

Motion Induced by Capillarity

64. THE INTERFACIAL REGION

The boundary between contiguous bulk phases of matter is known as the interfacial region or, simply, the interface [1].

The interfacial region is that thin layer surrounding a geometric surface of separation, within which the physical properties differ noticeably from those in either of the bulk phases. The thickness of this layer is illdefined because the variation of physical properties across it is continuous. Under conditions well away from the critical point, however, the layer is only a few molecules thick and, in any event, is very small compared to the wavelength of visible light. This is obvious from the reflection of light from the surface of a liquid. Close to the critical point the thickness of the interfacial region increases to become quite appreciable.

Here, we adopt an approximation in which the interface is infinitely thin; i.e., we regard the phase boundary as a geometric surface, and assume that the properties right up to the interface are unchanged from those of the respective bulk phases.

Since the thickness of the interface is of the order of molecular dimensions, such an approximation is fully justified in treating the macroscopic properties of liquids. Because the properties of matter in the interfacial region differ from those in bulk, the interface has free energy per molecule F^Σ which is peculiar to it.

We consider only the case of one-component systems.

The surface free energy is defined as

$$F^\Sigma = F - (F_1 + F_2),$$

where F is the total free energy of the system consisting of two phases separated by an interface, and $F_1 + F_2$ is the sum of the free energies of the two bulk phases, computed on the assumption that both remain homogeneous right up to the surface of separation. This surface free energy is the thermodynamic potential for which temperature T and surface area Σ are the independent variables; therefore

$$dF^s = -S^s dT + \sigma d\Sigma,$$

where S^s is the surface entropy.

The quantity*

$$\sigma = \left(\frac{\partial F^s}{\partial \Sigma} \right)_T$$

is the surface free energy per unit area at constant temperature. It is obvious that the work of reversible isothermal expansion of the surface dA is equal to the decrease in free energy, i.e.,

$$dA = -\sigma d\Sigma.$$

The quantity σ is known as the interfacial tension or surface tension.

The surface free energy in a one-component system is fully determined by two parameters, for example by the temperature T and surface area Σ . The surface tension σ , therefore, is a function only of temperature T .

The surface tension of liquids decreases with temperature. There is, however, no generally accepted or sufficiently well grounded theory describing the dependence of surface tension on temperature. The general character of this dependence becomes apparent only near the critical point.

65. CONDITIONS OF EQUILIBRIUM BETWEEN TWO FLUID PHASES AT REST

Let us determine the conditions for thermodynamic equilibrium in a two-phase, gas-liquid system, separated by an interface possessing surface tension σ [2].

The first obvious equilibrium condition is the equality of temperature in both phases. Having assumed the temperatures of the two phases to be the same, let us determine the equilibrium conditions at constant temperature.

Thermodynamic equilibrium in an isothermal system requires that the free energy of the system be a minimum; i.e., the following condition must be fulfilled

$$\delta F = 0,$$

where δF is an arbitrary and infinitesimal variation of the free energy of the system. Let us imagine two cylinders, one in each of

*This definition is valid only for the one-component systems that are considered here.

$$\frac{\partial V_x}{\partial Y} - \left| \frac{\partial \sigma}{\partial X} \right| \frac{1}{\mu U} \frac{L}{l} = \frac{\mu' U'}{\mu U} \frac{\partial V'_x}{\partial Y} \quad (66.7)$$

Assuming the dimensionless derivative $\frac{\partial V_x}{\partial X}$ to be of the order of unity, the surface tension term may be omitted if

$$\frac{L}{l} \left| \frac{\partial \sigma}{\partial X} \right| \frac{1}{\mu U} \ll 1 \quad (66.8)$$

$$\left| \frac{\partial \sigma}{\partial X} \right| \frac{L^2}{\rho \nu^2} \ll \text{Re} \quad (66.9)$$

Since the motion of the liquid was assumed to be viscous, the Reynolds number must be small compared to unity. Therefore, formula (66.9) may now be rewritten

$$\left| \frac{\partial \sigma}{\partial X} \right| \frac{L^2}{\rho \nu^2} \ll 1. \quad (66.10)$$

It follows from (66.10) that the effect of the varying surface tension on the liquid motion may be disregarded for changes in surface tension such that

$$\left| \frac{\partial \sigma}{\partial X} \right| \ll \frac{\rho \nu^2}{L^2}.$$

Thus, when the liquid velocity is low and the flow region is sufficiently thick, the effect of surface forces arising in variations of surface tension from one point to another may be neglected only at very small values of $\frac{\partial \sigma}{\partial X}$.

Of course, the characteristic thickness L must not be too large, if the Reynolds number is to remain small compared to unity.

67. RATE OF CAPILLARY RISE

As the simplest example of capillary motion, we examine the rise of liquid in a cylindrical capillary.

Capillary rise of liquids is often encountered in practice and in nature; it plays an important role in liquid motion through porous media.

The surface of a liquid filling a vertical capillary is subjected to a capillary force equal to $p_\sigma \cdot S$, where p_σ is the capillary pressure and S is the free surface of the liquid. Capillary pressure is equal to $p_\sigma = \frac{2\sigma}{r}$ and the liquid column of height h exerts a hydrostatic pressure equal to ρgh . The liquid is, therefore, subject to the difference

in pressures $\Delta p = p_\sigma - \rho gh$. Under the influence of this pressure difference, the liquid moves at a rate which may be easily computed.

Since the pressure gradient along the capillary is constant, the Poiseuille equation may be used to compute the rate of the rise. We may write

$$v = \frac{dh}{dt} = \frac{r^2}{8\mu} \frac{\Delta p}{h} \quad (67.1)$$

where v is the rate of rise produced by the pressure difference.

Substituting the value of Δp , we find

$$\frac{dh}{dt} = \frac{r^2}{8\mu h} \left(\frac{2\sigma}{r} - \rho gh \right). \quad (67.2)$$

Integrating this equation, we obtain

$$t = \frac{8\mu}{r^2 \rho g} \left(h_0 \ln \frac{h_0}{h_0 - h} - h \right) \quad (67.3)$$

In order to simplify equation (67.3), we have designated the equilibrium height of capillary rise by h_0 , which is defined by $\frac{2\sigma}{r} - \rho gh_0 = 0$.

Equation (67.3) shows that although infinite time is necessary for a rise of the liquid to its maximum height, the liquid actually reaches a height that differs little from the maximum in a relatively short period of time.

Similar considerations for the case of a horizontal capillary lead to the following expression for the time it takes the liquid to travel a distance l along the capillary:

$$t = \frac{2\eta l^3}{r^3 a}$$

In arriving at formula (67.3), we employed Poiseuille's law (67.1) which is valid for steady flow. In real cases, however, capillary rise is not a strictly steady-state phenomenon.

At large values of t , capillary rise becomes quasi-stationary. Therefore, formula (67.3) should be used only for large values of t , i.e., when $t \gg \frac{\rho r^2}{\mu}$.

Experiments conducted by S. S. Kozlovskii [4] with transformer oil confirmed the applicability of formula (67.3) to the capillary rise of liquids in a glass tube when $t \gg \frac{\rho r^2}{\mu}$.

68. THERMOCAPILLARY MOTION

As a second example of capillary motion, we examine the motion of a liquid with varying surface tension. The variation in surface tension from one point to another leads to the appearance of tangential stresses on the liquid surface as described by equation (65.27).

The reason for the variation in surface tension of the liquid is not important here. Later, we present numerous examples of reasons for the variation in surface tension, such as the introduction of surface-active substances with concentrations that vary from point to point, the presence of a varying electric charge on the liquid surface, and so on.

The simplest reason, however, is the variation in surface temperature.

Let us assume that the liquid is placed in a vessel whose sides are at different temperatures. The surface temperature of the liquid will, in that case, vary from point to point. Since the surface tension of the liquid is a function of temperature, it will also vary from point to point across the surface. When tangential forces act on the liquid surface, a motion will be produced. This motion is known as capillary convection. Obviously, the temperature difference in the vessel walls will produce the usual convective motion within the liquid in addition to the capillary convection. In certain cases, however, the usual convection will play a relatively unimportant role. When the surface of the liquid is sufficiently large compared to its volume, e.g., if the liquid is poured into a sufficiently wide shallow pan, the usual thermal convection will produce liquid velocities that are small compared to those caused by capillary convection. Indeed, the surface effects in this case must be large compared to those in the bulk of the liquid, because the surface dimensions are relatively large, and the surface tension forces are very significant compared to the gravitational forces, which are proportional to extremely small changes in liquid density.

Quantitative calculations confirm these qualitative considerations [5].

We examine the motion of a liquid poured into a shallow pan to a depth h . The two walls of the pan are at temperatures T_1 and T_2 , with $T_2 > T_1$. We assume that the usual mixing by thermal convection may be neglected and that the temperature is constant along the vessel. This assumption is justified later.

Let us find the expression for the variation in surface tension of the liquid. We take the x axis in the direction of the temperature gradient, and the y axis in the direction perpendicular to the surface of the liquid. The variation in surface tension is given by

$$\text{grad } \sigma = -\frac{\partial \sigma}{\partial T} \text{grad } T. \quad (68.1)$$

The liquid surface is at the plane $y = 0$, and the bottom of the pan is at the plane $y = h$.

The temperature coefficient for the surface tension of all liquids $\left(\frac{\partial \sigma}{\partial T}\right) < 0$; i.e., σ decreases with increasing liquid temperature. As a first approximation, we assume that the temperature gradient is constant along the length of the pan

$$\sigma = \sigma(T_1) + \left(\frac{\partial \sigma}{\partial T}\right) \frac{T_2 - T_1}{l} x. \quad (68.2)$$

The surface tension varies from point to point along that surface, attaining a maximum at the colder wall of the pan, and decreasing linearly in the direction of the warmer wall.

According to expression (65.27), the force exerted per 1 cm² of surface is

$$p_t = \frac{\partial \sigma}{\partial x} = \left(\frac{\partial \sigma}{\partial T}\right) \text{grad } T. \quad (68.3)$$

We determine the motion of the liquid produced by this force. Since the depth of the pan is very small compared to its other dimensions, and the assumption has been made that usual convection can be neglected, the hydrodynamic equations can be simplified.

Since there is no temperature gradient across the pan, there will be no motion in that direction. Furthermore, in the absence of convection arising in heating of the liquid, there can be no forces exerted in the direction of the y axis. The velocity component in the y direction therefore is zero. The equation for the velocity component in the x direction, in accordance with expression (1.2), is

$$\frac{\partial p}{\partial x} = \mu \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right). \quad (68.4)$$

Since the depth of the pan is very small in comparison to its other dimensions, the derivative $\partial v_x / \partial x$ will be very small in comparison with the derivative $\partial v_x / \partial y$. Hence, we may omit the term $\partial^2 v_x / \partial x^2$ in equation (68.4) as a higher order infinitesimal. We then obtain

$$\frac{\partial p}{\partial x} = \mu \frac{\partial^2 v_x}{\partial y^2}. \quad (68.5)$$

Again, since the pan is shallow, it may be assumed that the pressure is not a function of the distance y . This is clearly evident from the equation for the velocity component in the y direction

$$\frac{\partial p}{\partial y} = 0. \quad (68.6)$$

In equation (68.5), therefore, the pressure p may be considered a function of the distance x only.

The system of equations (68.5) and (68.6) must be completed with the continuity equation. In this case, the continuity equation can be conveniently expressed in terms of the total flow of the liquid in the pan by setting the equation equal to zero. Indeed, the flow of liquid at the surface, set in motion by surface forces, is accompanied by flow in the opposite direction in the remainder of the vessel. The reverse flow is due to the pressure gradient along the pan as given in equation (68.5).

Thus, the continuity equation in this case becomes

$$\int_0^h v_x dy = 0. \quad (68.7)$$

We can now write the system of boundary conditions for equations (68.5) to (68.7). At the bottom of the vessel, the liquid velocity is zero, and

$$(v_x)_{y=h} = 0. \quad (68.8)$$

The condition of continuity of the tangential stress component must be fulfilled at the free liquid surface; i.e., the viscous stress and the surface force per unit area must be equal:

$$\mu \left(\frac{\partial v_x}{\partial y} \right)_{y=0} = p_t. \quad (68.9)$$

Using the definition of p_t given above, the boundary condition at the surface is

$$\mu \left(\frac{\partial v_x}{\partial y} \right)_{y=0} = \frac{\partial \sigma}{\partial l} \text{grad } T. \quad (68.10)$$

Integrating equation (68.5), and remembering that pressure changes only in the x direction, we obtain

$$v_x = a + by + \frac{1}{2} \frac{1}{\mu} \cdot \frac{\partial p}{\partial x} \cdot y^2. \quad (68.11)$$

Boundary conditions (68.8) and (68.10) yield the following values for the constants a and b :

$$b = -\frac{1}{\mu} \frac{\partial \sigma}{\partial x}; \quad a = \frac{1}{\mu} \frac{\partial \sigma}{\partial x} h - \frac{1}{2\mu} \frac{\partial p}{\partial x} h^2.$$

As an important example of an actual operation in which thermocapillary motion plays the principal part, we now examine the mass transfer through a thin liquid film.

The transfer of oxygen through thin layers of a liquid plays an important role in metal corrosion when the metal is covered with a film of electrolyte. The electrolyte is in contact with the atmosphere, and equilibrium concentration is established on its outer surface.

The corrosion rate strongly depends on the magnitude of the oxygen flux to the metal surface.

The convective diffusion equation in the thin film is

$$v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2},$$

where v_x is determined from equation (68.11). On the assumption that the diffusion resistance is in a region of low velocities (i.e., the thickness of the diffusion layer is small compared to that of the film), the following expression may be written for v_x

$$v_x \approx \alpha y',$$

where y' is the vertical distance $y' = y - h$, measured from the bottom, and $\alpha = \frac{1}{2\mu} \frac{\partial \sigma}{\partial x}$. The boundary conditions in this case are

$$\begin{aligned} c &\rightarrow c_0 & \text{as } y' &\rightarrow \infty, \\ c &= 0 & \text{at } y' &= 0. \end{aligned}$$

Thus, we obtain

$$v_x = \frac{1}{\mu} \frac{\partial \sigma}{\partial x} (h - y) - \frac{1}{2\mu} \cdot \frac{\partial p}{\partial x} (h^2 - y^2). \quad (68.11')$$

Substituting the velocity as given above into the continuity equation, we get

$$\frac{\partial p}{\partial x} = \frac{3}{2h} \frac{\partial \sigma}{\partial x}.$$

Integrating the equation for the pressure gradient, we find the pressure distribution in the liquid

$$p = p_0 + \frac{3}{2h} [\sigma(x) - \sigma(0)]. \quad (68.12)$$

The constant p_0 is an undetermined constant pressure.

Using the pressure gradient as given in equation (68.12), we arrive at the final formula for velocity distribution

$$v_x = \frac{1}{4\eta\mu} \frac{\partial \sigma}{\partial T} (3y^3 - 4hy + h^2) \frac{dT}{dx}. \quad (68.13)$$

The maximum velocity of the liquid at the surface is

$$(v_x)_{y=0} = \frac{1}{4\mu} \cdot \frac{\partial \sigma}{\partial T} \cdot h \cdot \frac{dT}{dx}. \quad (68.14)$$

The velocity increases with the temperature gradient and with the depth of the liquid layer in the pan. This is true only for thin liquid layers. If the depth of the vessel becomes sufficiently great, the above solution will not apply, because it was obtained on the assumption that the following inequality is valid:

$$v_x \frac{\partial v_x}{\partial x} \ll \nu \frac{\partial^2 v_x}{\partial y^2};$$

i.e., it was assumed that the depth h^2 of the liquid layer is small compared to $\frac{\nu l}{|v_x|}$. Using expression (68.14), the following inequality is the condition for applicability of our solution,

$$h^3 \ll \frac{4\nu^2 \rho l}{\left| \frac{\partial \sigma}{\partial T} \right| \left| \frac{\partial T}{\partial x} \right|}. \quad (68.15)$$

The velocities arising in the liquid under the action of the surface forces are quite large. For example, for water, at $|\text{grad } T| = 0.1$ degree/cm, in a vessel whose depth is $h = 0.03$ cm, and where $\frac{\partial \sigma}{\partial T} = -0.15$ erg/cm²·degree, we find:

$$(v_x)_{y=0} = 0.1 \text{ cm/sec.}$$

Such velocities are substantially greater than those arising in the liquid due to ordinary convection, which in turn is caused by the density differences in the liquid at the walls.

It should also be borne in mind that equation (68.14) was derived on the assumption that the value of the Reynolds number is low. This equation may be used only when

$$\text{Re} = \frac{(v_x)_{y=0} h}{\nu} = \frac{1}{4\mu\nu^2} \frac{\partial \sigma}{\partial T} \frac{dT}{dx} h^2 \ll 1. \quad (68.16)$$

The above inequality corresponds to the general condition (66.10).

The diffusion problem is found to be identical with that of diffusion at the inlet section of a tube as presented in Sec. 20. Using equation (20.11), the mass flux equation is

$$I_{\text{diff}} \approx 0.6 \frac{c_0 S D^{2/3}}{L^{1/2}} \left(\frac{1}{\mu} \frac{\partial \sigma}{\partial x} \right)^{1/3},$$

where S is the area of the film and L its length (the larger dimension).

The mass flux is independent of the film thickness provided the latter is large compared to the thickness of the diffusion layer; i.e.,

$$\delta' = L^{1/3} D^{1/3} \frac{1}{\left(\frac{1}{\mu} \frac{\partial \sigma}{\partial x}\right)^{1/3}} \ll h.$$

At values for δ' of the order of h , the flux is given by

$$I \sim \frac{Dc_0S}{h}.$$

The expressions given above were derived by I. L. Rosenfel'd and K. A. Zhigalova [6].

Measured values of the average current density equal to $\frac{IFn}{S}$, using oxygen, are shown in Figure 69.

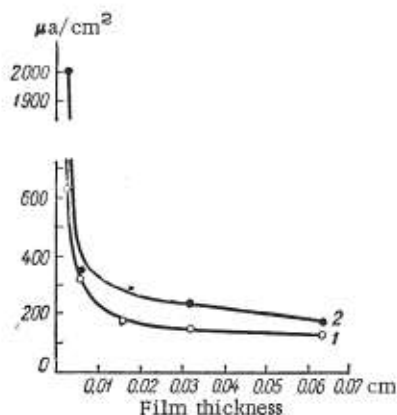


Figure 69. Dependence of the rate of oxygen reduction on the thickness of the electrolyte film. The electrolyte is 0.1 N NaCl; the cathode material is copper. Vapor pressure of water: 1) 17 mm Hg; 2) 1.15 mm Hg.

We see that the theoretical requirement that I be independent of h is found at $h > 3 \cdot 10^{-2}$ cm. In this case $\delta' \approx \frac{4}{100}h$.

An estimate of the value of $\frac{\partial \sigma}{\partial x}$ in these experiments gives $\frac{\partial \sigma}{\partial x} \sim 1$ (at a film length L of a few centimeters). Such variation in surface tension occurred because of nonuniformity of evaporation, change in solution composition during electrolysis, and changes in concentration of the electrolyte in various parts of the film.

Thermocapillary motion causes the formation of various types of films in an unevenly heated liquid.

69. EFFECT OF SURFACE-ACTIVE SUBSTANCES ON LIQUID FLOW

Experiments with liquids having clean surfaces are relatively rare in actual practice. Usually, the liquid is covered with surface-active substances to a greater or lesser degree [7].

Such a film modifies the forces exerted on the surface of the fluid. The modification is not simply the reduction of the surface tension. It involves tangential forces arising on the liquid surface.

This leads to a change in forces of capillarity as well as to the appearance of additional surface forces which are equal in magnitude to the capillary pressure.

The presence of surface-active substances, therefore, may lead to a significant change in the hydrodynamic regime. Indeed, the motion of the liquid and the change in shape of the surface caused by the motion lead to a change in the distribution of the concentration of the surface-active substance. Thus, the concentration of the latter varies from point to point on the surface

$$\Gamma = \Gamma(x, y, z),$$

where (x, y, z) are related to each other by the equation for the surface. A change in concentration of the surface-active substance results in a variation in surface tension along the surface. Therefore, capillary pressure; i.e., the normal force acting per 1 cm² of surface area

$$p_n = \frac{2\sigma(\Gamma)}{R} \quad (69.1)$$

will be different at different points on the surface.

When the surface tension of the liquid varies from point to point, then, a tangential force arises on the liquid surface in addition to the capillary pressure. The tangential force is directed from points of greater to points of lesser surface tension. This force per unit of liquid surface area is given by

$$p_t = \text{grad } \sigma = \frac{\partial \sigma}{\partial \Gamma} \text{grad } \Gamma \quad (69.2)$$

and is directed tangentially to the surface.

Thus, the presence of surface-active substances leads to the appearance of surface forces and changes the boundary conditions that must be fulfilled by the liquid velocity in the surface.

Motion of Drops and Bubbles in Fluid Media

70. MOTION OF LIQUID DROPS IN FLUID MEDIA

The motion of liquid drops in a fluid medium has been studied extensively both experimentally and theoretically. The study of this process yields important conclusions concerning the properties of the interface between two liquids, and between a liquid and a gas when the medium in which the drop moves is a gas.

The study of the laws governing drop motion in a fluid medium is essential in the solution of experimental and practical engineering problems. This includes various experiments on the motion of drops in an emulsion, extraction from liquid drops, the subdivision and atomization of drops in fuel injection into internal combustion engines, motion of raindrops, etc.

The motion of liquid mercury and other metallic drops in electrolytic solutions is characterized by the existence of charges on the surfaces of these drops. It will, therefore, be considered separately in Chapter IX.

The motion of liquid drops is closely tied to the size of the diffusional flux to the drop-solution interface. Finding the latter is a matter of great practical and theoretical significance. Problems related to diffusion at the drop-solution interface are discussed in Section 72.

We shall first consider the motion of drops so small that the motion is in the viscous regime ($Re \ll 1$). We have to deal most frequently with the fall of drops in a gravitational field. In what follows, therefore, we shall assume that gravity is the driving force.

The motion of a solid sphere for $Re \ll 1$ is determined by the well-known Stokes formula.

Computations by Rybczynski [1] and those undertaken independently by Hadamard [2] have shown that a change in the boundary conditions on the surface of a drop leads to a significant change in the velocity of the falling drop. Since we shall later need to

perform computations similar to those made in the derivation of the Rybczyński-Hadamard formula, we present its complete derivation here.

Let us consider the fall of a liquid drop in a liquid medium, the liquids being immiscible and differing in density and viscosity. Let the viscosity of the liquid medium be μ , and its density, ρ . The same properties for the drop are μ' and ρ' .

Let us direct the x axis vertically downward, so that the gravitational force acting on the drop is directed along the x axis and is

$$F = (\rho - \rho')g \cdot V,$$

where V is the volume of the drop.

Under the action of the force of gravity, the drop falls in the liquid at a certain velocity U . During its motion, the liquid within the drop attains a velocity v' , while the liquid medium surrounding the drop attains a velocity v . In this case, the drop preserves its spherical shape while falling and is not deformed. Some time after the start of the fall, the motion of the drop in the liquid medium becomes steady.

The Navier-Stokes equations for the steady motion of the liquid medium and for the liquid within the drop have the form

$$\text{grad } p = \mu \Delta v + i(\rho - \rho')g, \quad (70.1)$$

where p is the pressure and i is the unit vector in the positive direction of the x axis. Correspondingly

$$\text{grad } p' = \mu' \Delta v', \quad (70.2)$$

where p' is the pressure in the liquid inside the drop. Velocities v and v' satisfy the continuity equation

$$\left. \begin{aligned} \text{div } v &= 0, \\ \text{div } v' &= 0. \end{aligned} \right\} \quad (70.3)$$

It is convenient to reduce equation (70.1) to a form similar to (70.2) by introducing an additional effective pressure instead of the external force [3],

$$\pi = (\rho - \rho')gx = \frac{Fx}{V}.$$

It is not difficult to see that when the shear stress which includes this effective pressure is integrated over the surface, the total force exerted on the spherical drop will be precisely equal to the force F .

Equation (70.1) then acquires the form

$$\text{grad } (p - \pi) = \mu \Delta v, \quad (70.4)$$

which is similar to (70.2).

The similarity of the equations describing the motion of the inner and outer liquids makes the computations simpler.

To find the distributions of the velocities v and v' and of the pressures p and p' , the system of equations (70.1) to (70.4) must be solved taking the appropriate boundary conditions into consideration.

The symmetry of the problem suggests using a system of spherical coordinates (r, θ, φ) with the origin placed at the center of the drop. The angle θ is measured counterclockwise from the point of incidence of the flow.

Since the motion of the drop is symmetrical with respect to the x axis, the velocities of the inner and outer liquids are not functions of the angle φ ; i.e., they have the following components $v_r(r, \theta)$, $v_\theta(r, \theta)$, $v'_r(r, \theta)$, and $v'_\theta(r, \theta)$.

The Navier-Stokes equations in spherical coordinates have the form

$$\frac{\partial p}{\partial r} = \mu \left(\frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} + \frac{2}{r} \frac{\partial v_r}{\partial r} + \frac{\cot \theta}{r^2} \frac{\partial v_r}{\partial \theta} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} - \frac{2v_r}{r^2} - \frac{2 \cot \theta}{r^2} v_\theta \right), \quad (70.5)$$

$$\frac{1}{r} \frac{\partial p}{\partial \theta} = \mu \left(\frac{\partial^2 v_\theta}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r} \frac{\partial v_\theta}{\partial r} + \frac{\operatorname{ctg} \theta}{r^2} \frac{\partial v_\theta}{\partial \theta} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r^2 \sin^2 \theta} \right), \quad (70.6)$$

and the continuity equation has the form

$$\frac{\partial v_r}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{2v_r}{r} + \frac{v_\theta \cot \theta}{r} = 0. \quad (70.7)$$

The equations of motion for the inner liquid have similar forms.

In order to formulate the boundary conditions, it is convenient to pass to a system of coordinates which moves with the center of gravity of the falling drop. In such a system, the drop as a whole is considered motionless, while the outer liquid, which, as a whole, moves in the direction opposite to that of the actual motion of the drop, moves at a velocity $(-U)$ (U being the velocity of the drop's motion).

Thus, far from the falling drop, the velocity distribution in the liquid medium has the form

$$\left. \begin{aligned} v_r &= -U \cos \theta, \\ v_\theta &= +U \sin \theta \end{aligned} \right\} \quad \text{as } r \rightarrow \infty, \quad (70.8)$$

The normal component p_{rr} and the tangential component $p_{r\theta}$ of the viscous stress tensor are continuous at the liquid interface. In spherical coordinates the normal and tangential components of the stress tensor have the form

$$\left. \begin{aligned} p_{rr} &= -p + 2\mu \frac{\partial v_r}{\partial r}, \\ p_{r\theta} &= \mu \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right). \end{aligned} \right\} \quad (70.9)$$

The pressure in the expression for the normal component p_{rr} of the stress tensor is the total pressure in the liquid.

In our notation, the total pressure in the outer liquid is $(p - \pi)$. The boundary conditions for the stresses on the surface of the drop, at $r = a$, can therefore be written in the form

$$-(p - \pi) + 2\mu \left(\frac{\partial v_r}{\partial r} \right)_{r=a} = -p' + 2\mu' \left(\frac{\partial v'_r}{\partial r} \right)_{r=a}, \quad (70.10)$$

$$\mu \left(\frac{1}{r} \frac{\partial v_r}{\partial \theta} + \frac{\partial v_\theta}{\partial r} - \frac{v_\theta}{r} \right)_{r=a} = \mu' \left(\frac{1}{r} \frac{\partial v'_r}{\partial \theta} + \frac{\partial v'_\theta}{\partial r} - \frac{v'_\theta}{r} \right)_{r=a}. \quad (70.11)$$

In addition, the velocities of the inner and outer liquids must satisfy the following conditions on the surface of the drop:

1) The normal components of the inner and outer fluid velocities must be zero

$$v_r = v'_r = 0 \quad \text{at} \quad r = a. \quad (70.12)$$

Indeed, since the drop is not deformed and its surface does not pulsate (at high velocities, this is not so; see Section 79) and since the inner and outer liquids are immiscible, the surface of the liquid drop is the same as the impenetrable surface of a solid particle.

2) The boundary condition for the tangential velocity components on the liquid interface is significantly different from the boundary condition on a solid surface.

The tangential velocity components of the two liquids at the interface between them must be continuous; i.e.,

$$v_\theta = v'_\theta \quad \text{at} \quad r = a. \quad (70.13)$$

The continuity requirement for the tangential velocity component at the interface between the liquids follows directly from the well-known experimental fact that there is no slip between liquids at their interface.

The last condition which must be satisfied by the liquid within the drop is a condition which replaces conditions (70.8) for the velocity of the outer liquid. This condition states that the velocity components v'_r and v'_θ must remain finite at all points within the drop, particularly at the center of the drop (the origin of the coordinates):

$$v'_r \text{ and } v'_\theta \text{ are finite at } r = 0. \quad (70.14)$$

The solution of equations (70.1) to (70.4) for boundary conditions (70.8) to (70.14) allows us to find the velocity and pressure distributions in the liquids.

The boundary conditions (70.8) at infinity show that a solution of equations (70.1) to (70.4) should be sought in the form

$$\left. \begin{aligned} v_r &= f(r) \cos \theta; & v_\theta &= \varphi(r) \sin \theta, \\ p &= \psi(r) \cos \theta \end{aligned} \right\} \quad (70.15)$$

and similarly

$$\left. \begin{aligned} v'_r &= f'(r) \cos \theta; & v'_\theta &= \varphi'(r) \sin \theta, \\ p' &= \psi'(r) \cos \theta. \end{aligned} \right\}$$

Substituting these solutions (70.15) into equations (70.5), (70.6), and (70.7), we find:

$$\frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr} - \frac{4(f+\varphi)}{r^2} = \frac{d\psi}{dr}, \quad (70.16)$$

$$\frac{d^2 \varphi}{dr^2} + \frac{2}{r} \frac{d\varphi}{dr} - \frac{2(f+\varphi)}{r^2} = -\frac{\psi}{r}, \quad (70.17)$$

$$\frac{df}{dr} + \frac{2(f+\varphi)}{r} = 0. \quad (70.18)$$

A similar system of equations is obtained for the inner liquid. Expressions (70.16) to (70.18) are a system of linear, ordinary differential equations, which may be solved easily. Namely, we obtain from equation (70.18):

$$\varphi = -\frac{r}{2} \frac{df}{dr} - f. \quad (70.19)$$

Substituting the value of φ into equation (70.17), we obtain:

$$\frac{\psi}{r} = \frac{d^2}{dr^2} \left(\frac{r}{2} \frac{df}{dr} + f \right) + \frac{2}{r} \frac{d}{dr} \left(\frac{r}{2} \frac{df}{dr} + f \right) - \frac{1}{r} \frac{df}{dr}, \quad (70.20)$$

or

$$\psi = \frac{1}{2} r^3 \frac{d^3 f}{dr^3} + 3r \frac{d^2 f}{dr^2} + 2 \frac{df}{dr}.$$

Substituting the value of ψ into equation (70.16), we obtain:

$$r^3 \frac{d^4 f}{dr^4} + 8r^2 \frac{d^3 f}{dr^3} + 8r \frac{d^2 f}{dr^2} - 8 \frac{df}{dr} = 0. \quad (70.21)$$

Expression (70.21) is an Euler equation. In accordance with the general theory of integration of equations of this type, we shall seek

a solution in the form

$$f \approx r^n.$$

For n we then have the equation

$$n(n-1)(n-2)(n-3) + 8n(n-1)(n-2) + 8n(n-1) - 8n = 0,$$

or

$$n(n-2)(n+1)(n+3) = 0.$$

The roots of this are:

$$n_1 = 0; \quad n_2 = +2; \quad n_3 = -1; \quad n_4 = -3.$$

Therefore, we obtain for f :

$$f = \frac{b_1}{r^3} + \frac{b_2}{r} + b_3 + a_1 r^2. \quad (70.22)$$

On substituting f into equations (70.20) and (70.19), we obtain:

$$\varphi = \frac{b_1}{2r^3} - \frac{b_2}{2r} - b_3 - 2a_1 r^2, \quad (70.23)$$

$$\psi = \frac{b_2}{r^2} + 10a_1 r. \quad (70.24)$$

Substituting the above determined values of the functions f , φ , and ψ from (70.22), (70.23), and (70.24) into (70.15), we obtain:

$$v_r = \left(\frac{b_1}{r^3} + \frac{b_2}{r} + b_3 + a_1 r^2 \right) \cos \theta, \quad (70.25)$$

$$v_\theta = \left(\frac{b_1}{2r^3} - \frac{b_2}{2r} - b_3 - 2a_1 r^2 \right) \sin \theta, \quad (70.26)$$

$$p = \mu \left(\frac{b_2}{r^2} + 10a_1 r \right) \cos \theta. \quad (70.27)$$

The expressions for the velocity components and the pressure (70.25) to (70.27) represent the general solution of equations (70.1) to (70.3). Exactly the same expressions can be written for the velocity and pressure distributions within the drop. The values of the constants should be selected so as to satisfy conditions (70.8) to (70.14). In order for the outer solution to satisfy conditions (70.8), it is necessary that the constant a_1 for the outer liquid be equal to zero. Otherwise v_r and $v_\theta \rightarrow \infty$ as $r \rightarrow \infty$. Thus, the outer solution must have the form

$$v_r = \left(\frac{b_0}{r} + \frac{b_1}{r^2} + b_3 \right) \cos \theta, \quad (70.28)$$

$$v_\theta = \left(\frac{b_1}{2r^3} - \frac{b_2}{2r} - b_3 \right) \sin \theta, \quad (70.29)$$

$$p = \mu \frac{b_0}{r^2} \cos \theta. \quad (70.30)$$

In accordance with (70.14), the velocity distribution within the drop must be so expressed that the velocity components have a finite value at $r = 0$. For this, the constants for $\frac{1}{r}$ and $\frac{1}{r^2}$ in the inner solution must be equated to zero. The velocity and pressure distributions within the drop have the form

$$v'_r = (a_1 r^2 + a_2) \cos \theta, \quad (70.31)$$

$$v'_\theta = -(2a_1 r^2 + a_2) \sin \theta, \quad (70.32)$$

$$p' = \mu' a_0 + 10\mu' a_1 r \cos \theta. \quad (70.33)$$

Five unknowns, b_1 , b_2 , b_3 , a_1 , and a_2 , are involved in equations (70.28) to (70.33). The boundary conditions (70.8) to (70.13) contain six equations for the determination of these constants and of a sixth, the quantity U . In the course of the calculations, the constant in (70.33) was equated to zero. This arbitrary step is related to the fact that only the pressure difference in the liquid has a definite value. Substituting the expressions (70.28) and (70.29) into boundary condition (70.8), we find:

$$b_3 = -U. \quad (70.34)$$

Substituting the values of the corresponding quantities v_r , v'_r , v_θ , v'_θ , p , p' , and π into conditions (70.10) to (70.13) and following elementary, although somewhat lengthy computations, we obtain

$$U = \frac{2(\rho' - \rho)ga^2}{3\mu} \frac{\mu + \mu'}{2\mu + 3\mu'}. \quad (70.35)$$

This formula is known as the Rybczynski-Hadamard formula. It passes into the Stokes equation

$$U_{St} = \frac{2}{9} \frac{(\rho' - \rho)ga^2}{\mu}, \quad (70.36)$$

when the viscosity of the interior liquid is large, $\mu' \gg \mu$.

Comparing expressions (70.36) and (70.35), we note that

$$\frac{U}{U_{St}} = 3 \frac{\mu + \mu'}{2\mu + 3\mu'} > 1. \quad (70.37)$$

The meaning of this result is simple. Due to the mobility of the interface, the velocity gradients present in the liquid are smaller than those in the case of a solid interface. Decreasing the velocity gradients leads to a decrease in the energy dissipated in the liquid.

With the same driving force (gravity) and a smaller energy dissipation, the velocity of steady fall of a liquid drop should be greater than the velocity of fall of a solid sphere.

The liquid on the surface of the drop moves at a velocity

$$(v_\theta)_{r=a} = v_0 \sin \theta, \quad (70.38)$$

where v_0 is the magnitude of the velocity at the drop's equator,

$$v_0 = \frac{\mu}{2} \frac{U}{\mu + \mu'}. \quad (70.39)$$

For $\mu' \gg \mu$, the velocity on the surface is small and in the limit becomes zero (the case of a solid surface). For $\mu' \approx \mu$, $v_0 \approx \frac{U}{4}$, and for $\mu \gg \mu'$, v_0 has its maximum value: $v_0 \approx \frac{U}{2}$.

71. COMPARISON OF THE RYBCZYŃSKI-HADAMARD FORMULA WITH EXPERIMENTAL DATA

Comparisons of the Rybczyński-Hadamard formula with experimental data have been made in many instances. In the extremely careful measurements made by A. A. Lebedev [4], the velocities of fall of mercury drops in castor oil coincided exactly with the velocities for solid spheres. Similar results have been obtained by other investigators [5,6]. On the basis of these data it was generally concluded that the Rybczyński-Hadamard formula is not applicable under actual conditions. As an explanation of this contradiction between theory and experiment, Boussinesq [7] advanced the hypothesis that a thin layer of higher viscosity exists near a liquid interface. This assumption of the existence of increased viscosity in a thin, but macroscopic, layer near the interface has received wide acceptance and will be examined in greater detail later. According to Boussinesq's theory, velocity of fall of the drop is given by the formula

$$U = \frac{2}{3} \frac{\rho - \rho'}{\mu} g a^2 \frac{\mu + \mu' + \frac{2e}{3a}}{2\mu + 3\mu' + \frac{2e}{a}}. \quad (71.1)$$

the adsorption-desorption process, in this case, may be considered to be as rapid as desired, so that the concentration of the solution near the surface has a value c_1 which is in equilibrium with Γ , but differs from the concentration c_0 in the bulk of the solution. The quantity c_0 evidently corresponds to the equilibrium concentration Γ_0 on the surface.

As a result, there is a flow of surface-active material between the solution adhering to the drop and the bulk of the solution. The density of this flux can evidently be expressed in the form

$$J_n = D \left(\frac{\partial c}{\partial r} \right)_{r=a}, \quad (75.1)$$

where D is the diffusion coefficient of surface-active molecules and the derivative is evaluated at the surface of the drop.

Therefore in the case of rapid kinetics, j_n in the boundary condition (73.12) has the form of expression (75.1), and the boundary condition itself assumes the form (if surface diffusion is neglected)

$$D \left(\frac{\partial c}{\partial r} \right)_{r=a} = \Gamma_0 \operatorname{div}_s \mathbf{v}_t. \quad (75.2)$$

To find the general solution of the hydrodynamic equations with boundary condition (75.2), it is also necessary to find the concentration distribution in the solution. The latter is determined by the equation of convective diffusion

$$\mathbf{v} \operatorname{grad} c = D \Delta c. \quad (75.3)$$

The solution of the system of hydrodynamic and convective transfer equations with the appropriate boundary conditions presents very serious mathematical difficulties.

Namely, the system of equations (70.1) to (70.4) and (75.3) does not allow solutions that are dependent on the angle θ in the form of the first spherical (Legendre) function and its derivative (i.e., as $\cos \theta$ and $\sin \theta$). This indicates that the shape of the drop must necessarily deviate from spherical, and the method of solution developed by us for the case discussed above cannot be strictly applied to the solution of the problem posed here. Henceforth, we limit ourselves to a qualitative explanation.

In order to obtain an approximate expression for the velocity of the drop's motion, let us assume that the variation in the surface tension along the drop is small compared to its absolute value, so that we can neglect the deviation in the shape of the drop from spherical. Let us further assume that we can also neglect the dependence of the diffusional flux on the angle θ and that we may replace the true value of the flux in expression (75.1) by its mean value over the drop.*

* Editor's note: Actually we shall replace the true value of the thickness of the diffusion boundary layer by its mean value over the drop [see (75.4)]. The mean flux is zero.

The mean value \bar{j}_n of the flux can then be presented in the form

$$\bar{j}_n = D \frac{\Delta c}{\delta}, \quad (75.4)$$

where Δc is the difference in concentration between the bulk of the solution and a point near the surface and δ is the average thickness of the diffusion layer.

Assuming the shape of the drop to be constant, let us write the tangential velocity component on the surface in the form $v_0 \sin \theta$ and, utilizing formula (73.10) and the value for j_n from expression (75.4), let us write boundary condition (75.2) in the form

$$\frac{D \Delta c}{\delta} = \frac{2v_0 \Gamma_0 \cos \theta}{a}. \quad (75.4')$$

Assuming, further, that

$$\Delta c = \frac{\partial c}{\partial \Gamma} \Delta \Gamma = - \frac{\partial c}{\partial \Gamma} (\Gamma - \Gamma_0) = - \frac{\partial c}{\partial \Gamma} \Gamma',$$

we find the expression for the distribution of the amount of molecules adsorbed along the surface

$$\Gamma' = - \frac{\delta}{D} \frac{2v_0 \Gamma_0 \cos \theta}{a \left(\frac{\partial c}{\partial \Gamma} \right)}. \quad (75.5)$$

Relation (75.5) is analogous to expression (74.3) for the capillary pressure.

The distribution of surface tension along the drop can be derived from the approximate dependence of Γ' on the angle θ :

$$\begin{aligned} \sigma &= \sigma_{\pi/2} + \int_{\pi/2}^{\theta} \frac{\partial \sigma}{\partial \vartheta} d\vartheta = \int \frac{\partial \sigma}{\partial \Gamma} \frac{\partial \Gamma}{\partial \vartheta} d\vartheta + \sigma_{\pi/2} = \\ &= \sigma_{\pi/2} - \frac{\partial \sigma}{\partial \Gamma} \frac{2\Gamma_0 v_0 \delta}{Da \left(\frac{\partial c}{\partial \Gamma} \right)} \cos \theta = \sigma_{\pi/2} - \frac{2\Gamma_0 v_0 \delta}{Da} \left(\frac{\partial \sigma}{\partial c} \right) \cos \theta, \end{aligned} \quad (75.6)$$

where $\sigma_{\pi/2}$ is the surface tension on the drop's equator.

Knowing the dependence of the surface tension on the angle θ , it is possible to proceed with the formulation of boundary conditions and to the determination of the constants b_1, b_2, b_3, a_1 , and a_2 in the expressions for the components of the velocity, the velocity U of the fall of the drop, and the constant v_0 which we introduced into the expression for the tangential velocity component on the surface of the drop (a total of seven constants).

Computations no different from those preceding lead to expressions for U and v_0 that are identical with (74.10) and (74.11), in which the quantity γ_2 has the value

$$\gamma_2 = \frac{2RT\Gamma_0^2 \delta}{3Da c_0}. \quad (75.7)$$

If Γ_0 is expressed by formula (74.16), we have for γ_2 :

$$\gamma_2 = \frac{2RT\bar{\gamma}}{3Da} \cdot \frac{k^2 c_0}{\left(1 + \frac{k c_0}{\Gamma_\infty}\right)^2} = \frac{2RT\bar{\gamma}}{3Da} \cdot k\Gamma_0 \left(1 - \frac{\Gamma_0}{\Gamma_\infty}\right). \quad (75.8)$$

All quantities in formula (75.8), except the adsorption coefficient k , are either weak functions or are independent of the nature of the surface-active material. The retardation coefficient, therefore, is proportional to the square of the adsorbability k^2 of the material. If the dependence of the retardation coefficient γ_2 on the nature of the material is studied in a homologous hydrocarbon series, then, according to formula (75.8), at small adsorbabilities, the retardation coefficient is proportional to the square of the Traube coefficient.

As the concentration Γ_0 increases, so does γ_2 , which attains a maximum value at $\Gamma_0 = \frac{\Gamma_\infty}{2}$. At the maximum point,

$$(\gamma_2)_{\max} = \frac{k\Gamma_\infty RT\bar{\gamma}}{3aD}. \quad (75.9)$$

A further increase in the concentration of the solution leads to a decrease in γ_2 .

For the quantitative estimation of γ_2 , we may utilize the values for δ derived in Sections 14 and 72 for two limiting cases — a liquid drop and a solid sphere.

As may be seen from a comparison of expressions (14.17) and (72.8), the quantity δ is several times greater in the first case. This reflects the more favorable conditions of convective diffusion in the case of the liquid-liquid interface.

To estimate the maximum value of γ_2 that may be anticipated in the case of retardation by highly soluble surface-active substances, it is necessary to replace δ in formula (75.7) by its value from expression (14.17), thereby assuming that the motion of the liquid on the surface of the drop is fully damped by the surface-active substance.

Thus,

$$\gamma_2 = \frac{2RT\Gamma_0^2}{3Dac_0} \left(\frac{Da^2}{U}\right)^{1/2}. \quad (75.10)$$

In a case of weak retardation, for example, at sufficiently small concentrations of surface-active substances, we obtain a more correct value for γ_2 by replacing δ in formula (75.8) by its value from expression (72.8),

$$\gamma_2 = \frac{2RT\Gamma_0}{Dac_0} \left(\frac{Da}{U}\right)^{1/2}. \quad (75.11)$$

We see that the retardation decreases with increasing velocity in proportion to U^n , where n is between $1/3$ and $1/2$.

Let us now examine the retardation caused by a surface-active material which dissolves so slowly that it can be considered to remain on the surface of the drop during the entire period of the latter's motion. For the sake of brevity, let us agree to call such materials

insoluble. Their flux to the surface j_n is equal to zero, so the only mechanism for equalizing the concentration of the surface-active material along the surface of the drop is surface diffusion.

The distribution of the concentration of surface-active materials over the surface of the drop is determined by the equation of surface convective diffusion

$$\operatorname{div}_s(\Gamma v_t) = D_s \Delta \Gamma,$$

or, in spherical coordinates,

$$\frac{1}{a \sin \theta} \frac{\partial}{\partial \theta} (\sin^2 \theta \cdot \Gamma \cdot v_\theta) = \frac{D_s}{a^2} \cdot \frac{1}{\sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Gamma}{\partial \theta} \right), \quad (75.12)$$

where D_s is the surface diffusion coefficient of the surface-active material.

Assuming, as before, that the variations in concentration are small and that the velocity of motion of the liquid along the surface is equal to $v_0 \sin \theta$, we find:

$$2av_0\Gamma_0 \cos \theta = -\frac{D_s}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Gamma}{\partial \theta} \right),$$

or

$$\Gamma = -\frac{2av_0\Gamma_0}{D_s} \cos \theta. \quad (75.13)$$

Thus, the distribution of surface-active material on the surface, in this instance, is quite similar to that characterized by expression (75.5), differing from it only by the value of the constant coefficient. Therefore, without repeating the computations of the preceding section, it is possible to write the following expression for the velocity of fall of the drop:

$$U = 3U_0 \frac{\mu + \mu' + \gamma_3}{2\mu + 3\mu' + 3\gamma_3}, \quad (75.14)$$

where the coefficient is $\gamma_3 = \frac{2a\Gamma_0}{3D_s} \left| \frac{\partial \sigma}{\partial \Gamma} \right|$ and expresses the retardation of the drop by the surface-active material. For small degrees of surface coverage by the adsorbed surface-active material,

$$\gamma_3 = \frac{2\Gamma_0 a}{3D_s} \left| \frac{\partial \sigma}{\partial \Gamma} \right| \approx \frac{2\Gamma_0 a RT}{3D_s}, \quad (75.15)$$

i.e., the retardation increases in proportion to the amount adsorbed.

76. COMPARISON OF DIFFERENT THEORIES

In the study of Boussinesq [7], the following expression was derived for the velocity of drop fall

$$U = \frac{2}{3} \frac{(\rho - \rho') g a^2}{\mu} \cdot \frac{\mu + \mu' + \frac{2e}{3a}}{2\mu + 3(\mu' + \frac{2e}{a})}, \quad (76.1)$$

where e is the surface viscosity coefficient.*

Surface viscosity is defined by Boussinesq as the coefficient in the relation

$$\Delta \sigma = e \operatorname{div}_s \mathbf{v}_t,$$

whence

$$e = \frac{\Delta \sigma}{\operatorname{div}_s \mathbf{v}_t}. \quad (76.2)$$

Thus, the quantity e , which has been introduced, does not represent ordinary viscosity, but a second viscosity for the surface motion.

Using the values derived for $\operatorname{div}_s \mathbf{v}_t$ and $\Delta \sigma$, it is possible to find the quantity in our theory which corresponds to Boussinesq's surface viscosity. It is clear that various values can be derived for e , depending on the nature of the slow step that controls the over-all kinetics of the exchange.

Namely, from formulas (76.1) and (74.10) and from a comparison of formula (76.2) with expressions (73.10) and (75.6) for the case where the controlling step of the process is the diffusion of the material in the bulk of the solution, we find:

$$e = \left| \frac{\partial \sigma}{\partial c} \right| \frac{\Gamma_0 \delta}{D} = \frac{3\gamma_2 a}{2}. \quad (76.3)$$

Similarly, in the case of surface diffusion, using the same formulas and (75.13), taking the value of v_0 into account, we have:

$$e = \left| \frac{\partial \sigma}{\partial \Gamma} \right| \frac{\Gamma_0 a^2}{D_s} = \frac{3\gamma_3 a}{2}. \quad (76.4)$$

Thus, the assumption that the retardation is controlled by a constant surface viscosity and is a function exclusively of the surface properties of the liquid is not justified in either instance. This is especially important in the case of insoluble films because it is precisely in this case that the existence of a surface viscosity, in the sense of Boussinesq, would appear to be most likely. It is only under conditions of solubility of surface-active materials and slow kinetics of adsorption that the quantity e is in reality determined by surface properties and, as seen from expressions (74.5) and (74.3) and from definitions (76.2) and (73.10), can be formulated as follows:

*An incorrect value for the numerical coefficient of e is given in this study by Boussinesq.

$$e = \left| \frac{\partial \sigma}{\partial \Gamma} \right| \frac{\Gamma_0}{\alpha}. \quad (76.5)$$

The fact that, in the case of slow adsorption kinetics, the quantity e is a function neither of the radius nor of the flow regime follows directly from the fact that the equalization of the excess surface concentration depends here only on conditions in the surface layer and on the value of the concentration in the bulk phase. The latter, by assumption, remains constant. Nevertheless, in this case too, the similarity with Boussinesq's conclusion is purely formal since the physical meaning of the coefficient in the theory developed by us is quite different and, in contrast with the Boussinesq surface viscosity concept, cannot be understood without taking into account the existence of the bulk phase. With these reservations, the quantity $e = \frac{\gamma a}{2}$ may be regarded as the measure of a certain dynamic elasticity of the surface layer which determines its ability to resist lasting deformation and which is comparable to the elasticity values of surface layers derived by Gibbs [14].

Gibbs examined the change in the interfacial tension when the extent of the surface varies and introduced the concept of the elasticity E of a thin liquid lamella between two gaseous phases, defining E by the equation

$$2d\sigma = \frac{E dS}{S}. \quad (76.6)$$

The factor of 2 in the Gibbs equation indicates the presence of two interfaces. In defining the quantity E , Gibbs accepted the proposition that equilibrium always exists between the surface of the layer and adjacent parts of the body of the layer, because any disturbances of the layer accompanying the changes in S are for all practical purposes immediately negated because of the thinness of the film. On the contrary, the equilization of the concentrations in the thin layer along the surface may virtually be neglected. Under these conditions, the value of E can be easily computed from the quantities which determine the equilibrium state of the system. Let us apply Gibbs' argument to the analogous case that we are examining. Namely, let us assume that the adsorbed material is evenly distributed between the surface and the volume V of a certain phase that is adjacent to a second phase not containing that component, and let us designate by g the over-all amount of material that is being adsorbed. Obviously,

$$E = S \left(\frac{\partial \sigma}{\partial S} \right)_g = S \frac{\partial \sigma}{\partial c} \left(\frac{\partial c}{\partial S} \right)_g,$$

and, since

$$S\Gamma_0 + Vc = g,$$

then

$$E = -S \frac{d\sigma}{dc} \cdot \frac{\Gamma_0}{V + S \frac{\partial \Gamma_0}{\partial c}} \quad (76.7)$$

Equation (76.7) is equivalent to the Gibbs equation (655) in the cited reference. Let us examine separately two limiting cases, when $S\Gamma_0 \ll Vc$, i.e., when the amount of material on the surface is negligible compared to its amount in the volume, and the reverse case when $S\Gamma_0 \gg cV$. In the first instance, it follows from equation (76.7) that

$$E = -\frac{d\sigma}{dc} \cdot \frac{\Gamma_0 S}{V} = \frac{RT\Gamma_0^2}{c} \cdot \frac{S}{V} = \frac{RT\Gamma_0^2}{ch} \quad (76.8)$$

where $h = \frac{V}{S}$ is the thickness of the layer. In the second case

$$E = \Gamma_0 \left| \frac{\partial \sigma}{\partial \Gamma} \right| \quad (76.9)$$

or for small degrees of filling of the surface

$$E = RT\Gamma_0 \quad (76.10)$$

Equation (76.8) is very similar to the relation which we derived for e in the case of retardation under conditions of slow diffusion in the volume:

$$e = \frac{RT\Gamma_0^2}{c} \cdot \frac{1}{D}$$

The latter expression, however, instead of the reciprocal of the thickness of the layer $1/h$, contains the quantity δ/D , which has the dimensions $\text{cm}^{-1} \text{ sec}$. This difference in dimensions is quite natural since the equilibrium elasticity E of the film as interpreted by Gibbs expresses the variation in the surface tension for a given deformation. The ratio e/E must, therefore, have time as its dimension. Similarly, for the case of retarded surface diffusion, the quantity $e = \Gamma_0 \left| \frac{\partial \sigma}{\partial \Gamma} \right| \frac{a^2}{D_s}$ differs from the expression obtained for the elasticity of an insoluble film by the coefficient a^2/D_s , which also has the dimension of time. It is easy to see that the ratio e/E always defines to an order of magnitude the time needed for diffusion, under the given conditions of the system, to equalize the disturbed equilibrium of surface and volume concentrations caused by a single deformation of the surface.

77. COMPARISON OF THE DIFFERENT RETARDING MECHANISMS

As before, we shall designate the retardation coefficient by γ ; the cases where adsorption, diffusion in the volume, or diffusion on

the surface constitutes the slow step of the process are distinguished by the subscripts 1, 2, and 3, respectively. Let us first clarify the relative importance of the volume and surface diffusions. Since these two processes are parallel, the more rapid will be decisive. On it will depend the rate of establishment of a state of equilibrium concentrations. The more rapid process will evidently lead to the smaller value for γ .

In accord with equations (75.7) and (75.15),

$$\frac{\gamma_2}{\gamma_3} = \left(\frac{2RT\Gamma_0^2 \delta}{3Dac_0} \right) : \left(\frac{2a\Gamma_0}{3D_s} \left| \frac{\partial \tau}{\partial \Gamma} \right| \right) = \frac{RT\Gamma_0 \delta D_s}{Dc_0 a^2 \left| \frac{\partial \tau}{\partial \Gamma} \right|}.$$

When the surface is sparsely covered with the material being adsorbed, this expression can be simplified because $\frac{\partial \sigma}{\partial \Gamma} \approx -RT$ and, therefore,

$$\frac{\gamma_2}{\gamma_3} = \frac{\Gamma_0 \delta D_s}{Dc_0 a^2}. \quad (77.1)$$

When this phenomenon is studied with the usual dropping mercury electrode, a and δ have the values: $a \approx 5 \cdot 10^{-8}$ and $\delta \approx 3 \cdot 10^{-8}$. Taking into account the fact that D and D_s are quantities of the same order,* it follows from equation (77.1) that

$$\frac{\gamma_2}{\gamma_3} \approx \frac{\Gamma_0}{c_0}. \quad (77.2)$$

For surface diffusion to be significant compared with diffusion in the bulk phase, it is necessary for the relation $\frac{\gamma_2}{\gamma_3} \geq 1$ to be satisfied. For a 0.01 M solution of tertiary amyl alcohol in 1N NaCl, according to the data of A. N. Frumkin [15], $\frac{\Gamma_0}{c_0} \approx 10^{-6}$ on a mercury-solution interface. Surface diffusion, therefore, is significantly manifested only for materials whose surface activity exceeds that of the substance which we have chosen as a typical example of a soluble, surface-active compound. Such materials, however, are virtually insoluble. The importance of surface diffusion may increase if the equalization of concentrations in the volume phase is

*Apparently there are no experimental data for D_s in the case of liquid interfaces. It can be assumed, however, at least for materials which do not have an excessively long hydrocarbon chain and when the surface is sparsely covered, that D_s on a water surface and on a water-mercury interface do not differ from D in terms of orders of magnitude.

additionally retarded by the slowness of the adsorption step. This retardation, however, would hardly be sufficiently significant to cause an equalization of the large differences between the rates of the surface and the volume phase processes. Thus, if the surface-active material is transferred from the solution to the surface of the drop, the surface diffusion process apparently plays no significant part in the equalization of the concentration differences which appear because of convective transfer. This reasoning is no longer valid for drops of microscopic dimensions, at a $\approx 10^{-4}$ for example. In this case, the surface diffusion rate may become comparable to that in the volume phase.

Let us now compare the rate of diffusion in the volume phase with the rate of the adsorption process. Since these two processes are consecutive, the decisive role in determining the over-all rate of the reaction is exerted by the slower process, which accordingly contributes the larger value to the retardation coefficient γ . For this computation, we employ only the first kinetic interpretation of the Langmuir isotherm. According to equations (75.7) and (74.18)

$$\frac{\gamma_2}{\gamma_1} = \left(\frac{2RT\Gamma_0^2 \delta}{3Dac_0} \right) : \left(\frac{2RT}{a} \cdot \frac{\Gamma_0}{3z_0} \right) \approx \frac{\Gamma_0 \delta \alpha_0}{Dc_0} = \frac{\delta_0 \delta}{D} \left(1 - \frac{\Gamma_0}{\Gamma_\infty} \right). \quad (77.3)$$

Thus, the ratio of the diffusion retardation to that of adsorption decreases with an increase in the concentration of the solution and a decrease in δ , i.e., with an increase in the velocity of motion.

As shown by elementary computations, when a clean interface comes in contact with a solution of constant concentration c_0 , the coating of the interface changes with time according to the following relation:

$$\Gamma = \Gamma_0 \left[1 - \exp \left(- \frac{\alpha_0 t}{1 - \frac{\Gamma_0}{\Gamma_\infty}} \right) \right]. \quad (77.4)$$

Thus, the quantity $\frac{1}{\alpha_0} = \left(1 - \frac{\Gamma_0}{\Gamma_\infty} \right)$ should be regarded as the time τ_A required for the establishment of an adsorption equilibrium, and therefore

$$\alpha_0 = \frac{1 - \frac{\Gamma_0}{\Gamma_\infty}}{\tau_A}. \quad (77.5)$$

Substituting the value of α_0 from (77.5) into (77.3), we obtain:

$$\frac{\gamma_2}{\gamma_1} = \frac{\Gamma_0 \delta \left(1 - \frac{\Gamma_0}{\Gamma_\infty} \right)}{Dc_0 \tau_A}. \quad (77.6)$$

It follows from equation (77.6) that, for the condition $\frac{\gamma_2}{\gamma_1} < 1$ to be satisfied, it is necessary that

$$\tau_A > \frac{\Gamma_0 \delta \left(1 - \frac{\Gamma_0}{\Gamma_\infty}\right)}{D c_0} = \frac{k \delta}{D} \left(1 - \frac{\Gamma_0}{\Gamma_\infty}\right)^2. \quad (77.7)$$

In the case of a dilute solution of tertiary amyl alcohol which we examined, $\frac{\Gamma_0}{c_0} \approx 10^{-5}$, $\delta \approx 3 \cdot 10^{-3}$, $D \approx 10^{-5}$, and $1 - \frac{\Gamma_0}{\Gamma_\infty} \approx 1$. Thus, it follows from inequality (77.7) that

$$\tau_A > 3 \cdot 10^{-3} \text{ sec.}$$

In other words, for the retardation to be controlled by adsorption kinetics rather than by diffusion, the time for establishing an adsorption equilibrium must exceed several milliseconds. Such a value of τ_A is possible. The choice between the adsorption and the diffusion mechanisms, therefore, can be made only on the basis of experimental data and, in particular, on the basis of studies of the effect of stirring, which has different effects on the magnitude of the retardation coefficient γ in the two cases.

It follows from formulas (75.7) and (74.18) that the coefficient γ for both of these retardation mechanisms increases with a decrease in the radius a . As a result, in the case of drops of colloidal dimensions, it may be anticipated that the presence of even negligible amounts of surface-active impurities in the solution will lead to a loss of surface mobility. Thus, under ordinary conditions such drops should behave as solid spheres. Certain limitations are imposed on this conclusion by the decrease in γ_3 with a decrease in a .

78. LIMITS OF APPLICABILITY OF THE THEORY

The applicability of the above theory for the fall of a drop in a medium containing surface-active substances is limited, first of all, by the requirement that the Reynolds number be small during the drop's motion.

The second condition is the fulfillment of the inequality $|\Gamma'| \ll \Gamma_0$, which indicates the applicability of equation (73.12) or of the equivalent inequality $(\Delta\sigma) \ll \sigma_0 - \sigma$, where $\Delta\sigma$ is the variation of the surface tension caused by convective transfer and σ_0 is the surface tension of the liquid phase interface when $\Gamma_0 = 0$. Attainment of this condition may be difficult in many cases. We shall use this second inequality for a quantitative study. The maximum value for $|\Delta\sigma|$ according to equation (75.6) is

$$|\Delta\sigma| = \sigma(0) - \sigma\left(\frac{\pi}{2}\right) = \frac{2RT\Gamma_0^2 \sin \theta_0}{Dac_0} = \gamma v_0, \quad (78.1)$$

where $\sigma(0)$ and $\sigma\left(\frac{\pi}{2}\right)$ are values of σ at $\theta = 0$ and $\theta = \frac{\pi}{2}$.

Thus, the inequality under examination is equivalent to the relation

$$\gamma v_0 \ll |\sigma_0 - \sigma|, \quad (78.2)$$

The physical meaning of this limitation is that the changes in surface concentration become comparable to the initial concentration when these changes are equalized slowly. In the lower part of the drop, in particular, this may lead to complete removal of the adsorption layer from the surface and to an approach of the surface tension toward σ_0 . It is evident that under these conditions the true retardation will lag behind the values computed from the formulas and as derived for γ .

For a freely falling drop and considerable retardation, v_0 is equal to $\frac{\mu U_0}{2\gamma}$, according to equation (74.11). Substituting this value and the expression for U_0 given by the Stokes formula into equation (78.1), we obtain:

$$|\Delta\sigma| = \frac{\mu U_0}{2} = \frac{1}{9}(\rho' - \rho)ga^2. \quad (78.3)$$

From this simple relation, the following criterion for the applicability of the theory can be derived. The quantity $2|\Delta\sigma|$ is equal to the difference in interfacial tensions between the fore and aft ends of the drop. This quantity evidently cannot exceed a certain limit $|\Delta\sigma_{\max}|$, equal to the maximum decrease in the initial interfacial tension observed in solutions of the given surface-active material. Applicability of the theory, therefore, requires that

$$\frac{2}{9}(\rho' - \rho)ga^2 \ll |\Delta\sigma|_{\max},$$

or

$$a \ll \left[\frac{9}{2} \frac{|\Delta\sigma|_{\max}}{(\rho' - \rho)g} \right]^{1/2}. \quad (78.4)$$

This inequality determines the value of a certain critical radius a_{cr} above which the retardation due to changes in the interfacial tension no longer compensates for the viscous stresses, and the drop moves like a liquid drop. This critical radius was first introduced by Bond (see Section 71) on the basis of dimensional analysis and experimental data.

For $|\sigma_0 - \sigma| < \frac{1}{2}|\Delta\sigma_{\max}|$, deviations from the quantitative theory of retardation should begin at smaller values of a , determined by the inequality

$$a \ll \left[\frac{3(\sigma_0 - \sigma)}{(\rho' - \rho)g} \right]^{1/2}. \quad (78.5)$$

Thus, for example, if adsorption on the mercury-water interface leads to a one unit decrease in σ_0 , the retardation that it causes in the free fall of the mercury drop can become apparent only at $a_{cr} \approx 6 \cdot 10^{-2}$ cm.

In conclusion, it is interesting to draw attention to the following. For very large values of the retardation coefficient γ , while equation (74.11) is still strictly applicable, the quantity v_0 is very small. As a passes through a_{cr} , v_0 begins to rise sharply because retardation cannot arrest the surface motion. This conclusion is in agreement with the results of Bond's measurement of the velocity of the drop's fall. Thus, under these conditions, the surface behaves as though it possesses the property of non-Newtonian viscosity.

Let us now examine the limits of applicability of the theory in the case of retardation of surface motion by a layer of insoluble material. It follows from equation (75.15) that extremely small amounts of insoluble substances must have a strong retarding effect on the tangential motion of the surface. Indeed, noticeable retardation will start if

$$3\gamma_3 = \frac{2RT\Gamma_0 a}{D_s} > 2\mu + 3\mu', \quad (78.6)$$

i.e.,

$$\sigma_0 - \sigma \approx RT\Gamma_0 > \frac{D_s(2\mu + 3\mu')}{2a}.$$

Since, for a water-mercury interface, $2\mu + 3\mu' = 0.068$, assuming $D_s \approx 10^{-5}$ and $a = 5 \cdot 10^{-2}$, we have $\sigma_0 - \sigma > 10^{-5}$, where $\sigma_0 - \sigma$ characterizes the decrease in interfacial tension caused by the presence of an insoluble surface-active material. Since such a "cleansing" of a motionless surface to rid it of all insoluble impurities in fulfillment of the condition $\sigma_0 - \sigma < 10^{-5}$ is probably unattainable in practice, it appears that the conclusion to be drawn from equation (78.4) is that tangential motions on macroscopic surfaces can never in general be observed. At sufficiently small Γ_0 , however, the theory is found to be applicable only in cases of very low velocities of motion. At significant velocities, due to convective transfer, most of the surface is cleansed of the insoluble material, which accumulates in a small area. This fact is well known from the practice of cleaning water surfaces by means of an air jet.

Indeed, it follows from the condition $|\Gamma'| < \Gamma_0$ and equation (75.13) that:

$$v_0 < \frac{D_s}{2a},$$

whence, for the same values for the parameters a and D_s , we obtain

$$v_0 \ll 10^{-4} \text{ cm/sec.}$$

If, instead of surface velocity v_0 , the over-all velocity U is given, the limits of applicability of the theory are determined, as in the case of retardation by a soluble material, by the condition

$$\frac{\mu U}{2} \ll |\sigma_0 - \sigma|, \quad (78.7)$$

or, for a freely falling drop, by the equivalent condition

$$(\sigma_0 - \sigma) \gg \frac{(\rho' - \rho) a^2}{3}.$$

At the same time, the condition for strong retardation (78.6) must be fulfilled

$$(\sigma_0 - \sigma) > \frac{D_s (2\mu + 3\mu')}{2a},$$

which is possible only if

$$(\sigma_0 - \sigma) > \frac{D_s (2\mu + 3\mu')}{2a_0},$$

where a_0 is the value of the radius determined from the equation

$$\frac{(\rho' - \rho) a_0^2}{3} = \frac{D_s (2\mu + 3\mu')}{2a_0}. \quad (78.8)$$

For the case of a freely falling drop of mercury in water, on the basis of equation (78.8), we find that $a_0 \approx 4 \cdot 10^{-4}$ and, consequently,

$$\sigma_0 - \sigma > 10^{-8}.$$

This value for $\sigma_0 - \sigma$ is not as small as the value derived previously without taking into account the limits of the theory's applicability. Nevertheless, it is still very small. For $a > a_0$, the lower limit of $\sigma_0 - \sigma$, at which retardation is apparent, is defined by equation (78.5). For $a > a_0$, it is defined by equation (78.6). If the inevitable contamination of the surface of the drop is estimated as corresponding to $\sigma_0 - \sigma \approx 10^{-2}$ it follows from inequalities (78.5) and (78.6) that, in the range of values for a from $5 \cdot 10^{-5}$ to 10^{-3} , the drops must virtually behave as solid spheres.

79. MOTION OF LARGE DROPS

We have examined above the motion of drops of relatively small dimensions, where the regime of motion is viscous, i.e., when the Reynolds numbers are small. In actual practice, however, the motion of relatively large drops is often encountered, where the Reynolds numbers are considerably greater than unity.

Let us first examine drop motion in air. In this case, the density and viscosity of the medium are extremely low compared to those for the drop. Its motion, therefore, is no different from that of a solid body of the same shape and dimensions.

In the case of fall in a gravitational field, the drop's velocity can be derived from the following obvious relation

$$\rho' g V = K \rho \frac{U^2}{2} S$$

or

$$U = \left(\frac{2\rho' g V}{K_f \rho S} \right)^{1/2} = \sqrt{\frac{2}{3} \frac{\rho' g a}{K_f \rho}}. \quad (79.1)$$

Here, ρ' is the density of the liquid, ρ that of air, and S is the area of the midsection (the largest crosssection) of the drop. The drag coefficient K_f is of the order of 0.5 for a body of spherical shape.

The measured free fall velocities of individual drops in air, under normal conditions, agree well with equation (79.1) for drops ranging within the following size limits: $0.01 \leq a \leq 0.05$ cm.

Larger drops are deformed and their shape changes greatly from spherical. The drop flattens out during its fall and gradually acquires the shape of a convex bean with unequal sides. This deformation is accompanied by pulsations of relatively small amplitude. The velocity of fall ceases to follow (79.1) but increases with an increase in the radius more slowly than indicated by (79.1).

For drops 0.2 to 0.3 cm in radius, the velocity of fall is a weak function of the radius. Experimental data on this subject are not very accurate, but all authors have noted a limit on the velocity vs. dimension curve.

The limiting velocity, according to data of Khrgian [16], is 917 cm/sec. According to other authors it is somewhat smaller. Humphreys [17] sets the limiting velocity at 800 cm/sec.

Upon further increase in the radius of the falling drop, the large drop breaks up into smaller ones. This phenomenon of fragmentation will be examined in more detail later. A rigorous examination of the motion of a deformed and pulsating drop presents enormous difficulties. The velocity of fall of such drops, nevertheless, can be estimated.

In the air passing by the drop at the velocity U , a pressure difference appears between the fore and aft portions of the drop which, according to the Bernoulli law, is

$$\Delta p = \frac{\rho}{2} U^2.$$

The drop is deformed under the influence of this pressure difference. Capillary pressure prevents further deformation, and as a result of the competing effects of these forces, the drop acquires a certain steady shape related to the given velocity U .

The condition for the balance of the pressure and capillary forces can be written in the form

$$\Delta p S \delta h + \gamma \delta S = 0, \quad (79.2)$$

where S is the area of the deformed drop and h is the drop's dimension in the direction of the motion.

The first term of (79.2) represents the action of pressure forces expended in the deformation δh . The second term represents the effect of the forces of surface tension for this deformation.

it is obvious that, for a constant volume of drop, the following condition must be fulfilled

$$Sh = V = \frac{4\pi}{3} a^3 = \text{const.} \quad (79.3)$$

From (79.2) we obtain

$$\frac{\Delta p S}{\sigma} = - \frac{\partial S}{\partial h}, \quad (79.4)$$

and from (79.3), we have:

$$\frac{\partial S}{\partial h} = - \frac{V}{h^2} = - \frac{S}{h}. \quad (79.5)$$

Combining (79.4) and (79.5), we find, to an order of magnitude, that the thickness of the drop is

$$h = \frac{\sigma}{\Delta p} \sim \frac{2\sigma}{\rho U^2}. \quad (79.6)$$

Its surface, to an order of magnitude, is

$$S = \frac{V}{h} \approx \frac{\rho U^2 V}{2\sigma}. \quad (79.7)$$

Let us now write the equation of motion for a beanlike drop in a gravitational field.

We have, evidently,

$$K_f \frac{\rho U^2}{2} S = \rho' g V.$$

The drag coefficient K_f has its usual value, which is close to unity.

Substituting the value of the area of the midsection from (79.7) we obtain:

$$K_f \frac{V \rho^2 U^4}{4\sigma} \approx \rho' g V,$$

whence

$$U \approx \sqrt[4]{\frac{4\rho' g \sigma}{K_f \rho^2}}. \quad (79.8)$$

The velocity U is found to be independent of the dimensions of the drop and to be inversely proportional to the square root of the density of the medium and proportional to the $1/4$ power of the surface tension.

The meaning of this result is quite obvious: with an increase in velocity, the drop is flattened out, and its area consequently increases, which leads to a greater hydrodynamic resistance. The increased resistance compensates exactly for the increase in the driving force.

The greater the surface tension of the liquid, the less pronounced is the deformation of the drop. The velocity of fall, therefore, is higher for particles which have a greater surface tension and become less flattened.

Substituting the value of g and of the density of air under normal conditions, and assuming that $K_f = 1$, we find:

$$U \sim 740 \text{ cm/sec.}$$

For $K_f = 0.5$, we have $U \sim 860 \text{ cm/sec.}$

Considering the rough nature of the computations, it should be pointed out that the numerical value of U is unexpectedly close to experimental values. Unfortunately we do not have experimental material at our disposal that would allow the dependence of U on surface tension σ to be established. That alone would permit a test of equation (79.8).

In the case of a drop moving in a dense medium—for example, a liquid drop falling in another liquid—the picture becomes more complex. Apparently, here there is also a certain range of dimensions for which a formula of the type of (79.1) is applicable. Since the density of the medium, however, is usually comparable to that of the liquid in the drop, instead of (79.1) we must write

$$U = \sqrt{\frac{2}{3} \frac{(\rho' - \rho) g a}{K_f \rho}}. \quad (79.9)$$

The velocity of the fall, therefore, is much slower than in air.

Consequently, the dynamic force which deforms a drop falling in a liquid medium is smaller than in the case of fall in air, in the ratio $\frac{\rho' - \rho}{\rho}$. Deformation and transition to a constant fall velocity should take place for drops of larger dimensions.

It should be pointed out that what is frequently encountered in practice is not the motion of individual drops, but the motion of a whole system or column of drops, moving at small distances from each other. In this case, the conditions of the motion change and the preceding reasoning loses its validity. This interaction between drops plays an important role and, to a large extent, determines the nature of the motion of the system.

80. MOTION AND DISSOLUTION OF GAS BUBBLES IN LIQUIDS

The problem of the motion of gas bubbles in liquids has attracted the attention of numerous investigators, for a great variety of reasons. In the first place, the study of the motion of gas bubbles can furnish valuable information on the properties of the simplest phase interface, that of a liquid-gas interface. In the second place, the problem of the motion of gas bubbles is of considerable importance in engineering. It is sufficient to point out that, over such wide

industrial fields as basic chemicals, foods, and concentration of ores, there is widespread use of processes and equipment in which the operations are directly related to the laws governing the motion of gas or steam bubbles. We have in mind the bubbling of gases through liquids, a process used in many branches of the chemical and food industries and in the flotation process for the concentration of ores. Thus, for example, many chemical production processes involve the absorption of a great variety of gaseous substances by various liquid reagents in specially constructed absorbers. The gases are bubbled into the liquids. The bubbling of carbon dioxide in saturation boilers in the sugar beet industry is one of the basic processes for sugar production, etc. For these reasons bubble motion has been studied from every aspect in many theoretical and experimental investigations.

The regime of bubble motion varies considerably with the Reynolds number $Re = \frac{Ua}{\nu}$, where U is the velocity of bubble motion, a is the bubble radius, and ν is the kinematic viscosity of the liquid in which the bubble moves.

In the following, we shall treat systematically bubble motion in different regimes, i.e., at various values of the Reynolds number. Experimentally, bubble motion has been studied in various media and for different bubble diameters [18, 19, 34].

The results of all these studies can be summarized as follows. Bubbles with diameters less than 0.01 cm rise like solid spherical particles (in accordance with Stokes' law). For diameters in excess of 0.01 cm ($Re > 1$), the velocity of rise deviates from that indicated by Stokes' law. The resistance to the rising bubble is larger than in the viscous regime. In the region of Reynolds numbers from $Re \geq 1$ to $Re < 10,000$, the law of resistance has the same form as in the case of solid spheres (at the same Reynolds numbers).

For Reynolds numbers above 200 to 300, the law of resistance is usually expressed approximately by the formula

$$F = K_f \frac{\rho U^2 \pi a^2}{2},$$

where the drag coefficient K_f is equal to 0.6.* The shape of the bubble remains almost exactly spherical. On the basis of the resistance law stated above, the velocity of the bubble's rise can be determined from the relation

$$F_g V = W,$$

where F_g is the buoyancy force exerted per 1 cm³ of the bubble's volume and V is its volume. This gives

*Actually, in the range of Reynolds numbers from 200 to 1000, this coefficient varies from about 0.65 to about 0.55.

$$\rho g \cdot \frac{4}{3} \pi a^3 = 0.6 \rho \frac{U^2}{2} \pi a^2,$$

whence

$$U \approx 2 \sqrt{\frac{ga}{0.9}}.$$

At Reynolds numbers close to 700, which corresponds to bubble diameters of 0.2 to 0.3 cm, the nature of the motion of the bubbles changes sharply, and they start to be noticeably deformed, acquiring the shape of flattened ellipsoids whose minor axis is in the direction of bubble motion (Figure 70). At the same time, the bubbles begin to

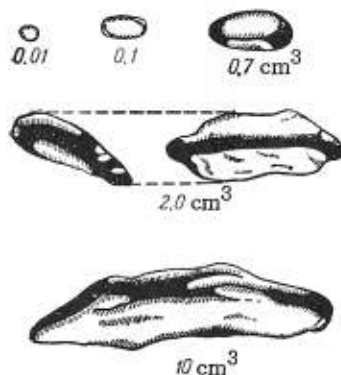


Figure 70. Shapes of air bubbles rising in water (approximately $\frac{1}{2}$ actual size).

vibrate, and they rise by a spiral motion instead of in a straight line. The velocity of motion of bubbles with diameters of 0.2 to 1.5 cm is almost independent of the bubble diameter and amounts to about 28 to 30 cm/sec (the corresponding Reynolds numbers lie within the range of 700 to 4500). Bubbles of larger diameters rise at somewhat greater velocities, namely at about 35 to 40 cm/sec, but are not very stable and tend to subdivide into smaller bubbles. This picture of bubble motion can be interpreted theoretically. Bowden termed the Reynolds number of a bubble moving within the range of $Re = 1$ to $Re = 700$ to 800 as moderate, and Reynolds numbers above 800 as large. It follows from what has been said that for motion at moderate Reynolds numbers, the shape of the bubble remains unchanged and can be considered spherical. At large Reynolds numbers, the bubble loses its spherical shape.

81. MOTION OF VERY SMALL BUBBLES

The motion of very small bubbles corresponds to Reynolds numbers that are small. This means that the regime of liquid motion near the surface of the bubble is viscous.

In the initial studies devoted to the investigation of the motion of small bubbles, resistance was computed by means of the usual Stokes formula. Rayleigh had already pointed out, however, that the existence of a tangential motion near the gas-liquid interface should change the velocity distribution in the liquid when a gas bubble moves in it, compared to the liquid movement (at the same velocity) for

the fall of a solid sphere. The problem of gas bubble motion is closely related to that of the motion of a liquid drop in a liquid medium, a problem which we examined in Section 70. The velocity of rise of a gas bubble in a liquid can be derived from formula (70.35), provided that μ' and ρ' are assumed to be negligible compared to the viscosity μ and the density ρ of the medium. This gives:

$$U = -\frac{1}{3} \frac{ga^2}{\nu}, \quad (81.1)$$

where g is the gravitational acceleration, ν is the kinematic viscosity of the liquid, and a is the radius of the bubble. The minus sign in expression (81.1) indicates that the bubbles rise in the gravitational field.

Formula (81.1) is applicable for small Reynolds numbers, $Re \ll 1$, i.e., when the following inequality holds

$$\frac{ga^3}{3\nu^2} \ll 1. \quad (81.2)$$

For a bubble moving through water, this yields:

$$a \ll 2 \cdot 10^{-2} \text{ cm.}$$

For motion in more viscous liquids, the Rybczynski-Hadamard formula is applicable to larger bubbles.

Comparing the velocity of rise of a bubble calculated from (81.1) with Stokes' law, we see that it is greater than the velocity of a solid sphere of the same density by the ratio $\frac{1}{3} : \frac{2}{9} = \frac{3}{2}$. This is due to the fact that the velocity of the liquid does not become zero at the gas-liquid interface, as it does at a solid surface, but is equal to

$$v_0 = \frac{U_0}{2}$$

according to expression (70.39). This is the reason why the velocity difference between the motionless liquid and the surface of a bubble is smaller than for a solid sphere. Thus, the corresponding energy dissipation is also smaller.

Many investigators have devoted effort to the study of the velocity of rise of small bubbles. Thus, Allen [20] measured the velocity of rising air bubbles in water and in aniline, presenting his data in graphic form showing the drag coefficient as a function of the Reynolds number.

The theoretical value of the drag coefficient for a gas bubble is

$$K_f = \frac{W}{\frac{\rho U^2}{2} \pi a^2} = \frac{8\nu}{Ua} = \frac{8}{Re},$$

where $Re = \frac{Ua}{\nu}$, i.e., one and one-half times smaller than for a solid sphere.

As noted from Figure 71 (see Section 83), Allen's experimental data completely disagree with the theory and lead to values for the drag coefficient which coincide exactly with the drag on a solid sphere.

The results of measurements made by other students are in good agreement with Allen's data and force us to the general conclusion that, at small Reynolds numbers, gas bubbles move like solid spheres. This fact has usually been interpreted as a confirmation of the Boussinesq theory presented previously (see Section 71).

Actually, the apparent "solidification" of moving bubbles is related to the effect of surface-active materials present in water, in aniline, and in other liquid media. None of the experimenters took any special measures to rid the liquids of surface-active substances when conducting their measurements. The rise velocity of a gas bubble in a liquid medium is expressed by (74.10), where the value of the retardation coefficient is governed by expression (74.8) or by (75.8). Since $\gamma \approx \frac{1}{a}$, an estimate of the values of γ for small bubble radii shows that, for $a < 10^{-2}$, the magnitude of γ substantially exceeds the viscosity μ , even in the presence of minute traces of surface-active substances. In this way, it is possible to anticipate that gas bubbles of very small dimensions should move in the same manner as solid spheres in all liquid media that have not been specially treated to rid them of surface-active materials. This conclusion has been fully confirmed in experiments conducted by A. V. Gorodetskaya. It will be shown later that all available experimental data on gas bubble motion become understandable if the presence of surface-active materials is taken into account, and that there is no need for such unfounded hypotheses as that of Boussinesq.

82. MOTION OF MEDIUM-SIZE BUBBLES

Let us examine bubble motion at moderate Reynolds numbers [21]. In the motion of a solid body at Reynolds numbers $Re \gg 1$, a hydrodynamic boundary layer exists near the surface of the solid body.

The reason for its appearance, as shown in Section 3, is that for $Re \gg 1$, the motion should be viewed as the flow of an ideal fluid, devoid of friction and capable of slipping along the solid surface. Such slippage is impossible in an actual fluid, and the velocity at the surface itself must be zero.

Let us pass to a system in which the bubble is at rest and the liquid moves at a velocity U . At large Reynolds numbers, the liquid can be considered ideal, and the energy dissipated due to viscous friction can be neglected,

Thus, the ratio of the irrotational portion of the motion to the rotational portion is characterized, as previously (cf. Section 118), by the ratio A/C . In the case of a pure liquid, this ratio, according to (118.1), is

$$\frac{A}{C} \approx \frac{\omega_0}{\nu k^2}. \quad (121.35)$$

In the case of a surface covered by an incompressible film, this ratio, according to (121.33), is given by

$$\frac{A}{C} \approx \frac{l}{k} \approx \sqrt{\frac{\omega_0}{\nu k^2}}. \quad (121.36)$$

Comparing (121.36) and (121.35), we see that the ratio A/C in the latter case is much smaller than in the first. This signifies that the rotational part of the motion is considerably increased by the presence of an incompressible film, because when the tangential velocity component becomes zero on the surface, the change in velocity across the surface layer is much sharper than in the case of a clean surface.

The increase in the rotational part of the motion, according to expression (1.15), leads to additional dissipation and damping of capillary waves.

The damping coefficient generally lies between β_0 and β_{lim} , and is strongly dependent on the properties of the film. Condensed films with densely packed molecular chains and with low compressibility exhibit the best damping properties. Such materials are fatty acids, triglycerides and other similar substances. Such insoluble surface-active agents as acetamides, phenols, nitriles and other materials with chains at angles to one another are materials with the least damping properties.

Let us turn to the analysis of damping of longer waves with a frequency

$$\omega_0 = \sqrt{gk}.$$

Substituting this value for ω_0 into boundary conditions (121.24) and (121.25), disregarding the quantities $\sqrt{\frac{\nu k^2}{\omega_0}}$ and $\frac{\nu k^2}{\omega_0}$ that are small compared to unity, and substituting the value of l/k from expression (117.17), we get the boundary conditions

$$\left(\frac{23}{\sqrt{gk}} + \frac{2\nu k^{3/2}}{\sqrt{g}} \right) A - C = 0, \quad (121.37)$$

$$\left(\frac{1k^2}{g} + \frac{2l\nu k^{3/2}}{\sqrt{g}} \right) A + l \left(1 - \frac{\sqrt{l\nu k^{5/4}}}{g^{3/4}\nu^{1/2}} \right) C = 0. \quad (121.38)$$

It is evident from (121.37) and (121.38) that two regions of gravity waves exist: a region where the wave vector $k \approx k_1$, where k_1 can be approximated by

$$\frac{\epsilon k_1^{5/4}}{g^{3/4} \nu^{1/2}} \approx 1$$

or by

$$k_1 \approx \frac{g^{3/2} \nu^{3/2}}{\epsilon^{3/2}}.$$

The other region is defined by the condition $k \approx k_2$, where k_2 is computed from the following:

$$\frac{\epsilon k_2}{g} \approx \frac{2\nu k_2^{3/2}}{Vg}.$$

The latter gives

$$k_2 \approx \frac{\nu^2 g}{\epsilon^2}.$$

A comparison of k_1 and k_2 shows that $k_1 > k_2$.

At representative values for ν and ϵ , $k_1 \approx \frac{1}{3} \text{ cm}^{-1}$, so that $\lambda_1 = \frac{2\pi}{k_1} \approx 15 \text{ cm}$, $k_2 \approx 10^{-3} \text{ cm}^{-1}$ and $\lambda = \frac{2\pi}{k_2} \approx 10^3 \text{ cm}$. In the region of $k \approx k_1$, i.e., in the region of centimeter wavelengths, $\frac{\epsilon k^2}{g} \approx \sqrt{\frac{2\nu k^{3/2}}{g}}$.

Thus, the second term $\frac{2\nu k^{3/2}}{\sqrt{g}}$ in boundary condition (121.38) may be disregarded compared to the first term $\frac{\epsilon k^2}{g}$.

From conditions (121.37) and (121.38), we then find the expression for the real part of the damping coefficient

$$\beta = \frac{1}{2\sqrt{2}} \cdot \frac{g^{1/4} \epsilon^{1/2} \nu^{1/2} k^{1/4}}{\epsilon^2 k^{3/2} + \nu g^{3/2} - \sqrt{2} \epsilon^{1/2} \nu^{1/2} g^{1/4} k^{1/4}}. \quad (121.39)$$

An approximation of the real part gives

$$\beta \approx \sqrt{\nu g^{1/2} k^{5/2}}. \quad (121.40)$$

The ratio of β to the damping coefficient β_0 in a pure liquid, therefore, has the form

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

i.e., the ratio is large compared to unity. Thus, the damping effect of the film remains fairly effective for waves of such lengths.

In the region $k \approx k_2$, i.e., in the region of very long waves, in condition (121.38)

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

and therefore this term can also be disregarded.

From conditions (121.37) and (121.38) we find

$$\beta = -2\nu k^2;$$

i.e., this region is characterized by natural damping. The effect of the film is merely a small change of frequency which is of no interest. For even longer waves the latter change disappears.

Thus, the damping action of surface-active agents according to the hydrodynamic theory of damping of capillary waves can be explained without resorting to any special hypotheses regarding special properties of these materials. It is found that the damping effect occurs throughout the wave spectrum, starting from the shortest capillary waves up to centimeter-long gravity waves.

In the limiting case the film behaves as a thin incompressible membrane that covers the surface of the liquid. This should not lead to the conclusion, however, that the damping properties of surface-active agents are independent of their nature. The damping coefficient, as seen from equations (121.30) and (121.39), is determined by the value of the coefficient of elasticity [see equation (121.17)]. The damping coefficient increases with increase in ϵ , and becomes independent of ϵ only in the limiting case. The damping effect of insoluble surface-active agents increases with the concentration Γ . That surface-active agent for which the value of $\partial\sigma/\partial\Gamma$ is the highest has the greatest damping effect. However, only in the limiting cases, involving very few of the surface-active agents, does the damping effect cease to be a function of the nature of the material.

The dependence of the damping effect on the nature of the surface-active agent is even more pronounced in the case of soluble materials — a case examined in the next section.

We now turn to the analysis of viscosity in surface-active agents. We showed in Section 77 that the effect of surface-active substances on the regime of liquid motion in steady-state is equivalent to the introduction of a certain new viscosity ϵ . This viscosity is not only a function of the properties, but also of the nature of the processes which control the rate at which equilibrium between surface and substrate is approached.

We introduce the surface viscosity coefficient for the case of a non-steady-state process. By definition (cf. Section 77), the surface viscosity coefficient is

$$\epsilon = \frac{\partial \Delta \sigma}{\partial \operatorname{div}_s \mathbf{v}} = \frac{\partial \sigma}{\partial \Gamma} \frac{\partial \Delta \Gamma}{\partial \operatorname{div}_s \mathbf{v}} = \frac{\partial \sigma}{\partial \Gamma} \frac{\partial \Delta \Gamma}{\partial \left(\frac{\partial v_x}{\partial x} \right)} = \frac{\partial \sigma}{\partial \Gamma} \cdot \frac{1}{ik} \frac{\partial \Gamma}{\partial v_x}.$$

But, according to equations (98.14) and (98.1),

$$\Delta\Gamma = -\frac{i k \Gamma_0}{\alpha} v_x;$$

therefore,

$$e = -\frac{\Gamma_0}{\alpha} \cdot \frac{\partial \sigma}{\partial \Gamma} = -\frac{\epsilon}{\alpha} \approx -\frac{\epsilon}{\omega_0}.$$

We see that surface viscosity cannot be viewed as a constant that characterizes the properties of the liquid, because it depends on the wave frequency ω_0 . Nevertheless, with this exception e may be regarded as a dynamic characteristic of the surface-active film and one which characterizes the relaxation processes in the material. The quantity ϵ , introduced by us, is the constant that characterizes the properties of the material. Thus, our previous examination, based on the introduction of the constant ϵ , adequately accounts for the surface viscosity. On the contrary, the introduction of surface viscosity as a constant to characterize the properties of the film is inadmissible.

In the light of the preceding discussion and bearing in mind the reasoning set forth in Section 77, it is clear that our analysis of the elastic properties of the film and our disregard of the viscous properties is purely a matter of terminology. We could have equally introduced the concept of surface viscosity and could have argued in terms of the viscosity of the film without mentioning its elastic properties.

The terminology adopted seems more appropriate to us because of the variable nature of the viscosity e , which cannot be a constant of the material. Non-steady-state processes involving surface-active agents, in this respect, are found to be similar to steady-state processes.

122. DAMPING OF WAVES BY SOLUBLE SURFACE-ACTIVE AGENTS

Surface-active agents, especially inorganic materials, are usually measurably soluble. This property affects their damping action. Let us consider the damping effect of soluble surfactants.

When a state of equilibrium exists between the surface and the bulk of the liquid, an equilibrium distribution of the surface-active agent is established. When the surface is deformed by waves of frequency ω_0 or of period $1/\omega_0$, two limiting cases are possible: 1) the relaxation time for equilibrium to become established between the surface and the body of the liquid (more exactly, the portion of the liquid body contiguous to the surface) is large compared to the wave period $1/\omega_0$, and 2) this time interval is small compared to $1/\omega_0$.

The deformation in the first instance occurs so rapidly that an equilibrium between the surface and the bulk of the liquid is not established, and the molecules do not have enough time to pass from the body of the solution to the surface and back again. Here, the presence of the bulk of the solution does not affect the process and all conclusions of the preceding section remain valid.

In the second case, we may assume that the surface and bulk of the solution are continually in a state of statistical equilibrium. This is the case of our further examination.

As before, let Γ_0 denote the surface concentration of an undeformed surface, and let Γ' denote the total change in concentration — resulting from surface deformation.

Similarly, let c and c' be the concentrations in the bulk of the solution and its change resulting from diffusion of the dissolved substance from the bulk of the solution to the surface when the latter is deformed.

Then, the equilibrium condition between the bulk and surface solutions is given by

$$\mu_n(\Gamma_0 + \Gamma') = \mu_p(c + c'), \quad (122.1)$$

where μ_n is the chemical potential of the solution on the surface and μ_p is the chemical potential in the bulk of the solution.

The value of the chemical potential in the bulk of the solution is taken near the surface, i.e., at $z = 0$.

Since the surface deformation and, therefore, the change in concentration are infinitely small, the chemical potentials may be expanded into a power series of which only the leading terms need be retained

$$\Gamma' = \frac{\left(\frac{\partial \mu_p}{\partial c}\right)}{\left(\frac{\partial \mu_n}{\partial \Gamma_0}\right)} c', \quad (122.2)$$

and, since the solution in the bulk can usually be considered weak, we have

$$\mu_p = RT \ln c_0 + \psi(p, T),$$

where T is the absolute temperature and p is pressure. Whence,

$$\Gamma' = \frac{RT}{c_0} \frac{1}{\left(\frac{\partial \mu_n}{\partial \Gamma_0}\right)} c'. \quad (122.3)$$

The value of c' is taken near the surface, i.e., at $z = 0$.

The change in surface concentration is related to two factors: surface deformation and diffusional flow from the body of the solution, which reduces this change. Therefore, considering the

equation of conservation of matter for Γ' , and without taking surface diffusion into consideration, we have with an accuracy to first order infinitesimals:

$$\frac{\partial \Gamma'}{\partial t} + \Gamma_0 \frac{\partial v_x}{\partial x} = D \left(\frac{\partial c'}{\partial z} \right)_{z=0}. \quad (122.4)$$

The right side of equation (122.4) is the diffusional flow from the bulk and D is the diffusion coefficient.

In the absence of diffusional flow, expression (122.4) is similar to (121.8).

To find the diffusional flow from the bulk of the solution, the diffusion equation for c' must be solved considering boundary conditions (122.2) and (122.4). However, since the boundary conditions include terms determined by the fluid flow equations, the diffusion equation with boundary conditions (122.2) and (122.4) must be solved simultaneously with the fluid flow equation and appropriate boundary conditions, which are

$$p_0 = \sigma \frac{\partial^2 \zeta}{\partial x^2}, \quad (122.5)$$

$$p_t = -\frac{\epsilon}{\Gamma} \frac{\partial \Gamma'}{\partial x}. \quad (122.6)$$

Condition (122.5) is equivalent to (121.6), and condition (122.6), although similar to (121.7), in this case has a different meaning for $\frac{\partial \Gamma'}{\partial x}$.

Substituting (122.3) into (122.4) we obtain, finally,

$$\frac{RT}{c_0} \frac{1}{\left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} \left(\frac{\partial c'}{\partial t} \right)_{t=0} = -\Gamma_0 \frac{\partial v_x}{\partial x} - D \left(\frac{\partial c'}{\partial z} \right)_{z=0}. \quad (122.7)$$

The concentration distribution in the bulk of the solution is given by the diffusion equation

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (122.8)$$

The solution of the hydrodynamic equations is

$$v_x = (ikAe^{kz} - iCe^{lz}) e^{ikx+at}, \quad (122.9)$$

$$v_z = (kAe^{kz} + ikCe^{lz}) e^{ikx+at}. \quad (122.10)$$

Therefore, a solution of (122.8) that satisfies boundary condition (122.7) must be sought in the following form:

$$c' = Bf(z) e^{ikx+at}.$$

Substituting this expression for c' into (122.8), we get

$$c' = Be^{\sqrt{\frac{a+Dk^2}{D}}z} e^{ikx+at}, \quad (122.11)$$

The amplitude of diffusion waves in equation (122.11) may be found from (122.7) by substituting the values of c' and v_x from equations (122.11) and (122.9), respectively. Then

$$B = \frac{\Gamma_0 l k (ikA - lC)}{\frac{RT\alpha}{c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} + \sqrt{D} \sqrt{\alpha + Dk^2}},$$

whence

$$\begin{aligned} c' &= \frac{\Gamma_0 l k (ikA - lC)}{\frac{RT\alpha}{c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} + \sqrt{D} \sqrt{\alpha + Dk^2}} e^{\sqrt{\frac{\alpha + Dk^2}{D}}} e^{ikx + \alpha t}, \\ \Gamma' &= \frac{RT}{c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} c' = \frac{\Gamma_0 l k (ikA - lC)}{\alpha + \frac{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}{RT} \sqrt{\alpha + Dk^2}} e^{ikx + \alpha t} = \\ &= \frac{\Gamma_0 \frac{\partial v_x}{\partial x}}{\alpha + \frac{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}{RT} \sqrt{\alpha + Dk^2}}. \end{aligned} \quad (122.12)$$

Boundary condition (69.5), therefore, may be written as

$$p_t = \frac{\frac{\varepsilon}{\alpha}}{1 + \frac{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}{\alpha RT} \sqrt{\alpha + Dk^2}} \frac{\partial^2 v_x}{\partial x^2}. \quad (122.13)$$

Condition (122.13) shows that, in the case of a soluble substance, the following parameter plays the role of the elastic constant (elasticity coefficient)

$$\varepsilon' = \frac{\varepsilon}{1 + \frac{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}{\alpha RT} \sqrt{\alpha + Dk^2}}.$$

Since the diffusion coefficient in the bulk of the solution is of the same order of magnitude on the surface, we may again assume [see (121.12)] that $\alpha \gg Dk^2$, and as

$$\varepsilon' = \frac{\varepsilon}{1 + \frac{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}{RT \sqrt{\alpha}}}. \quad (122.14)$$

This parameter is found to be a function not only of the elastic properties of the film, but also of the diffusion coefficient, of the bulk concentration and of the frequency.

It is not difficult to see that, as the bulk concentration decreases, i.e., as $c_0 \rightarrow 0$, this effective elastic constant (coefficient of elasticity) becomes equal to ϵ . On the contrary, when c_0 increases, the effective elastic constant decreases. In the limit as $c_0 \rightarrow \infty$ it becomes zero. Although this expression of course falls far short of high concentrations, because it depends on dilute solution approximations for chemical potentials, it nevertheless indicates the general trend of the elasticity coefficient.

By setting $\alpha = i\omega_0 + \beta$ and substituting the values (122.9) and (122.10) into boundary conditions (121.4) and (122.13), we obtain the equations for determining β . In this case we will limit our discussion to the most interesting case of capillary waves and, as previously, assume that $\frac{\nu k^2}{\omega_0} \ll 1$ and $\frac{\epsilon}{\sigma} \approx 1$. We now discuss the case when

$$\frac{\sqrt{D}c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right)}{RT \sqrt{\omega_0}} \gg 1.$$

Indeed, it is easily observed that if

$$\frac{\sqrt{D}c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right)}{RT \sqrt{\omega_0}} \ll 1,$$

then the above term may be omitted, and we revert to the case of an insoluble material. If, however,

$$\frac{\sqrt{D}c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right)}{RT \sqrt{\omega_0}} \approx 1,$$

then simple computations show that we obtain the damping coefficient given by (121.32). If

$$\frac{\sqrt{D}c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right)}{RT \sqrt{\omega_0}} \gg 1,$$

then, disregarding the small terms, we get

$$\left[i \frac{2\nu k^2}{\omega_0} + \frac{\epsilon k^2}{\omega_0^2} \frac{RT \sqrt{I_0}}{c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right) \sqrt{D}} \right] A - \\ - i \left[-1 + \frac{\epsilon k^2}{\omega_0^2} \sqrt{\frac{i\omega_0}{\nu k^2}} \frac{RT}{c_0 \left(\frac{\partial \mu_n}{\partial I_0} \right) \sqrt{D}} - \frac{2\beta}{\omega_0} \right] C = 0, \quad (122.15)$$

$$\left(2 \frac{\beta}{\omega_0} + \frac{2\nu k^2}{\omega_0} \right) A - C = 0. \quad (122.16)$$

Equation (122.15) shows that there are two regions:

$$\frac{RT \sqrt{\omega_0}}{c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right) \sqrt{D}} \approx \sqrt{\frac{\nu k^2}{\omega_0}}$$

or

$$\left. \begin{aligned} k^{1/2} &\approx \frac{\nu^{1/2} \sqrt{D} c_0}{\sigma^{1/4} RT} \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right) \\ \text{and} \quad \frac{RT \sqrt{\omega_0}}{c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right) \sqrt{D}} &\approx \frac{\nu k^2}{\omega_0} \end{aligned} \right\} \quad (122.17)$$

or

$$k^{1/2} \approx \frac{\nu \sqrt{D} c_0}{\sigma^{3/4} RT} \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right) \quad (122.18)$$

Omitting the small terms from equation (122.15), we obtain the following damping coefficients.

In the first region

$$\beta_1 = -\frac{1}{2\sqrt{2}} - \frac{\varepsilon RT k^{3/4}}{\sqrt{D} \sigma^{1/4} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} \frac{1 + \frac{\varepsilon RT k^{1/2}}{\sqrt{D} \sigma^{1/2} \nu^{1/2}}}{1 + \frac{\varepsilon^2 (RT)^2 k}{D \sigma \nu}}. \quad (122.19)$$

The damping coefficient in the first region is approximately equal to $\beta_1 \approx \nu^{1/2} \sigma^{1/4} k^{7/4}$. Although the damping coefficient in this region is somewhat lowered, owing to influx of molecules from the bulk of the solution, it nevertheless in order of magnitude agrees with the damping coefficient of an insoluble film.

In the region that is intermediate between the first and the second, i.e., at

$$\sqrt{\frac{\nu k^2}{\omega_0}} \gg \frac{RT \sqrt{\omega}}{\sqrt{D} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)} \gg \frac{\nu k^2}{\omega_0},$$

the damping coefficient is

$$\beta_{1,2} = -\frac{1}{2\sqrt{2}} - \frac{\varepsilon RT k^{3/4}}{2\sqrt{2} \sqrt{D} \sigma^{1/4} c_0 \left(\frac{\partial \mu_n}{\partial \Gamma_0} \right)}. \quad (122.20)$$

Finally, in the second region

$$\beta_2 = -2\nu k_2.$$

Thus, in the second region, where the wavelengths are long or the concentration in the bulk of the solution is very high, the damping coefficient is equal to that in a pure liquid. This result could have

been predicted, because, at a sufficiently high bulk concentration, the solution becomes homogeneous and only its surface tension differs from that in a pure liquid.

We see, therefore, that the solubility of a surface-active agent lessens its damping effect by reducing the constant ϵ . The decrease is the greater the smaller the frequency of the waves and the higher the equilibrium concentration (solubility) of the agent in the bulk of the solution.

Thus, a reduction in the damping effect primarily affects the long waves. This is in accordance with available experimental data on the damping effect of surfactants. The use of organic oils as wave-damping agents was recommended in early maritime handbooks. Substances with the best damping effects are seal oil and fish oils which are rich in fatty acids. The least effective are petroleum and kerosene.

These properties of surfactants are related to their solubility and to the value of the elastic constant. The fatty acids are least soluble and the mineral oils are most soluble. Unfortunately all available data on the damping of waves, including the data of R. N. Ivanov (although his experiments were conducted after the publication of the hydrodynamic theory, Ivanov did not refer to it — see [15]), are only qualitative and cannot be used for definitive verification of the theory.

Let us now consider application of the results presented here to the purely practical problem of damping of waves under actual conditions at sea.

The damping effect, as we have seen, influences short waves only. Long gravity waves are not damped by surface-active agents. Surfactants can generally affect only that liquid motion in which viscosity effects are present. In other words, the effect of surface-active agents can be manifested only at small Reynolds numbers or in the boundary layer.

In sea waves with high amplitudes, the motion is turbulent, rather than viscous. Therefore, surface-active agents exert no direct effect on such wave motion. They damp the ripples and small waves that cover the surface of the large ones. This influences the nature of the wave motion in the sense that it reduces the interaction between the wind and the waves. A smooth wave surface devoid of ripples, etc., reduces the transfer of energy from the wind to the wave. This results in reduced asymmetry of the wave and eliminates the deformation of waves which presents a dangerous condition for ships. In other words, the usual wave action is replaced by so-called swells.

123. BREAK-UP OF A LIQUID JET AT LOW FLOW VELOCITIES. THE CASE OF SYMMETRICAL DEFORMATIONS

One of the most important problems in capillary hydrodynamics, which has attracted the attention of such outstanding scientists as

Rayleigh [10] and Bohr [11], is the break-up of a liquid jet emanating from a nozzle or a spout into droplets. Interest in this problem has not diminished because of fuel injection systems in internal combustion engines, of emulsification and of many other problems. To the contrary, the problem of break-up of jets under the influence of dynamic air action — air in which the jet motion occurs — has become important along with the study of break-up of a jet caused by capillary forces, the problem that occupied Rayleigh and Bohr. We begin our analysis of the process of jet break-up with the case of a jet at low flow velocities.

At low jet velocities with reference to gas velocities, break-up occurs owing to the action of capillary forces. The surface energy of a cylindrical liquid jet is not a minimum.

As the jet breaks up into droplets, the surface energy decreases, since the liquid approaches its optimum, spherical shape.

Let us consider a cylindrical jet of radius a , issuing from a nozzle at a velocity u_0 . As it issues from the nozzle, the jet surface is always subjected to disturbances. No matter how well the surface of the nozzle may be polished, a certain roughness of the surface is inevitable. Vibrations of the nozzle, motion of the air surrounding the jet, presence of turbulence in the liquid moving within the nozzle — all may serve as the source of initial disturbances. Later we examine the motion of a liquid surface that has been subjected to an arbitrarily small disturbance.

The basic characteristics of jet break-up are the duration of the interval it remains unbroken and the size of the drops that are formed. The time interval prior to break-up determines the distance of propagation of the jet and the nature of its break-up.

Owing to the symmetry of the problem, the hydrodynamic equations must be written in a cylindrical coordinate system. For the time being, we examine only those disturbances in which there is no motion of the liquid around its axis of symmetry, i.e., disturbances for which we may assume the velocity components $v_\theta = 0$. We term such waves "symmetrical." The jet cross section, in the case of symmetrical waves, remains circular and either contracts or expands.

Equations of liquid motion in a jet with symmetrical waves are conveniently given in cylindrical coordinates

$$\frac{\partial v_r}{\partial t} = -\frac{1}{\rho} \frac{\partial p}{\partial r} + \nu \left[\frac{\partial^2 v_r}{\partial z^2} + \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} (r \cdot v_r) \right) \right], \quad (123.1)$$

$$\frac{\partial v_z}{\partial t} = -\frac{1}{\rho} \frac{\partial p}{\partial z} + \nu \left[\frac{\partial^2 v_z}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left(r \cdot \frac{\partial v_z}{\partial r} \right) \right], \quad (123.2)$$

where v_r is the radial velocity component, and v_z is the velocity component along the jet axis. Since the deformations are small, the second-order terms have been omitted.

The continuity equation is given as

$$\frac{\partial v_z}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \cdot v_r) = 0. \quad (123.3)$$

Boundary conditions for the jet surface must be known. The equation for a jet surface disturbed by some wave $\zeta(r, z, t)$, where ζ is the displacement of a point on the surface, is

$$r = a + \zeta(z, t).$$

Assuming that ζ is very small compared to a , we may write the boundary conditions in the form (117.5) as

$$\left. \begin{aligned} p_{rr} &= p_r, \\ p_{rz} &= 0 \end{aligned} \right\} \text{ at } r \approx a. \quad (123.4)$$

Moreover, the velocity components along the jet axis, i.e., at $r = 0$, must be finite.

The solution of the problem is approached similarly as in the case of wave motion on a plane surface of a viscous liquid. We denote the velocity in a viscous liquid by [12]

$$v_r = v_r^{(0)} + u_1, \quad (123.5)$$

$$v_z = v_z^{(0)} + u_2, \quad (123.6)$$

where quantities with the superscript zero are identical with the corresponding quantities in an ideal liquid.

The pressure should be the same as in an ideal liquid, because it is evident that the presence of viscosity affects the wave frequency but not the pressure within the liquid.

In an ideal liquid, and using cylindrical coordinates, the velocity is related to the velocity potential φ by

$$v_r^{(0)} = \frac{\partial \varphi}{\partial r}, \quad v_z^{(0)} = \frac{\partial \varphi}{\partial z} \quad (123.7)$$

and

$$\Delta \varphi = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \varphi}{\partial r} \right) + \frac{\partial^2 \varphi}{\partial z^2} = 0. \quad (123.8)$$

The pressure is given by

$$p = -\rho \frac{\partial \varphi}{\partial t}. \quad (123.9)$$

The continuity equation shows that u_1 and u_2 are related by

$$\frac{\partial u_2}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r u_1) = 0.$$

Thus, u_1 and u_2 may be given by

$$\left. \begin{aligned} u_1 &= -\frac{1}{r} \frac{\partial \psi}{\partial z}, \\ u_2 &= \frac{1}{r} \frac{\partial \psi}{\partial r}. \end{aligned} \right\} \quad (123.10)$$

where ψ is as yet an unspecified function of the coordinates and of time.

Substituting the expressions for velocity components into (123.1) and (123.2), and considering the equations for u_1 and u_2 , we obtain

$$\begin{aligned} \frac{\partial v_r^{(0)}}{\partial t} - \frac{1}{r} \frac{\partial}{\partial z} \frac{\partial \psi}{\partial t} &= \\ &= -\frac{1}{\rho} \frac{\partial p^{(0)}}{\partial r} + \nu \Delta v_r^{(0)} - \nu \frac{1}{r} \frac{\partial}{\partial z} \left[\frac{\partial^2 \psi}{\partial z^2} + r \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial}{\partial r} \psi \right) \right], \\ \frac{\partial v_z^{(0)}}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} \frac{\partial \psi}{\partial t} &= \\ &= -\frac{1}{\rho} \frac{\partial p^{(0)}}{\partial z} + \nu \Delta v_z^{(0)} + \nu \frac{1}{r} \frac{\partial}{\partial r} \left[\frac{\partial^2 \psi}{\partial z^2} + r \frac{\partial}{\partial r} \left(\frac{1}{r} \frac{\partial \psi}{\partial r} \right) \right]. \end{aligned}$$

Since

$$\begin{aligned} \Delta v_r^{(0)} &= \frac{\partial}{\partial r} \Delta \varphi = 0, \\ \Delta v_z^{(0)} &= \frac{\partial}{\partial z} \Delta \varphi = 0, \\ \frac{\partial v_z^{(0)}}{\partial t} &= \frac{\partial^2 \varphi}{\partial z \partial t} = -\frac{1}{\rho} \frac{\partial p^{(0)}}{\partial z}. \end{aligned}$$

we find that function ψ must satisfy the following equation:

$$\frac{\partial^2 \psi}{\partial r^2} - \frac{1}{r} \frac{\partial \psi}{\partial r} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{\nu} \frac{\partial \psi}{\partial t}. \quad (123.11)$$

We are interested in wave motion in the liquid. We therefore seek a solution for φ and ψ as periodic functions in z and exponential functions in t :

$$\varphi = \Phi(r) e^{ikz + \alpha t}, \quad (123.12)$$

$$\psi = \Psi(r) e^{ikz + \alpha t}. \quad (123.13)$$

Substituting (123.12) and (123.13) into (123.8) and (123.11), we get

$$\frac{d^2 \Phi}{dr^2} + \frac{1}{r} \frac{d\Phi}{dr} - k^2 \Phi(r) = 0, \quad (123.14)$$

$$\frac{d^2 \Psi}{dr^2} - \frac{1}{r} \frac{d\Psi}{dr} - \left(k^2 + \frac{\alpha}{\nu} \right) \Psi = 0. \quad (123.15)$$

The solution of equation (123.14) that retains a finite value along the axis of the jet [13] is

$$\Phi = C_1 I_0(kr), \quad (123.16)$$

where $I_0(kr)$ is the Bessel function of zero order with imaginary argument

$$I_0(kr) = J_0(ikr).$$

We seek a solution of equation (123.15) in the form

$$\Psi(r) = ry(r).$$

Then, for $y(r)$, we have

$$y'' + \frac{y'}{r} - \left(l^2 + \frac{1}{r^2}\right)y = 0, \quad (123.17)$$

where l , as in Section 117, is defined by

$$l^2 = k^2 + \frac{\alpha}{\nu}. \quad (123.18)$$

The solution of equation (123.17) that remains finite along the jet axis is

$$y = C_2 I_1(lr),$$

where $I_1(lr)$ is the Bessel function of first order with imaginary argument

$$I_1(lr) = \frac{1}{l} J_1(illr).$$

Finally, we obtain

$$\varphi = C_1 I_0(kr) e^{ikz + \alpha t}, \quad (123.19)$$

$$\psi = C_2 r I_1(lr) e^{ikz + \alpha t}. \quad (123.20)$$

The velocity and pressure profiles are found from φ and ψ using equations (123.7) and (123.10)

$$v_r = -ik \{iC_1 I_0'(kr) + C_2 I_1(lr)\} e^{ikz + \alpha t}, \quad (123.21)$$

$$v_z = k \left\{ iC_1 I_0(kr) + C_2 \left[\frac{I_1(lr)}{kr} + \frac{l}{k} I_1'(lr) \right] \right\} e^{ikz + \alpha t}, \quad (123.22)$$

$$p = -\rho \alpha C_1 \cdot I_0(kr) e^{ikz + \alpha t}. \quad (123.23)$$

Equations (123.21) to (123.23) contain three unknown quantities: the amplitudes C_1 and C_2 and the complex frequency α . The second boundary condition (123.4) allows one of the amplitudes to be expressed in terms of the other. The other boundary condition can

then be used to derive the equation for α . We first compute the tangential component of the stress tensor at the liquid surface. Obviously, we have

$$p_{rz} = \mu \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z} \right)_{r=a}. \quad (123.24)$$

Setting this equation equal to 0, we find the relation between C_1 and C_2 :

$$C_1 = C_2 \frac{I_1(la) \left[\frac{a}{v} + 2k^2 \right]}{2ik^2 I_1(ka)} = C_2 \frac{I_1(la) (l^2 + k^2)}{2ik^2 I_1(ka)}. \quad (123.25)$$

The first boundary condition (123.4) contains p_{rr} and p_σ . The former can be computed directly

$$p_{rr} = 2\rho\nu k e^{ikz+at} \left\{ -kC_1 I_1'(kr) - lC_2 I_1'(lr) + \frac{aC_1}{2\nu k} I_0(kr) \right\}. \quad (123.26)$$

Capillary pressure, in cylindrical coordinates, is obtained from equation (65.17)

$$p_s = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{\sigma}{a} - \frac{\sigma}{a^2} \left(\zeta + a^2 \frac{\partial^2 \zeta}{\partial z^2} \right), \quad (123.27)$$

where ζ is the displacement of the jet surface. It is obviously not a function of the azimuthal angle θ and, therefore, the term involving the derivative $\frac{\partial^2 \zeta}{\partial \theta^2}$ was omitted in (123.27). The value of the displacement of the surface for small displacements is related to the radial velocity component on the surface by

$$\zeta = \int (v_r)_{r=a} dt = \frac{ik}{a} [lC_1 I_1(ka) - C_2 I_1(la)] e^{ikz+at}.$$

Substituting this value for ζ into (123.27), we get

$$p_s = -\frac{\sigma}{a^2} (1 - k^2 a^2) \zeta.$$

(The reference pressure is $p = \frac{\sigma}{a}$.) Substituting the values found for p_{rr} and p_σ into boundary condition (123.4) and, eliminating the constants C_1 and C_2 by using equation (123.25), we get the equation for α ,

$$\begin{aligned} a^2 + \frac{2\nu k^2}{I_0(ka)} \left[I_1'(ka) - \frac{2kl}{k^2 + l^2} \cdot \frac{I_1(ka)}{I_1(la)} I_1'(la) \right] a = \\ = \frac{ak}{\rho a^2} (1 - k^2 a^2) \frac{I_1(ka)}{I_0(ka)} \cdot \frac{l^2 - k^2}{l^2 + k^2}. \end{aligned} \quad (123.28)$$

In the general case this equation is highly complex [since, according to (123.18), l is a function of α] and cannot be solved

analytically. We confine our analysis here to the two limiting cases: liquids with very low viscosity and liquids with very high viscosity. If the viscosity is low, and the following inequality holds in the wavelength region of interest*:

$$\frac{\alpha}{\nu} \gg k^2, \quad (123.29)$$

then we may write that

$$l \gg k.$$

It is easy to demonstrate (see below) that for $l \gg k$ the linear term in equation (123.28) is small and can be omitted.

Equation (123.28) then acquires a simple form

$$a^2 = \frac{\sigma k}{\rho a^2} (1 - k^2 a^2) \frac{I_1(ka)}{I_0(ka)}. \quad (123.30)$$

In the region where the wavelengths are small compared to the jet radius a the value of α is imaginary and

$$ka > 1.$$

For $ka \gg 1$, we have, in accordance with the well-known formula of the theory of Bessel functions [13],

$$I_n(x) \sim \frac{e^x}{\sqrt{2\pi x}}, \quad (123.31)$$

$$I_1(ka) \approx I_0(ka) \approx \frac{e^{ka}}{\sqrt{2\pi ka}}.$$

Setting the frequency $\omega = -i\alpha$, we get

$$\omega = \sqrt{\frac{\sigma k^3}{\rho}};$$

which corresponds to the frequency of capillary waves on the surface of a low-viscosity liquid.

Of greater interest is the case of long waves, for which the following inequality is satisfied

$$ka = \frac{2\pi a}{\lambda} < 1. \quad (123.32)$$

The quantity α for such waves has a positive real value. Positive values of α correspond to an unlimited rate of growth of wave

*It will be shown below that in this region the wavelength is considerably larger than the jet radius a .

amplitude. It is shown in the theory of turbulence that an exponential growth of wave amplitude signifies the appearance of continuous turbulence eddies in the liquid. The scale of these eddies is of the order of one wavelength. The presence of turbulence eddies in a liquid with a free surface leads to disruption of the surface and ejection of liquid. In the case of a cylindrical liquid jet, the exponential growth of wave amplitude with time leads to instability of its surface and break-up of the jet into drops. The jet surface is unstable for all wavelengths that satisfy the inequality (123.32). Equation (123.30), however, exhibits a maximum at $ka < 1$ for a given wavelength. The position of this maximum is determined by

$$\frac{\partial \alpha^2}{\partial k} = 0 = \frac{I_1'(ka) I_0(ka) - I_0'(ka) I_1(ka)}{I_0^2(ka)} (1 - k^2 a^2) - \frac{I_1(ka)}{I_0(ka)} 2ak.$$

A numerical solution of this equation shows that the maximum corresponds to a value of the wave number k equal to

$$k_{\max} = \frac{2\pi}{9.02a} = 0.70 \cdot \frac{1}{a}, \quad (123.33)$$

or to a wavelength

$$\lambda_{\max} = 9.02a. \quad (123.34)$$

This equation was first derived by Rayleigh. The value of α for this maximum can be easily found by substituting the numerical values of the Bessel functions:

$$\alpha_{\max} = 0.12 \sqrt{\frac{\sigma}{\rho a^3}}. \quad (123.35)$$

The wave number $k = k_{\max}$ corresponds to the greatest instability in waves. With $k = k_{\max}$ the instability is much greater than in waves with wave numbers satisfying the inequality (123.32). The maximum of the function $\alpha^2(k)$ is sharply defined. Since the amplitude grows exponentially in time, any increase in wave amplitude with a length λ that corresponds to the maximum α is decisive in the break-up of the jet.

During the time interval

$$\tau = \frac{1}{\alpha_{\max}} = 8.46 \sqrt{\frac{\rho a^3}{\sigma}} \quad (123.36)$$

the amplitude increases e times. Break-up of the jet produces drops whose size is of the order of λ_{\max} , i.e., about nine times greater than the radius a of the jet. The length of the jet prior to break-up is of basic interest. If this distance is small and the change in the jet velocity can be neglected, then the length is given by

$$L \approx u_0 \tau = 8.46 u_0 \sqrt{\frac{\rho a^3}{\sigma}}. \quad (123.37)$$

This formula shows that the intact length of the jet is proportional to the $3/2$ power of its radius and inversely proportional to the square root of the dynamic surface tension σ/ρ . Curiously enough, the intact length of the jet is very small, or at least much smaller than is usually assumed on the basis of visual observations. Thus, for example, for $u_0 \approx 100$ cm/sec, $\sigma/\rho \approx 80$ and $a \approx 1$ cm, we obtain $L \approx 10$ cm.

Visual observations fail to give correct values for the length of the unbroken jet due to an optical illusion — the apparent merging of the moving drops into a solid stream. Figure 102 shows the break-up of a jet recorded by flash photography [14].



Figure 102. Break-up of horizontal water jet into drops.

We will now define the limits of applicability of equation (123.27). Substituting equations (123.35) and (123.33) into (123.29), we get

$$\sqrt{\frac{a\sigma}{\rho\nu^2}} \gg 1. \quad (123.38)$$

It is evident that inequality (123.38) is also a condition determining the smallness of the linear term in (123.28) compared to the constant.

For water, condition (123.38) is satisfied in almost every case. In the case of a liquid like glycerine ($\nu \sim 10$, $\sigma/\rho \sim 30$), condition (123.38) holds for a jet radius $a > 3$ cm. At even higher viscosities equation (123.37) holds for even larger radii. It is simple to analyze another limiting case, where an inequality opposite to (123.29) is satisfied for a highly viscous liquid. For this case equation (123.28) can be again greatly simplified. It is more meaningful, however, to analyze a more generalized case. This is presented in the next section.

124. BREAK-UP OF A LIQUID JET AT LOW FLOW VELOCITIES. THE CASE OF ARBITRARY DEFORMATIONS

In the preceding section we examined the break-up of a jet resulting from the appearance of symmetrical waves on its surface. It was found that break-up of the jet is caused by waves with a length approximately 10 times the radius of the jet. Accounting for