Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Physics. — Prof. J. D. VAN DER WAALS offers on behalf of Dr. G. BAKKER of Schiedam a paper on: " *The potential function* $\varphi(r) = \dfrac{Ae^{-qr} + Be^{qr}}{r}$ *and* $\varphi(r) = \dfrac{A \sin(qr + \alpha)}{r}$ *and the potential function of* VAN DER WAALS".

In a previous paper I have pointed out that these potential functions lend to a spherical homogeneous shell or to a massive sphere, the density of which is a function of the distance from the centre, the property to attract an external point as if the mass were concentrated in the centre, if we leave a factor, depending on the radius, out of account. The differential equations, which are satisfied by these functions, are resp.:

$$\frac{d^2\varphi}{dx^2} + \frac{2}{r}\frac{d\varphi}{dr} = q^2\varphi \quad \ldots \ldots \ldots (1)$$

and

$$\frac{d^2\varphi}{dr^2} + \frac{2}{r}\frac{d\varphi}{dr} = -q^2\varphi \quad \ldots \ldots \ldots (2)$$

If we substitute $x^2 + y^2 + z^2$ for r^2, these equations may also be written:

$$\nabla^2\varphi = q^2\varphi. \quad \ldots \ldots \ldots \ldots (1a)$$

and

$$\nabla^2\varphi = -q^2\varphi \quad \ldots \ldots \ldots (2a)$$

The resemblance of these differential equations with the well-known equation $\nabla^2\varphi = 0$ for the potential of NEWTON, made it probable that these potential functions would have more in common. The analogy was even closer than I expected. I found e. g. that the action between two systems of agens, spread over arbitrary spaces and surfaces, may be substituted by a system of tensions in the medium in a similar way as MAXWELL did for electric agens.

In the first place we state the following theorems:

I. If ψ represents the potential in a point x, y, z of an agens which fills several spaces continuously, and is spread over several surfaces, the potential function being $\varphi(r) = \dfrac{Ae^{-qr} + Be^{qr}}{r}$, we find for the potential, with the exception of some points and surfaces the differential equation:

$$\nabla^2\psi = q^2\psi - 4\pi(A + B)\varrho \quad \ldots \ldots \ldots (3)$$

in which ϱ represents the density in that point.

18*

II. If ψ_1 represents the potential in a point x, y, z of an agens which fills several spaces continuously and is spread over several surfaces, the potential function being $\varphi_1(r) = \dfrac{A \sin(qr + \alpha)}{r}$, we get for the potential the differential equation:

$$\nabla^2 \psi_1 = - q^2 \psi_1 - 4 \pi \varrho A \sin \alpha \quad . \quad . \quad . \quad . \quad (4)$$

some points and surfaces being excepted; ϱ represents the density in that point.

It is easy to find equation:

$$\frac{A e^{-qr} + B e^{qr}}{r} - \frac{A + B}{r} = q(B - A) + \frac{(A + B) q^2 r}{\pi 2} + \frac{(B - A) q^3 r^2}{\pi 3} + .$$

Let us put:

$$\frac{A e^{-qr} + B e^{qr}}{r} - \frac{A + B}{r} = u \quad . \quad . \quad . \quad . \quad (5)$$

By applying the operation ∇^2 to the two members of the last equation but one, taking into account that $\nabla^2 \dfrac{A + B}{r} = 0$, we find:

$$\nabla^2 \frac{A e^{-qr} + B e^{qr}}{r} = \nabla^2 u = q^2 \left\{ \frac{A + B}{r} + (B - A) q + \frac{(A + B) q^2 r}{r} + \right\} =$$

$$= q^2 \frac{A e^{-qr} + B e^{qr}}{r} \quad \text{or}$$

$$\nabla^2 \varphi = \nabla^2 u = q^2 \varphi \quad . \quad . \quad . \quad . \quad (6)$$

The proof of the first theorem is based on this consideration. The potential ψ in a point x, y, z of an agens with a cubic density ϱ and a surface density σ, becomes if the potential function is $\varphi(r)$:

$$\psi = \Sigma \int \varrho \, \varphi(r) \, d\tau + \Sigma \int \sigma \, \varphi(r) \, ds$$

if r represents the distance from point x, y, z to the elements of space or of surface for which the density is represented by ϱ or σ.

We have:

$$\varphi(r) = \frac{A + B}{r} + u \quad \text{(equation 5)}$$

The potential may be written:

$$\psi = \Sigma \int \frac{(A+B)\varrho}{r} \, d\tau + \Sigma \int \frac{(A+B)\sigma}{r} \, ds + \Sigma \int \varrho u \, d\tau + \Sigma \int \sigma u \, ds$$

or

$$\psi = (A+B) \left\{ \Sigma \int \frac{\varrho \, d\tau}{r} + \Sigma \int \frac{\sigma \, ds}{r} \right\} + \Sigma \int \varrho u \, d\tau + \Sigma \int \sigma u \, ds$$

If we apply to both members the operation ∇^2, we get:

1st
$$\nabla^2 \left\{ \Sigma \int \frac{\varrho \, d\tau}{r} + \Sigma \int \frac{\sigma \, ds}{r} \right\} = - 4\pi \varrho$$

and because $\nabla^2 u = q^2 \varphi$ (see equation 6):

2nd
$$\nabla^2 \Sigma \int \varrho u \, d\tau + \nabla^2 \Sigma \int \sigma u \, ds = \Sigma \int \varrho \nabla^2 u \, d\tau + \Sigma \int \sigma \nabla^2 u \, ds =$$

$$= q^2 \, \Sigma \int \varrho \, \varphi \, d\tau + q^2 \, \Sigma \int \sigma \, \varphi \, ds = q^2 \, \psi$$

Hence:
$$\nabla^2 \psi = q^2 \psi - 4\pi (A+B) \varrho \quad \cdots \cdots \quad (7)$$

To prove the second theorem, we point out that:

$$A \sin (qr + \alpha) = A \cos \alpha \sin qr + A \sin \alpha \cos qr$$

If we substitute a new constant A_1 for $A \cos \alpha$ and B for $A \sin \alpha$ we may write the potential function $\varphi_1 (r)$ as follows:

$$\varphi_1 (r) = \frac{A_1 \sin qr + B \cos qr}{r}$$

We find easily:

$$\frac{A_1 \sin qr + B \cos qr}{r} - \frac{B}{r} = A_1 q - \frac{B q^2 r}{\pi 2} -$$

$$- \frac{A_1 q^3 r^2}{\pi 3} + \frac{B q^4 r^3}{\pi 4} + \frac{A_1 q^5 r^4}{\pi 5} -$$

If we put $\varphi_1 (r) - \dfrac{B}{r} = v$ and apply the operation ∇^2, we get :

$$\nabla^2 v = -q^2 \left(\frac{B}{r} + A_1 q - \frac{B q^2 r}{\pi 2} - \frac{A_1 q^3 r^2}{\pi 3} - \cdots \right) =$$

$$= -q^2 \left(\frac{B}{r} + u \right) = -q^2 \varphi_1 \quad . \quad . \quad (8)$$

and on this the proof of the second theorem is based.

Now we have for the potential in a point:

$$\psi = \Sigma \int \varrho \, \varphi_1 \, (r) \, d\tau + \Sigma \int \sigma \, \varphi_1 \, (r) \, ds$$

Now $\varphi_1 \, (r) = \frac{B}{r} + v.$ So also:

$$\psi = \Sigma \int \frac{B \varrho \, d\tau}{r} + \Sigma \int \frac{B \sigma \, ds}{r} + \Sigma \int \varrho v \, d\tau + \Sigma \int \sigma v \, ds \, .$$

If we apply to both members the operation ∇^2 we find in a similar way as we did when proving the preceding theorem:

$$\nabla^2 \psi = -4 \pi B \varrho + \Sigma \int \varrho \, \nabla^2 v \, d\tau + \Sigma \int \sigma \, \nabla^2 v \, ds \quad . \quad . \quad (9)$$

Now we get in consequence of (7):

$$\Sigma \int \varrho \, \nabla^2 v \, d\tau = -q^2 \, \Sigma \int \varrho \, \varphi_1 \, d\tau$$

and in the same way:

$$\Sigma \int \sigma \, \nabla^2 v \, ds = -q^2 \, \Sigma \int \sigma \, \varphi_1 \, ds$$

or

$$\Sigma \int \varrho \, \nabla^2 v \, d\tau + \Sigma \int \sigma \, \nabla^2 v \, ds = -q^2 \left(\Sigma \int \varrho \, \varphi_1 \, d\tau + \Sigma \int \sigma \varphi_1 \, ds \right) = -q^2 \psi$$

Equation (8) becomes:

$$\nabla^2 \psi = -4 \pi B \varrho - q^2 \psi$$

or because $B = A \sin \alpha$:

$$\nabla^2 \psi = -q^2 \psi - 4 \pi A \sin \alpha \, \varrho \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Let us now prove the reversed theorem of Theorem I [1]).

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[1]) With that modification that B is put 0.

III. If ψ and ϱ are functions of x, y and z, ψ satisfying the three following conditions:

1st ψ and its first derivatives with respect to x, y and z are continuous everywhere.

2nd some isolated points, lines and surfaces excepted, ψ fulfils in an acyclic region, the equation:

$$\nabla^2 \psi = q^2 \psi - 4 \pi A \varrho.$$

3rd the products $x\psi$, $y\psi$, $z\psi$, $x^2 \dfrac{d\psi}{dx}$, $y^2 \dfrac{d\psi}{dy}$ and $z^2 \dfrac{d\psi}{dz}$ become nowhere infinite; then the potential of an agens, the density of which is ϱ, is for that region ψ, the potential function being:

$$\varphi(r) = \frac{Ae^{-qr}}{r}$$

In order to prove this theorem, we take into account that the potential of an agens, for which the potential function is $\dfrac{Ae^{-qr}}{r}$, fulfils the differential equation:

$$\nabla^2 \psi = q^2 \psi - 4 \pi A \varrho \quad \ldots \ldots \ldots (11)$$

which is a special case of equation (3). If we can prove that on the given conditions only one solution of (11) is possible, the theorem is proved. We shall do so by proving that if there are two solutions, the difference of these functions will be zero everywhere.

If ψ and v are two solutions of equation (11) and if we put $\psi - v = u$, the new function u will satisfy the equation:

$$\nabla^2 u = q^2 u.$$

As ψ and v and their first derivatives with respect to x, y and z are supposed to be continuous everywhere, this is also the case with the function u and we may make use for this quantity of the well-known theorem of GREEN. This furnishes the equation:

$$\int (\nabla^2 u) u \, d\tau = \int u \left(\frac{du}{dx} \cos \alpha + \frac{du}{dy} \cos \beta + \frac{du}{dz} \cos \gamma \right) ds -$$

$$- \int \left\{ \left(\frac{du}{dx} \right)^2 + \left(\frac{du}{dy} \right)^2 + \left(\frac{du}{dz} \right)^2 \right\} d\tau \quad . \quad . \quad (12)$$

If we subtract $\int q^2\, u^2\, d\tau$ from the two members of this equation, we get:

$$\int (\nabla^2 u - q^2 u)\, u\, d\tau = \int u \left(\frac{du}{dx} \cos \alpha + \frac{du}{dy} \cos \beta + \frac{du}{dz} \cos \gamma \right) ds -$$

$$- \int \left\{ \left(\frac{du}{dx}\right)^2 + \left(\frac{du}{dy}\right)^2 + \left(\frac{du}{dz}\right)^2 + q^2 u^2 \right\} d\tau$$

Dirichlet [1]) in his proof of a corresponding theorem concerning the potential function $\dfrac{1}{r}$, has surrounded the spaces that present a singularity by closely surrounding surfaces, and he construed a cube, the centre of which coincides with the origin of the coordinate system, while it compasses all the spaces that present a singularity. By doing so we may make use of the above equation for the space contained between the sides of the cube and the surfaces construed round the places which offer a singularity. The first term of the right-hand member consists of the sum of a number of surface integrals, which are reduced to zero for the surfaces of the cube, when the edges of the cube increase infinitely, while the surface integrals taken over the surfaces which enclose the places offering a singularity, furnish two values of opposite sign, so that the result for every surface is zero. Then $\nabla^2 u = q^2 u$. The volume integral of the left-hand member is therefore also zero.

So:

$$\int \left\{ \left(\frac{du}{dx}\right)^2 + \left(\frac{du}{du}\right)^2 + \left(\frac{du}{dz}\right)^2 + q^2 u^2 \right\} d\tau = 0$$

from which follows:

$$u = 0 \quad \text{or} \quad \psi = v \quad q.\, d.\, e.$$

In these considerations the more general function :

$$\varphi (r) = \frac{A e^{-qr} + B e^{qr}}{r}$$

must be excluded as potential function.

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[1]) Vorlesungen über die im umgekehrten Verhältniss des Quadrats der Entfernung wirkenden Krafte von P. G. Lejeune-Dirichlet. blz. 32.

In this case the following equation would hold for points which are at an infinite distance from the agens:

$$\psi = M \frac{Ae^{-qr} + Be^{qr}}{r}$$

M representing the whole mass.

According to the third condition $r\,\psi$ will nowhere become infinite.

Now $r\,\psi = M(Ae^{-qr} + Be^{qr})$ and e^{qr} become infinite, if $r = \infty$. Only for $B = 0$ this objection has no weight. We shall therefore confine ourselves to the function of VAN DER WAALS and a general reversion of theorem I cannot be proved in this way. Such a theorem, however, would not be of much importance here, as for $B \gtrless 0$ the potential function has properties, which are never found when examining molecular forces.

Potential energy in the unity of volume.

Let us seek the potential energy of an agens spread continuously over several spaces for the potential function of VAN DER WAALS, which we write:

$$\varphi(r) = -f \frac{e^{-qr}}{r}$$

If ψ is the potential and ϱ the density, we get for this quantity:

$$W = \frac{1}{2} \int \psi \varrho \, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

We consider this as being taken over the infinite space. Now we get according to equation (11)

$$\nabla^2 \psi = q^2 \psi + 4\pi f \varrho$$

and so

$$\varrho = \frac{\nabla^2 \psi - q^2 \psi}{4\pi f}$$

By substitution in (13):

$$W = \frac{1}{8\pi f} \int \psi \nabla^2 \psi \, d\tau - \frac{q^2}{8\pi f} \int \psi^2 \, d\tau \quad . \quad . \quad . \quad (14)$$

Now we have:

$$\int \psi \, \nabla^2 \, \psi \, d\tau = \int \psi \frac{d^2\psi}{dx^2} \, d\tau + \int \psi \frac{d^2\psi}{dy^2} \, d\tau + \int \psi \frac{d^2\psi}{dz^2} \, d\tau \quad . \quad (15)$$

By partial integration:

$$\int \psi \frac{d^2\psi}{dx^2} \, d\tau = \iint \frac{d\psi}{dx} \, \psi \, dy \, dz - \int \left(\frac{d\psi}{dx}\right)^2 d\tau$$

Because ψ and $\dfrac{d\psi}{dx}$ become [1]) zero at infinite distance from the agens, the surface integral becomes zero and so:

$$\int \psi \frac{d^2\psi}{dx^2} \, d\tau = - \int \left(\frac{d\psi}{dx}\right)^2 d\tau \ .$$

By substituting in equation (14) this expression for $\displaystyle\int \psi \, \frac{d^2\psi}{dx^2} \, d\tau$ and the corresponding expressions for the other surface integrals of (15), we find:

$$W = - \frac{1}{8\,\pi\,f} \int \Sigma \left(\frac{d\psi}{dx}\right)^2 d\tau - \frac{q^2}{8\,\pi\,f} \int \psi^2 \, d\tau$$

$$\left\{ \Sigma \left(\frac{d\psi}{dx}\right)^2 = \left(\frac{d\psi}{dx}\right)^2 + \left(\frac{d\psi}{dy}\right)^2 + \left(\frac{d\psi}{dz}\right)^2 \right\}.$$

The energy in the unity of volume becomes therefore:

$$- \frac{1}{8\,\pi\,f} \left\{ \Sigma \left(\frac{d\psi}{dx}\right)^2 + q^2 \, \psi^2 \right\} .$$

Let us put:

$$R^2 = \left(\frac{d\psi}{dx}\right)^2 + \left(\frac{d\psi}{dy}\right)^2 + \left(\frac{d\psi}{dz}\right)^2$$

then we may also write:

$$- \frac{R^2 + q^2 \, \psi^2 \ ^{2)}}{8\,\pi\,f} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

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[1]) If the members of the last equation are added to those of the corresponding equation for the other axes, we may consider the surface integrals together as being one surface integral over a sphere. If $r = \infty$, this integral becomes 0.

[2]) $q \, \psi$ has the dimension of a force, for q is the reverse of a length.

or substituting $\dfrac{1}{\lambda}$ for q:

$$ -\frac{1}{8\,\pi\,f}\left(R^2 + \frac{\psi^2}{\lambda^2} \right) \quad . \quad . \quad . \quad . \quad . \quad (16a) $$

If $f = 1$ and $q = 0$, we find once more the well-known expression:

$$ -\frac{R^2}{8\,\pi} . $$

This expression is negative, because the constant of the potential function is equated to zero. So it represents without the — sign the work required to separate different parts of the agens at an infinite distance from one another, when the forces are attractive.

Tension in the medium.

MAXWELL has proved that the force which two electric systems exercise on each other, may be considered as a simple system of tensions in the medium. The same applies to the general potential function $\varphi\,(r) = \dfrac{A\,e^{-qr} + B\,e^{qr}}{r}$ and so also to the potential function of VAN DER WAALS.

Imagine an agens spread over different spaces, for which the potential function $\varphi\,(r)$ holds good, and enclose a certain region by a closed surface. Call this region system I and all other space system II. The resultant of the X-components of the forces exercised by system II on system I is:

$$ X_1 = -\int \frac{d\psi}{dx}\,\varrho\,d\tau \;{}^{1)} $$

According to equation (3):

$$ \varrho = \frac{q\,\psi - \nabla^2\,\psi}{4\,\pi\,(A + B)} $$

so

$$ 4\,\pi\,(A + B)\,X_1 = \int \nabla^2\,\psi\,\frac{d\psi}{dx}\,d\tau - q^2 \int \psi\frac{d\psi}{dx}\,d\tau . $$

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[1] Here the same remark holds good as I have made repeatedly in such like calculations. See e.g. Journal de Physique 1899, p. 546. Generally this expression for X_1 is proved in a lengthy way.

Now we get (see MAXWELL 1873, blz. 129, I):

$$\nabla^2 \psi \frac{d\psi}{dx} = \frac{d\psi}{dx}\left(\frac{d^2\psi}{dx^2} + \frac{d^2w}{dy^2} + \frac{d\psi^2}{dz^2}\right) =$$

$$= \frac{1}{2}\frac{d}{dx}\left\{\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dz}\right)^2\right\} + \frac{d}{dy}\left(\frac{d\psi}{dx}\frac{d\psi}{dz}\right).$$

Let us put:

$$\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A+B)\,p_{xx}$$

$$\left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A+B)\,p_{yy}$$

$$\left(\frac{d\psi}{dz}\right)^2 - \left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - q^2\,\psi^2 = 8\,\pi\,(A+B)\,p_{zz}$$

$$\frac{d\psi}{dy}\frac{d\psi}{dz} = 4\,\pi\,(A+B)\,p_{yz} = 4\,\pi\,(A+B)\,p_{zy}$$

$$\frac{d\psi}{dz}\frac{d\psi}{dx} = 4\,\pi\,(A+B)\,p_{zx} = 4\,\pi\,(A+B)\,p_{xz}$$

$$\frac{d\psi}{dx}\frac{d\psi}{dy} = 4\,\pi\,(A+B)\,p_{xy} = 4\,\pi\,(A+B)\,p_{xy}$$

then we get:

$$-\frac{1}{4\,\pi}\frac{d\psi}{dx}\nabla^2\psi = (A+B)\left\{\frac{dp_{xx}}{dx} + \frac{dp_{yx}}{dy} + \frac{dp_{zx}}{dz}\right\}$$

and so:

$$X_1 = \left(\int \frac{dp_{xx}}{dx} + \frac{dp_{yx}}{dy} + \frac{dp_{zx}}{dz}\right) d\tau$$

or as a surface integral on the surface, which encloses system I:

$$X_1 = \int (l\,p_{xx} + m\,p_{yx} + n\,p_{zx})\,ds$$

and in the same way:

$$Y_1 = \int (l\,p_{xy} + m\,p_{yy} + n\,p_{zy})\,ds$$

$$Z_1 = \int (l\,p_{xz} + m\,p_{yz} + n\,p_{zz})\,ds$$

In exactly the same way as MAXWELL we may conclude from this that, when a part of the whole system is enclosed by a potential surface, we may consider the action of the other part on the enclosed part of the system as a tension (or pressure), normal to that potential surface, so in the direction of the lines of force, and a pressure (or tension) round the lines of force normal to them. The value of the tension is here:

$$\frac{R^2 - q^2\, w^2}{8\,\pi\,(A + B)} \quad \text{or if } B = 0 \text{ and } A = -f: \quad \frac{R^2 - q^2\,\psi^2}{8\,\pi\,f}$$

The quantity q is the reciprocal value of λ in the potential function of VAN DER WAALS. Hence:

$$- \frac{1}{8\,\pi\,f}\ \left(R^2 - \frac{\psi^2}{\lambda^2}\right).$$

If $R^2 > \dfrac{\psi^2}{\lambda^2}$, the expression becomes negative and the tension becomes a pressure. The value of this expression becomes:

$$\frac{1}{8\,\pi\,f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right) \quad\quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If we take the surface element for which the tension or pressure is to be determined, normal to the lines of force and represent by l, m and n the direction cosines of the normal measured outwards, then the x-component of the force, acting on the element (considered as a part of a closed surface) is:

$$l\,p_{xx} + m\,p_{yz} + n\,p_{xz}\ .$$

Now:

$$8\,\pi\,(A + B)\,\{l\,p_{xx} + m\,p_{yz} + n\,p_{xz}\} =$$

$$= l\left\{\left(\frac{d\psi}{dx}\right)^2 - \left(\frac{d\psi}{dy}\right)^2 - \left(\frac{d\psi}{dz}\right)^2 - q^2\,\psi^2\right\} + 2\,m\,\frac{d\psi}{dx}\,\frac{d\psi}{dy} + 2\,n\,\frac{d\psi}{dx}\,\frac{d\psi}{dz}$$

and we get the relation:

$$l\,\frac{d\psi}{dx} + m\,\frac{d\psi}{dy} + n\,\frac{d\psi}{dz} = 0\ .$$

By combining these two equations, we find easily:

$$8 \pi (A + B) \{l\, p_{xx} + m\, p_{yz} + n\, p_{xz}\} =$$

$$= - l \left\{ \left(\frac{d\psi}{dx}\right)^2 + \left(\frac{d\psi}{dy}\right)^2 + \left(\frac{d\psi}{dz}\right)^2 + q^2\, \psi^2 \right\}.$$

As we have taken the force as a vector in the direction of the normal measured outwards, the above equation indicates the force which acts on the element from the inside towards the outside. The expression between the braces in the right-hand member is always positive, and we get therefore a negative tension or a positive pressure:

$$\frac{R^2 + q^2\, \psi^2}{8 \pi (A + B)}$$

For the potential function of VAN DER WAALS $B = 0$, $A = - f$ and $q = \dfrac{1}{\lambda}$, so we find here a (positive) *tension*:

$$\frac{1}{8 \pi f} \left(R^2 + \frac{\psi^2}{\lambda^2} \right)$$

For an electric system the system of forces may be described as a system of *tensions* in the direction of the lines of force and a system of *pressures* normal to the lines of force, here however we see that we must assume both tensions and pressures in the direction of the lines of force. Normal to the lines of force there are only tensions, whereas for electric agens the reverse is found. For electric agens the numeric value of the tension is equal to that of the pressure; in our case the tension is not equal to the pressure, except where ψ and R are zero. For the potential energy per unit of volume we found:

$$W = - \frac{1}{8 \pi f} \left(R^2 + \frac{\psi^2}{\lambda^2} \right)$$

from which follows that:

the absolute value of the potential energy per unit of volume is equal to the tension normal to the lines of force.

The Surface-tension and the Molecular Pressure.

Let us imagine a liquid in equilibrium with its saturated vapour. In the transition layer we may assume the lines of force to be normal to the surface separating the two phases. Let us imagine this surface to be horizontal, therefore the lines of force in the capillary layer as being vertical. If the above considerations are correct, and if we assume that the substance fills the space continuously with a mean density, we shall find for the surface tension exactly the same value as is deduced from the calculations of VAN DER WAALS in his "Theorie der capillariteit". Let us first calculate the molecular pressure; i. e. the force, with which a column of the surface layer with the unity of transverse section is attracted downwards in the direction of the liquid by the surrounding substance.

Per unit of surface we found a pressure, indicated by the formula:

$$D = \frac{1}{8\pi f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right).$$

The force we are speaking of, which we shall call K, is nothing but the difference between the absolute values of the pressure D on the upper and the lower surfaces of the column of the surface layer. Let us call the potential in the vapour ψ_2 and in the liquid ψ_1, and let us bear in mind that both in the vapour and in the liquid R may be put equal to zero, then we find:

$$K = \frac{1}{8\pi f \lambda^2}\left(-\psi_2{}^2 + \psi_1{}^2\right) = \frac{\psi_1{}^2 - \psi_2{}^2}{8\pi f \lambda^2} \quad \text{[1]}$$

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[1] The pressures in consideration are here negative and therefore properly speaking, tensions. For the rest the ideas tension and pressure are somewhat arbitrary. There is no objection to adding an everywhere equal amount to the pressure and the tension through the whole mass. The new system of pressures and tensions will give a representation of the system of forces as well as the original. This appears immediately from the form of the space-integral, which represents the force between two parts of the system :

$$X_1 = \int\left(\frac{dp_{xx}}{dx} + \frac{dp_{xy}}{dy} + \frac{dp_{xz}}{dz}\right)d\tau$$

The coefficient of $d\tau$ consists of the sum of three differential coefficients. Therefore constant amounts may be added to p_{xx}, p_{xy} and p_{xz}.

If the hydrostatic pressure through the whole mass is equal to the external pressure and if only the pressure of the air acts on the system, the pressure $\frac{1}{8\pi f}\left(R^2 - \frac{\psi^2}{\lambda^2}\right)$ is equal to the pressure with reversed sign, leaving a constant out of account.

As further

$$\psi_1 = - 4 \pi f \lambda^2 \varrho_1 \quad \text{and} \quad \psi_2 = - 4 \pi f \lambda^2 \varrho_2$$

or

$$\psi_1 = - 2 a \varrho_1 \quad \text{and} \quad \psi_2 = - 2 a \varrho_2$$

we may also write:

$$K = \frac{4 a^2 \varrho_1^2 - 4 a^2 \varrho_2^2}{4 a} = a \, (\varrho_1^2 - \varrho_2^2) \quad \ldots \quad (20)$$

If we neglect ϱ_2 with respect to ϱ_1, we get the well-known expresssion of LAPLACE:

$$K = a \, \varrho_1^2$$

LAPLACE, however, proved this relation only in the supposition that the density in the liquid (also in the surface layer) is constant everywhere.

For the tension *normal* to the lines of force, so in our case in the direction parallel to the separating surface, we found:

$$\frac{1}{8 \pi f} \left(R^2 + \frac{\psi^2}{\lambda^2} \right).$$

This expression holds for a unit of surface. For an elementary-rectangle of transverse section of the capillary layer, (i. e. normal to the potential surfaces), two sides of which are parallel to the potential surfaces and have the length of a unit, whereas the other two sides have the direction of the tangents of the surface and a differential length dh, we get:

$$\frac{1}{8 \pi f} \left(R^2 + \frac{\psi^2}{\lambda^2} \right) dh .$$

The total tension in the capillary layer will be equal to the sum of these differential-expressions, i. e.:

$$S^{[1]} = \frac{1}{8 \pi f} \int_1^2 R^2 \, dh + \frac{1}{8 \pi f \lambda^2} \int_1^2 \psi^2 \, dh \quad \ldots \quad (23)$$

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[1] This quantity S is *not* the quantity H of LAPLACE.

The limits 1 en 2 relate to liquid and vapour.
In the theory of VAN DER WAALS is:

$$\psi = -2\,a\,\varrho - \frac{2\,c_2}{2}\frac{d^2\varrho}{dh^2} - \frac{2\,c_4}{\pi\,4}\frac{d^4\varrho}{dh^5} -$$

for

$$-R = -2\,a\frac{d\varrho}{dh} - \frac{2\,c_2}{2}\frac{d^3\varrho}{dh^3} - \frac{2\,c_4}{\pi\,4}\frac{d^5\varrho}{dh^5} -$$

By substitution of the squares of these expressions in (23), making use of the expressions:

$$\lambda^2 = \frac{\dfrac{c_2}{2}}{a} = \frac{\dfrac{c_4}{\pi\,4}}{\dfrac{c_2}{2}} = \frac{\dfrac{c_6}{\pi\,6}}{\dfrac{c_4}{\pi\,4}} = \cdots$$

we find easily:

$$S = a\int_1^2 \varrho^2\,dh - a\,\lambda^2 \int_1^2\left(\frac{d\varrho}{dh}\right)^2 dh + a\,\lambda^4 \int_1^2\left(\frac{d^2\varrho}{dh^2}\right)^2 dh$$

As the tension normal to the lines of force per unit of surface was equal to the potential energy per unit of volume with reversed sign, we have also found this energy.

We can also easily derive the value of the energy directly from the equation for the energy, with which the energy of the unit of mass in a point of the surface layer exceeds that in a point within the liquid. Prof. VAN DER WAALS finds for this:

$$-a\,(\varrho - \varrho_1) - \frac{c_2}{\pi\,2}\frac{d^2\varrho}{dh^2} - \frac{c_4}{\pi\,4}\frac{d_4\varrho}{dh^4} -$$

For the whole separating layer we get per unit of surface a potential energy:

$$-a\int_1^2\varrho^2\,dh + a\,\varrho_1\int_1^2\varrho\,dh - \frac{c_2}{\pi\,2}\int_1^2\varrho\frac{d^2\varrho}{dh^2}\,dh - \frac{c_4}{\pi\,4}\int_1^2\varrho\frac{d^4\varrho}{dh^4}\,dh -$$

$$\int\varrho\,dh = \text{ mass of the separating layer per unit of surface } = m.$$

19

We get further:

$$\int_1^2 \varrho \frac{d^2\varrho}{dh^2}\, dh = \int_1^2 \varrho\, d\frac{d\varrho}{dh} = -\int_1^2 \left(\frac{d\varrho}{dh}\right)^2 dh \ ^{1})$$

$$\int_1^2 \varrho \frac{d^4\varrho}{dh^4}\, dh = \int_1^2 \varrho\, d\frac{d^3\varrho}{dh^3} = -\int_1^2 \frac{d^3\varrho}{dh^3}\frac{d\varrho}{dh}\, dh = -\int_1^2 \frac{d\varrho}{dh}\, d\frac{d^2\varrho}{dh^2} = \int_1^2 \left(\frac{d^2\varrho}{dh^2}\right)^2 dh$$

The potential energy per unit of surface becomes:

$$W = -a\int_1^2 \varrho^2\, dh + a\,\varrho_1\, m + \frac{c_2}{\pi 2}\int_1^2 \left(\frac{d\varrho}{dh}\right)^2 dh - \frac{c_4}{\pi 4}\int_1^2 \left(\frac{d^2\varrho}{dh^2}\right)^2 dh + \ . \ .$$

As zero position we have taken that of the liquid. If we take infinite rarefaction as zero position, we get $a\,\varrho_1\, m = 0$ and so:

$$S = -W$$

Astronomy. — S. L. Veenstra: "*On the Systematic Corrections of the proper motions of the stars, contained in* Auwers'-Bradley-*Catalogue, and the coordinates of the Apex of the solar motion in Space*". (Communicated by Prof. J. C. Kapteyn.)

The materials for these investigations have been taken from an yet unpublished catalogue, prepared by Prof Kapteyn. This catalogue contains for all the Bradley-stars, observed in both coordinates (with the exception of the Pleiades, the Hyades and the fainter components of physical double-stars) the position, the total proper motion μ, its components v and τ, in the direction from the apex and perpendicular to that direction and the quantities λ and χ [2]), respectively the distance from star to apex, and the angle between the great circle on which this distance is measured and the declination-circle.

The quantities v, τ, λ and χ have been calculated with different

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[1]) The differential-quotients $\frac{d\rho}{dh}$, $\frac{d^2\rho}{dh^2}$ etc. are zero outside the separating layer.

[2]) In the *printed* catalogue the quantities χ have not been included.