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$$\Delta F^0_R = 4\Delta F^0 f_S + 2\Delta F^0 f_{H_2O} + 2\Delta F^0 f_{OH^-} - \Delta F^0 f_{SO_4} = -3\Delta F^0 f_{H_2S} = 0 - 113.4 - 75.18 + 177.34 + 19.62 = 8.38$$

at unit activity and standard temperature and pressure (f is the particular species). Actual pressure and temperature are different but will not change the magnitude of the result. Then at equilibrium $\Delta F^0_R = -RT \ln k$:

$$-RT \ln k = 8.38, \text{ and } k = 10^{-6.16} = \frac{(S^0)^4(OH^-)^2(H_2O)^2}{(SO^4)\ (H_2S)^3_{aq}}$$

where R and T are the gas constant and absolute pressure, and k is the equilibrium constant. For $pH = 7$ or $(OH) = 10^{-7}$, $(S^0) = 1$ (solid has unit activity), $(SO_4) = 0.01$; ignoring activity coefficients, we obtain $(H_2S)_{aq} = 10^{-2}$. Thus, more than 0.01 mole of H_2S per liter (360 mg/liter) would theoretically be required to produce solid S^0 under the assumed conditions. Note, however, that Millet, cited by Postgate (*14*), demonstrated that sulfite, which can readily react with H_2S to produce sulfur, can be an intermediate in bacterial sulfate reduction.
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22 May 1970

Surface Films Compacted by Moving Water: Demarcation Lines Reveal Film Edges

Abstract. *When water flows under the edge of a surface film the large viscous shear stress at the edge prevents the film from spreading and raises a ridge on the water surface. Near the top of its downstream flank the ridge has an abrupt change in curvature that we see as a line on the water.*

On a calm day an observer who finds the right place on a stream or river will see an unobtrusive yet startling phenomenon, a line on the surface of the water. The line may lie still, or it may contort itself, one way and another, in response to eddies. Very likely he will think a spider thread has fallen onto the water and try to cut it with his canoe paddle. As the disturbance caused by the cutting fades, the line reappears, mended and whole.

With luck the observer will see a little animal supported by surface tension drift across the line, hop back to the other side, drift across, hop back, and so on through many repetitions. The line divides good surface from bad, in the little animal's view. If conditions are right, our observer will see that the bad surface looks dirtier than the good, with more specks of debris upon it. And if he uses the water surface as a mirror, he will see that it forms a shallow ridge, a centimeter or so wide, with the line about at its top.

The line is a line of demarcation, D-line for short, between surface regions with different amounts of contamination. What can maintain such a discontinuity against the tendency of surface films to spread into equilibrium? What causes the D-ridge on which the line sits? The line itself must be some sort of kink in the profile of the ridge; but what sort, and how is it produced?

The next clue requires a lake shore and an onshore breeze. Stick a shovel into the lake and heave the water upward to make a local upwelling. If the breeze has compacted a dense enough film of contaminants, a D-line will form at the outward-flowing edges of the upwelling boil of water. As the boil quiets down, the loop of line will contract and eventually "annihilate" itself, launching a ring of ripples as it does so. If the film is less compacted, the D-line may weaken and become invisible without contracting. Squeeze the film between a boat and the shore: The D-line will run its full course through contraction and annihilation.

Now invert the experiment. Go to where there is an offshore breeze and touch the surface with a pipe cleaner soaked in Mazola corn oil. The oil will spread, sending before it an expanding circle of ripples. Look sharp at the right moment and you will see that a ring of D-line gets left behind by the

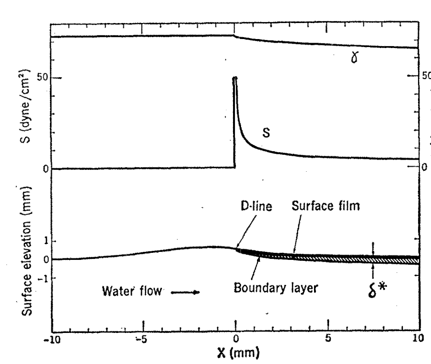
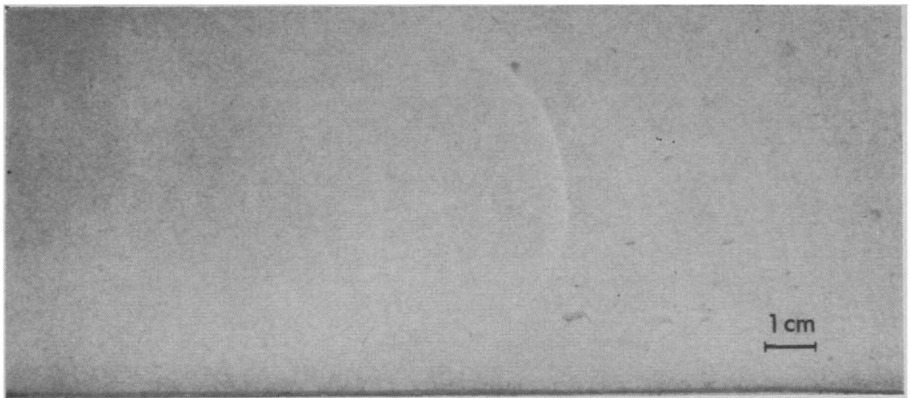


Fig. 1. The D-ridge elevation profile at a water speed below 23.2 cm/sec, showing the surface film downstream of the D-line, and the displacement thickness δ* of the boundary layer beneath the film. The D-line is perpendicular to the paper, and the surface dam is off scale to the right. Also illustrated are the shear stress S exerted on the film by the flowing water at a speed of 23.2 cm/sec, and the surface tension γ. Note how γ is reduced by the shear stress.



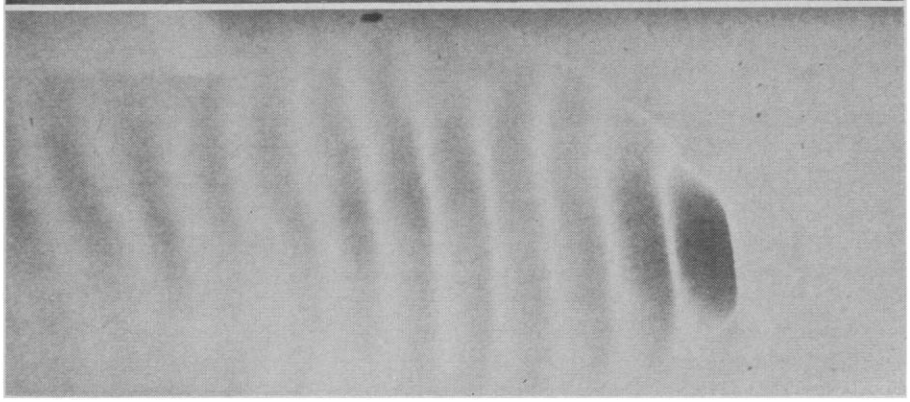


Fig. 2 (top). A D-ridge, seen by the way it focuses sunlight on the bottom of the channel. The water flows from left to right in all figures. Fig. 3 (bottom). Ripples upstream of the D-ridge at a water speed higher than the minimum speed (23.2 cm/sec) of surface waves, as seen by the sunlight they focus.

ripples, expands more and more slowly while becoming fainter and fainter, takes on a wiggly shape, and finally gets too faint to see. A film expanding over stationary water makes a D-line, just as does water flowing outward under a stationary or inward-moving film. The D-line is a dynamic phenomenon, caused by relative motion between a surface film and the water beneath.

A surface film moving relative to the liquid below it will drag the uppermost part of the liquid along with itself, forming a boundary layer. The mathematics of boundary layers is so difficult that solutions have been worked out only for the simplest physical situations. One of these is fairly close to what happens when D-lines occur in nature, and we can contrive an experiment in which the correspondence is almost perfect.

Consider a channel whose downstream end is dammed at the surface but not below. Water can flow down the channel, but a surface film cannot escape; nor, if the arriving water carries very little film substance on its surface, will the trapped film gain material. It will rest on the water as a stationary, unchanging ceiling. Except for the fact that the ceiling is not quite flat, the situation is the same as that on one side of an infinitely thin, plane lamina lying edge-on to a flow of liquid, a classic solved problem in boundary layer theory.

Near its upstream end the boundary layer is sure to be laminar; thus its displacement thickness δ^* is given (*1*, p. 123) by

$$\delta^* = 1.72 \left(\frac{\nu x}{u}\right)^{\frac{1}{2}} \qquad (1)$$

where x is the distance from the upstream end of the film, ν is the kinematic viscosity of the water, and u is the speed of the water flow outside the boundary layer. The boundary layer forms a blunt wedge under the film, as shown in Fig. 1. Near $x = 0$ this formula is inaccurate even for an ideal lamina of infinitesimal thickness, and the thickness of the film, though small, is finite. But the leading edge of the boundary layer is nevertheless blunt, even if Eq. 1 does not give its shape accurately.

The nonzero thickness of the boundary layer requires that a finite amount of water in and beneath it suffer finite accelerations, which will be largest near $x = 0$. Accelerations require forces; forces have reactions; and the reactions make the elevation of the water surface that we see as the D-ridge.

Figure 2 shows a D-line on a water stream 3 cm deep flowing in a channel 7.5 cm wide. More precisely, Fig. 2 shows sunlight focused into a line at the bottom of the channel by a part of the D-ridge that presents a convex surface upward to the air. The water was diverted from a small stream tributary to Lake Placid in northern New York State. The film was natural contamination present in the stream water, with, perhaps, additions of saliva or spray enamel, used on occasion to shift the line quickly to a convenient point in the channel for photography. The D-line and D-ridge look the same, no matter what substance is used to form the film.

The height of the D-ridge increases rapidly with water speed, but no dramatic change occurs in its shape until at above 23.2 cm/sec (slightly modified, no doubt, by the finite depth of the water), the lowest speed at which surface waves can propagate (*2*), a stationary train of ripples appears upstream of the D-line, as shown in Fig. 3. At lower water speed any ripples would travel upstream and not stay in station with the D-line.

Figure 4 shows a D-line in a much wider stream about 2 cm deep, at a water speed somewhat below the threshold for stationary ripples. The line of sight is at about 30° to the water surface and end-on to the D-line. Horizontal in Fig. 4 is a fishline 0.2 mm in diameter, whose reflection gives, approximately, a 2 cos 30° magnification (all too little) of the elevation profile of the water surface at right angles to the D-line.

The distorted lattice is the reflection of a wire screen (3-mm mesh), itself visible in the background. Downward displacement of the image of any of the less sloping set of screen wires is proportional to the slope of the water surface, upward from the left to right, to which is added, unfortunately, a contribution from the square of the slope of the water surface. The D-line is where the wire images have a downward kink. Because the images are kinked but unbroken, the D-line is a discontinuity in the curvature of the water surface, but not in its slope.

Looking more steeply downward at the water reduces the effect of the square of the slope, and Fig. 5, taken at a camera angle of 60°, is more nearly a plot of the slope of the water surface. Using this information to supplement the fishline reflection in Fig. 4, we arrive at the D-ridge profile given in Fig. 1, for which I claim no great accuracy.

Ripples are visible in Fig. 4, but these were not stationary. As the water speed approaches the stationary wave threshold, the stream becomes very susceptible to the excitation of waves that move slowly upstream. An upstream wind amplifies these waves. It may also initiate them, and so may turbulence produced by the surface dam. The waves are not shown in Fig. 1.

The tipped screen technique described above, driven hard, could detect the presence of a D-ridge down to a water speed of 1 cm/sec, but a speed of 3 cm/sec was needed to verify that the profile was about the same shape as at higher speeds.

Marked changes of the D-ridge profile with water speed would be expected only near the stationary ripple threshold, and in Fig. 6 we find them. A small increase in water speed from that of Fig. 5 produces a region of nearly constant maximum slope just downstream of the D-line and steepens the upstream upslope relative to the downstream downslope.

Even at lower speeds the dynamics of the D-ridge is complicated, but two main effects seem to be at work. The blunt wedge of boundary layer forces the water outside it to curve down, and to accelerate in a downstream direction in order to pass through the reduced cross section left available. The down-curving path of the water requires an upward reaction on the surface near the D-line, which distorts it into a ridge. The downstream acceleration requires a drop in pressure as the water passes under the nose of the wedge, and this implies a concave-up increment in the curvature of the tensioned surface as we pass from upstream to downstream of the D-line. The sum of these two effects is a ridge with an abrupt change in curvature near its top on the downstream side, which is what we saw in Figs. 4 and 5.

The shearing liquid in the boundary layer applies to the film above it a downstream shear stress S given (*1*, p. 120) by

$$S = 0.332\, \rho u^{3/2} (\nu/x)^{\frac{1}{2}}$$

plotted in Fig. 1 for $u = 23.2$ cm/sec, which must be balanced by the negative of the gradient of the surface tension γ of the film-covered water; hence

$$0.332\, \rho u^{3/2} (\nu/x)^{\frac{1}{2}} = S = -\frac{d\gamma}{dx} \quad (2)$$

where ρ is the density of the water.

Equation 2, like Eq. 1, is inaccurate near $x = 0$, and for the same reasons. But although the shear stress does not go to infinity as x goes to zero, it is still very high, and it is this initial shove that the water delivers as it first encounters the film that keeps the edge of the film from spreading.

We can integrate Eq. 2 to get

$$\gamma = 0.664\, \rho u^{3/2} (\nu x)^{\frac{1}{2}} + \text{constant}$$

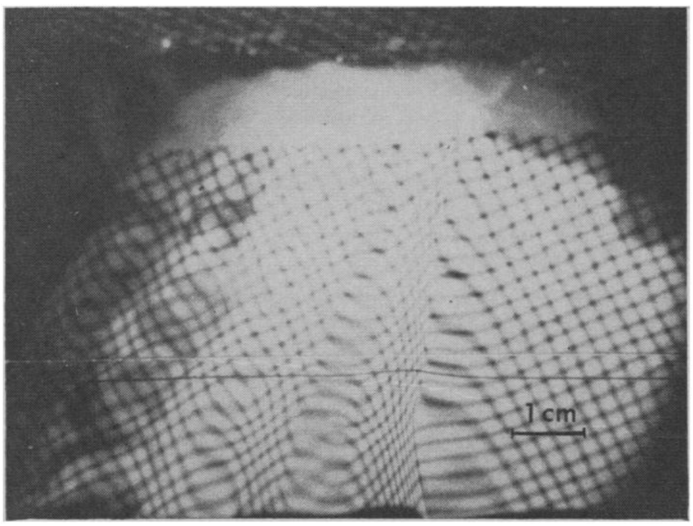
Because at $x = 0$ the film meets pure water with a surface tension of γ_0, the constant equals γ_0, and we have

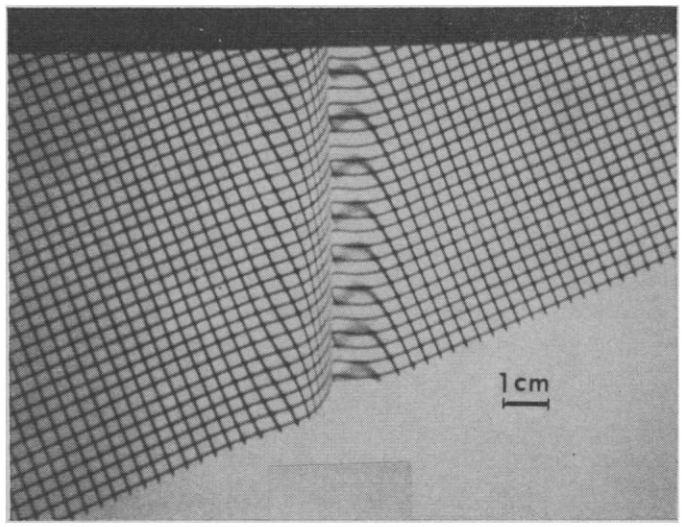
$$\gamma_0 - \gamma = \beta = 0.664\, \rho u^{3/2} (\nu x)^{\frac{1}{2}} \quad (3)$$

where β is the surface tension deficit, or surface "pressure." At any water speed the surface pressure has a fixed relation to x, shown in Fig. 1 for $u = 23.2$ cm/sec, and the film automatically adjusts its areal density, and therefore β, at every point so as to obey this relation.

At sufficiently large x Eq. 3 says that γ becomes negative, or that β exceeds γ_0. But a surface with negative γ is unstable against buckling, and it concertinas, sometimes visibly, at its downstream end until the film is short enough so that γ drops only to zero at the surface dam.

Although buckling collapse sets an absolute upper limit to the surface pressure, many films, oils, for example,





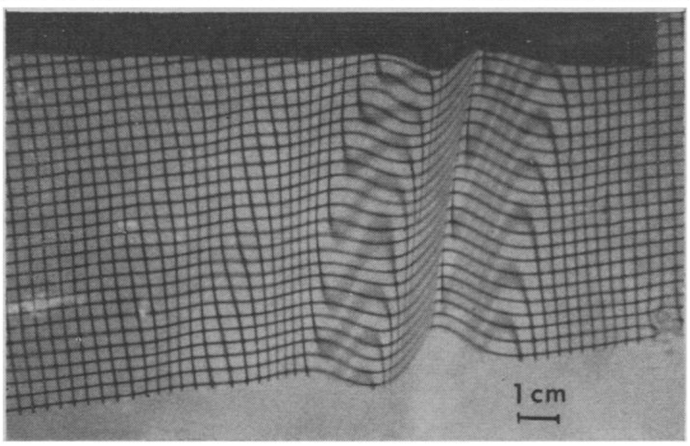


Fig. 4 (above left). D-ridge elevation profile at below 23.2 cm/sec, given by the distortion of the reflection of a horizontal fishline.

Fig. 5 (above right). Profile of the D-ridge slope at less than 23.2 cm/sec, given by the distortion of the reflection of a tipped wire mesh.

Fig. 6 (below left). Profile of the D-ridge slope at a slightly higher water speed than that of Fig. 5. The amplitude has increased more than the photographs suggest, because in Fig. 6 the sensitivity has been lowered by reducing the tilt of the screen.

have lower maximum surface pressures, above which they collapse without buckling. If in Eq. 3 we set β equal to the limiting surface pressure β_{max}, however caused, we can solve for x_{max}, the maximum length of film. For $u = 23.2$ cm/sec and $\beta_{max} = 73$ dyne/cm, x_{max} is about 1 m.

The Reynolds number $(ux)/\nu$ at x_{max} is 2.32×10^5, which is low enough so that the entire length of the boundary layer is certain to be laminar (*1*, p. 37). If the boundary layer becomes turbulent, Eq. 3 overestimates x_{max}, but this can occur only for longer films with, perhaps surprisingly, lower water speeds. Raising u lowers the Reynolds number at x_{max} because x_{max} varies as u^{-3}.

A surface dam is a special case of upwelling and subsidence. Water subsides to get underneath it and then upwells on the downstream side. A stream with a succession of surface dams will be covered with film only for a short distance upstream of each dam. Except for what little material has diffused to the surface since the last upwelling, the rest of the stream will have no covering.

This will be true of upwelling and subsidence of any origin, be it bottom conformation and eddies in streams, density gradient waves in the sea (*3*), or whatever mechanism causes the linear pattern of upwellings and subsidences that go along with wind slicks (*4*). Suppose an array of linear upwellings 100 m apart makes the water flow at 10 cm/sec toward linear subsidences between them. Any film will be compressed into sharp-edged bands over the subsidences. The bands will be only 7 m wide if the collapse surface pressure of the film is 40 dyne/cm.

The sharpness of these edges is suggested by indicators other than the D-line, often when u is too low, or the water is too rough for D-lines to be seen. In wind slicks the film makes its presence known by damping short-wavelength waves. The transition from a ripply to a glassy surface occupies a distance of 30 cm or so, most of which may be the distance that the ripples have to run within the slick to be attenuated to insignificance. A sharper transition is revealed if we spray the water with a garden hose. The spray, splashing into the water, makes many little drops that skid across a clean water surface only to drown within a centimeter or so of the same line at the edge of a slick, a line well on the ripply side of the transition zone defined by the damping of the wavelets.

The sharp edges are predicted by Eq. 3, which applies exactly only if the water which approaches the edge carries no film material on its surface. This is never precisely true, and we can arrange cases where considerable material is carried. Will the film on the approaching water remain undisturbed until it hits and adds to the trapped film at a line of discontinuity; or will the jump in surface pressure occur more gradually? We might expect the latter to occur, unless the film has a very special relation of surface pressure to areal density. Yet if a drop of Mazola oil is added to an expanded Mazola oil slick, an expanding D-line is formed; so if the discontinuity is no longer ideal, the transition is still quite abrupt.

The D-line is not the only demarcation line to be found on water. Lines can often be seen at the meeting of waters of different properties, as when fresh water runs over salt water (*5*). But when we see a thread-narrow line we should suspect the presence of a natural or man-made contaminant film. D-lines will form on flowing Bethesda tap water, and on the cold, clear water of an Adirondack mountain brook.

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Planetary Albedo Changes Due to Aerosols

Abstract. *Absorption and scattering by aerosols and reflection of solar radiation from the surface determine the sign of the change in the planetary albedo caused by the presence of aerosols. This change in planetary albedo results in atmospheric heating or cooling. Small changes in the ratio of absorption to scattering over time can reverse such heating or cooling trends.*

In the past few years there has been growing concern over the effects of pollutants on the environment. Although greater attention has been devoted to biological effects, there are also possibly significant meteorological effects. This paper concerns changes in the planetary albedo which, in turn, affect the temperature of the earth. The planetary albedo is the proportion of the incoming solar energy that is reflected back to space by the earth and the atmosphere.

Until recently, it had been believed that an increase in carbon dioxide was contributing to an increase in the mean annual worldwide temperature (*1*). However, the decrease in the worldwide temperature since 1945 has required further hypothesis. McCormick and Ludwig (*2*) suggested that increased aerosol content resulting from pollution increased the backscattered component of incoming solar radiation and thereby caused the cooling. However, Charlson and Pilat (*3*) showed that an aerosol layer, by absorbing solar radiation, could have the opposite effect, that is, warming, and that other hypotheses are required to explain the observed cooling. I shall show here that the ratio of absorption to scattering and the surface (or lower cloud layer) albedo are important parameters in determining the temperature change.

A relationship between the planetary albedo, the incoming solar radiation, and the outgoing infrared radiation, which is a function of the mean temperature for a spherical body under the influence of solar radiation at the mean distance of the earth from the sun, is given by

$$(1 - A)\, S = 4\sigma T^4 \qquad (1)$$

where S is the incident solar radiation on a horizontal surface (integrated over wavelength), A is the planetary albedo, σ is the Stefan-Boltzmann constant, and T is the mean radiative temperature of the sphere.

It should be emphasized that the mean radiative temperature is the temperature one would obtain by radiometric observation from outside the atmosphere. The surface temperature of the earth is dependent on convection, conduction, evaporation, and the solar and infrared radiation fluxes. Angström (*4*) stated that a change in the mean temperature "can only be taken as a rough estimate" of a change in the surface temperature. This report is concerned with changes in the mean