

The Damping of Waves by Surface-Active Substances. I

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The damping effect produced by surface-active substances has been the subject of very numerous experimental investigations¹. It appears, however, that no quantitative theory of this phenomenon has hitherto been advanced; nor can even any fundamental assumptions, which could serve as a basis for an exact theory, be considered as fully developed.

In one of the recent papers devoted to the damping effect of surface-active substances Shuleikin² suggested that the damping of waves on the surface of a liquid should be due to irreversible energy losses on friction in the surface film, associated with the anomalously high viscosity of monolayers.

Similar hypotheses were advanced by a number of authors³ in connection with other processes taking place in monolayers.

From a theoretical standpoint, however, such assumptions seem to be ill-founded and scarcely plausible.

On the other hand, Lamb⁴ suggested the idea (which, as will be shown below, is quite correct) that the damping effect of a film must be due to its inextensibility.

¹ Atken, Proc. Roy. Soc., Edinburgh, 12, 56 (1883); V. Shuleikin, "The Physics of the Sea" (1933).

² V. Shuleikin, Bull. Acad. Sci. USSR, Geophys. Ser., (1937). V. Shuleikin, "The Physics of the Sea" (1933).

³ Mayers and Harkins, J. Chem. Phys., 5, 601 (1937); Kirkwood, J. Chem. Phys., 6, 298 (1938).

⁴ Lamb, "Hydrodynamics", Cambridge (1932).

This hypothesis, however, is not supported by any direct evidence, since the elastic moduli of monolayers have been measured experimentally and cannot be said to be particularly high.

In the present work it is shown that the spreading of a surface active film over the surface of a viscous liquid results in a radical alteration of the boundary conditions at the liquid-gas interface. Eventually, the whole character of motion of the liquid is also altered, and the intensity of the vortices in the boundary layer of the liquid increases, which leads to a greater dissipation of energy.

1. Motion of liquid

Let us consider the motion of a viscous liquid whose surface is covered by a film of a surface-active substance.

As is known, the equations of motion of a liquid are:

$$\begin{aligned} \frac{\partial \vec{v}}{\partial t} + (\vec{v} \nabla) \vec{v} &= -\frac{1}{\rho} \nabla p + \frac{\eta_1}{\rho} \nabla^2 \vec{v} + \frac{\eta_2}{\rho} \Delta (\nabla \vec{v}) + \vec{F}, \\ \frac{\partial \rho}{\partial t} + \operatorname{div} \rho \vec{v} &= 0, \end{aligned} \quad (1)$$

where $\vec{v}$ is the velocity, ρ —density of the liquid, p —pressure within the liquid, η_1 and η_2 —viscosity coefficients and $\vec{F}$ —external volume forces per unit mass.

Assuming the liquid to be incompressible and its motion sufficiently slow, we may rewrite eqs. (1) in a simpler form:

$$\begin{aligned} \frac{\partial \vec{v}}{\partial t} &= -\frac{1}{\rho} \nabla p + \frac{\eta_1}{\rho} \nabla^2 \vec{v} + \vec{F}, \\ \operatorname{div} \vec{v} &= 0. \end{aligned} \quad \begin{aligned} (2) \\ (2') \end{aligned}$$

Giving the z axis a vertical direction, we shall look for a solution of eqs. (2) in the form of plane waves in the xoz plane.

As is known⁴, eqs. (2) may be solved with the aid of potentials φ and ψ related to the velocity components by the following equations:

$$v_x = -\frac{\partial \varphi}{\partial x} - \frac{\partial \psi}{\partial z}, \quad (3)$$

$$v_z = -\frac{\partial \varphi}{\partial z} + \frac{\partial \psi}{\partial x}. \quad (3')$$

Substitution of (3) and (3') in eqs. (2) and (2') leads to three equations

$$\Delta\varphi = 0, \quad (4)$$

$$\frac{\partial\psi}{\partial t} - \eta\Delta\psi = 0, \quad (5)$$

$$\frac{\partial\varphi}{\partial t} - \frac{p}{\rho} - gz = 0, \quad (6)$$

in which $\eta = \frac{\eta_1}{\rho}$ is the kinematic viscosity and $F_z = g$ is the acceleration of gravity. The solutions of eqs. (4) and (5) have the form:

$$\begin{aligned} \varphi &= Ae^{kx} e^{ikx+\alpha t} + Be^{-kx} e^{ikx+\alpha t}, \\ \psi &= Ce^{lx} e^{ikx+\alpha t} + De^{-lx} e^{ikx+\alpha t}. \end{aligned}$$

Assuming, for the sake of simplicity, that the liquid is contained in a vessel of infinite depth, we may put $B = D = 0$ in order to satisfy the conditions: $\varphi = 0$; $\psi = 0$ when $x = -\infty$ (the x axis is directed vertically upwards, so that only negative values of x are considered). We accordingly have

$$\varphi = Ae^{kx} e^{ikx+\alpha t}, \quad (7)$$

$$\psi = Ce^{lx} e^{ikx+\alpha t}. \quad (7')$$

The quantities l and k are not independent, but are connected by the relation:

$$l = \sqrt{k^2 + \frac{\alpha}{\eta}}. \quad (8)$$

Substituting the expressions for φ and ψ in eqs. (3), (3') and (6), we obtain

$$v_x = -(ikAe^{kx} + lCe^{lx}) e^{ikx+\alpha t}, \quad (9)$$

$$v_z = -(kAe^{kx} - ikCe^{lx}) e^{ikx+\alpha t}, \quad (9')$$

$$p = \alpha\rho Ae^{kx} e^{ikx+\alpha t} - \rho gz. \quad (10)$$

Let us now find the displacements of particles on the surface. Let ξ denote the horizontal displacement on the surface of the liquid and ζ the vertical displacement. Then we have to a usual approximation

$$\frac{\partial\xi}{\partial t} \cong v_x \Big|_{z=0}, \quad (11)$$

$$\frac{\partial\zeta}{\partial t} \cong v_z \Big|_{z=0}, \quad (11')$$

whence

$$\bar{\eta} = -\frac{ikA + lC}{\alpha} e^{ikx + \alpha t}, \quad (12)$$

$$\zeta = -\frac{kA - ikC}{\alpha} e^{ikx + \alpha t}. \quad (12')$$

Finally, we shall subsequently require the expressions for the normal and vertical components of the stress tensor. The normal component is given by

$$\begin{aligned} p_{xx} = -p + 2\eta_1 \frac{\partial v_x}{\partial z} = & -\rho \chi A e^{kx} e^{ikx + \alpha t} + \rho g z - \\ & - 2\eta_1 (k^2 A e^{kx} - ikl C e^{lx}) e^{ikx + \alpha t}, \end{aligned} \quad (13)$$

whilst the tangential component is

$$\begin{aligned} p_{xz} = \eta_1 \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) = & -\eta_1 [2ik^2 A e^{kx} + (l^2 + k^2) C e^{lx}] e^{ikx + \alpha t} = \\ = & -[2i\eta_1 k^2 A e^{kx} + (2\eta_1 k^2 + \rho \chi) C e^{lx}] e^{ikx + \alpha t}. \end{aligned} \quad (13')$$

The frequency, α , which is generally a complex quantity, must be expressed in terms of the wave-number, k , by means of the boundary conditions to the determination of which we shall now proceed.

2. Boundary conditions

As is known, the boundary conditions are given by the conditions of continuity of the stress tensor components. We, therefore, have to determine the forces acting on a surface covered by a film of a surface-active substance. Equating the components of the forces acting on the film to the corresponding components of the stress tensor in the liquid, we shall find the equation determining β .

Let the thermodynamic potential of a plane surface covered by a surface-active substance be given by

$$\Phi_0 = \int \varphi(v_0) dS_0 \quad (14)$$

where v_0 is the surface concentration and $\varphi(v_0)$ the thermodynamic potential per unit surface. The integration is carried out over the whole

surface. When waves are generated on the surface of the liquid, the area of the free surface and, consequently, the surface concentration in the film are altered.

It follows that, generally, the thermodynamic potential of the surface is also altered.

If $v = v_0 + v'$ is the surface concentration on the deformed surface, the corresponding thermodynamic potential will be

$$\Phi = \int \varphi(v_0 + v') dS, \quad (14')$$

where integration is made over the deformed surface. The deformation of the surface consists in that each of its elements having an area $dS_0 = dx dy$ is either stretched or compressed to a new area

$$dS = \sqrt{(dx + \xi(x))^2 + (\zeta(x))^2} dy = dS_0 + \frac{dS'}{dS_0} dS_0,$$

where $\frac{dS'}{dS_0}$ is the relative change of area of the surface element. Neglecting the infinitesimal terms of higher orders of smallness, we may write:

$$\frac{dS'}{dS_0} = \frac{dS - dS_0}{dS_0} \cong \frac{\partial \xi}{\partial x} + \frac{1}{2} \left(\frac{\partial \zeta}{\partial x} \right)^2. \quad (15)$$

Let us now find the change in the free energy accompanying the deformation of the surface. Let it be assumed that the total number, N , of particles adsorbed on the surface remains unchanged on deformation. This is actually the case whenever the monolayer is insoluble in the substrate. The case of a soluble film will be discussed elsewhere.

The change of the free energy is given by

$$\Delta\Phi = \int \varphi(v_0 + v') dS - \int \varphi(v_0) dS_0, \quad (16)$$

and we may write simultaneously

$$\delta N = 0, \quad (17)$$

From eqs. (15) and (17) we get:

$$v' = \frac{dN}{dS_0} - \frac{dN}{dS_0 + \frac{dS'}{dS_0} dS_0} \cong v_0 \left[\frac{\partial \xi}{\partial x} + \frac{1}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 - \left(\frac{\partial \xi}{\partial x} \right)^2 \right]. \quad (18)$$

The same result may be attained from the condition of continuity.

Expanding $\varphi(v_0 + v')$ in powers of v' , and substituting v' from eq. (18) and $\frac{dS'}{dS_0}$ from eq. (15), we obtain to within the second order of smallness

$$\begin{aligned} \Delta\Phi = \int \left(\varphi(v_0) - v_0 \left(\frac{\partial \varphi}{\partial v} \right)_{v=v_0} \right) \left(\frac{\partial \xi}{\partial x} + \frac{1}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 \right) dx dy + \\ + \frac{1}{2} \int v_0^2 \left(\frac{\partial^2 \varphi}{\partial v^2} \right)_{v=v_0} \left(\frac{\partial \xi}{\partial x} \right)^2 dx dy. \end{aligned} \quad (19)$$

It is known, however, that the surface tension, σ , is related to the chemical potential, μ , by the equations

$$\mu = \frac{\partial \Phi}{\partial n} = \frac{\partial \varphi}{\partial v}, \quad (20)$$

$$\sigma_0 = \frac{\partial \Phi}{\partial S} = \varphi(v) - v_0 \frac{\partial \varphi}{\partial v} = \varphi - v_0 \mu. \quad (21)$$

Therefore, adopting the notation

$$\epsilon_0 = v_0^2 \left(\frac{\partial^2 \varphi}{\partial v^2} \right)_{v=v_0} \quad (22)$$

we have

$$\Delta\Phi = \int \sigma_0 \left[\frac{\partial \xi}{\partial x} + \frac{1}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 \right] dx dy + \int \frac{\epsilon_0}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 dx dy.$$

The change of the free energy equals the potential energy of the surface layer on deformation:

$$u = \int \sigma_0 \left[\frac{\partial \xi}{\partial x} + \frac{1}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 \right] dx dy + \int \frac{\epsilon_0}{2} \left(\frac{\partial \xi}{\partial x} \right)^2 dx dy. \quad (23)$$

Letting the quantity (23) vary with the corresponding parameters ξ and ζ , we may find the forces acting on the film. Designating the

normal resultant of the forces applied to one cm.² of the film by F_z , we shall have

$$\delta u_z = - \int F_z \delta \zeta \, dx \, dy = \int \sigma_0 \frac{\partial \zeta}{\partial x} \frac{\partial \delta \zeta}{\partial x} \, dx \, dy$$

or, integrating by parts,

$$\delta u_z = - \int F_z \delta \zeta \, dx \, dy = - \int \sigma_0 \frac{\partial^2 \zeta}{\partial x^2} \, dx \, dy$$

whence

$$F_z = \sigma_0 \frac{\partial^2 \zeta}{\partial x^2}. \quad (24)$$

Eq. (24) is the usual expression for the Laplacean force of surface tension.

Similarly, for the tangential resultant F_x of the forces acting on one cm.² of the film, we obtain

$$\begin{aligned} \delta u_x &= - \int F_x \delta \xi \, dx \, dy = \int \epsilon_0 \frac{\partial \delta \xi}{\partial x} \, dx \, dy + \int \epsilon_0 \frac{\partial \xi}{\partial x} \frac{\partial \delta \xi}{\partial x} \, dx \, dy = \\ &= - \int \epsilon_0 \frac{\partial^2 \xi}{\partial x^2} \, dx \, dy, \end{aligned}$$

whence

$$F_x = \epsilon_0 \frac{\partial^2 \xi}{\partial x^2}. \quad (25)$$

Neglecting all expansion terms higher than the first, we may rewrite eq. (25) as follows:

$$F_x \simeq - \frac{\epsilon_0}{v_0} \frac{\partial v}{\partial x}, \quad (26)$$

taking account of eq. (18).

It follows from eqs. (25) and (26) that the quantity ϵ_0 characterizes the elastic properties of the film and represents nothing but the two-dimensional compressibility modulus of the film. From the definition of ϵ_0 it follows that

$$\epsilon_0 = - v_0 \left(\frac{\partial \sigma_0}{\partial v} \right).$$

In the sequel it will be convenient to introduce the quantity $\epsilon = \frac{\epsilon_0}{\rho}$, where ρ is the density of the liquid substrate. This quantity will be called the elastic constant of the film.

When the concentrations of the substance constituting the surface film are high and correspond to the condensed state, the numerical

value of the elastic constant proves to be of the same order as the surface tension of the system, σ_0 . When the surface concentration tends to zero, ϵ also tends to zero, whilst σ_0 tends to the surface tension of the pure liquid substrate.

In the sequel we shall have to deal not with σ_0 itself but with the quantity $\frac{\sigma_0}{\rho}$ which we shall designate by σ .

3. Damping coefficient.

Using expressions (24) and (25) for the components of the force acting on cm.^2 of the film, we may write the boundary conditions which determine the character of motion of a liquid carrying a surface film.

Namely, the projections of the forces should be equated to the corresponding components of the stress tensor on the surface of the liquid ($z = \zeta$).

The continuity of the normal component of the stress tensor requires that

$$(p_{zz})_{z=\zeta} = F_z,$$

whilst the continuity of the tangential component gives

$$(p_{xz})_{z=\zeta} = F_x.$$

ζ being an infinitely small quantity, we may write to a usual approximation:

$$(p_{zz})_{z=0} = F_z, \quad (27)$$

$$(p_{xz})_{z=0} = F_x. \quad (28)$$

In the case of a clean surface the boundary conditions are

$$(p_{zz})_{z=0} = F_z \quad (27')$$

and

$$(p_{xz})_{z=0} = 0, \quad (28')$$

where the expression for F_z has the same form, except that, instead of the surface tension, σ , of the system film-substrate, there appears the surface tension of the pure substrate. We thus see that the boundary conditions in a liquid covered by a surface film essentially differ from those of a pure liquid.

Substituting in boundary condition (28) the values of p_{xx} and F_z from (13'), (25) and (11), we have

$$-2i\eta_1 k^2 A - \eta_1 (l^2 + k^2) C = \epsilon \frac{ik^3 A + k^2 l C}{\alpha}. \quad (29)$$

Introducing the kinematic viscosity, ν , and the quantity

$$\omega^2 = gk + \sigma k^3 \quad (30)$$

we obtain

$$\left(\frac{\epsilon k^3}{\omega^2} + \frac{2\eta k^2 \alpha}{\omega^2} \right) A - i \left(\frac{\alpha^2}{\omega^2} + \frac{2\eta k^2 \alpha}{\omega^2} + \frac{\epsilon k^2 l}{\omega^2} \right) C = 0. \quad (31)$$

Similarly, from eqs. (13), (24) and (27) we find the second boundary condition:

$$\left(\frac{\alpha^2}{\omega^2} + \frac{2\eta k^2 \alpha}{\omega^2} + 1 \right) A - i \left(\frac{2\eta k l \alpha}{\omega^2} + 1 \right) C = 0. \quad (32)$$

In the case of a clean surface the boundary condition (32) for the normal components of the stress tensor has the same form, except that σ should be substituted for surface tension of the pure liquid, whereas condition (31), according to eq. (28), assumes the form:

$$\frac{2\eta k^2 \alpha}{\omega^2} A - i \left(\frac{\alpha^2}{\omega^2} + \frac{2\eta k^2 \alpha}{\omega^2} \right) C = 0. \quad (31')$$

The quantity ω , defined by eq. (30), is the frequency of surface waves in an ideal liquid. Assuming the viscosity η to be sufficiently small, we shall look for the frequency α as defined by

$$\alpha = \pm i\omega + \beta, \quad (33)$$

where β is the damping coefficient which, *ex hypothesi*, is small compared to ω , so that $\frac{\beta}{\omega}$ is small compared to unity.

In solving eqs. (31) and (32) it is useful to note that the quantity $\frac{\eta k^2}{\omega}$ involved is always small compared to unity provided the wave-length is not excessively small.

In fact,

$$\frac{\eta k^2}{\omega} < \frac{\eta k}{C_m} = \frac{2\pi\eta}{\lambda C_m},$$

where C_m is the minimum velocity of propagation of surface waves, given by

$$C_m = \sqrt[4]{4\sigma g}.$$

Assuming reasonable values for σ , ρ and τ_0 we find

$$\frac{\eta k^2}{\omega} < \frac{5 \times 10^{-3}}{\lambda}.$$

In the sequel we shall confine ourselves to such wave-lengths as satisfy the inequality $\frac{5 \times 10^{-3}}{\lambda} \ll 1$ since the applicability of hydrodynamics to very short wave-lengths becomes doubtful.

The further solution of the equations would be more convenient to proceed with when carried out for each individual case separately.

1. Capillary waves. As is known, for capillary waves we may write $\sigma k^3 \gg gk$, whence

$$\omega \approx \sqrt{\sigma k^3}. \quad (34)$$

Then boundary condition (32), after substituting α from (33) and ω from (34) and neglecting the terms of the order of $\left(\frac{\beta}{\omega}\right)^3$, assumes the form

$$\left(\frac{\epsilon}{\sigma} + \frac{2i\eta k^2}{\omega}\right) A - i\left(-1 - \frac{2\beta}{\omega} + \frac{2i\eta k^2}{\omega} + \frac{\epsilon l}{\sigma h}\right) C = 0. \quad (32')$$

According to eq. (8) we have

$$\frac{l}{k} = \sqrt{1 + \frac{i\omega}{\eta k^2}} \approx \sqrt{\frac{i\omega}{\eta k^2}}, \quad (8')$$

$\frac{l}{k}$ obeying the inequality $\frac{l}{k} \gg 1$ provided the wave-lengths are not too small.

Then, neglecting the corresponding terms in (32'), we find that the boundary condition is expressed by the relation:

$$kA - \mathcal{U}C = 0. \quad (35)$$

However, comparing eq. (35) with (12) we can see that condition (35) is nothing else but the requirement

$$(v_x)_{z=0} = 0, \quad (35')$$

i. e., the requirement that the horizontal component of velocity on the surface of the liquid should be equal to zero.

It follows that with respect to capillary waves—at least not too short ones—an adsorbed film behaves as an incompressible system, *i. e.*, as a true solid.

In the case under consideration the boundary condition for the normal component of the stress tensor (31) assumes the following form:

$$\left(\frac{2i\beta}{\omega} + \frac{2i\eta k^2}{\omega}\right)A - i\left(1 + \frac{2i\eta k l}{\omega}\right)C = 0. \quad (36)$$

Eliminating the coefficients A and C from eqs. (35) and (36) and substituting $\sqrt{\frac{i\omega}{\eta k^2}}$ for $\frac{l}{k}$, we obtain for the damping coefficient

$$\beta = -\frac{\eta^{1/2} k \omega^{1/2}}{2\sqrt{2}} = -\frac{\eta^{1/2} \sigma^{1/2} k^{7/2}}{2\sqrt{2}}, \quad (37)$$

where the imaginary part of β , which is small compared to ω , is dropped.

In the case of a clean surface the damping coefficient may be found from eqs. (31) and (32) and proves to be

$$\beta_0 = -2\eta k^2.$$

From the assumption made it follows that the ratio of the two values

$$\frac{\beta}{\beta_0} = \frac{1}{4\sqrt{2}} \frac{\omega^{1/2}}{\eta^{1/2} k}$$

is large compared to unity, *i. e.*, an incompressible film produces a considerable increase in the damping coefficient. Moreover, in so far as $\varepsilon \cong \sigma$, the value of the damping coefficient depends no longer upon the elasticity of the film, but is solely determined by the viscosity of the liquid and the surface tension of the system liquid-film.

2. Capillary-gravitational waves. In the intermediate region between capillary and gravitational waves the frequency, ω , is connected with the wave-number, k , by the relation

$$\omega = \sqrt{gk + \sigma k^3}.$$

In this region $k \cong \sqrt{\frac{g}{\sigma}}$. It will be readily seen that in this instance all the conditions considered in the preceding case are fulfilled, *i. e.*,

$$\left|\frac{l}{k}\right| \gg 1 \quad \text{and} \quad \frac{\varepsilon k^3}{\omega^2} \cong 1.$$

It follows that in this region too, the damping coefficient is given by formula (37).

In the case under consideration the damping effect of surface films is therefore also very strong and, at sufficiently high concentrations, independent of the properties of the film.

The origin of the additional energy losses (in excess of those occurring in an uncontaminated liquid) which result in the damping of waves will be clear from the following considerations. Let us calculate the vorticity at an arbitrary point in the liquid. By definition we have

$$\Gamma = \frac{\partial v_x}{\partial x} - \frac{\partial v_z}{\partial z} = \nabla^2 \psi = \frac{\alpha}{\eta} C e^{i z} e^{\alpha x + \alpha t}.$$

In an uncontaminated liquid, from the condition that p_{xx} must be equal to zero, it may be readily found that

$$\frac{C_0}{A_0} = - \frac{2i\eta k^2}{\alpha + 2\eta k^2},$$

where

$$\alpha = i\omega + \beta_0 = i\omega - 2\eta k^2$$

whence

$$\frac{C_0}{A_0} = - \frac{2\eta k^2}{\omega},$$

i. e., the ratio $\frac{C_0}{A_0}$ is small. The motion of the liquid is therefore almost irrotational.

In the case of a liquid contaminated with a film, eq. (35) yields

$$\left| \frac{C}{A} \right| = \left| \frac{k}{i} \right| = \sqrt{\frac{2\eta k^2}{\omega}}.$$

Hence the ratio

$$\left(\frac{C_0}{A_0} \right) : \left(\frac{C}{A} \right) = \sqrt{\frac{2\eta k^2}{\omega}}$$

is small compared to unity, *i. e.*, the intensity of vortices in a liquid covered by a film is correspondingly greater than in an uncontaminated liquid.

The presence of additional vortices results in irreversible energy losses and eventually produces the damping of waves.

3. Gravitational waves. In this case $gk \gg \sigma k^3$, whence

$$\omega \simeq \sqrt{gk}.$$

Substituting this expression for ω in boundary conditions (31) and (32), neglecting the quantities $\frac{\eta k^2}{\omega}$ and $\sqrt{\frac{\eta k^2}{\omega}}$ which are small compared to unity, and substituting $\frac{l}{k}$ from eq. (34), we find that the boundary conditions assume the following form:

$$\left(\frac{2\beta}{\sqrt{gk}} + \frac{2\eta k^{3/2}}{\sqrt{g}} \right) A - C = 0, \quad (38)$$

$$\left(\frac{\epsilon k^2}{g} + \frac{2i\eta k^{3/2}}{\sqrt{g}} \right) A + i \left(1 - \frac{\sqrt{\epsilon} \epsilon k^{5/4}}{g^{3/4} \eta^{1/2}} \right) C = 0. \quad (39)$$

From eqs. (38) and (39) it may be seen that gravitational waves fall into two regions: a region in which the wave-vector $k \cong k_1$, where k_1 is such that $\frac{\epsilon k_1^{5/4}}{g^{3/4} \eta^{1/2}} \sim 1$, i. e., $k_1 \cong \frac{g^{3/2} \eta^{2/3}}{\epsilon^{1/6}}$, and another region in which $k \sim k_2$, where $\frac{\epsilon k_2^2}{g} \cong \frac{2\eta k_2^{3/2}}{\sqrt{g}}$, i. e., $k_2 \cong \frac{\eta^2 g}{\epsilon^2}$.

It will be readily seen that $k_1 > k_2$. With reasonable values of η and ϵ , $k_1 \cong \frac{1}{3} \text{ cm.}^{-1}$, so that $\lambda_1 = \frac{2\pi}{k_1} \cong 15 \text{ cm.}$ whilst $k_2 \cong 10^{-3} \text{ cm.}^{-1}$ and $\lambda_2 = \frac{2\pi}{k_2} \sim 10^3 \text{ cm.}$

In the region of $k \sim k_1$, i. e., for centimeter waves,

$$\frac{\epsilon k^2}{g} \cong \sqrt{\frac{2\eta k^{3/2}}{\sqrt{g}}},$$

so that $\frac{2i\eta k^{3/2}}{\sqrt{g}}$ in eq. (39) may be neglected as compared to $\frac{\epsilon k^2}{g}$.

Then from eqs. (38) and (39) we obtain

$$\beta = -\frac{1}{2\sqrt{2}} \frac{g^{1/4} \epsilon^2 \eta^{1/2} k^{13/4}}{\epsilon^2 k^{5/2} + \eta g^{3/2} - \sqrt{2} \epsilon \eta^{1/2} g^{3/4} k^{5/4}},$$

where the imaginary component of β , being but a small correction to frequency, has been dropped. The order of magnitude of the real component of β is

$$\beta \cong \sqrt{\eta g^{1/2} k^{5/2}}.$$

The ratio of β to the damping coefficient, β_0 , in the pure liquid is therefore given by

$$\frac{\beta}{\beta_0} \approx \sqrt{\frac{g^{1/2}}{\eta k^{3/2}}},$$

i. e., is large compared to unity.

The damping effect of the film is thus still comparatively strong even for such large wave-lengths.

In the region of $k \approx k_2$, *i. e.*, for very long waves, we have

$$\frac{\epsilon k^{5/4}}{g^{3/4} \eta^{1/2}} \ll 1$$

and this term can be neglected in eq. (39).

From eqs. (38) and (39) we obtain

$$\beta = -2\gamma k^2,$$

i. e., in this region we have but natural damping. The effect of the film is confined to a slight change in the frequency which we have not quoted in this paper. At still longer wave-lengths this latter also vanishes.

Conclusion

We thus see that when exact account is taken of the presence of a film on the surface of a liquid, the calculated values of the damping coefficient prove to be higher than the corresponding values for the clean surface. The calculation requires no special hypotheses regarding the nature of the irreversible energy losses in the film.

It is shown that, with respect to short waves, a monomolecular film of sufficient surface concentration behaves as an incompressible system, *i. e.*, as a true solid.

It seems difficult to carry out a quantitative comparison of the results obtained with the experimental data, the latter being usually of a qualitative nature.

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