XLIX. On the theory of surface forces. II

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To cite this article: G. Bakker (1907) XLIX. On the theory of surface forces. II, Philosophical Magazine Series 6, 14:82, 509-528, DOI: [10.1080/14786440709463710](https://doi.org/10.1080/14786440709463710)

To link to this article: <http://dx.doi.org/10.1080/14786440709463710>

Published online: 16 Apr 2009.

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XLIX. *On the Theory of Surface Forces. II.*

By G. BAKKER*.

§ 1. *Observations of Isaac Newton.*

IF films of liquids, such as oil-films on water or films of a solution of soap in water, become continually thinner and thinner, there appear suddenly, as every one knows, on the thinnest places of the brilliant surface circular black spots. These spots gradually enlarge so that the surface of the film seems to be perforated with holes. This observation was made first by Isaac Newton.

I will demonstrate how this phenomenon can be explained in a theory of surface-forces, in which the capillary layer is considered as a gradual transition of the liquid phase to the vapour phase, such as those of Lord Rayleigh† by means of the properties of the theoretical isotherms of James Thomson and van der Waals.

Reinold and Rücker‡ have made the very important discovery that the black spot, always formed before an undisturbed film of soap solution breaks, has a uniform or nearly uniform thickness of about eleven or twelve micro-millimetres, while the thickness of the remaining parts of the film exceeds fifty micro-millimetres. The sharp boundary of the black spots is also a consequence of the relative great difference between the thickness of the spots and the remaining parts of the film. Let us now consider a liquid membrane, the breadth being equal to the unit, lying between two solid strips supported on the right and the left by cords stretched in a vessel containing nothing but water vapour (see fig. 1).

Fig. 1.

The liquid film cannot be in equilibrium unless the strips are bound to the walls of the vessel§. When thus the thickness of the film *exceeds sufficiently* twofold the thickness of the capillary layer, the tensions in the strings, which bind the strips

* Communicated by the Author.

† "On the Theory of Surface Forces, II." *Phil. Mag.* Feb. 1892, p. 209.‡ *Proc. Roy. Soc.* June 21, 1877; and *Trans. Roy. Soc.* April 19, 1883.§ *Phil. Mag.* for December 1906, p. 563.

to the walls of the vessel, are twofold the surface-tension H of the theory of Laplace. (Fig. 2 presents a part of the liquid film of fig. 1 on an enlarged scale.)

Fig. 2.

If the film is thick enough we have between the capillary layers AB and A_1B_1 liquid, while we have between A and B as well between A_1 and B_1 a gradual transition of the density. Above B_1 as well below B we have saturated vapour. If we gradually draw out the film it becomes thinner and thinner. If there is still sufficient liquid between A and A_1 , we have thus, in supposing a gradual variation of the density between A and B as well as between A_1 and B_1 , all the densities of the theoretical isotherms of James Thomson between A and B as well between A_1 and B_1 of fig. 3, and

Fig. 3.

thus likewise the densities of the phases, which would be unstable if they were isolated. The liquid layers CD and C_1D_1 (fig. 2) are thus in equilibrium with the aid of the matter between C_1 and C , the matter above D_1 and the matter below D . If we continue to thin the film (fig. 2) the densities C and C_1 , which correspond with the unstable phases C and C_1 (fig. 3) of the theoretical isotherm, will finally

touch each other in forming a new state of equilibrium, and because *the new film, not containing the densities between $C-D$ and C_1-D_1 is not complete, it becomes suddenly thinner.*

Although it is possible that the two layers AD and A_1D_1 precipitate in each other sooner than we have supposed, I believe I have demonstrated that the observation of Newton may be predicted by a theory of the capillary layer, such as the theory of Rayleigh or the theory of van der Waals, where the layer is considered as a continual transition of the liquid-density to the vapour-density.

In his popular Lectures and Addresses, vol. i. pp. 8 & 9 (1891), Sir William Thomson (Lord Kelvin) says:—"The abrupt commencement and the permanent stability of the black film demonstrate a proposition of fundamental importance in the molecular theory:—The tension of the film, which is sensibly constant when the thickness exceeds fifty micro-millimetres, diminishes to a minimum, and begins to increase again when the thickness is diminished to ten micro-millimetres. It seems not possible to explain this fact by any imaginable law of force between the different portions of the film supposed homogeneous, and we are forced to the conclusion that it depends upon molecular heterogeneousness."

Whereas my considerations are very well applicable to a theory of the capillary layer in which the forces of cohesion are considered as the attractive forces between the *elements of volume* of the liquid, it seems that the conclusion of Lord Kelvin, where he says that the abrupt commencement and the permanent stability of the black film depend upon molecular heterogeneousness, is not indispensable. Further, the author continues (*l. c.*):—"When the homogeneous molar theory is thus disproved by observation, and its assumption of a law of attraction augmenting more rapidly than according to the Newtonian law when the distance becomes less than fifty micro-millimetres is proved to be insufficient, may we not go farther and say that it is unnecessary to assume any deviation from the Newtonian law of force varying inversely as the square of the distance, continuously from the millionth of a micro-millimetre to the distance of the remotest star or remotest piece of matter in the universe; and, until we see how gravity itself is to be explained, as Newton and Faraday thought it must be explained, by some continuous action of intervening or surrounding matter, may we not be temporarily satisfied to explain capillary attraction merely as Newtonian attraction intensified in virtue of intensely dense molecules movable among one another, of which the aggregate constitutes a mass, of liquid or solid."

Though I cannot comprehend that the phenomenon, discussed by Lord Kelvin, requires the molecular heterogeneity of matter, I have nevertheless always considered the idea, whereby capillary attraction is explained as merely Newtonian attraction of dense molecules (Laplace, Secchi, Kelvin), as a magnificent idea, that is not to be rejected before the contrary is proved. So I have found* for a medium the following formula for the potential function $\phi(r)$ of the forces between their *elements*, accepting the Newtonian law of forces between the *molecules* and assuming the law of dispersion of Boltzmann :

$$\phi(r) = -f \frac{r + D}{r^2} e^{\frac{\lambda}{r+D}}$$

where $\lambda = \frac{f\mu}{RT}$ and r = distance between the elements of the volume of the medium ; R = constant of the gas ; T = absolute temperature ; D = diameter of the molecules ; f = constant of the gravitation ; μ = weight of one molecule. The meaning is that the *potential energy* of the elements of the homogeneous medium should be the same as that of the molecules of the gas.

If μ is sufficiently large, the influence of the factor $e^{\frac{\lambda}{r+D}}$ may be important. Because λ is varying inversely as the absolute temperature, we see that for our medium at a sufficiently elevated temperature the potential function approaches to

$$\phi(r) = -f \frac{r + D}{r^2},$$

and when, moreover, the medium is sufficiently rarefied the function becomes :

$$\phi(r) = -\frac{f}{r},$$

so that the cohesion becomes practically null. We find also, in accordance with the consideration of Lord Kelvin, in his popular Lectures and Addresses (vol. i. p. 59, 1891), that the Newtonian law of attraction between the *molecules* may be very well in harmony with the properties of the forces between the *volume elements* of the homogeneous medium, considered in the ordinary capillary theory.

If my consideration upon the abrupt commencement and the permanent stability of the black spot is exact, the *twofold* thickness of the *complete* capillary layer of soap-solution at

* *Ann. der Phys.* 4^e Folge (1903) p. 216.

ordinary temperature is, in virtue of the measurements of Reinold and Rücker, inferior to $50\ \mu\mu$, while *twofold* the *incomplete* capillary layer of the black spot is more than $10\ \mu\mu$. Putting h for the thickness of the (complete) capillary layer of a soap-solution, we have also :

$$\begin{aligned} 50\ \mu\mu &> 2h > 10\ \mu\mu \\ 25\ \mu\mu &> h > 5\ \mu\mu. \end{aligned} \quad . \quad . \quad . \quad . \quad (1)$$

Observation.—That we may have in the black spots the same tension as in the complete capillary layer may very well be in accordance with the expression which I have found for the surface-tension H of Laplace; *i. e.* :

$$H = \frac{1}{4\pi f} \int_1^2 \left(\frac{dV}{dh} \right)^2 dh; \quad . \quad . \quad . \quad . \quad (I.)*$$

f denotes the constant in the used potential function for the forces of cohesion: $-f e^{-\frac{r}{\lambda}}$ and dh is the differential of the normal to the surface of the layer. The order of greatness of H is also :

$$\frac{1}{4\pi f} \frac{(V_2 - V_1)^2}{h}, \quad . \quad . \quad . \quad . \quad (II.)^\dagger$$

where h denotes the thickness of the capillary layer and V_2 and V_1 are successively the potentials in the vapour and liquid phase. For a black spot we must change V_1 into the potential of a point in equal distances of the two planes which limit the black film, and just as h is smaller for a black spot than for a *complete* capillary layer, so also the difference between the potential in the vapour phase V_2 and the potential in the point at equal distances from the two planes which limit the black film is smaller than the difference $V_2 - V_1$ for the

* G. Bakker, "On the Theory of Surface Forces," Phil. Mag. Dec. 1906, p. 562.

† If a denotes the coefficient of the well-known expression of Laplace for the so-called molecular pressure $a\rho^2$, Gauss and van der Waals have found for the potential of the forces between the *volume-elements* of a homogeneous phase $-2a\rho$, where ρ denotes the density. Formula (II.) becomes therefore

$$\frac{1}{\pi f} \cdot \frac{a^2(\rho_1 - \rho_2)^2}{h}.$$

In this paper I find in § 3 [see formula (17)] for H the formula

$$H = \frac{6}{5\pi f} \cdot \frac{a^2(\rho_1 - \rho_2)^2}{h}.$$

complete capillary layer. The surface-tension in the black spot can also be very well equal to the tension H in the complete capillary layer.

It may not be superfluous to remark that, though the surface-tension in the black spots may have the same *value* as in the complete capillary layer, the tension is nevertheless a quantity of somewhat other signification, the ordinary constant of Laplace being the surface-tension in a *complete* capillary layer.

§ 2. *The Hydrostatic Pressure in the Capillary Layer and in the Black Spot.*

If we consider again the liquid-film of fig. 1, we may easily demonstrate that for low temperatures, for instance near the melting-point, the pressure *parallel* to the surfaces, which limit the film, may be *large* and *negative*. Indeed the part of the film to the right of the plane BB_1 (perpendicular on AA_1) is in equilibrium firstly with an external force at A_1 , which we measure as twofold the surface-tension, and secondly with the influence of the part of the film to the left of BB_1 on the considered part. *Between* the two capillary layers which limit the film the matter is in the *ordinary homogeneous liquid state*, and therefore the pressure is equal to the exterior pressure or the vapour-pressure. As near the melting-point the vapour-pressure may be neglected, the pressure *between* the capillary layers of the liquid may be considered as null. The cohesion and thermic pressure in the *interior* of the film (between the capillary layers) are therefore nearly equal. On the contrary, *in the capillary layers which limit the considered film* we must have a force *directed to the left*, which is in equilibrium with half the force in the strings which bind the strips to the walls of the vessel. The value of this force is therefore the constant of Laplace, H . This force, being *outward relative to the considered part* (between BB_1 and A_1), *must be reckoned as a negative pressure*, which means that the cohesion in the capillary layer parallel to their surface is at low temperatures larger than the thermic pressure.

If p_2 denotes the pressure in a direction parallel to the surface, dh denoting the differential of the normal to the surface, the condition of the equilibrium demands:

$$2 \int_1^2 p_2 dh + 2H = 0. \quad . \quad . \quad . \quad (2a)$$

Putting

$$\frac{1}{h} \int_1^2 p_2 dh = \bar{p},$$

where h denotes the thickness of the capillary layer, and p the average pressure in the direction of the surface, we have

$$\bar{p} = -\frac{H}{h}. \quad \dots \dots \dots (2b)$$

For water the surface-tension being $H=76$ (dyne pro cm. or erg pro cm.²), and adopting in connexion with the investigations of Reinold and Rücker, $h=10 \mu\mu$, we find for water at ordinary temperature :

$$\bar{p} = -\frac{76}{10^{-6}} = -76 \cdot 10^6 \text{ or nearly } -76 \text{ atmospheres.}$$

Whereas the black spots may be in equilibrium with the complete capillary layer, and the thickness of the black spots may be less than $5 \mu\mu$ (Reinold and Rücker), *the absolute value of the negative pressure in the black spots of a film of soap-solution may be larger than 150 atmospheres.*

That the pressure *perpendicular* to the surface of the capillary layer must be equal to the vapour-pressure, we see in considering the well-known statement of the theory of elastic forces:

$$\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{yy}}{\partial y} + \frac{\partial p_{zz}}{\partial z} = 0^*;$$

when we choose the z -axis normal to the surface.

The gradient of the properties of the capillary layer being normal to its surface :

$$\frac{\partial p_{xx}}{\partial x} = 0, \quad \frac{\partial p_{yy}}{\partial y} = 0;$$

Hence

$$\frac{\partial p_{zz}}{\partial z} = 0 \quad \text{or} \quad p_{zz} = \text{constant.}$$

In the homogeneous phases of the liquid and the vapour adjacent to the capillary layer, the pressure being the vapour-pressure, we have :

$$p_{zz} = \text{vapour-pressure} = p_1, \\ \text{putting } p_1 = \text{vapour-pressure.}$$

§ 3. *The average value $\bar{p}$ of the Pressure p_2 parallel to the surface of the Capillary Layer and the Theoretical Isotherm of James Thomson and van der Waals.*

When we may not neglect the vapour-pressure p_1 we must complete the equation (2a) to

$$2 \int_1^2 p_2 dh - 2p_1 h + 2H = 0.$$

* Gravitation is not considered.

Hence

$$h = \frac{H}{p_1 - \bar{p}}.$$

We will now demonstrate that, if F (fig. 4) is the point on the theoretical isotherm such that

$$\text{surface NHGMLN} = \text{surface LFGM},$$

we can put

$$\bar{p} = RF.$$

Fig. 4.

F is the point where $\int_1 v dp = 0$, and where also the thermodynamical potential has the same value as in the homogeneous liquid and vapour phase. If μ_1 is this value, we put generally

$$\int_1 v dp = \mu - \mu_1.$$

If p denotes the pressure in a *homogeneous* phase having the same density as in a point of the capillary layer, we shall have

$$p = \theta - a\rho^2 \quad \text{or} \quad dp = d\theta - 2a\rho d\rho,$$

where θ designs the thermic pressure. If V denotes further the potential of the forces of cohesion, we have:

$$d\theta = -\rho dV.$$

Eliminating $d\theta$ between these differential equations:

$$vdp + 2a d\rho = -dV.$$

$$\text{Integrating:} \quad \int_1 v d\rho + 2a(\rho - \rho_1) = V_1 - V, \quad . \quad . \quad . \quad (3)$$

where the index belongs to the liquid phase. Now for this phase we have

$$V_1 = -2a\rho_1 \quad (\text{Gauss and van der Waals})$$

and equation (3) becomes:

$$V + 2a\rho = \mu_1 - \mu. \quad . \quad . \quad . \quad . \quad (4)$$

For the potential V of the forces of cohesion I have found*

$$\lambda^2 \frac{d^2 V}{dh^2} = V + 2a\rho. \quad . \quad . \quad . \quad (5)$$

Hence

$$\lambda^2 \frac{d^2 V}{dh^2} = \mu_1 - \mu. \quad . \quad . \quad . \quad (6)$$

The member on the right being for a point on the theoretical isotherm nothing but the integral $-\int_1 v dp$, is given by the superficies (for the point F for instance):

$$-NHGM + LFCM.$$

The member on the right becomes also null in the *three* points

H , F , and K ,

and therefore we have for these points equally: $\frac{d^2 V}{dh^2} = 0$.

The curve, which presents the potential of the forces of cohesion V as function of h must, therefore, be asymptote to two straight lines belonging to the potentials of the homogeneous liquid and vapour phase; moreover, this curve must have a point of inflexion Q (fig. 5).

Fig. 5.

The value of $\frac{dV}{dh}$ is also at this point a maximum. This value of the strength of the force may be calculated in the following manner:—

The hydrostatic pressure *perpendicular* to the surface of the capillary layer is equal to the vapour-pressure, and can be considered as the difference between the thermic pressure θ and the cohesion in the same direction. Now I have found

* Phil. Mag. for Dec. 1906, p. 565, equation (11).

for this cohesion*

$$S_1 = -\frac{1}{8\pi f} \left\{ \left(\frac{dV}{dh} \right)^2 - \frac{V^2}{\lambda} \right\},$$

the potential function of the forces of cohesion being $-f e^{-\frac{r}{\lambda}}$.

$$\text{We have also: } p_1 = \theta - \frac{V^2}{8\pi f \lambda^2} + \frac{1}{8\pi f} \left(\frac{dV}{dh} \right)^2. \quad (7)$$

Remarking that $2\pi f \lambda^2 = a \dagger$,

$$\frac{\lambda^2}{4a} \left(\frac{dV}{dh} \right)^2 = p_1 - \theta + \frac{V^2}{4a}. \quad (8)$$

For the point of inflexion Q_1 we have $\frac{d^2V}{dh^2} = 0$; hence

$$V + 2a\rho = 0. \quad (9)$$

See equation (5).

Moreover if p denotes the pressure in a *homogeneous* phase with a density equal to the density in the considered point of the capillary layer, we have

$$p = \theta - a\rho^2. \quad (10)$$

Eliminating θ and V between (7), (9), and (10), we get

$$\frac{\lambda^2}{4a} \left(\frac{dV}{dh} \right)^2 = p_1 - p$$

or

$$\frac{dV}{dh} = \frac{2\sqrt{a}}{\lambda} \sqrt{p_1 - p} = 2\sqrt{2\pi f} \sqrt{p_1 - p}, \quad (11)$$

$p_1 - p$ being denoted by the distance SF in fig. (4).

Although in a theory of capillary attraction, where use is made of a potential function of the form

$$-f e^{-\frac{r}{\lambda}},$$

the thickness of the capillary layer becomes infinite and the V-curve of fig. 5 is asymptote to BB' and CC' , we have practically considered the capillary layer only as a layer for which the gradient of the potential V cannot be neglected in

* Phil. Mag. for Dec. 1906, p. 564.

† Loc. cit. p. 561.

calculating the value of the capillary tension :

$$H = \frac{1}{4\pi f} \int_{-\infty}^{\infty} \left(\frac{dV}{dh} \right)^2 dh,$$

and we may write :

$$H = \frac{1}{4\pi f} \int_1^2 \left(\frac{dV}{dh} \right)^2 dh, \quad . \quad . \quad . \quad (12)$$

where the indices refer to the points where the phases may be considered practically as homogeneous (liquid- and vapour-phase).

For the same reason the curve PQS in fig. 5 is considered as being touched respectively in the points S and P by the straight lines CC' and BB' *.

The consideration of fig. 5 gives for the curve, which $\frac{dV}{dh}$ presents in function of h , the curve in fig. 6.

Fig. 6.

The points V and W in fig. (6) correspond respectively with the points G and P in fig. (4).

* The superficies PSTP' = $\int_1^2 V dh$ in fig. 5 has a simple signification. Indeed, in integrating the two members of the equation (5), remarking that $\frac{dV}{dh}$ is null for the homogeneous phases, we get

$$\lambda^2 \int_1^2 \frac{d^2 V}{dh^2} dh = \int_1^2 V dh + 2a \int_1^2 \rho dh = 0.$$

Now, $\int_1^2 \rho dh$ denotes the mass of the capillary layer per unit of superficies; hence

$$\text{Superficies PSTP}' = -2am.$$

This equation is independent of the potential function used. Indeed, the equation (3) in the theory of surface-forces of Rayleigh (Phil. Mag. Febr. 1892) gives immediately :

$$\int_1^2 V dh = 2K \int_1^2 \rho dh = 2Km.$$

Practically, we consider the curve LVQWM, where VL and WM are the tangents at the points V and W and calculate the superficies between that curve and LM as parabolic segments. Hence

$$\begin{aligned}\text{Superficies LVQWML} &= \int_1^2 \frac{dV}{dh} dh = V_2 - V_1 = 2a(\rho_1 - \rho_2) \\ &= \frac{2}{3} \text{LM} \times \text{QS} = \frac{4}{3} \text{LM} \sqrt{2\pi f} \sqrt{p_1 - p}. \quad (13)\end{aligned}$$

QS being the maximum value of $\frac{dV}{dh}$, given by equation 11.

The distance between the centre of gravity and LM is, in virtue of the equations (12) and (9), expressed by

$$\frac{1}{2} \int_1^2 \left(\frac{dV}{dh} \right)^2 dh : \int_1^2 \frac{dV}{dh} = 2\pi f H : 2a(\rho_1 - \rho_2), \quad (14)$$

and equally by

$$\frac{2}{3} \text{QS} = \frac{2}{3} \cdot 2 \sqrt{2\pi f} \sqrt{p_1 - p}. \quad (15)$$

The expressions (14) and (15) give

$$\sqrt{p_1 - p} = \frac{5}{8} \sqrt{2\pi f} \frac{H}{a(\rho_1 - \rho_2)}. \quad (16)$$

Eliminating respectively $\sqrt{p_1 - p}$ and $a(\rho_1 - \rho_2)$ between the equations (16) and (13), we have for LM :

$$\text{LM} = \frac{6}{5\pi f} \frac{a^2(\rho_1 - \rho_2)^2}{H} = \frac{15}{16} \frac{H}{p_1 - p}, \quad (17)$$

where p is denoted by the distance RF in fig. (4).

Practically, I put also for the thickness of the capillary layer :

$$h = \frac{H}{p_1 - p}. \quad (18)$$

Further I have found * for the capillary tension :

$$H = \int_1^2 (p_1 - p_2) dh.$$

This equation and (18) give :

$$p_1 h - \int_1^2 p_2 dh = p_1 h - \bar{p} h$$

or

$$p = \frac{1}{h} \int_1^2 p_2 dh = p = \text{RF in fig. 4.}$$

* Phil. Mag. for December 1906, p. 563.

That is to say :

The average value $\bar{p}$ of the pressure p_2 parallel to the surface of the capillary layer may be considered as equal to the pressure of the theoretical isotherm in the point F (fig. 4), where the thermodynamic potential μ is equal to their value in the homogeneous phases H and K.

The equation

$$\frac{6}{5\pi f} \frac{a^2(\rho_1 - \rho_2)^2}{H} = \frac{15}{16} \frac{H}{p_1 - \bar{p}} \quad . \quad . \quad (17)$$

may be written

$$p_1 - \bar{p} = p_1 - \bar{p} = \frac{25\pi f}{32a^2} \left[\frac{H}{\rho_1 - \rho_2} \right]^2. \quad (17a)$$

In this formula for the difference between the pressure p_1 resp. *perpendicular* and the (average) pressure *parallel* to the surface of the capillary layer, f denotes the constant of the used potential function :

$$-f \frac{e^{-\frac{r}{\lambda}}}{r},$$

while a is the coefficient of the expression $a\rho^2$ of Laplace for the so-called molecular pressure or the function a in the equation of state of van der Waals. Although a is a function of the temperature, we will, as a first approximation, consider a and f as constants ; k being a new constant, we have also

$$p_1 - \bar{p} = k \left[\frac{H}{\rho_1 - \rho_2} \right]^2.$$

Now $\frac{H}{\rho_1 - \rho_2}$ is proportional to the rise of a liquid in a capillary tube and therefore proportional to $T_k - T^*$, where T_k is the critical temperature and T the temperature of observation. We have also (when the liquid wets the walls of the tube) :

$$p_1 - \bar{p} = \alpha \left(1 - \frac{T}{T_k} \right)^2. \quad . \quad . \quad . \quad . \quad (19)$$

α being a constant.

* E. C. de Vries, Inaugural-dissertation, and *Arch. Néerl. Science*, xxviii. pp. 210-219 (1894), and J. E. Verschaffelt, *Koninkl. Akad. v. Wetensch.* at Amsterdam, April 1896.

If the pressure is expressed in atmospheres, I have found for ether*:

$$p_1 - \bar{p} = 238 \left(1 - \frac{T}{T_k}\right)^2, \quad T = \text{absol. temp.,}$$

and for the temperature at which the (average) pressure $\bar{p}$ parallel to the surface of the capillary layer is null:

$$T = 0.82 T_k.$$

For this temperature (110°·7 Cels.) the point F in fig. 4 lies thus on the volume-axis, which is in accordance with the calculation of van der Waals, which shows (a conceived as a constant) that at the temperature $T = 0.844 T_k$ the volume-axis is a *tangent* to the theoretical isotherm†. For the temperature $T = 0.82 T_k$, p being null, we have for the thickness of the capillary layer:

$$h = \frac{H}{p_1} = \frac{\text{surface-tension}}{\text{vapour-tension}},$$

which gives for ether,

$$h = 8.5 \mu\mu.$$

At 110°·7 Cels., I find thus for the thickness of the capillary layer of ether a value of the same order of greatness as the thickness of the capillary layer of a solution of soap in water at ordinary temperatures according to the measurements of Reinold and Rücker.

§ 4. *The Gradient of p_2 and the Relation between the Pressure p_2 and the Density ρ for a Point in the Capillary Layer.*

While the pressure p_1 perpendicular to the surface of the capillary layer is a constant and equal to the vapour-pressure (see above, the end of § 2; we continue to consider the capillary layer as plane), the pressure p_2 parallel to their surface has a gradient. We will demonstrate how one can find the relation between p_2 and the reciprocal value $v = \frac{1}{\rho}$ of the density in a point of the capillary layer. For the cohesions resp. *in* the direction of the lines of force (that is to say in the direction normal to the surface of the capillary layer) and perpendicular to the lines of force (and therefore

* *Zeitschr. f. phys. Chem.* li. p. 358 (1905).

† van der Waals, *Continuïteit der gas en vloeistofoestand*.

parallel to the surface of the capillary layer) I have found*, the potential function of the forces of cohesion being

$$-f \frac{e^{-\frac{r}{\lambda}}}{r} :$$

and

$$S_1 = -\frac{1}{8\pi f} \left\{ \left(\frac{dV}{dh} \right)^2 - \frac{V^2}{\lambda^2} \right\}$$

$$S_2 = \frac{1}{8\pi f} \left\{ \left(\frac{dV}{dh} \right)^2 + \frac{V^2}{\lambda^2} \right\}.$$

The hydrostatic pressure being, in every direction, the difference between the thermic pressure θ and the cohesion, we have

$$p_1 = \theta - \left\{ \frac{V^2}{8\pi f \lambda^2} - \frac{1}{8\pi f} \left(\frac{dV}{dh} \right)^2 \right\}. \quad . \quad . \quad (20)$$

$$p_2 = \theta - \left\{ \frac{V^2}{8\pi f \lambda^2} + \frac{1}{8\pi f} \left(\frac{dV}{dh} \right)^2 \right\}. \quad . \quad . \quad (21)$$

and therefore

$$p_1 - p_2 = \frac{1}{4\pi f} \left(\frac{dV}{dh} \right)^2. \quad . \quad . \quad . \quad (22)$$

Now the pressures p_1 and p_2 are respectively the maximal and minimal value of the hydrostatic pressure in any direction in the considered point and the equation (22) shows therefore that:—

The departure from the law of Pascal in a point of the capillary layer is proportional to the square of the intensity of the force of cohesion.

Differentiating the equation (22), p_1 being a constant, we find :

$$-\frac{dp_2}{dh} = \frac{1}{2\pi f} \frac{dV}{dh} \frac{d^2V}{dh^2}. \quad . \quad . \quad . \quad (23)$$

Now we have found [see above, equation (6)]

$$\lambda^2 \frac{d^2V}{dh^2} = \mu_1 - \mu, \quad . \quad . \quad . \quad (6)$$

where μ is the thermodynamic potential for the considered point in the capillary layer and μ_1 its value in the liquid- and vapour-phase. We have therefore

$$-\frac{dp_2}{dh} = \frac{1}{2\pi f \lambda^2} \frac{dV}{dh} (\mu_1 - \mu). \quad . \quad . \quad . \quad (24)$$

* Phil. Mag. for Dec. 1906, p. 564.

In three points of the theoretical isotherm (fig. 4) the thermodynamic potential has the same value *i. e.*, in the points H, K, and F; H and K are the points where the physical isotherm (HK) cuts the theoretical, while we have for the point F:

$$\text{surface NHGM} = \text{surface LFGM.}$$

Between H and F, $\mu_1 > \mu$; in the point F, $\mu = \mu_1$; and between F and K, $\mu > \mu_1$. Now I have demonstrated that $\frac{dV}{dh}$ * is always positive in the capillary layer; $\frac{dp_2}{dh}$ has therefore in the equation (24) the same sign as $\mu - \mu_1$. If we therefore denote a point in the capillary layer by the corresponding point † of the theoretical isotherm, we have:

$$\text{between H and F, } \frac{dp_2}{dh} < 0;$$

$$\text{in F, } \frac{dp_2}{dh} = 0;$$

$$\text{between F and K, } \frac{dp_2}{dh} > 0.$$

The hydrostatic pressure p_2 parallel to the surface of the capillary layer diminishes therefore between H and F, has a

Fig. 7.

minimum value in F, and increases between F and K. The curve which presents p_2 as a function of h has therefore a shape as in fig. 7. AB is the thickness of the capillary layer.

* *Zeitschr. f. Phys. Chem.* xlii. p. 71 (1902).

† That is to say, that this point corresponds with the same density as the density in the considered point of the capillary layer.

The surface of RDQESR is given by $\int_1^2 (p_1 - p_2) dh$ and presents the value of the constant of Laplace. Now (see above) the pressure p for the point F at which $\mu = \mu_1$ has the same value as the average pressure $p = \frac{1}{h} \int_1^2 p_2 dh$ in the capillary layer. Hence

$$\text{surface RDQESR} = (p_1 - p)h, \quad . \quad . \quad . \quad (25)$$

where h denotes the thickness of the capillary layer.

The equations (20) and (21) give further by addition :

$$\frac{p_1 + p_2}{2} = \theta - \frac{V^2}{8\pi f \lambda^2}, \quad . \quad . \quad . \quad . \quad (26)$$

Now for the point Q in fig. 7, which corresponds with the point F in fig. 4, we have $\mu = \mu_1$, and the equation (4) gives therefore for the point Q in fig. 7,

$$V = -2a\rho.$$

If p denotes the pressure of the isotherm in the point F, we have :

$$\theta = p + a\rho^2.$$

The equation (26) becomes therefore for the point F in fig. 4 or the point Q in fig. 7 :

$$\frac{p_1 + p_2}{2} = p + a\rho^2 - \frac{4a^2\rho^2}{8\pi f \lambda^2}.$$

$$\text{Further, } 2\pi f \lambda^2 = a^* ; \text{ hence } p = \frac{p_1 + p_2}{2}.$$

By substitution of this value of p in the equation (25), we find :

$$\text{surface RDQESR} = \frac{1}{2}(p_1 - p_2)h = \frac{1}{2} \text{ surface RUVSR}.$$

If, however, we would bring the properties of the theoretical isotherm into connexion with those of the capillary layer, we must find the relation between p_2 and $v \left(= \frac{1}{\rho} \right)$. Therefore we depart from the equation (26) and make use of the equation of state of van der Waals, which gives for the thermic pressure :

$$\theta = \frac{RT}{v-b}, \quad \text{and thus} \quad \frac{p_1 + p_2}{2} = \frac{RT}{v-b} - \frac{V^2}{4a}. \quad . \quad (27)$$

* Phil. Mag. for December 1906, p. 564.

Now

$$d\theta = -\rho dV;$$

or

$$dV = -vd\theta = -RTvd \frac{1}{v-b}.$$

Integrating,

$$V - V_1 = RT \log \frac{v-b}{v_1-b} - RTb \left(\frac{1}{v-b} - \frac{1}{v_1-b} \right),$$

where the index corresponds to the liquid state. Further,

$$V_1 = -2a\rho_1 = -\frac{2a}{V_1} \\ \text{(Gauss and van der Waals)*.}$$

By substitution in (27),

$$\frac{p_1 + p_2}{2} = \frac{RT}{v-b} - \frac{1}{4a} \left\{ RT \log \frac{v-b}{v_1-b} + RTb \frac{v-v_1}{(v-b)(v_1-b)} - \frac{2a}{v_1} \right\}^2. \quad (28)$$

Since the hydrostatic pressure p_1 is nothing but the vapour-pressure and thus at a definite temperature a constant, the equation (28) may be considered as the relation between p_2 and v . For the point H in fig. 4, $v=v_1$ and $p_1=p_2$; the equation (28) properly becomes therefore for the point H :

$$p_1 = \frac{RT}{v_1-b} - \frac{1}{4a} \frac{4a}{v_1^2} = \frac{RT}{v_1-b} - \frac{a}{v_1^2}.$$

By the aid of the well-known relation

$$RT \log \frac{v_2-b}{v_1-b} = a \left(\frac{1}{v} - \frac{1}{v_2} \right) + p_1(v_2-v_1),$$

we find easily that for the point K in fig. 4 the equation (28) properly becomes

$$p_1 = \frac{RT}{v_2-b} - \frac{a}{v_2^2}.$$

As, however, the equation (28) is not easily to be discussed, we start immediately from equation (24)

$$dp_2 = \frac{\mu - \mu_1}{a} dV. \quad . \quad . \quad (24)$$

Now, $d\theta = -\rho dV$ or $dV = -vd\theta$, and, still ever adopting

* Hence it has often been wrongly concluded that the potential energy of the forces between the *molecules* should be $-ap$.

(30) gives therefore

$$\frac{d^2 p_2}{dv^2} = \frac{RT(v+b)}{a(v-b)^3} (\mu_1 - \mu).$$

In the point U just beneath the point G, $\mu_1 - \mu > 0$ and the p_2-v curve turns therefore the convex side to the volume-axis. Because at the point H the tangent is parallel to the volume-axis, the p_2-v curve has a point of flexion between H and U. In the same manner we find that the p_2-v curve HUVWK has also a point of flexion between W and V, where V is the point just beneath P.

The curve HUVWK gives therefore together with the empiric isotherm HK a complete image of the relation between the hydrostatic pressures (p_1 and p_2) and the reciprocal value $v = \frac{1}{\rho}$ of the density in a point of the capillary layer, whereas the state of every point of the capillary is completely described by these three things.

L. *Condensation Nuclei produced by Cooling Gases to Low Temperatures.* By GWILYM OWEN, B.A., M.Sc., Assistant Lecturer and Demonstrator in Physics in the University of Liverpool, and A. LL. HUGHES, B.Sc.*

WE have recently examined the condition in which air is evolved from charcoal after absorption in a dry and dust-free state at the temperature of liquid air, in order to determine whether it remains dust-free when liberated by warming the charcoal to atmospheric temperature. The charcoal was contained in the bend of a small glass U-tube connected to the cloud chamber of a Wilson's expansion apparatus; and, after the liquid air used for the cooling was removed and a sufficient time was allowed for the evolved air to regain the temperature of the atmosphere, a sample of the air was admitted through a glass tap into the cloud chamber. It was at once found that the evolved air contained large numbers of nuclei, sufficient, in fact, to produce dense showers; but when a control experiment was performed without any charcoal in the U-tube, a similar number of nuclei appeared. The experiments therefore were indecisive as to whether the escape of the absorbed air caused disintegration of the charcoal, but they raised the very interesting question as to the cause of the showers obtained in the expansion chamber when air which had merely passed through a process of cooling

* Communicated by Prof. L. R. Wilberforce, M.A.