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Propagation Characteristics of Capillary Ripples, I.
The Theory of Velocity Dispersion and Amplitude
Attenuation of Plane Capillary Waves on
Viscoelastic Films*

MASTER

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ABSTRACT

The boundary value problem for velocity of propagation and attenuation of capillary ripples over viscoelastic surface films is set up and solved from the viewpoint of continuum hydrodynamics. Both soluble and insoluble films are treated. Successive approximation methods are used to derive explicit formulae for velocity of propagation and amplitude

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attenuation; formulae for these quantities accurate to second order are given for slightly viscoelastic and highly viscoelastic films, and formulae accurate to first order are given for films of intermediate viscoelasticity.

INTRODUCTION

The theoretical study of capillary ripples began with Kelvin (1), who derived an equation for the frequency dependence of the velocity of propagation of capillary ripples over clean liquid surfaces. The attenuation of capillary ripples on rigid films was briefly discussed by Lamb (2) and studied carefully by Levich (3, 4). Levich's formulation of boundary conditions was basically thermodynamic; treatments of this same problem with hydrodynamic boundary condition formulation are due to Wieghardt (5) and Dorrestein (6). The dependence of velocity of propagation of ripples on film or medium viscoelastic properties had not been investigated, nor had ripple attenuation been investigated for other than rigid film boundary conditions, prior to the initiation of this research.

Very recently Goodrich (7, 8) has published results of his theoretical and experimental attack on this problem. The theoretical attack somewhat resembles our own in concept. Goodrich's treatment includes a more complete characterization of film viscoelasticity in terms of number of viscoelastic properties than ours, whereas our treatment, due in part to the simplified treatment of film viscoelasticity, lends itself to successive approximation solutions for velocity of propagation and amplitude attenuation capable of simple comparison with experiment. Our experimental approach, to be described in the following paper, is quite different from that of Goodrich.

The study of velocity dispersion with frequency and amplitude attenuation in the propagation of capillary ripples appears to offer interesting possibilities for the investigation of viscoelastic properties of surface films. A recent review by Tschoegl (9) emphasizes the dearth of information in this area. For this purpose a theoretical formulation including both elastic and viscous relaxation parameters is necessary, and it is also highly desirable that the formulation be suited for all film compositions (from dilute to concentrated monolayers) and for appreciable film solubility. The theory to be developed herein results in such a formulation.

THEORETICAL

We shall be interested in capillary ripples produced by a bar lying in the surface of a liquid and oscillating normal to the plane of the surface at rest. Let the y axis be normal to the surface at rest, $y = 0$ be the equation of that surface, and negative values of y correspond to points within the liquid. Let the z axis be the rest position of the bar, and let the bar be placed in periodic motion in the plane $x = 0$, moving always parallel to its rest position and oscillating about $y = 0$. Then waves will be propagated in the x direction, and their motion will depend on the coordinates x , y , and t but not on z . We shall suppose the amplitudes of these waves to be small compared to their wave lengths. We shall further suppose the liquid to be incompressible.

Let ρ be the density of the liquid, g the gravitational constant, $\mathbf{q}$ the (vector) acceleration of gravity and μ the coefficient of viscosity. Let

$\underline{q}$ be the vector particle velocity* with components q_x , q_y and p the pressure; $\underline{q}$ and p will be functions of x , y , and t . Then the Navier-Stokes equation for incompressible fluids is (10)

$$\rho \left\{ \frac{\partial \underline{q}}{\partial t} + (\underline{q} \cdot \nabla) \underline{q} \right\} = -\nabla p + \mu \nabla^2 \underline{q} - \rho \underline{g} \quad [1]$$

subject to the continuity equation for incompressible fluids

$$\nabla \cdot \underline{q} = 0. \quad [2]$$

We have the problem of finding a solution to Eq. [1], subject to Eq. [2] and other appropriate boundary conditions, applicable to the propagation of plane waves through a viscous medium bounded by a viscoelastic film. We proceed as follows:

A. Linearization and General Solution of Navier-Stokes

Equation Appropriate for Capillary Ripples (11)

We shall suppose $\underline{q}$ and all its derivatives small in first order. Where ω is the angular frequency of the generator bar, a the wave amplitude, and λ the wave length; the expected orders of magnitude of terms in Eq. [1] are $\omega^2 a$ for $\frac{\partial \underline{q}}{\partial t}$, $\omega^2 a \left(\frac{a}{\lambda}\right)$ for $(\underline{q} \cdot \nabla) \underline{q}$, and $\mu \omega a / \lambda^2$ for $\mu \nabla^2 \underline{q}$. We therefore suppose specifically that $\omega^2 a \ll g$, $\frac{a}{\lambda} \ll 1$. Hence to zeroth-order Eq. [1] becomes

$$0 = -\frac{\partial p}{\partial y} - \rho g \quad [3a]$$

* Bold face letters denote vectors, common letters are scalars. ∇ is a vector operator; $\nabla \cdot \underline{q} \equiv \text{div } \underline{q}$, $\nabla p \equiv \text{grad } p$, $\nabla \times \underline{q} \equiv \text{curl } \underline{q}$, $\nabla^2 \equiv (\nabla \cdot \nabla) \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$.

$$0 = \frac{\partial p}{\partial x} \quad [3b]$$

and if we take $p = 0$ when $y = 0$ we have to zeroth order

$$p = -\rho g y. \quad [4]$$

Let $p = \Delta p - \rho g y$; then by [4] Δp is small in first order. Substituting this expression in Eq. [1] and neglecting second order terms we find to first order

$$\rho \frac{\partial \underline{q}}{\partial t} = -\nabla(\Delta p) + \mu \nabla^2 \underline{q} \quad [5]$$

subject to Eq. [2].

We now resolve $\underline{q}$ into components $\underline{q}_1, \underline{q}_2$ such that $\underline{q} = \underline{q}_1 + \underline{q}_2$, $\nabla \times \underline{q}_1 = 0$, $\nabla \cdot \underline{q}_2 = 0$. That this resolution is valid and unique except for a constant vector is a general theorem of vector analysis particularly well discussed by Sommerfeld (12). Then there exists a scalar function $\phi(x, y, t)$ such that $\underline{q}_1 = -\nabla \phi$. We shall further undertake to establish a stream function $\Psi(x, y, t)$ such that $q_{2x} = -\frac{\partial \Psi}{\partial y}$, $q_{2y} = \frac{\partial \Psi}{\partial x}$; if this function can be established the vector $\underline{q}_2$ will evidently satisfy $\nabla \cdot \underline{q}_2 = 0$. Equation [5] may now be rewritten

$$-\frac{\partial^2 \phi}{\partial t \partial x} - \frac{\partial^2 \Psi}{\partial t \partial y} = -\frac{1}{\rho} \frac{\partial \Delta p}{\partial x} - \frac{\mu}{\rho} \frac{\partial}{\partial y} \nabla^2 \Psi \quad [6a]$$

$$-\frac{\partial^2 \phi}{\partial t \partial y} + \frac{\partial^2 \Psi}{\partial t \partial x} = -\frac{1}{\rho} \frac{\partial \Delta p}{\partial y} + \frac{\mu}{\rho} \frac{\partial}{\partial x} \nabla^2 \Psi \quad [6b]$$

in which we have used $\nabla^2 \underline{q}_1 = -\nabla^2(\nabla \phi) = -\nabla(\nabla^2 \phi) = 0$, since

$\nabla \cdot \underline{q}_2 = 0$ and Eq. [2] together imply $\nabla \cdot \underline{q}_1 = 0$. Equations [6a] and [6b] will be simultaneously satisfied if

$$\frac{\partial \Psi}{\partial t} = \frac{\mu}{\rho} \nabla^2 \Psi \quad [7a]$$

$$\frac{\partial \phi}{\partial t} = \frac{\Delta p}{\rho} \quad [7b]$$

and we seek functions ϕ and Ψ satisfying these equations and the further equation, implied by Eq. [2]

$$\nabla^2 \phi = 0. \quad [7c]$$

The oscillations of the generator bar will cause waves to be propagated in the + x direction; let k be their wave number, α their damping coefficient, and let $\underline{k} = k + i\alpha$. Then we suppose ϕ and Ψ to be of the form

$$\phi = Y_1(y) e^{i(\underline{k}x - \omega t)} \quad [8a]$$

$$\Psi = Y_2(y) e^{i(\underline{k}x - \omega t)} \quad [8b]$$

and find that the functions defined in Eqs. [8a] and [8b] satisfy Eqs. [7c] and [7a] respectively if

$$Y_1 = A e^{\underline{k}y} + A' e^{-\underline{k}y} \quad [9a]$$

$$Y_2 = B e^{my} + B' e^{-my} \quad [9b]$$

where A , A' , B , and B' are complex constants and $m^2 = \underline{k}^2 - \frac{i\rho}{\mu} \omega$. Now

if the waves are generated in a trough of finite depth l , we must have

$$Y_1 = 0, Y_2 = 0 \text{ when } y = -l, \text{ so that } A' = -A e^{-2\underline{k}l}, Y_1 = A \{ e^{\underline{k}y} - e^{-(2\underline{k}l - \underline{k}y)} \}.$$

We shall be interested in physical situations in which $k \geq 24 \text{ cm}^{-1}$, $l \geq 2 \text{ cm}$.

Hence $e^{-(2\underline{k}l - \underline{k}y)} \leq e^{-48}$ and is negligible. We may therefore neglect the

constant A' , and for similar reasons (by choice of the root m of m^2 whose

real part is positive) we may also neglect the constant B' . This amounts to treating the waves as propagated on a medium whose depth is infinite, and the discussion just given indicates that this treatment will be appropriate for experimental results such as might be obtained, for example, with films on liquids in Langmuir troughs. For deep media we therefore have

$$\phi = Ae^{\frac{ky}{\omega}} e^{i(kx - \omega t)} \quad [10a]$$

$$\psi = Be^{my} e^{i(kx - \omega t)} \quad [10b]$$

and from [7b]

$$\Delta p = -ipA\omega e^{\frac{ky}{\omega}} e^{i(kx - \omega t)}, \quad [10c]$$

B. The Diffusion and Surface Transfer Problem

Because of the periodic deformation of the surface there will be a periodic departure of the surface concentration Γ (moles/cm²) from its equilibrium value Γ_0 for the surface at rest; if the concentration of solute C (moles/cm³) is appreciable there will result a periodic transfer of solute from bulk to surface and a diffusion of solute within the bulk. The following boundary value problem arises:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right), \quad x > 0, \quad y < 0 \quad [11a]$$

$$C(x, y, t)_{y \rightarrow -\infty} = C_0 \quad [11b]$$

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x} [\Gamma q_x]_{y \rightarrow 0^-} - R = 0 \quad [11c]$$

where C_0 is the mean bulk concentration, R the rate of transfer of solute from bulk to surface (moles/cm² sec), q_x is the x component of the particle velocity, and D is the solute diffusion coefficient. Equation [11c] is the surface analog of the bulk continuity equation with source-sink term.

Let $C = C_0 + \Delta C$, $\Gamma = \Gamma_0 + \Delta \Gamma$, and suppose $\Delta \Gamma$, ΔC , q_x and their derivatives are all small in first order (amplitude of oscillation small compared to wave length). Then to first order

$$\frac{\partial \Delta C}{\partial t} = D \left[\frac{\partial^2 \Delta C}{\partial x^2} + \frac{\partial^2 \Delta C}{\partial y^2} \right], \quad x > 0, y < 0 \quad [12a]$$

$$\Delta C(x, y, t)_{y \rightarrow -\infty} = 0 \quad [12b]$$

$$\frac{\partial \Delta \Gamma}{\partial t} + \Gamma_0 \left(\frac{\partial q_x}{\partial x} \right)_{y \rightarrow 0^-} - R = 0. \quad [12c]$$

We suppose that $\Delta C = Y_3(y) e^{i(\underline{k}x - \omega t)}$ and find that to satisfy [12a] we must set $Y_3 = E e^{ny} + E' e^{-ny}$, where $n^2 = \underline{k}^2 - \frac{i\omega}{D}$, E and E' are complex constants. Let n be the root of n^2 whose real part is positive; then to satisfy [12b] we must choose $E' = 0$. Hence

$$\Delta C = E e^{ny} e^{i(\underline{k}x - \omega t)} \quad [13]$$

satisfies Eqs. [12a] and [12b].

We now turn to boundary condition [12c]. In general R may depend on $\Delta \Gamma$, ΔC , and $\left(\frac{\partial \Delta C}{\partial y} \right)_{y \rightarrow 0^-}$; the dependence will reflect the kinetic mechanism of transfer from bulk to surface, and for the problem under consideration the transfer will result from small deviations from equilibrium. We shall suppose this transfer to be diffusion limited. Then

$\Gamma(x, t)$ is in equilibrium with $C(x, 0, t)$, $R = -D(\frac{\partial \Delta C}{\partial y})_{y \rightarrow 0^-}$, $\Delta \Gamma = (\frac{d\Gamma}{dC})_{C_0} \Delta C_{y \rightarrow 0^-}$,
 $\frac{\partial \Delta \Gamma}{\partial t} = (\frac{d\Gamma}{dC})_{C_0} (\frac{\partial \Delta C}{\partial t})_{y \rightarrow 0^-}$. Hence Eq. [12c] becomes

$$(\frac{d\Gamma}{dC})_{C_0} (\frac{\partial \Delta C}{\partial t})_{y \rightarrow 0^-} + \Gamma_0 (\frac{\partial q_x}{\partial x})_{y \rightarrow 0^-} + D(\frac{\partial \Delta C}{\partial y})_{y \rightarrow 0^-} = 0. \quad [14]$$

From the definitions of the functions ϕ and Ψ , $q_x = -\frac{\partial \phi}{\partial x} - \frac{\partial \Psi}{\partial y}$,
 $(\frac{\partial q_x}{\partial x})_{y \rightarrow 0^-} = -(\frac{\partial^2 \phi}{\partial x^2})_{y \rightarrow 0^-} - (\frac{\partial^2 \Psi}{\partial x \partial y})_{y \rightarrow 0^-}$. Hence using the expressions
for ϕ and Ψ given in Eqs. [10a], [10b] and the expression for ΔC given
in Eq. [13] we find that to satisfy [14] we must set $E = -\Gamma_0(k^2 A - ikmB)$
 $/[nD - i\omega(\frac{d\Gamma}{dC})_{C_0}]$, and hence the solution to the boundary value problem
[11a-c] appropriate for concentration changes resulting from capillary
ripple propagation and diffusion-controlled adsorption is

$$\Delta C = -\frac{\Gamma_0(k^2 A - ikmB)}{nD - i\omega(\frac{d\Gamma}{dC})_{C_0}} e^{ny} e^{i(kx - \omega t)}. \quad [15]$$

Since the surface concentration is assumed to be in equilibrium with
 $C(x, 0, t)$ we have for small displacements

$$\Delta \Gamma = (\frac{d\Gamma}{dC})_{C_0} \Delta C_{y \rightarrow 0^-} = -(\frac{d\Gamma}{dC})_{C_0} \frac{\Gamma_0(k^2 A - ikmB)}{nD - i\omega(\frac{d\Gamma}{dC})_{C_0}} e^{i(kx - \omega t)} \quad [16a]$$

$$= -\Gamma_0 \frac{\frac{k}{\omega} [mB + ikA]}{1 + \frac{inD}{\omega} (\frac{d\Gamma}{dC})_{C_0}} e^{i(kx - \omega t)}. \quad [16b]$$

C. The Surface Stress Boundary Conditions

The components of the stress tensor for an incompressible fluid are

$$\sigma_{ij} = -p\delta_{ij} + \mu \left\{ \frac{\partial q_{x_i}}{\partial x_j} + \frac{\partial q_{x_j}}{\partial x_i} \right\} \quad [17]$$

where x_i, x_j take on the values x, y, z ; $\delta_{ij} = 1$ if $i = j$ and $\delta_{ij} = 0$ if $i \neq j$.

The boundary condition will be written in terms of the normal and tangential stresses at the surface. Since we shall be concerned with capillary ripples of amplitude small compared to wave length the normal to the surface will be very nearly in the y direction. Hence the normal stress will be very nearly $(\sigma_{yy})_{y \rightarrow 0^-}$ and the tangential stresses very nearly $(\sigma_{xy})_{y \rightarrow 0^-}, (\sigma_{yz})_{y \rightarrow 0^-}$ with $(\sigma_{yz})_{y \rightarrow 0^-} = 0$ for the plane ripple propagation problem here formulated. Therefore

$$\begin{aligned} (\sigma_{xy})_{y \rightarrow 0^-} &= \mu \left\{ \frac{\partial q_x}{\partial y} + \frac{\partial q_y}{\partial x} \right\}_{y \rightarrow 0^-} = \mu \left\{ \frac{\partial^2 \Psi}{\partial x^2} - \frac{\partial^2 \Psi}{\partial y^2} - 2 \frac{\partial^2 \phi}{\partial x \partial y} \right\}_{y \rightarrow 0^-} \\ &= -\mu \{ B(\underline{k}^2 + m^2) + 2i\underline{k}^2 A \} e^{i(\underline{k}x - \omega t)} \end{aligned} \quad [18a]$$

$$\begin{aligned} (\sigma_{yy})_{y \rightarrow 0^-} &= -P_{y \rightarrow 0^-} + 2\mu \left(\frac{\partial q_y}{\partial y} \right)_{y \rightarrow 0^-} = -(\Delta p)_{y \rightarrow 0^-} + 2\mu \left[-\frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial x \partial y} \right]_{y \rightarrow 0^-} \\ &= \{ i\rho A\omega - 2\mu(A\underline{k}^2 - iBm\underline{k}) \} e^{i(\underline{k}x - \omega t)} \end{aligned} \quad [18b]$$

using Eqs. [10a], [10b] and [10c].

We now consider the surface stresses in terms of properties of the surface film. Suppose we have a film on the plane surface of a liquid in an apparatus such as a Langmuir trough, rectangular in shape with unit

width and length A_0 . Let F_0 be the force exerted on a barrier confining the film from the film side when the system is at rest and at equilibrium. If the barrier is moved with a velocity $\dot{A}$ the surface force will be altered due to the film elasticity by an amount proportional to the change in area, and may also be altered due to relaxation processes by an amount proportional to the velocity of displacement. We may therefore represent the surface force F at some new area A by

$$F = F_0 + k_e \frac{A - A_0}{A_0} + \frac{k_v}{A_0} \frac{dA}{dt} \quad [19a]$$

If we now choose Γ = surface concentration, moles/cm² as independent variable instead of A we have also

$$\begin{aligned} F &= F_0 - k_e \frac{\Gamma - \Gamma_0}{\Gamma_0} - \frac{k_v}{\Gamma_0} \frac{d\Gamma}{dt} \\ &= F_0 - k_e \frac{\Delta\Gamma}{\Gamma_0} - \frac{k_v}{\Gamma_0} \frac{d\Delta\Gamma}{dt} \end{aligned} \quad [19b]$$

and the tangential stress at x will be given by

$$\sigma_{xy} = \frac{\partial F}{\partial x} = - \frac{k_e}{\Gamma_0} \frac{\partial \Delta\Gamma}{\partial x} - \frac{k_v}{\Gamma_0} \frac{\partial^2 \Delta\Gamma}{\partial x \partial y} \quad [20]$$

The normal stress results from the boundary tension of the film-covered liquid and the local curvature due to capillary ripples. Where γ is the boundary tension, R_1 and R_2 the principle radii of curvature at a point on the surface, $\sigma_{yy} = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$. If $\Delta y = f(x)$ is the equation of the surface at some instant t and ripple amplitude is small compared to wave length then to terms in first order $\left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{\partial^2 \Delta y}{\partial x^2}$.

But

$$\begin{aligned} \Delta y &= \int (q_y)_{y \rightarrow 0^-} dt = \int \left(-\frac{\partial \phi}{\partial y} + \frac{\partial \psi}{\partial x} \right)_{y \rightarrow 0^-} dt \\ &= \frac{i}{\omega} e^{i(\underline{k}x - \omega t)} \{ -A\underline{k} + i\underline{k}B \}. \end{aligned} \quad [21]$$

Hence

$$\sigma_{yy} = \frac{k^3 \gamma}{\omega} \{ iA + B \} e^{i(\underline{k}x - \omega t)} \quad [22]$$

while from Eqs. [20] and [16b]

$$\sigma_{xy} = \frac{\frac{k}{\omega} [mB + i\underline{k}A]}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\underline{\Gamma}} \right)_{C_0}} \{ i\underline{k}k_e + \underline{k}k_v \omega \} e^{i(\underline{k}x - \omega t)} \quad [23]$$

Comparing Eqs. [18a] and [23] we find

$$-\mu \{ B(\underline{k}^2 + m^2) + 2iA\underline{k}^2 \} = \frac{\frac{k^2}{\omega} (mB + i\underline{k}A)}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\underline{\Gamma}} \right)_{C_0}} (ik_e + \omega k_v) \quad [24]$$

and comparing Eqs. [17b] and [22] we find

$$ipA\omega - 2\mu(A\underline{k}^2 - iBm\underline{k}) = \frac{k^3 \gamma}{\omega} (iA + B). \quad [25]$$

Eqs. [24] and [25] furnish two linear homogeneous equations in the two unknown constants A and B, and a nontrivial solution of them exists only if the determinant of their coefficients is zero. We divide both sides of Eqs. [24] and [25] by $\frac{\gamma k^3}{\omega}$ and rearrange to obtain

$$A \left\{ i \frac{2\mu\omega}{\gamma \underline{k}} - \frac{\frac{k_e}{\gamma} - i\omega \frac{k_v}{\gamma}}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\underline{\Gamma}} \right)_{C_0}} \right\} + B \left\{ \left(1 + \frac{m^2}{\underline{k}^2} \right) \frac{\mu\omega}{\gamma \underline{k}} + \frac{i \frac{k_e m}{\gamma \underline{k}} + \omega \frac{k_v m}{\gamma \underline{k}}}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\underline{\Gamma}} \right)_{C_0}} \right\} = 0 \quad [24a]$$

$$A \left\{ i \left(\frac{\rho \omega^2}{\gamma \underline{k}^3} - 1 \right) - \frac{2\mu\omega}{\gamma \underline{k}} \right\} + B \left\{ i \frac{2\mu\omega m}{\gamma \underline{k}^2} - 1 \right\} = 0 \quad [25a]$$

in which coefficients of A and B have been collected in sets of dimensionless groups. For a non-trivial solution for the coefficients A and B we must therefore have

$$\begin{vmatrix} \left\{ i \frac{2\mu\omega}{\gamma \underline{k}} - \frac{\frac{k_e}{\gamma} - i\omega \frac{k_v}{\gamma}}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\Gamma} \right)_{C_0}} \right\} & \left\{ \left(1 + \frac{m^2}{\underline{k}^2} \right) \frac{\mu\omega}{\gamma \underline{k}} + \frac{i \frac{k_e m}{\gamma \underline{k}} + \omega \frac{k_v m}{\gamma \underline{k}}}{1 + \frac{i n D}{\omega} \left(\frac{dC}{d\Gamma} \right)_{C_0}} \right\} \\ \left\{ i \left(\frac{\rho \omega^2}{\gamma \underline{k}^3} - 1 \right) - \frac{2\mu\omega}{\gamma \underline{k}} \right\} & \left\{ i \frac{2\mu\omega m}{\gamma \underline{k}^2} - 1 \right\} \end{vmatrix} = 0 \quad [26]$$

in which μ is the bulk viscosity, $\omega = 2\pi\nu$, where ν is the ripple frequency, $\underline{k} = k + i\alpha$ is the complex ripple wave number (k is the wave number, α the damping coefficient), γ the boundary tension, k_e the film elasticity, k_v the film relaxation parameter [see Eq. 19a], D the solute diffusion coefficient, $\left(\frac{d\Gamma}{dC} \right)_{C_0}$ the slope of the equilibrium adsorption isotherm at concentration C_0 , ρ the bulk density, $m = \left\{ \underline{k}^2 - i \frac{\rho\omega}{\mu} \right\}^{1/2}$, and $n = \left\{ \underline{k}^2 - \frac{i\omega}{D} \right\}^{1/2}$ (m and n are both chosen as roots whose real parts are positive). Since Eq. [26] is complex it permits two variables, say k and α , to be established in terms of the remaining variables.

D. Evaluation of Ripple Wave Number and Damping Coefficient

Let $y_1 = \frac{\rho\omega^2}{\gamma \underline{k}^3}$, $y_2 = \frac{\alpha}{k}$. We choose these two dimensionless groups as our two dependent variables to be established by Eq. [26]. It will be convenient to introduce the auxiliary variables v and ϕ defined by $1 + iy_2 = ve^{i\phi}$. Thus $v = \sqrt{1 + y_2^2}$, $\phi = \tan^{-1} y_2$, $\frac{k}{\underline{k}} = ve^{i\phi}$. We note that

if the capillary ripples are to persist over an appreciable number of wave lengths, α/k must be small compared to unity, so that $y_2 \ll 1$, $v \approx 1$, $\phi \ll 1$, $\phi \approx y_2$.

$$\text{Let } \frac{\mu\omega}{\gamma k} = u_1, \left\{ \frac{k_e}{\gamma} - i\omega \frac{k_v}{\gamma} \right\} / \left\{ 1 + \frac{i n D}{\omega} \left(\frac{dC}{d\Gamma} \right)_{C_0} \right\} = u_2 e^{i\theta_2}, \frac{m}{k} = u_3 e^{i\theta_3}.$$

u_3 and θ_3 are not independent variables in this problem, but may be expressed in terms of the variables y_1 , y_2 , and u_1 or y_1 , v , ϕ , and u_1

$$\text{previously introduced. Thus } u_3 e^{i\theta_3} = \frac{m}{k} = \left\{ \frac{k^2}{k^2} - \frac{i\rho\omega^2}{\mu k^2} \right\}^{1/2} = \left\{ \frac{k^2}{k^2} - i \frac{\rho\omega^2}{\gamma k^3} \frac{\gamma k}{\mu\omega} \right\}^{1/2} \\ = \left\{ v^2 e^{2i\phi} - i y_1 / u_1 \right\}^{1/2}. \quad u_2 \text{ and } \theta_2 \text{ are independent variables; it will}$$

be noted that the three independent dimensionless variables k_e/γ , $\omega k_v/\gamma$, and $\frac{nD}{\omega} \left(\frac{dC}{d\Gamma} \right)_{C_0}$ occur together in such a way as to be represented by a single complex variable. We shall consider the resolution of u_2 and θ_2 later.

On replacing terms in Eq. [26] by corresponding dimensionless variables we obtain

$$0 = \begin{vmatrix} \left\{ 2i \frac{u_1}{v} e^{-i\phi} - u_2 e^{i\theta_2} \right\} & \left\{ \left(1 + \frac{u_3^2}{v^2} e^{2i(\theta_3 - \phi)} \right) \frac{u_1}{v} e^{-i\phi} + i \frac{u_2 u_3}{v} e^{i(\theta_3 + \theta_2 - \phi)} \right\} \\ \left\{ i \left(\frac{y_1}{v} e^{-3i\phi} - 1 \right) - 2 \frac{u_1}{v} e^{-i\phi} \right\} & \left\{ 2i \frac{u_1 u_3}{v^2} e^{i(\theta_3 - 2\phi)} - 1 \right\} \end{vmatrix} \quad [27]$$

or

$$i \left(\frac{y_1}{v} e^{-3i\phi} - 1 \right) \left(\frac{u_1}{v} e^{-i\phi} + \frac{u_1 u_3^2}{v^3} e^{i(2\theta_3 - 3\phi)} - 2 \frac{u_1}{v^2} e^{-2i\phi} - 2 \frac{u_1^2 u_3^2}{v^4} e^{2i(\theta_3 - 2\phi)} \right) \\ + 2i \frac{u_1}{v} e^{-i\phi} + 4 \frac{u_1^2 u_3}{v^3} e^{i(\theta_3 - 3\phi)} = u_2 e^{i\theta_2} \left\{ 1 + \frac{y_1 u_3}{v^4} e^{i(\theta_3 - 4\phi)} - \frac{u_3}{v} e^{i(\theta_3 - \phi)} \right\}. \quad [28]$$

Two limiting behaviors are implied by Eq. [28]; if u_2 is very small (very slightly viscoelastic films) the right side of Eq. [28] may be neglected, while if u_2 is very large (highly viscoelastic films) the left side of Eq. [28] may be neglected and the coefficient of u_2 on the right side equated to zero. We shall first consider these two limiting cases, and then proceed to the case of films of intermediate viscoelasticity.

(a) Non-viscoelastic Film, $u_2 \approx 0$

Suppose u_1 is small in first order, and y_1 is of order unity. Then $u_1 u_3^2$ is of order unity, and terms in $u_1^2 u_3^2, u_1^2 u_3$ are at least small in first order. Suppose y_2 and hence ϕ are small in first order; then $v = \sqrt{1 + y_2^2} = 1$ to terms in first order. To zeroth order we have from Eq. [28]

$$i(y_1 - 1) u_1 u_3^2 e^{2i\theta_3} = 0 \quad (\text{zeroth order}) \quad [29]$$

and so

$$(y_1)_0 = 1 \quad (\text{zeroth order}). \quad [30]$$

Since $y_1 = \frac{\rho\omega^2}{\gamma k}$, the zeroth order solution is Lord Kelvin's Equation for capillary ripple propagation.

Let $y_1 = 1 + \Delta y_1$, with Δy_1 supposed small in first order. To first order we also have $y_2 = \phi$, $e^{-i\phi} = 1 - iy_2$, $u_3 e^{i\theta_3} = \left\{ v^2 e^{2i\phi} - \frac{y_1}{u_1} \right\}^{1/2} \approx \left\{ -i(1 + \Delta y_1) + u_1 \right\}^{1/2} u_1^{-1/2}$ or $u_3 e^{i\theta_3} \approx u_1^{-1/2} e^{-i\pi/4} (1 + \frac{1}{2} \Delta y_1 + \frac{1}{2} i u_1)$.

Hence to first order we have from Eq. [28]

$$\Delta y_1 - 3iy_2 + 4iu_1 + 4u_1^{3/2} e^{-i\pi/4} = 0 \quad (\text{first order}) \quad [31]$$

whence to first order

$$\Delta y_1 = -2\sqrt{2} u_1^{3/2} \quad [32]$$

$$y_2 = \frac{4}{3} u_1 - \frac{2\sqrt{2}}{3} u_1^{3/2} \quad [33]$$

Using the zeroth order result (Kelvin's Equation) for k we have

$$u_1 = \frac{\mu\omega}{\gamma k} = \frac{\mu\omega}{\gamma} \left(\frac{\gamma}{\rho\omega^2}\right)^{1/3} = \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/3} \quad \text{Hence to terms in first order, from}$$

[30] and [32] we have

$$y_1 = 1 - 2\sqrt{2} u_1^{3/2} \quad [34a]$$

or

$$k = \left(\frac{\rho\omega^2}{\gamma}\right)^{1/3} \left\{ 1 - 2\sqrt{2} \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/2} \right\}^{-1/3} \approx \left(\frac{\rho\omega^2}{\gamma}\right)^{1/3} \left\{ 1 + \frac{2\sqrt{2}}{3} \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/2} \right\} \quad [34b]$$

and from [33]

$$\alpha = \frac{4}{3} \frac{\mu\omega}{\gamma} \left[1 - \frac{\sqrt{2}}{2} \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/2} \right] \quad [35]$$

We see from their derivations that Eqs. [30-35] should also be valid for viscoelastic films for which u_2 is an order of magnitude smaller than u_1 .

(b) Highly Viscoelastic Films, $u_2 \gg 1$

In this case terms on the left side of Eq. [28] are orders of magnitude smaller than those on the right, and the coefficient of $u_2 e^{i\theta_2}$ on the right side must be zero. We obtain the equation

$$y_1 - v^3 e^{3i\phi} + \frac{v^4}{u_3} e^{i(4\phi - \theta_3)} = 0 \quad [36]$$

We suppose ϕ and $\frac{1}{u_3}$ small in first order; then $v = 1$ to first order and

$$(y_1)_0 = 1 \quad (\text{zeroth order}). \quad [37]$$

i. e. we again obtain Kelvin's Equation as a zeroth order result. Let $y_1 = 1 + \Delta y_1$, with Δy_1 supposed small in first order. To first order we have again $u_3 e^{i\theta_3} = u_1^{-1/2} e^{-i\pi/4} (1 + \frac{1}{2} \Delta y_1 + \frac{1}{2} i u_1)$ so that to first order Eq. [36] becomes

$$\Delta y_1 + \frac{\sqrt{2}}{2} u_1^{1/2} - 3iy_2 + i \frac{\sqrt{2}}{2} u_1^{1/2} = 0 \quad [38]$$

whence

$$\Delta y_1 = -\frac{\sqrt{2}}{2} u_1^{1/2} \quad [39]$$

$$y_2 = \frac{\sqrt{2}}{6} u_1^{1/2} \quad [40]$$

These calculations are readily extended to second order, with the results

$$y_1 = 1 - \frac{\sqrt{2}}{2} u_1^{1/2} + \frac{1}{4} u_1 \quad [41]$$

$$y_2 = \frac{\sqrt{2}}{6} u_1^{1/2} + \frac{11}{36} u_1 \quad [42]$$

To express wave number and damping coefficient in terms of physical quantities correct to second order it is necessary to use a value of k correct to first order, i. e. $k = \left(\frac{\rho\omega^2}{\gamma}\right)^{1/3} \left[1 + \frac{\sqrt{2}}{6} \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/6}\right]$, in the expression for u_1 . We find that also to second order

$$k = \left(\frac{\rho\omega^2}{\gamma}\right)^{1/3} \left[1 + \frac{\sqrt{2}}{6} \left(\frac{\omega\mu^3}{\rho\gamma^2}\right)^{1/6}\right] \quad [43]$$

while

$$\alpha = \frac{\sqrt{2}}{6} \left(\frac{\rho \omega^2}{\gamma} \right)^{1/3} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \left[1 + \sqrt{2} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \right]. \quad [44]$$

(c) Films of Intermediate Viscoelasticity

If u_1 is taken as a parameter of smallness, we have seen in parts (a) and (b) that the solution $y_1 = 1$ causes both right and left sides of Eq. [28] to vanish in zeroth order, and hence this is also a zeroth order solution to Eq. [28]. Hence we again set $y_1 = 1 + \Delta y_1$, and suppose Δy_1 , y_2 , ϕ , and u_1 small. We shall therefore again find that to first order $u_3 e^{i\theta_3} = u_1^{-1/2} e^{-i\pi/4} \left[1 + \frac{1}{2} \Delta y_1 + \frac{1}{2} i u_1 \right]$. To terms in first order Eq. [28] becomes (note that the left side of Eq. [31] is the first order approximation to the left side of Eq. [28], and the left side of Eq. [38] multiplied by $\frac{u_2 u_3}{v^4} e^{i(\theta_2 + \theta_3 - 4\phi)}$ is the first order approximation to the right side of Eq. [28])

$$\Delta y_1 - 3iy_2 + 4iu_1 + 4u_1^{3/2} e^{-i\pi/4} = \frac{u_2 u_3}{v^4} e^{i(\theta_2 + \theta_3 - 4\phi)} [\Delta y_1 - 3iy_2 + e^{i\pi/4} u_1^{1/2}] \quad [45a]$$

$$= \frac{u_2}{u_1^{1/2}} e^{i(\theta_2 - \frac{\pi}{4})} [\Delta y_1 - 3iy_2 + e^{i\pi/4} u_1^{1/2}]. \quad [45b]$$

Hence

$$(\Delta y_1 - 3iy_2) \left[1 - \frac{u_2}{u_1^{1/2}} e^{i(\theta_2 - \frac{\pi}{4})} \right] = -4iu_1 - 4u_1^{3/2} e^{-i\pi/4} + u_2 e^{i\theta_2}. \quad [46]$$

On rearranging and rationalizing Eq. [46] we obtain

$$\Delta y_1 = - \frac{2\sqrt{2} u_1^{3/2} - u_2(1 + 4u_1) \cos \theta_2 - 4u_2 u_1^{1/2} \sin(\theta_2 - \frac{\pi}{4}) + \frac{\sqrt{2}}{2} \frac{u_2^2}{u_1^{1/2}}}{1 - 2 \frac{u_2}{u_1^{1/2}} \cos(\theta_2 - \frac{\pi}{4}) + \frac{u_2^2}{u_1}} \quad [47]$$

$$y_2 = \frac{4u_1 - 2\sqrt{2} u_1^{3/2} - u_2(1 - 4u_1) \sin \theta_2 - 4u_2 u_1^{1/2} \cos(\theta_2 - \frac{\pi}{4}) + \frac{\sqrt{2}}{2} \frac{u_2^2}{u_1^{1/2}}}{3[1 - 2 \frac{u_2}{u_1^{1/2}} \cos(\theta_2 - \frac{\pi}{4}) + \frac{u_2^2}{u_1}]} \quad [48]$$

Note that as $u_2 \rightarrow 0$ Eqs. [47] and [48] reduce to Eqs. [32] and [33] respectively, and that as $u_2 \rightarrow \infty$ Eqs. [47] and [48] reduce to Eqs. [39] and [40], respectively. Equations [47] and [48] can be used to provide corrections to the limiting equations [32, 33, 39, 40] as follows:

For slightly viscoelastic films (u_2 small but not negligible)

$$y_1 = 1 - 2\sqrt{2} u_1^{3/2} + u_2 \cos \theta_2 + 4u_2 u_1^{1/2} \sin(\theta_2 - \frac{\pi}{4}) \quad [49]$$

$$y_2 = \frac{4}{3} u_1 - \frac{2\sqrt{2}}{3} u_1^{3/2} - \frac{1}{3} u_2 \sin \theta_2 + \frac{4}{3} u_2 u_1^{1/2} \cos(\theta_2 - \frac{\pi}{4}) \quad [50]$$

while for viscoelastic films (u_2 large but not infinite)

$$y_1 = 1 - \frac{\sqrt{2}}{2} u_1^{1/2} + \frac{1}{4} u_1 - \frac{u_1}{u_2} \sin \theta_2 + \frac{4u_1^{3/2}}{u_2} \sin(\theta_2 - \frac{\pi}{4}) \quad [51]$$

$$y_2 = \frac{\sqrt{2}}{6} u_1^{1/2} + \frac{11}{36} u_1 + \frac{1}{3} \frac{u_1}{u_2} \cos \theta_2 - \frac{4u_1^{3/2}}{3u_2} \cos(\theta_2 - \frac{\pi}{4}) \quad [52]$$

Equations for non-viscoelastic films (Eqs. [32-5]) are hence correct to terms of order $u_1^{3/2}$ if the viscoelastic parameter u_2 is small compared to $u_1^{3/2}$, and are in error by an amount of the order u_2 for small u_2 in general. Equations for highly viscoelastic films (Eqs. [41-4]) are correct to terms of order u_1 provided $\frac{u_1}{u_2}$ is small compared to u_1 , i. e. provided u_2 is large compared to unity, and are in error by an amount of the order $\frac{u_1}{u_2}$ for u_2 large ($\frac{u_1}{u_2}$ small) in general.

We shall see subsequently that the parameter θ_2 may be expected to assume values in the range $-\frac{\pi}{2} \leq \theta_2 \leq \frac{\pi}{4}$, and it must therefore be noted that the denominators in Eqs. [47] and [48] become zero for $\theta_2 = \frac{\pi}{4}$, $u_2 = u_1^{1/2}$. The first approximation solution to Eq. [28] is therefore invalid for $\theta_2 = \frac{\pi}{4}$, $u_2 = u_1^{1/2}$, and is seriously inaccurate for values of θ_2 and u_2 close to this singularity. To second order, the real and imaginary parts of Eq. [28] lead to the two simultaneous quadratic equations in the quantities $\Delta y_1, y_2$:

$$\begin{aligned} & \Delta y_1 \left[1 - \frac{u_2}{u_1^{1/2}} \left\{ \cos \left(\theta_2 - \frac{\pi}{4} \right) - \frac{1}{2} u_1 \sin \left(\theta_2 - \frac{\pi}{4} \right) \right\} \right] + y_2 \left[13u_1 \right. \\ & \quad \left. - 3 \frac{u_2}{u_1^{1/2}} \left\{ \sin \left(\theta_2 - \frac{\pi}{4} \right) + \frac{1}{2} u_1 \cos \left(\theta_2 - \frac{\pi}{4} \right) \right\} \right] + \Delta y_1^2 \left[1 - \frac{1}{2} \frac{u_2}{u_1^{1/2}} \cos \left(\theta_2 - \frac{\pi}{4} \right) \right] \\ & \quad - y_2^2 \left[15 - 9 \frac{u_2}{u_1^{1/2}} \cos \left(\theta_2 - \frac{\pi}{4} \right) \right] - \frac{11}{2} y_2 \Delta y_1 \frac{u_2}{u_1^{1/2}} \sin \left(\theta_2 - \frac{\pi}{4} \right) \\ & = - 2\sqrt{2} u_1^{3/2} + u_2 \cos \theta_2 \end{aligned} \quad [53]$$

$$\begin{aligned}
& \Delta y_1 \left[-3u_1 + \frac{u_2}{u_1} \frac{1}{2} \left\{ \sin(\theta_2 - \frac{\pi}{4}) + \frac{1}{2} u_1 \cos(\theta_2 - \frac{\pi}{4}) \right\} \right] \\
& + 3y_2 \left[1 - \frac{u_2}{u_1} \frac{1}{2} \left\{ \cos(\theta_2 - \frac{\pi}{4}) - \frac{1}{2} u_1 \sin(\theta_2 - \frac{\pi}{4}) \right\} \right] + \frac{1}{2} \Delta y_1^2 \frac{u_2}{u_1} \frac{1}{2} \sin(\theta_2 - \frac{\pi}{4}) \\
& - 9y_2^2 \frac{u_2}{u_1} \frac{1}{2} \sin(\theta_2 - \frac{\pi}{4}) + y_2 \Delta y_1 \left[9 - \frac{11}{2} \frac{u_2}{u_1} \frac{1}{2} \cos(\theta_2 - \frac{\pi}{4}) \right] \\
& = 4u_1 - 2\sqrt{2} u_1^{3/2} - u_2 \sin \theta_2. \quad [54]
\end{aligned}$$

These equations must be solved simultaneously for reasonably accurate values of Δy_1 and y_2 in the neighborhood of the singularity of Eqs. [47] and [48]. More accurate results can be obtained with considerably more labor by numerical solution of Eq. [28] (see Appendix).

DISCUSSION

The successive approximation solutions to Eq. [28] for non-viscoelastic (Eqs. [32-5]), slightly viscoelastic (Eqs. [49-50]), highly viscoelastic (Eqs. [51-2]) and infinitely viscoelastic (Eqs. [41-4]) are expansions in powers of the dimensionless variable $u_1 = \frac{\mu\omega}{\gamma k} \approx \left(\frac{\omega\mu^3}{\rho\gamma^2} \right)^{1/3} = \left(\frac{2\pi\nu\mu^3}{\rho\gamma^2} \right)^{1/3}$. For dilute aqueous solutions of surface active solutes at 25°C we may suppose $\mu = 9 \times 10^{-3}$ poise, $\rho = 1 \text{ gm/cm}^3$, $\gamma = 50 \text{ dynes/cm}$. Then $u_1 \approx 1.2 \times 10^{-2} \left(\frac{\nu}{1000} \right)^{1/3}$; since it seems unlikely at present that we shall be studying capillary ripples at frequencies far greater than 10^3 cycles per second we may suppose $u_1 \approx 10^{-2}$ for dilute aqueous systems. Then Eqs. [34a-34b], which carry these expansions to terms in $u_1^{3/2}$ (but neglect terms of the order u_1^2) should represent y_1 and k to about 1 part

in 10^4 , provided the viscoelastic parameter u_2 is of the order 10^{-4} or less. Under these same circumstances Eqs. [33, 35] should represent y_2 and α to about 1 part in 10^2 . Equations [41-4] are expansions including terms in u_1 , but neglecting terms in $u_1^{3/2}$; they should represent y_1 and k to 1 part in 10^3 , and y_2 and α to 1 part in 10^2 , provided $\frac{u_1}{u_2}$ is of order 10^{-3} or less, i.e. provided u_2 is of order 10 or greater. Measurements of ripple wave number and amplitude attenuation accurate to 1% on aqueous systems will only be able to characterize films as negligibly viscoelastic (if $u_2 < 10^{-4}$) or very highly viscoelastic (if $u_2 > 10$), but will only be able to establish the parameter u_2 with a precision of 10% if $10^{-3} < u_2 < 1$. Equations [49-50] (which include terms in u_2 but neglect terms in $u_2 u_1^{1/2}$) will extend the ranges of Eqs. [32-5] from $u_2 < 10^{-4}$ to $u_2 < 10^{-3}$. Equations [51-2] (which include terms in $\frac{u_1}{u_2}$ but neglect terms in $u_1^{3/2}/u_2$) will extend the ranges of Eqs. [41-4] from $u_2 > 10$ to $u_2 > 1$.

Equations [47-8] should be used for the calculation of ripple wave number k and ripple amplitude attenuation α in the intermediate viscoelasticity range $10^{-3} \leq u_2 \leq 1$. In this range k and α depend importantly on the parameters u_2 and θ_2 given by $u_2 e^{i\theta_2} = \left\{ \frac{k_e}{\gamma} - i\omega \frac{k_v}{\gamma} \right\} / \left\{ 1 + \frac{i\omega D}{\omega} \left(\frac{dC}{d\Gamma} \right) C_0 \right\}$. Now n is the root with positive real part of $n^2 = \underline{k}^2 - \frac{i\omega}{D}$. Since $\underline{k}^2 = k^2 (1 + iy_2)^2$, it is easily shown from the limiting forms previously given for k and y_2 that for $D \leq 10^{-5} \text{ cm}^2/\text{sec}$, $\omega \leq 10^4 \text{ sec}^{-1}$ (it is doubtful that other cases are of interest) $\frac{\omega}{D}$ is about five orders of magnitude greater than $\underline{k}^2$, so that to excellent approximation $n = \left(\frac{\omega}{D} \right)^{1/2} e^{-\pi i/4}$, $\frac{i\omega D}{\omega} = \left(\frac{D}{\omega} \right)^{1/2} e^{\pi i/4}$. Substituting this result in the equation defining $u_2 e^{i\theta_2}$ and rationalizing we

obtain

$$u_2 e^{i\theta_2} = \frac{k_e + \frac{1}{2} \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} (k_e - \omega k_v) - i \left[\omega k_v + \frac{1}{2} \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} (k_e + \omega k_v) \right]}{\gamma \left[1 + \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} + \frac{D}{\omega} \left(\frac{dC}{d\Gamma}\right)_{C_0}^2 \right]} \quad [53]$$

whence

$$u_2 = \frac{(k_e^2 + \omega^2 k_v^2)^{1/2}}{\gamma} \frac{1 + \frac{1}{2} \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0}}{i + \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} + \frac{D}{\omega} \left(\frac{dC}{d\Gamma}\right)_{C_0}^2} \quad [54]$$

$$\tan \theta_2 = - \frac{2\omega k_v + \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} (k_e + \omega k_v)}{2k_e + \left(\frac{2D}{\omega}\right)^{1/2} \left(\frac{dC}{d\Gamma}\right)_{C_0} (k_e - \omega k_v)} \quad [55]$$

From Eq. [55] it follows that θ_2 is limited to the range $-\frac{\pi}{2} \leq \theta_2 \leq \frac{\pi}{4}$. There is no information available concerning the relaxation parameter k_v ; if values of k_v are such that $k_e \gg \omega k_v$, θ_2 is further limited to the range $-\frac{\pi}{4} \leq \theta_2 \leq 0$.

Figures 1 and 2 present the dependence of y_1 and y_2 on θ_2 and u_2 for $u_1 = 10^{-2}$, a physically representative value, as obtained by numerical solution of Eq. [28] (see appendix). For comparison, limiting curves for slightly viscoelastic and viscoelastic films [Eqs. 49-52] are also shown, and appear adequately to represent the numerical solutions for u_2 less than 10^{-2} or greater than 1.

In comparing the present work with previous treatments it was noted that there appears to be a discrepancy in sign of the tangential component of the stress tensor due to the surface film (see Eq. [20]) chosen by Goodrich (7) on the one hand, and by Levich (3, 4) and ourselves on the other. That our choice of sign is correct is most easily recognized by equating tangential stress tensor components given by Eqs. [17] and [20], and considering the special case $k_v = 0$, $q_y = 0$ which might correspond to the steady flow of a surface film in a channel under a spreading pressure gradient. Clearly, for steady flow $\frac{\partial \Delta \Gamma}{\partial x} < 0$ implies $\frac{\partial q_x}{\partial y} > 0$, so that the right side of Eq. [20] must be opposite in sign to the right side of the tangential component of Eq. [17]. It is interesting to note that an error in sign at this point (equivalent to reversing the sign of u_2 in our equations) does not alter limiting results at either very low or very high surface viscoelasticities, but leads to serious discrepancies, including negative damping coefficients, in the intermediate u_2 region. Since there seems to be a sparsity of data in this region such theoretical implications apparently have simply not been explored heretofore.

The present work is the first to extend calculation of the capillary ripple wave number beyond the zeroth order or Kelvin Equation result (see Eqs. [34b, 43, 47, 49, 51]) for non-viscoelastic, intermediate, or highly viscoelastic films. We shall show in subsequent papers that deviation from Kelvin's Equation is experimentally detectable and is in accord with our theory. Equations equivalent to the leading term in Eq. [35] have been given by Lamb (12) and Goodrich (7), and to the leading term in [42] by Levich (3); second order developments of the damping coefficients for non-viscoelastic [Eq. 35], highly viscoelastic [Eq. 44],

and developments for regions of intermediate viscoelasticity [Eqs. 48, 50, 52] are to the best of our knowledge new. Subsequent papers will show that equations for non-viscoelastic and highly viscoelastic films are in good agreement with experimental data for such films; films of intermediate viscoelasticity suitable for testing the corresponding equations have so far not been encountered.

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APPENDIX

Equation [28] was solved numerically to a high degree of approximation in the following manner. Let $W = \frac{u_2}{u_1}^{1/2}$, $\Psi = \theta_2 - \frac{\pi}{4}$. Then Eq. [28] can be written in the form

$$We^{i\Psi} = \frac{\nu}{\delta}$$

where

$$\nu = i[y_1 - (1 + iy_2)^3][u_1 - \frac{i[y_1 + iu_1(1 + iy_2)^2]}{(1 + iy_2)^2}] - 2u_1^2(1 + iy_2)^2$$

$$+ 2iu_1[y_1 + iu_1(1 + iy_2)^2] + 2iu_1(1 + iy_2)^3$$

$$+ 4u_1^{3/2}e^{-\frac{\pi i}{4}}(1 + iy_2)[y_1 + iu_1(1 + iy_2)^2]^{1/2}$$

$$\delta = [y_1 + iu_1(1 + iy_2)^2]^{1/2}[y_1 - (1 + iy_2)^3] + u_1^{1/2}e^{\frac{\pi i}{4}}(1 + iy_2)^4$$

ν and δ do not contain W or Ψ . To a precision of one part in 10^6 for $u_1 \approx 10^{-2}$ we have by binomial expansion

$$[y_1 + iu_1(1 + iy_2)^2]^{1/2} = y_1^{1/2}[1 - \frac{u_1}{y_1}y_2 + \frac{1}{8}(\frac{u_1}{y_1})^2(1 - 6y_2^2 + y_2^4)$$

$$+ i\{\frac{1}{2}\frac{u_1}{y_1}(1 - y_2^2) + \frac{1}{2}(\frac{u_1}{y_1})^2(y_2 - y_2^3)\}]$$

Rationalizing the expression for $\frac{v}{\delta}$ we obtain.

$$W = \sqrt{\frac{A^2 + B^2}{C^2 + D^2}}, \quad \tan \Psi = \frac{BC - AD}{AC + BD}$$

where

$$A = \frac{y_1^2(1 - y_2^2)}{(1 + y_2^2)^2} - y_1 - 4u_1^2(1 - y_2^2) \\ + 2\sqrt{2}u_1^{3/2}y_1^{1/2}\left[1 + y_2 + \frac{1}{2}\left(\frac{u_1}{y_1}\right)(1 - 3y_2 - 3y_2^2 + y_2^3)\right]$$

$$+ \frac{1}{8}\left(\frac{u_1}{y_1}\right)^2(1 + 5y_2 - 10y_2^2 - 10y_2^3 + 5y_2^4 + y_2^5)]$$

$$B = 4u_1y_1 - \frac{2y_2y_1^2}{(1 + y_2^2)^2} - y_1y_2 - 8u_1^2y_2$$

$$+ 2\sqrt{2}u_1^{3/2}y_1^{1/2}\left[-1 + y_2 + \frac{1}{2}\left(\frac{u_1}{y_1}\right)(1 + 3y_2 - 3y_2^2 - y_2^3)\right]$$

$$+ \frac{1}{8}\left(\frac{u_1}{y_1}\right)^2(-1 + 5y_2 + 10y_2^2 - 10y_2^3 - 5y_2^4 + y_2^5)]$$

$$C = y_1^{1/2}\left[y_1 - 1 + 3y_2^2 + \frac{1}{2}\left(\frac{u_1}{y_1}\right)(-2y_1y_2 + 5y_2 - 10y_2^3 + y_2^5)\right]$$

$$+ \frac{1}{8}\left(\frac{u_1}{y_1}\right)^2(-1 + y_1 + 21y_2^2 - 6y_1y_2^2 - 35y_2^4 + y_1y_2^4 + 7y_2^6)]$$

$$+ \frac{u_1^{1/2}}{\sqrt{2}}[1 - 4y_2 - 6y_2^2 + 4y_2^3 + y_2^4]$$

$$\begin{aligned}
D = & y_1^{1/2} [-3y_2 + y_2^3 + \frac{1}{2}(\frac{u_1}{y_1})(y_1 - 1 + 10y_2^2 - y_1y_2^2 - 5y_2^4) \\
& + \frac{1}{8}(\frac{u_1}{y_1})^2(-7y_2 + 4y_1y_2 + 35y_2^3 - 4y_1y_2^3 - 21y_2^5 + y_2^7)] \\
& + \frac{u_1^{1/2}}{\sqrt{2}} (1 + 4y_2 - 6y_2^2 - 4y_2^3 + y_2^4)
\end{aligned}$$

To prepare Figs. 1 and 2, values of W and Ψ corresponding to $u_1 = 0.0100$, y_2 ranging from 0.005 to 0.055 in increments of 0.001, and y_1 ranging from 0.90 to 1.05 in increments of 0.01 were calculated and tabulated by the Cyclone computer at Iowa State University. Values of y_1 , y_2 and W corresponding to specified values of θ_2 (-90° , -45° , 0° , and 45° in this instance) were then obtained by interpolation from these tables. Over the range covered by the tables it was apparent that the solutions for each angle consisted of two branches, and the branch satisfying the limiting solutions Eqs. [49-52] was selected.

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FIGURE CAPTIONS

Fig. 1 - Dependence of reduced velocity of propagation $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ on viscoelastic parameters u_2 and θ_2 for $u_1 = \frac{\mu\omega}{\gamma k} = 10^{-2}$.

Fig. 2 - Dependence of reduced damping coefficient $y_2 = \frac{\alpha}{k}$ on viscoelastic parameters u_2 and θ_2 for $u_1 = 10^{-2}$.

Fig. 1 - Dependence of reduced velocity of propagation $\gamma_1 = \frac{\rho\omega^2}{\gamma k^3}$ on viscoelastic parameters u_2 and θ_2 for $u_1 = \frac{\mu\omega}{\gamma k} = 10^{-2}$.

Fig. 2 - Dependence of reduced damping coefficient $y_2 = \frac{\alpha}{k}$ on viscoelastic parameters u_2 and θ_2 for $u_1 = 10^{-2}$.

END