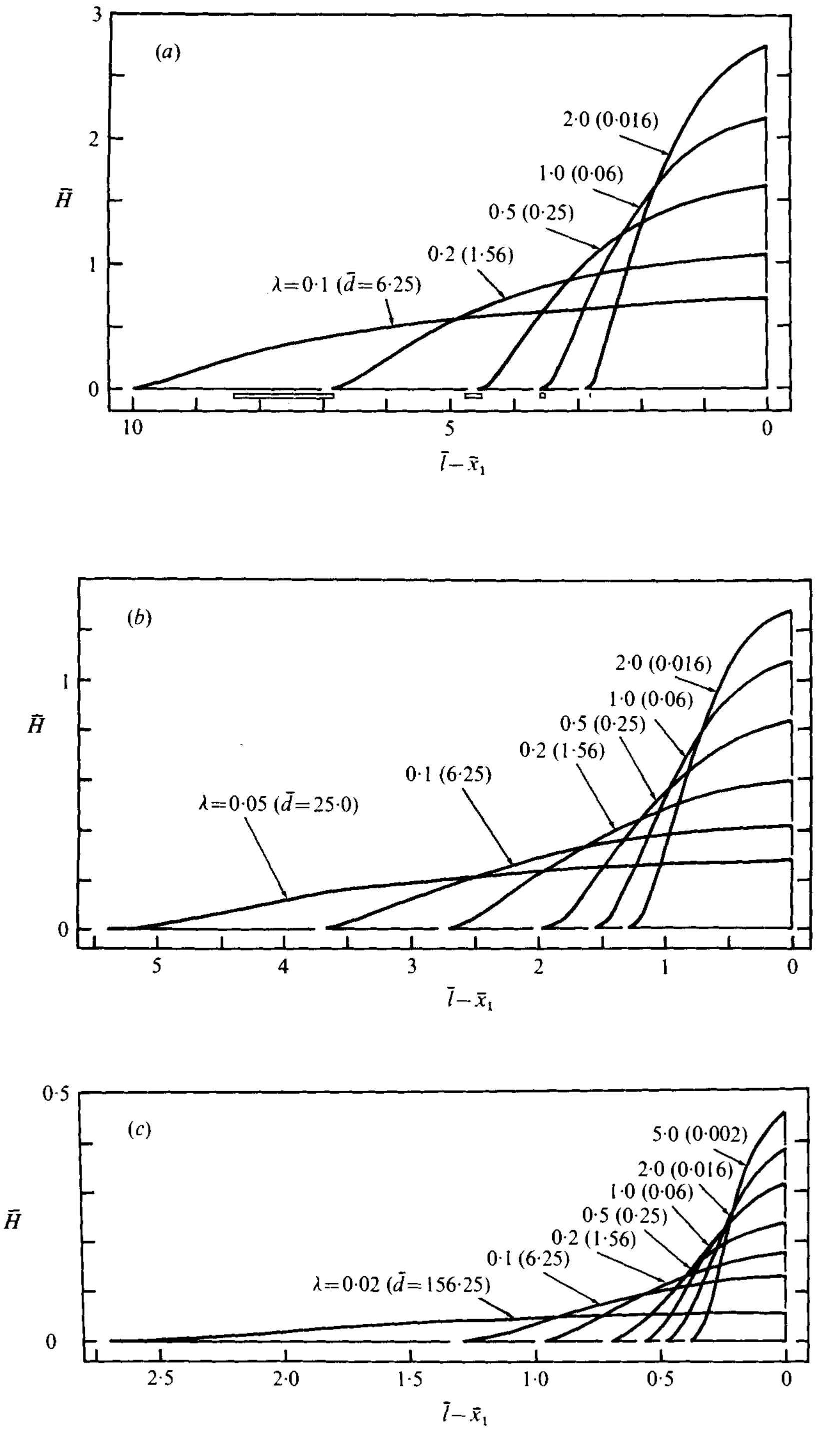

FIGURE 3. $\bar{H}$ as a function of $l-\bar{x}_1$ for different values of λ with (*a*) $\bar{V} = 5$, (*b*) $\bar{V} = 1$ and (*c*) $\bar{V} = 0{\cdot}1$. The values of $\bar{d}$ are shown in parentheses; $S > 0$.

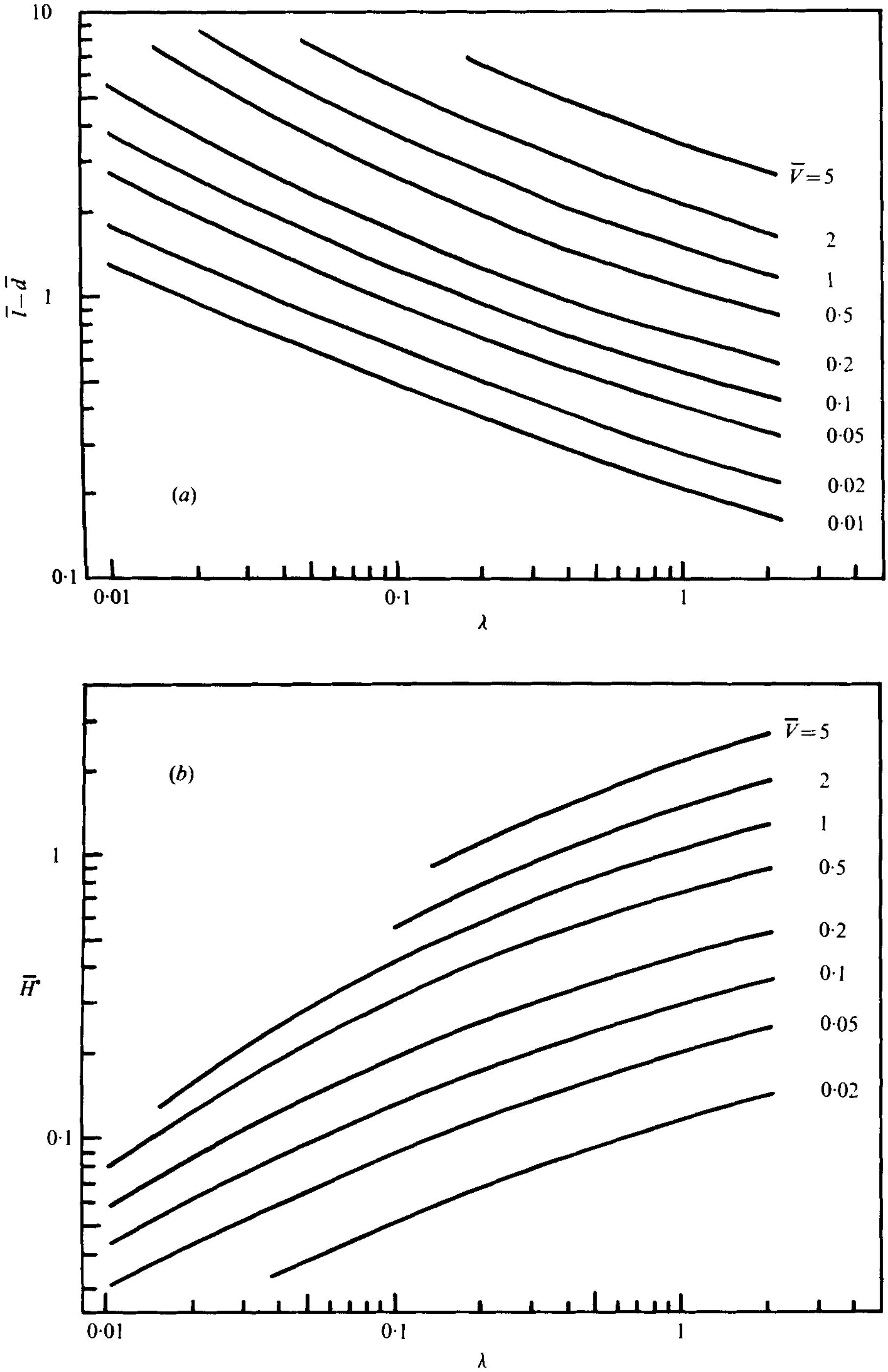

FIGURE 4. (*a*) $\bar{l}-\bar{d}$ and (*b*) $\bar{H}^*$ as functions of $\bar{V}$ and λ; $S > 0$.

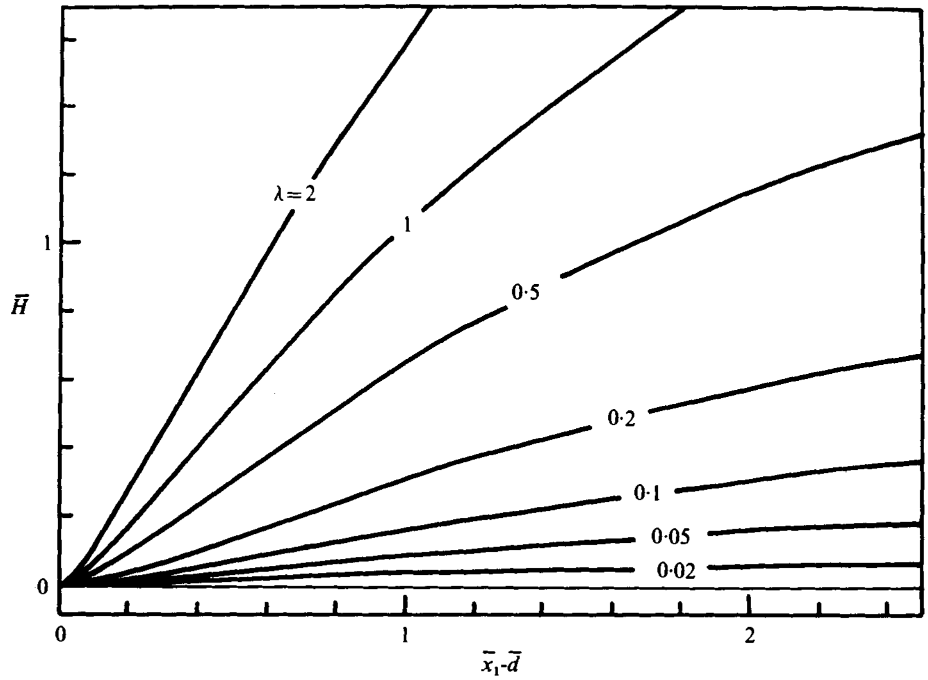

FIGURE 5. $\bar{H}$ as a function of $\bar{x}_1 - \bar{d}$ for different values of λ in the limit $\bar{V} \to \infty$; $S > 0$.

$\bar{V}$	V (cm²)	λ	U (cm s⁻¹)	$\bar{H}$	H' (cm)
5	2·37	5	243	0·5	0·303
1	0·474	2	132	1	0·607
0·1	0·047	1	83·1	2	1·21
		0·5	52·3		
		0·2	28·4	$\bar{x}_1$	x_1' (cm)
		0·1	17·9	1	0·781
		0·05	11·3	5	3·91
		0·02	6·12	10	7·81

$\rho_1 = 0{\cdot}934$ g cm^{-3} $\rho_2 = 1{\cdot}0$ g cm^{-3} $\mu_1 = 10$ cP $\mu_2 = 1{\cdot}0$ cP
$\sigma_{12} = 39{\cdot}5$ dyne cm^{-1} $\sigma_{13} = 20{\cdot}1$ dyne cm^{-1} $S = 11{\cdot}9$ dyne cm^{-1}

TABLE 1. Values of parameters for Dow-Corning 100 Silicone fluid (10 cS) spreading on water.

Second, the condition (3.14) for the neglect of inertia effects within the oil may, by writing B as $H'(dH'/dx_1')^{-1}$, be expressed in terms of local quantities as

$$\left(\frac{dH'}{dx_1'}\right)\frac{U'H'}{\nu_1} \ll 1, \tag{7.5}$$

where $\nu_1 = \mu_1/\rho_1$ and U' is the local characteristic velocity of the oil, which, for the situation where (6.19) is satisfied, is very much smaller than U, so that by (6.18)

$$U' \sim \frac{\mu_2}{\mu_1}\frac{H'}{\delta}U. \tag{7.6}$$

Thus since the boundary-layer thickness δ is of order $(\nu_2 x_1'/U)^{\frac{1}{2}}$, where $\nu_2 = \mu_2/\rho_2$, the condition (7.5) may be written as

$$\left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{U}{\nu_1}\right)^{\frac{3}{2}}H'^2(x_1')^{-\frac{1}{2}}\frac{dH'}{dx_1'} \ll 1, \tag{7.7}$$

which, by (6.24), reduces to

$$\left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{3}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{3}{2}}\left(\bar{H}^2(\bar{x}_1)^{-\frac{1}{2}}\frac{d\bar{H}}{d\bar{x}_1}\right)_{\max} \ll 1. \tag{7.8}$$

Again $(\bar{H}^2(\bar{x}_1)^{-\frac{1}{2}}d\bar{H}/d\bar{x}_1)_{\max}$ tends to zero (see figures 2 and 3) as $\lambda \to 0$, so that (7.5) is satisfied if *either*

$$\left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{3}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{3}{2}} \ll 1 \quad \text{with} \quad \lambda \quad \text{of order unity} \tag{7.9a}$$

or

$$\lambda \ll 1 \quad \text{with} \quad \left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{3}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{3}{2}} \quad \text{of order unity.} \tag{7.9b}$$

It is noted that (7.9*a*) is satisfied if either (i) the oil viscosity μ_1 is sufficiently large or (ii) the flow velocity U of the water is sufficiently small.

Third, condition (6.19), which implies that the velocity U' at the oil–water interface is much smaller than U, may be written as

$$\frac{\mu_2}{\mu_1}H'\left(\frac{U}{\nu_2 x_1'}\right)^{\frac{1}{2}} \ll 1 \tag{7.10}$$

or, in terms of the variables defined by (6.24), as

$$\left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{1}{2}}(\bar{H}(\bar{x}_1)^{-\frac{1}{2}})_{\max} \ll 1. \tag{7.11}$$

Thus (6.19) is satisfied if *either*

$$\left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{1}{2}} \ll 1 \quad \text{with} \quad \lambda \quad \text{of order unity} \tag{7.12a}$$

or

$$\lambda \ll 1 \quad \text{with} \quad \left(\frac{\nu_1}{\nu_2}\right)^{\frac{1}{2}}\frac{\mu_2}{\mu_1}\left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}}\left(\frac{DU}{\nu_1}\right)^{\frac{1}{2}} \quad \text{of order unity.} \tag{7.12b}$$

Like (7.9*a*), condition (7.12*a*) is satisfied if either (i) μ_1 is sufficiently large or (ii) U is sufficiently small.

Finally, it is noted that conditions (6.20), which, like (6.19), were included only to simplify the numerical computation, represent conditions on the properties of the spreading fluid. While the condition $\rho_2/\rho_1 - 1 \ll 1$ is fairly well satisfied for many spreading fluids (like that in table 1), the other condition $\sigma_{12}/\sigma_{13} \ll 1$ in (6.20) is more difficult to satisfy.

If it is assumed that a volume of oil undergoing unidirectional unsteady spreading on water at rest in a channel behaves as if it were in a steady state at each instant of its movement, we may use the steady-state solution to calculate its spreading rate by integrating the equation

$$U = \frac{dl}{dt} \quad \text{or} \quad t = \int_0^l \frac{dl}{U(l)}, \tag{7.13}$$

where $U(l)$ is derived from the calculated relation between l and U (or λ). This was done by Huh *et al.* (1975), who showed that the predicted spreading rate calculated by this method gave reasonable agreement with experiment.

In the theory described in §6 no attempt has been made to determine the stability of the steady-state systems considered. However, stable steady-state situations are known to exist, as for example in the control of oil spilled on flowing water by a mechanical barrier (boom). Aspects of this problem that need further study include (*a*) what happens when the conditions of validity discussed briefly above are not satisfied, (*b*) the effect of surface waves generated by the oil spreading (McCutchen 1970), and (*c*) the possibility of turbulent motion in the boundary layer.

Our study has demonstrated how the spreading of oil on a water surface may be investigated when monolayer and bulk-layer regions exist simultaneously. However, it should be pointed out that the model of spreading described here is not universally valid and that other possibilities can exist. For example, if the spreading fluid is slightly soluble in the water, mutual saturation may cause the value of the spreading coefficient S to change from positive to negative (Adamson 1967). If this occurs the oil film retracts to form a liquid lens.

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Appendix. Asymptotic solution of (6.27) at $\bar{y}_1 = 0$

If we write $\bar{y}_1 = \delta\hat{y}_1$, where $\hat{y}_1$ is of order unity and $\delta \ll 1$, (6.27) becomes

$$-\bar{H}\frac{d^3\bar{H}}{d\hat{y}_1^3} + \delta^2\bar{H}\frac{d\bar{H}}{d\hat{y}_1} = 4\lambda^2\delta^3 - 32\lambda^4\hat{y}_1\delta^4 + \dots, \tag{A 1}$$

so that if

$$\bar{H} = \delta^{\frac{3}{2}}\bar{H}_0 + \delta^p\bar{H}_1 + \dots, \tag{A 2}$$

where $\frac{3}{2} < p < \frac{5}{2}$, we obtain by substituting into (A 1) and equating like powers of δ

$$-\bar{H}_0\, d^3\bar{H}_0/d\hat{y}_1^3 = 4\lambda^2 \tag{A 3}$$

and

$$-\bar{H}_0\, d^3\bar{H}_1/d\hat{y}_1^3 - \bar{H}_1 d^3\bar{H}_0/d\hat{y}_1^3 = 0. \tag{A 4}$$

Also, the boundary conditions (6.28*a*) imply that $\bar{H}_0$, $\bar{H}_1$, $d\bar{H}_0/d\hat{y}_1$ and $d\bar{H}_1/d\hat{y}_1$ are all zero at $\hat{y}_1 = 0$. The solution of (A 3) for $\bar{H}_0$ satisfying the boundary conditions is

$$\bar{H}_0 = (\tfrac{32}{3})^{\frac{1}{2}}\lambda\hat{y}_1^{\frac{3}{2}}, \tag{A 5}$$

which when substituted into (A 4) yields

$$\hat{y}_1^3 d^3\bar{H}_1/d\hat{y}_1^3 - \tfrac{3}{8}\bar{H}_1 = 0. \tag{A 6}$$

This has a solution satisfying the required boundary conditions which may be written as

$$\bar{H}_1 = c\hat{y}_1^{\frac{1}{4}(5+\sqrt{13})}, \tag{A 7}$$

where c is an arbitrary constant. Substituting the values of $\bar{H}_0$ and $\bar{H}_1$ into (A 2) and noting that the resulting expression must be a function of $\bar{y}_1$ only, it is seen that $p = \frac{1}{4}(5+\sqrt{13})$ and

$$\bar{H} = (\tfrac{32}{3})^{\frac{1}{2}}\lambda\bar{y}_1^{\frac{3}{2}} + c\bar{y}_1^{\frac{1}{4}(5+\sqrt{13})} + \dots. \tag{A 8}$$

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