

BRIEF COMMUNICATION

AXISYMMETRIC FLOW DRIVEN BY A SURFACE TENSION GRADIENT AT A MOBILE INTERFACE

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INTRODUCTION

Surface tension gradients at mobile interfaces produce a variety of fluid motions. An example reviewed by Scriven & Sternling (1960) is the Marangoni effect in which surface tension gradients arising from concentration differences drive the flow. Varying surface tension also accompanies thermal and electric potential differences at interfaces; resulting flows have been analyzed by Levich (1962) and Newman (1973a).

Another flow caused by an electric potential gradient is currently being used in connection with the study of bubble nucleation at an ideal surface. Within electrolytic gas evolution, a phenomenon central to the aluminum and chlorine industries, nucleation of gas bubbles is the first step in the bubble-growth process. Complicated by the fact that even polished electrodes are microscopically rough and hence provide active bubble-generating sites, the fundamental study of nucleation on an ideal surface requires use of a mercury pool as the negative electrode.

A diagram of the experimental apparatus appears in figure 1. When current is passed through the cell, hydrogen ions are discharged on the mercury and water is split to make oxygen at the anode. The tube in the center of the vessel makes the pool center ohmically favorable, hence the current density (c.d.) at the pool's center is higher than at the edge. Because of this nonuniform c.d., the double layer potential at the interface increases from more negative to less negative and hence the surface tension increases radially. The low surface tension mercury at the axis flows to relieve the high surface tension at the periphery; hence mercury and the aqueous phase are "pumped" outward by the varying potential at the surface and return from above and below to maintain steady flow. In contrast to a solid interface where the velocity goes to zero, the radial velocity at the mercury interface is a maximum. Thus the center portion of the electrode is continuously renewed and makes an ideally clean and smooth surface for nucleation studies. The flow complicates the study because dissolved hydrogen gas is convected away from the surface; hence the flow velocities must be analyzed. In this paper, the flow in such a system under special circumstances is described.

ANALYSIS

The Navier-Stokes equation must be solved with the continuity equation in each phase. The steady-state cylindrical-coordinate form of these two equations is†

$$\frac{1}{r} \frac{\partial}{\partial r} (rv_r) + \frac{\partial v_z}{\partial z} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} = 0 \quad [1]$$

†Where no subscript appears, the equations apply to either region.

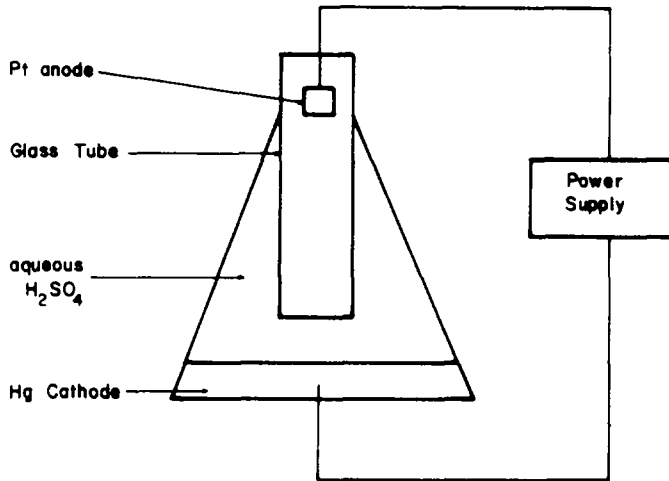


Figure 1. A schematic of the interface showing the coordinates. In practice, phase 1 was aqueous. Phase 2 was mercury.

$$-\frac{v_\theta^2}{r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + v_r \frac{\partial v_r}{\partial r} + v_z \frac{\partial v_r}{\partial z} = \nu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial (rv_r)}{\partial r} \right) + \frac{\partial^2 v_r}{\partial z^2} \right. \\ \left. + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} \right] - \frac{1}{\rho} \frac{\partial \mathcal{P}}{\partial r} \quad [2]$$

$$v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} = -\frac{1}{\rho r} \frac{\partial \mathcal{P}}{\partial \theta} + \nu \left[\frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial (rv_\theta)}{\partial r} \right) \right. \\ \left. + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2} \right] \quad [3]$$

$$\frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_r \frac{\partial v_z}{\partial r} + v_z \frac{\partial v_z}{\partial z} = \nu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{\partial^2 v_z}{\partial z^2} \right. \\ \left. + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} \right] - \frac{1}{\rho} \frac{\partial \mathcal{P}}{\partial z}. \quad [4]$$

Assuming that the surface remains flat, that the regions are unbounded, and proceeding analogously with the von Karman (1921) solution for flow at a rotating disk, one seeks solutions of the following forms in both phases 1 and 2.

$$v_r = rf(z) \quad [5]$$

$$v_z = h(z) \quad [6]$$

$$P = \mathcal{P}(z). \quad [7]$$

After substituting these relations into the preceding equations, one obtains:

$$2f + h' = 0 \quad [8]$$

$$f^2 + hf' = \nu f'' \quad [9]$$

$$hh' + \frac{P'}{\rho} = \nu h'' \quad [10]$$

The boundary conditions are no flow through the interface, no slip at the interface,

vanishing radial velocity far from the interface, and the force balance at the interface. In addition, the dynamic pressure must be specified at one point. Mathematically, the first three conditions are

$$z = 0 \quad h = 0 \quad [11]$$

$$z = 0 \quad f_1 = f_2 \quad [12]$$

$$z = \infty, -\infty \quad f_1 = f_2 = 0 \quad [13]$$

where "1" denotes aqueous phase and "2" denotes mercury. The fourth boundary condition is equivalence between the driving force for motion (the surface tension gradient) and the retarding viscous forces in both phases,

$$z = 0, \tau_{zr_1} - \tau_{zr_2} = \frac{d\sigma}{dr} \quad [14]$$

where τ is the shear stress and σ the surface tension.

After inserting expressions [5] and [6] for the velocities, one finds

$$-\mu_1 f'_1 + \mu_2 f'_2 = \frac{1}{r} \frac{d\sigma}{dr} \quad [15]$$

The surface tension must vary with the square of the radius for the equations and boundary conditions to be independent of radius.

$$\sigma = \frac{ar^2}{2} + b \quad [16]$$

This is a purely physical requirement for this solution to work. For a given cell geometry, one must solve Laplace's equation for the potential with kinetic boundary conditions (Newman 1973c) and convert the potential variation along the mercury surface to a surface tension variation via electrocapillary curves in order to determine the degree to which the actual variation of surface tension could be approximated by an equation such as [16]. Substituting [16] into [15], one obtains

$$-\mu_1 f'_1 + \mu_2 f'_2 = a. \quad [17]$$

The dynamic pressure \mathcal{P} is set to zero at the interface.

The equations are made dimensionless by introducing the following definitions:

$$v_r = rf_0 F, \quad f_0 = az_0/\mu \quad [18]$$

$$v_z = h_0 H, \quad h_0 = az_0^2/\mu \quad [19]$$

$$z = z_0 Z, \quad z_0 = (\mu^2 \rho a)^{1/3} \quad [20]$$

$$P = p_0 \pi. \quad [21]$$

Equations [8]–[10] become:

$$2F + H' = 0 \quad [22]$$

$$F^2 + HF' = F'' \quad [23]$$

$$HH' + \pi' = H'' \quad [24]$$

Boundary conditions [11]–[13] and [17] become:

$$Z = 0 \quad H = 0 \quad [25]$$

$$Z = 0 \quad F_1 = \left(\frac{\mu_1 \rho_1}{\mu_2 \rho_2} \right)^{1/3} F_2 \quad [26]$$

$$Z = \pm \infty \quad F = 0 \quad [27]$$

$$Z = 0 \quad -F_1' + F_2' = 1. \quad [28]$$

Also,

$$Z = 0 \quad \pi = 0. \quad [29]$$

One can see from boundary condition [26] that the general functions F , H and π in both phases are correct for the specified ratio of the fluids' viscosities, but are independent of the radial surface tension constants a and b .

Equations [22]–[24] are coupled nonlinear ordinary differential equations. Equations [22] and [23] are solved first; then [24] is integrated to find the pressure.

$$\pi = H' - \frac{1}{2} H^2. \quad [30]$$

Assuming a value for F_1 at the interface, which completely specifies the problem in region 1, I compute functions F_1 , H_1 and the derivative F_1' at the interface. Then F_2' at the interface is computed from [28]; this quantity in turn completely specifies the functions in region 2. Upon determining the functions in region 2, I recalculate F_1 at the interface, compare it with the original estimate, and repeat the process until the values no longer change. The equations were linearized about a trial solution, put into finite difference form, and solved by Newman's (1975) BAND program for solution of simultaneous ordinary differential equations.

RESULTS AND DISCUSSION

The functions F , H , and π for a mercury/water system appear in figures 2 and 3. The radial velocities are largest at the interface where the driving force for flow originates. Zero at the interface, the axial flows reach a maximum some distance away. I estimated a value of " a ", corresponding to a potential varying radially at 1 volt per centimeter, to be 240 dynes/cm³.[†] Resulting velocities were calculated for the system mercury/water at 10°C.

radial velocity of interface 1 cm from axis = 48 cm/sec
 maximum velocity in z direction (Hg) = 0.39 cm/sec
 distance from interface of v_z maximum (Hg) = 1.3 (10⁻²) cm
 Maximum velocity in z direction (H₂O) = 1.2 cm/sec
 distance from interface of v_z maximum (H₂O) = 4.5 (10⁻⁵) cm.

The significant changes in velocity in both phases occur within a millimeter of the surface.

[†]Given a value for the radial variation of potential, one can deduce the surface tension change accompanying this variation from an electrocapillary curve (Newman 1973, p. 153). One volt per centimeter is an atypically high variation of potential over the surface of many electrochemical cells, but in this case the experiment is designed to make use of this flow and hence a high gradient is used.

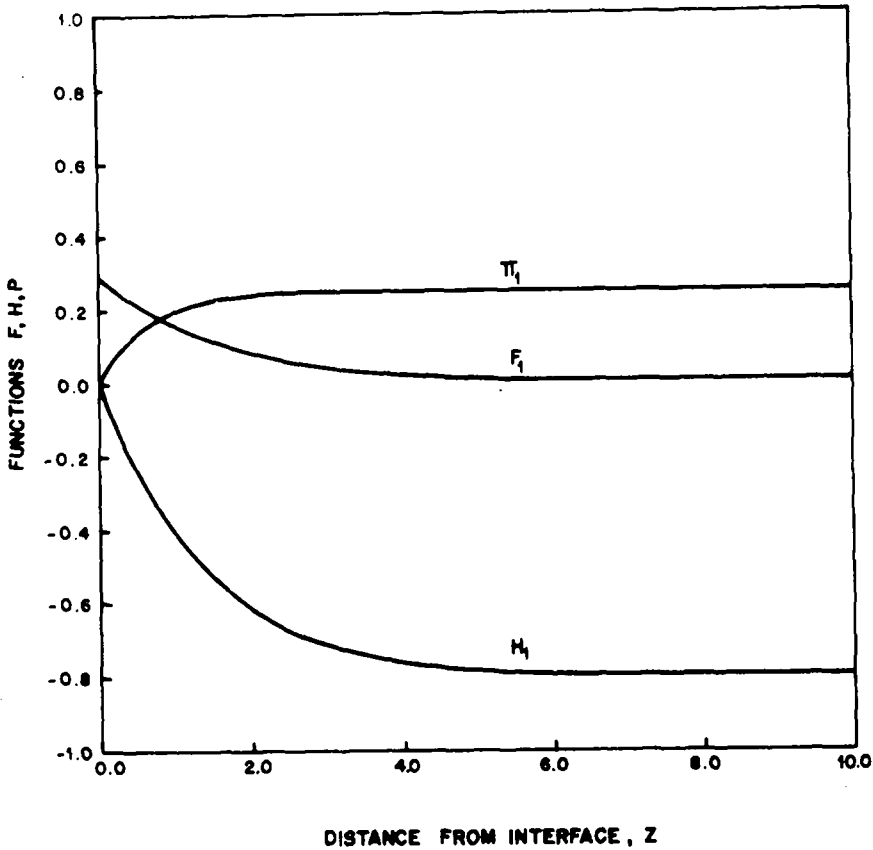


Figure 2. The dimensionless z -dependent velocity and pressure functions for phase 1. $(\mu_1\rho_1/\mu_2\rho_2)^{1/3} = 0.3928$.

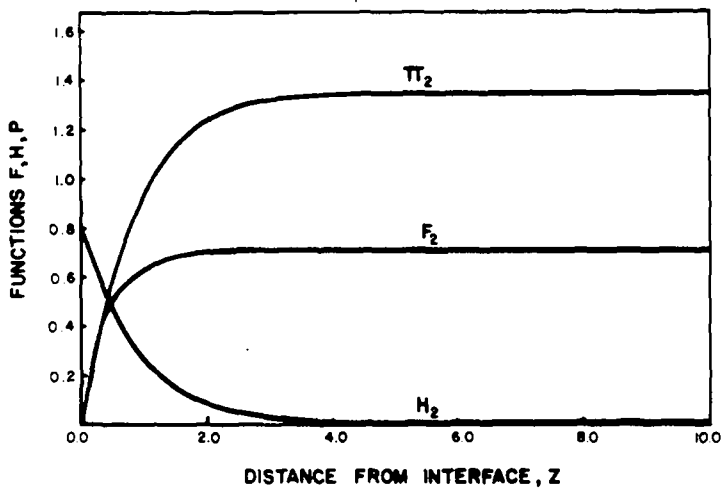


Figure 3. The dimensionless z -dependent velocity and pressure functions for phase 2. $(\mu_1\rho_1/\mu_2\rho_2)^{1/3} = 0.3928$.

CONCLUSIONS

The velocities and pressure in an axisymmetric surface tension-driven flow at the interface between two phases have been calculated. Using the von Karman assumptions about axisymmetric flows near an interface, I showed that the interface is uniformly accessible if the surface tension increases with the square of the radius. The flows in both phases depend on the ratios

of the viscosities and densities of the phases. Significant velocity changes occur in a region next to the interface less than 0.1 cm thick.

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