Hydrodynamic Effects on an Interfacial Film

Abstract. *An interfacial film collected on the upstream face of a barrier on the surface of flowing water (i) develops in two or three distinct stages, (ii) has an equilibrium length inversely proportional to the velocity squared, (iii) exhibits a linear decrease in surface tension, and (iv) exhibits an interfacial shear force proportional to the velocity.*

Obstruction of the free surface of water flowing in an open channel, with the bulk allowed to flow through undisturbed, causes a spontaneous surface film to accumulate on the upstream side of the barrier. At low surface velocities the film attains a length of 1 m or more; its upstream edge is marked by a small stationary ripple on the surface. The film layer is additive, as is evidenced by the way it grows, and distinguishable by the ripple at its upstream end and the relatively little surface motion between the ripple and the barrier.

Our apparatus was not degreased and we used ordinary tap water. The chemical nature of the film was not determined; we presume, however, that the barrier collected surface-active material contained in the air-water interface. Detailed study of the growth properties of such films was reported by Merson and Quinn (*1*); by carefully controlling the chemical purity of their system, they investigated the growth properties of films formed with various surfactants. Theoretical and experimental investigation of the vertical velocity distribution beneath such a film has been reported (*2*). We now report some physical measurements of the surfactant film with a flowing substrate.

We halted the free surface of flow in an open channel with a barrier that just touched the surface from above. Water was recirculated in a flume 1.13 m wide, 8 cm deep, and 4 m long; its upstream end was packed with metal shavings and a metal honeycomb to effect uniform flow conditions transverse to the direction of flow. The velocity of the flow was controlled by adjustment of a valve in the discharge side of the pump or by alteration in the depth in the channel. The surface velocity was measured by timing the movement of surface floats both upstream and downstream of the film. The barrier was a glass tube, 13 mm in diameter, with rubber stoppers in its ends to seal them to the channel wall. Experiments (*1*) with barriers of brass, plexiglass, and Teflon had shown that, despite differing menisci, film growth was unaffected by the various methods of touching the surface with the barrier.

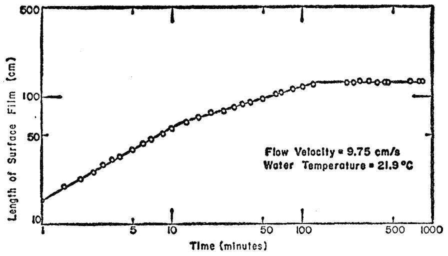


Fig. 1. Typical growth rate of the surface film.

Immediately after placement of a barrier across the surface of a uniform flow, a small ripple appeared, marking the upstream end of the film; at this stage the film was but a few millimeters long. With time the film lengthened, at first rapidly and later more slowly, until finally a steady-state length was established (Fig. 1). The growth curve shows two or three distinct stages of development: the first is believed to be the period during which a monomolecular layer is collected; the later stages are believed to reflect condensation as additional material is collected, as the edgewise compressive stress at the barrier increases, and as desorption from the film balances the continual supply of surfactant. We made no attempt to control the availability of the surface-active material, so that the quantitative features of the growth curves were not generally reproducible, but characteristics of growth, including the changes in slope, were always the same.

Merson and Quinn (*1*) showed that the growth should be linear with time if the film is incompressible and no desorption is assumed, that the growth should be linear with the square root of time if the film is compressible and no desorption is assumed, and that the growth rate decays exponentially if Langmuir desorption kinetics are assumed. The growth characteristics (Fig. 1) indicate definite changes in the nature of the film as it lengthens. The broken accumulation curve indicates a growing expanded phase during the first 12 minutes, and a fully grown expanded phase, plus a growing condensed phase, between 12 and 115 minutes. Because of the continuing supply of surface-active material from upstream, the fully developed film probably grew continuously at the upstream end and failed at the barrier.

The steady-state length was sensitive to velocity, and a steady-state surface film immediately adapted its length to changes in velocity. The effect of variation in the substrate velocity on one of the collected layers is shown in Fig. 2; except for the longest lengths of film, the length is proportional to the square of the surface velocity. We believe that the longest lengths were affected by entrance effects of the channel flow.

A very striking feature of the film was the continuous, slow, unsteady, strong, two-dimensional circulation pattern within it, made evident by a sprinkling of aluminum powder; it consisted of regularly spaced, unsteady channels oriented parallel to the direction of the substrate flow. These circulation channels, about 1 cm in width, extended most of the length of the film and alternated in direction of flow. The patterns indicate that the condensed phase is fluid and that the condensation is more or less reversible. The circulation velocity was ⩾ 50 percent lower than the substrate velocity. At the barrier, as well as at the upstream edge of the film, the flow of the circulation channel divided and reversed its direction. The circulation patterns are assumed to reflect Marangoni effects (*3*).

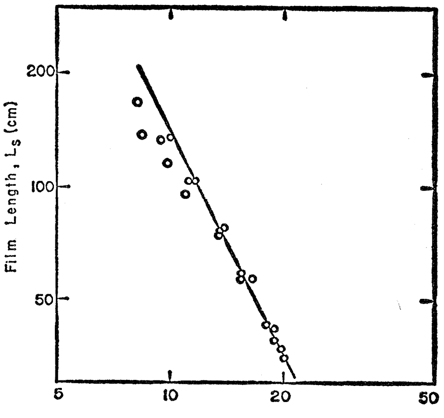


Fig. 2. Typical dependence of film length on velocity for a given accumulation of surface-film material.

Similar, strong, definite circulation patterns within the film have been reported, but only two counterrotating circulations (*1, 2*). The circulations observed by us consisted of a whole series of parallel, longitudinal currents alternating in direction. Merson and Quinn (*1*) used a channel 3.1 cm wide; Kenning and Cooper (*2*), 2.4 cm. Our very wide channel was chosen to create a large central portion of the film that was unaffected by the wall boundary layer; the straightness of the leading edge showed that a uniform central portion was achieved. At the outside edges, however, the surface-velocity boundary layer was evident; here the circulations were affected by the transverse variation of the surface velocity and were wider.

The surface tension was measured with a du Nouy tensiometer at various points in several constant-length films under steady-state conditions. The total drop in surface tension was always about 45 dyne/cm, so that the gradient of surface tension was related to the total steady-state length of the layer. For any one velocity the surface tension drops linearly with distance from the leading edge for most of the length of the layer; only a short length near the leading edge does not exhibit this linearity. If all surface-tension values are adjusted so that the linear relation passes through zero at the leading edge, the data may be plotted as in Fig. 3. Except for a leading-edge portion, it follows that the decrease in surface tension is directly proportional to (i) distance from the leading edge, and (ii) the square of the velocity. A Weber number,

$$N_w = \rho L_s V^2/(\sigma_o - \sigma_i - \sigma)$$

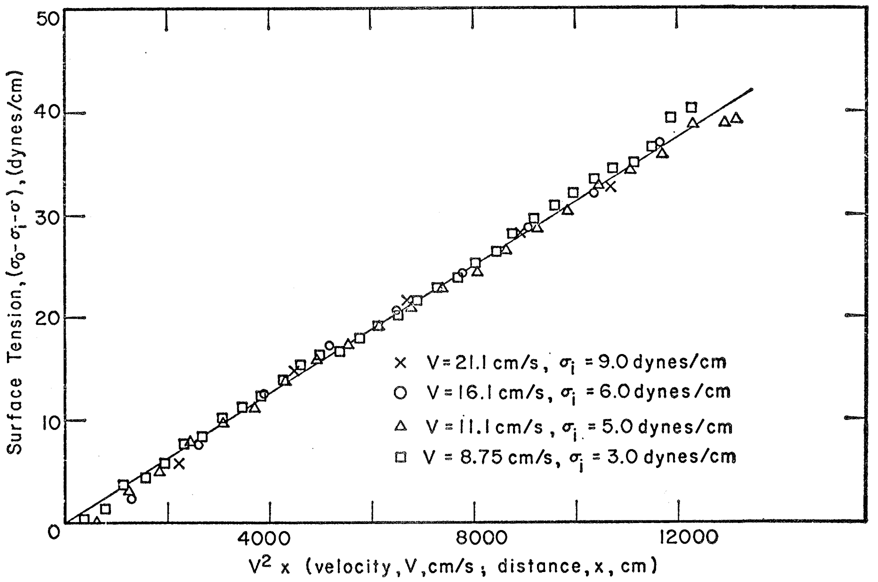
is constant and equal to 620 for this phenomenon (*4*).

The strong surface-tension gradient was also observed qualitatively in two other ways: (i) capillary waves in the film were strongly refracted as they propagated through regions of decreasing surface tension; (ii) when benzene (or any similar liquid having lower surface tension than water) was dropped on the film at various points behind the leading edge, it spread readily near the leading edge but coalesced near the barrier. The benzene spread at points behind the leading edge as far as a point at which the water-air surface tension was reduced to that of benzene-air; further downstream from this point to the barrier, the benzene coalesced. Precisely at the critical point the benzene tried to spread on one side and coalesce on the other.

We tried to measure the total force exerted on the surface film by the substrate flow. Suspended from the ceiling (a height of 3 m) and with its length slightly less than the width of the channel, the barrier acted as a pendulum; it just touched the surface, and leakage of the film material past its ends was minimal.

When the barrier was lifted from the water, the flow set at some constant velocity, and the barrier then placed in contact with the surface, a surface layer again built out from the barrier. For this constant velocity, the pendulum barrier deflected varying degrees from its equilibrium position, depending on the length of the film.

Deflection was measured as a function of film length for several velocities; each velocity was held constant, and deflection was noted for various lengths of the film as it grew outward. For each velocity, deflection was a linear function of length *L*, with some initial deflection for zero length; we believe that this initial deflection was due to the hydrodynamic effect on the



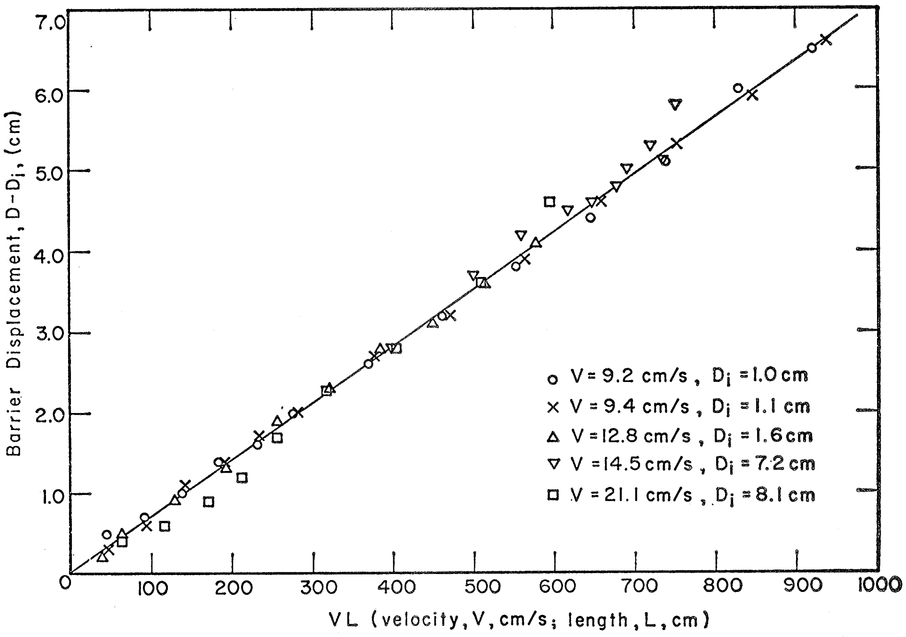


Fig. 3 (top). The linear dependence of the drop in surface tension on the square of the velocity and the first power of distance downstream from the leading edge of the film. Fig. 4 (bottom). The linear dependence of displacement of the barrier on the first power of the velocity and on the length of the film.

barrier itself. When each deflection is corrected so that zero deflection occurs at zero length of the film, the remaining deflection reflects the shear force on the film, and perhaps such secondary effects as the changing angle of contact of the surface, and the changing column of water supported by the barrier and the connecting surfaces. Each deflection curve was adjusted to give zero deflection at zero length (Fig. 4). The deflection (thus the force) is a linear function of velocity and of length.

Since the viscosity of the water was not varied, we cannot define the dependence of force on viscosity, but we suspect that the force is a linear function of Reynolds number VL/ν. Full interpretation of the barrier deflection may require knowledge of the wetting angle and the height of liquid supported by the barrier.

It is well known that for parallel flow along a rigid flat plate with a sharp leading edge the total force is proportional to the three-halves power of velocity and to the one-half power of length. If the plate itself is fluid (as is the film layer), measurements indicate that the force is linear with velocity and that the shear stress is constant along the film.

Thus our observations indicate that the barrier collected surface-active material from upstream; the film was subjected to the drag of the water flowing under it and was restrained by the barrier.

The expanded phase made up approximately half the length of a fully developed film (Fig. 1). The lack of evidence of discontinuity of surface tension along the films (Fig. 3) indicates that perhaps the drag on the expanded and condensed phases is the same.

When an axial force (usually called surface pressure) is applied to a monolayer, it is counterbalanced by a decrease in surface tension (*5*). In our studies, a shear force was applied to the film, but our findings indicate that the shear stress is proportional to the first power of velocity, whereas the surface-tension gradient is proportional to the second power—that is, the surface-tension gradient will not generally balance the shear stress. Evidence of the effect of this imbalance of forces on a particle of the surface film is the cellular circulation pattern observed.

The irregularity of the decrease in surface tension near the leading edge probably reflects the curvature of the film at the ripple. The film surface appeared to be elevated slightly at the leading edge, requiring extra forces to support its elevated mass.

As an idealization, let us suppose that the linear relation between the decrease in surface tension and the square of the velocity was also true for the leading portion of the surface layer: $\sigma_o - \sigma = KV^2x$. Since the drop in surface tension between the leading edge and the barrier is always the same, it follows that the equilibrium length is inversely proportional to the square of the velocity, and this is approximately true (Fig. 2).

The classical treatment of a fluid sphere moving in a fluid medium assumes no special interfacial effects, considering only the respective viscosities of sphere and medium. But gas bubbles often move as if they are encapsulated in a rigid shell. It is usually assumed that a film of surfactant collects at the interface and that the flow around the sphere (*2*), with its resultant shear stress, compresses the surfactant and pushes it to the rear of the sphere. Since surface tension is strongly altered by small concentrations of surfactant, it is assumed that the shear stress creates surface-tension gradients from the front to the rear of the sphere. The nature of these gradients and the relation between them and the shear stress are not understood, however.

We report, for a simple two-dimensional flow, observations of surface-tension gradients created by the flow, the magnitudes of the gradients, and the dependence of the gradients on velocity and distance from the leading edge; the total forces on films of various lengths were also noted. Without measuring surface-tension gradients in growing films, however, one cannot relate interfacial shear stresses with corresponding surface-tension gradients. We did not study the effect of variations in substrate viscosity or density, or the effect of film chemistry.

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References and Notes

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4. Symbols: D, displacement of pendulum barrier; D_i, end-effect correction for displacement; K, proportionality constant; L, length of surface film not in equilibrium; L_s, steady-state length of surface film; N_w, Weber number; V, velocity of surface of free stream; x, distance downstream from leading edge of surface film; ν, kinematic viscosity of water; σ, surface tension within surface film; σ_o, surface tension of free stream; σ_i, end-effect correction on surface tension.
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6. Supported by grant G-14557 from the National Science Foundation. We thank H. A. Einstein for suggestions.

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A New Allotropic Form of Carbon from the Ries Crater

Abstract. *A new allotropic form of carbon occurs in shock-fused graphite gneisses in the Ries Crater, Bavaria. The assemblage in which it occurs consists of hexagonal graphite, rutile, pseudobrookite, magnetite, nickeliferous pyrrhotite, and baddeleyite. Electron-probe analyses indicate that the new phase is pure carbon. It is opaque and much more strongly reflecting than hexagonal graphite. Measurement of x-ray diffraction powder patterns leads to cell dimensions $a = 8.948 \pm 0.009$, $c = 14.078 \pm 0.017$ angstroms, with a primitive hexagonal lattice.*

The material was recognized as a possible new mineral because of its distinctive optical properties in polished sections of shock-fused graphite gneisses from the Ries Crater in Germany. The mineral is slightly harder than graphite, and its reflection color is metallic gray to white. It occurs as relatively thin lamellae (3 to 15 μm wide) alternating with graphite and perpendicular to the 0001 face of graphite (Fig. 1). No anisotropism was observed, probably on account of the extremely small grain size.

Detailed optical studies in reflected light of numerous shocked graphite gneiss specimens from different localities in the Ries Crater revealed that only a small fraction of the graphites contain the new form of carbon. The new mineral, which very probably has been formed from hexagonal graphite by