

*Citation:*

H. Hulshof, The direct deduction of the capillary constant  $\sigma$  as a surfacetension, in:  
KNAW, Proceedings, 2, 1899-1900, Amsterdam, 1900, pp. 389-406

If we take  $T_1 = 2 T_k$  and for  $v_1$  the value for the greatest cooling according to the process  $\chi_1 = \chi_2$ , so  $v_1 = 2,2 b$ , and for  $v_2$  a value, which corresponds to  $p_2 = 20$  atm., then even by this one expansion the air would have been cooled already far below the critical point. Lord RAYLEIGH has already pointed out, that the process of LINDE might be improved by causing the expanding gas to perform more work. It remains therefore desirable to find an arrangement, by which the expansion approaches more nearly an isentropic process than is the case in the apparatus of LINDE.

**Physics.** — Prof. J. D. VAN DER WAALS presents for the proceedings a communication of Mr. H. HULSHOF at Delft, on: *“The direct deduction of the capillary constant  $\sigma$  as a surface-tension.”*

The amount of the capillary tension and the capillary energy, as found by Prof. VAN DER WAALS in his *Théorie Thermodynamique de la capillarité*, may also be determined directly. The existence of capillary tension is undoubtedly the consequence of molecular attraction. Therefore we shall have to examine the influence of molecular attraction in the capillary layer, i.e. we shall have to determine the value of the molecular pressure for an arbitrary point of the capillary layer. The equation of state gives  $a\rho^2$  for the value of the molecular pressure; the equation of state, however, comprises only those cases, in which the distribution of matter is homogeneous. As the molecular pressure is the direct consequence of the attraction, which the particles exercise on one another and is therefore determined in a point by the condition of the surroundings, it may be expected that for not homogeneous distribution of matter the molecular pressure in different directions will have different values. The existence of capillary tension is to be ascribed to the fact, that in the capillary layer the molecular pressure in the direction of the surface of the liquid is different from that in the direction normal to the surface.

When the matter is homogeneously distributed the molecular pressure per surface element  $do$  is equal to the force with which all the matter on one side of the plane in which  $do$  is situated, attracts in the direction towards this plane the material cylinder with  $do$  as base, situated on the other side of the plane. In the capillary layer we can also define the molecular pressure in the same way.

Therefore we shall determine the molecular pressure in a point  $A$  of the capillary layer:

- $a$ . in the direction normal to the surface of the liquid;
- $b$ . in the direction parallel to the surface.

$a$ . Through  $A$  we lay a plane parallel to the surface of the liquid. The force with which the layer of a thickness  $du$ , parallel to the separating layer, at a distance  $u$  below the plane laid through  $A$ , attracts the unity of mass  $f$ ,  $h_1 c M$  above this plane, is:

$$- d\psi(u + h_1),$$

on the supposition that the examined layer has the unity of density.

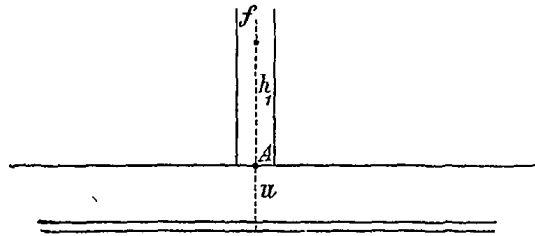


Fig. I

The density in a layer parallel to the surface of the liquid is the same everywhere. We give therefore, the density as a function of the distance from the plane laid through  $A$ . If

we call the normal  $h$  and take as positive direction that one turned towards the vapour phasis, so that  $h = 0$  is situated in the homogeneous liquid phasis, the density of the layer with a thickness  $du$  will be:

$$\rho - u \frac{d\rho}{dh} + \frac{u^2}{1.2} \frac{d^2\rho}{dh^2} - \text{etc.}$$

where  $\rho$ ,  $\frac{d\rho}{dh}$ ,  $\frac{d^2\rho}{dh^2}$  have the values which these quantities have in point  $A$ . For all layers below the plane through it, the attraction is:

$$\int_{u=0}^{u=\infty} \left( \rho - u \frac{d\rho}{dh} + \frac{u^2}{1.2} \frac{d^2\rho}{dh^2} \right) d\psi(u + h_1).$$

Let us imagine in  $f$  not the unity of mass, but let us consider there a volume-element with a thickness of  $dh_1$  and for the sake of simplicity with a base of  $1 \text{ cm.}^2$  instead of  $do$ . The density of this volume-element being:

$$\varrho + h_1 \frac{d\varrho}{dh} + \frac{h_1^2}{1.2} \frac{d^2\varrho}{dh^2} + \text{etc.}$$

the attraction which is to be calculated may be represented by:

$$\int_0^\infty \left( \varrho + h_1 \frac{d\varrho}{dh} + \frac{h_1^2}{1.2} \frac{d^2\varrho}{dh^2} \right) dh_1 \int_{u=0}^{u=\infty} \left( \varrho - u \frac{d\varrho}{dh} + \frac{u^2}{1.2} \frac{d^2\varrho}{dh^2} \right) d\psi(u + h_1)$$

$$\int_{u=0}^{u=\infty} -\varrho d\psi(u + h_1) = \varrho \psi(h_1)$$

$$\int_{u=0}^{u=\infty} u \frac{d\varrho}{dh} d\psi(u + h_1) = \left[ u \frac{d\varrho}{dh} \psi(u + h) \right]_{u=0}^{u=\infty} - \frac{d\varrho}{dh} \int_{u=0}^{u=\infty} \psi(u + h_1) du$$

The integrated term is zero for the two limits.

$$\int_{u=0}^{u=\infty} -\frac{u^2}{1.2} \frac{d^2\varrho}{dh^2} d\psi(u + h_1) = \left[ -\frac{u^2}{1.2} \frac{d^2\varrho}{dh^2} \psi(u + h_1) \right]_{u=0}^{u=\infty} +$$

$$+ \frac{d^2\varrho}{dh^2} \int_{u=0}^{u=\infty} \psi(u + h_1) u du$$

The integrated term is here also zero for the two limits.  
The integral becomes therefore:

$$\int_0^\infty \left( \varrho + h_1 \frac{d\varrho}{dh} + \frac{h_1^2}{1.2} \frac{d^2\varrho}{dh^2} \right) dh_1 \left[ \varrho \psi(h_1) - \frac{d\varrho}{dh} \int_{u=0}^{u=\infty} \psi(u + h_1) du + \right.$$

$$\left. + \frac{d^2\varrho}{dh^2} \int_{u=0}^{u=\infty} \psi(u + h_1) u du \right]$$

$$\int_0^\infty \varrho dh_1 \varrho \psi(h_1) = \varrho^2 \int_0^\infty \psi(h_1) dh_1 = a\varrho^2 \dots \dots (1) (1')$$

$$\begin{aligned}
-\int_0^{\infty} \varrho dh_1 \frac{d\varrho}{dh} \int_{u=0}^{u=\infty} \psi(u+h_1) du &= -\varrho \frac{d\varrho}{dh} \int_0^{\infty} dh_1 \int_{u=0}^{u=\infty} \psi(u+h_1) du = \\
&+ \varrho \frac{d\varrho}{dh} \int_0^{\infty} dh_1 \int_{u=0}^{u=\infty} d\pi(u+h_1) \quad . \quad (1) (2')
\end{aligned}$$

We put  $\psi(u) du = -d\pi(u)$  and suppose, as is usually done that  $\pi(\infty)$  is equal to zero. The latter expression may be transformed into:

$$-\varrho \frac{d\varrho}{dh} \int_0^{\infty} \pi(h_1) dh_1 = \left[ -\varrho \frac{d\varrho}{dh} h_1 \pi(h_1) \right]_0^{\infty} - \varrho \frac{d\varrho}{dh} \int_0^{\infty} h_1 \psi(h_1) dh_1$$

The integrated term is zero for the two limits.

$$\begin{aligned}
\int_0^{\infty} \varrho dh_1 \frac{d^2\varrho}{dh^2} \int_{u=0}^{u=\infty} \psi(u+h_1) u du &= -\varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} dh_1 \int_{u=0}^{u=\infty} u d.\pi(u+h_1) = \\
&= -\varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} dh_1 \left[ u \pi(u+h_1) \right]_{u=0}^{u=\infty} + \varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} dh_1 \int_{u=0}^{u=\infty} \pi(u+h_1) du \quad \dots (1) (3')
\end{aligned}$$

Here too the integrated term is zero for the two limits.

We put  $\pi(x) dx = -d\chi(x)$  and suppose as usual that  $\chi(\infty) = 0$ . The latter expression may be transformed into:

$$\begin{aligned}
-\varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} dh_1 \int_{u=0}^{u=\infty} d.\chi(u+h_1) &= -\varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} dh_1 \left[ \chi(u+h_1) \right]_{u=0}^{u=\infty} = \\
&= \varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} \chi(h_1) dh_1 = \varrho \frac{d^2\varrho}{dh^2} \left[ h_1 \chi(h_1) \right]_0^{\infty} + \varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} h_1 \pi(h_1) dh_1.
\end{aligned}$$

The integrated term is zero for the two limits; so the expression becomes:

$$\varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} \pi(h_1) d. \frac{h_1^2}{2} = \varrho \frac{d^2\varrho}{dh^2} \left[ \pi(h_1) \frac{h_1^2}{2} \right]_0^{\infty} + \varrho \frac{d^2\varrho}{dh^2} \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1$$

The integrated form is again zero for the two limits.

$$\int_0^{\infty} h_1 \frac{d\rho}{dh} \rho \psi(h_1) dh_1 = \rho \frac{d\rho}{dh} \int_0^{\infty} h_1 \psi(h_1) dh_1 \dots (2) (1')$$

$$\begin{aligned} \int_0^{\infty} h_1 \frac{d\rho}{dh} dh_1 \frac{d\rho}{dh} \int_{u=0}^{u=\infty} \psi(u+h_1) du &= - \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} h_1 dh_1 \int_{u=0}^{u=\infty} \psi(u+h_1) du = \\ &= \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} h_1 dh_1 \int_{u=0}^{u=\infty} d \cdot \pi(u+h_1) = \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} h_1 dh_1 \left[ \pi(u+h_1) \right]_{u=0}^{u=\infty} \\ &= - \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} h_1 dh_1 \pi(h_1) = - \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} \pi(h_1) d \cdot \frac{h_1^2}{2} = \\ &= - \left( \frac{d\rho}{dh} \right)^2 \left[ \pi(h_1) \frac{h_1^2}{2} \right]_0^{\infty} - \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1 \dots (2) (2') \end{aligned}$$

The integrated form is zero for the two limits.

$$\int_0^{\infty} \frac{h_1^2}{1.2} \frac{d^2\rho}{dh^2} dh_1 \rho \psi(h_1) = \rho \frac{d^2\rho}{dh^2} \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1 \dots (3) (1')$$

$$\int_0^{\infty} h_1 \frac{d\rho}{dh} dh_1 \int_{u=0}^{u=\infty} \frac{d^2\rho}{dh^2} \psi(u+h_1) u du = \frac{d\rho}{dh} \frac{d^2\rho}{dh^2} \int_0^{\infty} h_1 dh_1 \int_{u=0}^{u=\infty} \psi(u+h_1) u du \dots (2) (3')$$

This expression has the dimension  $\int_0^{\infty} h_1^3 \psi(h_1) dh_1$  and will be neglected by us as well as (3) (2') and (3) (3').

For the molecular pressure in the direction normal to the surface of the liquid we find therefore:

$$\begin{aligned} \rho \rho^2 - \rho \frac{d\rho}{dh} \int_0^{\infty} h_1 \psi(h_1) dh_1 + \rho \frac{d^2\rho}{dh^2} \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1 + \rho \frac{d\rho}{dh} \int_0^{\infty} h_1 \psi(h_1) dh_1 - \\ - \left( \frac{d\rho}{dh} \right)^2 \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1 + \rho \frac{d^2\rho}{dh^2} \int_0^{\infty} \frac{h_1^2}{2} \psi(h_1) dh_1 \end{aligned}$$

or

$$a\rho^2 + \rho \frac{d^2\varrho}{dh^2} \int_0^\infty h_1^2 \psi(h_1) dh_1 - \left(\frac{d\rho}{dh}\right)^2 \int_0^\infty \frac{h_1^2}{2} \psi(h_1) dh_1$$

We put  $\int_0^\infty h_1 \psi(h_1) dh_1 = c_1$  and  $\int_0^\infty h_1^2 \psi(h_1) dh_1 = c_2$ , therefore the expression for the molecular pressure is transformed into:

$$a\rho^2 + c_2 \rho \frac{d^2\varrho}{dh^2} - \frac{c_2}{2} \left(\frac{d\rho}{dh}\right)^2$$

If we add to this molecular pressure the external pressure  $p_1$ , we may equate this sum to  $p + a\rho^2$ , if  $p$  represents the pressure, which belongs to a homogeneous phasis with the density  $\rho$ .

$$p_1 + a\rho^2 + c_2 \rho \frac{d^2\varrho}{dh^2} - \frac{c_2}{2} \left(\frac{d\rho}{dh}\right)^2 = p + a\rho^2$$

$$p_1 - p = -c_2 \rho \frac{d^2\varrho}{dh^2} - \frac{c_2}{2} \left(\frac{d\rho}{dh}\right)^2$$

This relation is the same as has been deduced by Prof. VAN DER WAALS.

b. We shall now calculate the molecular pressure in the direction of the surface of the liquid. For this purpose we suppose a plane laid through  $A$ , normal to the capillary layer, and in  $A$  a cylinder

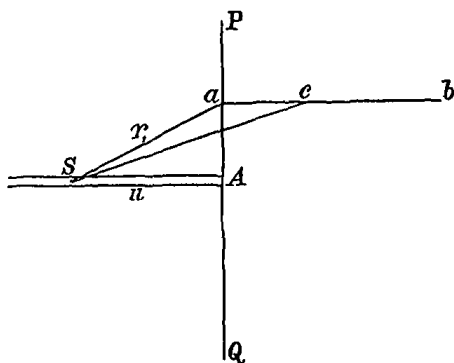


Fig. 2.

with a thickness  $do$  normal to that plane. The matter in the cylinder has everywhere the same density. The unity of mass in  $c$  acts on the unity of mass in  $S$  with a force  $\varphi(r)$ , if  $r$  represents the distance  $Sc$ . The component of this force in the direction normal to  $PQ$  is  $\varphi(r) \cos \underline{Sca}$  or  $\varphi(r) \frac{dr}{dz}$  if we

call the direction  $ab$  the direction  $z$ .

The material cylinder  $ab \perp PQ$ , with a thickness  $do'$  and with a

unity of density acts therefore on the unity of mass in  $S$  with a force, of which the component in the direction  $\perp PQ$  is:

$$do' \int_{r=r_1}^{r=\infty} \varphi(r) \frac{dr}{dz} dz = do' \int_{r_1}^{\infty} \varphi(r) dr = do' \zeta(r_1),$$

where we assume that  $d \cdot \zeta(r) = -\varphi(r) dr$  and  $\zeta(\infty) = 0$ .

Let us now imagine in the plane  $PQ$  a system of polar coordinates with  $A$  as origin and the line  $\perp$  to the paper as fixed axis. We take as surface element  $y dy d\varphi$ . Let the density in  $A$  be  $\rho$ , then in an arbitrary point of the plane  $PQ$  the density is:

$$\rho + \frac{d\rho}{dh} y \sin \varphi + \frac{1}{2} \frac{d^2\rho}{dh^2} y^2 \sin^2 \varphi + \dots$$

It is easy to see that if the terms  $\rho + \frac{d\rho}{dh} y \sin \varphi$  alone existed, the attraction which the substance right of  $PQ$  would exercise on the unity of mass in the direction  $\perp PQ$ , would be the same as in case of a homogeneous density  $\rho$  and therefore:

$$\rho \psi(u).$$

We have still to add to this attraction:

$$\int_{y=0}^{y=\infty} \int_{\varphi=0}^{\varphi=2\pi} \frac{1}{2} \frac{d^2\rho}{dh^2} y^2 \sin^2 \varphi y dy d\varphi \zeta(r) .$$

$$\int_0^{2\pi} \sin^2 \varphi d\varphi = \pi$$

and so the expression becomes:

$$\frac{1}{2} \frac{d^2\rho}{dh^2} \int_0^{\infty} \zeta(r) \pi y^3 dy = \frac{1}{4} \frac{d^2\rho}{dh^2} \int_{r=u}^{r=\infty} 2\pi \zeta(r) (r^2 - u^2) r dr$$

for  $r^2 = u^2 + y^2$  and so  $r dr = y dy$ .

For this latter expression we may also write:



$$\begin{aligned}
-\frac{1}{4} \frac{d^2 \rho}{dh^2} \int_{r=u}^{r=\infty} (r^2 - u^2) d\psi(r) &= \\
&= \left[ -\frac{1}{4} \frac{d^2 \rho}{dh^2} (r^2 - u^2) \psi(r) \right]_{r=u}^{r=\infty} + \frac{1}{2} \frac{d^2 \rho}{dh^2} \int_{r=u}^{r=\infty} \psi(r) r dr .
\end{aligned}$$

This integrated term is zero for the two limits.

So we find for the component of the attraction  $\perp PQ$ :

$$\rho \psi(u) + \frac{1}{2} \frac{d^2 \rho}{dh^2} \int_u^{\infty} \psi(r) r dr$$

and therefore for the attraction of the cylinder:

$$do \int_0^{\infty} \rho du \left[ \rho \psi(u) + \frac{1}{2} \frac{d^2 \rho}{dh^2} \int_u^{\infty} \psi(r) r dr \right]$$

and for the molecular pressure in the direction of the capillary layer:

$$\int_0^{\infty} \rho du \left[ \rho \psi(u) + \frac{1}{2} \frac{d^2 \rho}{dh^2} \int_u^{\infty} \psi(r) r dr \right] .$$

This expression becomes:

$$\rho^2 \int_0^{\infty} \psi(u) du - \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} du \int_u^{\infty} r d\pi(r) .$$

The latter term may be transformed into:

$$\begin{aligned}
& -\frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} du \left[ u \pi(u) \right]_u^{\infty} + \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} du \int_u^{\infty} \pi(r) dr = \\
& = \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} u \pi(u) du + \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} \chi(u) du = \\
& = \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} u \pi(u) du + \left[ \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} u \chi(u) \right]_0^{\infty} + \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} u \pi(u) du .
\end{aligned}$$

The integrated term is zero for the two limits and so we keep :

$$\frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} 2 u \pi (u) du = \left[ \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} u^2 \pi (u) \right]_0^{\infty} + \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} u^2 \psi (u) du .$$

Also this integrated term is zero for the two limits.

We find therefore for the molecular pressure in the direction of the capillary layer :

$$\rho^2 \int_0^{\infty} \psi (u) du + \frac{1}{2} \rho \frac{d^2 \rho}{dh^2} \int_0^{\infty} u^2 \psi (u) du$$

or

$$a \rho^2 + \frac{c_2}{2} \rho \frac{d^2 \rho}{dh^2} .$$

The pressure in consequence of the attraction has therefore another value in the direction of the capillary layer than in the direction normal to this layer. In the direction of the capillary layer a surplus of molecular pressure will exist in consequence of the attraction. This surplus will amount to :

$$a \rho^2 + \frac{c_2}{2} \rho \frac{d^2 \rho}{dh^2} - a \rho^2 - c_2 \rho \frac{d^2 \rho}{dh^2} + \frac{c_2}{2} \left( \frac{d\rho}{dh} \right)^2$$

or

$$- \frac{c_2}{2} \rho \frac{d^2 \rho}{dh^2} + \frac{c_2}{2} \left( \frac{d\rho}{dh} \right)^2 .$$

This surplus of pressure taken over a surface  $\perp$  to the bordering layer whose length in the direction of the capillary layer is 1 cm. and whose breadth is equal to the thickness of the capillary layer, furnishes the value of the capillary tension :

$$\int \left\{ - \frac{c_2}{2} \rho \frac{d^2 \rho}{dh^2} + \frac{c_2}{2} \left( \frac{d\rho}{dh} \right)^2 \right\} dh ,$$

which integral is to be taken over the whole thickness of the capillary layer.

We may make also another representation to ourselves of the capillary tension. Let us bear in mind that the thermal pressure  $\vartheta = \frac{RT}{V-b}$  in any point has the same value in all directions. If now in consequence of the molecular attraction the molecular pressure

has different values in different directions, the condition, which is thereby brought about, may be compared with a condition where the pressure has a different value in different directions. If we call the quantity which is to be considered as the pressure in the direction  $\perp$  to the capillary layer,  $p_1$  and that in the direction of the capillary layer, the following formula would hold:

$$p_1 + a \varrho^2 + c_2 \varrho \frac{d^2 \varrho}{dh^2} - \frac{c_2}{2} \varrho \left( \frac{d\varrho}{dh} \right)^2 = p_2 + a \varrho^2 + \frac{c_2}{2} \varrho \frac{d^2 \varrho}{dh^2}$$

or

$$p_1 - p_2 = -\frac{c_2}{2} \varrho \frac{d^2 \varrho}{dh^2} + \frac{c_2}{2} \left( \frac{d\varrho}{dh} \right)^2.$$

This difference in pressure taken over a surface normal to the bordering layer, with a length of 1 cm. and a breadth equal to the thickness of the capillary layer, furnishes the value of the capillary tension:

$$\int (p_1 - p_2) dh.$$

The work which is to be performed for enlarging the surface with 1 cm.<sup>2</sup>, the temperature remaining constant, so the capillary energy is:

$$\sigma = \int (p_1 - p_2) dh = \int \left\{ -\frac{c_2}{2} \varrho \frac{d^2 \varrho}{dh^2} + \frac{c_2}{2} \left( \frac{d\varrho}{dh} \right)^2 \right\} dh.$$

With the aid of this latter consideration we can easily show that the capillary energy is equal to the amount with which the thermodynamic potential of the bordering layer, taken over a cylinder whose section is 1 cm.<sup>2</sup> and whose height is equal to the thickness of the capillary layer, exceeds the thermodynamic potential of the same mass in the homogeneous vapour- or liquid-phases.

**Astronomy.** — “*Determination of the latitude of Ambriz and of San Salvador (Portuguese West-Africa).*” By C. SANDERS (Communicated by Dr. E. F. VAN DE SANDE BAKHUYZEN).

During a several years' residence on the West coast of Africa I spent as much as I could of my leisure in making observations for determining geographical positions. Till now, besides a rather