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Suppression of Capillary Waves by Surface-Active Films

David Nelson

November 1985

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ABSTRACT

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1.0 INTRODUCTION

The calming effect of oily materials on water waves has fascinated scientists and seafarers since antiquity. In a famous experiment, Benjamin Franklin observed that a teaspoon of oil spread rapidly to cover approximately half an acre on a pond, producing an area "smooth as a looking glass."¹ Assuming that the teaspoon contained about 5 cm³ of oil, we can calculate that Franklin's film was about 20 Angstroms (2×10^{-7} cm) thick. Recently, sun-glint photographs of the western Mediterranean Ocean taken from the Space Shuttle have revealed a complicated pattern of quiescent regions, which reflect the sun specularly, as well as regions of diffuse reflection, presumably due to a profusion of capillary waves.² The regions of specular reflection have been attributed to sea slicks, possibly of natural origin. (Diatoms, for example, contain droplets of oil to assist in flotation and/or as an emergency food supply.³)

As representative surface-active materials, we may consider saturated fatty acids (lipids) with the chemical formula $\text{CH}_3 - (\text{CH}_2)_n - \text{COOH}$, where n is usually between 10 and 20. The polar head group is, for all practical purposes, infinitely soluble in water; the hydrocarbon tail, however, is hydrophobic, because it disrupts the delicate network of hydrogen bonds which characterize short range order in liquid H_2O . The competing hydrophillic and

hydrophobic tendencies tend to pin such "amphiphilic" molecules normal to an air-water interface, with the tails directed towards the atmosphere. Since amphiphiles typically measure 20 \AA along their long axis, Franklin's film was one molecular layer thick.

How can such a thin layer cause a pronounced change in the wave properties? The well-known reduction in surface tension due to the surfactant produces only a minor change in the velocity of the waves. Hydrodynamic theories of how surface-active films affect capillary-gravity wave damping have been worked out by Reynolds,⁴ Levich,⁵ and Dorrestein,⁶ who find effects which are most pronounced in the capillary wave part of the spectrum. The basic idea is that the finite compressibility of a lipid monolayer modifies the boundary conditions at an air-water interface. This change in boundary conditions will affect the flow below the surface down to a viscous penetration depth δ ,⁷

$$\delta = \sqrt{2\nu/\omega} , \quad (1.1)$$

where ν is the kinematic viscosity of water and ω is the angular frequency of the wave. Since δ is of order $10^{-2} - 10^{-3}$ cm for capillary waves with wavelengths of order .1 to 1 cm, surfactant molecules influence the flow down to a depth which vastly exceeds their size.

When surfactants are present, the vorticity in the viscous penetration depth increases, increasing the damping by factors as large as 2 to 4 relative to a clean surface.

Although remarkable, it seems unlikely that this enhanced damping could, by itself, account for interfaces which are "as smooth as a looking glass" when covered with an oily film. On a clean surface, a 0.5 cm capillary wave, for example, decays in a time which is more than twenty times its basic period. Capillary waves, once generated, will persist for several wave periods even when the damping is enhanced by surface-active films. The damping can never become very large, because the dissipation is confined to the viscous penetration depth, which depends only weakly on the surfactant concentration. The kinetic energy of the flow is distributed over a much larger volume, whose depth is comparable to the wavelength. The decay rate is increased by at most a factor three even in the extreme case of films which are incompressible or have infinite viscosities.

Sea slicks can also inhibit the generation of capillary waves by the wind.⁸ For clean surfaces, Lamb discusses a Kelvin-Helmholtz-like instability leading to wave growth above a critical wind speed of 6.5 m/sec.⁹ Lamb points out, however, that waves are apparently generated by other means at considerably lower velocities. A number of alternative theoretical approaches are available.¹⁰ Using one

such approach, Miles finds a minimum wind speed of about 1 m/sec for a clean surface, and estimates that an incompressible film increases this threshold by an order of magnitude.¹¹

In this report, we study a different mechanism for wave generation, namely turbulent fluctuations of the wind about its mean velocity. If a wave with a particular wavevector and frequency is already present, it will be acted upon most strongly by those components of the fluctuating atmospheric Reynold's stress with matching wavevectors and frequencies. This particular generation mechanism has been explored for clean surfaces by Lamb⁹ and by Phillips.¹²

By calculating the response of capillary waves to fluctuating Reynold's stresses within linearized hydrodynamics, we show that surfactants produce a pronounced reduction in the response to stresses parallel to the surface. If only tangential stresses are present, a modest amount of surfactant can reduce the root mean square amplitude of capillary waves by a factor of 10 or more relative to a clean surface; the root mean square amplitude tends to zero in the limit of an incompressible film. There is also a reduction in the response to fluctuating normal stresses, although here the effect is only a factor of 2 or 3. The different responses to parallel and normal stresses agrees with a suggestion by Dorrestein.⁶ Little is known about the relative strengths of fluctuating tangential and

normal stresses near the ocean surface. If these stresses are equal, the root mean square wave amplitudes will be reduced by a factor of about 6. If tangential stresses dominate, however, the suppression of capillary waves by surfactants could be much more effective, especially for films with low compressibilities.

In Section 2.0, we review some elementary properties of lipid films which will be needed later in the report. The hydrodynamic theory of damping of capillary-gravity waves by surfactants is reviewed in Section 3.0. This theory allows the damping to be predicted directly from laboratory measurements of pressure-area isotherms; in some cases, knowledge of film viscosities may also be necessary. Finally, in Section 4.0, we calculate the effect of lipid monolayers on the response to fluctuating atmospheric Reynold's stresses at the sea surface.

2.0 PROPERTIES OF SURFACE-ACTIVE FILMS

Figure 1 shows a typical experimental setup for studying surface-active films in the laboratory.¹³ Lipid molecules are confined to a region of area A by a float. The air-water surface tension $\sigma_{H_2O} \approx 74$ dyne/cm is reduced by the presence of the lipid monolayer. As a result, the film exerts a pressure π on the float as it tries to spread and cover the clean water surface. Upon measuring the pressure necessary to confine the film to different areas at constant temperature T, one obtains a pressure-area isotherm like that shown in Figure 2. It is easily shown that the pressure π gives the reduction in the surface tension due to the presence of the film,¹³

$$\sigma = \sigma_{H_2O} - \pi , \quad (2.1)$$

where σ is the surface tension with the film present. To a first approximation, pressure-area isotherms at temperature T are often described by a two-dimensional ideal gas equation of state,

$$\pi = Nk_B T/A , \quad (2.2)$$

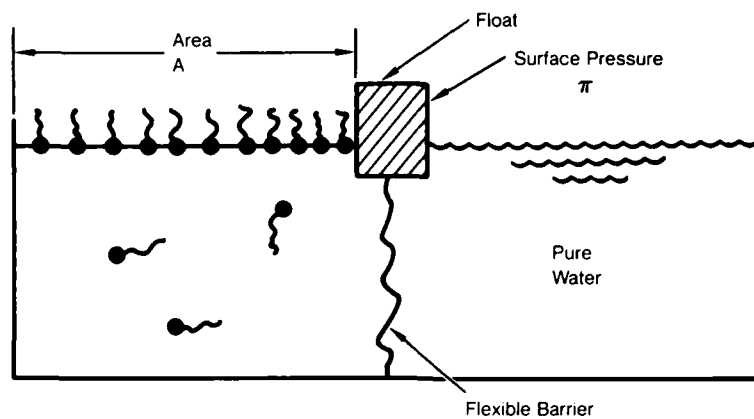


Figure 1. Experimental setup for measuring surfactant properties.

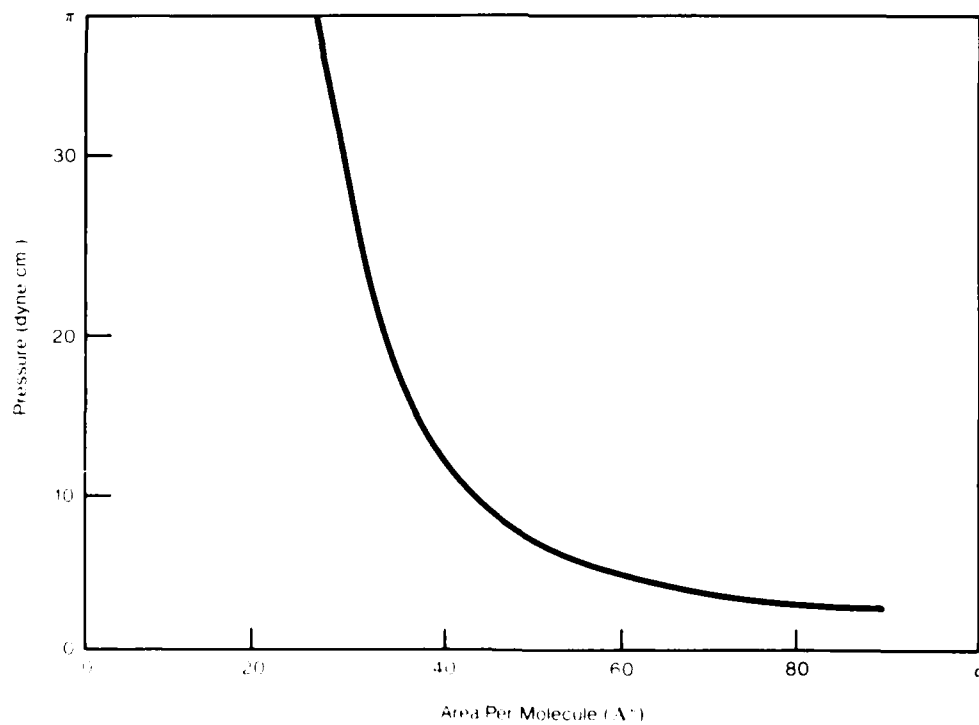


Figure 2. Typical pressure-area isotherm

where N is the total number of lipid molecules in the film. In real films, the pressure rises more steeply with decreasing area than predicted by Equation (2.2), due to hard core repulsions between lipids.

At high lipid densities, there can be anomalies in pressure-area isotherms due to phase transitions in the film. Many different phases are possible, including solids, liquids, gases, tilted liquids, expanded liquids, tilted solids, etc.¹⁴ In principle, there could be enhanced damping of surface waves if the periodic pressure variations in a wave were to drive a film back and forth across one of these transitions. It seems improbable, however, that naturally occurring slicks would appear exactly at a density corresponding to one of these phase transitions. The densities in sea slicks, moreover, are probably those of a dilute liquid or moderately dense gas,² for which most of these transitions are absent.

Besides reducing the surface tension, surface-active monolayers also cause the air-water interface to behave like an elastic membrane. When the surface distorts, there are now elastic restoring forces in the plane of the film. The elasticity arises because the surface tension depends on the concentration $\Gamma = N/A$ of surfactant. Consider, for example, the behavior of the teaspoon of oil discussed in the Introduction. The film initially spreads rapidly with a

velocity of about 10 cm/sec.¹³ It eventually stops spreading, however, at monolayer thicknesses, because further dilution of the film would increase the surface tension.

To calculate the force which stops the spreading, consider the free energy of a film of area A,

$$F = \sigma A + \sigma_{H_2O} \tilde{A} \quad (2.3)$$

where \tilde{A} is the area which is free of film. Let us compute the change in free energy associated with a small change in the film area,

$A \rightarrow A + \delta A$, $\tilde{A} \rightarrow \tilde{A} - \delta A$. The surfactant concentration changes according to

$$\Gamma = N/A$$

$$\rightarrow \frac{N}{A+\delta A} = \Gamma \left[1 - \frac{\delta A}{A} \right] . \quad (2.4)$$

Because the surface tension depends on Γ , there will be a corresponding change in $\sigma(\Gamma)$,

$$\begin{aligned} \sigma(\Gamma) &\rightarrow \sigma\left(\Gamma \left[1 - \frac{\delta A}{A} \right]\right) \\ &\approx \sigma(\Gamma) - \Gamma \frac{d\sigma}{d\Gamma} \frac{\delta A}{A} . \end{aligned} \quad (2.5)$$

Adding up the changes in Equation (2.3), we see that the change in free energy is

$$\delta F = [\sigma - \sigma_{H_2O} - \Gamma \frac{d\sigma}{d\Gamma}] \delta A . \quad (2.6)$$

Stability of the film requires that this change vanish, which means that the "spreading pressure" $\pi_s \equiv \sigma_{H_2O} - \sigma$ must be balanced by the term arising from density dependence of the surface tension,

$$\pi_s = - \Gamma \frac{d\sigma}{d\Gamma} . \quad (2.7)$$

The quantity

$$B \equiv - \Gamma \frac{d\sigma}{d\Gamma} \geq 0 , \quad (2.8)$$

acts like an elastic bulk modulus of the film, and will play an important role in the hydrodynamic theory discussed in the next two sections. Note that for a thick film, σ is independent of Γ , so that this bulk modulus vanishes. For a film which has spread to monolayer thicknesses with no external constraints, Equation (2.7) shows that B equals the spreading pressure. Films can also be compressed, by artificial barriers like that shown in Figure 1, or by internal waves at sea.¹⁵ In this case, we have, using Equation (2.1)

$$\begin{aligned}
 B &= \Gamma \frac{d(\pi_{\text{H}_2\text{O}} - \pi)}{d\Gamma} \\
 &= -A \frac{d\pi}{dA} .
 \end{aligned}
 \tag{2.9}$$

Equation (2.9) shows that B is the inverse two-dimensional compressibility and can be determined by differentiating pressure-area isotherms. For an ideal gas (which would spread to infinite dilution unless it were confined), we have

$$B = k_B T/a ,
 \tag{2.10}$$

where $a = A/N$ is the area per molecule.

3.0 DAMPING OF CAPILLARY-GRAVITY WAVES BY SURFACTANTS

Assume the mean air-water interface is normal to the z-axis, and consider the propagation of a deep water surface wave in the x-direction (See Figure 3). Following the methods of References 4-6, we write x- and z-components of the velocity as

$$v_x = \partial_x \phi - \partial_z \psi \quad (3.1a)$$

$$v_y = \partial_z \phi + \partial_x \psi \quad (3.1b)$$

where ϕ and ψ are functions of x , z , and time t . The function ϕ describes inviscid, incompressible potential flow and satisfies Laplace's equation,

$$\nabla^2 \phi = 0 . \quad (3.2)$$

The linearized incompressible Navier-Stokes equations,

$$\begin{aligned} \partial_t \vec{v} &= - \frac{1}{\rho_0} \vec{\nabla} p + \nu \nabla^2 \vec{v} , \\ \vec{\nabla} \cdot \vec{v} &= 0 , \end{aligned} \quad (3.3)$$

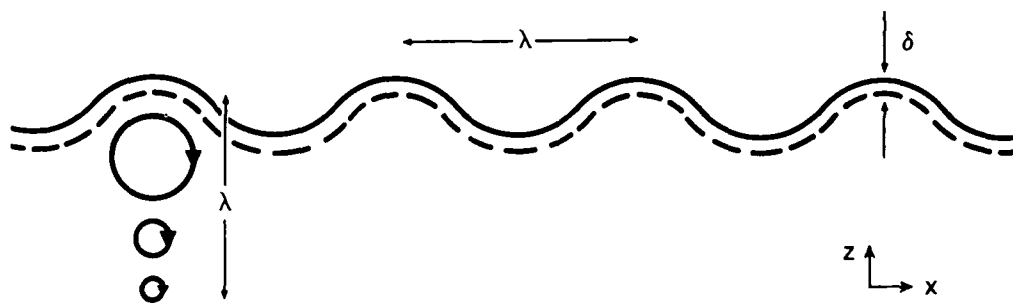


Figure 3 Characteristic dimensions of a capillary wave. The potential flow is approximately circular, and dies out at depths comparable to the wavelength λ . The viscous penetration depth δ is typically much smaller than λ .

will be satisfied, provided ψ satisfies

$$\partial_t \psi = \nu \nabla^2 \psi \quad (3.4)$$

where ν is the kinematic shear viscosity and ρ_0 is the density.

Restricting our attention to deep water waves, we write ϕ and ψ as periodic functions of x and t which are exponentially damped in the negative z direction.

$$\phi(x, z, t) = A e^{ikx + kz - i\omega t}, \quad (3.5a)$$

$$\psi(x, z, t) = C e^{ikx + \ell z - i\omega t}, \quad (3.5b)$$

where A and C are complex amplitudes which will be determined by boundary conditions. The undisturbed surface is taken to be $z = 0$. The ansatz (3.5a) for ϕ automatically satisfies Laplace's equation; ψ will satisfy Equation (3.4) provided that ℓ is related to k by

$$\ell^2 = k^2 - i\omega/\nu. \quad (3.6)$$

The form of ϕ and ψ means that the velocities v_x and v_y may be written

$$v_x = (ikAe^{kz} - lBe^{lz}) e^{ikx - i\omega t} \quad (3.7a)$$

$$v_z = (kAe^{kz} + ikBe^{lz}) e^{ikx - i\omega t} . \quad (3.7b)$$

We require that ϕ satisfy the inviscid Navier-Stokes equations, which means that the pressure is given by,

$$p = -\rho_0 g z + i\omega \rho_0 A e^{ikx + kz - i\omega t} , \quad (3.8)$$

where g is the gravitational constant, and we take the pressure at the undeformed interface to be zero. Boundary conditions will ultimately be specified at the displaced interface $z = \zeta(x,t)$. Since $\partial_t \zeta = v_z$ in the limit of small velocities and displacements, we have using Equation (3.7b) that

$$\zeta(x,t) = \frac{kA + ikB}{-i\omega} e^{ikx - i\omega t} . \quad (3.9)$$

Because ϕ obeys Laplace's equation, its contribution to the viscous damping in the Navier-Stokes equations vanishes. Dissipation comes from the rotational part of the flow, which is controlled by ψ :

$$\vec{\nabla} \times \vec{v} = - (\nabla^2 \psi) \hat{y} . \quad (3.10)$$

We shall be primarily interested in waves with wavelengths $\lambda = 2\pi/k$ which are much larger than, say, 10^{-3} cm. For such waves, which are only weakly damped, it is an excellent approximation to neglect the k^2 term in Equation (3.6) and write

$$l = \frac{1}{\sqrt{2}} \sqrt{\frac{\omega}{\nu}} - \frac{i}{\sqrt{2}} \sqrt{\frac{\omega}{\nu}} . \quad (3.11)$$

The decay of the function ψ in the z -direction is controlled by the real part of l , which is just the reciprocal of the viscous penetration depth δ defined in the introduction. Equation (3.11) is a good approximation for l whenever the wavelength is much greater than the viscous penetration depth,

$$\lambda \gg \delta . \quad (3.12)$$

Dissipation occurs only within the viscous penetration depth; its strength is given by the complex amplitude C in Equation (3.5), which is in turn determined by the boundary conditions. The flow is guaranteed to be potential flow at depths much greater than δ , regardless of the boundary conditions (see Figure 3).

At the interface there are boundary conditions on both the normal and tangential forces. The normal boundary condition is obtained by equating the zz -component of the fluid stress tensor, evaluated at $z = \zeta(x,t)$, to the usual capillary restoring force,⁷

$$(-p + 2\eta \partial_z v_z)|_{z = \zeta} = \sigma \frac{\partial^2 \zeta}{\partial x^2}. \quad (3.13)$$

In the linearized theory, surfactants only affect the normal boundary condition by changing the surface tension σ according to Equation (2.1). The tangential boundary condition follows from requiring that the xz -component of the fluid stress tensor, evaluated at $z = \zeta(x,t)$, match the forces arising from the flow of the surfactant within the surface. In analogy with three-dimensional compressible fluids, we define a two-dimensional viscous stress tensor⁶,

$$\begin{aligned} \sigma_{ij}^{(2)} = & -\pi \delta_{ij} + \eta_2 (\partial_i v_j + \partial_j v_i - \delta_{ij} \partial_k v_k) \\ & + \zeta_2 \delta_{ij} \partial_k v_k \end{aligned} \quad (3.14)$$

where i and j denote directions in the (x,y) -plane, and η_2 and ζ_2 are two-dimensional shear and bulk viscosities. We assume the lipid molecules are constrained to move at velocities given by the bulk

expressions (3.7) evaluated at the interface. Since v_y is zero, the force due to the surfactant at the interface is directed along the x-axis and equals

$$\begin{aligned} F_S &= \partial_x \sigma_{xx}^{(2)} \\ &= -\partial_x \pi + \mu_2 \partial_x^2 v_x \end{aligned} \quad (3.15)$$

where we have defined a composite two-dimensional viscosity μ_2 ,

$$\mu_2 = \eta_2 + \zeta_2. \quad (3.16)$$

Upon recognizing that π is, up to an additive constant, just the negative of the surface tension (see Equation (2.1)), we see that the tangential boundary condition becomes

$$\eta(\partial_z v_x + \partial_x v_z) \Big|_{z=\zeta} = \frac{\partial \sigma}{\partial x} + \mu_2 \partial_x^2 v_x. \quad (3.17)$$

To proceed further, we need to know the space and time dependence of σ induced by the wave motion. Assuming that σ changes by virtue of changes in the surfactant concentration Γ , we have

$$\frac{\partial \sigma}{\partial x} = \frac{\partial \sigma}{\partial \Gamma} \frac{\partial \Gamma}{\partial x}, \quad (3.18)$$

so we need to know $\Gamma(x,t)$. Assuming that Γ undergoes both diffusion and convection at the interface, we have⁵

$$\partial_t \Gamma + \vec{\nabla}(\vec{v}\Gamma) = D \nabla^2 \Gamma . \quad (3.19)$$

The two-dimensional diffusion constant D will be controlled by diffusion of the lipid polar head groups at the interface through water. It certainly cannot be much greater than, say, 10^{-5} cm²/sec, a typical diffusion constant in a bulk liquid. Under these conditions, the convective part of Equation (3.19) dominates over diffusion. We neglect the finite solubility of lipid molecules in water which, according to Levich,⁵ decreases the ability of surfactants to damp surface waves. Neglecting D , and writing Γ in terms of the deviation $\Gamma'(x,t)$ from its equilibrium value Γ_0 ,

$$\Gamma(x,t) = \Gamma_0 + \Gamma'(x,t) , \quad (3.20)$$

we have, to lowest order in the small quantities v_x and Γ' ,

$$\partial_t \Gamma' = - \Gamma_0 \partial_x v_x , \quad (3.21)$$

or, integrating with respect to time and differentiating with respect to x ,

$$\frac{\partial \Gamma'}{\partial x} = \frac{-i\Gamma_0}{\omega} \partial_x^2 v_x. \quad (3.22)$$

Combining Equation (3.22) with Equations (3.18) and (3.17), we see that the tangential boundary condition becomes

$$\eta(\partial_z v_z + \partial_x v_x) \Big|_{z=\zeta} = \left(\frac{iB}{\omega} + \mu_2\right) \partial_x^2 v_x \quad (3.23)$$

where we have introduced the surfactant bulk modulus B defined by Equation (2.8). Note that the bulk modulus can be regarded as contributing to a frequency-dependent two-dimensional viscosity. The angular frequency of a .5 cm capillary wave is about 300 Hz. For a moderately dense film, with 40 \AA^2 per molecule, the ideal gas formula (2.10) gives $B = 10 \text{ dyne/cm}$. Under these conditions, the contribution of the bulk modulus to the effective viscosity is

$$\frac{B}{\omega} \sim 3 \times 10^{-2} \text{ dyne-sec/cm}. \quad (3.24)$$

Since typical intrinsic film viscosities are less than or equal to $10^{-4} \text{ dyne-sec/cm}$,¹⁶ we shall neglect the intrinsic viscosity in most of what follows.

Setting μ_2 to zero, and using Equations (3.7a), (3.7b), (3.8), and (3.9) in the boundary conditions (3.13) and (3.23), we find two homogeneous equations for the complex amplitudes A and C, namely

$$(-\omega^2 + \omega_0^2 - 2i\nu\omega k^2) A + (i\omega_0^2 + 2\nu k l \omega) C = 0, \quad (3.25a)$$

$$(2\nu\omega k^2 + iBk^3/\rho_0) A + (\omega^2 + 2i\nu\omega k^2 - \frac{Bk^2 l}{\rho_0}) C = 0 \quad (3.25b)$$

where

$$\omega_0(k) \equiv \sqrt{gk + \sigma k^3/\rho_0}. \quad (3.26)$$

Simultaneous solutions are only possible if the determinant of coefficients vanishes,

$$\Delta(k, \omega) \equiv \det \begin{pmatrix} -\omega^2 + \omega_0^2 - 2i\nu\omega k^2, & i\omega_0^2 + 2\nu k l \omega \\ 2\nu\omega k^2 + 2Bk^3/\rho_0, & \omega^2 + 2i\nu\omega k^2 - \frac{Bk^2 l}{\rho_0} \end{pmatrix} = 0, \quad (3.27)$$

which defines implicitly the dispersion relation $\omega = \omega(k)$ of capillary-gravity waves. If there is no surfactant present, $B = 0$,

and Equation (3.27) leads in the limit $\lambda \gg \delta$ to the standard result,⁵

$$\omega(k) = \omega_0(k) - 2i\nu k^2. \quad (3.28)$$

Suppose, on the other hand $B = \infty$, so that the film is incompressible. This is the limiting case discussed by Lamb.⁹ From Equation (3.25b), we have that

$$ikA - \frac{1}{2}B = 0. \quad (3.29)$$

which, in view of Equation (3.7a), means that the tangential component of velocity vanishes, $v_x = 0$. As shown, for example, in the book by Levich,⁵ the solution of (3.27) in the capillary wave part of the spectrum ($\lambda < 1.7$ cm) is then

$$\omega(k) = \sqrt{\frac{\sigma k^3}{\rho_0}} - \frac{1}{\sqrt{2}} \left(\frac{\nu^2 \sigma}{\rho_0} \right)^{1/4} k^{7/4}, \quad (3.30)$$

where we have neglected a small shift in a real part of the frequency. The ratio of the imaginary part of (3.30) to the damping $2\nu k^2$ for a clean surface is

$$\frac{\text{Im } \omega}{2\nu k^2} = \frac{1}{4\sqrt{2}} \sqrt{\frac{(\sigma k^3 / \rho_0)^{1/2}}{\nu k^2}}$$

$$\approx 3 \lambda^{1/4}, \quad (3.31)$$

where the wavelength in the last line is measured in centimeters. Although an equation like (3.31) is cited in most texts as the reason oil calms troubled waters, the enhanced damping is really not very impressive, especially for wavelengths much less than a centimeter.

To examine this question further, we have solved Equation (3.27) numerically for a range of different values of B. To simplify the discussion, we model the surfactant by an ideal gas, and imagine that it is gradually compressed by increasing the pressure π which confines it. Comparing Equations (2.1) and (2.2), we see that $B = \pi$ in this approximation. The pressure also enters the surface tension through Equation (2.1). Experiments which measure capillary wave damping¹⁶⁻¹⁸ typically use a transducer at a fixed frequency, and measure an inverse attention length k_d by fitting the envelope of the wave train to an exponential decay, $\sim \exp(-k_d x)$. Numerical solutions of Equation (3.27) at a fixed real wavevector k lead to a complex frequency of the form

$$\omega = \omega_0(k) - i\gamma(k) \quad (3.32)$$

where $\omega_0(k)$ is given approximately by (3.28) and $\gamma(k)$ represents the damping. To make contact with the experiments, we need to analytically continue to real frequencies and complex wavevectors. Let k_0 be the real wavevector such that $\omega_0(k_0)$ equals the real frequency ω in question. Replacing k by $k_0 + ik_d$ in Equation (3.32), and expanding in the small quantity k_d , we find that

$$k_d = \gamma(k_0) / \left[\left. \frac{d\omega_0}{dk} \right|_{k = k_0} \right]. \quad (3.33)$$

The group velocity rather than the phase velocity enters because a spatially narrow transducer at fixed frequency generates a band of wavelengths in the vicinity of k_0 .

Figure 4 shows a plot of k_d vs. pressure for a 0.52 cm capillary wave. Also shown is the damping for an incompressible film. The damping increases with increasing surfactant concentration, and remarkably, goes through a maximum before approaching the result for an incompressible film at high pressure. This nonmonotonic behavior has been observed in many laboratory experiments¹⁶⁻¹⁷, including those on naturally occurring sea surface films.¹⁸ It was first pointed out theoretically by Dorrestein.⁶ Note that the damping can actually exceed the result for an incompressible film. As noted by

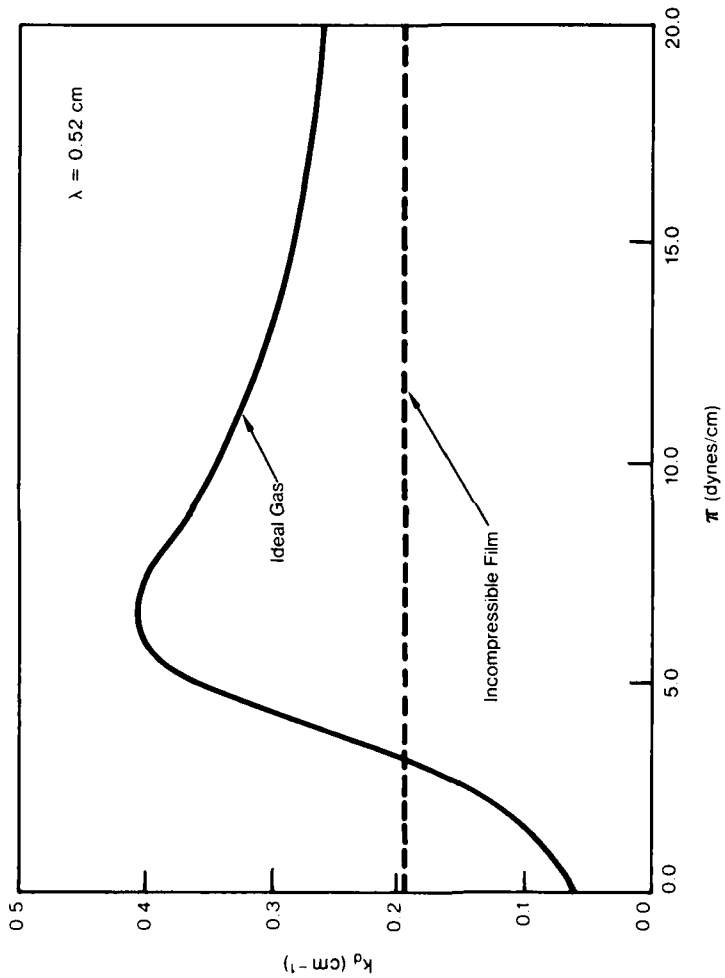


Figure 4 Damping as a function of pressure assuming the surfactant behaves like an ideal gas. The weak pressure dependence for an incompressible film arises from the pressure dependence of the surface tension.

Davies and Vose¹⁷, this must be due to an appreciable tendency of the horizontal velocity near the surface to reverse relative to the horizontal velocity in the bulk. The effect of a finite intrinsic surface viscosity is to reduce the maximum, ultimately leading to a monotonic variation in the limit of large viscosities.⁶ Although the enhanced damping at intermediate pressures is larger than that predicted by Equation (3.30), it is still not a particularly dramatic effect.

4.0 EFFECT OF TURBULENT FLUCTUATIONS IN THE ATMOSPHERE

The linearized hydrodynamic theory described in Section 3 is easily generalized to allow a coupling to fluctuating components of the Reynolds stress in the wind. Upon adding the zz and xz components of the atmospheric stress tensor p'_{ij} at the interface to the boundary conditions (3.13) and (3.23), we have

$$(-p + 2\eta\partial_z v_z)|_{z=\zeta} - \sigma \frac{\partial^2 \zeta}{\partial x^2} = p'_{zz}(x,t), \quad (4.1)$$

$$\eta(\partial_z v_x + \partial_x v_z)|_{z=\zeta} - \left(\frac{iB}{\omega} + \mu\right)\partial_x^2 v_x = p'_{xz}(x,t), \quad (4.2)$$

where $p'_{zz}(x,t)$ and $p'_{xz}(x,t)$ are fluctuating random variables. Effects due to the mean wind velocity, embodied in the average values of p'_{zz} and p'_{xz} , can amplify or diminish preexisting capillary waves, depending on the circumstances.¹⁹

Here, we study generation of capillary waves due to fluctuations in p'_{zz} and p'_{xz} about their mean values. Assuming a wind speed of 1m/sec at a height of 1 meter above the ocean, we estimate that turbulent fluctuations in the bulk stress tensor should be present down to a Kolmogorov scale of about .03 cm., which includes the capillary wave part of the spectrum. Because little is known about such fluctuations close to an air-water interface, we shall simply assume that

the fluctuating components of the wind stress are unaffected by the presence or absence of surfactant, and compare the mean square wave amplitudes generated at a various wave vectors and frequencies.

Consider the response to one particular Fourier component of the fluctuating wind stress tensor at the interface,

$$p'_{zz}(x,t) = p_{zz}^0 e^{ikx-i\omega t}; \quad p'_{xz}(x,t) = p_{xz}^0 e^{ikx-i\omega t} \quad (4.3)$$

where, in contrast to Section 3.0, both k and ω are real. The analysis of Section 3.0 (again setting the 2d viscosity μ_2 to zero) now leads to a matrix equation for the amplitudes A and C , namely

$$\begin{pmatrix} -\omega^2 + \omega_0^2 - 2i\gamma\omega k^2, & i\omega_0^2 + 2\nu\omega k\ell \\ 2\nu\omega k^2 + iBk^3/\rho_0, & \omega^2 + 2i\nu\omega k^2 - Bk^2\ell/\rho_0 \end{pmatrix} \begin{pmatrix} A \\ C \end{pmatrix} = \begin{pmatrix} -i\omega p_{zz}^0 \\ -i\omega p_{xz}^0 \end{pmatrix}. \quad (4.4)$$

The amplitudes which follow from (4.4) are

$$A = -i\omega[(i\omega_0^2 + 2\nu\omega k\ell)p_{zz}^0 + (2\nu\omega k^2 - Bk^3/\rho_0)p_{xz}^0]/\Delta(k,\omega) \quad (4.5a)$$

$$C = -i\omega[(\omega^2 + 2i\nu\omega k^2 - Bk^2\ell/\rho_0)p_{zz}^0 + (-\omega^2 + \omega_0^2)p_{xz}^0]/\Delta(k,\omega) \quad (4.5b)$$

where $\Delta(k, \omega)$ is the determinant defined in Equation (3.27). We can now obtain the space and time dependence of the interface height via Equation (3.9).

Suppose that p_{zz}° and p_{xz}° are chosen from an ensemble of randomly chosen amplitudes, and assume for simplicity that p_{zz}° and p_{xz}° are statistically independent. It then follows from Equations (4.5) and (3.9) that

$$\overline{\eta^2(x, t)} = S_L(k, \omega) \overline{(p_{zz}^{\circ})^2} + S_T(k, \omega) \overline{(p_{xz}^{\circ})^2} \quad (4.6)$$

where the bar denotes an ensemble average and

$$S_L(k, \omega) = k^2 |i\omega_0^2 + 2\nu k l \omega - i\omega^2 + 2\nu k^2 \omega - iBk^3 l / \rho_0|^2 / |\Delta(k, \omega)|^2 \quad (4.7a)$$

$$S_T(k, \omega) = k^2 |2\nu k l \omega - Bk^3 l / \rho_0 + i\omega^2 - i\omega_0^2 + 2\nu k^2 \omega|^2 / |\Delta(k, \omega)|^2 \quad (4.7b)$$

$S_L(k, \omega)$ and $S_T(k, \omega)$ are response functions describing how the interface reacts to longitudinal (i.e., normal to the surface) and transverse stresses respectively. Figure 5 shows the real part of the capillary-gravity wave dispersion relation (3.26). It is

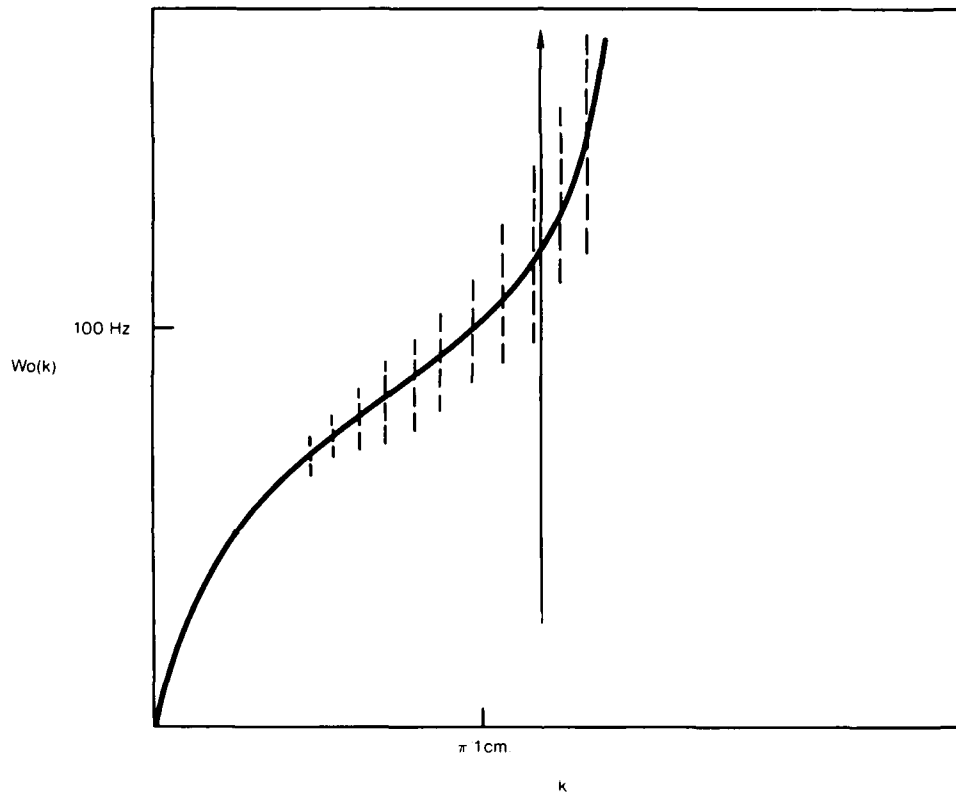


Figure 5. Capillary-gravity wave dispersion relation. The imaginary part of the frequency at fixed real wavevector is represented by the size of vertical dashed lines.

instructive to imagine fixing the wavevector and varying frequency along the vertical line shown in the figure. The response functions S_L and S_T should become large when the frequency passes through $\omega_0(k)$. The width of this resonance is proportional to the damping discussed in Section 3.0. The height of the resonance is a measure of how easy it is to generate waves at the resonance frequency.

Figures 6a and b contrast the response with and without a surface film in the gravity wave part of the spectrum. The wavelength is one meter, we have assumed that the surface film has a compressibility of 10 dyne/cm. On a clean surface, there is an extremely narrow resonance at $\omega_0 = 7.85216$ Hz. The surfactant shifts the resonant frequency and leads to a small increase in the damping, as measured by the half-width at half-maximum. The heights of the resonances are depressed only slightly by the surface film. Figure 6 shows that there will be persistent long wavelength "oily swells" in sea slicks, notwithstanding the presence of a surface film. This result is to be expected, since the right-hand side of Equation (3.23) becomes negligible compared to the left-hand side at sufficiently long wavelengths.

The results for capillary waves with wavelength 0.52 cm are shown in Figures 7a and 7b. Here, the effect of a surface film is much more remarkable. Particularly striking is the reduction in the

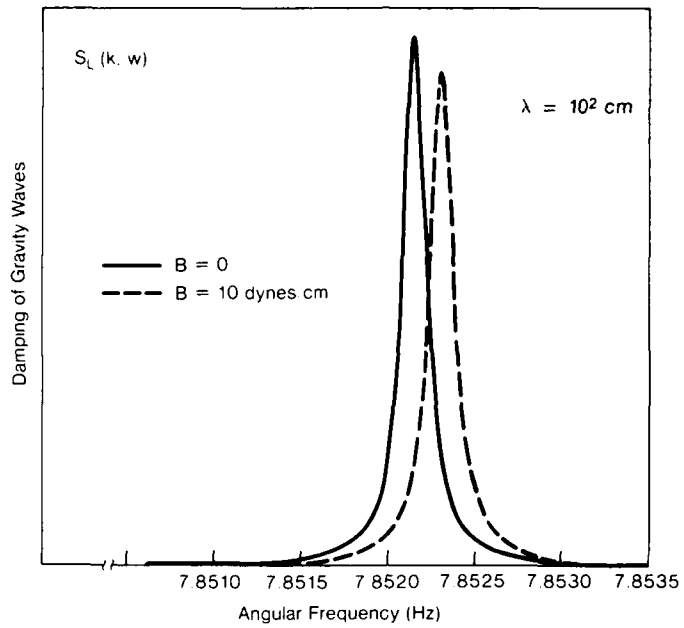


Figure 6a. Longitudinal response functions in the gravity wave part of the spectrum.

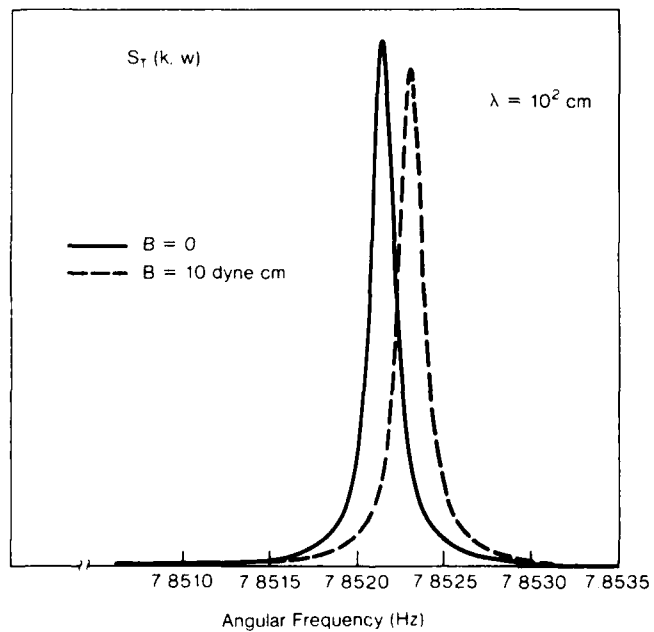


Figure 6b. Transverse response functions in the gravity wave part of the spectrum.

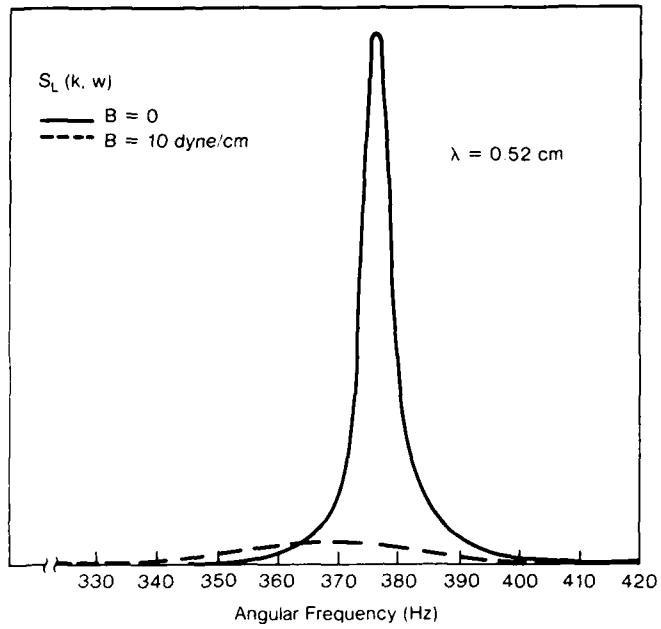


Figure 7a. Longitudinal response functions in the capillary wave part of the spectrum.

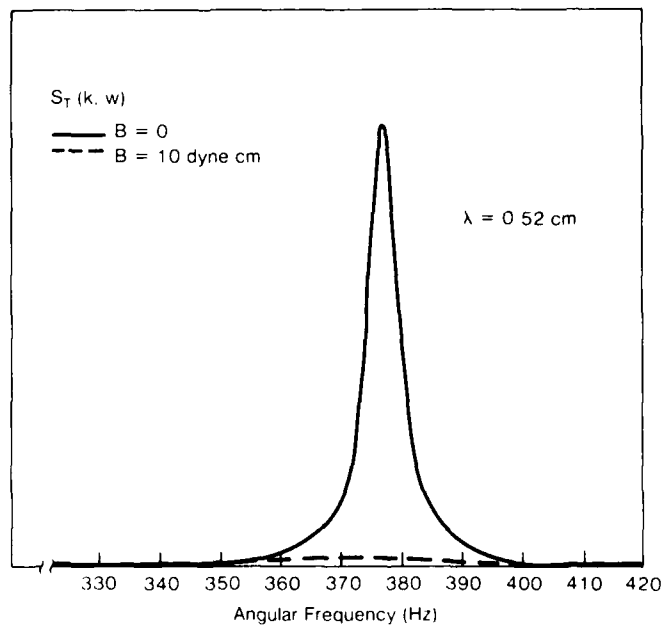


Figure 7b. Transverse response functions in the capillary wave part of the spectrum.

heights of the response functions. The longitudinal response is down by a factor of 20 and the transverse response is barely visible (down by a factor of 60). A significant increase in the damping is also apparent, as well as a small shift in the resonant frequency

($\omega_0 = 369.06$ Hz for a clean surface). Figure 7 shows that oil calms troubled waters not only because of this increased damping, but also because it is very difficult to generate large amplitude capillary waves.

The reduced amplitude for capillary waves is most pronounced in the transverse response function. In contrast to the damping, which approaches a finite limit for an incompressible film, the amplitudes generated by transverse fluctuations actually vanish as B tends to infinity. To see this in more detail, we start with the time-dependent boundary conditions (3.13) and (3.23), including the effect of a transverse wind stress $p_{xz}(x,t)$,

$$2\eta \frac{\partial_z v_x}{\omega_0} + \rho_0 g \zeta + \rho_0 \frac{\partial \phi}{\partial t} - \sigma \frac{\partial^2 \zeta}{\partial x^2} = 0, \quad (4.8a)$$

$$\eta (\partial_x v_z + \partial_z v_x) - \frac{iB}{\omega_0} \partial_x^2 v_x = p_{xz}(x,t), \quad (4.8b)$$

where we have set $\mu_2 = 0$ and used Equation (3.8) for the pressure. All quantities in Equations (4.8) are to be evaluated with $z = \zeta$.

The effect of viscosity in these boundary conditions can be neglected in the large B limit. Upon setting $\eta = 0$, using (3.1) and differentiating each equation with respect to time, we find Equations for ϕ and ψ , namely

$$\rho_0 g (\partial_z \phi - \partial_x \psi) + \rho_0 \partial_t^2 \phi - \sigma \partial_x^2 (\partial_z \phi - \partial_x \psi) = 0 \quad (4.9a)$$

$$B \partial_x^2 (\partial_x \phi + \partial_z \psi) = \partial_t p_{xz}. \quad (4.9b)$$

We now assume that ϕ and ψ can be written

$$\phi = A(t) e^{ikx + kz - i\omega_0(k)t} \quad (4.10a)$$

$$\psi = C(t) e^{ikx + lz - i\omega_0(k)t} \quad (4.10b)$$

where k is real, $\omega_0(k)$ is given by Equation (3.26), and $A(t)$ and $C(t)$ are slowly varying functions of time. The wave represented by Equation (4.10) will be acted upon most strongly by that Fourier component of p_{xz} whose wavevector and frequency match k and $\omega_0(k)$. As discussed, for example, by Longuet-Higgins¹⁹, the wave will be most strongly amplified when the phase of p_{xz} makes this variable stress a maximum at the wave crests and a minimum at the troughs. Assume for simplicity that only this mode is present, and that it

varies as in Equation (4.3). When Equations (4.10a) and (4.10b) are substituted in (4.9), the result is two ordinary differential equations for $A(t)$ and $C(t)$, namely

$$\dot{A}(t) + i\ddot{A}(t)/2\omega_0 + \frac{1}{2}\omega_0 C(t) = 0 \quad (4.11a)$$

$$ik^3 A(t) + k^2 \ell C(t) = -i\omega_0 p_{xz}^0. \quad (4.11b)$$

We now confine our attention to the capillary wave part of the spectrum. Neglecting the second order time derivative in (4.11a), and using (4.11b) to eliminate $C(t)$, we find a simple differential equation for $A(t)$ (ignoring a contribution to the imaginary part of A), namely,

$$\frac{dA}{dt} = -\frac{1}{2\sqrt{2}} \left(\frac{\sigma v}{\rho_0}\right)^{2^{1/4}} k^{7/4} A + \frac{1}{2\sqrt{2}} \left(\frac{\sigma k^3}{\rho_0}\right)^{3/4} \frac{\sqrt{v}}{Bk^2} p_{xz}^0. \quad (4.12)$$

If $p_{xz}^0 = 0$, the wave dies out, and $A(t)$ decays with the damping rate of an incompressible surfactant, given by the imaginary part of Equation (3.30). For a nonzero tangential stress, $A(t)$ approaches

$$A_\omega^{\text{surf}} = \omega_0 p_{xz}^0 / Bk^3 \quad (4.13)$$

for long times, a limit which tends to zero for large B .

Equation (4.12) should be contrasted with the result for a clean surface, which is¹⁹

$$\frac{dA}{dt} = -2vk^2A + p_{xz}^0/2\rho_0. \quad (4.14)$$

This equation has the long time limit

$$A_\infty^{\text{clean}} = p_{xz}^0/4vk^2\rho_0. \quad (4.15)$$

The ratio $A_\infty^{\text{clean}}/A_\infty^{\text{surf}}$ can be made arbitrarily large as B becomes large, i.e., for sufficiently incompressible films.

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