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THE THERMODYNAMIC THEORY OF CAPILLARITY UNDER THE HYPOTHESIS OF A CONTINUOUS VARIATION OF DENSITY

J. D. van der Waals

1. INTRODUCTION

Laplace considered capillary phenomena to be in the domain of statics. Gauss shared this idea; it was by applying the principle of virtual velocities, which allows us to find the conditions of equilibrium in statics, that he was able to formulate the laws of these phenomena. Neither author supposed that the molecules were in thermal motion either in the body of the fluid or in the boundary layer; and if we recall the era in which their theories were developed, this should not surprise us. The molecules for them are therefore at rest; and if this is really the case then the phenomenon is purely static.

But such a hypothesis is directly contrary to present ideas on the nature of heat, which suppose the molecules to be in rapid movement. The phenomenon ought therefore, following this new theory, to be of a thermodynamic nature; and we shall not discover the laws of capillarity by applying a principle that is valid only in statics; we must start from a principle which shows us the state of a substance in thermodynamic equilibrium. Such equilibrium is not a state of rest but a steady state of motion.

A thermodynamic theory of capillarity has already been developed by Gibbs. His paper, "On the equilibrium of heterogeneous substances," is in the main devoted to these phenomena; the author takes more than a hundred pages to explain their nature and to discuss both well-known and less well-known applications. Equation (502) of Gibbs' paper can be regarded as the essence of the new theory.

Gibbs himself has observed (footnote p. 432 [p. 267]) that it is possible to interpret capillary phenomena in quite another way. Now circumstances which need not be mentioned here led me to conceive a different theory of these phenomena; and I think that there is some interest in making it known, all the more because in my view objections can be raised against a supposition which Gibbs has had to use to arrive at his fundamental equation (502).

According to Gibbs' theory, capillary phenomena are present only if there is a discontinuity between the portions of fluid that are face-to-face. The chapter of his paper that discusses capillarity carries, in fact, the title, "Influence of surfaces of discontinuity, etc." In contrast, the method that I propose to develop in the following pages is not a satisfactory treatment unless the density of the body varies continuously at and near its transition layer. It will not be without interest to show that the two apparently contradictory hypotheses lead to values of the same order of magnitude for the capillary tension and energy.

2. THE THERMODYNAMIC PRINCIPLE OF EQUILIBRIUM

The thermodynamic principle of equilibrium can be formulated as follows: Matter distributes itself in a space in such a way that, for a given energy, the entropy attains a maximum. This principle, which Gibbs takes as the basis of his researches, is already found in essence in the work of Clausius. The latter shows in fact that if irreversible, and therefore clearly nonequilibrium changes are made, the entropy of a system increases.

The truth of this proposition can be shown without difficulty in one or two cases of irreversibility, as for example the case of inequality of temperature or of a nonzero difference of pressure. But these facts are far from leading logically to the conclusion that a maximum in entropy necessarily implies a state of equilibrium. Hence we must recognize that the principle is not proved by this argument; it is, however, rendered all the more probable. However, the truth of the principle of thermodynamic equilibrium is no more in doubt than that of several other similar principles, which have been deduced by generalization from our observation of particular cases. In my view, the logical basis of the principle of conservation of energy is no more certain.

The total entropy can be represented $\int \rho\eta \, dk$; where dk is an element of volume of the given space, ρ the density in this element, and η the entropy per unit mass in the state present in this element of volume. Similarly $\int \rho\epsilon \, dk$ expresses the total energy, and $\int \rho \, dk$ the given amount of substance.

The principle of equilibrium implies therefore that if

$$\int \rho \, dk = c_1 \quad \text{and} \quad \int \rho\epsilon \, dk = c_2 \tag{2.1}$$

then matter distributes itself in the volume in such a way that $\int \rho\eta \, dk$ attains a maximum value. In other words, when equilibrium is established, we have

$$\delta \int \rho\eta \, dk = 0$$

subject to the conditions (2.1).

We can invert the principle of equilibrium as follows: A given amount of matter distributes itself in a given space in such a way that, for a given value of the total entropy, the total energy has a minimum, or

$$\delta \int \rho\epsilon \, dk = 0 \tag{2.2}$$

when

$$\int \rho \, dk = c_1 \quad \text{and} \quad \int \rho\eta \, dk = c_2 \tag{2.3}$$

Finally, the form in which the same principle is most easily applied, which I have used in my work[3] "Molecular Theory etc.", and which I propose to use in the present work, is the following: A given substance distributes itself in a given space, at a given temperature, in such a way that $\int \rho(\epsilon - \tau_1\eta) \, dk$ becomes a minimum. This third form follows from the

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[3] Molecular Theory of a substance formed from two different components; *Z. Phys. Chem.* **5**:133 (1890), or *Arch. Néerl.* **24**:1 (1891).

second as follows. Let l be a constant factor; then it follows, by the rules of the calculus of variations, that

$$\delta \int \rho(\epsilon - l\eta)\, dk = 0 \qquad \text{when} \quad \int \rho\, dk = c_1 \tag{2.4}$$

is equivalent to Eqs. (2.2) and (2.3).

In other words, every solution of Eqs. (2.2) and (2.3) satisfies also (2.4), and vice versa. We need only to define the significance of l. To do this we take the temperature as one of the parameters that determines the state at any point in the space.

If the other arbitrary parameters do not change—if therefore the density also remains constant—it follows that

$$\frac{d\epsilon}{d\tau} - l\frac{d\eta}{d\tau} = 0$$

By comparing this with one of the first equations of the mechanical theory of heat

$$\tau\, d\eta = d\epsilon + p\, dV$$

we see that l represents the temperature τ_1, which must be constant since we have equilibrium. This third form of the principle of equilibrium is more simple to apply than the two preceding ones, since three equations are reduced to two, without loss of generality. The supplementary condition of constant temperature τ_1 excludes no imaginable state of equilibrium. It is also simpler since $(\epsilon - \tau_1\eta)$, which we call the free energy, can be found immediately from the equation of state, at least for homogeneous phases.

There is also a fourth form in which one can express the thermodynamic principle of equilibrium: A given amount of matter distributes itself, at given temperature and pressure, in such a way that the total value of $\epsilon - \tau_1\eta + p_1 V$ becomes a minimum. It is not difficult to deduce this from the preceding form. It yields solutions which are valid only when the pressure remains constant, and so when external forces are excluded. It is thus less general than the third form.

3. APPLICATION TO THE EQUILIBRIUM OF A SINGLE SUBSTANCE WITHOUT CONSIDERATION OF CAPILLARY PHENOMENA

The state at any point in a given space is determined by the density or specific volume, the temperature being specified. This is not to say, however, that ϵ or $\epsilon - \tau_1\eta$ is completely determined by this density; each depends equally on the density at neighboring points. But the error that we commit in assuming a dependence on the density only at the point considered vanishes completely when the state of equilibrium is that of a homogeneous distribution of the substance. There remains only an error at the limits where the substance is in contact with the boundaries. When the substance separates in a vessel into two parts of unequal density, there also will be an error for another layer, namely the transition layer between the two parts. If, however, the state of equilibrium is one where there is a change of density throughout the vessel, as in a substance under the action of gravity, then the error becomes general, however feeble it may be. The only circumstances that we are concerned with are those arising from capillarity. Thus if we admit that ϵ, and hence also $\epsilon - \tau_1\eta$, is determined at each point only by the density at that point, then we shall find the conditions of equilibrium, neglecting the capillary phenomena.

If we represent $\epsilon - \tau_1\eta$ by ψ, then these conditions are $\delta \int \rho\psi \, dk = 0$ and $\int \rho \, dk = C$.

The application of these formulas can be reduced to the calculation of the variation of an integral without additional conditions by subtracting a constant multiple of the second integral from the first, and so by writing

$$\delta \int \rho(\psi - \mu_1) \, dk = 0$$

or

$$\int \delta\rho \, dk \, (\psi + \rho \, \partial\psi/\partial\rho - \mu_1) = 0$$

It follows therefore that at any point in the space we have

$$\psi + \rho \, \partial\psi/\partial\rho = \mu_1 \qquad \text{or} \qquad \psi - V \, \partial\psi/\partial V = \mu_1$$

or again

$$\epsilon - \tau_1\eta + p_1 V = \mu_1$$

The density at each point must therefore be such that the two quantities τ_1 and μ_1 have everywhere the same values. If there are no external forces, then there is a third quantity, namely the pressure p, which must satisfy the same condition. This last rule follows from the differential equation

$$d\epsilon - \tau_1 \, d\eta + p \, dV + V \, dp = 0$$

Since, when ϵ is not a function of position, we have $d\epsilon = \tau_1 \, d\eta - p \, dV$, then dp will be zero, or $p = \text{const} = p_1$.

The condition of equality of the three quantities τ_1, μ_1, and p_1 can be satisfied, in the case of one single substance, only if there is a unique homo-

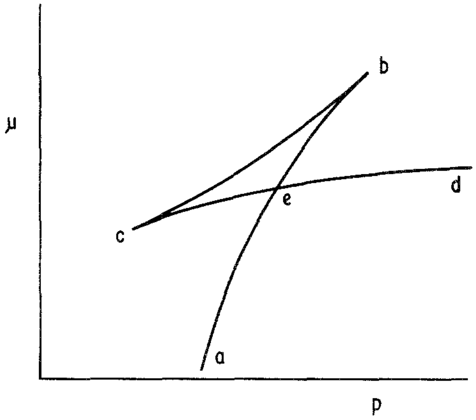

Fig. 1

geneous phase, or two phases of this kind, occupying the whole of the vessel (Fig. 1).

The conditions that we shall derive make the first variation $\delta \int \rho(\psi - \mu_1)\, dk$ equal to zero. For these to lead to the integral being a minimum we need to show that $\delta^2 \int > 0$. Now

$$\delta^2 \int \rho(\psi - \mu_1)\, dk = \frac{1}{2}\int (\delta\rho)^2 \frac{\partial^2}{\partial\rho^2}[\rho(\psi - \mu_1)]\, dk$$

or

$$2(\partial\psi/\partial\rho) + \rho(\partial^2\psi/\partial\rho^2) > 0$$

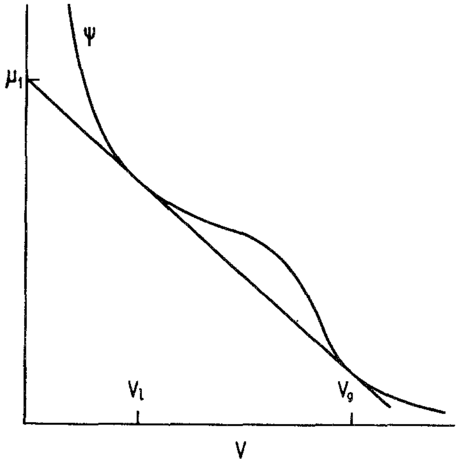

Fig. 2

This last condition is simplified when we write $1/V$ in place of ρ; it becomes then

$$(\partial^2\psi/\partial V^2) > 0 \qquad \text{or} \qquad -(\partial p/\partial V) > 0$$

An arbitrary amount of material cannot therefore distribute itself in a vessel of a capacity determined by the requirement that the phase be homogeneous; that is, if the quantity is supposed given, e.g., unit mass, it cannot be distributed homogeneously in a vessel of any capacity whatsoever. It is only when the volume has a value such that the curve of ψ is convex downward for homogeneous states that the phase is stable (Fig. 2). There is instability at volumes between the points of inflection of the curve, and in these cases there can be no homogeneous phase. The substance must divide itself into two different phases, each of the density given by the volumes corresponding to the points of contact of the double tangent. And even if a state were to be stable when homogeneous, but if separation is nevertheless possible, then the homogeneous phase will not be found. In these circumstances ψ satisfies the condition of being at a minimum. But if the separation occurs, the sum of the values of ψ for the two layers is even smaller; this state has therefore the greater stability. The sum of the values of ψ is given by a point on the double tangent. We see therefore that the stability of a state shows that it can exist—but that to show the stability of a phase we must search for other possible states, for which the total value of ψ is less than the minimum previously found. If there is separation, we shall find certain points, namely those in the transition layer, for which the value of $\epsilon - \tau_1\eta$ is not solely a function of density, as had hitherto been supposed at all points in the vessel. In other words, these conditions which the two coexisting phases ought to satisfy are still open to the objection that they have been derived from an inadequate treatment.

4. DEDUCTION OF THE STATE OF EQUILIBRIUM, TAKING ACCOUNT OF CAPILLARITY

We shall obtain a complete solution of the problem of capillarity if we can express $\epsilon - \tau_1\eta$ at each point as a function of the density at that point and of the differences of density in the neighboring phases, out to a distance limited by the range over which the molecular forces act. We should therefore describe a sphere about each point of radius equal to this distance, assume an arbitrary distribution of matter within this sphere, and then find a way of expressing the energy and entropy as a function of the density at the center and of such parameters as are needed for the surrounding density. In choosing arbitrarily this distribution of density within the sphere of interaction we should naturally be guided by what we know in advance about the state of equilibrium. We should therefore have regard both to sudden jumps of density as well as to continuous variations. The latter are always present. A layer of a gaseous substance, condensed on a solid body, will show a continuous, even if rapid, variation, while the vapor above a liquid undergoes a condensation which, originally at least, will be continuous.

However, the difficulty of obtaining an expression for the energy when there is a discontinuity of density has led me to attempt the calculation only for the case of continuous variation. The energy does not then depend only on the density, but the other parameters which appear in the expression $\epsilon - \tau_1\eta$ for this point soon become apparent.

In fact, if we draw a straight line on which we measure a distance h, then the new parameters are expressed by $d\rho/dh$, $d^2\rho/dh^2$, etc. If we know in advance that the density has a constant value in parallel layers, then the line should be drawn only in one direction, namely that perpendicular to the layers.

5. CALCULATION OF THE ENERGY FOR THE CASE OF A CONTINUOUS VARIATION OF DENSITY THROUGH PARALLEL LAYERS

Let us consider a liquid in the lower part of a vessel with vertical sides, with a saturated vapor above it. Let the densities be ρ_1 and ρ_2 with $\rho_1 > \rho_2$, and let the surface of separation be horizontal. This can be brought out only under the influence of gravity, but we put aside the useless complications which arise from external forces, and we allow gravitation no other role but that of keeping the layers planar. If, however, the inconsistency of such a course raises objections, then we could take a horizontal membrane of liquid separating two gaseous layers.

Let us draw now a straight line perpendicular to the layers, on which we denote a distance h. Let $h = 0$ be taken in the middle of the greater of the two densities, that is, ρ_1. At this point the energy per unit mass is a function of ρ_1 only and can be represented by $\epsilon_1 = C - a\rho_1$, where a is the constant which enters in the equation of state when one takes unit density to be that of the vapor at 0° and 76 cm pressure. The constant C is the kinetic energy, which can be treated as invariant, since τ_1 remains constant. If we now move unit mass from the zone where the density is constant ρ_1 to a point in the intermediate layer where the density is ρ and the energy ϵ, then we no longer have at this place the relation $\epsilon = C - a\rho$, except in one particular case, and that is when the sphere of attraction centered on the point considered has in its lower half a greater density precisely equal to and distributed in just the same way as the lower density in the upper half of the sphere. We can conclude at once that the correction to the equation $\epsilon = C - a\rho$ is not confined to a term in $d\rho/dh$. If $f(h)$ is the force holding back the unit mass as it rises, then

$$\epsilon = \epsilon_1 + \tfrac{1}{2}\int_0^h f(h)\,dh \tag{5.1}$$

In fact the work of bringing about the travel through the distance h is $\int_0^h f(h)\,dh$, and half of this work is recovered in the form of an increase of energy of the particle considered; the other half is added to the energy of the surrounding matter. We must therefore determine $f(h)$ to know the energy of unit mass at height h.

To do this we suppose for the moment that the layers acting on the unit mass are situated at distances u from the layer that encloses it. We take u positive for layers above this, and negative for those below. To find $f(h)$ we must subtract from the attractive force of the lower layers, directed downward, that of the upper layers directed in the opposite sense.

Let us then cut in a lower layer at distance u a ring of thickness du, whose center is the foot of the perpendicular dropped from the point at which we propose to find $f(h)$. Let t be radius of this ring, and $2\pi t\,dt\,du$ its volume. The vertical component of the attraction is

$$\rho_{h-u}2\pi t\,dt\,du\,(u/r)\varphi(r)$$

where r is the distance from the point considered to any point in the ring, and $\varphi(r)$ the force between two unit masses at a separation r. The vertical component of attraction of the whole layer du is therefore

$$\int_{t=0}^{t=\infty} \rho_{h-u}2\pi t\,dt\,du\,(u/r)\varphi(r)$$

where $r^2 = u^2 + t^2$ or $r\,dr = t\,dt$, so that the vertical component can be written

$$\int_{r=u}^{r=\infty} \rho_{h-u}2\pi u\,du\,\varphi(r)\,dr$$

Let us now put $\varphi(r)\,dr = d\zeta(r)$ when the last integral becomes $\rho_{h-u}2\pi u\,\zeta(u)\,du$, if we introduce the known limit $\zeta(\infty) = 0$. Let us similarly put $2\pi u\zeta(u)\,du = d\psi(u)$; we can now represent the attraction exerted by the layer as $-\rho_{h-u}\,d\psi(u)$. If the density of all layers at distance greater than u remains constant, then their total attraction is $\rho_{h-u}\psi(u)$, a result which explains the significance of $\psi(u)$. That is, this function represents the attraction on unit mass of all layers between u and ∞ when they have a constant density of unity. If the attractive power stops at the distance of the radius of the sphere at attraction, then $\psi(u)$ represents the force exerted by a spherical segment or cap, starting at a distance u, and filled with a substance of unit density.

Let there be two layers, one at $h - u$ and the other at $h + u$; they exert together a downward force expressed by

$$d\psi(u)\{-\rho_{h-u} + \rho_{h+u}\}$$

For the set of layers the downward force is

$$-\int_0^\infty d\psi(u)\{\rho_{h-u} - \rho_{h+u}\}$$

or, integrating by parts,

$$-\psi(u)[\rho_{h-u} - \rho_{h+u}]_0^\infty + \int_0^\infty \psi(u)\,du\left\{\frac{\partial\rho_{h-u}}{\partial u} - \frac{\partial\rho_{h+u}}{\partial u}\right\}$$

The integrated term is zero at the two limits; for $u = \infty$, since $\psi(\infty) = 0$; and for $u = 0$, since $\rho_{h-0} = \rho_{h+0}$. We have therefore

$$f(h) = \int_0^\infty \psi(u)\,du\left\{\frac{\partial\rho_{h-u}}{\partial u} - \frac{\partial\rho_{h+u}}{\partial u}\right\}$$

Moreover,

$$\rho_{h-u} = \rho_h - u\frac{\partial\rho_h}{\partial h} + \frac{u^2}{2!}\frac{\partial^2\rho_h}{\partial h^2}, \quad \text{etc.}$$

$$\frac{\partial\rho_{h-u}}{\partial u} = -\frac{\partial\rho_h}{\partial h} + u\frac{\partial^2\rho_h}{\partial h^2}, \quad \text{etc.}$$

Similarly,

$$\frac{\partial\rho_{h+u}}{\partial u} = \frac{\partial\rho_h}{\partial u} + u\frac{\partial^2\rho_h}{\partial h^2}, \quad \text{etc.}$$

or

$$f(h) = \int_0^\infty 2\psi(u)\,du\left\{-\frac{\partial\rho_h}{\partial h} - \frac{u^2}{2!}\frac{\partial^3\rho_h}{\partial h^3} - \cdots\right\}$$

or, restricting ourselves to the two leading terms,

$$f(h) = -2\frac{\partial\rho_h}{\partial h}\int_0^\infty \psi(u)\,du - \frac{2}{2!}\frac{\partial^3\rho_h}{\partial h^3}\int_0^\infty u^2\psi(u)\,du$$

The second of these integrals is much smaller than the first since each element of the second contains an additional factor of $u^2/2$, and u is always very small, at most equal to the radius of the sphere of attraction. The first of these two integrals is nothing but the quantity K of Laplace, for a density of unity. The missing integral $\int_0^\infty u\psi(u)\,du$ is his quantity H for the same density.

We find for $\int_0^h f(h)\,dh$

$$-2(\rho_h - \rho_1)\int_0^\infty \psi(u)\,du - \left[\frac{\partial^2\rho_h}{\partial h^2} - \left(\frac{\partial^2\rho_h}{\partial h^2}\right)_{h=0}\right]\int_0^\infty u^2\psi(u)\,du$$

Since the origin of h is in the homogeneous fluid, where the density is ρ_1, we have $(d^2\rho_h/dh^2)_{h=0} = 0$.

Equation (5.1) therefore becomes

$$\epsilon = C - a\rho_1 - (\rho - \rho_1)\int_0^\infty \psi(u)\,du - \frac{1}{2}\frac{d^2\rho}{dh^2}\int_0^\infty u^2\psi(u)\,du$$

From the way it occurs in the equation of state we have $a = \int_0^\infty \psi(u)\,du$; and if we put

$$c_1 = \int_0^\infty u\psi(u)\,du \qquad \text{and} \qquad c_2 = \int_0^\infty u^2\psi(u)\,du$$

we can represent the energy of unit mass at point h by .

$$\epsilon = C - a\rho - \tfrac{1}{2}c_2\, d^2\rho/dh^2$$

If in the calculation of ρ_{h-u} and ρ_{h+u} we had not limited ourselves to a few terms, we should have found

$$\epsilon = C - a\rho - \frac{c_2}{2!}\frac{d^2\rho}{dh^2} - \frac{c_4}{4!}\frac{d^4\rho}{dh^4}, \quad \text{etc.}$$

It is certainly striking that the term thought by Laplace to be characteristic of capillarity is just that missing from the equation for the energy, and which therefore should be missing also in the subsequent development of this theory of capillary action. The term which should account for these phenomena is c_2, and this quantity is as many times smaller than c_1 as c_1 is smaller than a. This circumstance could easily lead to the belief that we should find from the hypothesis of a continuous variation of density that the capillary energy would be so small that it disagreed with the value found experimentally, at least unless we ascribe to the sphere of attraction dimensions which, in their turn, will disagree with other observations. We show below, however, that these difficulties are imaginary. A more serious obstacle arises in trying to decide if the expression $\epsilon = C - a\rho - \tfrac{1}{2}c_2\, d^2\rho/dh^2$ is an adequate approximation. The successive coefficients, c_4, c_6, etc., are of such size that c_6/c_4 is of the same degree of smallness as c_4/c_2 and c_2/a, an order that we can put equal to that of the square of the radius of the sphere of attraction. The successive factors by which these terms are multiplied can, however, be increasing, since we can consider $(d^2\rho/dh^2)/\rho = (d^4\rho/dh^4)/(d^2\rho/dh^2)$, etc., as inversely proportional to the square of the thickness of the transition layer. Everything depends, therefore, on knowing if this thickness is large relative to the radius of the sphere of attraction, and it seems to me that there is nothing against this supposition; on the contrary, optical observations seem to show that it really is so. While this point would justify a more profound examination, I shall provisionally restrict myself to the term containing the factor c_2, and return in Section 15 to the complete equation.

Before being able to give a value to $\psi = \epsilon - \tau_1\eta$, we must resolve the question of whether the value of η in the transition layer is determined by the density alone, as I think to be the case. Gibbs himself evidently inclines to the same view (p. 382 [p. 221] of the well-known memoir). The entropy, it seems to me, is determined at each point by the molecular speeds and the number of collisions. Be that as it may, we lack all evidence from which we could deduce what the effect on the entropy would be of a change of state in the surrounding mass. I therefore think it excusable, if not quite justified, if I take the entropy to be a function only of density in the following development.

6. FORM OF THE INTEGRAL OF THE FREE ENERGY FOR THE CASE OF VARIATION OF DENSITY AND DEDUCTION OF THE LAW OF VARIABILITY OF DENSITY

The free energy, for a phase of specific volume V, is equal to $-\int p\,dV$. If the equation of state is known, we can therefore calculate it at once. If $p = R\tau/(V-b) - a/V^2$, then $\psi = -R\tau \ln(V-b) - a/V$, or $-R\tau\ln(\rho^{-1}-b) - a\rho$. For the case of variable density we must, from what has been said above, add to this the term $-\frac{1}{2}c_2\, d^2\rho/dh^2$. In order to separate the consequences of a particular form of the equation of state from those that are independent of it, I shall represent $-\int p\,dV$ by $f(\rho)$. The total value of the free energy is therefore $\int \rho[f(\rho) - \frac{1}{2}c_2\, d^2\rho/dh^2]\,dh$, if the vessel has unit cross section and parallel walls, while $\int \rho\,dh$ represents the fixed quantity of matter.

Hence at equilibrium

$$\delta\int \rho[f(\rho) - \tfrac{1}{2}c_2\, d^2\rho/dh^2]\,dh = 0$$

when $\int \rho\,dh = C$.

Let us subtract μ_1 times the second integral from the first, and we have then only to find the conditions under which

$$\delta\int \rho[f(\rho) - \tfrac{1}{2}c_2\, d^2\rho/dh^2 - \mu_1]\,dh = 0$$

This is a known problem in the calculus of variations whose solution can be described succinctly. The integrand contains two parameters, ρ and $(d^2\rho/dh^2)$, and we can vary both, but not independently.[4]

Let us, for brevity, denote the integral by I, so that

$$\delta I = \int \delta\rho \left[f(\rho) + \rho \frac{\partial f}{\partial \rho} - \frac{c_2}{2} \frac{d^2\rho}{dh^2} - \mu_1 \right] dh - \int \frac{c_2}{2} \rho \, \delta\left(\frac{d^2\rho}{dh^2}\right) dh$$

Integration by parts changes the last term into a form in which $\delta\rho$ appears in the integrand.

Thus

$$\begin{aligned} -\frac{c_2}{2} \int \rho \, \delta\left(\frac{d^2\rho}{dh^2}\right) dh &= -\frac{c_2}{2} \int \rho \, d\left(\delta \frac{d\rho}{dh}\right) \\ &= -\frac{c_2}{2} \left\{ \left[\rho \, \delta\left(\frac{d\rho}{dh}\right) \right]_-^+ - \int \delta\left(\frac{d\rho}{dh}\right)\left(\frac{d\rho}{dh}\right) dh \right\} \\ &= -\frac{c_2}{2} \left\{ \left[\rho \, \delta\left(\frac{d\rho}{dh}\right) \right]_-^+ - \left[\frac{d\rho}{dh} \delta\rho \right]_-^+ + \int \delta\rho \frac{d^2\rho}{dh^2} dh \right\} \\ &= -\frac{c_2}{2} \int \delta\rho \frac{d^2\rho}{dh^2} dh \end{aligned}$$

So that

$$\delta I = \int \delta\rho \left[f(\rho) + \rho \frac{\partial f}{\partial \rho} - c_2 \frac{d^2\rho}{dh^2} - \mu_1 \right] dh$$

The conditions which must be satisfied for all the contents of the vessel to be at equilibrium are found by putting the coefficient of $\delta\rho$ equal to zero, so that

$$f(\rho) + \rho \frac{\partial f}{\partial \rho} - c_2 \frac{d^2\rho}{dh^2} - \mu_1 = 0 \tag{6.1}$$

At the boundaries of the vessel liquid and vapor are sufficiently far from the transition layer that we may suppose the densities to be homogeneous; we have therefore $d^2\rho/dh^2 = 0$. In other words, we recover the same conditions of equilibrium that we had when we had neglected capillary phenomena, namely

$$\epsilon_1 - \tau_1\eta_1 + p_1 V_1 = \mu_1 \qquad \text{and} \qquad \epsilon_2 - \tau_1\eta_2 + p_1 V_2 = \mu_1$$

μ_1 is therefore what we ordinarily call the thermodynamic potential. Since $d\rho/dh$ always vanishes at a sufficient distance from the transition layer, the conditions for the integrated terms to vanish are satisfied.

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[4] We do not consider here possible changes of c_2 with the state of the fluid, that is, with ρ and τ. See Appendix.

Yet if we calculate the magnitude of $\epsilon - \tau_1\eta + pV$ for different parts of the transition layer we do not obtain the value μ_1. The difference is found, in general, to be

$$\sum_1^\infty \frac{c_{2n}}{2\cdot n!}\left(\frac{d^{2n}\rho}{dh^{2n}}\right)$$

or, if we restrict ourselves to the first term,

$$\epsilon - \tau_1\eta + pV - \mu_1 = \tfrac{1}{2}c_2\, d^2\rho/dh^2$$

We might consider nevertheless that p, for all parts of the vessel and so for the transition layer, represents the magnitude of $-\partial f/\partial V$, or, in other words, the function of V given by the equation of state as the value of p for a homogeneous phase when the density is uniform. We cannot therefore consider p in the transition layer as representing the pressure, properly defined. The value of p at any arbitrary point is a function which represents the pressure when the portion of material considered is not surrounded by parts of a different density. As soon as we leave the transition layer the value of p and of the real pressure coincide.

Equation (6.1) defines the law of variation of density in the transition layer, as follows

$$c_2\, d^2\rho/dh^2 = f(\rho) + \rho\, \partial f/\partial \rho - \mu_1 \tag{6.2}$$

It is not hard to see how the density of the liquid passes, according to this equation, into that of the vapor. Let us write it

$$c_2\, d^2(1/V)/dh^2 = \psi' + pV - \mu_1 \tag{6.3}$$

where ψ' and p represent the values of these functions in a homogeneous phase of specific volume V. In Fig. 2 the course of ψ' is represented in the following way. If we place a tangent to the curve of ψ' the intercept on the axis of ψ' is equal to $\psi' + pV$, as in Eq. (6.3), where μ_1 is the intercept of the double tangent on the ψ' axis. On the liquid side of the transition layer we have $\psi' + pV = \mu_1$ and $d^2\rho/dh^2$ has therefore an initial value of zero. At larger volumes, and so smaller values of ρ, the function $\psi' + pV - \mu_1$ is negative. This holds true as long as we have not reached the volume for which $\psi' + pV - \mu_1$ has returned to zero. This volume can be found by drawing a tangent to the curve of ψ' from the point on the ψ' axis where it is cut by the double tangent. The point of tangency is necessarily on the unstable part of the isotherm. For larger volumes $\psi' + pV$ is always larger than μ_1; $d^2\rho/dh^2$ therefore remains positive until the density of the vapor is

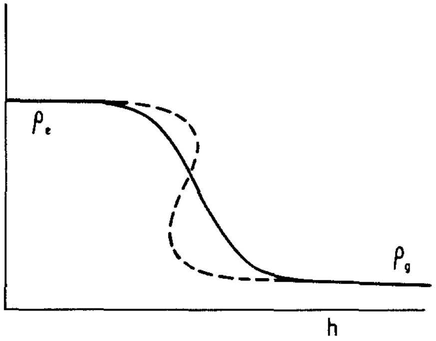

Fig. 3

reached, where it finally returns to zero. If we take the axis of h perpendicular to the transition layer, the density will be represented by a curve of very simple form—the full line in Fig. 3.

We could also have deduced this change of density by using Fig. 1. In this figure $\psi' + pV$ is the ordinate. It is true that the abscissa is now the pressure p, but since the course of the isotherm tells us the relation between p and V, or between p and ρ, this causes no problem. The value of μ_1 is the ordinate of point e in this figure. Starting from e and remaining on the liquid branch, we next reach point c. The quantity $\psi' + pV - \mu_1$ is negative in this interval and has its greatest negative value at point c, and similarly for $d^2\rho/dh^2$. If we now leave c on the unstable branch $\psi' + pV$ returns toward μ_1. The difference becomes zero at a point between c and b, which can be found by drawing a line parallel to the p axis through point e to cut the curve cb. At point b, the function $\psi' + pV - \mu_1$ reaches its greatest positive value; it is here therefore that we have the value of p, and hence of ρ, for which the curve $\rho = F(h)$ has the greatest value of $d^2\rho/dh^2$.

7. INVESTIGATION OF STABILITY

If the change of density in the transition layer is as described above, then there will be certain densities which would belong to the unstable state if they were to exist for a nonzero space; this is a necessary consequence of the hypothesis of a continuous change of density. If we can show the stability of such a distribution of density, it will follow that phases that would be unstable when distributed over a nonzero space can be stable when they become the transition between different densities.

We must look for the criterion of equilibrium in the sign of the expression $\delta^2 I$. If this expression be positive, the free energy is at a minimum when matter is distributed in the way described, and such a distribution should therefore be possible. For a variation, we have

$$\Delta I = \delta \int \rho \, dh \left\{ f(\rho) - \frac{c_2}{2} \frac{d^2\rho}{dh^2} - \mu_1 \right\} + \frac{1}{2} \delta^2 \int \rho \, dh \left\{ f(\rho) - \frac{c_2}{2} \frac{d^2\rho}{dh^2} - \mu_1 \right\} \tag{7.1}$$

while from (6.2) it follows that $\delta \int$ will be zero, so that the sign of ΔI will be that of the second term in (7.1). Let us write q for $d^2\rho/dh^2$ and henceforth drop the subscript 2 from c_2. That is,

$$I = \int dh \, \{\rho[f(\rho) - \mu_1] - \tfrac{1}{2} c_2 \rho q\}$$

$$\delta I = \int dh \, \{\delta\rho \, (\partial/\partial\rho)_{q=\text{const}}[\rho f(\rho) - \rho\mu_1 - \tfrac{1}{2} c\rho q] - \tfrac{1}{2} c\rho \, \delta q\}$$

$$\delta^2 I = \frac{1}{2} \int dh \left\{ (\delta\rho)^2 \frac{\partial^2 \rho f(\rho)}{\partial\rho^2} - c \, \delta\rho \, \delta q \right\}$$

Let us rewrite the second term as

$$-\tfrac{1}{2} c \int dh \, \delta\rho \, \delta q$$

Since

$$\delta q = \delta(d^2\rho/dh^2) = (d/dh)[\delta(d\rho/dh)]$$

we can write for this expression (dropping for the moment the factor $-c/2$),

$$\left[\delta\rho \, \delta\left(\frac{d\rho}{dh}\right) \right]_-^+ - \int \delta\left(\frac{d\rho}{dh}\right) \frac{d\delta\rho}{dh} \, dh$$

$$= \left[\delta\rho \, \delta\left(\frac{d\rho}{dh}\right) \right]_-^+ - \int d(\delta\rho) \frac{d\delta\rho}{dh}$$

$$= \left[\delta\rho \, \delta\left(\frac{d\rho}{dh}\right) \right]_-^+ - \left[\delta\rho \frac{d\delta\rho}{dh} \right]_-^+ - \int \delta\rho \, dh \frac{d^2\delta\rho}{dh^2}$$

The integrated terms cancel, $\delta \, d\rho/dh$ having the same value as $d\delta\rho/dh$. We have therefore

$$\delta^2 I = \frac{1}{2} \int dh \, \delta\rho \left\{ \frac{\partial^2[\rho f(\rho)]}{\delta\rho^2} \, \delta\rho - c \frac{d^2\delta\rho}{dh^2} \right\}$$

$$= \frac{1}{2} \int dh \, \delta\rho \left\{ \frac{\partial^2[\rho(f(\rho) - \mu_1)]}{\delta\rho^2} \, \delta\rho - c \frac{d^2\delta\rho}{dh^2} \right\}$$

while

$$\delta I = \int dh \, \delta\rho \left\{ \frac{\partial[\rho(f(\rho) - \mu_1)]}{\delta\rho} - c \frac{d^2\rho}{dh^2} \right\}$$

Now we can always find a set of values for $\delta\rho$ such that

$$\frac{\partial^2[\rho(f(\rho) - \mu_1)]}{\delta\rho^2}\,\delta\rho' = c\frac{d^2\delta\rho'}{dh^2}$$

and so for which $\delta^2 I = 0$.

Such a set of variations occurs if we displace the layer parallel to itself, while conforming to the law of variation of densities for the case of equilibrium, and at the same time letting $\delta\rho'$ be the variation of density occurring at each point.

That is, let $\rho = F(h)$, and let the variation δh be denoted by α; then $\delta\rho' = \alpha(d\rho/dh)$. The state of equilibrium of the layer satisfies the equation

$$\frac{\partial}{\partial\rho}[\rho(f(\rho) - \mu_1)] - c\frac{d^2\rho}{dh^2} = 0$$

and since, by differentiation of the equation of equilibrium

$$\frac{\partial^2}{\partial\rho^2}[\rho(f(\rho) - \mu_1)]\,d\rho = c\frac{d^2}{dh^2}\left\{\frac{d\rho}{dh}\right\}dh$$

we find also

$$\frac{\partial^2}{\partial\rho^2}[\rho(f(\rho) - \mu_1)]\alpha\frac{d\rho}{dh} = c\frac{d^2}{dh^2}\left\{\alpha\frac{d\rho}{dh}\right\}$$

or

$$\frac{\partial^2}{\partial\rho^2}[\rho(f(\rho) - \mu_1)]\,\delta\rho' = c\frac{d^2}{dh^2}(\delta\rho')$$

Such a set of variations can be imagined, but it does not satisfy the conditions of the problem, at least when we have liquid in the lower part of the vessel and vapor in the upper. In the second case, when we have vapor above and below a liquid membrane, this set is possible. By displacing the membrane we have therefore realized a state of neutral equilibrium; but even although this set of variations of ρ is now possible, we must, in order to examine the stability of a given density in the transition layer, consider also another set of variations $\delta\rho$, which we can represent by $t\,\delta\rho'$. We have then

$$\frac{d^2(\delta\rho)}{dh^2} = t\frac{d^2(\delta\rho')}{dh^2} + 2\frac{dt}{dh}\frac{d(\delta\rho')}{dh} + \delta\rho'\frac{d^2t}{dh^2}$$

which gives

$$\delta^2 I = \frac{1}{2}\int t\,\delta\rho'\,dh\left\{\frac{\partial^2[\rho(f(\rho) - \mu_1)]}{\delta\rho^2}t\,\delta\rho' - c\left(t\frac{d^2(\delta\rho')}{dh^2} + 2\frac{dt}{dh}\frac{d(\delta\rho')}{dh} + \delta\rho'\frac{d^2t}{dh^2}\right)\right\}$$

or, in a simpler form,

$$\begin{aligned}\delta^2 I &= -\frac{c}{2}\int t\,\delta\rho'\left\{2\frac{dt}{dh}\frac{d(\delta\rho')}{dh} + \delta\rho'\frac{d^2t}{dh^2}\right\}dh \\ &= -\frac{c}{2}\int t\left\{\frac{dt}{dh}\frac{d(\delta\rho')^2}{dh} + (\delta\rho')^2\frac{d^2t}{dh^2}\right\}dh \\ &= -\frac{c}{2}\int t\,dh\,\frac{d}{dh}\left[(\delta\rho')^2\frac{dt}{dh}\right]\end{aligned}$$

Integrating by parts,

$$\delta^2 I = -\left[\frac{c}{2}\,t(\delta\rho')^2\frac{dt}{dh}\right]_-^+ + \frac{c}{2}\int(\delta\rho')^2\left(\frac{dt}{dh}\right)^2 dh$$

The integrated terms, which we can write as $-(c/2)\,\delta\rho\,\delta\rho'\,(dt/dh)$, cancel at the limits, where the densities of the liquid and vapor are fixed, and it then becomes a simple matter to find the influence of any distribution of density in the transition layer. There remains only the term

$$\delta^2 I = \tfrac{1}{2}c\int(\delta\rho')^2(dt/dh)^2\,dh$$

This integral is positive since all its elements are squares. It is zero only if t is constant, but then we recover the parallel displacement already considered.

8. THE CONSTANCY OF THE PRESSURE, BOTH IN THE INTERIOR OF THE LIQUID AND THE VAPOR AND IN THE TRANSITION LAYER

We have obtained Eq. (6.2) for the state of equilibrium. If on the right we replace ρ by $1/V$, we have

$$-\int p\,dV + pV - \mu_1 = c\,d^2\rho/dh^2 \tag{8.1}$$

where p now represents the pressure of a homogeneous phase of specific volume V. By differentiation,

$$V\,dp = c\,d(d^2\rho/dh^2) \qquad \text{or} \qquad dp = c\rho\,d(d^2\rho/dh^2)$$

and by integration of the last equation

$$p + k = c\{\rho\,d^2\rho/dh^2 - \tfrac{1}{2}(d\rho/dh)^2\}$$

We can establish at once the meaning of the new constant k. In the middle of the liquid or of the vapor, where both $d\rho/dh$ and $d^2\rho/dh^2$ are zero, we have $p + k = 0$ or $k = -p_1$, where p_1 is the external pressure, which has therefore the property of being a constant throughout the whole extent of the vessel. We shall write henceforth for the transition layer

$$p_1 = p - c\{\rho\, d^2\rho/dh^2 - \tfrac{1}{2}(d\rho/dh)^2\} \tag{8.2}$$

and if we substitute for p from the equation of state, we have

$$p_1 = R\tau\left(\frac{1}{\rho} - b\right)^{-1} - a\rho^2 - c\left\{\rho\frac{d^2\rho}{dh^2} - \frac{1}{2}\left(\frac{d\rho}{dh}\right)^2\right\}$$

This last equation allows us to find the pressure when we know the density ρ and the values of $d\rho/dh$ and $d^2\rho/dh^2$ in a planar layer.

It follows that the pressure in a planar layer is independent of the sign of $d\rho/dh$, a result which could have been seen in advance, for the sign depends on the direction in which h is increasing, which can clearly have no effect on the pressure. The sign of $d^2\rho/dh^2$, on the contrary, is independent of the direction in which h is measured.

We can now calculate the value of $\epsilon - \tau_1\eta + p_1V$ which we need in order to find the capillary energy. Let us write

$$\epsilon - \tau_1\eta + p_1V = \epsilon - \tau_1\eta + pV + (p_1 - p)V$$

when the condition of equilibrium gives us, for the first terms,

$$\epsilon - \tau_1\eta + pV = \mu_1 + \tfrac{1}{2}c\, d^2\rho/dh^2$$

The last term $(p_1 - p)V = (p_1 - p)\rho^{-1}$ follows from (8.2), and so we have

$$\epsilon - \tau_1\eta + p_1V = \mu_1 + \frac{c}{2}\left\{\frac{1}{\rho}\left(\frac{d\rho}{dh}\right)^2 - \frac{d^2\rho}{dh^2}\right\}$$

Whether we take for the thermodynamic potential of the portions of fluid in the transition layer either $\epsilon - \tau_1\eta + pV$ or $\epsilon - \tau_1\eta + p_1V$, we cannot ascribe to it the constant value μ_1 found at any point in the vessel where $d\rho/dh$ and $d^2\rho/dh^2$ are zero. It is, however, this assumption that Gibbs makes when he deduces his fundamental equation (502), as he shows on p. 384 [p. 223]. However, his demonstration seems to me to contain an error of the same kind that we should have committed if, in the integral that also contains derivatives—in our case it has not only ρ but also $d^2\rho/dh^2$—we had considered variation with respect to ρ only, and neglected the necessary and consequent variation with respect to $d^2\rho/dh^2$. In my view, the fact that the potential $\epsilon - \tau_1\eta + p_1V$ is, on average, greater in the transition layer than in the homogeneous phases is just the reason for the existence of the capillary energy. Gibbs rectifies his error, it is true, by introducing the term $\sigma\, dS$ into Eq. (493), and so his Eq. (502) is perfectly correct; but he should have had other reasons for introducing the term $\sigma\, dS$, and it is, I think, the inequality of the thermodynamic potential which should have been his starting point.

9. CAPILLARY ENERGY

Let us consider a space where there is a constant pressure p_1 and a constant temperature τ_1, where, for example, there may be a liquid and its saturated vapor. Let us now divide in this space a portion of matter into a part of specific volume V_2, energy ϵ_2, and entropy η_2, and one of specific volume V_1, energy ϵ_1, and entropy η_1. If we have only to supply heat to bring about this new state, then

$$\epsilon_1 = \tau_1\eta_1 + p_1V_1 = \epsilon_2 - \tau_1\eta_2 + p_1V_2$$

This follows at once from the differential equation

$$d\epsilon = \tau_1\, d\eta - p_1\, dV$$

Since p_1 and τ_1 are constants, integration gives

$$\epsilon_1 - \epsilon_2 = \tau_1(\eta_1 - \eta_2) - p_1(V_1 - V_2)$$

If $(\epsilon_1 - \tau_1\eta_1 + p_1V_1) > (\epsilon_2 - \tau_1\eta_2 + p_1V_2)$, then in addition to the heat supplied, we must also furnish energy of a special kind, and so do an amount of work equal to the difference.

The case of a capillary layer is one where there is equilibrium notwithstanding an excess of $\epsilon - \tau_1\eta + p_1V$ in this layer over the value found in other parts of the system. If therefore, as before, ϵ, η, and V represent energy, entropy, and volume per unit mass, then

$$\sigma = \int \rho\, dh\, (\epsilon - \tau_1\eta + p_1V - \mu_1) \qquad (9.1)$$

is the capillary energy per unit surface. If S is the cross section of the vessel, then the capillary energy of the free surface of the liquid is σS.

Equation (9.1) is basically the same as Eq. (502) of Gibbs, as I shall now show. Gibbs' equation is written

$$\epsilon_E = \tau_1\eta_E + \sigma S + \mu_1 m_E$$

He introduces a surface of separation, which need not coincide with the surface of discontinuity, but which is parallel with this plane and at a very short distance from it.

The quantity ϵ_E is the excess of energy, in the transition layer, over that which we should find if, on both sides of the surface of separation, we chose an energy density near this surface equal to that found at a great distance; and similarly for η_E and m_E. The last quantity is therefore the excess of matter present in the surface layer over that found on the supposition above. Let ρ_1 and ρ_2 be the constant densities, ρ_1' and ρ_2' the real densities, ϵ_1 and ϵ_2 the constant energies per unit mass, ϵ_1' and ϵ_2' the real values, and similarly for the entropy. We have then

$$\epsilon_E = \int \epsilon_1'\rho_1'\,dh_1 + \int \epsilon_2'\rho_2'\,dh_2 - \int \epsilon_1\rho_1\,dh_1 - \int \epsilon_2\rho_2\,dh_2$$

$$\eta_E = \int \eta_1'\rho_1'\,dh_1 + \int \eta_2'\rho_2'\,dh_2 - \int \eta_1\rho_1\,dh_1 - \int \eta_2\rho_2\,dh_2$$

and so

$$\begin{aligned}\epsilon_E - \tau_1\eta_E = {} & \int \rho_1'\,dh_1\,(\epsilon_1' - \tau_1\eta_1') + \int \rho_2'\,dh_2\,(\epsilon_2' - \tau_1\eta_2') \\ & - \int \rho_1\,dh_1\,(\epsilon_1 - \tau_1\eta_1) - \int \rho_2\,dh_2\,(\epsilon_2 - \tau_1\eta_2)\end{aligned}$$

Let us add $\int p_1\,dh_1$ to the first positive and the first negative integrals, and similarly $\int p_1\,dh_2$ to the second positive and negative integrals. We do not change the value of the right-hand side and obtain

$$\begin{aligned}\epsilon_E - \tau_1\eta_E = {} & \int \rho_1'\,dh_1\,(\epsilon_1' - \tau_1\eta_1' + p_1V_1') \\ & + \int \rho_2'\,dh_2\,(\epsilon_2' - \tau_1\eta_2' + p_1V_2') - \mu_1\int \rho_1\,dh_1 - \mu_2\int \rho_2\,dh_2 \\ = {} & \int \rho_1'\,dh_1\,(\epsilon_1' - \tau_1\eta_1' + p_1V_1' - \mu_1) \\ & + \int \rho_2'\,dh_2\,(\epsilon_2' - \tau_1\eta_2' + p_1V_2' - \mu_1) \\ & + \mu_1\left\{\int \rho_1'\,dh_1 + \int \rho_2'\,dh_2 - \int \rho_1\,dh_1 - \int \rho_2\,dh_2\right\}\end{aligned}$$

The coefficient of μ_1 is what Gibbs calls m_E and, whatever the position of the surface of separation, the other integrals can be combined to give[5]

$$\int \rho\,dh\,(\epsilon - \tau_1\eta + p_1V - \mu_1)$$

We find therefore that

$$\epsilon_E = \tau_1\eta_E + S\int \rho\,dh\,(\epsilon - \tau_1\eta + p_1V - \mu_1) + \mu_1 m_E$$

---

[5] This and preceding quantities should be multiplied by S, the cross section of the vessel.

The definition of σ, as it follows from Gibbs' development, leads directly to the same function as the theory developed in this paper; that is, we arrive again at (9.1).

This integral should really be taken over the whole height of the vessel, but in practice we need to take into account only those points where $d\rho/dh$ and $d^2\rho/dh^2$ have a nonnegligible value. We have shown above that we can equally well write

$$\sigma = \frac{c}{2}\int dh\left\{\left(\frac{d\rho}{dh}\right)^2 - \rho\frac{d^2\rho}{dh^2}\right\}$$

However, the two terms in this integral are equal when we take the integration over the whole height of the layer:

$$\int\left(\frac{d\rho}{dh}\right)^2 dh = \int\frac{d\rho}{dh}\,d\rho = \left[\rho\frac{d\rho}{dh}\right]_-^+ - \int\rho\frac{d^2\rho}{dh^2}\,dh$$

At the limits we have $d\rho/dh = 0$. We can therefore write for σ either

$$\sigma = c\int(d\rho/dh)^2\,dh$$

or

$$\sigma = -c\int\rho(d^2\rho/dh^2)\,dh$$

However, all parts of the layer do not contribute to the capillary energy. Let us examine this point by writing (9.1) as

$$\sigma = \int\rho(\epsilon - \tau_1\eta + pV - \mu_1)\,dh + \int(p_1 - p)\,dh$$

or, from (6.2),

$$\sigma = \int\rho\,\tfrac{1}{2}c(d^2\rho/dh^2)\,dh + \int(p_1 - p)\,dh$$

Let ψ' and p be again the values of these functions in a homogeneous phase, so that from (6.1)

$$\sigma = \int dh\,\{p_1 - p + \tfrac{1}{2}\rho(\psi' + pV - \mu_1)\}$$

If σ comprised only the first term, $\int dh\,(p_1 - p)$, then all the layers whose densities are above that of the point where the empirical isotherm cuts the theoretical one on its unstable branch would contribute positively to the integral, while, conversely, all layers of lower densities would contribute negatively. The addition of the second term, however, brings the limit where the positive values pass the negative nearer to the side of the lower densities. At the start of the layer $(p_1 - p) + (\psi' + pV - \mu_1)/2V$ is zero. Let us return to Fig. 1; the maximum value is on the unstable branch a little above c. For a point at the height of e on the unstable branch, we have $\psi' + pV - \mu_1 = 0$; but since $p_1 - p$ is still positive, we have not yet reached the point where we pass into the region of negative values. At a point vertically above e we have $p_1 - p = 0$, but here $\psi' + pV - \mu_1$ is positive, so this is again not the point at which the change is reached. At the extreme value of h the value is zero, as at the start. But it is easy to show that the value is negative at a short distance from this limit. We have

$$d\left\{p_1 - p + \frac{1}{2}\frac{\psi' + pV - \mu_1}{V}\right\} = -\frac{1}{2}\left\{dp + \frac{\psi' + pV - \mu_1}{V^2}\,dV\right\}$$

since $d(\psi' + pV - \mu_1) = V\,dp$.

It follows from the theoretical isotherm that the value of p is decreasing here, and since $\psi' + pV - \mu_1$ can be neglected, that differential $(-\frac{1}{2}dp)$ is positive. That is, in its limiting behavior the function is increasing, and since its final value is zero, it must be negative at a small distance short of the limit. The meaning of all this is that those layers that we can think of as expanded liquid contribute to the capillary energy, while those that we think of as compressed gas diminish this energy. No doubt this rule is quite general. Thus a gaseous layer, condensed on a solid boundary, diminishes the capillary energy of the surface layer.

10. CAPILLARITY FOR A SPHERE

It is worthwhile for several reasons to solve the capillary problem for cases other than that of a mass bounded by a plane surface. Let us choose, for example, a spherical mass, so that we can remove all considerations of gravity from the problem.

It is of interest to see how the capillary pressure comes into play under these conditions, and how far the properties of a spherical surface layer differ from those of a planar layer. We can then decide how far we are justified in considering, as we usually do, that the two cases have equal energies per unit surface. Let us take a spherical mass in a vessel of the same shape and with the same center; the density can then be taken to be constant throughout any spherical layer. The only difficulty is the calculation of ϵ for unit mass at a point in the surface.

To do this let us calculate the force exerted by unit mass toward the center when this mass is in a layer of variable density at a distance R from the center (compare the method of calculation in Section 5). A plane layer perpendicular to the radius R exerts an attraction

$$\int_{r=u}^{r=\infty} \rho 2\pi u\, du\, \varphi(r)\, dr$$

where u is the distance of the unit mass above this layer. Let P be the foot of the perpendicular and Q an arbitrary point in the planar layer. Integrating by parts, we find for the attraction

$$2\pi u\, du\left\{\rho_P \zeta(u) + \int_{r=u}^{r=\infty} \zeta(r)\, dr\, \frac{d(\rho_Q)}{dr}\right\}$$

Now we can put $(d\rho_Q/dR_Q)(dR_Q/dr)$ for $d\rho_Q/dr$, and since

$$R_Q{}^2 = (R-u)^2 + r^2 - u^2 = R^2 - 2uR + r^2$$

we have also $dR_Q/dr = r/R_Q$ or $d\rho_Q/dr = (d\rho_Q/dR_Q)(r/R_Q)$. If we are content with the same degree of approximation to which we have restricted ourselves in the case of plane layers, that is, if we neglect all coefficients above c_2, we can put $d\rho_Q/dR_Q = d\rho_P/dR_P$, and equate the attraction of the layer to

$$2\pi u\, du\left\{\zeta(u)\rho_P + \int_{r=u}^{r=\infty} \zeta(r)\, \frac{r}{R_P}\, \frac{d(\rho_P)}{dR_P}\, dr\right\}$$

or

$$2\pi u\, du\, \zeta(u)\rho_{R-u} + \frac{u\psi(u)}{R_P}\, du\, \frac{d(\rho_{R-u})}{dR_P}$$

Subtract from this the value of the force of attraction exerted upward by a layer, namely

$$2\pi u\, du\, \zeta(u)\rho_{R+u} + \frac{u\psi(u)}{R_P}\, du\, \frac{d(\rho_{R+u})}{dR_P}$$

to give the force directed toward the center

$$\begin{aligned} f(R) &= \int_0^\infty -d\psi(u)\,\{\rho_{R-u} - \rho_{R+u}\} \\ &\quad + \int_0^\infty u\psi(u)\, du\left\{\frac{1}{R_P}\frac{d(\rho_{R-u})}{dR_P} - \frac{1}{R_P}\frac{d(\rho_{R+u})}{dR_P}\right\} \\ &= \int_0^\infty \psi(u)\, du\, \frac{d(\rho_{R-u} - \rho_{R+u})}{du} \\ &\quad + \int_0^\infty u\psi(u)\, du\, \frac{1}{R_P}\, \frac{d(\rho_{R-u} - \rho_{R+u})}{dR_P} \end{aligned}$$

In the first integral we can restrict $(d/du)(\rho_{R-u} - \rho_{R+u})$ to the two terms $-(2\,d\rho_R/dR + u^2\,d^3\rho_R/dR^3)$. Since

$$\frac{1}{R_P}\frac{d(\rho_{R+u})}{dR_P} = \frac{1}{R}\frac{d\rho_R}{dR} + u\left(\frac{1}{R}\frac{d^2\rho_R}{dR^2} - \frac{1}{R^2}\frac{d\rho_R}{dR}\right) + \cdots$$

we can replace

$$\frac{1}{R_P}\frac{d}{dR_P}(\rho_{R-u} - \rho_{R+u}) \qquad \text{by} \qquad -u\left(\frac{2}{R}\frac{d^2\rho_R}{dR^2} - \frac{2}{R^2}\frac{d\rho_R}{dR}\right)$$

We then have

$$f(R) = -\left\{\left(2a - \frac{2c}{R^2}\frac{d\rho}{dR} + c\frac{d^3\rho}{dR^3} + \frac{2c}{R}\frac{d^2\rho}{dR^2}\right\}\right.$$

and the value of ϵ becomes

$$\epsilon = C - a\rho - \frac{c}{2}\frac{d^2\rho}{dR^2} - \frac{c}{R}\frac{d\rho}{dR}$$

The conditions of equilibrium are now given by the equation

$$\delta I = \delta\int 4\pi R^2\,dR\,\rho\left\{f(\rho) - \mu_1 - \frac{c}{R}\frac{d\rho}{dR} - \frac{c}{2}\frac{d^2\rho}{dR^2}\right\}$$

After reduction, the coefficient of $\delta\rho$, which must be equal to zero, can be expressed

$$f(\rho) + \rho\frac{\partial f}{\partial\rho} - c\frac{d^2\rho}{dR^2} - \frac{2c}{R}\frac{d\rho}{dR} - \mu_1 = 0$$

[The integrated terms require that $d\rho/dR$ and $\delta(d\rho/dR)$ vanish at the limits.]

In this case also we see that where there is a uniform density, and so where $d\rho/dR$ and $d^2\rho/dR^2$ are zero, we must have $f(\rho) + \rho\,df/d\rho = \mu_1$; that is to say, the value of this function must be the same at all such points. If therefore we assume that the liquid is placed in the middle and the vapor at the outside of the vessel, we shall have

$$\epsilon_l - \tau_1\eta_l + p_l V_l = \epsilon_v - \tau_1\eta_v + p_v V_v$$

However, the values of p_l and p_v are no longer equal, as is the case for a planar boundary surface. To find the relation between these two quantities we can choose between two different routes. First, we can differentiate the equation of equilibrium,

$$f(\rho) + \rho\frac{\partial f}{\partial\rho} - \mu_1 = c\frac{d^2\rho}{dR^2} + \frac{2c}{R}\frac{d\rho}{dR} \tag{10.1}$$

that is (cf. Section 8)

$$-\int p\,dV + pV - \mu_1 = c\frac{d^2\rho}{dR^2} + \frac{2c}{R}\frac{d\rho}{dR}$$

It follows then that

$$V\,dp = c\,d\left(\frac{d^2\rho}{dR^2}\right) + 2c\,d\left(\frac{1}{R}\frac{d\rho}{dR}\right)$$

We obtain by integration

$$p + k = c\left\{\rho\frac{d^2\rho}{dR^2} - \frac{1}{2}\left(\frac{d\rho}{dR}\right)^2\right\} + 2c\frac{\rho}{R}\frac{d\rho}{dR} - 2c\int\frac{dR}{R}\left(\frac{d\rho}{dR}\right)^2$$

Let us now consider two points, one inside the transition layer—and so, on our hypothesis, in the homogeneous liquid—and at distance R_1 from the center. Let the pressure at this place be p_l. The other point is outside the transition layer, that is, in the vapor at a distance R_2 and with a pressure p_v. We can write

$$p_l - p_v = 2c\int_{R_1}^{R_2}\frac{1}{R}\left(\frac{d\rho}{dR}\right)^2 dR$$

Had we assumed that the vapor had been at the center and the liquid on the outside, then we should have found that the pressure inside exceeded that outside by

$$\int_{R_1}^{R_2}\frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR$$

where the integral is taken through the whole thickness of the transition layer.

As for a plane surface, let σ denote

$$c\int_{R_1}^{R_2}(d\rho/dR)^2\,dR$$

which we shall shortly examine more closely, and let us ignore the small variation in R arising from the nonzero thickness of the transition layer. Then

$$p_l = p_v + 2\sigma/R$$

This is the well-known formula of the usual theory of capillarity.

If the liquid is in the middle of the vessel and the vapor around the outside, then $\epsilon - \tau_1\eta + pV$ is the same in the two homogeneous phases; but since the pressure is different—that of the liquid exceeding that of the vapor—the state of both the saturated vapor and the liquid differ from those found for a planar surface. Figure 1 allows us to determine the states of the phases under these conditions. We merely draw a short line parallel to the p axis, with one of its ends resting on the branch describing the state of the vapor and the other on that of the liquid, and of a length equal to the difference of pressure. Since the pressure of the liquid is greater than that of the vapor, this line lies above point e. We see therefore that both vapor and liquid are in compressed states. In the opposite case, when the vapor is in the middle and the liquid in the outer part of the vessel, the small line lies below point e, and the state of the two phases is reversed.

In the first case the excess of the pressure of the vapor over the normal saturated vapor pressure Δp_v can be found as follows:

$$\Delta(\psi' + pV) = \Delta p_l/\rho_l = \Delta p_v/\rho_v$$

Now $\Delta p_l = 2\sigma/R + \Delta p_v$ and so

$$\Delta p_v = \frac{\rho_v}{\rho_l - \rho_v}\frac{2\sigma}{R}$$

Conversely, when the vapor is in the middle and the liquid on the outside, we have $\Delta p_v = -[\rho_v/(\rho_l - \rho_v)]2\sigma/R$. These results are known, but have been derived here in a novel way.

We can now determine the function p in a second way by integrating the equation of equilibrium with respect to ρ.

From Eq. (10.1) we deduce that

$$\rho(\psi' + pV - \mu_1) - \int_{p_l}^{p} dp = \frac{c}{2}\left(\frac{d\rho}{dR}\right)^2 + \int_{R_1}^{R} \frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR$$

or, when the second point is placed in the homogeneous region,

$$p_l - p_v = \int \frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR$$

The first deduction gives us the value of p at a point in the transition layer

$$p - p_l = c\left\{\rho\frac{d^2\rho}{dR^2} - \frac{1}{2}\left(\frac{d\rho}{dR}\right)^2 + \right\}\frac{2c\rho}{R}\frac{d\rho}{dR} - \int_{R_1}^{R} \frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR$$

or

$$p - \left\{p_l - \int_{R_1}^{R} \frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR\right\} = c\left\{\rho\frac{d^2\rho}{dR^2} - \frac{1}{2}\left(\frac{d\rho}{dR}\right)^2 + \frac{2\rho}{R}\frac{d\rho}{dR}\right\}$$

The question now arises as what we must consider to be the pressure in an arbitrarily chosen layer. It is the quantity p_s, where

$$p_s = p_l - \int_{R_1}^{R} \frac{2c}{R}\left(\frac{d\rho}{dR}\right)^2 dR \qquad (10.2)$$

On introducing the equation of state, we get

$$p_s = R\tau\left(\frac{1}{\rho} - b\right)^{-1} - a\rho^2 - c\left\{\rho\frac{d^2\rho}{dR^2} - \frac{1}{2}\left(\frac{d\rho}{dR}\right)^2 + \frac{2\rho}{R}\frac{d\rho}{dR}\right\} \tag{10.3}$$

The term we have subtracted from p_l to give the true pressure in (10.2) does not disappear when we make $d\rho/dR$ and $d^2\rho/dR^2$ vanish in the layer itself. On the contrary, it represents the sum of all contributions from distant layers that can be thought of as influencing the pressure. Now the true pressure in a layer should be determined by the state in that layer, that is, by ρ, $d\rho/dR$, and $d^2\rho/dR^2$; and it is just this that Eq. (10.3) expresses. Equation (10.2) gives the pressure at a point in the layer as a function of that at a distant point and the density changes that lie between these points, while Eq. (10.3) expresses it as a function of the properties at the point in question. We have to examine first what we must take the external pressure to be, before being able to find an expression for the capillary energy per unit surface of a spherical mass.

To obtain the energy of the whole layer we must determine

$$\int 4\pi R^2\, dR\, \rho\{\epsilon - \tau_1\eta + p_s V - \mu_1\}$$

If we write

$$\epsilon - \tau_1\eta + p_s V - \mu_1 = \epsilon - \tau_1\eta + pV - \mu_1 + (p_s - p)V$$

if we remember that

$$\epsilon - \tau_1\eta + p_l V = f(\rho) + \rho\frac{\partial f}{\partial\rho} - \frac{c}{R}\frac{d\rho}{dR} - \frac{c}{2}\frac{d^2\rho}{dR^2}$$

and use again (10.1), then we shall have

$$\epsilon - \tau_1\eta + pV - \mu_1 = \frac{c}{R}\frac{d\rho}{dR} + \frac{c}{2}\frac{d^2\rho}{dR^2}$$

On using the equation

$$p_s - p = -c\left\{\rho\frac{d^2\rho}{dR^2} - \frac{1}{2}\left(\frac{d\rho}{dR}\right)^2 + \frac{2\rho}{R}\frac{d\rho}{dR}\right\}$$

we obtain

$$\int 4\pi R^2\, dR\, \rho(\epsilon - \tau_1\eta + p_s V - \mu_1) = c\int 4\pi R^2\, dR\left\{\left(\frac{d\rho}{dR}\right)^2 - \frac{1}{2R^2}\frac{d}{dR}\left(R^2\rho\frac{d\rho}{dR}\right)\right\}$$

The terms that comprise this integral vanish in all parts of the space where $d\rho/dR$ is zero; hence it is zero for both homogeneous liquid and vapor. In the capillary layer, since $R^2\rho\, d\rho/dR$ vanishes at the limits, its value becomes

$$c\int 4\pi R^2(d\rho/dR)^2\, dR$$

If we neglect the variation in R, the layer having a finite thickness, then the energy per unit surface is

$$\sigma = c\int (d\rho/dR)^2\, dR$$

In the case of a planar layer we determine ρ as a function of h from Eq. (6.1), while for a spherical surface

$$\frac{c}{R^2}\frac{d}{dR}\left(R^2\frac{d\rho}{dR}\right) = f(\rho) + \rho\frac{\partial f}{\partial\rho} - \mu_1$$

Since R is large relative to the thickness of the layer, we can treat this difference of form as quite insignificant.

11. VALUE OF THE CAPILLARY ENERGY NEAR THE CRITICAL TEMPERATURE

In the expression

$$\sigma = c\int (d\rho/dh)^2\, dh = c\int_{\rho_v}^{\rho_l} (d\rho/dh)\, d\rho$$

we can replace $d\rho/dh$ by a function of ρ of the kind we have deduced above (Section 6). If the integration is then possible, we shall obtain σ as a function of the two coexistent densities ρ_l and ρ_v. We need therefore the value of $d\rho/dh$, and this we can get from Eqs. (8.1) and (8.2).

On introducing the equation of state into (8.1) we obtain

$$c\frac{d^2\rho}{dh^2} = \frac{p}{\rho} - R\tau_1 \ln\left(\frac{1}{\rho} - b\right) - a\rho - \mu_1$$

and so we can obtain $d\rho/dh$ from (8.2). We thus find for σ,

$$\sigma = (2c)^{1/2}\int_{\rho_v}^{\rho_l} d\rho\left\{p_1 - \mu_1\rho - a\rho^2 - R\tau_1\rho\ln\left(\frac{1}{\rho} - b\right)\right\}^{1/2}$$

This result allows us to obtain at once a general property of σ, even without being able to carry out the integration. The terms under the root are necessarily of the same dimensions. Consider the term $a\rho^2$; its integral will have the dimensions of $\rho^2 a^{1/2}$, and so contribute to σ a term $k\rho_l^2(ac)^{1/2}$, where k is a numerical coefficient.

According to the theory of Laplace we have $\sigma = c_1 \cdot \frac{1}{2}(\rho_l - \rho_v)^2$, or $\sigma = k'\rho_l{}^2 c_1$. Since the radius of the sphere of attraction enters as a square root in our calculation of σ, we can deduce that it has a size similar to that which follows from Laplace's theory. That is, the values of c_1 and $(ac)^{1/2}$ are of the same order of magnitude.

Although we cannot in general calculate the integral σ, we can determine its value near the critical temperature with sufficient accuracy. To this end, let us write

$$\sigma = (2c)^{1/2} \int_{V_l}^{V_v} \frac{dV}{V^{5/2}} \left\{ p(V - V_l) - \int_{V_l}^{V} p \, dV \right\}^{1/2}$$

and replace p and V by ϵp_k and nV_k, where p_k and V_k are the critical values of p and V. We find

$$\sigma = \left(\frac{2cp_k}{V_k{}^2} \right)^{1/2} \int_{n_1}^{n_2} \frac{dn}{n^{5/2}} \left\{ \epsilon_1 (n - n_1) - \int_{n_1}^{n} \epsilon \, dn \right\}^{1/2}$$

We may expand the function

$$f(n) = \epsilon_1 (n - n_1) - \int_{n_1}^{n} \epsilon \, dn$$

in powers of $(n - n_1)$ by means of Taylor's theorem. Now it is evident that $f(n_1) = 0$, and since $f'(n) = \epsilon_1 - \epsilon$, we have also $f'(n_1) = 0$. Furthermore, $f''(n) = -\partial\epsilon/\partial n$, $f'''(n) = -\partial^2\epsilon/\partial n^2$, etc., and so

$$f(n) = -(n - n_1)^2 \left\{ \frac{1}{2!} \left(\frac{\partial \epsilon}{\partial n} \right)_1 + \frac{n - n_1}{3!} \left(\frac{\partial^2 \epsilon}{\partial n^2} \right)_1 + \frac{(n - n_1)^2}{4!} \left(\frac{\partial^3 \epsilon}{\partial n^3} \right)_1 \cdots \right\}$$

Near the critical point $(\partial\epsilon/\partial n)_1$ and $(\partial^2\epsilon/\partial n^2)_1$ are small, since they vanish at the critical point itself. We can therefore see at once that we must retain three terms in the series which multiplies $(n - n_1)^2$, but that higher terms can be neglected, at least when $n - n_1$ remains small. If we retain the three terms shown with their coefficient $(n - n_1)^2$, then we can see that the series is a square. When solved as an equation of second degree, it should naturally give n_2 as a root. It follows that since $f(n)$ contains $(n - n_1)^2$ as a factor, then equally it will contain $(n - n_2)^2$. But we can also show this directly without recourse to this argument by considering that, for $n = n_2$, ϵ must take the value ϵ_1. Let us expand

$$\epsilon = \epsilon_1 + (n - n_1) \left(\frac{\partial \epsilon}{\partial n} \right)_1 + \frac{(n - n_1)^2}{2!} \left(\frac{\partial^2 \epsilon}{\partial n^2} \right)_1 + \frac{(n - n_1)^3}{3!} \left(\frac{\partial^3 \epsilon}{\partial n^3} \right)_1$$

and putting $\epsilon = \epsilon_1$ and $n = n_2$ (liquid pressure = vapor pressure), then

$$\left(\frac{\partial \epsilon}{\partial n} \right)_1 + \frac{n_2 - n_1}{2!} \left(\frac{\partial^2 \epsilon}{\partial n^2} \right)_1 + \frac{(n_2 - n_1)^2}{3!} \left(\frac{\partial^3 \epsilon}{\partial n^3} \right)_1 = 0$$

By comparing this equation with $f(n_2) = 0$ (Maxwell's theorem), that is,

$$\frac{1}{2!}\left(\frac{\partial\epsilon}{\partial n}\right)_1 + \frac{n_2 - n_1}{3!}\left(\frac{\partial^2\epsilon}{\partial n^2}\right)_1 + \frac{(n_2 - n_1)^2}{4!}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1 = 0 \qquad (11.1)$$

we find

$$\left(\frac{\partial\epsilon}{\partial n}\right)_1 = \frac{1}{12}(n_2 - n_1)^2\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1$$

$$\left(\frac{\partial^2\epsilon}{\partial n^2}\right)_1 = -\frac{1}{2}(n_2 - n_1)\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1$$

and so can verify easily the statement above.

We find therefore that

$$f(n) = -\frac{1}{4}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1 (n - n_1)^2(n_2 - n)^2$$

and so

$$\sigma = \left(\frac{2cp_k}{V_k^2}\right)^{1/2}\left[-\frac{1}{4!}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1\right]^{1/2}\int_{n_1}^{n_2}\frac{dn}{n^{5/2}}(n - n_1)(n_2 - n)$$

Now at the critical point n becomes unity, and if we stay close to the critical temperature, n_1 is smaller than unity and n_2 greater. So we can achieve an adequate approximation by putting $n = 1$ in the denominator and $n = n_1 + \Delta$ in the numerator. The integral then becomes

$$\int_0^{n_2 - n_1} d\Delta \cdot \Delta[(n_2 - n_1) - \Delta]$$

and its value is $\frac{1}{6}(n_2 - n_1)^3$.

Hence

$$\sigma = \left(\frac{2cp_k}{V_k^2}\right)^{1/2}\left[-\frac{1}{4!}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1\right]^{1/2}\frac{(n_2 - n_1)^3}{6}$$

If we can equate $(\partial^3\epsilon/\partial n^3)_1$ to -9, its value at the critical point from the equation of state, this expression becomes

$$\sigma = \left(\frac{2cp_k}{V_k^2}\right)^{1/2}\left(\frac{3}{8}\right)^{1/2}\frac{(n_2 - n_1)^3}{12}$$

or, putting $a\rho_k^2/3$ for p_k,

$$\sigma = (ca)^{1/2}\rho_k^2[(n_2 - n_1)^3/12] \qquad (11.2)$$

From Laplace's theory we have

$$\sigma = \rho_k^2\int u\psi(u)\,du\,\tfrac{1}{2}(n_2 - n_1)^2 \qquad (11.3)$$

Let us consider

$$(ac)^{1/2} = \left\{ \int \psi(u)\,du \int u^2\psi(u)\,du \right\}^{1/2}$$

which is of the same order of magnitude as $\int u\psi(u)\,du$. Then whenever $n_2 - n_1$ is not itself very small, we shall obtain about the same value for the capillary energy σ from either of the last two equations (11.2) or (11.3), without having to choose any particular size for the radius of the sphere of attraction. The only difference is that in Laplace's theory the capillary energy near the critical temperature is proportional to the square of the difference of density of liquid and vapor, while the thermodynamic theory, with the hypothesis of a continuous density transition, shows that this energy is proportional to the cube of these differences.

From the result $\sigma = \frac{1}{12}(ca)^{1/2}\rho_k{}^2(n_2 - n_1)^3$ we can deduce how σ behaves as a function of τ, at least in the neighborhood of τ_k, since we know how $n_2 - n_1$ depends on the temperature. Mathias[6] has given empirical formulas for the liquid and vapor densities which we could use here, but since we have followed a strictly theoretical path so far, it is important to examine the extent to which theory can lead to these experimentally verified formulas.

We have shown above that (11.1) is a perfect square, and so

$$\frac{4}{2!}\left(\frac{\partial\epsilon}{\partial n}\right)_1 \frac{1}{4!}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1 = \left\{\frac{1}{3!}\left(\frac{\partial^2\epsilon}{\partial n^2}\right)_1\right\}^2$$

This equation should hold true as long as we remain in the *immediate* neighborhood of the critical temperature.

The quantities $(\partial\epsilon/\partial n)_1$, etc., do not have the values they possess at the critical point, but those that belong to $n_k + dn$ and $m_k + dm$, where $\tau = m\tau_k$. If the state denoted by the index 1 is the liquid, then dn and dm are negative. By expanding $\partial\epsilon/\partial n$, etc., we find

$$\left(\frac{\partial\epsilon}{\partial n}\right)_1 = \left(\frac{\partial\epsilon}{\partial n}\right)_k + \left(\frac{\partial^2\epsilon}{\partial n\,\partial m}\right)_k dm + \left(\frac{\partial^2\epsilon}{\partial n^2}\right)_k dn$$
$$+ \frac{1}{2}\left\{\left(\frac{\partial^3\epsilon}{\partial n\,\partial m^2}\right)_k dm^2 + 2\left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k dm\,dn + \left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k dn^2\right\}$$

$$\left(\frac{\partial^2\epsilon}{\partial n^2}\right)_1 = \left(\frac{\partial^2\epsilon}{\partial n^2}\right)_k + \left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k dm + \left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k dn$$

$$\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_1 = \left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k$$

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[6] *Ann. de Toulouse* 5:1 (1891).

We thus obtain a relation between dn and dm by noting that $(\partial\epsilon/\partial n)_k$ and $(\partial^2\epsilon/\partial n^2)_k$ are zero:

$$\frac{4}{2!}\,\frac{1}{4!}\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k\left\{\left(\frac{\partial^2\epsilon}{\partial n\,\partial m}\right)_k dm\right.$$
$$\left.+\frac{1}{2}\left[\left(\frac{\partial^3\epsilon}{\partial n\,\partial m^2}\right)_k dm^2+2\left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k dm\,dn+\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k dn^2\right]\right\}$$
$$=\left(\frac{1}{3!}\right)^2\left\{\left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k dm+\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k dn\right\}^2$$

The solution of this equation in dn shows that dn^2 and dm are of the same degree of smallness; we can therefore neglect the term in dm^2 by comparison with that in dm. We have therefore

$$\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k dn^2+2\left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k dn\,dm+6\left(\frac{\partial^2\epsilon}{\partial n\,\partial m}\right)_k dm=0$$

when

$$dn=\left(\frac{\partial^3\epsilon}{\partial n^2\,\partial m}\right)_k\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k^{-1} dm\pm\left\{-6\,dm\left(\frac{\partial^2\epsilon}{\partial n\,\partial m}\right)_k\left(\frac{\partial^3\epsilon}{\partial n^3}\right)_k^{-1}\right\}^{1/2}$$

The negative value of dn is therefore $a\alpha\,dm-\beta(-dm)^{1/2}$, where α and β represent the coefficients. The positive or vapor value is $-\alpha\,dm+\beta(-dm)^{1/2}$, or, replacing $-dm$ by $1-m$ and dn by n_l-n_k,

$$n_l-n_k=\alpha(1-m)-\beta(1-m)^{1/2}$$

and

$$n_v-n_k=\alpha(1-m)+\beta(1-m)^{1/2}$$

or

$$n_v-n_l=n_2-n_1=2\beta(1-m)^{1/2}$$

If we introduce this value of n_2-n_1 into the expression for σ, it becomes

$$\sigma=\frac{2}{3}(ac)^{1/2}\rho_k{}^2\beta^3\left(\frac{\tau_k-\tau}{\tau_k}\right)^{3/2}$$

The value of β implied by the equation of state $\epsilon=8m/(3n-1)-3/n^2$ is found to be 2. The equation of state $\epsilon=8m/(3n-1)-3/mn^2$ or $\epsilon=8m/(3n-1)-3[\exp(1-m)]/m^2$ (van Laar) would make it $2\sqrt{2}=2.83$. The empirical formula of Mathias, for which the coefficients have been calculated to give good agreement down to $m=0.8$, leads to rather larger a value, which we can fix at about 3.5. It follows from the form of the temperature coefficient of σ, that is, of $[(\tau_k-\tau)/\tau_k]^{3/2}$, that not only does σ vanish at the critical temperature—a consequence which should naturally follow from all theories—but also that $d\sigma/d\tau$ is zero at that temperature.

When therefore σ is represented as a function of τ the curve touches that τ axis at $\tau = \tau_k$, while it follows from Eq. (11.3) that this curve cuts the τ axis at an acute angle.[7]

12. THE DIMENSIONS OF THE CAPILLARY LAYER

The equation

$$\left(\frac{c}{2}\right)^{1/2} \frac{d\rho}{dh} = \left\{p_1 - \mu_1\rho - a\rho^2 - R\tau\rho \ln\left(\frac{1}{\rho} - b\right)\right\}^{1/2}$$

can be considered to be a differential equation for determining h. Let us therefore reduce it to the form

$$dh = (c/2)^{1/2} V_k^{-1} p_k^{-1/2} n^{-3/2} \left[\epsilon_1(n - n_1) - \int_{n_1}^{n} \epsilon \, dn\right]^{-1/2} dn$$

or, near τ_k, to

$$dh = \left(\frac{c}{2}\right)^{1/2} V_k^{-1} p_k^{-1/2} \left[-\frac{1}{4!}\left(\frac{\partial^3 \epsilon}{\partial n^3}\right)_k\right]^{-1/2} n^{-3/2}(n - n_1)^{-1}(n_2 - n)^{-1} \, dn$$

$$= 2\left(\frac{\int u^2\psi(u) \, du}{\int \psi(u) \, du}\right)^{1/2} n^{-3/2}(n - n_1)^{-1}(n_2 - n)^{-1} \, dn$$

Let us take

$$\int u^2\psi(u) \, du = u_1{}^2 \int \psi(u) \, du$$

where u_1 is comparable with the radius of the sphere of attraction. We have then

$$h = 2u_1 \int_{n_1}^{n_2} \frac{dn}{n^{3/2}(n - n_1)(n_2 - n)}$$

and it follows at once that h will be large compared with n_1.[8] For maximum simplicity we take the factor $n^{3/2}$ equal to unity in making the integration,

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[7] This is consistent with the observations of E. C. de Vries (Metingen over den invloed der temperatuur etc., Proefschrift, Leiden, 1893), to which Prof. Kamerlingh Onnes has drawn my attention, where the author confirms the first form of the curve that I have developed in this theory, which had indeed already been implicit in my train of thought in 1888. The figures reported by de Vries on p. 47, in the column headed CH, do not, it is true, agree with $[(\tau_k - \tau)/\tau_k]^{3/2}$, but with an exponent that can be found to be about 1.23, increasing slowly as one approaches more closely to the critical temperature.

[8] If we accept the law $\psi(u) = \exp(-u/\lambda)$, where λ is a constant (see Section 15), then $u_1 = \lambda\sqrt{2}$. If we make certain assumptions, we find that for ether $\lambda = 1.74 \times 10^{-8}$ cm and $u_1 = 2.46 \times 10^{-8}$ cm. [This form of intermolecular potential was discussed in detail in Appendix 5 of the original paper.]

and put the limits equal to n_2' and n_1' in order to avoid a difficulty that becomes apparent at once. We have then

$$h = \frac{2u_1}{n_2 - n_1} \ln\left[\frac{n_2' - n_1}{n_2 - n_2'} \frac{n_2 - n_1'}{n_1' - n_1}\right]$$

If we now let the limits coincide with n_2 and n_1, then h becomes infinite; however, it does not seem to me that this result invalidates the present theory. Let us take n_2' and n_1' so close to n_2 and n_1 that they would be experimentally indistinguishable from them, e.g., $n_1' - n_1 = n_2 - n_2' = 10^{-6}(n_2 - n_1)$; then

$$h = 2u_1(n_2 - n_1)^{-1} \ln(10^{12})$$

Thus at temperatures where $n_2 - n_1$ is a small fraction, e.g., 1/10, h will still, for these limits, be less than 600 times u_1. It is only when $h = 2000u_1$ that we reach a value equal to that of the wavelength of visible light. Now the temperature at which $n_2 - n_1 = 1/10$ is very close to the critical. The fact that, for the limits chosen above, the value of h must become infinite when $n_2 - n_1 = 0$ is not a problem. We have, it is true, a layer of infinite thickness, but its properties do not differ from those of the vapor and the liquid at the same limit. We can conclude from this that the thickness of the layer increases with rising temperature.

13. THERMAL PROPERTIES OF THE CAPILLARY LAYER

Let us consider a vessel containing a liquid and vapor, the liquid being bounded by a plane surface, e.g., a taut membrane of liquid. There will be the same pressure everywhere in the vessel; let this be p, and let the temperature be τ.

Let m_1 be again the mass of the liquid, ϵ_1 the energy of this mass, etc. The following equations apply to the three masses:

$$\epsilon_1 - \tau\eta_1 + pV_1 = m_1\mu_1$$

$$\epsilon_2 - \tau\eta_2 + pV_2 = m_2\mu_1$$

$$\epsilon_s - \tau\eta_s + pV_s = m_s\mu_1 + \sigma S$$

Suppose that there is a small change; then we shall have

$$d\epsilon_1 - \tau\, d\eta_1 + p\, dV_1 = \mu_1\, dm_1$$

$$d\epsilon_2 - \tau\, d\eta_2 + p\, dV_2 = \mu_1\, dm_2$$

$$d\epsilon_s - \tau\, d\eta_s + p\, dV_s = \mu_1\, dm_s + \sigma\, dS$$

If the total amount of matter is unchanged, then $dm_1 + dm_2 + dm_s = 0$, and similarly if there is no change of volume, $dV_1 + dV_2 + dV_s = 0$. Then

$$dE - \tau\, d\eta = \sigma\, dS \qquad \text{or} \qquad \tau\, d\eta = dE - \sigma\, dS$$

where E and η are the total energy and entropy in the vessel. If we compare this with the equation

$$\tau\, d\eta = dE + p\, dV$$

then we can conclude that the relations for p given by the mechanical theory of heat can be applied without modification to $-\sigma$. Had the volume not been supposed to be constant, we should have had

$$\tau\, d\eta = dE + p\, dV - \sigma\, dS$$

If we now consider E as function of τ, V, and S, the last equation becomes

$$\tau\, d\eta = \left(\frac{\partial E}{\partial \tau}\right)_{VS} d\tau + \left[\left(\frac{\partial E}{\partial V}\right)_{\tau S} + p\right] dV + \left[\left(\frac{\partial E}{\partial S}\right)_{\tau V} - \sigma\right] dS$$

Since $d\eta$ must be a total differential, and since $d\tau$, dV, and dS are mutually independent, we deduce in the usual way that

$$\tau\, d\eta = \left(\frac{\partial E}{\partial \tau}\right)_{VS} d\tau + \tau\left(\frac{\partial p}{\partial \tau}\right)_{VS} dV - \tau\left(\frac{\partial \sigma}{\partial \tau}\right)_{SV} dS$$

We deduce that if the surface is increased at constant volume, then it is necessary, to maintain the temperature constant, to add an amount of heat given by the equation[9] $(\partial Q/\partial S)_{V,\tau} = -\tau(\partial\sigma/\partial\tau)_{S,V}$ {see Gibbs, pp. 434 and 436 [pp. 269 and 271], Eqs. (587), (593)}. Since σ is a function only of the temperature, we can replace $(\partial\sigma/\partial\tau)_{S,V}$ simply by $d\sigma/d\tau$. This follows moreover from the relation $(\partial^2 p/\partial\tau\, \partial S)_V = -(\partial^2\sigma/\partial\tau\, \partial V)_S$.

The equation $p\, dV = \tau\, d\eta - dE + \sigma\, dS$ allows us to reach the same conclusion by noting that the state is determined by η, p, and S, and by remembering that dV is a total differential:

$$dV = \left(\frac{\partial \tau}{\partial p}\right)_{\eta S} d\eta - \left(\frac{\partial E}{\partial p}\right)_{\eta S} \frac{dp}{p} + \left(\frac{\partial \sigma}{\partial p}\right)_{\eta S} dS$$

Suppose now that no heat be added, and so that $d\eta = 0$, and that the lowering of temperature be compensated by condensation, so that $dp = 0$; it follows that

$$(\partial V/\partial S)_{\eta p} = (\partial\sigma/\partial p)_{\eta S}$$

---

[9] It follows from this equation that, since at the critical temperature $\sigma = 0$ and so $(\partial Q/\partial S)_{\tau,V} = 0$, then $d\sigma/d\tau$ is also zero, as follows from my theory, and in agreement with the observations of de Vries.

The work done on the contents by the external pressure p, which diminishes the volume by virtue of the condensation, is equal to $-p(\partial V/\partial S)_{\eta,p}$. From the last equation, this work is therefore

$$-p(\partial V/\partial S)_{\eta p} = -p(\partial \sigma/\partial p)_{\eta S}$$

This relation can be put into a form that we shall be able to derive at once from other considerations. Since σ is a function only of the temperature, and so independent of S and η, this work can also be expressed as $-p(d\sigma/d\tau)(d\tau/dp)$. Here p represents the pressure of the saturated vapor, and so[10] $\tau\, dp/d\tau = r/u$, and the work is $-(up/r)\tau\, d\sigma/d\tau$ [Gibbs, Eqs. (592) and (595)].

The heat that we must add at constant volume to increase the surface by unit area while holding the temperature constant is $-\tau\, d\sigma/d\tau$. If, however, we do not add this heat, then the vapor condenses; and when this happens the external work provides part of the heat that is liberated, and this part is represented by the fraction pu/r.

If we determine the value of $(\partial E/\partial S)_{V,\tau}$, we find it to be $\sigma - \tau\, d\sigma/d\tau$. This does not contradict Section 9, where we have put the capillary energy equal to σ. When we increase the layer by unit surface area, for example, by stretching a membrane, we do work equal to σ, which is added therefore to the energy of the membrane. We must in addition furnish a quantity of heat equal to $-\tau\, d\sigma/d\tau$. The total increase in energy is therefore $\sigma - \tau\, d\sigma/d\tau$. In Section 9 we have denoted the special work to be done by σ, not counting the added heat, in agreement with the arguments above. It is this quantity that is generally called the capillary constant.

14. DISCONTINUOUS BOUNDARY LAYER

The form found for the capillary constant in the case of a gradual transition of density allows us to calculate also the usual value that follows from the theory of Laplace when the changes are discontinuous. Let

$$\sigma = \int u^2\psi(u)\, du \int \frac{d\rho_h}{dh}\, d\rho_h = \int \left\{ u\psi(u)\, du \int u \frac{d\rho_h}{dh}\, d\rho_h \right\}$$

Now we have

$$\rho_{h-u} = \rho_h - u\frac{d\rho_h}{dh} + \frac{u^2}{2}\frac{d^2\rho_h}{dh^2} \cdots$$

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[10] The values of p and of $dp/d\tau$ are not changed by the presence of the surface layer, or, rather, the usual relations of the mechanical theory of heat are equally valid for a liquid and vapor separated by a planar layer. [r and u, not defined in the original paper, were symbols commonly used for ΔH and ΔV.]

When h is smaller than u, as is the case if h is really zero, then $\rho_{h-u} = \rho_1$, and so

$$u\frac{d\rho_h}{dh} = \rho_h - \rho_1 + \frac{u^2}{2}\frac{d^2\rho_h}{dh^2}$$

If we now recall that

$$\int \frac{d^2\rho}{dh^2}\,d\rho = \frac{1}{2}\left(\frac{d\rho}{dh}\right)^2$$

which can be put equal to zero at the limits (and similarly for the higher terms), then all that remains of σ is

$$\tfrac{1}{2}\int u\psi(u)\,du\cdot(\rho_1 - \rho_2)^2$$

But we recognize that this last equation is not in accord with the temperature dependence of the capillary energy. To avoid this difficulty we should have to adopt the hypothesis that the way the molecular forces act is different for the liquid and the vapor, a hypothesis which is not supported by the continuity existing between these states. Moreover, such a supposition would explain nothing; it amounts only to an admission of our inability to explain capillary phenomena, because we have insufficient information.

The state described in the preceding pages can certainly exist; that has been proved by the study of stability. If we want to show that another state is impossible, we must prove not only that the free energy is at a minimum for the case of a continuous transition, but also that there is not a state of the same energy with an even smaller value; such a demonstration is difficult. However, the theory that supposes a discontinuity has not even been tested to see if such a state is one of equilibrium, and still less to see if it is stable. I think therefore that I have the right to conclude that for the moment the hypothesis of continuity has the greater probability.

15. SOLUTION OF THE COMPLETE DIFFERENTIAL EQUATION

The solution of the capillary problem given above would be completely rigorous if all the coefficients c_{2n} for $n > 1$ were equal to zero. The way in which we obtain these functions $\int u^4\psi(u)\,du$, etc., makes this condition unlikely. We must therefore expect that the solution given above should only be an approximation. We cannot exclude the possibility that the complete solution, should it be realizable, might tell us something of the limits of the temperature above which there is a continuous transition, as we have assumed above, and below which there might be a real discontinuity. The complete solution is unfortunately impossible because we do not know the value of the functions c_{2n}.

The more rapidly these functions decrease, the more closely the solution above approaches the true one. If we assume a relation between c_2 and c_4, etc., which obviously exaggerates the sizes of the successive coefficients, and if we can solve the problem, then the true solution will undoubtedly lie between that obtained by putting c_4, c_6, etc., equal to zero and that obtained by giving these functions too great a value. I have therefore looked for a solution on the hypothesis that

$$ac_4/4! = (c_2/2!)^2, \qquad a^2c_6/6! = (c_2/2!)^3, \qquad \text{etc.}$$

and so

$$\frac{1}{4!}\int \psi(u)\,du \int u^4\psi(u)\,du = \left\{\frac{1}{2!}\int u^2\psi(u)\,du\right\}^2 \qquad \text{etc.}$$

These relations between the coefficients follow rigorously if it is assumed that $\psi(u) = \exp(-u/\lambda)$. With this hypothesis, and putting $c_2 = c$, we have

$$\frac{2}{2!}\,c\,\frac{d^2\rho}{dh^2} + \frac{2}{4!}\,c_4\,\frac{d^4\rho}{dh^4} + \text{etc.} = f(\rho) - \mu_1$$

$$\frac{c^2}{2a}\,\frac{d^4\rho}{dh^4} + \text{etc.} = \frac{c}{2a}\left\{\frac{\partial f}{\partial \rho}\,\frac{d^2\rho}{dh^2} + \frac{\partial^2 f}{\partial \rho^2}\left(\frac{d\rho}{dh}\right)^2\right\}$$

or

$$f(\rho) - \mu_1 - c\,\frac{d^2\rho}{dh^2} = \frac{c}{2a}\left\{\frac{\partial f}{\partial \rho}\,\frac{d^2\rho}{dh^2} + \frac{\partial^2 f}{\partial \rho^2}\left(\frac{d\rho}{dh}\right)^2\right\}$$

Hence

$$f(\rho) - \mu_1 - \frac{c}{2a}\,\frac{\partial^2 f}{\partial \rho^2}\left(\frac{d\rho}{dh}\right)^2 = c\left\{1 + \frac{1}{2a}\,\frac{\partial f}{\partial \rho}\right\}\frac{d^2\rho}{dh^2} \qquad (15.1)$$

The function of $f(\rho)$ now represents what previously was $f(\rho) + \rho\, df/d\rho$, and $f(\rho) - \mu_1$ becomes the function

$$pV - p_1V_1 - \int_{V_1}^{V} p\,dV$$

when this is expressed as a function of ρ by substituting $1/\rho$ for V. If we mark on the ρ axis the lengths ρ_2 and ρ_1, then, since

$$\frac{\partial f(\rho)}{\partial \rho} = \frac{1}{\rho}\frac{dp}{d\rho} = -V^3\,\frac{dp}{dV}$$

the curve $f(\rho) - \mu_1$ has a sinusoidal form, that is, the ordinates are positive at first for a certain range, and then negative. They start and end with the value zero and change smoothly.

Let us represent this by

$$\sum \beta_m \sin[2m\pi(\rho - \rho_2)/(\rho_1 - \rho_2)]$$

If we are satisfied with one term, then we solve Eq. (15.1) by putting

$$f(\rho) - \mu_1 = ak(\rho_1 - \rho_2)\sin[2\pi(\rho - \rho_2)/(\rho_1 - \rho_2)]$$

Since $\partial^2 f/\partial\rho^2 = -4\pi^2 f(\rho_1 - \rho_2)^{-2}$, Eq. (15.1) can also be written

$$[f(\rho) - \mu_1]\left\{1 + \frac{4\pi^2 c}{2a(\rho_1 - \rho_2)^2}\left(\frac{d\rho}{dh}\right)^2\right\} = c\left[1 + \frac{1}{2a}\frac{\partial f}{\partial\rho}\right]\frac{d^2\rho}{dh^2}$$

and so

$$\begin{aligned} c\frac{d^2\rho}{dh^2}&\left\{1 + \frac{4\pi^2 c}{2a(\rho_1 - \rho_2)^2}\left(\frac{d\rho}{dh}\right)^2\right\}^{-1} \\ &= [f(\rho) - \mu_1]\left(1 + \frac{1}{2a}\frac{\partial f}{\partial\rho}\right)^{-1} \\ &= ak(\rho_1 - \rho_2)\sin\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\left\{1 + \pi k\cos\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\right\}^{-1} \end{aligned}$$

or

$$\begin{aligned} \frac{c}{2}d\left(\frac{d\rho}{dh}\right)^2&\left\{1 + \frac{4\pi^2 c}{2a(\rho_1 - \rho_2)^2}\left(\frac{d\rho}{dh}\right)^2\right\}^{-1} \\ &= -\frac{ak}{2\pi}(\rho_1 - \rho_2)^2\, d\cos\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\left\{1 + \pi k\cos\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\right\}^{-1} \end{aligned}$$

of which the integral is

$$\begin{aligned} 1 + \frac{4\pi^2 c}{2a(\rho_1 - \rho_2)^2}\left(\frac{d\rho}{dh}\right)^2 &= C\left\{1 + \pi k\cos\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\right\}^{-2} \\ &= (1 + \pi k)^2\left\{1 + \pi k\cos\left[2\pi\frac{\rho - \rho_2}{\rho_1 - \rho_2}\right]\right\}^{-2} \end{aligned} \tag{15.2}$$

where the constant C has been chosen so that $d\rho/dh = 0$ when $\rho = \rho_1$ and ρ_2.

I have derived Eq. (15.2) because it can give us an idea of how it should be possible to decide if the transition layer is continuous or if it has a discontinuity. This equation makes $d\rho/dh$ infinite when $\cos[2\pi(\rho - \rho_2)/(\rho_1 - \rho_2)] = -1/\pi k$. For very small values of k this condition cannot be satisfied. If we take $1/\pi k = 1$, then there will be an element of the curve $\rho = f(h)$ where the tangent is perpendicular to the h axis, and for larger values of k it may be assumed that there is a discontinuity. For $1/\pi k < 1$ the curve represented by (15.2) has the form shown by the dashed line in Fig. 3, that is, a curve for which, at certain values of h, there are three different densities, and this is an absurdity.

However, this is not to be feared near the critical temperature where k is very small. I have verified that k approaches zero as τ approaches τ_k, so that the value of σ as calculated above is the same as the approximate value for these temperatures.

Without having recourse to Eq. (15.2), we can deduce from (15.1) that the particular case $d\rho/dh = \infty$ will occur when $1 + (2a)^{-1}\,\partial f/\partial\rho = 0$. If we start from the liquid side, $f(\rho) - \mu_1$ becomes negative and $\partial^2 f/\partial\rho^2$ is positive. The left-hand side of (15.1) is therefore entirely negative, and so also is $d^2\rho/dh^2$, since $1 + (2a)^{-1}\,\partial f/\partial\rho$ is positive. If $d\rho/dh$ rises toward an infinite value, then a little before this point is reached the sign of the left-hand side will remain negative, unless we have the special case that $\partial^2 f/\partial\rho^2$ changes sign. But then the sign of $d^2\rho/dh^2$ will change also, and so the same thing must occur for the coefficient of $d^2\rho/dh^2$, that is, $1 + (2a)^{-1}\,\partial f/\partial\rho$.

This allows us to find, from the equation describing the state of the liquid, the temperature at which $d\rho/dh$ becomes infinite for the first time. We know that $df/d\rho = \rho^{-1}\,dp/d\rho$, or $-2a\rho = dp/d\rho$, and since $dp/d\rho$ is negative, this temperature must be on the unstable branch of the isotherm. The equation $\partial p/\partial\rho = -2a\rho$, or $dp/dV = 2a/V^3$, or again $R\tau(V-b)^{-2} = 0$, requires that $\tau = 0$.

If we had represented the equation of equilibrium

$$\sum \frac{c_{2n}}{2n!}\frac{d^{2n}\rho}{dh^{2n}} = \frac{f(\rho) - \mu_1}{2}$$

by

$$c\frac{d^2\rho}{dh^2} + m\frac{c^2}{a}\frac{d^4\rho}{dh^4} + \text{etc.} = f(\rho) - \mu_1$$

thus attributing to the successive coefficients a value m times greater [always supposing that the $(mc/a)^n\, d^{2n}\rho/dh^{2n}$ converge to zero], then we should have found that the condition under which $d\rho/dh$ becomes infinite was the equation $1 + (m/2a)\,\partial f/\partial\rho = 0$. It gives

$$R\tau = a\frac{(V-b)^2}{V^3}\left(2 - \frac{2}{m}\right)$$

The two equal roots are given by $V = 3b$ and $\tau/\tau_k = 1 - (8m)^{-1}$, so that it is only if m becomes infinite that the discontinuity would occur near τ_k. The hypothesis $m = 1$ leads to continuity at all temperatures, and seems to me to be the truth. As I have pointed out above, it follows from the hypothesis $\psi(u) = \exp(-u/\lambda)$. Since I wrote these pages I have been able to convince myself that this function agrees with all the known mathematical properties of the molecular interactions. It leads to the expression

$$P = C - (f/u)\exp(-u/\lambda)$$

for the potential between two material points placed at a separation u. The expression $\exp(-u/\lambda)$ can be thought of as an extinction factor, in which λ, which is nothing but the ratio of the two constants H and K in Laplace's theory, is so small that the molecular interaction diminishes exceedingly rapidly.

Since I now no longer believe the supposition $m = 1$ to be arbitrary, but to be in accord with the facts, I have derived the form of σ from the differential equation (15.1). If we provisionally retain the factor m, we find that $m = 0$ leads to the previously obtained approximate value of σ, and $m = 1$ to the exact value. If the equation is

$$f = c\frac{d^2\rho}{dh^2} + m\frac{c^2}{a}\frac{d^4\rho}{dh^4} + \cdots$$

we derive from it

$$f = c\frac{d^2}{dh^2}\left(\rho + \frac{m}{2a}f\right)$$

Multiply both sides by $d\rho + (m/2a)\,df$ and obtain, after integration,

$$\rho f + (p_1 + p) + \frac{m}{4a}f^2 = \frac{c}{2}\left(\frac{d\rho}{dh}\right)^2\left(1 + \frac{m}{2a}\frac{\partial f}{\partial \rho}\right)^2$$

from which we find, after using the relations found above,

$$\sigma = \frac{c}{2}\int dh\left\{\left[\frac{d}{dh}\left(\rho + \frac{m}{2a}f\right)\right]^2 - \left(\rho + \frac{m}{2a}f\right)\frac{d^2}{dh^2}\left(\rho + \frac{m}{2a}f\right)\right\}$$

or

$$\sigma = c\int dh\left(\frac{d\rho}{dh}\right)^2\left(1 + \frac{m}{2a}\frac{df}{d\rho}\right)^2$$

We should now ask if we can demonstrate also the stability of the general case. The number of differentials which have to be taken into account makes this very difficult. It follows from

$$I = \int \rho\,dh\left[f(\rho) - \mu_1 - a\lambda^2\frac{d^2\rho}{dh^2} - a\lambda^4\frac{d^4\rho}{dh^4}\cdots\right]$$

that

$$\delta^2 I = \frac{1}{2}\int \rho\, dh \left[(\delta\rho)^2 \frac{\partial^2}{\partial\rho^2}\,[\rho f(\rho) - \mu_1] \right.$$
$$\left. - 2a\lambda^2\, \delta\rho\, \delta\left(\frac{d^2\rho}{dh^2}\right) - 2a\lambda^4\, \delta\rho\, \delta\left(\frac{d^4\rho}{dh^4}\right) \cdots \right]$$

(see Section 7), or, after integration by parts,

$$\delta^2 I = \frac{1}{2}\int \rho\, dh \left[(\delta\rho)^2 \frac{\partial^2}{\delta\rho^2}\,[\rho f(\rho) - \mu_1] \right.$$
$$\left. - 2a\lambda^2\, \delta\rho\, \frac{d^2(\delta\rho)}{dh^2} - 2a\lambda^4\, \delta\rho\, \frac{d^4(\delta\rho)}{dh^4} \cdots \right]$$

The artifice of Section 7 does not work in this case. But in comparing the calculations with those of Section 7, after having introduced $t(d\rho/dh)\alpha$ in place of $\delta\rho$, one can see at once the conditions under which I was able to determine the sign of the second-order variation in the simple case. The number of separate problems for which one can fix the conditions of maximum and minimum values is very small. But it must be noted that the state of equilibrium implies, just as for the simple case, that the densities in the superficial layer are those that, extended throughout a nonzero space, would give rise to an unstable state. Nevertheless the demonstration of stability holds in Section 7 for the simple case, and so there is no good reason to suppose that it cannot hold also in the more general case.

At the critical temperature the result given by the complete equation differs so little from the value described previously that we can use the latter without modification.

APPENDIX (see Section 6)

To keep matters simple we have used here a particular form of the equation of state, but the conclusions are quite independent of this choice. When therefore G. Bakker[11] claims that I have used the hypothesis $\epsilon = \phi(v) + \psi(\tau)$, it must be said that my conclusions do not depend on this choice. The result that the free energy is equal to $f(\rho) - \frac{1}{2}c_2\, d^2\rho/dh^2$ at height h in a planar transition layer is independent of it. We know that c_2 in this expression represents an integral that is independent of the distribution of matter, and that $f(\rho)$ is the free energy in surroundings of homogeneous density. The fact that the passage to the transition layer takes place only gradually

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[11] *Z. Phys. Chem.* **12**: 284 (1893).

has also been established without appeal to this hypothesis; and this independence extends to the estimation of the order of magnitude of c_2. An expression of the form $f(\rho) = \frac{1}{2}c_2\, d^2\rho/dh^2$ is obtained even on a kinetic hypothesis which supposes that the mean value of the potential energy is affected only by the direct collisions of the molecules.

Let us consider a special case where the molecular pressure depends also on the temperature, and is put equal to $a_0 f(\tau)/V^2$. Since $d\epsilon/dV = \tau(dp/d\tau)_V - p$, we have

$$\epsilon = c - a_0\rho[f(\tau) - \tau f'(\tau)]$$

The term $-a_0\rho f(\tau)$, which for brevity we denote ϵ_k, is to the molecular pressure $K = \rho^2 a_0 f(\tau) = -\rho\epsilon_k$ as the potential of the plane surface of liquid of homogeneous density is to the force with which an elementary column of infinite length of the same liquid resting on it is attracted by a unit section. We require that the liquid is of homogeneous density not only in the sense of molecular theory, but also from a mathematical point of view, and that the particles of the liquid exert mutual forces which derive from a potential. If, as is usual, we take a layer of thickness dh at height h in the column above the liquid of density ρ, if moreover, the potential of the liquid bounded by a plane is P_h at height h, then the force per unit surface acting on this layer is $(dP_h/dh)\rho\, dh$, and the effect exerted on the whole column by unit surface is

$$K' = \int_0^\infty \rho\, dP = -\rho P_0$$

where P_0 is the potential of the liquid at the surface.

In place of the mathematical liquid uniformly filling space, we can suppose also a liquid in which matter is concentrated in molecules, but where the probability that any molecule finds itself at a given point in space is always the same. This supposes that the molecules are distributed in a totally arbitrary way, and that larger or smaller separations are not, as in the kinetic problem, favored in the way that probability indicates. It must further be assumed that the interaction between two molecules is determined only by the position of a single point in each molecule.

If everything were really thus, then we could express the relation between ϵ_k and K as above; the first part of the energy $\epsilon_k = -a_0\rho f(\tau)$ is the work done against displacement forces, the potential of which determines the molecular pressure.

But if the real state of affairs in liquids departs from this picture, as I now show—and it is this that I allow in my theory when a depends on the temperature—then we must consider the second fraction $a\rho\tau f'(\tau)$ as a complementary energy. We can say of this energy that it belongs to the molecules by virtue of the particular state in which they find themselves for the values of ρ and τ. It will be clear that in my theory of capillarity this second part of the energy plays a role only in very special conditions. It suffices to say that it is the value of $\epsilon - \tau\eta$, and not that of ϵ, that matters, and in the case we are considering $\tau\eta$ gives us a term which annuls the one in question. In general, after subtracting a pure function of temperature, we have $\epsilon - \tau\eta = \int p \, dV$, and we find again for $\epsilon - \tau\eta$ in homogeneous surroundings

$$\psi = -a_0 \rho f(\tau) - R\tau \ln(\rho^{-1} - b)$$

We find similarly the expression that I have used in the text for points where the density is not uniform, provided that the second part of the energy $a_0 \rho \tau f'(\tau)$ depends only on the local state at these points, that is, on τ and ρ, and not on $d^2\rho/dh^2$, $d^4\rho/dh^4$, etc. I know of no evidence I could invoke against this last hypothesis. It is in complete agreement with what I have assumed previously; that is, that the entropy is determined only by ρ and τ in places where the density is not homogeneous.

When I have had to calculate the difference between ϵ and ϵ_1, I have therefore never taken account of the displacement forces. The form of the integrals c_2, c_4, etc., becomes complicated as soon as one abandons the idea of an absolutely uniform probability for the distribution of molecular centers in the space around a given molecular center. Such considerations guide us wholly when in the domain of kinetic theory, and although they show us that c_2, etc., could depend on the state, that is, on τ and ρ at the place one evaluates the integral, we cannot yet expect the kinetic theory to tell us this dependence. I have therefore excluded this complication from my theory, and have not discussed here how one could study, by purely thermodynamic arguments, the way in which c_2, etc., could depend on the density.