

## The containment of an oil slick by a boom placed across a uniform stream

By N. D. DI PIETRO† AND R. G. COX

McGill University, Department of Civil Engineering and Applied Mechanics,  
817 Sherbrooke St West, Montreal PQ H3A 2K6.

(Received 2 December 1977 and in revised form 15 March 1979)

A small region (called the surface tension region) where pressure differences across the oil–water and oil–air interfaces are important is shown to exist between the gravity viscous and monolayer regions in a spreading oil slick (Di Pietro, Huh & Cox 1978). The importance of this new region is that (i) it is necessary in order to connect the gravity–viscous and monolayer regions and (ii) it is a region where slopes of interfaces are large. This idea is used to find the thickness profile of an oil layer contained upstream of a barrier (an oil boom) placed across a channel in which water is flowing at a constant velocity. The assumption is also made that the velocity difference across the oil layer is small compared with the water velocity. The general conditions for the validity of the results are then discussed together with the modifications to the theory which are necessary if the boundary layer in the water below the oil should be turbulent rather than laminar. Good agreement is found to exist between experimental results for unsteady spreading on quiescent water in a channel and the results of the theory applied to this situation assuming quasi-steady spreading.

---

### 1. Introduction

The behaviour of a liquid (such as an oil) spreading on the horizontal surface of a second, immiscible, liquid (such as water) as the result of gravity and surface tension forces is considered. It is known (Adamson 1967) that when the Harkins spreading coefficient (Harkins 1952) is negative, the spreading liquid spreads on a quiescent substrate to form an equilibrium shape in the form of a lens, whereas when the spreading coefficient is positive, it continues to spread indefinitely until all the available substrate surface is covered by a layer which may be of molecular thickness (Pujado & Scriven 1972). We consider here only this latter situation for which many experiments have been undertaken to observe the rates of spreading (Landt & Volmer 1926; von Guttenberg 1941; Burgers, Grep & Korvezee 1950; Lugton & Vines 1960; Marwedel & Jepsen–Marwedel 1961; Banks 1957; Ahmad & Hansen 1972; Langmuir 1936). It has been observed that with some systems, the deposition of an oil on the water–air interface results in a band of molecular thickness (which will be referred to as the monolayer) to spread ahead of the bulk liquid (Mercer 1939; Zisman 1941; Mar & Mason 1968).

Recent attempts to understand the mechanics of the spreading process have been made by Fay (1969), Hoult (1972), Buckmaster (1973), Wicks (1969) and Garrett &

† Present address: SNC/Foster Wheeler Ltd., 1 Complex Desjardins, Montreal, Quebec.

Barger (1970), who have derived estimates of spreading rates for situations where various driving and dissipation forces are assumed to dominate. Di Pietro (1975) and Di Pietro *et al.* (1978; hereafter referred to as DHC) have given a detailed derivation of the equations determining the spreading for both the monolayer and also for the thicker region of the spreading liquid (which will be referred to as the bulk layer) where it may be considered as a continuum. For the monolayer spreading they assumed that horizontal gradients of surface tension due to variations in monolayer thickness (or equivalently to the surface concentration of the spreading liquid) caused the spreading. The equations they obtained consisted of (a) a continuity equation for the spreading liquid, (b) a balance between the surface tension gradient and the drag due to the boundary layer in the substrate, (c) an experimentally determined relation between the surface tension and the concentration of the spreading liquid, and (d) a relation between the velocity and stress at the monolayer obtained by solving the boundary-layer equations within the substrate liquid. However in the bulk layer they assumed that gravity and surface tension (resulting in pressure differences across the various interfaces) cause the spreading and by the use of lubrication theory obtained the equations determining the spreading. These consisted of (a) a continuity equation for the spreading liquid, (b) a vertical force balance equation, (c) a horizontal force balance equation, and (d) a relation between the velocity and stress on the spreading liquid due to the substrate obtained by solving the boundary-layer equations within the substrate.

As a special case, DHC also considered the steady-state situation where, on a substrate liquid flowing with a constant speed  $U$  along a channel, a constant volume per unit width  $V$  of spreading liquid is held against the flow by means of a barrier placed perpendicular to the flow and projecting below the water surface a distance sufficiently large to prevent the spreading liquid from seeping past (figure 2). For this situation, they solved numerically the equations for both the monolayer and bulk layer when certain additional simplifying assumptions were made. In this manner the horizontal sizes of monolayer and bulk layer were obtained as well as the spreading-layer thickness at the barrier.

The purpose of the present paper is to investigate new perturbation solutions of the governing equations. It is seen that over most of the region occupied by the bulk layer, gravity rather than surface tension is the driving force. This we will refer to as the gravity-viscous region (see Hoult 1972). However at the edge of the bulk layer, between this gravity-viscous region and the monolayer there exists a small region of only a few millimetres in width where surface tension replaces gravity as the driving force. This region, which will be referred to as the surface-tension region, is found to be important because (i) it is necessary in order to connect the solutions in the gravity-viscous and monolayer regions, and (ii) it is a region where the slopes of the interfaces are largest and is thus important in considering the validity of the theory.

A simplification of the general theory for when the velocity variation across the bulk layer is either much smaller or much larger than that across the substrate boundary layer is then discussed.

These results are then applied to the steady-state situation (considered by DHC), where on a substrate liquid flowing along a channel with velocity  $U$ , a volume  $V$  per unit width of spreading liquid is held against the flow by a barrier projecting below

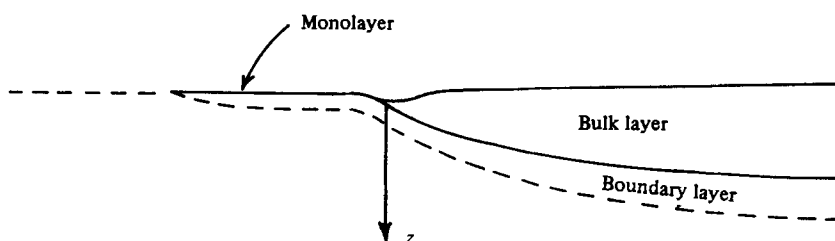


FIGURE 1. The spreading of an oil (phase 1) on the surface of water (phase 2).

the water surface. The spreading liquid thickness profile is thus found for the situation where the velocity difference across the spreading layer is everywhere small. In particular the total length of the spreading layer and its depth at the barrier are found as functions of  $U$  and  $V$ . Such calculations are useful in determining the effectiveness of oil containment booms. The general conditions of validity of the results are then discussed together with the modifications to the theory which occur as the result of the substrate boundary layer becoming turbulent.

Finally, a comparison is made between the available experimental results for unsteady spreading of a fixed volume of liquid on the surface of a quiescent substrate contained in a channel and the predictions obtained from the theoretical results obtained in this paper when applied to this situation (assuming motion to be quasi-steady).

## 2. Surface tension and gravity-viscous regions

We consider for the moment the general situation in which a liquid, phase 1 (which will be referred to as an oil), spreads over the surface of a substrate liquid, phase 2 (water), which may either be quiescent or moving with some prescribed motion.

As shown in figure 1 (using the same notation as DHC), the viscosity and density of the oil are denoted by  $\mu_1$  and  $\rho_1$  and of the water by  $\mu_2$  and  $\rho_2$ . The surface tensions of the oil-water, oil-air and water-air interfaces are respectively written as  $\sigma_{12}$ ,  $\sigma_{13}$  and  $\sigma_{23}$ , so that the Harkins spreading coefficient referred to in § 1 is

$$S = \sigma_{23} - (\sigma_{12} + \sigma_{13}). \tag{2.1}$$

Since the capillary length-scale  $(\sigma_{13}/\rho_1 g)^{\frac{1}{2}}$  for the oil-air interface and

$$(\sigma_{12}/(\rho_2 - \rho_1) g)^{\frac{1}{2}}$$

for the oil-water interface are normally of the order of a few millimetres, they are usually very much smaller than the characteristic horizontal length scale  $B$  of the region occupied by the oil (except for the initial stages of spreading of a very small volume of oil). It will thus be assumed that the two capillary length-scales are of the same order of magnitude and that

$$\eta \equiv \left( \frac{\sigma_{12}}{(\rho_2 - \rho_1) g} \right)^{\frac{1}{2}} / B \ll 1, \tag{2.2}$$

so that expansions may be made in terms of this parameter  $\eta$ . Taking Cartesian axes  $x, y, z$  with the  $z$  axis vertically downwards (see figure 1), and the origin on the same

level as the undisturbed water-air interface (in the absence of flow), we let the oil-water, oil-air and water-air interfaces be given by  $z = h_{12}$ ,  $h_{13}$  and  $h_{23}$  respectively so that within the bulk layer, the layer thickness  $H = h_{12} - h_{13}$ . We define 'outer' non-dimensional independent variables as

$$\hat{x} = x/B, \quad \hat{y} = y/B, \quad \hat{t} = tU/B, \tag{2.3}$$

and dependent variables as

$$\left. \begin{aligned} \hat{H} &= H \left( \frac{(\rho_2 - \rho_1)g}{\sigma_{12}} \right)^{\frac{1}{2}}, \quad \hat{h}_{12} = h_{12} \left( \frac{(\rho_2 - \rho_1)g}{\sigma_{12}} \right)^{\frac{1}{2}}, \quad \hat{h}_{13} = h_{13} \left( \frac{(\rho_2 - \rho_1)g}{\sigma_{12}} \right)^{\frac{1}{2}}, \\ \hat{\mathbf{u}}^* &= \mathbf{u}^*/U, \quad \hat{\boldsymbol{\tau}}^* = \boldsymbol{\tau}^*/\mu_1 U \left( \frac{(\rho_2 - \rho_1)g}{\sigma_{12}} \right)^{\frac{1}{2}}, \end{aligned} \right\} \tag{2.4}$$

where  $U$  is a characteristic spreading speed,  $\mathbf{u}^*$  the (horizontal) velocity and  $\boldsymbol{\tau}^*$  the stress on the oil at the oil-water interface. The equations valid for the bulk layer obtained by DHC may then be written as

$$\frac{\partial \hat{H}}{\partial \hat{t}} + \hat{\nabla} \cdot (\hat{H} \hat{\mathbf{u}}^*) - \frac{1}{3} \hat{\nabla} \cdot (\hat{H}^2 \hat{\boldsymbol{\tau}}^*) = 0, \tag{2.5}$$

$$\eta^2 \hat{\nabla}^2 \left( \hat{h}_{12} + \frac{\sigma_{13}}{\sigma_{12}} \hat{h}_{13} \right) - \left( \hat{h}_{12} + \frac{\rho_1}{\rho_2 - \rho_1} \hat{h}_{13} \right) = 0, \tag{2.6}$$

and

$$\lambda \hat{\boldsymbol{\tau}}^* = \hat{H} (\hat{\nabla} \hat{h}_2 - \eta^2 \hat{\nabla}^2 \hat{h}_{12}), \tag{2.7}$$

where

$$\lambda = \frac{\mu_1 UB}{\sigma_{12}} \left( \frac{(\rho_2 - \rho_1)g}{\sigma_{12}} \right)^{\frac{1}{2}}, \tag{2.8}$$

and where  $\hat{\nabla}$ ,  $\hat{\nabla}^2$ , etc., are horizontal surface operators with respect to the  $\hat{x}$ ,  $\hat{y}$  variables (i.e.  $\hat{\nabla} \equiv \partial/\partial \hat{x}, \partial/\partial \hat{y}$ ).

Expanding  $\hat{h}_{13}$ ,  $\hat{h}_{12}$ ,  $\hat{H}$  and  $\hat{\mathbf{u}}^*$  (and also if necessary  $\hat{\boldsymbol{\tau}}^*$ ) in terms of  $\eta$  as

$$\left. \begin{aligned} \hat{h}_{13} &= (\hat{h}_{13})_0 + \eta(\hat{h}_{13})_1 + \dots, \\ \hat{h}_{12} &= (\hat{h}_{12})_0 + \eta(\hat{h}_{12})_1 + \dots, \\ \hat{H} &= \hat{H}_0 + \eta \hat{H}_1 + \dots, \\ \hat{\mathbf{u}}^* &= \hat{\mathbf{u}}_0^* + \eta \hat{\mathbf{u}}_1^* + \dots, \end{aligned} \right\} \tag{2.9}$$

and substituting into (2.5) to (2.7), it is seen that the lowest-order solution satisfies

$$\frac{\partial \hat{H}_0}{\partial \hat{t}} + \hat{\nabla} \cdot (\hat{H}_0 \hat{\mathbf{u}}_0^*) - \frac{1}{3} \hat{\nabla} \cdot (\hat{H}_0^2 \hat{\boldsymbol{\tau}}_0^*) = 0, \tag{2.10}$$

$$(\hat{h}_{12})_0 + \frac{\rho_1}{\rho_2 - \rho_1} (\hat{h}_{13})_0 = 0 \tag{2.11}$$

and

$$\lambda \hat{\boldsymbol{\tau}}_0^* = \hat{H}_0 \hat{\nabla} (\hat{h}_{12})_0. \tag{2.12}$$

In these equations the terms involving the interfacial tensions of the surfaces do not appear. Also since these terms involve higher-order derivatives, it is expected that in order to make an expansion in terms of  $\eta$ , another region of expansion (of boundary-

layer type) must exist possibly at the contact line where the bulk layer joins the monolayer. Also from (2.11) it is observed that

$$(\hat{h}_{12})_0 = \frac{\rho_1}{\rho_2} \hat{H}_0 \quad \text{since} \quad \hat{H}_0 = (\hat{h}_{12})_0 - (\hat{h}_{13})_0,$$

so that (2.12) may be written

$$\hat{\tau}^* = \frac{\rho_1}{\lambda \rho_2} \hat{H}_0 \hat{\nabla} \hat{H}_0 = \frac{\rho_1}{2\lambda \rho_2} \hat{\nabla} \hat{H}_0^2. \quad (2.13)$$

At any point on the contact line, take  $\hat{x}$  normal and  $\hat{y}$  tangential to the contact line with the  $\hat{x}$  axis directed towards the bulk region. Expanding the stress  $\hat{\tau}^*$  as a Taylor series for small  $\hat{x}$  and noting that since  $\sigma = \sigma_{12} + \sigma_{13}$  is constant along the contact line and that in the monolayer  $\nabla \sigma + \hat{\tau}^* = 0$ , it follows that  $\hat{\tau}_x^* = 0$  while  $\hat{\tau}_y^*$  may be taken to be constant to the lowest order in  $\hat{x}$ . Thus as  $\hat{x} \rightarrow 0$ , it follows from (2.13) that

$$\frac{\partial}{\partial \hat{y}} \hat{H}_0^2 = 0, \quad \frac{\partial}{\partial \hat{x}} \hat{H}_0^2 \sim \frac{2\lambda \rho_2}{\rho_1} \hat{\tau}_y^* + O(\hat{x}),$$

giving

$$\hat{H}_0 \sim \left( \frac{2\lambda \rho_2}{\rho_1} \hat{\tau}_y^* \right)^{\frac{1}{2}} \hat{x}^{\frac{1}{2}} + O(\hat{x}^{\frac{3}{2}}) \quad \text{as} \quad \hat{x} \rightarrow 0. \quad (2.14a)$$

Thus by (2.11)

$$(\hat{h}_{12})_0 \sim \frac{\rho_1}{\rho_2} \left( \frac{2\lambda \rho_2}{\rho_1} \hat{\tau}_y^* \right)^{\frac{1}{2}} \hat{x}^{\frac{1}{2}} + O(\hat{x}^{\frac{3}{2}}), \quad (2.14b)$$

$$(\hat{h}_{13})_0 \sim -\frac{(\rho_2 - \rho_1)}{\rho_2} \left( \frac{2\lambda \rho_2}{\rho_1} \hat{\tau}_y^* \right)^{\frac{1}{2}} \hat{x}^{\frac{1}{2}} + O(\hat{x}^{\frac{3}{2}}) \quad \text{as} \quad \hat{x} \rightarrow 0. \quad (2.14c)$$

Equation (2.13) and hence the above expansions for  $\hat{x} \rightarrow 0$  cannot apply at the contact line since in general  $\hat{\tau}^*$  would be non-zero in (2.13) whereas by the continuity of the interfaces and by the balance of vertical force components (see DHC) both  $\hat{H}_0$  and  $\hat{\nabla} \hat{H}_0$  must be zero.

Thus at a general point on the contact line an 'inner' expansion in  $\eta$  is made by choosing the  $\hat{x}, \hat{y}$  co-ordinates with origin at the chosen point on the contact line and defining inner  $\bar{x}, \bar{y}$  co-ordinates as

$$\bar{x} = \hat{x}/\eta, \quad \bar{y} = \hat{y}/\eta \quad \text{and} \quad \bar{t} = \hat{t}. \quad (2.15)$$

If the origin of co-ordinates moves with fluid at the contact line, then in the  $\bar{x}, \bar{y}$  variables, the equations (2.5) to (2.7) remain valid except that  $\hat{\mathbf{u}}^*$  is now interpreted as the fluid velocity relative to the moving origin so that  $\hat{\mathbf{u}}^* = 0$  at  $\hat{x} = \hat{y} = 0$ . If the contact line is assumed to be smooth with curvature of order unity, then it may be written as

$$\hat{x} = A\hat{y}^2, \quad (2.16)$$

where  $A$  is of order unity.

Thus in inner variables it is

$$\bar{x} = A\eta\bar{y}^2 \quad (2.17)$$

so that to lowest order in  $\eta$  the contact line can be taken as the straight line  $\bar{x} = 0$ .

In terms of these inner variables, the values of  $\hat{H}$ ,  $\hat{h}_{12}$  and  $\hat{h}_{13}$  from (2.14) become

$$\hat{H} \sim \eta^{\frac{1}{2}} \left( \frac{2\lambda\rho_2}{\rho_1} \hat{\tau}_x^* \right)^{\frac{1}{2}} \bar{x}^{\frac{1}{2}} + O(\eta^{\frac{3}{2}}), \quad (2.18a)$$

$$\hat{h}_{12} \sim \eta^{\frac{1}{2}} \frac{\rho_1}{\rho_2} \left( \frac{2\lambda\rho_2}{\rho_1} \hat{\tau}_x^* \right)^{\frac{1}{2}} \bar{x}^{\frac{1}{2}} + O(\eta^{\frac{3}{2}}), \quad (2.18b)$$

$$\hat{h}_{13} \sim -\eta^{\frac{1}{2}} \left( \frac{\rho_2 - \rho_1}{\rho_2} \right) \left( \frac{2\lambda\rho_2}{\rho_1} \hat{\tau}_x^* \right)^{\frac{1}{2}} \bar{x}^{\frac{1}{2}} + O(\eta^{\frac{3}{2}}), \quad (2.18c)$$

from which it is seen that matching on to the inner expansion requires that  $\hat{H}$ ,  $\hat{h}_{12}$  and  $\hat{h}_{13}$  must be of order  $\eta^{\frac{1}{2}}$ . Thus we define inner dependent variables such that

$$\bar{H} = \hat{H}\eta^{-\frac{1}{2}}, \quad \bar{h}_{12} = \hat{h}_{12}\eta^{-\frac{1}{2}}, \quad \bar{h}_{13} = \hat{h}_{13}\eta^{-\frac{1}{2}}, \quad \bar{\mathbf{u}}^* = \hat{\mathbf{u}}^*\eta^{-\frac{1}{2}}, \quad \bar{\tau}^* = \hat{\tau}^*, \quad (2.19)$$

so that in the inner region of expansion (2.5) to (2.7) become

$$\left. \begin{aligned} \eta^{\frac{1}{2}} \frac{\partial \bar{H}}{\partial \bar{t}} + \bar{\nabla} \cdot (\bar{H} \bar{\mathbf{u}}^*) - \frac{1}{3} \bar{\nabla} \cdot (\bar{H}^2 \bar{\tau}^*) &= 0, \\ \bar{\nabla}^2 \left( \bar{h}_{12} + \frac{\sigma_{13}}{\sigma_{12}} \bar{h}_{13} \right) - \left( \bar{h}_{12} + \frac{\rho_1}{\rho_2 - \rho_1} \bar{h}_{13} \right) &= 0 \end{aligned} \right\} \quad (2.20)$$

and

$$\lambda \bar{\tau}^* = \bar{H} (\bar{\nabla} \bar{h}_{12} - \bar{\nabla} \bar{\nabla}^2 \bar{h}_{12}).$$

Thus we expand  $\bar{h}_{13}$  as

$$\bar{h}_{13} = (\bar{h}_{13})_0 + o(\eta^0) \quad \text{as } \eta \rightarrow 0 \quad (2.21)$$

with similar expansions for  $\bar{h}_{12}$ ,  $\bar{H}$  and  $\bar{\mathbf{u}}^*$ . Thus

$$\left. \begin{aligned} \bar{\nabla} \cdot (\bar{H}_0 \bar{\mathbf{u}}_0^*) - \frac{1}{3} \bar{\nabla} \cdot (\bar{H}_0^2 \bar{\tau}_0^*) &= 0, \\ \bar{\nabla}^2 \left( (\bar{h}_{12})_0 + \frac{\sigma_{13}}{\sigma_{12}} (\bar{h}_{13})_0 \right) - \left( (\bar{h}_{12})_0 + \frac{\rho_1}{\rho_2 - \rho_1} (\bar{h}_{13})_0 \right) &= 0 \end{aligned} \right\} \quad (2.22)$$

and

$$\lambda \bar{\tau}_0^* = \bar{H}_0 (\bar{\nabla} (\bar{h}_{12})_0 - \bar{\nabla} \bar{\nabla}^2 (\bar{h}_{12})_0).$$

The second term in the expansion (2.21) is, for unsteady motions (such as the expansion of a given volume of oil from some point), of order  $\eta^{\frac{1}{2}}$ . However for steady motions such as the one considered later for the containment of oil upstream of a boom across a uniform stream, the term  $\eta^{\frac{1}{2}} \partial \bar{H} / \partial \bar{t}$  appearing in (2.20) is zero so that the second term in the expansion (2.21) is of order  $\eta^{-1}$  [which is required for the matching onto the term of order  $\eta^{\frac{1}{2}}$  in (2.18)].

At  $\bar{x} = 0$ , the contact line, since the interfaces must meet and since vertical force components must balance,

$$(\bar{h}_{12})_0 = (\bar{h}_{13})_0 = \bar{h}_{23}, \quad (2.23a)$$

$$\frac{\partial}{\partial \bar{x}} (\bar{h}_{12})_0 = \frac{\partial}{\partial \bar{x}} (\bar{h}_{13})_0 = \frac{\partial}{\partial \bar{x}} \bar{h}_{23}, \quad (2.23b)$$

where  $\bar{h}_{23} = \eta^{-\frac{1}{2}} ((\rho_2 - \rho_1)g / \sigma_{12})^{\frac{1}{2}} h_{23}$  and  $\partial \bar{h}_{23} / \partial \bar{x}$  at the contact line are functions of

$\bar{y}$  which to the lowest order in  $\eta$  may be taken as constants. Also the required matching on to the outer expansion is, by (2.18),

$$(\bar{h}_{12})_0 \sim \frac{\rho_1}{\rho_2} \left( \frac{2\lambda\rho_2}{\rho_1} \bar{\tau}_x^* \right)^{\frac{1}{2}} \bar{x}^{\frac{1}{2}}, \tag{2.24a}$$

$$(\bar{h}_{13})_0 \sim -\frac{\rho_2 - \rho_1}{\rho_2} \left( \frac{2\lambda\rho_2}{\rho_1} \bar{\tau}_x^* \right)^{\frac{1}{2}} \bar{x}^{\frac{1}{2}} \text{ as } \bar{x} \rightarrow \infty. \tag{2.24b}$$

Thus it is seen that the boundary conditions for  $(\bar{h}_{12})_0$  and  $(\bar{h}_{13})_0$  do not involve  $\bar{y}$  so that one expects the solution of (2.22) satisfying these boundary conditions for a given value of  $\bar{\tau}^*$  to be a function of  $\bar{x}$  only. Thus (2.22) takes the form

$$\left. \begin{aligned} \frac{\partial}{\partial \bar{x}} (\bar{H}_0 (\bar{u}_0^*)_x) - \frac{1}{3} \frac{\partial}{\partial \bar{x}} (\bar{H}_0^3 \bar{\tau}_x^*) &= 0, \\ \frac{\partial^2}{\partial \bar{x}^2} \left\{ (\bar{h}_{12})_0 + \frac{\sigma_{13}}{\sigma_{12}} (\bar{h}_{13})_0 \right\} - \left\{ (\bar{h}_{12})_0 + \frac{\rho_1}{\rho_2 - \rho_1} (\bar{h}_{12})_0 \right\} &= 0, \\ \lambda \bar{\tau}_x^* &= \bar{H}_0 \left\{ \frac{\partial}{\partial \bar{x}} (\bar{h}_{12})_0 - \frac{\partial^3}{\partial \bar{x}^3} (\bar{h}_{12})_0 \right\}. \end{aligned} \right\} \tag{2.25}$$

It is noted that whereas in the outer region of expansion gravity effects dominate over surface tension effects (the surface tension effects being negligible at lowest order), in the inner region these effects are equally important. However, in this inner region there is the simplification that at the lowest order there is (i) no variation in the  $\bar{y}$  direction [i.e., the flow is two-dimensional] and (ii) the stress  $\bar{\tau}^*$  is in the  $\bar{x}$  direction and may be taken to be constant. For convenience we will refer to the outer region as the gravity-viscous region [being the same as the gravity-viscous region referred to by Fay (1969) and Hault (1972)] and to the inner region as the surface-tension region.

### 3. Small and large velocity variations across the oil layer

The dimensional velocity at the oil-air interface  $\mathbf{u}(h_{13})$  is given by DHC as

$$\begin{aligned} \mathbf{u}(h_{13}) - \mathbf{u}^* &= -\frac{1}{2\mu_1} H^2 [-\rho_1 g \nabla h_{13} + \sigma_{13} \nabla \nabla^2 h_{13}] \\ &= -\frac{1}{2\mu_1} H \boldsymbol{\tau}^*. \end{aligned} \tag{3.1}$$

Thus since the stress  $\boldsymbol{\tau}^*$  due to the boundary layer is of order  $\mu_2(\Delta \mathbf{u})_{BL}/\delta$  where  $(\Delta \mathbf{u})_{BL}$  is the velocity difference across the boundary layer and  $\delta$  is the boundary-layer thickness, it follows that

$$\left| \frac{(\Delta \mathbf{u})_{oil}}{(\Delta \mathbf{u})_{BL}} \right| \approx \frac{\mu_2 H}{\mu_1 \delta}, \tag{3.2}$$

where  $(\Delta \mathbf{u})_{oil} = |\mathbf{u}(h_{13}) - \mathbf{u}^*|$  is the velocity difference across the oil layer. Thus if

$$\frac{\mu_2 H}{\mu_1 \delta} \ll 1 \tag{3.3}$$

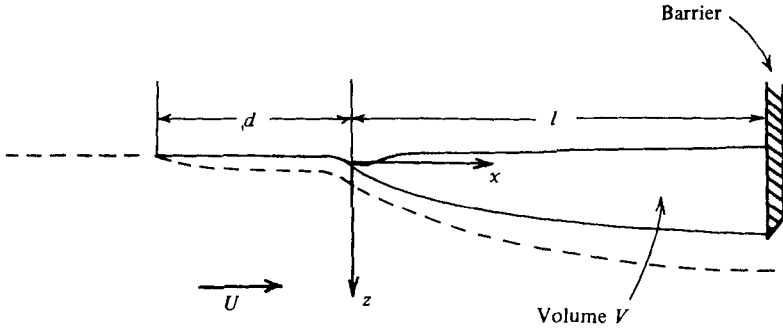


FIGURE 2. A volume  $V$  per unit width of oil held against a flow of velocity  $U$  along a channel by means of a barrier projecting below the water surface.

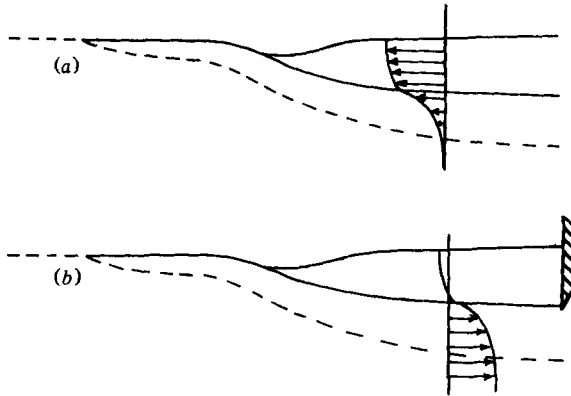


FIGURE 3. Sketch of velocity profiles for the case of a small velocity difference across the oil layer for (a) spreading on a quiescent substrate and (b) spreading against a uniform flow upstream of a barrier.

it follows that the magnitude of the velocity difference across the oil is very much smaller than that across the boundary layer.

For oil spreading on water at rest  $(\Delta u)_{oil} = |\mathbf{u}^*|$ , so that by writing the continuity equation (see DHC) in the form

$$\frac{\partial H}{\partial t} + \nabla \cdot (H\mathbf{u}^*) - \frac{1}{3} \nabla \cdot \left( \frac{H^2}{\mu_1} \boldsymbol{\tau}^* \right) = 0,$$

it is observed that whereas the first two terms are of order  $H|\mathbf{u}^*|/B$  the third term is of order  $H|\mathbf{u}^*| B^{-1}(\mu_2 H/\mu_1 \delta)$  and is thus negligible so that

$$\frac{\partial H}{\partial t} + \nabla \cdot (H\mathbf{u}^*) = 0. \tag{3.4}$$

This is the expected form of the continuity equation since the velocity is approximately  $\mathbf{u}^*$  at all points across the oil layer (see figure 3a).

For oil held in a steady-state configuration upstream from a barrier in a uniform flow along a channel (figure 2) (the case considered by DHC),  $|\mathbf{u}^*| \simeq 0$  so that the boundary layer in the water is the Blasius boundary layer (see figure 3b) for which



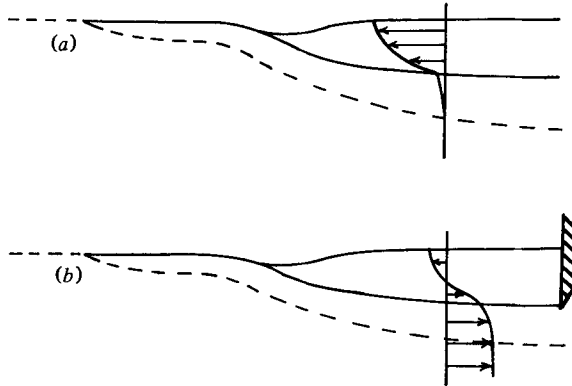


FIGURE 4. Sketch of velocity profiles for the case of a large velocity difference across the oil layer for (a) spreading on a quiescent substrate and (b) spreading against a uniform flow upstream of a barrier.

the value of  $\tau^*$  is known. The thickness of the oil is then determined by the horizontal and vertical force balance equations alone (see DHC).

If the opposite situation to that discussed above holds so that

$$\frac{\mu_2 H}{\mu_1 \delta} \gg 1, \tag{3.5}$$

then the magnitude of the velocity difference across the oil is very much larger than that across the boundary layer (see figure 4). The velocity  $\mathbf{u}^*$  may then be taken as the given velocity of the water below the boundary layer (e.g.  $\mathbf{u}^* = 0$  for oil spreading on water at rest) and so the thickness of the oil may be obtained from the vertical force balance and continuity equations alone (see DHC) while the horizontal force balance equation gives the value of  $\tau^*$ . The boundary-layer equations valid in the water may then be solved with this known value of  $\tau^*$ .

#### 4. Spreading of oil against a uniform flow

The steady-state situation considered by DHC is now discussed where on water flowing with velocity  $U$  along a channel, a fixed volume of oil is held against the flow by means of a barrier (see figure 2). We take the origin of axes at the contact line (between monolayer and surface tension region) with the  $x$  axis in the direction of the flow and let the position of the leading edge of the monolayer be  $x = -d$  and of the barrier be  $x = l$ . Then since the flux of oil is zero at all points in the monolayer region (see DHC),  $\mathbf{u}^* = 0$  there. It is also zero in the surface tension and gravity-viscous regions at all values of  $x$  for which (3.3) is satisfied.

We will assume that in fact (3.3) is satisfied throughout (i.e. for  $0 < x < l$ ) (and examine later the conditions of validity of this assumption) so that the boundary layer in the water is a Blasius boundary layer which exerts a stress  $\tau^* = (\tau^*, 0, 0)$  on the oil given by

$$\tau^* = \alpha(\mu_2 \rho_2 U^3)^{\frac{1}{2}} (x+d)^{-\frac{1}{2}} \quad \text{where} \quad \alpha = 0.33206. \tag{4.1}$$

In the monolayer region ( $-d < x < 0$ ), the horizontal force balance equation

$$\nabla\sigma + \tau^* = 0$$

may be integrated to give

$$\sigma = \sigma_{23} - 2\alpha(\mu_2\rho_2 U^3)^{\frac{1}{2}}(x+d)^{\frac{1}{2}}, \quad (4.2)$$

where it has been noted that  $\sigma = \sigma_{23}$  at  $x = -d$ . Since at the contact line  $x = 0$ ,  $\sigma$  is equal to  $\sigma_{12} + \sigma_{13}$ , it follows that

$$d = S^2/4\alpha^2 U^3 \mu_2 \rho_2, \quad (4.3)$$

where  $S$  is the spreading coefficient given by (2.1).

In the bulk region, the oil thickness is determined by the vertical and horizontal force balance equations (see DHC), which take the form

$$\frac{d^2}{dx^2}(\sigma_{12}h_{12} + \sigma_{13}h_{13}) - g[(\rho_2 - \rho_1)h_{12} + \rho_1 h_{13}] = 0, \quad (4.4a)$$

$$H \left[ (\rho_2 - \rho_1)g \frac{dh_{12}}{dx} - \sigma_{12} \frac{d^3 h_{12}}{dx^3} \right] = \alpha(\mu_2\rho_2 U^3)^{\frac{1}{2}}(x+d)^{-\frac{1}{2}}. \quad (4.4b)$$

It is assumed that  $d$  and  $l$  are both much larger than the capillary length scales so that an expansion may be made in the surface tension (inner) and gravity-viscous (outer) regions as described in § 2. Taking the length scale  $B$  to be equal to  $d$ , the expansion parameter  $\eta$  is

$$\eta \equiv \left( \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \right)^{\frac{1}{2}} \frac{4\alpha^2 U^3 \mu_2 \rho_2}{S^2}. \quad (4.5)$$

Expressing (4.4a, b) in outer variables (as in § 2), one obtains

$$\eta^2 \frac{d^2}{d\hat{x}^2} \left( \hat{h}_{12} + \frac{\sigma_{13}}{\sigma_{12}} \hat{h}_{13} \right) - \left( \hat{h}_{12} + \frac{\rho_1}{\rho_2 - \rho_1} \hat{h}_{13} \right) = 0, \quad (4.6a)$$

$$\hat{H} \left( \frac{d\hat{h}_{12}}{d\hat{x}} - \eta^2 \frac{d^3 \hat{h}_{12}}{d\hat{x}^3} \right) = \frac{1}{2} \frac{S}{\sigma_{12}} (\hat{x} + 1)^{-\frac{1}{2}}. \quad (4.6b)$$

Substituting into these equations the expansions (2.9), it is seen that  $(\hat{h}_{13})_0$ ,  $(\hat{h}_{12})_0$  and  $\hat{H}_0$  satisfy [see (2.11) and (2.12)]

$$(\hat{h}_{12})_0 + \frac{\rho_1}{\rho_2 - \rho_1} (\hat{h}_{13})_0 = 0, \quad (4.7a)$$

$$\hat{H}_0 \frac{d(\hat{h}_{12})_0}{d\hat{x}} = \frac{1}{2} \frac{S}{\sigma_{12}} (\hat{x} + 1)^{-\frac{1}{2}}, \quad (4.7b)$$

while  $(\hat{h}_{13})_1$ ,  $(\hat{h}_{12})_1$  and  $\hat{H}_1$  satisfy

$$(\hat{h}_{12})_1 + \frac{\rho_1}{\rho_2 - \rho_1} (\hat{h}_{13})_1 = 0, \quad (4.8a)$$

$$\hat{H}_1 \frac{d(\hat{h}_{12})_0}{d\hat{x}} + \hat{H}_0 \frac{d(\hat{h}_{12})_1}{d\hat{x}} = 0. \quad (4.8b)$$

Since  $\hat{H}_0 = (\hat{h}_{12})_0 - (\hat{h}_{13})_0$ , the quantities  $(\hat{h}_{12})_0$  and  $(\hat{h}_{13})_0$  may be eliminated from (4.7a, b) to give

$$\hat{H}_0 \frac{d\hat{H}_0}{d\hat{x}} = \frac{1}{2} \left( \frac{\rho_2}{\rho_1} \right) \left( \frac{S}{\sigma_{12}} \right) (\hat{x} + 1)^{-\frac{1}{2}}, \quad (4.9)$$

which possesses the general solution

$$\hat{H}_0 = \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [2(\hat{x} + 1)^{\frac{1}{2}} + K_1]^{\frac{1}{2}}$$

where  $K_1$  is a constant.

Since for matching on to the inner expansion  $\hat{H}_0 \rightarrow 0$  as  $\hat{x} \rightarrow 0$  it follows that  $K_1 = -2$ , therefore

$$\hat{H}_0 = \sqrt{2} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}}. \tag{4.10a}$$

Thus, from (4.7a),

$$(\hat{h}_{12})_0 = \sqrt{2} \left(\frac{\rho_1}{\rho_2}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}}, \tag{4.10b}$$

$$(\hat{h}_{13})_0 = -\sqrt{2} \frac{\rho_2 - \rho_1}{(\rho_1 \rho_2)^{\frac{1}{2}}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}}. \tag{4.10c}$$

The solution of (4.8a, b) is obtained as

$$\left. \begin{aligned} \hat{H}_1 &= K \left(\frac{\rho_2}{\rho_1}\right) \left(\frac{S}{\sigma_{12}}\right) (\hat{H}_0)^{-1}, \\ (\hat{h}_{12})_1 &= K \left(\frac{S}{\sigma_{12}}\right) (\hat{H}_0)^{-1}, \\ (\hat{h}_{13})_1 &= -K \left(\frac{\rho_2 - \rho_1}{\rho_1}\right) \left(\frac{S}{\sigma_{12}}\right) (\hat{H}_0)^{-1}, \end{aligned} \right\} \tag{4.11}$$

where  $K$  is an arbitrary constant of integration. Thus the outer expansion is

$$\hat{H} = \sqrt{2} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \{[\sqrt{(\hat{x} + 1)} - 1]^{\frac{1}{2}} + \frac{1}{2} K \eta [\sqrt{(\hat{x} + 1)} - 1]^{-\frac{1}{2}} + \dots\} \tag{4.12}$$

with

$$\hat{h}_{12} = \frac{\rho_1}{\rho_2} \hat{H} \quad \text{and} \quad \hat{h}_{13} = -\frac{\rho_2 - \rho_1}{\rho_2} \hat{H}.$$

As  $x \rightarrow 0$ ,

$$\hat{H} \sim \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \{[\hat{x}^{\frac{1}{2}} - \frac{1}{8} \hat{x}^{\frac{3}{2}} + \dots] + \eta K [\hat{x}^{-\frac{1}{2}} + \frac{1}{8} \hat{x}^{\frac{1}{2}} + \dots] + \dots\}, \tag{4.13}$$

which when expressed in inner variables defined as in § 2, becomes

$$\hat{H} \sim \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \{\eta^{\frac{1}{2}} [\bar{x}^{\frac{1}{2}} + K \bar{x}^{-\frac{1}{2}} + \dots] + \eta^{\frac{1}{2}} [-\frac{1}{8} \bar{x}^{\frac{3}{2}} + \frac{1}{8} K \bar{x}^{\frac{1}{2}} + \dots] + \dots\}. \tag{4.14}$$

Thus if the inner expansion is of the form (2.21), it is seen that matching requires that

$$\bar{H}_0 \sim \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [\bar{x}^{\frac{1}{2}} + K \bar{x}^{-\frac{1}{2}} + \dots], \tag{4.15a}$$

$$\bar{H}_1 \sim \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [-\frac{1}{8} \bar{x}^{\frac{3}{2}} + \frac{1}{8} K \bar{x}^{\frac{1}{2}} + \dots] \quad \text{as} \quad \bar{x} \rightarrow \infty \tag{4.15b}$$

with similar asymptotic forms for  $(\bar{h}_{12})_0$ ,  $(\bar{h}_{12})_1$ ,  $(\bar{h}_{13})_0$  and  $(\bar{h}_{13})_1$  being determined by

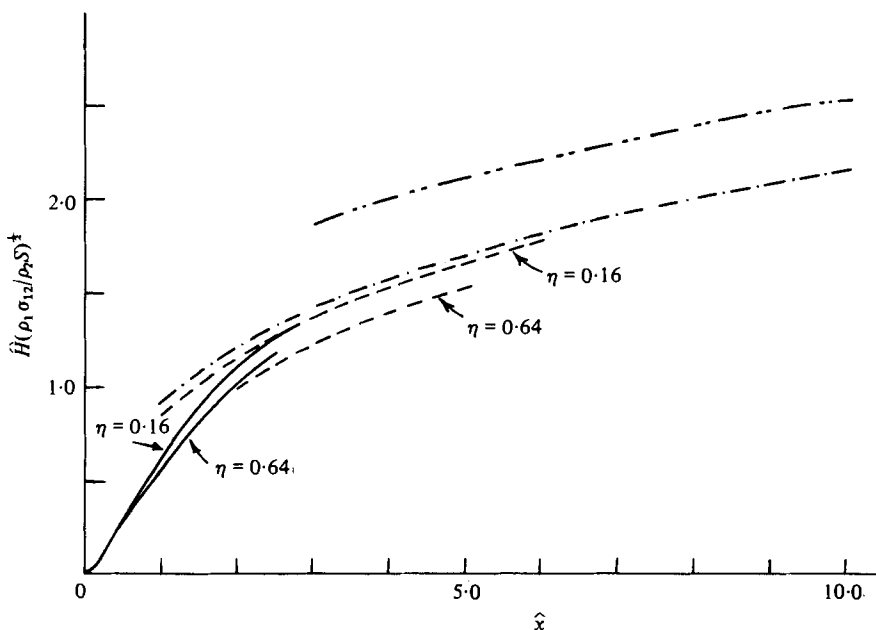


FIGURE 5. Values of  $\hat{H}(\rho_1/\rho_2)^{\frac{1}{2}}(\sigma_{12}/S)^{\frac{1}{2}}$  as a function of  $\hat{x}$ : - · - ·, values given by (4.13) for  $\eta = 0$ ; - - -, values given by (4.13) for  $\eta = 0.16$  and  $\eta = 0.64$ ; —, numerical values determined by DHC for  $\eta = 0.16$  and  $\eta = 0.64$ ; - - - -, asymptotic form for  $\hat{x} \rightarrow \infty$  given by (4.24).

$(\bar{h}_{12})_0 = (\rho_1/\rho_2)\bar{H}_0$ ,  $(\bar{h}_{13})_0 = -[(\rho_2 - \rho_1)/\rho_2]\bar{H}_0$ , etc. Expressing (4.4a, b) in inner variables, one obtains

$$\frac{d^2}{d\bar{x}^2} \left( \bar{h}_{12} + \frac{\sigma_{13}}{\sigma_{12}} \bar{h}_{13} \right) - \left( \bar{h}_{12} + \frac{\rho_1}{\rho_2 - \rho_1} \bar{h}_{13} \right) = 0, \quad (4.16a)$$

$$\bar{H} \left\{ \frac{d\bar{h}_{12}}{d\bar{x}} - \frac{d^3\bar{h}_{12}}{d\bar{x}^3} \right\} = \frac{1}{2} \frac{S}{\sigma_{12}} (1 + \eta\bar{x})^{-\frac{1}{2}}, \quad (4.16b)$$

which, upon substitution of the expansions (2.21), yields the equations for  $\bar{H}_0$ ,  $(\bar{h}_{12})_0$ , etc., as

$$\frac{d^2}{d\bar{x}^2} \left\{ (\bar{h}_{12})_0 + \frac{\sigma_{13}}{\sigma_{12}} (\bar{h}_{13})_0 \right\} - \left\{ (\bar{h}_{12})_0 + \frac{\rho_1}{\rho_2 - \rho_1} (\bar{h}_{13})_0 \right\} = 0, \quad (4.17a)$$

$$\bar{H}_0 \left\{ \frac{d(\bar{h}_{12})_0}{d\bar{x}} - \frac{d^3(\bar{h}_{12})_0}{d\bar{x}^3} \right\} = \frac{1}{2} \frac{S}{\sigma_{12}} \quad (4.17b)$$

and the equations for  $\bar{H}_1$ ,  $(\bar{h}_{12})_1$ , etc., as

$$\frac{d^2}{d\bar{x}^2} \left\{ (\bar{h}_{12})_1 + \frac{\sigma_{13}}{\sigma_{12}} (\bar{h}_{13})_1 \right\} - \left\{ (\bar{h}_{12})_1 + \frac{\rho_1}{\rho_2 - \rho_1} (\bar{h}_{13})_1 \right\} = 0, \quad (4.18a)$$

$$\bar{H}_0 \left\{ \frac{d(\bar{h}_{12})_1}{d\bar{x}} - \frac{d^3(\bar{h}_{12})_1}{d\bar{x}^3} \right\} + \bar{H}_1 \left\{ \frac{d(\bar{h}_{12})_0}{d\bar{x}} - \frac{d^3(\bar{h}_{12})_0}{d\bar{x}^3} \right\} = -\frac{1}{4} \frac{S}{\sigma_{12}} \bar{x}. \quad (4.18b)$$

The lowest-order inner solution thus satisfies (4.17a, b) and the required boundary conditions at  $\bar{x} = 0$ , namely

$$(\bar{h}_{12})_0 = (\bar{h}_{13})_0 = (\bar{h}_{23})_0 \quad (4.19a)$$

and

$$\left(\frac{d(\bar{h}_{12})_0}{d\bar{x}}\right) = \left(\frac{d(\bar{h}_{13})_0}{d\bar{x}}\right) = \left(\frac{d(\bar{h}_{23})_0}{d\bar{x}}\right). \quad (4.19b)$$

The normal stress balance across the monolayer (see DHC) yields, for  $-d < x < 0$ ,

$$\frac{d^2(\bar{h}_{23})_0}{d\bar{x}^2} - \frac{\rho_2}{\rho_2 - \rho_1} \frac{\sigma_{12}}{\sigma} (\bar{h}_{23})_0 = 0. \quad (4.20)$$

The asymptotic solution of (4.17a, b) for  $\bar{x} \rightarrow \infty$  may [by substituting  $\bar{x} = \epsilon^{-1}\hat{x}$  where  $\epsilon \rightarrow 0$ ] be found to be exactly that given by (4.15a) so that the matching condition is thus satisfied. In general the equations (4.17a, b) and (4.20) with boundary conditions (4.19a, b) must be solved numerically, a comparison with the asymptotic form (4.15a) then giving the value of the constant  $K$ . This value is a function of  $\rho_1/\rho_2$ ,  $\sigma_{13}/\sigma_{12}$  and  $\sigma(x)/\sigma_{12}$  [but not of  $S/\sigma_{12}$  since from (4.17) it is seen that  $\bar{H}_0$ ,  $(\bar{h}_{12})_0$  and  $(\bar{h}_{13})_0$  may all be taken proportional to  $(S/\sigma_{12})^{\frac{1}{2}}$ ]. For the particular case for which  $(\rho_2/\rho_1 - 1) \ll 1$  and  $\sigma_{12}/\sigma_{13} \ll 1$  (which implies that  $h_{13}$  and  $h_{23}$  are negligibly small), numerical solutions were obtained by DHC and a comparison of their results with (4.15a) gives  $K = -0.42$  for that particular situation. Values of  $\hat{H}$  given by (4.12) and valid in the outer region of expansion have been plotted in figure 5 where the numerical solutions of DHC are given for comparison.

It is noted that

$$\hat{H} \sim \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \hat{x}^{\frac{1}{2}} \quad \text{as } \hat{x} \rightarrow 0, \quad (4.21)$$

from which it is seen that it is impossible (as mentioned previously) to join this solution on to the monolayer solution without the intervening inner (surface tension) region.

Also, from (4.12), it is seen that

$$\hat{H} = \sqrt{2} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \hat{x}^{\frac{1}{2}} \quad \text{as } \hat{x} \rightarrow \infty. \quad (4.22)$$

The volume  $V$  per unit width of oil is

$$V = \int_0^l H dx \quad (4.23)$$

if the amount of oil in the monolayer is negligible. Thus writing

$$V = \left(\frac{\sigma_{12}}{(\rho_2 - \rho_1)g}\right)^{\frac{1}{2}} \frac{S^2}{4\alpha^2 U^3 \mu_2 \rho_2} \hat{V} \quad (4.24a)$$

and

$$l = \frac{S^2}{4\alpha^2 U^3 \mu_2 \rho_2} \hat{l} = d\hat{l}, \quad (4.24b)$$

it is seen that

$$\hat{V} = \int_0^{\hat{l}} \hat{H} d\hat{x}. \quad (4.25)$$

Dividing the range of integration into two parts, one part being  $0 \leq \hat{x} < a$  (or

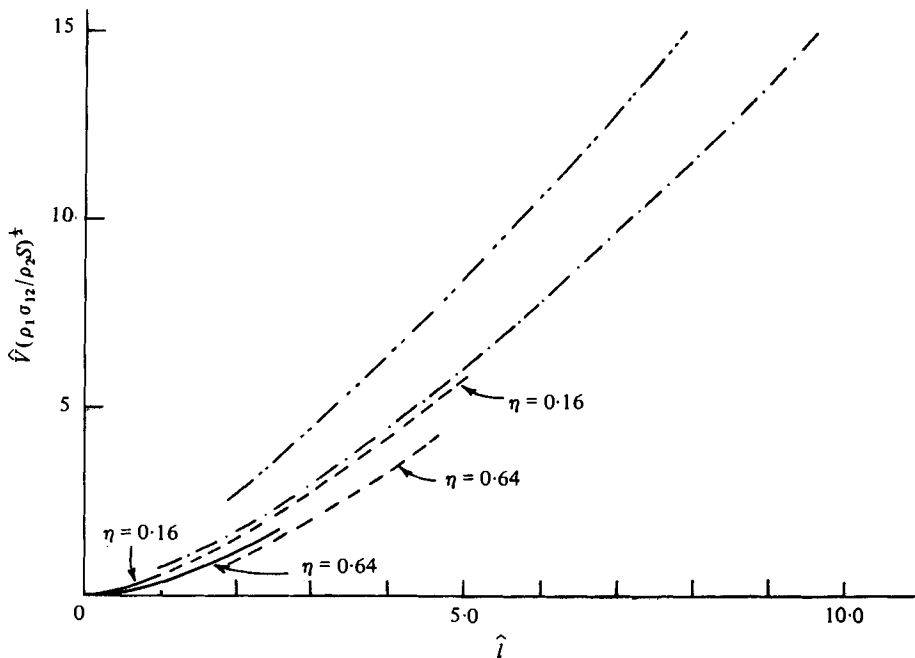


FIGURE 6. Values of  $\hat{V}(\rho_1/\rho_2)^{\frac{1}{2}} (\sigma_{12}/S)^{\frac{1}{2}}$  as a function of  $\hat{l}$ : ---, values given by (4.29) for  $\eta = 0$ ; - · - ·, values given by (4.29) for  $\eta = 0.16$  and  $\eta = 0.64$ . —, numerical values determined by DHC for  $\eta = 0.16$  and  $\eta = 0.64$ ; ····, asymptotic form for  $\hat{l} \rightarrow \infty$  [see (4.31)].

$0 \leq \bar{x} < a\eta^{-1}$ , where  $a \ll 1$  and the other  $a < \hat{x} \leq \hat{l}$ , it is seen that one may evaluate the integral over the former part using inner variables so that

$$\begin{aligned} \hat{V} &= \int_0^{a\eta^{-1}} \bar{H} \eta^{\frac{1}{2}} d\bar{x} + \int_a^{\hat{l}} \hat{H} d\hat{x} \\ &= \int_0^{a\eta^{-1}} \eta^{\frac{1}{2}} [\bar{H}_0 + \eta \bar{H}_1 + \dots] d\bar{x} + \int_a^{\hat{l}} [\hat{H}_0 + \eta \hat{H}_1 + \dots] d\hat{x}. \end{aligned} \tag{4.26}$$

Since as  $\eta \rightarrow 0$ ,  $a\eta^{-1} \rightarrow \infty$ , the first integral is evaluated by subtracting off from the integrand the part which makes the integral diverge as  $\eta \rightarrow 0$ . Thus (from (4.17)),

$$\begin{aligned} \hat{V} &= \eta^{\frac{1}{2}} \int_0^{a\eta^{-1}} \left\{ \bar{H}_0 - \left(\frac{\rho_1}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} [\bar{x}^{\frac{1}{2}} + K\bar{x}^{-\frac{1}{2}}] \right\} d\bar{x} \\ &\quad + \eta^{\frac{1}{2}} \int_0^{a\eta^{-1}} \left\{ \bar{H}_1 - \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \left[-\frac{1}{8}\bar{x}^{\frac{3}{2}} + \frac{1}{8}K\bar{x}^{\frac{1}{2}} + \dots\right] \right\} d\bar{x} \\ &\quad + \eta^{\frac{1}{2}} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \left\{ \frac{3}{8}\eta^{-\frac{1}{2}} a^{\frac{3}{2}} + 2K\eta^{-\frac{1}{2}} a^{\frac{1}{2}} \right\} \\ &\quad + \eta^{\frac{1}{2}} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \left\{ -\frac{1}{20}\eta^{-\frac{1}{2}} a^{\frac{5}{2}} + \frac{1}{12}K\eta^{-\frac{1}{2}} a^{\frac{3}{2}} + \dots \right\} \\ &\quad + \int_a^{\hat{l}} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} \sqrt{2\{[(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}} + \frac{1}{2}K\eta[(\hat{x} + 1)^{\frac{1}{2}} - 1]^{-\frac{1}{2}} + \dots\}} d\hat{x}, \end{aligned}$$

which, since  $a \ll 1$ , reduces to

$$\hat{V} = \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{\sigma_{12}}\right)^{\frac{1}{2}} 2\sqrt{2} \left\{ \frac{2}{3}[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{3}{2}} + \frac{2}{5}[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{5}{2}} + K\eta[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{3}{2}} + \frac{1}{3}K\eta[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{5}{2}} + O(\eta^{\frac{3}{2}}) \right\}. \quad (4.27)$$

Actually, if the contact angle is given at the barrier at  $x = l$ , the above volume will be in error by a term of order  $\eta$  (since  $V$  will be in error by an amount of order  $\sigma_{12}/(\rho_2 - \rho_1)g$ ). However, since the contact angle produced by the above solution (4.13) approaches  $90^\circ$  as  $\eta \rightarrow 0$ , it follows that the error in (4.27) must be  $o(\eta)$  for a given contact angle of  $90^\circ$  at the barrier (as was the case for the calculations of DHC).  $\hat{V}$  is plotted against  $\hat{l}$  in figure 6 where the numerical results of DHC are also given for comparison. In dimensional form (4.27) is

$$V = \left(\frac{S^5}{U^6 \mu_2^2 \rho_1 \rho_2 (\rho_2 - \rho_1) g}\right)^{\frac{1}{2}} \frac{\sqrt{2}}{2\alpha^2} \left\{ \frac{2}{3}[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{3}{2}} + \frac{2}{5}[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{5}{2}} + \dots \right\}. \quad (4.28)$$

When  $\hat{l}$  is large (i.e.  $l \gg d$ ) so that the bulk layer is much longer than the monolayer, (4.28) gives

$$V \simeq \frac{8}{5}(\alpha)^{\frac{1}{2}} \left(\frac{U^3 \mu_2 \rho_2^3 l^5}{\rho_1^2 (\rho_2 - \rho_1)^2 g^2}\right)^{\frac{1}{2}}, \quad (4.29)$$

so that in terms of volume  $V$  and flow velocity  $U$ , the length  $l$  of the bulk layer is

$$l \simeq \left(\frac{25}{64\alpha}\right)^{\frac{1}{2}} \left(\frac{V^4 \rho_1^2 (\rho_2 - \rho_1)^2 g^2}{U^3 \mu_2 \rho_2^3}\right)^{\frac{1}{2}}. \quad (4.30)$$

To prevent loss of oil under the barrier at  $x = l$  it must project a distance  $h_l$  below the undisturbed water level, where

$$h_l = h_{12}|_{x=l} = \left(\frac{\sigma_{12}}{(\rho_2 - \rho_1)g}\right)^{\frac{1}{2}} \hat{h}_{12}|_{\hat{x}=\hat{l}}, \quad (4.31)$$

which by (4.12), reduces to

$$h_l = \left(\frac{S}{(\rho_2 - \rho_1)g}\right)^{\frac{1}{2}} \left(\frac{\rho_1}{\rho_2}\right)^{\frac{1}{2}} \sqrt{2} \left\{ [(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{3}{2}} + \frac{1}{2}K\eta[(\hat{l}+1)^{\frac{1}{2}}-1]^{\frac{5}{2}} + \dots \right\}. \quad (4.32)$$

For the present case of  $\hat{l}$  large, this gives

$$h_l \simeq 2\alpha^{\frac{1}{2}} \left(\frac{U^3 \mu_2 \rho_1^2 l}{\rho_2 (\rho_2 - \rho_1)^2 g}\right)^{\frac{1}{2}} \quad (4.33)$$

or, by (4.30), in terms of  $U$  and  $V$  as

$$h_l \simeq (20\alpha^2)^{\frac{1}{2}} \left(\frac{U^3 V \mu_2 \rho_1^3}{\rho_2^2 (\rho_2 - \rho_1)^2 g^2}\right)^{\frac{1}{2}}. \quad (4.34)$$

Thus, the necessary barrier depth  $h_l$  increases with both  $U$  and  $V$  as expected. For a given barrier depth  $h_l$  and flow velocity  $U$ , the maximum volume  $V$  of oil retained (if  $l \gg d$ ) is thus

$$V \simeq \frac{1}{20\alpha^2} \frac{h_l^5 \rho_2^2 (\rho_2 - \rho_1)^2 g^2}{U^3 \mu_2 \rho_1^3}. \quad (4.35)$$

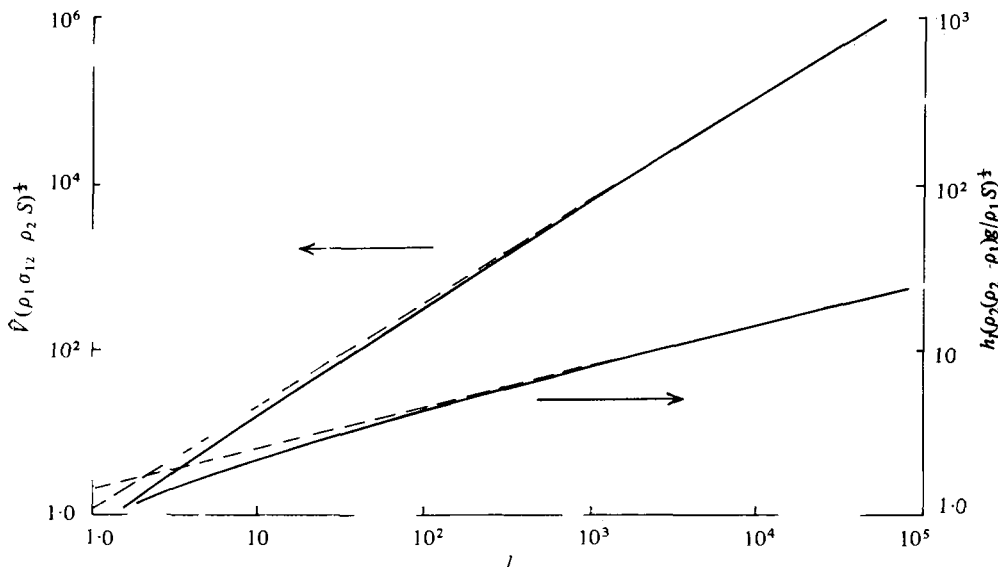


FIGURE 7. Values of  $\hat{V}(\rho_1/\rho_2)^{\frac{1}{2}}(\sigma_{12}/S)^{\frac{1}{2}} \equiv 4\alpha^2 V(U^6 \mu_2^2 \rho_1 \rho_2 (\rho_2 - \rho_1) g/S^5)^{\frac{1}{2}}$  and  $h_1(\rho_2(\rho_2 - \rho_1)g/\rho_1 S)^{\frac{1}{2}}$  as functions of  $l \equiv 4\alpha^2 l(U^3 \mu_2 \rho_2/S^2)$  for  $\eta = 0$ . —, values given by (4.27) and (4.13); ---, asymptotic forms for  $l \rightarrow \infty$ .

On the other hand, when the length of the bulk layer is much smaller than the monolayer (but also much larger than the capillary length scales) so that  $l$  is small, the length  $l$  of the bulk layer obtained from (4.28) is

$$l \simeq \left(\frac{9}{16\alpha^2}\right)^{\frac{1}{2}} \left(\frac{V^2 S \rho_1 (\rho_2 - \rho_1) g}{U^3 \mu_2 \rho_2^2}\right)^{\frac{1}{2}}. \tag{4.36}$$

The necessary barrier depth  $h_1$  for this case is [from equations (4.32) and (4.36)]

$$h_1 \simeq (6\alpha)^{\frac{1}{2}} \left(\frac{U^3 V \mu_2 \rho_1^2}{S(\rho_2 - \rho_1) \rho_2 g}\right)^{\frac{1}{2}}. \tag{4.37}$$

Again, for this case,  $h_1$  increases with both  $U$  and  $V$ . For given  $h_1$  and  $U$ , the maximum oil volume retained is obtained from (4.37) as

$$V \simeq \frac{1}{6\alpha^2} \frac{h_1^3 S(\rho_2 - \rho_1) \rho_2 g}{U^3 \mu_2}. \tag{4.38}$$

The condition  $l \gg d$  for the validity of (4.29), (4.30), (4.33), (4.34) and (4.35) may be expressed as

$$U \gg \left(\frac{2}{25\alpha^4}\right)^{\frac{1}{2}} \left(\frac{S^5}{V^2 \rho_1 \rho_2 (\rho_2 - \rho_1) g \mu_2^2}\right)^{\frac{1}{2}}, \tag{4.39}$$

so that it follows that the bulk layer is much larger than the monolayer at large flow speed  $U$  and/or large oil volume  $V$ . The condition  $l \ll d$  for validity of (4.36)–(4.38) is opposite to that given by (4.39). In figure 7, the values of

$$\hat{V}(\rho_1 \sigma_{12}/\rho_2 S)^{\frac{1}{2}} = 4\alpha^2 V(U^6 \mu_2^2 \rho_1 \rho_2 (\rho_2 - \rho_1) g/S^5)^{\frac{1}{2}}$$



given by (4.27) and of  $h_l(\rho_2(\rho_2 - \rho_1)g/\rho_1 S)^{\frac{1}{2}}$  given by (4.32) are plotted against  $\hat{l} = 4\alpha^2 l(U^3 \mu_2 \rho_2 / S^2)$  for  $\eta = 0$  together with their asymptotic forms (4.29) and (4.33) for  $\hat{l} \rightarrow \infty$ . These graphs enable one, for a given oil volume  $V$  and flow speed  $U$ , to obtain the bulk layer length  $l$  and the depth  $h_l$  at the barrier. Also for given barrier depth  $h_l$  and flow speed  $U$ , the maximum oil volume  $V$  (as well as bulk layer length  $l$ ) may be obtained.

The order of magnitude of the oil thickness in the surface tension region (i.e. for fixed  $\bar{x}$ ) at a position near where it joins the gravity viscous region may be obtained from (4.15a) as

$$\begin{aligned}
 H &= \left( \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \right)^{\frac{1}{2}} \eta^{\frac{1}{2}} \bar{H} \simeq \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \eta^{\frac{1}{2}} \left( \frac{\rho_2 S}{\rho_1 \sigma_{12}} \right)^{\frac{1}{2}} \\
 &\simeq 2\alpha \left( \frac{U^6 \sigma_{12} \mu_2^2 \rho_2^4}{S^2 \rho_1^2 (\rho_2 - \rho_1)^3 g^3} \right)^{\frac{1}{4}}.
 \end{aligned}
 \tag{4.40}$$

Also, in a similar manner the order of magnitude of the rate of increase  $dH/dx$  of oil layer thickness at such a position is

$$\begin{aligned}
 \frac{dH}{dx} &= \left( \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \right)^{\frac{1}{2}} \eta^{-\frac{1}{2}} \frac{4\alpha^2 U^3 \mu_2 \rho_2}{S^2} \frac{d\bar{H}}{d\bar{x}} \\
 &\simeq 2\alpha \left( \frac{U^6 \mu_2^2 \rho_2^4}{S^2 \sigma_{12} \rho_1^2 (\rho_2 - \rho_1)g} \right)^{\frac{1}{4}}.
 \end{aligned}
 \tag{4.41}$$

### 5. Conditions of validity

In the derivation of the results obtained in § 4, various assumptions have been made. These include (i) the assumption of a small velocity variation across the oil layer; (ii) the assumption that the monolayer and bulk layer lengths are much larger than the capillary length scale; (iii) the assumption that the interfaces have small slopes; (iv) the neglect of inertia effects in the oil; (v) the neglect of pressure variations in the substrate flow; (vi) the assumption that the boundary layer in the water is laminar; (vii) the assumption of no depletion of the monolayer. The necessary conditions for the applicability of each of these assumptions will now be discussed.

(i) *Small velocity variation across the oil layer.* The condition for the velocity variation across the oil layer to be much smaller than that across the boundary layer is given by (3.3). Since the order of magnitude of the boundary-layer thickness (as defined in § 3) is

$$\delta \simeq \frac{1}{\alpha} \left( \frac{\nu_2(x+d)}{U} \right)^{\frac{1}{2}} = \frac{1}{\alpha} \left( \frac{\nu_2 d}{U} \right)^{\frac{1}{2}} (\hat{x} + 1)^{\frac{1}{2}}
 \tag{5.1}$$

and the oil layer thickness in the gravity-viscous region is given by (4.12), it follows that (3.3), for the gravity-viscous region, is

$$\frac{\mu_2 H}{\mu_1 \delta} \simeq 2\sqrt{2} \alpha^2 \left( \frac{U^4 \rho_2^3}{S \rho_1 (\rho_2 - \rho_1) g} \right)^{\frac{1}{2}} \frac{\mu_2}{\mu_1} \left[ \frac{(\hat{x} + 1)^{\frac{1}{2}} - 1}{(\hat{x} + 1)} \right]^{\frac{1}{2}} \ll 1.
 \tag{5.2}$$

The function  $\{[(\hat{x} + 1)^{\frac{1}{2}} - 1]/(\hat{x} + 1)\}^{\frac{1}{2}}$  increases from zero at  $\hat{x} = 0$  to a maximum value

of  $\frac{1}{2}$  at  $\hat{x} = 3$  and then decrease to zero as  $\hat{x} \rightarrow \infty$ . Thus the condition (3.3) is satisfied for all  $\hat{x}$  if the maximum value of the left-hand side of (3.3) is small, i.e. if

$$U \ll \left( \frac{S\mu_1^2\rho_1(\rho_2 - \rho_1)g}{\mu_2^2\rho_2^3} \right)^{\frac{1}{4}}. \quad (5.3)$$

However, if (5.3) is not satisfied,  $\mu_2 H / \mu_1 \delta$  is only small for  $\hat{x} = x/d$  less than some critical value determined by (5.2). In fact,  $\mu_2 H / \mu_1 \delta$  will not be small even in the surface tension region if (3.3) is violated with  $H$  given by (4.40) and  $\delta$  by (5.1) (with  $\hat{x} \approx 0$ ), i.e. if

$$U \gg \left( \frac{S^6 \mu_1^4 \rho_1^2 (\rho_2 - \rho_1)^3 g^3}{\sigma_{12} \mu_2^8 \rho_2^8} \right)^{\frac{1}{14}}. \quad (5.4)$$

Should the condition (3.3) be violated for any value of  $x$ , then at that value of  $x$  and at all points downstream the boundary layer would not be of Blasius type.

(ii) *Lengths of monolayer and bulk layer large.* For the expansion procedure described in § 2 to be valid the capillary length scale must be much smaller than (a) the length of monolayer (so that  $\eta$  is small) and (b) the length of bulk layer. These conditions may be expressed as

$$\left( \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \right)^{\frac{1}{2}} \ll \frac{S^2}{U^3 \mu_2 \rho_2}$$

and

$$\left( \frac{\sigma_{12}}{(\rho_2 - \rho_1)g} \right)^{\frac{1}{2}} \ll l,$$

respectively. While the first condition may be written as

$$U \ll \left( \frac{S^4 (\rho_2 - \rho_1) g}{\sigma_{12} \mu_2^2 \rho_2^2} \right)^{\frac{1}{2}}, \quad (5.5)$$

the second may, by using (4.30) and (4.36), be expressed as

$$U \ll \left( \frac{V^8 \rho_1^4 (\rho_2 - \rho_1)^9 g^9}{\sigma_{12}^5 \mu_2^2 \rho_2^6} \right)^{\frac{1}{2}} \quad \text{for } l \gg d, \quad (5.6)$$

$$U \ll \left( \frac{V^4 S^2 \rho_1^2 (\rho_2 - \rho_1)^5 g^5}{\sigma_{12}^3 \mu_2^2 \rho_2^4} \right)^{\frac{1}{2}} \quad \text{for } l \ll d. \quad (5.7)$$

It is noted that whereas (5.5) is satisfied if the flow velocity  $U$  is small enough, (5.6) and (5.7) require that either  $U$  is small enough or the oil volume  $V$  is large enough.

(iii) *Slope of interfaces small.* For the lubrication theory described by DHC for the oil motion in the bulk layer to be valid  $dH/dx$  must be small everywhere. In the outer region of expansion  $dH/dx$  may be obtained from (4.10a) as

$$\frac{dH}{dx} = \sqrt{2} \alpha^2 \left( \frac{U^6 \mu_2^2 \rho_2^3}{S^3 \rho_1 (\rho_2 - \rho_1) g} \right)^{\frac{1}{2}} (1 + \hat{x})^{-\frac{1}{2}} [(1 + \hat{x})^{\frac{1}{2}} - 1]^{-\frac{1}{2}},$$

which is a monotonically decreasing function which  $\rightarrow \infty$  as  $\hat{x} \rightarrow 0$  and  $\rightarrow 0$  as  $\hat{x} \rightarrow \infty$ . Thus  $dH/dx$  must attain its maximum value in the surface tension region, this value being given by (4.41). Thus the condition that  $dH/dx$  is small everywhere, may be written as

$$U \ll \left( \frac{S^2 \sigma_{12} \rho_1^2 (\rho_2 - \rho_1) g}{\mu_2^2 \rho_2^4} \right)^{\frac{1}{2}}. \quad (5.8)$$

In a similar manner the condition for the slope of the oil-water interface to be small may be obtained as

$$U \ll \left( \frac{S^2 \sigma_{12} (\rho_2 - \rho_1) g}{\mu_2^2 \rho_1^2} \right)^{\frac{1}{4}}. \tag{5.9}$$

Should this condition be violated, then there is the possibility that one may get boundary-layer separation in the surface tension region which would affect both boundary layer and oil thickness profile downstream of this region. However, this would not occur (the boundary layer being modified only in a minor way) if the boundary-layer thickness  $(\nu_2 d/U)^{\frac{1}{2}}$  is very much larger than the depth variation of the oil-water interface in the surface tension region [determined in a manner similar to (4.40)], i.e. if

$$U \ll \left( \frac{S^6 (\rho_2 - \rho_1)^3 g^3}{\sigma_{12} \mu_2^2 \rho_1^2 \rho_2^4} \right)^{\frac{1}{4}}. \tag{5.10}$$

Thus if both (5.9) and (5.10) are violated, there is the possibility of boundary-layer separation.

(iv) *Neglect of inertia effects in the oil.* The condition for the neglect of inertia effects in the oil layer (see DHC) may be written as

$$\frac{U_c}{\nu_1} H \frac{dH}{dx} \ll 1, \tag{5.11}$$

where  $U_c$  is the characteristic velocity locally in the oil layer. For situations where the velocity variation across the oil layer is small compared to that across the boundary layer [see assumption (i) above],  $U_c \sim (\Delta u)_{o11}$  in (3.2) so that

$$U_c \simeq \frac{\mu_2 H}{\mu_1 \delta} U.$$

Thus, condition (5.11) becomes

$$\frac{\mu_2}{\mu_1} \frac{U}{\delta \nu_1} H^2 \frac{dH}{dx} \ll 1,$$

which when expressed in outer variables by (5.1), (2.3) and (2.4), becomes

$$\left( \frac{U^{12} \mu_2^4 \sigma_{12}^3 \rho_1^2 \rho_2^4}{S^6 \mu_1^4 (\rho_2 - \rho_1)^3 g^3} \right)^{\frac{1}{2}} \frac{1}{(\hat{x} + 1)^{\frac{1}{2}}} \hat{H}^2 \frac{d\hat{H}}{d\hat{x}} \ll 1.$$

Substituting the value of  $\hat{H}$  given by (4.10a), one obtains

$$\left( \frac{U^{12} \mu_2^4 \rho_2^7}{S^3 \mu_1^4 \rho_1 (\rho_2 - \rho_1)^3 g^3} \right)^{\frac{1}{2}} (\hat{x} + 1)^{-1} [(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}} \ll 1.$$

The expression  $(\hat{x} + 1)^{-1} [(\hat{x} + 1)^{\frac{1}{2}} - 1]^{\frac{1}{2}}$  increases from zero at  $\hat{x} = 0$  and attains a maximum value of  $9/16\sqrt{3}$  at  $\hat{x} = \frac{7}{9}$  and then decreases to zero as  $\hat{x} \rightarrow \infty$ . Thus, inertia effects in the oil are negligible everywhere if

$$U \ll \left( \frac{S^3 \mu_1^4 \rho_1 (\rho_2 - \rho_1)^3 g^3}{\mu_2^4 \rho_2^7} \right)^{\frac{1}{4}}. \tag{5.12}$$

(v) *Neglect of pressure variations in substrate flow.* The flow in the substrate is disturbed from its uniform motion by (i) the depression of the oil-water interface below the bulk layer and (ii) the finite thickness of the boundary layer. Since the

vertical component of velocity at the oil-water interface is of order  $U dh_{12}/dx$ , the inviscid disturbance flow due to the depression of the oil-water interface is of this order. Thus, the flow fluid in the water below the boundary layer is of the form  $U\mathbf{i} + O(U dh_{12}/dx)$ , where  $\mathbf{i}$  is unit vector in the  $x$  direction. Then, using Bernoulli's equation, we obtain the pressure variations in the substrate at any point near the oil-water interface as being of order  $\rho_2 U^2 dh_{12}/dx$ , giving rise to an additional stress on the oil of this order in the vertical direction. This has a negligible effect if it is small compared with the stress  $\rho_2 gH$ , i.e. if

$$\frac{U^2 dh_{12}}{gH dx} \ll 1, \quad (5.13)$$

or in terms of outer variables [using equation (4.10)], if

$$\left(\frac{U^5 \mu_2 \rho_1}{gS^2}\right) [(1 + \hat{x})^{\frac{1}{2}} - 1]^{-1} (1 + \hat{x})^{-\frac{1}{2}} \ll 1. \quad (5.14)$$

Since the expression  $[(1 + \hat{x})^{\frac{1}{2}} - 1]^{-1} (1 + \hat{x})^{-\frac{1}{2}}$  is unbounded as  $\hat{x} \rightarrow 0$ , it follows that the effect of substrate pressure variations is greatest in the surface tension region. Thus (5.13) is satisfied everywhere if it is satisfied for characteristic values of  $H$  and  $dh_{12}/dx$  valid in the surface tension region. This gives

$$U \ll \left(\frac{\sigma_{12} \rho_2^2 g}{\rho_1^2 (\rho_2 - \rho_1)}\right)^{\frac{1}{4}} \quad (5.15)$$

as the required condition for the neglect of substrate pressure variations due to depression of the oil-water interface.

In a similar manner it is seen that the substrate pressure variations due to the boundary-layer displacement thickness are negligible if

$$\frac{U^2}{g} \frac{1}{H} \frac{d\delta}{dx} \ll 1. \quad (5.16)$$

Again it is seen that this condition is most likely to be violated in the surface tension region, so that by substituting the characteristic values of  $H$  and  $\delta$  given by (4.40) and (5.1), the condition that the effect of the boundary-layer displacement thickness is negligible everywhere is that

$$U \ll \left(\frac{S^2 \sigma_{12} \rho_2^4 g}{\mu_2^2 \rho_1^2 (\rho_2 - \rho_1)^3}\right)^{\frac{1}{4}}. \quad (5.17)$$

However, this condition may be too severe since we have used the value  $\rho_2 U^2 d\delta/dx$  [which by (5.1) is of order  $\rho_2 U^2 (\nu_2/dU)^{\frac{1}{2}}$ ] for the order of magnitude of the pressure variations on the oil-water interface, whereas (Van Dyke 1964) it is known that for a boundary layer on a flat plate in a uniform stream the pressure variation is smaller by a factor of  $(\nu_2/dU)^{\frac{1}{2}}$ .

(vi) *Assumption that the boundary layer is laminar.* Throughout the entire monolayer and also for the bulk layer where condition (3.3) (that the velocity across the oil layer is small) is satisfied, the boundary layer in the substrate is identical to that on a flat plate. This boundary layer is laminar at a distance  $(x + d)$  from the leading edge of the monolayer if (Schlichting 1968)

$$\frac{U(x + d)}{\nu_2} < Re_c, \quad (5.18)$$

where  $Re_c$  is a critical Reynolds number whose value is of the order  $3.5 \times 10^5$  to  $1.0 \times 10^6$ . Thus, from (4.3), it is seen that the boundary layer is laminar beneath the entire monolayer if

$$U > [(2\alpha)^{-1} (Re_c)^{-\frac{1}{2}}] S / \mu_2, \tag{5.19}$$

this corresponding to a size  $d$  of monolayer with

$$d < (2\alpha) (Re_c)^{\frac{1}{2}} \frac{\mu_2^2}{\rho_2 S}, \tag{5.20}$$

which is approximately 60 m for  $S = 10 \text{ dyn cm}^{-1}$ . Also, when the size ( $l$ ) of the bulk layer is much larger than the size of the monolayer, it is seen from (4.30) and (5.18) that the boundary layer is laminar beneath the entire bulk layer if

$$U < \left(\frac{64\alpha}{25}\right) (Re_c)^{\frac{1}{2}} \frac{\mu_2^3}{\rho_1 \rho_2 (\rho_2 - \rho_1) g V^2}, \tag{5.21}$$

this corresponding to the size  $l$  of layer for which

$$l > \left(\frac{25}{64\alpha}\right) (Re_c)^{-\frac{1}{2}} \frac{\rho_1 (\rho_2 - \rho_1) g V^2}{\mu_2^2}. \tag{5.22}$$

(vii) *No depletion of monolayer.* It may be noted that if the volume  $V$  of oil is reduced keeping the flow velocity  $U$  fixed, then a stage will be reached when there will be no bulk layer. Should this occur then after a further reduction in  $V$ , the surface tension at the barrier will drop below the value  $\sigma_{12} + \sigma_{13}$  so that the monolayer length will no longer be given by (4.3). This will occur when

$$\frac{\epsilon S^2}{4\alpha^2 U^3 \mu_2 \rho_2} > V \quad \text{or} \quad U < \left(\frac{\epsilon S^2}{4\alpha^2 \mu_2 \rho_2 V}\right)^{\frac{1}{3}}, \tag{5.23}$$

where  $\epsilon$  is the mean thickness of the monolayer. Such a depleted monolayer therefore occurs for small oil volumes and for small substrate velocities.

## 6. The effect of the turbulent boundary layer

From (5.19) and (5.21) it is seen that the boundary layer in the substrate is predominately turbulent if

either 
$$U \ll [(2\alpha)^{-1} (Re_c)^{-\frac{1}{2}}] \frac{S}{\mu_2} \tag{6.1}$$

or 
$$U \gg \left(\frac{64\alpha}{25}\right) (Re_c)^{\frac{1}{2}} \frac{\mu_2^3}{\rho_1 \rho_2 (\rho_2 - \rho_1) g V^2}. \tag{6.2}$$

Under such conditions the stress  $\tau^*$  (assuming small velocity difference across the bulk layer) on the oil (Schlichting 1968) is

$$\tau^* = \alpha_t \rho_2 U^2 \left(\frac{U}{\nu_2}\right)^{-\frac{1}{2}} (x+d)^{-\frac{1}{2}} \quad \text{where} \quad \alpha_t = 0.029. \tag{6.3}$$

Repeating the previous analysis by replacing the expression (4.1) for  $\tau^*$  by (6.3), we obtain the following results.

(i) The length  $d$  of monolayer is [cf. equation (4.3)]

$$d = \left(\frac{5}{4}\alpha_t\right)^{-\frac{1}{2}} \left(\frac{S^5}{\mu_2 \rho_2^4 U^9}\right)^{\frac{1}{2}}. \quad (6.4)$$

The thickness  $H$  of the oil in the gravity viscous region is [cf. equation (4.10a)]

$$H = \sqrt{2} \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{S}{(\rho_2 - \rho_1)g}\right)^{\frac{1}{2}} \{(\hat{x} + 1)^{\frac{1}{2}} - 1\}^{\frac{1}{2}}, \quad (6.5)$$

where  $\hat{x} = x/d$  and  $d$  is the monolayer length given by (6.4). From this expression it is seen that the length  $l$  of the gravity viscous region, when it is much larger than  $d$ , is [cf. equation (4.30)]

$$l \simeq \left(\frac{7}{5}\right)^{\frac{2}{5}} \left(\frac{2}{5\alpha_t}\right)^{\frac{2}{5}} \left(\frac{\rho_1(\rho_2 - \rho_1)}{\rho_2^2}\right)^{\frac{2}{5}} \left(\frac{\rho_2 g^5 V^{10}}{\mu_2 U^9}\right)^{\frac{1}{5}}, \quad (6.6)$$

the height  $h_1$  of oil at the barrier then being [cf. equation (4.34)]

$$h_1 \simeq \left(\frac{7}{5}\right)^{\frac{2}{5}} \left(\frac{5\alpha_t}{2}\right)^{\frac{2}{5}} \left(\frac{\rho_2^2}{\rho_1(\rho_2 - \rho_1)}\right)^{\frac{2}{5}} \left(\frac{\mu_2 U^9 V^4}{\rho_2 g^5}\right)^{\frac{1}{5}} \quad (6.7)$$

(ii) The condition that  $l$  be very much larger than  $d$  [so that (6.6) and (6.7) are valid] is [cf. equation (4.39)]

$$U \gg 2^{\frac{2}{5}} \left(\frac{5}{7}\right)^{\frac{2}{5}} \left(\frac{2}{5\alpha_t}\right)^{\frac{2}{5}} \left(\frac{\rho_2^2}{\rho_1(\rho_2 - \rho_1)}\right)^{\frac{2}{5}} \left(\frac{S^7}{\mu_2 \rho_2^6 g^2 V^4}\right)^{\frac{1}{5}}. \quad (6.8)$$

(iii) The condition for small velocity variation across the bulk layer compared with  $U$ , which for a turbulent boundary layer should be more properly used in the form  $H\tau^*/\mu_1 U \ll 1$ , reduces to [cf. equation (5.2)]

$$\left(\frac{\rho_2^2}{\rho_1(\rho_2 - \rho_1)}\right)^{\frac{1}{2}} \left(\frac{\mu_2 \rho_2^2 S U^5}{\mu_1^4 g^2}\right)^{\frac{1}{2}} \frac{\{(1 + \hat{x})^{\frac{1}{2}} - 1\}^{\frac{1}{2}}}{(1 + \hat{x})^{\frac{1}{2}}} \ll 1. \quad (6.9)$$

Since the left-hand side increases monotonically with  $\hat{x}$  and  $\rightarrow \infty$  as  $\hat{x} \rightarrow \infty$ , it follows that the condition is most likely to be violated at the barrier at  $\hat{x} = l/d$ . Thus, for the gravity viscous dominated situation ( $l \gg d$ ), it is seen that the velocity variation across the oil is small everywhere if [cf. equation (5.3)]

$$U \ll \left(\frac{\rho_1(\rho_2 - \rho_1)}{\rho_2^2}\right)^{\frac{2}{11}} \left(\frac{\mu_1^7 g^3}{\mu_2^2 \rho_2^5 V}\right)^{\frac{1}{11}} \quad (6.10)$$

(iv) The length of the surface tension region is much smaller than the monolayer length  $d$  if [cf. equation (5.5)]

$$U \ll \left(\frac{(\rho_2 - \rho_1)^2 g^2 S^5}{\mu_2 \rho_2^4 \sigma_{12}^2}\right)^{\frac{1}{5}} \quad (6.11)$$

and much smaller than the bulk layer length if [cf. equation (5.6)]

$$U \ll \left(\frac{\rho_1(\rho_2 - \rho_1)}{\rho_2^2}\right)^{\frac{2}{5}} \left(\frac{\rho_2(\rho_2 - \rho_1)^7 g^{12} V^{10}}{\mu_2 \sigma_{12}^7}\right)^{\frac{1}{5}} \quad (6.12)$$

for  $l \gg d$ .

(v) For slopes of interfaces to be small (i.e.  $dH/dx \ll 1$ ) we require

$$\left(\frac{\rho_2^2}{\rho_1(\rho_2 - \rho_1)}\right)^{\frac{1}{2}} \left(\frac{\mu_2 \rho_2^2 U^8}{g^2 S^3}\right)^{\frac{1}{4}} \{(1 + \hat{x})^{\frac{1}{2}} - 1\}^{-\frac{1}{2}} (1 + \hat{x})^{-\frac{1}{2}} \ll 1,$$

the left-hand side of which is a monotonically decreasing function which  $\rightarrow \infty$  as  $\hat{x} \rightarrow 0$ . Thus, interface slopes are greatest close to surface tension region and the condition that they are small everywhere is thus [cf. equation (5.8)]

$$U \ll \left(\frac{\rho_1(\rho_2 - \rho_1)}{\rho_2^2}\right)^{\frac{1}{2}} \left(\frac{g^2 S \sigma_{12}^2}{\mu_2(\rho_2 - \rho_1)^2}\right)^{\frac{1}{4}}. \quad (6.13)$$

(vi) The condition for the neglect of inertia effects in the oil may be written as

$$\frac{\tau^*}{\mu_1 \nu_1} H^2 \frac{dH}{dx} \ll 1,$$

which reduces to

$$\left(\frac{\mu_2 \rho_2^7 U^9}{\mu_1^4 \rho_1(\rho_2 - \rho_1)^3 g^3}\right)^{\frac{1}{2}} \{(1 + \hat{x})^{\frac{1}{2}} - 1\}^{\frac{1}{2}} (1 + \hat{x})^{-\frac{3}{2}} \ll 1. \quad (6.14)$$

Thus, since the left-hand side is bounded for all  $\hat{x}$ , the condition for the neglect of inertia everywhere is [cf. equation (5.12)]

$$U \ll \left(\frac{\mu_1^4 \rho_1(\rho_2 - \rho_1)^3 g^3}{\mu_2 \rho_2^4}\right)^{\frac{1}{2}}. \quad (6.15)$$

(vii) The condition (5.13) for the neglect of pressure variations in the substrate flow now reduces to [cf. equation (5.14)]

$$\frac{U^2 \rho_1}{g \rho_2} \left(\frac{\mu_2 \rho_2^4 U^8}{S^5}\right)^{\frac{1}{4}} \{(1 + \hat{x})^{\frac{1}{2}} - 1\}^{-1} (1 + \hat{x})^{-\frac{1}{2}} \ll 1, \quad (6.16)$$

the left-hand side of which is unbounded as  $\hat{x} \rightarrow 0$ . Thus, the effect is most likely to be important in the surface tension region, the condition for its neglect everywhere being

$$U \ll \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}} \left(\frac{\sigma_{12} g}{(\rho_2 - \rho_1)}\right)^{\frac{1}{4}}, \quad (6.17)$$

which is seen to be identical with (5.15).

(viii) The condition for the monolayer to become depleted is [cf. equation (5.23)]

$$U < \left(\frac{5}{4} \alpha_t\right)^{-\frac{1}{2}} \left(\frac{S^5 \epsilon^4}{\mu_2 \rho_2^4 V^4}\right)^{\frac{1}{2}}. \quad (6.18)$$

## 7. Conclusions

For any particular spreading fluid, the general behaviour (determined by the results of §§ 4–6) of a volume  $V$  per unit width of the fluid held in a steady state configuration against a uniform flow  $U$  by a barrier may be represented on a  $UV$  graph on which the various spreading regimes are indicated. This has been done in figure 8 for a fluid for which  $\mu_1 = 10$  P,  $\rho_1 = 0.9$  g cm<sup>-3</sup>,  $S = \sigma_{12} = 10$  dyn cm<sup>-1</sup> spreading on water ( $\mu_2 = 10^{-2}$  P,  $\rho_2 = 1$  g cm<sup>-3</sup>). Thus the values of  $U$  and  $V$  for the gravity-viscous regions with laminar (region *A*) and turbulent (region *B*) boundary layers are shown, as are also the monolayer regions with laminar (region *C*) and tur-

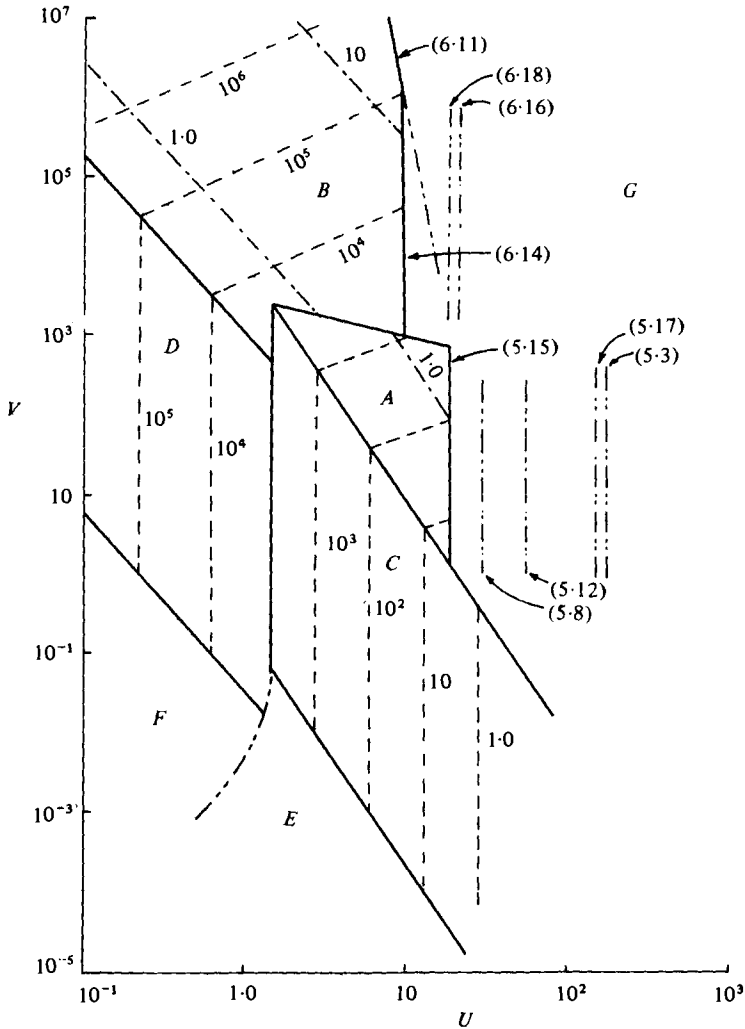


FIGURE 8. The various regimes of spreading behaviour for oil of volume  $V$  ( $\text{cm}^2$ ) per unit width held in a steady-state configuration against a uniform flow of velocity  $U$  ( $\text{cm s}^{-1}$ ) ( $\mu_1 = 10 \text{ P}$ ,  $\mu_2 = 10^{-2} \text{ P}$ ,  $\rho_1 = 0.9 \text{ g cm}^{-3}$ ,  $\rho_2 = 1.0 \text{ g cm}^{-3}$ ,  $S = \sigma_{12} = 10 \text{ dyn cm}^{-1}$ ). ---, lines of constant length of layer (measured in cm); - - - - , lines of constant layer thickness at barrier (measured in cm).

bulent (region  $D$ ) boundary layers and the depleted monolayers with laminar (region  $E$ ) and turbulent (region  $F$ ) boundary layers. The lines of constant layer length and of constant depth at the barrier have also been plotted. However, the boundary between the regions  $E$  and  $F$  of the depleted monolayer, as well as the lines of constant layer length in these regions  $E$  and  $F$ , have not been plotted as their form depends upon the specific  $(\sigma, H)$  relation for the monolayer. It is also found for this example that the gravity viscous regime for a laminar boundary layer (region  $A$ ) does not extend beyond a value of  $U = 18.7 \text{ cm s}^{-1}$  at which point the effect of substrate pressure variations [determined by (5.15)] become important. All the other limitations of the theory [determined by (5.3), (5.8), (5.12) and (5.17)] also shown in figure 8, are seen to occur



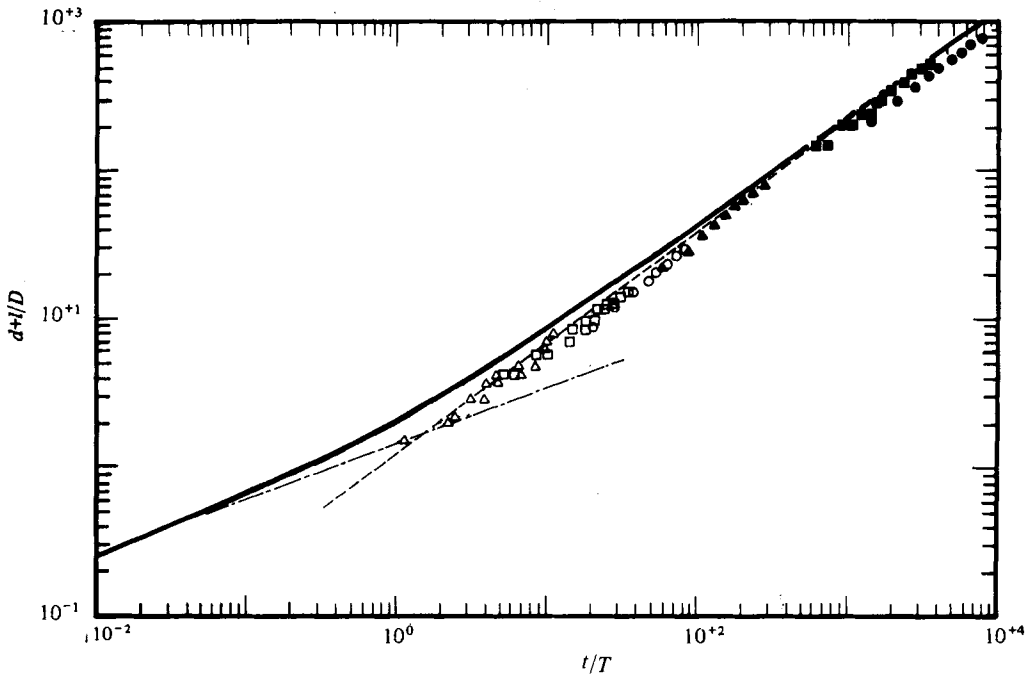


FIGURE 9. Experimentally obtained values (Huh *et al.* 1975) of dimensionless length  $d+l/D$  of oil spreading along a channel as a function of dimensionless time  $t/T$  for:  $\bullet$ ,  $V = 0.105 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 50 \text{ cSt}$ ;  $\blacksquare$ ,  $V = 0.105 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 10 \text{ cSt}$ ;  $\blacktriangle$ ,  $V = 0.7 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 10 \text{ cSt}$ ;  $\circ$ ,  $V = 1.75 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 10 \text{ cSt}$ ;  $\square$ ,  $V = 3.50 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 10 \text{ cSt}$ ;  $\triangle$ ,  $V = 6.99 \text{ cm}^2$ ,  $\mu_1/\rho_1 = 10 \text{ cSt}$ . The continuous line is theoretical result based on quasi-static assumption. - - -, asymptotic form for small  $t/T$  given by (7.1b), - - -, asymptotic form for large  $t/T$  given by (7.2b).

at higher values of  $U$ . The gravity viscous regime with turbulent boundary layer (region *B*) does not extend beyond  $U = 9.5 \text{ cm s}^{-1}$  [given by (6.14)] at which the slope of the oil-water interface becomes large. However, at large oil volumes ( $V > 1.23 \times 10^6 \text{ cm}^2$ ) the upper limit of  $U$  is determined by the condition (6.11) for small velocity variations across the oil layer. The other conditions of validity of the theory [determined by equations (6.16) and (6.18)] also shown in figure 8, are seen to occur at higher values of  $U$ . Beyond these upper limits of  $U$  for which the theory is valid (denoted by region *G*), the various effects discussed in § 5 would become important so that the general theory would have to be modified accordingly.

However, it should be emphasized that the boundaries between the regimes are not really sharp as shown in figure 8 since for values of  $U$  and  $V$  near a boundary line, regions corresponding to the regimes on either side of the boundary line can be expected to exist simultaneously. For example, near the boundary line between regimes *A* and *C*, one would have a gravity viscous region near the barrier and a monolayer region further from the barrier (separated from each other by a small surface tension region). Furthermore, it should be mentioned that what is shown in figure 8 is merely an example and that spreading fluids with different physical properties could have  $UV$  diagrams which are significantly different. Thus, while in the present example, the surface tension region is never dominant, there may be other spreading fluids for which it is for some region of the  $UV$  diagram.

From these results (and those in §§ 4–6) one can determine for any spreading fluid, the maximum volume of oil that can be held back by a containment boom of a given depth deployed across a stream flowing with a given velocity  $U$  (so long as  $U$  is not so large that one is within the unknown region  $G$ ).

While there appears to be no quantitative experimental results which can be directly compared with the results of the above theory, it is interesting to note that when these results are applied to the unsteady spreading of oil on the surface of quiescent water contained in a channel (by assuming that such spreading is quasi-steady) good agreement between theory and experiment is obtained (see Huh, Inoue & Mason, 1975). Thus by integrating numerically

$$U = \frac{d}{dt}(d+l)$$

with  $d$  given by (4.3) and with  $l$  by (4.28) a relation between  $(d+l)$  and  $t$  is obtained. This is plotted in figure 9 together with experimental results using the same dimensionless quantities as used by Huh *et al.* (1975), namely  $(d+l)/D$  and  $t/T$ , where

$$D = 5V/4(2S/\rho_1(1-\rho_1/\rho_2)g)^{\frac{1}{2}}$$

and

$$T = [25\alpha\rho_1(1-\rho_1/\rho_2)gV^2(\mu_2\rho_2)^{\frac{1}{2}}/16S^2]^{\frac{1}{3}}.$$

The asymptotic form for small  $t$  (for which  $l \gg d$ ), obtained from (4.30) with  $U = dl/dt$ , is

$$d+l \simeq l = \left(\frac{8}{3}\right)^{\frac{1}{3}} \left(\frac{25}{64\alpha}\right)^{\frac{1}{2}} \left(\frac{V^4\rho_1^2(\rho_2-\rho_1)^2g^2}{\mu_2\rho_2^3}\right)^{\frac{1}{3}} t^{\frac{1}{3}} = 1.5044 \left(\frac{V^4\rho_1^2(\rho_2-\rho_1)^2g^2}{\mu_2\rho_2^3}\right)^{\frac{1}{3}} t^{\frac{1}{3}} \quad (7.1a)$$

or

$$\frac{d+l}{D} = \left(\frac{8}{3}\right)^{\frac{1}{3}} \left(\frac{t}{T}\right)^{\frac{1}{3}} = 1.445 \left(\frac{t}{T}\right)^{\frac{1}{3}}. \quad (7.1b)$$

This is also plotted in figure 9. The experimental results of Suchon (1970) agrees well with the above equation (7.1a) (see Hault 1972) but have not been plotted on figure 9 since the value of  $S$  was not known for the liquids used. The asymptotic form for large  $t$  (for which  $d \gg l$ ) is obtained from (4.3) with  $U = d(d)/dt$  as

$$d+l \simeq d = \left(\frac{4}{3}\right)^{\frac{1}{2}} \left(\frac{1}{2\alpha}\right)^{\frac{1}{2}} \left(\frac{S^2}{\mu_2\rho_2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} = 1.523 \left(\frac{S^2}{\mu_2\rho_2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} \quad (7.2a)$$

or

$$\frac{d+l}{D} = \left(\frac{4}{3}\right)^{\frac{1}{2}} \left(\frac{t}{T}\right)^{\frac{1}{2}} = 1.241 \left(\frac{t}{T}\right)^{\frac{1}{2}}. \quad (7.2b)$$

This is also plotted on figure 9 for comparison.

The physical properties of the liquids used in the experimental results shown in figure 9 have been tabulated in table 1 from which it is seen that the experiments covered a range of  $l/d$  from 0.017 to 1.67. In particular the range of velocity  $U$  is shown for each experiment together with the conditions on  $U$  [given by (5.3), (5.9), (5.12), (5.15), (5.17) and (5.19)] for the validity of the theory. It is seen that all conditions are satisfied except for the experiments with high values of  $U$  (i.e. small values of  $l$  and  $d$ ) with an oil volume of 6.99 cm<sup>2</sup> for which inertia effects within the oil may be important. Although it may appear that inertia effects may not be negligible for

Symbol used in figure 9 ...	●	■	▲	○	□	△
Oil viscosity $\mu_1$ (P)	0.48	0.0934	0.0934	0.0934	0.0934	0.0934
Oil density $\rho_1$ (g cm <sup>-3</sup> )	0.96	0.934	0.934	0.934	0.934	0.934
Oil volume $V$ (cm <sup>3</sup> )	0.105	0.105	0.70	1.75	3.50	6.99
Spreading coefficient $S$ (dyn cm <sup>-1</sup> )	16.4	11.9	11.9	11.9	11.9	11.9
Oil-water interfacial tension $\sigma_{12}$ (dyne cm <sup>-1</sup> )	34.3	39.5	39.5	39.5	39.5	39.5
Range of monolayer length $d$ (cm)	28.4 -109.6	31.8 -106.3	26.2 -103.4	23.9 -91.6	18.0 -91.5	8.3 -77.5
Range of bulk layer length $l$ (cm)	1.19 -1.84	1.16 -2.39	4.4 -7.8	7.4 -12.8	11.2 -19.9	13.9 -33.7
Range of values of $l/d$	0.017 -0.042	0.022 -0.051	0.075 -0.17	0.14 -0.31	0.22 -0.62	0.43 -1.67
Range of velocity $U$ (cm s <sup>-1</sup> )	8.2 -12.9	6.7 -10.0	6.8 -10.7	7.0 -11.0	7.1 -12.1	7.5 -15.7
Conditions of validity:						
Small velocity variation across oil layer [see (5.3)], $U$ (cm s <sup>-1</sup> ) <	34.5	15.8	15.8	15.8	15.8	15.8
Small slopes of interfaces [see (5.9)] $U$ (cm s <sup>-1</sup> ) <	39.7	40.1	40.1	40.1	40.1	40.1
Neglect of inertia effects in oil layer [see (5.12)], $U$ (cm s <sup>-1</sup> ) <	18.2	11.0	11.0	11.0	11.0	11.0
Neglect of inertia effects in water, (i) condition (5.15), $U$ (cm s <sup>-1</sup> ) <	30.9	28.6	28.6	28.6	28.6	28.6
(ii) condition (5.17), $U$ (cm s <sup>-1</sup> ) <	340.0	245.0	245.0	245.0	245.0	245.0
Boundary layer is laminar [see (5.19)], $U$ (cm s <sup>-1</sup> ) >	3.2	2.3	2.3	2.3	2.3	2.3

TABLE 1. Comparison between the experimental situations examined by Inoue, Huh & Mason (1975) and the corresponding conditions of validity of the theory.

smaller oil volumes, this is not so, since the position  $\hat{x} = \frac{7}{8}$  where inertia effects become large does not exist owing to the small values of  $l/d$ .

This work was supported by the National Sciences and Engineering Research Council of Canada under grant no. A7007.

#### REFERENCES

- ADAMSON, A. W. 1967 *Physical Chemistry of Surfaces*. Interscience.  
 AHMAD, J. & HANSEN, R. S. 1972 *J. Colloid Interface Sci.* **38**, 601.  
 BANKS, W. H. 1957 *Proc. 2nd Int. Congr. Surface Activity*, vol. 1, p. 16.  
 BUCKMASTER, J. 1973 *J. Fluid Mech.* **59**, 481.  
 BURGERS, W. G., GREUP, D. H. & KORVEZEE, A. E. 1950 *Recueil* **69**, 921.  
 DI PIETRO, N. D. 1975 M.Sc. dissertation, McGill University, Montreal.  
 DI PIETRO, N. D., HUH, C. & COX, R. G. 1978 *J. Fluid Mech.* **84**, 529.  
 FAY, J. A. 1969 The spread of oil slicks on a calm sea. In *Oil on the Sea* (ed. D. P. Hoult). Plenum Press.

- GARRETT, W. D. & BARGER, W. R. 1970 *Envir. Sci. Tech.* **4**, 123.
- GUTTENBERG, W. VON 1941 *Z. Phys.* **118**, 22.
- HARKINS, W. D. 1952 *The Physical Chemistry of Surface Films*. New York: Reinhold.
- HOULT, D. P. 1972 *Ann. Rev. Fluid Mech.* **4**, 341.
- HUH, C., INOUE, M. & MASON, S. G. 1975 *Can. J. Chem. Engng* **53**, 367.
- LANDT, E. & VOLMER, M. 1926 *Z. Phys. Chem.* **122**, 398.
- LANGMUIR, I. 1936 *Science* **84**, 379.
- LUGTON, F. D. & VINES, R. G. 1960 *Australian J. Appl. Sci.* **11**, 497.
- MAR, A. & MASON, S. G. 1968 *Kolloid Z. Z. Polymere* **225**, 55.
- MARWEDEL, G. & JEBSEN-MARWEDEL, H. 1961 *Farbe u. Lack* **67**, 276.
- MERCER, E. H. 1939 *Proc. Phys. Soc.* **51**, 561.
- PUJADO, P. R. & SCRIVEN, L. E. 1972 *J. Colloid Interface Sci.* **40**, 82.
- SCHLICHTING, H. 1968 *Boundary Layer Theory*. McGraw Hill.
- SUCHON, W. 1970 An experimental investigation of oil spreading over water, M.S. thesis (Mech. Eng.), MIT.
- VAN DYKE, M. D. 1964 *Perturbation Methods in Fluid Mechanics*. Academic.
- WICKS, M. 1969 *Proc. Joint Conf. Prevention and Control of Oil Spills*. API and FWPCA, New York.
- ZISMAN, W. A. 1941 *J. Chem. Phys.* **9**, 534.