Deformation of Advancing Menisci

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To date there exists no complete treatment of the hydrodynamics of spreading of liquids on solids, which is consistent with the Navier-Stokes equations of motion. Consequently our understanding of such phenomena as capillary rise, multiphase flow through porous media, and spontaneous climbing or spreading of thin films on solids, is incomplete.

The basic difficulty lies in explaining the large translational velocities which must occur in the thin region at the leading edge of the film (near the three-phase interline). According to conventional hydrodynamic treatment the velocity should go to zero as the film thickness goes to zero. Available descriptions either ignore the details of the fluid flow near the leading edge (*1* to *3*) or offer empirical corrections to the meniscus shape in the form of a velocity-dependent apparent contact angle (*4*).

There is, however, ample reason to be concerned with such flow behavior. It has been shown that the optically measurable contact angle between an advancing meniscus and the adjacent solid is greater than the equilibrium contact angle and increases with velocity of advance (*4, 5*). As a result the component of the surface tension force in the direction of motion is less than for a static system. In addition a finite force is required to initiate motion, depending on equilibrium contact angle but in some cases apparently independent of surface roughness (*5*). Finally it has been reported that dry capillary tubes behave differently than previously wetted but well drained ones (*2*). It is therefore of interest to find out to what extent a hydrodynamic treatment can elucidate such phenomena and where it fails.

PHYSICOCHEMICAL THEORIES OF SPREADING

Although the thermodynamic conditions for wetting and spreading are well established, the method by which the liquid advances over the immobile solid surface is not well understood. Some model for spreading however must be postulated and several possibilities have been suggested.

The Distillation Theory.

Hardy (*6*) noted that if a drop of lubricant having an appreciable vapor pressure were placed on a surface of glass, its lubricating effects could be felt at some distance from the drop. Out of this grew the theory, which Hardy's experiments seemed to confirm, that a primary film of liquid was formed by condensation or adsorption from the vapor phase, and the bulk liquid then spread over it.

Multilayer adsorption is a well established process which at high relative saturation can give rise to films of appreciable thickness as can be seen from the familiar Brunauer-Emmett-Teller equation or various modifications of it.

Surface Diffusion Theory

For liquids of low vapor pressure the distillation process is doubtful. In fact Bascom, Cottington, and Singleterry (*7*) showed experimentally that a primary film spread over a long distance on a flat plate while no film was detected on another plate placed parallel and closer to the bulk film than the final spreading distance. They concluded from this that in their experiments the primary film must be advanced by surface diffusion and not through the vapor phase.

Long Range Intermolecular Forces

It has long been clear from theoretical and experimental evidence that many surface phenomena must be explained by the presence of unbalanced long range intermolecular forces, rather than nearest neighbor interactions (*8* to *10*). Examples of such forces include deep surface orientation of molecules, changes in viscosity of thin films compared to bulk values, electrical double layer or ionic atmospheres, etc.

It is not clear how long range forces should play a role in the spreading process, but changes in the double layer or distortion of it have been cited in explaining some spreading phenomena on mercury (*11*). It is also conceivable that changes in cohesive forces in very thin layers can give rise to slip conditions favorable to advancing the front. Perhaps the most interesting possibility is the suggestion of Derjaguin, et al. (*12*) that diffuse ionic atmospheres and molecular force-interactions give rise to what they have termed the disjoining pressure, which is analogous to osmotic pressure in that the chemical potential of the fluid film is changed by the presence of the interfaces. According to the theories of Derjaguin, et al., large pressure gradients could be expected in such thin films, which in turn could explain large translational velocities near the solid not expected from consideration of capillary forces alone.

Whatever the mechanism of film advancement it must be compatible with the Navier-Stokes equations in the bulk of the advancing liquid. In this paper we seek to determine the requirements of these equations by considering a very simple capillary phenomenon, with the hope that it may provide a guide in subsequent investigations of liquid behavior near solid surfaces. In the present analysis we ignore the possibility of slip between the solid and liquid, and base our treatment instead on postulated preformed liquid films, which may be produced by any combination of multilayer adsorption, distillation, or surface diffusion. We hope to consider the possibilities of slip in a subsequent paper.

MODEL OF AN ADVANCING FRONT BASED ON A PRIMARY FILM CONCEPT

We consider the system shown in Figure 1 which depicts a meniscus of liquid rising in a long capillary slit. The equilibrium contact angle is taken to be zero, that is the liquid wets the solid. We focus our attention on the thin terminal region of the meniscus where the free surface is nearly parallel to the solid wall or more precisely where $\left| \frac{dh}{dz} \right| << 1$. We anticipate that this region is of critical importance in determining the meniscus shape and the capillary rise behavior.

In this region we are able to make several useful simplifications:

1. the flow is essentially one-dimensional
2. gravitational effects are negligible compared to surface tension effects
3. curvature pressure or capillary pressure is transmitted undiminished across the film
4. acceleration and inertial effects can be neglected since the local Reynolds number will be small in the thin film region $\left(\frac{<v_z>h}{\nu} << 1 \right)$

The second assumption is good for capillary systems for which the dimensionless surface tension $\gamma/\rho g B^2$ is larger than 50. This restricts our quantitative results to capillary slits or tubes whose half width, or radius, is about 0.025 cm. or less for most organic liquids, but at our present level of treatment this does not affect the quantitative insight given by the analytical results obtained. Gravitational forces can be taken into consideration, and we are in fact doing so in further work now in progress. The most limiting of the above assumptions is the first one, since circulation or rolling action at the front is thereby excluded, but this seems reasonable for systems with small contact angle.

The equation of motion then takes the forms

$$\frac{\partial P}{\partial y} = \frac{\partial P}{\partial x} = 0 \tag{1}$$

$$-\frac{\partial P}{\partial z} + \mu \frac{\partial^2 v_z}{\partial y^2} = 0 \tag{2}$$

We now integrate Equation (2) with respect to y at constant z subject to the conventional Nusselt boundary conditions of no shear at the free surface and no slip at the solid:

$$\text{boundary condition 1.} \quad \text{at} \quad y = h \quad \frac{\partial v_z}{\partial y} = 0 \tag{3}$$

$$\text{boundary condition 2.} \quad \text{at} \quad y = 0 \quad v_z = 0 \tag{4}$$

Note that boundary condition 1 implies that surface tension gradients are absent.

This gives the velocity profile of the form:

$$v_z = \frac{1}{\mu} \left(\frac{\partial P}{\partial z} \right) \left(\frac{y^2}{2} - hy \right) \tag{5}$$

and an average velocity at any z is

$$<v_z> = -\frac{1}{\mu} \left(\frac{\partial P}{\partial z} \right) \frac{h^2}{3} \tag{6}$$

A mass balance for a segment dz of the film yields

$$\frac{\partial h}{\partial t} = -\frac{\partial (<v>h)}{\partial z} \tag{7}$$

Substituting for $<v>$ in this expression by using Equation (6) we obtain

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial z} \left[\frac{1}{\mu} \left(\frac{\partial P}{\partial z} \right) \frac{h^3}{3} \right] \tag{8}$$

This relation can be used to describe a wide variety of spreading phenomena provided an appropriate expression for P is known, but we shall limit further attention to one very simple operation, that is, steady flow upward in a vertical capillary slit at a constant velocity β. After sufficient time has elapsed, the meniscus will move at a velocity $v = \delta_z \beta$ and will maintain a constant shape which we wish to determine. The pressure in the thin meniscus region is effectively the surface pressure if we neglect the disjoining pressure contribution (12). Thus we can say

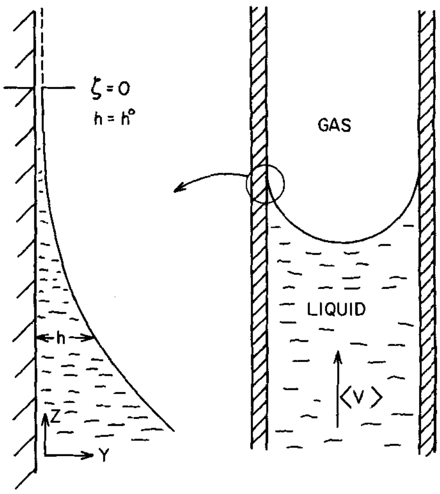

Fig. 1. Schematic representation of advancing front in a capillary.

$$P_G - P = \sigma \left(\frac{1}{R_c} \right) \tag{9}$$

For the region under consideration the radius of curvature R_c can be approximated as (13):

$$\frac{1}{R_c} \doteq \frac{\partial^2 h}{\partial z^2} \tag{10}$$

The sign of this expression is determined by recognizing that the local center of curvature is in the gas phase.

With these assumptions about the meniscus celerity and capillary pressure we can write Equation (8) in the form:

$$\beta \frac{dh}{d\zeta} = \frac{d}{d\zeta} \left[\frac{\sigma}{\mu} \frac{d^3 h}{d\zeta^3} \frac{h^3}{3} \right] \tag{11}$$

where $\zeta = z - \beta t$. We may immediately integrate Equation (11) once to get

$$\frac{d^3 h}{d\zeta^3} = \left[\frac{3\mu\beta}{\sigma} \right] \frac{h - h^o}{h^3} \tag{12}$$

where h^o is a constant of integration.

If $h^o = 0$ we see that as $h \to 0$ the third derivative becomes singular. In order to avoid this difficulty we postulate that the wall ahead of the advancing meniscus is covered with a flat film of liquid of thickness h^o, formed either by surface diffusion or a distillation mechanism, as discussed before.

We now introduce dimensionless variables, $\xi = \zeta/h^o$ and $\eta = h/h^o$. From Equation (12) we then get the expression:

$$\frac{d^3 \eta}{d\xi^3} = \left[\frac{3\mu\beta}{\sigma} \right] \frac{\eta - 1}{\eta^3} \tag{13}$$

We now note that $3\mu\beta/\sigma$ is a dimensionless group which for many fluids and most realistic values of β is small compared to unity. Thus for water at 20°C. and a celerity $\beta = 1$ cm./sec., which is of the order of magnitude for capillary rise experiments, we find $N = 3\mu\beta/\sigma = 3 \cdot 0.01 \cdot 1/72 = 4 \cdot 10^{-4}$. We are therefore led to attempt a perturbation solution of Equation (13) in terms of N.

In looking for boundary conditions it is of help to note that both as $\eta = 1$ and $\eta \to \infty$ then $d^3\eta/d(\xi)^3 \to 0$; hence the radius of curvature approaches a constant in both limits. This is consistent with expectations and for the case of $\eta \to \infty$ has already been discussed by Rose (*14*). We choose here to state boundary conditions at $\xi = 0$.

$$\text{boundary condition 1} \quad \text{at} \quad \xi = 0 \quad \frac{d^2\eta}{d\xi^2} = \frac{1}{H^*} \tag{14}$$

$$\text{boundary condition 2} \quad \text{at} \quad \xi = 0 \quad \frac{d\eta}{d\xi} = 0 \tag{15}$$

$$\text{boundary condition 3} \quad \text{at} \quad \xi = 0 \quad \eta = 1 \tag{16}$$

Here H^* is a dimensionless radius of curvature which is a function of system dimensions, rise rate, and primary film thickness and must be determined later.

We now write a perturbation expansion retaining only the first-order term

$$\eta = \eta^{(0)} + N\ \eta^{(1)} \tag{17}$$

The zeroth-order solution, which is exact for a small stationary meniscus, is of the form

$$\eta^{(0)} = \frac{1}{2B^*}\ \xi^2 + 1 \tag{18}$$

where $B^* = B/h^o$ is the dimensionless half width of the capillary slit. We now define $X = \xi/\sqrt{2}\,B^*$ for convenience; then the differential equation for the first order term becomes

$$\frac{d^3\eta^{(1)}}{dX^3} = (2B^*)^{3/2}\ \frac{X^2}{(X^2+1)^3} \tag{19}$$

The boundary conditions are
boundary condition 1 at $X = 0$

$$\frac{d^2\eta^{(1)}}{dX^2} = C^* = \left(\frac{2B^*}{H^*} - 2 \right) \tag{20}$$

C^* and H^* are both as yet undetermined.

$$\text{boundary condition 2} \quad \text{at} \quad X = 0 \quad \frac{d\eta^{(1)}}{dX} = 0 \tag{21}$$

$$\text{boundary condition 3} \quad \text{at} \quad X = 0 \quad \eta^{(1)} = 0 \tag{22}$$

This gives a first-order perturbation solution of the form

$$\eta^{(1)} = (2B^*)^{3/2}\left[\frac{1}{16}\,(X^2+3)\tan^{-1} X - \frac{3X}{16} + \frac{C^*X^2}{2} \right]$$

Thus the first-order perturbation expansion and its first and second derivatives in dimensionless distance X can be written as follows.

$$\eta - 1 = X^2 + N(2B^*)^{3/2}\left[\frac{1}{16}\,(X^2+3)\tan^{-1} X - \frac{3X}{16} + \frac{C^*X^2}{2} \right] \tag{24}$$

$$\frac{d\eta}{dX} = 2X + N(2B^*)^{3/2}\left[\frac{X}{8}\tan^{-1} X - \frac{X^2}{8(X^2+1)} + C^*X \right] \tag{25}$$

$$\frac{d^2\eta}{dX^2} = 2 + N(2B^*)^{3/2}\left[\frac{X}{8(X^2+1)} - \frac{X}{4(X^2+1)^2} + \frac{1}{8}\tan^{-1} X + C^* \right] \tag{26}$$

The first and second derivatives are related to the apparent contact angle and curvature respectively.

LIMITING EXPRESSIONS FOR SMALL h^o

We anticipate that the primary film thickness h^o will often be very small, much smaller than the precision with which the position ζ and the thickness h can be measured. We note that $X = \dfrac{\zeta}{\sqrt{2Bh^o}}$ may be rather large even when conventional methods of observing menisci in tubes or slits indicate that the contact point, $\zeta = 0$, is reached. Thus we are only able to observe optically positions for which $|X| >> 1$ and approximations to Equations (25) and (26) for $\sqrt{\dfrac{h^o}{2B}} << |X| << \sqrt{\dfrac{B}{2h^o}}$ will be particularly useful. It is easy to show that these are

$$\left(\frac{d\eta}{dX}\right)_{\text{app}} = 2X + N(2B^*)^{3/2}\left[\left(C^* - \frac{\pi}{16} \right) X - \frac{1}{8} \right] \tag{29}$$

$$\left(\frac{d^2\eta}{dX^2}\right)_{\text{app}} = 2 + N(2B^*)^{3/2}\left[C^* - \frac{\pi}{16} \right] \tag{30}$$

These approximations are quite valid for capillary radii or half widths of 0.025 cm. and the primary film thickness 10^{-5} cm. or less as suggested by Bascom, et al. (*7*).

These equations indicate that in general what we are able to see is a capillary meniscus of a circular cross-section. The subscript app denotes apparent values of $d\eta/dX$ and $d^2\eta/dX^2$, that is, their values observed at distances large compared to primary film thickness but small compared to the tube or slit dimensions. These two equations show that the motion of the system has two major effects on the meniscus shape:

1. There is an increase in the apparent contact angle with velocity described by

$$\tan\theta_{\text{app}} = \frac{1}{\sqrt{2B^*}}\left(\frac{d\eta}{dX}\right)_{\text{app}} = -\frac{NB^*}{4} \tag{31}$$

2. There is a corresponding change in the curvature, described by Equation (30)

The apparent inconsistency in letting X approach zero when it already was assumed to be larger than $\sqrt{\dfrac{h^o}{2B}}$ is justified when we remember that this is the "apparent" result obtained by the usual microscopic techniques which cannot see the true contact form, as pointed out before.

The direct effects of the motion are thus confined to a very small region near the wall. The bulk of the meniscus will still approximate very closely a spherical section for

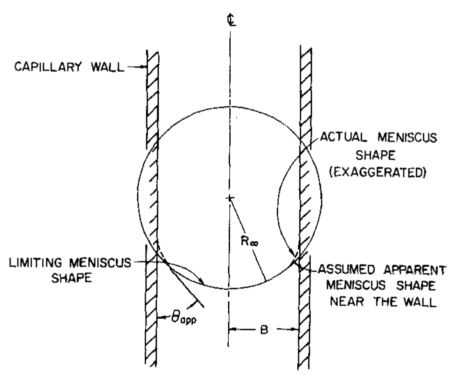

Fig. 2. Meniscus shape during capillary rise.

rise in a circular tube or a circular cylindrical section for rise between parallel plates, although its radius of curvature will be larger than at equilibrium.

It remains to determine this radius of curvature for the bulk section. To do this we must recognize that Equation (30) is a limiting expression for the spherical section shown in Figure 2, useful only when $\left| \frac{d\eta}{d\zeta} \right| << 1$. The radius of curvature in the bulk of the meniscus can then be shown to be the radius of a circle which intersects the tube wall at the apparent contact angle θ_{app} given by Equation (31). Thus by simple geometric arguments the bulk radius of curvature can be shown to be

$$R_\infty = B\sqrt{1 + \left(\frac{NB}{4h^o}\right)^2} = B\sqrt{1 + \tan^2 \theta_{app}} \quad (32)$$

We are now in a position to obtain the expression for C^* from Equation (30) since we have the limiting radius of curvature explicitly:

$$C^* = \frac{\pi}{16} + \frac{h^o}{NB} \left[\frac{1 - \sqrt{1 + \left(\frac{NB}{4h^o}\right)^2}}{\sqrt{1 + \left(\frac{NB}{4h^o}\right)^2} \cdot \sqrt{\frac{2B}{h^o}}} \right] \quad (33)$$

Note that R_∞ and C^* are functions of rise rate, capillary half width and the primary film thickness as expected.

DISCUSSION AND CONCLUSIONS

From the above simple analysis we have obtained some insight into the rise mechanism and found a way to interpret experiments, at least qualitatively.

First we note that the apparent contact angle is a rather doubtful concept and rests on the inability to observe the meniscus closely enough to see the true contact form. We can expect that some deviation from the spherical or cylindrical form may be seen near the wall by a careful observer, but the observed contact angle depends considerably on the care of the observed and the quality of his equipment (magnification of microscope, etc.). Thus we can expect considerable variation and irreproducibility in the observed data. This problem seems to be demonstrated by the data of Rose and Heins (*4*). Equation (31) indicates that $\tan \theta_{app}$ varies linearly with rate of rise, but the scatter of these data only allows us to conclude that the equation is not inconsistent with the data.

The radius of curvature of the meniscus at the center line or midplane of the capillary, on the other hand, provides an unambiguous means of determining the effect of motion on meniscus shape. It appears therefore that such measurements are to be preferred. The radius thus measured is related to system properties and parameters through Equation (32). This equation allows us to calculate the primary film thickness for any given rise rate and observed radius of curvature. The values of h^o thus calculated may then suggest which mechanism for primary film spreading, discussed before, may be operative and test whether the concept is useful at all.

The hypothesis of a primary film provides a ready explanation for the difference in behavior of dry and well-drained wet capillaries: the latter can be expected to be covered with a relatively thick primary film. This is for example a natural consequence of the Derjaguin hypothesis of a distinctive adsorptive phase (*12*). We cannot, however, explain why a finite force is required to initiate flow when the equilibrium contact angle is finite, as this situation is not consistent with our boundary conditions.

We have shown that a complete hydrodynamic theory for spontaneous spreading or capillary rise of liquids on a solid requires a separate physicochemical mechanism for advancing the liquid over the dry solid. Once we have decided on that mechanism we may solve the hydrodynamic equations to interpret the observed dependence of the meniscus shape in capillary rise experiments on the rise rate and the system properties.

Finally this represents only a first attempt at a hydrodynamic theory of spreading for liquids on solids. However, the importance of thin liquid films and triple interfaces in lubrication and in a wide variety of mass and heat transfer systems calls for much more effort in this area.

NOTATION

B = capillary slit half width, cm.
B^* = B/h^o dimensionless capillary slit half-width
C^* = constant of integration
H^* = dimensionless radius of curvature at $\xi = 0$
h^o = primary film thickness, cm.
h = local meniscus thickness, cm.
N = $3\mu\beta/\sigma$, dimensionless rise rate
P_G = gas phase pressure, dyne/sq.cm.
P = liquid phase pressure, dyne/sq.cm.
R_C = local radius of curvature, cm.
R_∞ = limiting radius of curvature at large X, cm.
t = time, sec.
v_z = velocity in the z-direction, cm./sec.
$\langle v \rangle$ = average velocity in the z-direction, cm./sec.
x, y, z = Cartesian coordinates
X = $\xi/\sqrt{2B^*} = \zeta/\sqrt{2Bh^o}$ dimensionless, reduced variable in the z-direction

Greek Symbols

β = meniscus celerity, cm./sec.
μ = viscosity, g./cm.·sec.
ν = kinematic viscosity, sq.cm./sec.
η = h/h^o dimensionless meniscus thickness
$\eta^{(0)}$, $\eta^{(1)}$ = zeroth- and first-order perturbation terms for η
ζ = $z - \beta t$ coordinate following the meniscus front
ξ = ζ/h^o reduced coordinate following meniscus motion
σ = surface tension, dyne/cm.

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