Physics. — *"On the Theory of the Friction of Liquids* II.*"* By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of March 29, 1919).

§ 4. *Distribution of density in a liquid flowing in a field of forces.* Before proceeding to the "friction by formation of groups", we shall discuss a simpler problem. We shall namely imagine that a gas streams in a field of force, and then examine what modifications are brought about by the streaming in the distribution of density as it would arise in a field of forces when there was no current. For this purpose we shall again imagine the simple case that the streaming takes place in the x-direction, and that the velocity may be represented by $u = az$. We shall further suppose that we have to do with a stationary current, so that in a point at rest in space the density and the velocity of the current are constant.

In order to examine the distribution of density which will present this stationary character, we shall assume that there are two causes that might give rise to a change in the density in a given point. the "molar" current, and the "diffusion" current. It is not to be denied that this distinction is artificial, and that the change of the quantity of substance in an element of space can of course always be found from the total current that flows in through the boundary surfaces. I shall, however, suppose that this total current may be thought composed of a molar current, to which I shall assign the unmodified velocity $u = az$, and a current which is the consequence of the inhomogeneous density in connection with the heat motion. The latter will be denoted by the name of diffusion current. I shall further assume that the change brought about by each of these two causes, can be computed independent of the other cause.

The quantity which enters a volume element per second through the molar current is:

$$\frac{dn}{dt} dx\, dy\, dz = -u \frac{\partial n}{\partial x} dx\, dy\, dz \quad . \quad . \quad . \quad . \quad (10)$$

In order to calculate the contribution of the diffusion-current we shall assume that the distribution of the velocities of the gas-mole-

cules at any point may be found in the following way. We shall, namely, assume the velocities of the molecules which have collided in a certain layer to consist of two components: 1. the velocity of current in the layer in which they have collided, and 2 the heat motion, of which latter it will be assumed that it is distributed over the different molecules according to MAXWELL's law. Undoubtedly we make an error when supposing these things, but we may expect that this will only be an error in a numerical coefficient, and that the · nature of the phenomenon and also the order of magnitude will be correctly represented by the formulae derived by the aid of these suppositions.

In order to examine the diffusion current through a plane A, we shall consider two planes lying on either side of the plane A at a distance $\frac{\sqrt{3}}{3} l$. ($l =$ mean length of path of the molecules). And we shall consider the molecules passing through the plane A as "emitted" from one of these two planes, by which we understand that they have had their last collision there. Let us first consider the molecules that collide in the $+$ plane [1]), and which possess a component of velocity normal to the plane A between w and $w + dw$. Arrived in the plane A these molecules have obtained a normal velocity w' determined by the equation:

$$\tfrac{1}{2} m w'^2 = \tfrac{1}{2} m w^2 + \frac{\partial \varepsilon}{\partial z} \frac{l\sqrt{3}}{3}. \qquad \cdot \quad \cdot$$

The number of molecules of this group passing per second and per unit of area through plane A, is when n represents the density of the molecules in A, and $n + \frac{\partial n}{\partial z} \frac{l\sqrt{3}}{3}$ that in the $+$ plane:

$$\frac{1}{\sqrt{\pi^3}} \left(n + \frac{\partial n}{\partial z} \frac{l\sqrt{3}}{3} \right) w' e^{-\frac{u^2 + v^2 + w'^2}{\sigma^2} + \frac{1}{kT} \frac{\partial z}{\partial z} \frac{l\sqrt{3}}{3}} d\frac{u}{\alpha} d\frac{v}{\alpha} d\frac{w'}{\alpha} . \quad . \quad (11)$$

When we pay only attention to the molecules emitted from the $+$ plane, w' must always have a value for which $\tfrac{1}{2} m w'^2$ is $> \frac{\partial \varepsilon}{\partial z} \frac{l\sqrt{3}}{3}$. In the direction from $+$ to $-$ however, there go, also molecules

---

[1]) i. e. the plane parallel to A at a distance $\tfrac{1}{3} l\sqrt{3}$ on the side where the potential energy ε of the molecules is greater than in A. The plane lying on the other side will be called the $-$ plane. The z-axis will be normal to A in the direction from the $-$ plane to the $+$ plane, so that $\frac{\partial \varepsilon}{\partial z} > 0$.

which have first passed through it in opposite direction with such a small velocity that they could not reach the + plane, but reversed their velocity in consequence of the force $-\dfrac{\partial \varepsilon}{\partial z}$ before having reached it. When also these molecules are taken into account the total diffusion current from + to — is found by integrating expression (11) with respect to u and v between $-\infty$ and $+\infty$ and with respect to w' between 0 and $-\infty$.

The molecules flowing in opposite i.e. in the + direction through the plane are found by taking a group of molecules emitted from the — plane:

$$\frac{1}{\sqrt{\pi^3}}\left(n - \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)w'e^{-\frac{u^2+v^2+w'^2}{\varsigma^2}-\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}}\,d\frac{u}{\alpha}\,d\frac{v}{\alpha}\,d\frac{w'}{\alpha}$$

and by integrating u and v in this between $-\infty$ and $+\infty$ and w' between 0 and $+\infty$.

Thus it is found that the plane A is passed per second and per unit of area in the — direction by the following number of molecules:

$$\frac{u}{2\sqrt{\pi}}\left\{\left(n + \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)e^{\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}} - \left(n - \frac{\partial n}{\partial z}\frac{l\sqrt{3}}{3}\right)e^{-\frac{1}{kT}\frac{\partial \varepsilon}{\partial z}\frac{l\sqrt{3}}{3}}\right\} =$$

$$= \frac{u\sqrt{3}}{3\sqrt{\pi}}l\left(\frac{\partial n}{\partial z} + n\frac{\partial \varepsilon}{\partial z}\frac{1}{kT}\right) = \frac{u\sqrt{3}}{3\sqrt{\pi}}\,nl\left(\frac{1}{n}\frac{\partial n}{\partial z} + \frac{\partial \varepsilon}{\partial z}\frac{1}{kT}\right). \quad . \quad . \quad (12)$$

In this we shall assume nl to be constant, though, strictly speaking, this is only allowed for gases at small densities. In the case of thermodynamic equilibrium this diffusion current must be zero through very plane, so that then $l(n) + \dfrac{\varepsilon}{kT} =$ constant, which gives the known distribution of the molecules in space in that case.

We shall make use of the value of the diffusion current in equation (12) in order to calculate how much enters through the six sides of a volume element $dx\,dy\,dz$. We find for this:

$$-\frac{\alpha\sqrt{3}}{3\sqrt{\pi}}\,nl\,\nabla^2\left\{l(n) + \frac{\varepsilon}{kT}\right\}dx\,dy\,dz,$$

so that we find for the condition for a stationary state in connection with equation (10):

$$+\frac{\alpha\sqrt{3}}{3\sqrt{\pi}}\,nl\,\nabla^2\left\{l(n) + \frac{\varepsilon}{kT}\right\} = u\frac{\partial n}{\partial x} \quad . \quad . \quad . \quad (13)$$

I shall here leave out of account the question what corrections

would have to be applied to the numerical factor and use equation (13) further uncorrected.

$l(n) + \dfrac{\varepsilon}{kT}$ is the quantity that GIBBS represents by μ and denotes by the name of thermodynamic potential. In the case of thermodynamic equilibrium it is constant, and equal to $l(n_0)$, when n_0 is the density in the point where the potential energy is put zero. In the case of no equilibrium considered by us I shall put:

$$l(n) + \frac{\varepsilon}{kT} - l(n_0) = w. \qquad \ldots \ldots \ldots \quad (14)$$

or taking into account that we suppose w to be small:

$$n = n_e\, e^{-\frac{\varepsilon}{kT}}(1+w) = n_0 e^{-\frac{\varepsilon}{kT}} + nw, \qquad \ldots \ldots \quad (14a)$$

so that nw represents the number of molecules that in consequence of the current is present in an element of space in excess above the normal number $n_0\, e^{-\frac{\varepsilon}{kT}}$. According to equation (13) w is found as the potential of imaginary agent, of which the density would

be: $\quad - \dfrac{\sqrt{3\pi}}{a \cdot nl}\, u\, \dfrac{\partial n}{\partial x}.$

To illustrate the meaning of the found formula we shall apply it for the following simple case: the field of forces arises from a single centre of forces, in which we lay the origin O of the system of coordinates, the force being only a function of r. If there was no current, this field of forces would in a gas give rise to a denser cloud round O, in which the density would only be a function of r. Let us now think the gas set flowing with a *constant* velocity u in the negative x-direction, and let us suppose this to bring about a *slight* variation in the density, so that by way of first approximation we may take in equation (13) the value of $\dfrac{\partial n}{\partial x}$ as it would be without current, hence:

$$\frac{\partial n}{\partial x} = - n_0 e^{-\frac{\varepsilon}{kT}} \frac{1}{kT} \frac{\partial \varepsilon}{\partial x} \qquad \ldots \ldots \ldots \quad (15)$$

which causes equation (13) to become:

$$\nabla^2 w = - \frac{\sqrt{3\pi}}{a \cdot nl}\, u\, \frac{n}{kT} \frac{\partial \varepsilon}{\partial x} \qquad \ldots \ldots \ldots \quad (13a)$$

The imaginary agent is then negative on the side of the positive x-axis, and has an equal, but positive value on the side of the negative x-axis. Then the potential w of this agent will be zero in

the yz plane, as is easily derived from considerations of symmetry, and will on either side of it present the same sign as the imaginary agent. The excess nw, therefore, also shows these signs, which comes to this that the cloud has shifted in the direction of the negative x-axis, as was to be expected.

When we no longer assume u to be constant, but $u = az$, w will obtain a positive sign in the 1st and the 3id quadrant, i.e. the cloud will be elongated in the direction of a line that forms an angle of $45°$ with the original axes and lies in the 1st and the 3id quadrant.

§ 5. *Distribution of the density in a flowing liquid at the critical point.* When after these preparatory remarks we proceed to the problem of the anomalies of density in a flowing liquid, we shall first have to calculate $\nabla^2 w$ according to equation (13a). For this purpose we first remark that the value given for $\nabla^2 w$ by this equation is only a consequence of the movement of the gas relative to the centre of force. When we put $u = $ constant, and if we then make the centre of force participate in the movement, it would of course come to the same thing as if everything was at rest. We shall, therefore, always have to take this relative velocity for u in equation (13a). The value of $\nabla^2 w$ in a volume element $dx\,dy\,dz = d\omega$ can now be calculated as the sum of contributions furnished by forces exerted by the substance in the different surrounding volume elements. When we call one of these surrounding elements $dx'\,dy'\,dz' = d\omega'$ and the density in it n', then the $n'd\omega'$ molecules in it can be conceived as a centre of force. When we put again $u = az$, the velocity of the substance in $d\omega$ relative this centre will amount to $a\,(z-z')$. Let us further represent the potential energy of two molecules at a mutual distance r by $\varphi(r)$, the contribution to $\nabla^2 w$ in $d\omega$ which is owing to the substance in $d\omega'$ is then:

$$- \frac{\sqrt{3\pi}}{a\,.\,nl}\frac{n}{kT}a\big(z-z'\big)\,n'd\omega'\,\frac{\partial\varphi(r')}{\partial r'}\frac{x-x'}{r'}$$

in which r' represents the distance of the spacial elements $d\omega$ and $d\omega'$. When we turn the axes $45°$ round the y-axis, and when we call the new axes ξ, η, ζ, we find for the total value of $\nabla^2 w$:

$$\nabla^2 w = - \frac{\sqrt{3\pi}}{al}\frac{a}{kT}\int n'\frac{\partial\varphi}{\partial r'}\frac{(\xi-\xi')^2-(\zeta-\zeta')^2}{2r'}\,d\omega' \quad . \quad . \quad . \quad (16)$$

This equation gives the distribution of the imaginary agent in space. We find from it for the value of w_1 in a volume element

$d\xi_1 \, d\eta_1 \, d\zeta_1 = d\omega_1$, when we represent the distance of an element $d\omega$ to $d\omega_1$ by r_1:

$$w_1 = + \frac{\sqrt{3\pi}}{al} \frac{a}{kT} \iint n' \frac{\partial \varphi}{\partial r'} \frac{(\xi - \xi')^2 - (\zeta - \zeta')^2}{2r'} \frac{1}{r_1} \, d\omega' d\omega \quad . \quad (17)$$

If n' were constant, we should of course find $\nabla^2 w = o$ and $w = o$. If, however, in a definite region n' is greater than in the surrounding volume elements, then in a line parallel to the ξ-axis and passing through the centre of this region $\nabla^2 w$ will be negative, and in a line parallel to the ζ-axis positive. The imaginary agent and w have then opposite signs, so that here also the condensed group will be elongated in a direction forming an angle of 45° with the original axes.

§ 6. *The application of the virial relation.* In order to calculate the stress tensor from the value found for w_1, we shall make use of the virial equation. We shall, however, have to demonstrate beforehand the applicability of this equation for the case under consideration. Let us for this purpose consider a definite volume in the space in which the flowing gas is found. We shall assign to it the shape of a rectangular parallelepiped and choose the coordinate axes parallel to the sides. As we think the state stationary, the expression $\Sigma \, m \, x \, \dot{x}$, in which the summation extends over all the molecules in the volume will be constant. The fact that through the boundary planes molecules enter and leave the considered space, does not affect this. We conclude from this that:

$$\frac{d}{dt}(\Sigma \, m \, x \, \dot{x}) = 0 = \Sigma \, m \, \dot{x}^2 + \Sigma \, x \, X + O \, m \, (x_1 - x_2) \int \dot{x}^2 f(\dot{x}) \, d\dot{x} \quad . \quad (18)$$

In this X is the x-component of the force acting on a molecule, x_1 and x_2 are the abscissae of the boundary planes of the parallelepiped normal to the x-axis, and O is the area of these planes. $f(\dot{x}) \, d\dot{x}$ denotes the number of molecules per c.c.m., of which the x-component of the velocity lies between $\dot{x}$ and $\dot{x} + d\dot{x}$. The latter term refers to the change in the value of $\Sigma \, m \, x \, \dot{x}$, which results from the molecules entering and leaving through the planes $x_1 = c$ and $x_2 = c$. The molecules entering and leaving through other boundary planes will yield on an average a contribution zero to $\frac{d}{dt} \Sigma \, m \, x \, \dot{x}$. Let us put:

$$\dot{x} = \dot{x}_{th} + u,$$

in which u represents the velocity of current and $\dot{x}_{th}$ the velocity of the heat motion, and let us take into consideration that

$$\Sigma \, 2 \, m \, u \, \dot{x}_{th} = 0.$$

$$\int 2 \, u \, \dot{x}_{th} \, f(\dot{x}) \, d\dot{x} = 0$$

and

$$\Sigma \, m \, u^2 + O \, m \, (x_1 - x_2) \, u^2 \int f(\dot{x}) \, d\dot{x} = 0.$$

Equation (18) then assumes the following form:

$$\Sigma \, m \, \dot{x}^2_{th} + \Sigma \, x \, X + O \, (x_1 - x_2) \, m \int \dot{x}^2_{th} \, f(\dot{x}) \, d\dot{x} = 0$$

Let us further split up X into X_1 and $\dot{X}_2$, in which X_1 refers to the mutual forces of the molecules in the considered volume and X_2 to the forces exerted by bodies lying outside the volume on the molecules contained in it. We shall only have to take forces X_2 into account that act in the planes $x_1 = c$ and $x_2 = c$; the others will be zero on an average. We shall further be allowed to put:

$$(\Sigma \, X_2)_{x_1} + m \, O \int \dot{x}_{th}^2 f(\dot{x}) \, d\dot{x} = p_{xx} \, O \quad . \quad . \quad . \quad (19)$$

in which $(\Sigma \, X_2)_{x_1}$ represents the sum of all the forces X_2 that act in the plane $x_1 = c$, and p_{xx} an element of the stress tensor in the well-known way. The lefthand member of (19), namely, indicates the total change of momentum which is caused by the substance on the lefthand side of the plane $x_1 = c$ in that on the righthand side both in consequence of transport by the molecules in their heat motion and in consequence of forces. As $O(x_2 - x_1) = V$ we find ·

$$p_{xx} \, V = \Sigma \, m \, \dot{x}^2 + \Sigma \, x \, X_1$$

or

$$p_{xx} = \frac{RT}{V} - \Sigma' \, x \, X_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

when the sign Σ' in the last equation represents a summation over all the molecules in a c.c.m.

§ 7. *The stress tensor in a flowing liquid.* When we now calculate $p_{\xi\xi}$ according to equation (20), we find:

$$p_{\xi\xi} = \frac{RT}{V} - \iint \frac{\partial \varphi}{\partial r_{12}} \, n_1 n_2 \, \frac{(\xi_2 - \xi_1)^2}{r_{12}} \, d\omega_1 d\omega_2, \quad . \quad . \quad . \quad (21)$$

in which $d\omega_1$ and $d\omega_2$ are two elements of space the distance of which is expressed by r_{12}, and in which the density of the molecules amounts respectively to n_1 and n_2. We now can put:

$$n_1 = \bar{n} + \Delta_1 + w_1(\bar{n} + \Delta_1)$$
$$n_2 = \bar{n} + \Delta_2 + w_2(\bar{n} + \Delta_2).$$

In this $\bar{n}$ represents the mean density, Δ the deviation, as we might expect it also without current, $w_1 n_1 = w_1 (\bar{n} + \bigtriangledown_1)$ representing according to § 4 the deviation from the mean density brought about by the current. Terms that would contain w^2, have been neglected. In the product $n_1 n_2$ the term $(\bar{n} + \Delta_1)(\bar{n} + \Delta_2)$ will yield the same value for all the coordinate directions. This term would also occur when there was no current, and its integral in equation (21) will produce the term $\dfrac{a}{v^2}$ of the hydrostatic pressure according to the

equation of state. Let us also remark that $\overline{n\Delta_1} = 0$ and $\overline{n\Delta_2} = 0$, then (21) may be written as follows:

$$p_{\xi\xi} - p = -\iint \frac{\partial \varphi}{\partial r_{12}} \frac{(\xi_2 - \xi_1)^2}{r_{12}} (w_1 n_1 \Delta_2 + w_2 n_2 \Delta_1 + n_1 w_1 n_2 w_2) d\omega_1\, d\omega_2 \quad (21a)$$

We shall neglect the third term. The 1st and the 2nd will be equal on an average, hence we may take twice the first. We shall substitute in it the value for w_1 that we have found in equation (17), in which we may replace n' by Δ', because when Δ' is everywhere zero, also w_1 becomes $= 0$. Thus we find·

$$p_{\xi\xi} - p = - \frac{\sqrt{3\pi}}{al} \frac{a}{kT} \iiiint n_1 \Delta_2 \Delta' \frac{\partial \varphi}{\partial r'} \frac{(\xi - \xi')^2 - (\zeta - \zeta')^2}{r'}$$
$$\frac{1}{r_1} \frac{\partial \varphi}{\partial r_{12}} \frac{(\xi_2 - \xi_1)^2}{r_{12}} d\omega' d\omega\, d\omega_1 d\omega_2. \quad\quad . \quad . \quad . \quad . \quad (21b)$$

and in the same way:

$$p_{\zeta\zeta} - p = - \frac{\sqrt{3\pi}}{dl} \frac{a}{kT} \iiiint n_1 \Delta_2 \Delta' \frac{\partial \varphi}{\partial r'} \frac{(\xi - \xi')^2 - (\zeta - \zeta')^2}{r'}$$
$$\frac{1}{r_1} \frac{\partial \varphi}{\partial r_{12}} \frac{(\zeta_2 - \xi_1)^2}{r_{12}} d\omega' d\omega\, d\omega\, d\omega_2.$$

It will hardly be possible to calculate the value of these expressions accurately. I shall confine myself to a rough estimation of the order of magnitude, and demonstrate that $p_{\xi\xi} - p$ and $p_{\zeta\zeta} - p$ assume equal but opposed values, which in virtue of the properties of the stress tension had to be the case.

If for two different elements of space the values for Δ were always independent of each other, $\overline{\Delta_2 \Delta'}$ would be $= 0$, except when we make the element $d\omega'$ coincide with $d\omega_2$. When we then made the value of $d\omega_2$ approach zero, the righthand member of $(21b)$ would become zero. The Δ's for different elements of space are, however, not independent, but when Δ_2 is e.g. positive, the Δ's in the adjacent elements will probably also be positive, so that the product $\Delta_2 \Delta' d\omega_2 d\omega'$ will be positive on an average not only for $d\omega' = d\omega_2$, but also for a finite region round $d\omega_2$. In this region I shall assign to Δ' not only the same sign, but also the same value as to Δ_2, and I shall assume that the size of the region is equal to the sphere of attraction of a molecule [1]. I shall further assume that we get a sufficient approximation for $p_{\xi\xi} - p$, when we assign the value n to n_1, and I shall write v for $\int n_1 \, d\omega'$, in which we extend the integration over the just-mentioned region. v then represents the mean number of molecules in a sphere of attraction. At the critical density I should then be inclined to ascribe to v a value between 5 and 25, though not much is to be said with certainty about this value. In consequence of these assumptions $(21b)$ passes into:

$$p_{\xi\xi} - p = -\frac{\sqrt{3\pi}}{al} \frac{av}{kT} \iiint \Delta_2{}^2 \frac{\partial \varphi}{\partial r_2} \frac{(\xi-\xi_2)^2-(\zeta-\zeta_2)^2}{r_2}$$

$$\frac{1}{r_1} \frac{\partial \varphi}{\partial r_{12}} \frac{(\xi_2-\xi_1)^2}{r_{12}} d\omega \, d\omega_1 d\omega_2 \quad . \quad . \quad . \quad . \quad . \quad (21c)$$

In order to find the sign of this expression, we transport the origin to the point $\xi_2 \, \eta_2 \, \zeta_2$, and first determine the sign of the quantity $\dfrac{\partial \varphi}{\partial r_2} \dfrac{(\xi-\xi_2)^2-(\zeta-\zeta_2)^2}{r_2} \equiv Q$. The bisextrices of the angles between the displaced ξ and ζ-axes, divide the plane into four quadrants; two of them contain the ξ-axis, and two the ζ-axis. In the two quadrants that contain the ξ-axis, Q will be > 0, in the others Q will be < 0. If we next inquire into the sign of $\int Q \dfrac{1}{r_1} d\omega = I$, this sign will depend on the situation of the point $\xi_1 \, \eta_1 \, \zeta_1$.

If this point lies in the quadrants where $Q > 0$, I will also be

---

[1] Not improbably it is greater; but as the elements $d\omega'$ and $d\omega_2$, the mutual distance of which is much greater, do not appreciably contribute to the value of the righthand member of $(21b)$, the restriction to this value may be justified.

> 0 and vice versa. Let us now finally form $\int I\,\dfrac{\partial \varphi}{\partial r_{12}}\dfrac{(\xi_2-\xi_1)^2}{r_{12}}\,d\omega_1$, and let us first integrate along a circle $r_{12} = $ constant; then the positive values of I will be multiplied by greater values of $(\xi_2-\xi_1)^2$ than the negative values, so that the positive sign results. If we had calculated $p_{\xi\varsigma}-p$, we had multiplied by $(\zeta_2-\zeta_1)^2$, so that then negative values of I had been multiplied by a greater factor, and the negative sign would have resulted.

In order to arrive at last at an estimation of the order of magnitude of $(p_{\xi\xi}-p)$, we observe that:

$$\int \frac{\partial \varphi}{\partial r}\, r\, dx\, dy\, dz = \frac{a}{N^2} \qquad \ldots \ldots (22)$$

in which **a** represents the known quantity a of the equation of state and N the number of molecules per molecular quantity.

We further assume that in the factor $\dfrac{1}{r_1}$ the radius of the sphere of attraction of the molecules (ϱ) may be written for r_1, and that the influence of the factors $\dfrac{(\xi-\xi_2)^2-(\zeta-\zeta_2)^2}{r_2{}^2}$ and $\dfrac{(\xi_2-\xi_1)^2}{r_{12}{}^2}$ will consist in this that the values which would be obtained by an omission of these factors, are multiplied by a moderate value μ, smaller than 1. •

Thus we find, when we also take into account that $NkT = RT$:

$$p_{\xi\xi} - p = -\frac{a\sqrt{3\pi}}{al\,RT}\,\nu\mu\,\overline{\Delta^2}\,\frac{(\mathbf{a})^2}{N^3}\,\frac{1}{\varrho} \qquad \ldots \ldots (21d)$$

If we had calculated p, we should also have found a term with $\overline{\Delta^2}$ in the virial of the attractive forces. If we call it p', then:

$$p' = \tfrac{1}{3}\,\overline{\Delta^2}\,\frac{\mathbf{a}}{N^2}$$

so that:

$$\frac{p_{\xi\xi}-p}{p'} = -\frac{a\sqrt{3\pi}}{3\alpha\,l\,RT}\,\nu\,\mu\,\frac{\mathbf{a}}{N}\,\frac{1}{\varrho} = \pm\,10^{-11}.$$

As our purpose was only a rough estimation, we have taken in this:

$$a = 1 \quad \text{and} \quad \nu\mu = 1$$
$$\alpha = 3.10^4$$
$$l = 10^{-7}$$
$$\varrho = 5.10^{-8}$$
$$N = 6.10^{23}$$

When we take for $p_k = 70$ atm. for CO_2 and $\eta = 0,000678$, we find:

$$\frac{\eta}{p} = \pm 10^{-11}$$

Now $p_k = $ round $\dfrac{1}{8} \dfrac{a}{v_k^2}$ and $p' = \dfrac{\overline{\Delta^2}}{\overline{n}^2} \dfrac{a}{v_k^2}$, hence if at the critical point the mean Δ becomes somewhat smaller, but of the same order of magnitude as $\overline{n}$, then $p_{k} - p$ will become of the same order of magnitude as η for a gradient of velocity $a = 1$, and must, therefore, certainly, be taken into account. On the strength of this we should have to expect that an abnormally great value of η would be found at the critical density, when for T_k we examined the value η as function of the density. WARBURG and VON BABO [1]) have determined η for CO_2 at 32,6° for different densities. η increases with the density. There does not appear any irregular increase at the critical density from their observations. It would be interesting when similar observations could be made at a temperature nearer T_k.

---

[1]) WIEDEMANN's Annalen. XVII p. 390. 1882.