CHAPTER VII

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

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

where S^{Σ} is the surface entropy.

The quantity*

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

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

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

the two phases, resting on a surface element $d\Sigma$, and let us relate all quantities to this element. The free energy of the system consists of the free energies of the bulk phase in each of the cylinders F_1 and F_2 of the surface free energy. Therefore,

$$\delta F = \delta F_1 + \delta F_2 + \delta F^{\Sigma} = 0. \tag{65.1}$$

The change in the free energy of the system at constant temperature can occur only as a result of changes in volume of the two phases and a change in area of the interface. The change in the free energy within the bulk phases at constant temperature is given by

$$\delta F_1 = -p_1 \delta V_1, \tag{65.2}$$

$$\delta F_2 = -p_2 \delta V_2, \tag{65.3}$$

where p_1 and p_2 are the absolute pressures and δV_1 and δV_2 are changes in the volumes of the two cylinders. The change in surface free energy at constant temperature equals

$$\delta F^{\Sigma} = \sigma\, d\Sigma. \tag{65.4}$$

Since the total volume of the system remains constant, an increase in the volume of one phase causes a corresponding decrease in the volume of the other; i.e.,

$$\delta V_1 = -\delta V_2. \tag{65.5}$$

Therefore, the total change in the free energy of system is

$$\delta F = -(p_1 - p_2)\,\delta V_1 + \sigma\,\delta\Sigma. \tag{65.6}$$

The relation between the two quantities δV and $\delta\Sigma$ should now be established. Let us first examine the case in which the curvature of the interface is very small. Here, in computing the change in free energy the interface may be considered a plane surface.

First, let us determine the variation in the surface area $\delta\Sigma$, if all of its elements are subjected to some arbitrary and infinitesimal displacement along the normal to an undeformed surface, i.e., the plane $z = 0$.

We consider a surface element $d\Sigma$ on the interface. The sides of the element are dx and dy and therefore $d\Sigma_0 = dxdy$. The deformation of the surface element occurs through extention or contraction, which transform the element of area to

$$d\Sigma = \sqrt{1 + \left(\frac{\partial\zeta}{\partial x}\right)^2}\, d\Sigma_0, \tag{65.7}$$

where ζ is the vertical displacement over the plane $z = 0$.

The formula takes into account only such deformations of linear elements on the surface (x, y) as result in a change of the surface area of the element $d\Sigma$.

For the sake of simplicity, we have also assumed that the displacements ζ occur in the plane y = const, producing a surface that is curved in only one direction.

At small displacements ζ, equation (65.7) may be approximated by

$$d\Sigma \approx \left(1+\frac{1}{2}\left(\frac{\partial\zeta}{\partial x}\right)^2\right) dx\,dy. \tag{65.8}$$

The surface area after deformation is

$$\Sigma = \int\int\left(1+\frac{1}{2}\left(\frac{\partial\zeta}{\partial x}\right)^2\right) dx\,dy.$$

The variation in the surface area is

$$\begin{aligned}\delta\Sigma &= \int\int \frac{\partial\zeta}{\partial x}\,\frac{\partial\,\delta\zeta}{\partial x}\,dx\,dy = \\ &= \int\left(\frac{\partial\zeta}{\partial x}\,\delta\zeta\Big|_1^2\right) dy - \int\int \frac{\partial^2\zeta}{\partial x^2}\,\delta\zeta\,dx\,dy = -\int\int \frac{\partial^2\zeta}{\partial x^2}\,\delta\zeta\,dx\,dy,\end{aligned} \tag{65.9}$$

since two surface points may be considered fixed, and $\delta\zeta_1 = \delta\zeta_2 = 0$.

The change in the volume δV_1 of the first phase produced by an infinitesimal displacement of points on the surface is

$$\delta V_1 = \int \delta\zeta\,dx\,dy. \tag{65.10}$$

Substituting expressions (65.9) and (65.10) into the equation of total change in the free energy of the system (65.6), we get

$$\delta F = \int\int\left[-(p_1-p_2)+\sigma\frac{\partial^2\zeta}{\partial x^2}\right]\delta\zeta\,dx\,dy. \tag{65.11}$$

In an equilibrium state the free energy is a minimum and $\delta F = 0$. Since $\delta\zeta$ is an arbitrary and an infinitesimal quantity, it follows from equation (65.11) that

$$p_1 - p_2 = -\sigma\frac{\partial^2\zeta}{\partial x^2}. \tag{65.12}$$

The difference in pressures in the two contiguous phases, in the presence of surface tension, is known as capillary pressure p_σ. It follows from (65.12) that, with small deformations of a surface curved only in one direction, we have

$$p_\sigma = p_1 - p_2 = -\sigma \frac{\partial^2 \zeta}{\partial x^2}. \tag{65.13}$$

The expression $p_\sigma = p_1 - p_2$ gives the change in mechanical equilibrium of two contiguous phases when the interface is not a plane. Formula (65.13) and analogous expressions that are derived below determine the shape of the free surface of the liquid.

A similar expression for capillary pressure can be derived for the case of a surface that is curved in two directions.

For subsequent discussion, we need to derive expressions for capillary pressure at small deformations of a cylindrical and a spherical surface.

The surface area in cylindrical coordinates (r, z, ψ) is

$$\Sigma = \int\int \sqrt{r^2 + r^2\left(\frac{\partial r}{\partial z}\right)^2 + \left(\frac{\partial r}{\partial \psi}\right)^2}\, d\psi\, dz. \tag{65.14}$$

Assuming that the undeformed cylindrical surface had a radius a, and that the deformed surface has a radius $a + \zeta(\psi, z)$, then the deformed surface for a small displacement $\zeta(\psi, z)$ is described by

$$\begin{aligned}\Sigma &= \int\int (a+\zeta)\sqrt{1 + \left(\frac{\partial \zeta}{\partial z}\right)^2 + \frac{1}{a^2}\left(\frac{\partial \zeta}{\partial \psi}\right)^2}\, dz\, d\psi \approx \\ &\approx \int\int (a+\zeta)\left[1 + \frac{1}{2}\left(\frac{\partial \zeta}{\partial z}\right)^2 + \frac{1}{2a^2}\left(\frac{\partial \zeta}{\partial \psi}\right)^2\right] dz\, d\psi \approx \\ &\approx \int\int \left[a + \zeta + \frac{a}{2}\left(\frac{\partial \zeta}{\partial z}\right)^2 + \frac{1}{2a}\left(\frac{\partial \zeta}{\partial \psi}\right)^2\right] dz\, d\psi.\end{aligned}$$

The variation of the surface area is

$$\delta\Sigma = \int\int \left[\delta\zeta + a\left(\frac{\partial \zeta}{\partial z}\right)\frac{\partial \delta\zeta}{\partial z} + \frac{1}{a}\left(\frac{\partial \zeta}{\partial \psi}\right)\frac{\partial \delta\zeta}{\partial \psi}\right] dz\, d\psi.$$

Integrating the second and third terms of the last equation by parts with respect to the variables z and ψ, we obtain

$$\begin{aligned}\int\int \frac{\partial \zeta}{\partial z}\frac{\partial \delta\zeta}{\partial z}\, dz\, d\psi &= \int \frac{\partial \zeta}{\partial z}\delta\zeta \Big|_0^L d\psi - \int\int \frac{\partial^2 \zeta}{\partial z^2}\delta\zeta\, dz\, d\psi = \\ &= -\int\int \frac{\partial^2 \zeta}{\partial z^2}\delta\zeta\, dz\, d\psi, \\ \int\int \frac{\partial \zeta}{\partial \psi}\frac{\partial \delta\zeta}{\partial \psi}\, dz\, d\psi &= \int \frac{\partial \zeta}{\partial \psi}\delta\zeta \Big|_0^{2\pi} dz - \int \frac{\partial^2 \zeta}{\partial \psi^2}\delta\zeta\, dz\, d\psi.\end{aligned}$$

Here, L designates the length of the cylinder. At the limits of integration the variation $\delta\zeta$ may be assumed to be zero.

We then find:

$$\delta\Sigma = \int\int \delta\zeta\left[1 - a\frac{\partial^2 \zeta}{\partial z^2} - \frac{1}{a}\frac{\partial^2 \zeta}{\partial \psi^2}\right] d\psi\, dz. \tag{65.15}$$

The variation in the volume for an infinitesimal displacement of the surface may be written in cylindrical coordinates in the form

$$\delta V = \int\int \delta\zeta\,(a+\zeta)\,dz\,d\psi. \tag{65.16}$$

Substituting (65.15) and (65.16) into (65.6), we get

$$\delta F = \int\int -(p_1 - p_2)\,\delta\zeta\,(a+\zeta)\,dz\,d\psi + \\ + \int\int \sigma\left[1 - a\frac{\partial^2\zeta}{\partial z^2} - \frac{1}{a}\frac{\partial^2\zeta}{\partial\psi^2}\right]\delta\zeta\,d\psi\,dz.$$

The condition of minimum free energy gives

$$-(p_1 - p_2) + \frac{\sigma}{a+\zeta}\left[1 - a\frac{\partial^2\zeta}{\partial z^2} - \frac{1}{a}\frac{\partial^2\zeta}{\partial\psi^2}\right] = 0,$$

whence

$$p_\sigma = (p_1 - p_2) \approx \frac{\sigma}{a} - \frac{\sigma}{a^2}\left[\zeta + a^2\frac{\partial^2\zeta}{\partial z^2} + \frac{\partial^2\zeta}{\partial\psi^2}\right].$$

The first term $\frac{\sigma}{a}$ is a constant that is immaterial here and may be omitted. We then have

$$p_\sigma \approx -\frac{\sigma}{a^2}\left[\zeta + a^2\frac{\partial^2\zeta}{\partial z^2} + \frac{\partial^2\zeta}{\partial\psi^2}\right]. \tag{65.17}$$

The capillary pressure in the case of deformation of a spherical surface may be derived in exactly the same manner.

In spherical coordinates (r, θ, ψ), the surface area is

$$\Sigma = \int\int \sqrt{1 + \frac{1}{r^2}\left(\frac{\partial r}{\partial\theta}\right)^2 + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial r}{\partial\psi}\right)^2}\, r^2 \sin\theta\, d\theta\, d\psi.$$

If the undeformed sphere has a radius R, then the radius of the deformed surface is R + $\zeta(\theta, \psi)$. For a small displacement ζ, the deformed surface is given by

$$\Sigma = \int\int \sqrt{1 + \frac{1}{R^2}\left(\frac{\partial\zeta}{\partial\theta}\right)^2 + \frac{1}{R^2\sin^2\theta}\left(\frac{\partial\zeta}{\partial\psi}\right)^2}\,(R+\zeta)^2 \sin\theta\, d\theta\, d\psi \approx \\ \approx \int\int \left[1 + \frac{1}{2R^2}\left(\frac{\partial\zeta}{\partial\theta}\right)^2 + \frac{1}{2R^2\sin^2\theta}\left(\frac{\partial\zeta}{\partial\psi}\right)^2\right](R+\zeta)^2 \sin\theta\, d\theta\, d\psi.$$

The variation of the surface is then expressed as follows:

$$\delta\Sigma = \int\int \left\{2\,(R+\zeta)\,\delta\zeta + \frac{\partial\zeta}{\partial\theta}\frac{\partial\delta\zeta}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial\zeta}{\partial\psi}\frac{\partial\delta\zeta}{\partial\psi}\right\}\sin\theta\, d\theta\, d\psi.$$

Integration of the last two terms by parts gives

$$\int \frac{\partial \zeta}{\partial \theta} \frac{\partial \delta \zeta}{\partial \theta} \sin \theta \, d\theta = \left[\left(\frac{\partial \zeta}{\partial \theta} \sin \theta \right) \delta \zeta \Big|_0^\pi \right] - \int \delta \zeta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \zeta}{\partial \theta} \right) d\theta,$$

$$\int \frac{\partial \zeta}{\partial \psi} \frac{\partial \delta \zeta}{\partial \psi} d\psi = \left[\frac{\partial \zeta}{\partial \psi} \delta \zeta \Big|_0^\pi \right] - \int \delta \zeta \frac{\partial^2 \zeta}{\partial \psi^2} d\psi.$$

Since the variation $\delta\zeta$ at the limits of integration is zero we find

$$\delta \Sigma = \int \int \left\{ 2(R+\zeta) - \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \zeta}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 \zeta}{\partial \psi^2} \right\} \delta \zeta \sin \theta \, d\theta \, d\psi. \quad (65.18)$$

The variation in the volume enclosed by the surface is

$$\delta V = \int \delta \zeta (R+\zeta)^2 \sin \theta \, d\theta \, d\psi. \quad (65.19)$$

Substituting (65.18) and (65.19) into (65.6) we have:

$$\delta F = \int \left\{ -(p_1 - p_2)(R+\zeta)^2 + 2\sigma(R+\zeta) - \right.$$
$$\left. - \frac{\sigma}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \zeta}{\partial \theta} \right) + \frac{\sigma}{\sin^2 \theta} \frac{\partial^2 \zeta}{\partial \psi^2} \right\} \delta \zeta \sin \theta \, d\theta \, d\psi.$$

The requirement of minimum free energy leads to the expression for capillary pressure

$$p_\sigma = -\frac{2\zeta\sigma}{R^2} - \frac{\sigma}{R^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \zeta}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 \zeta}{\partial \psi^2} \right]. \quad (65.20)$$

Equations (65.13), (65.17) and (65.20) are often presented in the following form:

$$p_\sigma = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad (65.21)$$

where R_1 and R_2 are the principal radii of curvature of the surface. Equation (65.21) is known as the Laplace equation. It may be shown that, at small curvatures (large radii of curvature), the expressions for the sum of the radii of curvature correspond to the formulas given above.

For simple geometric configurations, equation (65.15) may be fully integrated. For example, let a liquid be adjacent to one side of a plane vertical wall (Figure 68). Let us designate the height of the meniscus by y and its thickness by h, and let θ be the angle of contact between the liquid and the wall. Let the y axis be vertically upward, and the surface of the liquid be at the plane y = 0. The gas pressure p_2 is constant and may be selected as the reference for pressure measurements. The pressure in the liquid at rest is

$$p_1 = \text{const} - \rho g y. \qquad (65.22)$$

One of the radii of curvature, R_2, for example, is equal to zero.

Condition (65.21), therefore, gives

$$-\rho g y = \frac{\sigma}{R_1} + \text{const.} \qquad (65.23)$$

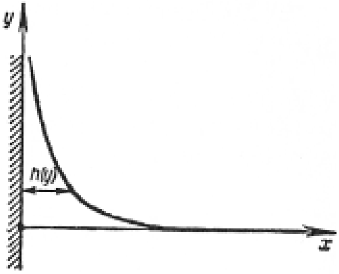

Figure 68. Meniscus at a vertical plate.

For the radius of curvature, we may write

$$\frac{1}{R_1} = -\frac{\frac{d^2h}{dx^2}}{\left(1+\left(\frac{dh}{dx}\right)^2\right)^{3/2}}. \qquad (65.24)$$

Assuming that the constant in equation (65.23) is equal to zero, we have

$$\frac{\frac{d^2h}{dx^2}}{\left(1+\left(\frac{dh}{dx}\right)^2\right)^{3/2}} = \frac{\rho g x}{\sigma}. \qquad (65.25)$$

Integrating twice equation (65.25) yields an expression which defines the shape of the surface

$$h(x) = -\sqrt{\frac{\sigma}{\rho g}} \operatorname{arg\,ch} 2\sqrt{\frac{\sigma}{\rho g x^2}} + \sqrt{\frac{2\sigma}{\rho g}} \sqrt{2 - \frac{\rho g x^2}{2\sigma}} + \text{const.} \qquad (65.26)$$

The constant here is determined by the magnitude of the angle of contact.*

Under given conditions, tangential forces may be extertedon the surface of the liquid, along with normal pressure. If the surface tension of the liquid changes from point to point, a tangential force will be exerted in addition to the pressure normal to the surface. This force is similar to the volume force that appears in a medium with nonuniform pressure, and its magnitude is determined by the surface tension gradient.

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*Editorial note. In the elegant study of M. M. Kusakov and D. N. Nekrasov [9], the capillary rise in capillaries of arbitrary shapes is examined.

The tangential force per unit area is

$$p_t = \operatorname{grad} \sigma. \tag{65.27}$$

The plus sign preceding the gradient indicates that the force P_t tends to move the surface of the liquid in a direction form lower to higher surface tension.

66. MOTION INDUCED BY CAPILLARITY

The presence of surface tension on the free surface of a liquid may, in certain cases, considerably affect the regime of motion of the liquid. Those cases of liquid motion in which surface tension plays an important role, are often described by the general term "capillary hydrodynamics."

The presence of an interface between fluid phases may exert an influence on the motion of the liquid in two instances: when the interface has finite curvature, and when the interfacial tension varies from point to point in the liquid surface. In both instances, forces appear in the interfacial region that generally affect the liquid motion. The effect of surface tension on the motion of the liquid is shown by a new system of boundary conditions for the interface between two contiguous liquids.

Let us set up a system of boundary conditions for the interface between two liquid phases.

As pointed out in Section 1, the following conditions obtain at the interface between two liquid phases:

1) The tangential velocity component at the liquid surface must be continuous:

$$v_t^{(1)} = v_t^{(2)}. \tag{66.1}$$

Condition (66.1) indicates that the molecular interactions of particles in both phases occur without slippage.

2) The velocity components normal to the interface of two immiscible phases equal zero:

$$v_n^{(1)} = v_n^{(2)} = 0. \tag{66.2}$$

The existence of interfacial tension has no effect on boundary conditions (66.1) and (66.2). In addition to these kinematic conditions, dynamic conditions must also be fulfilled at the interface.

3) Normal force components per unit area of the interface (normal components of the stress tensor) must be continuous:

$$p_{nn} + p_\sigma = p'_{nn}. \tag{66.3}$$

Condition (66.3) is the direct generalization of condition (65.13) and represents the balance of the normal component of forces exerted on the interface.

4) The tangential force component per unit area must be continuous. This is the condition of continuity of the tangential components of the stress tensor

$$p_{tt} + p_t = p'_{tt}. \tag{66.4}$$

The above boundary conditions include the quantities p_σ and p_t, which are functions of surface tension. It is obvious that the effect of surface tension is reflected in conditions (66.3) and (66.4). It should be noted here that while condition (66.3) can be fulfilled on the surface of a static liquid, condition (66.4) cannot be fulfilled under static conditions.

Indeed, the normal stress tensor component in a liquid at rest, according to formula (1.5), reduces to the usual pressure, and equations (66.3) and (65.13) will agree.

Conversely, by definition (1.5), the tangential stress tensor component vanishes for a liquid at rest. Boundary condition (66.4) in such a liquid, therefore, cannot be satisfied since $p_{tt} = p_{t't'} \neq 0$, and $p_t \neq 0$. The occurrence of variations in surface tension always sets the liquid into motion.

Another general remark can be made with respect to boundary conditions (66.3) and (66.4): there is no effect of the liquid surface in large scale motions.

The extent of this effect may be evaluated from boundary conditions (66.3) and (66.4). For example, when motion takes place in a field of gravity, it follows from condition (66.3) that capillary pressure may be neglected, provided that

$$p_\sigma \approx \frac{\sigma}{\lambda} \ll \rho g \lambda, \tag{66.5}$$

where λ is the scale of motion.

In other words, if the scale of motion λ is large in comparison with the capillary constant $\left(\frac{\sigma}{\rho g}\right)^{1/2}$, the surface forces do not affect the motion. For example, as shown in Sec. 93, surface tension affects the wave process on the surface of a liquid only in the case those waves whose length λ is shorter than $\left(\frac{\sigma}{\rho g}\right)^{1/2}$.

In general, the effect of varying surface tension on the motion of a liquid which has a free surface or which is contiguous to another liquid may be viewed as follows. Let us reduce the boundary conditions, for example, condition (66.4), to a dimensionless form. Assuming that the motion of the liquid is viscous, we may write

$$\frac{\mu U}{L}\frac{\partial V_x}{\partial Y} - \frac{1}{l}\frac{\partial \sigma}{\partial X} = \frac{\mu' U'}{L}\frac{\partial V'_x}{\partial Y} \tag{66.6}$$

or

$$\frac{\partial V_X}{\partial Y} - \left|\frac{\partial \sigma}{\partial X}\right| \frac{1}{\mu U} \frac{L}{l} = \frac{\mu' U'}{\mu U} \frac{\partial V'_X}{\partial Y} \tag{66.7}$$

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

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

$$\left|\frac{\partial \sigma}{\partial x}\right| \frac{L^2}{\rho \nu^2} \ll \mathrm{Re} \tag{66.9}$$

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

$$\left|\frac{\partial \sigma}{\partial x}\right| \frac{L^2}{\rho \nu^2} \ll 1. \tag{66.10}$$

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

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

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

Substituting the value of Δp, we find

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

Integrating this equation, we obtain

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

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:

$$t = \frac{2\mu l^2}{r\sigma}$$

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

$$\operatorname{grad} \sigma = \frac{\partial \sigma}{\partial T} \operatorname{grad} T. \tag{68.1}$$

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

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

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 cm^2 of surface is

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

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

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

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

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

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

$$\frac{\partial p}{\partial y} = 0. \tag{68.6}$$

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

$$\int_0^h v_x\,dy = 0. \tag{68.7}$$

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

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

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:

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

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

$$\mu\left(\frac{\partial v_x}{\partial y}\right)_{y=0} = \frac{\partial\sigma}{\partial T}\,\mathrm{grad}\,T. \tag{68.10}$$

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

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

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

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

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

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

Thus, we obtain

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

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

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

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

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

The maximum velocity of the liquid at the surface is

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

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,

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

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

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

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

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

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

$$I \sim \frac{Dc_0 S}{h}.$$

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.

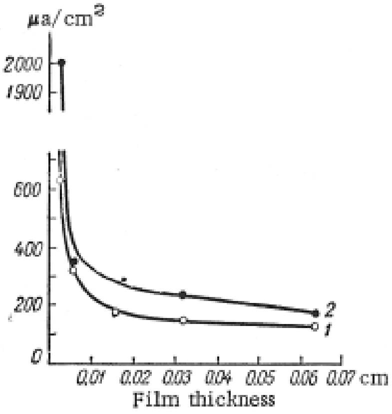

Figure 69. Dependence of the rate of oxygen reduction on the thickness of the electrolyte film. The electrolyte is 0.1 N NaCl; the cathode material is copper. Vapor pressure of water: 1) 17 mm Hg; 2) 1.15 mm Hg.

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 cm^2 of surface area

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

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

$$p_t = \operatorname{grad} \sigma = \frac{\partial \sigma}{\partial \Gamma} \operatorname{grad} \Gamma \tag{69.2}$$

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.

The boundary conditions at the interface between two liquids (or liquid-gas) are

$$p_{nn} + p_{\sigma} = p'_{nn}, \qquad (69.3)$$

$$p_{tt} + p_{t} = p'_{tt}, \qquad (69.4)$$

where p_{nn} and p_{tt} are the normal and tangential components of the viscous stress tensor, p_{σ} is the capillary pressure, and p_t is the tangential force (per 1 cm^2 of surface area).

The difference in boundary conditions on a liquid surface covered with a film, as compared to pure liquid, in turn leads to a different flow regime.

The effect of surface-active substances on liquid flow is apparent as long as the condition given in (69.4) is controlling. This condition concerns only the viscous stresses in the liquid. At high Reynolds numbers, therefore, when the viscous forces are small compared to inertia and the liquid viscosity is not important, the tangential velocity of the liquid is not limited in any way. Thus, at high Reynolds numbers, the presence of surface-active substances does not influence the liquid flow.* The meaning of this assertion is simple. At high liquid velocities, the surface-active substances will be entirely swept away (''blown off''). Conversely, in a viscous flow regime, the effect of surface-active substances could be very significant. It should be stressed that, along with the effect of the surface-active substance on liquid flow, the motion of the surface-active substance should also be examined. Indeed, the energy dissipation caused by irreversible processes occurs not only in the liquid, but also in the film formed by the surface-active substance. One can speak of a surface viscosity which manifests itself when there is motion in the film.

However, since films of surface-active substances generally are composed of a single layer of surface-active molecules, the dissipation of energy in this layer is small compared to that in the bulk phase. Later (Sec. 77) we discuss in detail the problem of viscosity of monolayers and the circumstances under which this viscosity is important. In any event, the viscosity of the monolayer can be taken into account in formulating all further equations. The viscosity of

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*It should be borne in mind, however, at high Reynolds numbers, that surface-active substances may have an indirect effect on the motion of the liquid. S. I. Kosterin and M. N. Rubanovich [8] showed that for liquid flow in a tube, the presence of surface-active substances may cause persistent foaming. The presence of numerous bubbles adhering to the tube walls leads to an increase in the hydrodynamic resistance coefficient (separating the bubbles from the walls requires the expenditure of a fairly considerable amount of energy).

the monolayer may be determined only from experimental data — data on the energy dissipation in liquids covered by a monolayer of surface-active materials. Experiments always measure the sum of the effects, and provide no subdivision of the energy dissipation into contributions from the surface and bulk phases.

For separate determination of the energy dissipated in the liquid phase and in the monolayer, it is necessary to know the flow regime in the presence of a surface-active material. Then, the energy dissipated in the liquid could be computed. The difference between the experimentally measured energy dissipation and the calculated figure (or of two equivalent quantities) then would represent the energy dissipation due to viscous flow in the surface phase.

It is shown later than in many instances — such as, for example, the fall of a droplet through a liquid when the liquid surface is covered by a surface-active substance — viscous motion in the monolayer and the energy dissipation caused by it are so small compared with the energy dissipation in the bulk phase that this portion of the energy dissipated may be disregarded. In this sense the viscosity of the monolayer need not be taken into account. It would be incorrect, however, to regard this conclusion as generally applicable.

In other instances, the energy dissipation in the monolayer may be so important that it must be taken into account in computing the total energy dissipated.

The presence of noticeable viscous energy dissipation in the monolayer can be determined only by experiments and calculations of the liquid flow regime. In these calculations the effect of surface-active substances should be considered.

The calculation must consider boundary conditions (69.3) and (69.4) at the surface of the liquid covered by an absorbed surface-active material.

The normal and tangential forces — p_σ and p_t, respectively — in expressions (69.3) and (69.4) may be computed, provided the distribution of the surface-active substance on the surface of the liquid, i.e., $\sigma(x, y, z)$, is known.

Assuming that $\sigma = \sigma(\Gamma)$ the distribution of the surface-active material on the moving liquid surface must be known in order to determine the surface forces.

This distribution is affected by several factors. First, the surface-active material on the surface is entrained by liquid flow. As a result, a convective flux of the surface-active substance arises along the liquid surface

$$j_{\text{surf}} = \Gamma v_t, \tag{69.5}$$

where v_t is the tangential liquid velocity at the surface. Since the concentration of the surface-active material on the surface varies from point to point, a diffusion of molecules of that material appears in the liquid surface. The diffusion proceeds from points of greater to points of lesser concentration. The diffusional mass flux arising on the surface is given by

$$\mathbf{j}_{\text{diff}} = -D_s \operatorname{grad} \Gamma, \tag{69.6}$$

where D_s is the surface diffusion coefficient.

If the surface-active material is soluble in the liquid, it can pass from the surface phase into the bulk phase, or vice versa, at any point on the surface.

Let j_n designate the mass flux per unit area from the surface to the bulk phase, or vice versa. The flux is governed by the slower of the two steps into which this may be subdivided in either direction:

1) the desorption (or adsorption) process, and

2) the passage of dissolved surface-active materials into the bulk of the solution (or their passage to the surface from the bulk of the solution).

The law of conservation of surface-active material may then be written

$$\frac{\partial \Gamma}{\partial t} + \operatorname{div} (\mathbf{j}_{\text{surf}} + \mathbf{j}_{\text{diff}}) + j_n = 0,$$

or

$$\frac{\partial \Gamma}{\partial t} + \operatorname{div} (\Gamma \mathbf{v}_t - D_s \operatorname{grad} \Gamma) + j_n = 0. \tag{69.7}$$

In the case of a plane liquid surface represented in Cartesian coordinates, we get

$$\frac{\partial \Gamma}{\partial t} + j_n + \frac{\partial}{\partial x}\left(\Gamma v_x - D_s \frac{\partial \Gamma}{\partial x}\right) + \frac{\partial}{\partial y}\left(\Gamma v_y - D_s \frac{\partial \Gamma}{\partial y}\right) = 0. \tag{69.8}$$

It follows from equation (69.7) that the distribution of the material in the surface may be found if the velocity distribution in the liquid is known (the flux j_n may be a function of the velocity distribution in the liquid, if the flux is determined by the rate of transfer of the surface-active material).

In turn, to find the velocity distribution, it is necessary to know the forces acting on the liquid surface, i.e., the distribution of the surface-active material.

Thus, in order to solve the complete problem of liquid flow in the presence of surface-active materials, it is necessary to solve simultaneously the equations of viscous liquid motion, with consideration of boundary conditions (69.3) and (69.4), and equation (69.7) for the conservation of surface-active material.