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On the characteristic equation of v.d.Waals, in:
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Physics. — Prof. VAN DER WAALS presents for the Proceedings of the meeting a paper of Prof. L. BOLTZMANN, foreign member of the Academy,: "*On the characteristic equation of* V. D. WAALS," with an accompanying letter from which the following extract has been taken.

VIENNA, March 2nd 1899.

Dear Sir,

Mr. VAN LAAR has sent me from Utrecht a calculation which he undertook at your demand. From this I have calculated the next correction term of your formula in the same way as I have followed in the second part of my gas-theory, and I take the liberty of sending the MS. to you. The result will differ in some respects from the one you obtained, but I should consider a discussion about it very interesting on mathematical grounds; not so much on physical grounds, as the further correction terms are certainly not calculable. Under slight pressures the observations are too inaccurate for this term to be useful, while for high pressures more approximation terms would be required. Moreover no observations have been made on *Hg*-vapour, argon, helium, where spherical molecules may be presumed. I should be pleased if you would lay my MS. before the Amsterdam Academy of Sciences and I should like it to be printed in its Proceedings, because I think this the best way to attain my purpose, viz. to incite those who are interested in this question to a discussion which might be useful to science. . . . .

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Yours truly
LUDWIG BOLTZMANN.

At the demand of Prof. VAN DER WAALS, Mr. VAN LAAR has calculated a formula which may be used for the calculation of a further approximation term in the former's formula. I shall show how Mr. VAN LAAR's formula may be used for the further development of my calculation relating to this subject, and make use of the same notations as in the second part of my "Lectures on Gas-theory", which I shall always briefly quote as l. c.

I. *Calculation of the space left for the centre of a new molecule to be introduced into the gas.*

Let V be the volume of a vessel, in which there are found n very

small, rigid spheres (molecules), all of them having the same properties and of the mass m and the diameter σ.

We represent by D_1 the first approximated value of the space D left for the centre of a molecule new added into the gas. This molecule has the same properties as the others. Then $D_1 = V$. As a second approximation we must subtract from this the volume of the distance-spheres of all the n molecules. The term distance-sphere stands here for a sphere concentric to the molecule and with the radius σ, so having a volume of $\frac{4}{3}\pi\sigma^3$. If we put $\frac{2\pi\sigma^3}{3m} = b$ and the total mass of the gas $m\,n = G$, then the sum of all the volumes of all the n distance-spheres is $2\,G\,b$ and the second approximated value of D is therefore

$$D_2 = V - 2\,G\,b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For the third approximation we must take into account that not the sum of the volumes of all the distance-spheres is to be subtracted from V, as here and there two distance spheres cover each other partially, and that then the space which is common to them, is to be subtracted but once. So we must add to D_2 the sum Z of all spaces which two distance-spheres have anywhere in common.

We find the volume Z in the following way: We construe round the centre of every one of the n molecules a spherical shell concentrical with the molecule, with an inner radius x and the very small thickness dx, which spherical shell we shall call S. The volume R, which is the sum of all the spherical shells S construed in such a way, is $4\pi n x^2 dx$. The number dn of the centres of the molecules which are found in any of these spherical shells is to the total number of the molecules in the first approximation as R is to the volume of the vessel V, so that we get

$$dn \; : \; n = 4\pi n x^2 dx \; : \; V \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$dn = \frac{4\pi n^2 x^2 dx}{V} \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The last expression gives the number of molecules whose centres lie at a distance between x and $x + dx$ from the centre of any other molecule. The number of the pairs of molecules, whose centra have a distance between these limits, is $\frac{1}{2}\,dn$. As soon as x is between σ and 2σ, the distance-spheres of the two molecules of

the pairs in question will have a lens-shaped space of the volume

$$2 K = \frac{\pi}{12} (16 \sigma^3 - 12 \sigma^2 x + x^3) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in common (l.c. p. 166) [1]). The sum of all these lens-shaped spaces which occur with all possible pairs of molecules, is represented by Z. Therefore

$$Z = \int K \, dn = \frac{\pi^2 n^2}{6 V} \int_\sigma^{2\sigma} x^2 \, dx \, (16 \sigma^3 - 12 \sigma^2 x + x^3) = \frac{17}{16} \frac{G^2 b^2}{V} \quad . \quad (5)$$

and

$$D_3 = V - 2 G b + Z \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The value of D, in which the approximation has been worked out one term further, is called D_4. To find it, we must first subtract from D_3 the sums of all volumes which belong to the distance-spheres of three molecules at the same time, and which is according to Mr. VAN LAAR

$$\frac{2 \beta G^3 b^3}{V^2}$$

in which β is the quantity which he has calculated and which he has also represented by β on the last page of his discussion. Secondly however we have also to add a correction term to Z, which we shall represent by ζ, so that

$$D_4 = V - 2 G b + \frac{17}{16} \frac{G^2 b^2}{V} - 2 \beta \frac{G^3 b^3}{V^2} + \zeta \quad . \quad . \quad . \quad (7)$$

We get the correction term ζ by the following consideration. The proportion (2) is only right as a first approximation. If we try to obtain to a greater accuracy, the last term of the proportion should not be represented simply by V, as the whole volume of the vessel is not at the disposal of all the n molecules. In the same way a correction term is to be inserted in the last member but one of the

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[1]) Compaie also. VAN DER WAALS, Amst. Acad 31 Oct. 1896 and 29 Oct. 1898.

proportion, while also a part of the volume, represented above by R, will fall in the distance-sphere of other molecules.

Next we may state the following rule. According to probability the relation between the number represented above by dn and the total number n of the molecules will be the same as between that part R_1 of the space R which is left for the centre of a new-added molecule and the whole space which is left inside the vessel for the centre of a new-added molecule. [1]

According to formula (1) the last mentioned space is $V - 2\,Gb$. The last term of the proportion (2) should therefore be represented by $V - 2\,Gb$ instead of by V. R_1 is still to be found. For this purpose we construe inside each of the above considered n spherical shells with a radius x and a thickness dx, which we have called the spherical shells S, a concentrical spherical shell with an inner radius y and a thickness dy. The latter spherical shells we shall call the spherical shells T. The sum of the number of the centra of molecules, which lie in any of the spherical shells T is, analogous to the equation (3)

$$d\nu = \frac{4\,\pi\,n^2\,y^2\,dy}{V} \quad \ldots \quad \ldots \quad (8)$$

The part

$$\pi\,x\,\frac{o^2 - (x - y)^2}{y}$$

of the surface lies within the distance spheres of every separate one of the molecules ; thence the part

$$\omega = \pi\,x\,dx\,\frac{\sigma^2 - (x - y)^2}{y} \quad \ldots \quad \ldots \quad (9)$$

of the inner space of the spherical shells in question with a radius x and a thickness dx, as an easy calculation shows. That part of the volumes of all the spherical shells S which is covered by the distance spheres of all the $d\nu$ molecules together is therefore $\omega\,d\nu$.

If no molecules were to be found inside the spherical shells S, we might integrate this expression with respect to y from $x - \sigma$ to $x + \sigma$ and

$$\int \omega\,d\nu = \frac{16\,\pi^2\,n^2\,x^2\,\sigma^3}{3\,V}\,dx = \frac{2\,b\,G}{V}\,.\,4\,\pi\,n\,x^2\,dx \quad \ldots \quad (10)$$

would follow.

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[1] For a fuller exposition of this rule comp. l. c. § 51.

Then the space of the sum of the volumes $R = 4 \pi n x^2 dx$ of all the spherical shells S together, which is enclosed in the distance spheres, would be to this total space R, as the whole space $2 G b$ occupied by the distance spheres of all the molecules of the gas to the whole volume of the vessel V, which was to be expected a priori.

In every spherical shell S, however, a molecule is found, so that the centre of another molecule cannot come closer than at a distance σ from the centre of the spherical shell. Therefore we have to subtract from the value (10).

$$\int_{y=x-\sigma}^{y=\sigma} \omega \, d\nu = \frac{4 \pi^2 n^2 x^2 dx}{V} \left(\frac{x^3}{12} - x \sigma^2 + \frac{4\sigma^3}{3} \right) = 4 \pi n x^2 dx \, \gamma,$$

in which

$$\gamma = \frac{\pi n}{12 V} (x^3 - 12 x \sigma^2 + 16 \sigma^3) .$$

Instead of the last term but one in the proportion (2) we have therefore to put

$$4 \pi n x^2 dx \left(1 - \frac{2 G b}{V} + \gamma \right).$$

As we ought to substitute $V \left(1 - \frac{2 G b}{V} \right)$ for the last term, it comes to the same thing as if the last term were left as it is, and as if

$$4 \pi n x^2 dx (1 + \gamma)$$

were substituted for the last term but one, at least if terms of still higher order are neglected.

We obtain therefore for dn the correction term

$$d\nu = \gamma \, dn$$

and for Z the correction term

$$\zeta = \int K \gamma \, d\nu = \frac{\pi^3 n^3}{72 V^2} \int_{\sigma}^{2\sigma} x^2 \, dx \, (x^3 - 12 \sigma^2 x + 16 \sigma^3)^2 =$$

$$= \frac{2357}{22680} \cdot \frac{\pi^3 n^3 \sigma^9}{V^2} = \frac{2357}{6720} \frac{G^3 b^3}{V^2} ;$$

By the substitution of these values, formula (7) becomes:

$$D_4 = V - 2\,G\,b + \frac{17}{16}\,\frac{G^2\,b^2}{V} + \left(\frac{2357}{6720} - 2\beta\right)\frac{G^3\,b^3}{V^2} =$$

$$= V - 2\,G\,b\left[1 - \frac{17}{32}\,\frac{G\,b}{V} + \left(\beta - \frac{2357}{13440}\right)\frac{G^2\,b^2}{V^2}\right] \quad (11)$$

This is therefore the space left in the vessel for the centre of a molecule, when terms of four different orders with respect to $\frac{G\,b}{V}$ are considered.

II. *Correction of the equation of* VAN DER WAALS.

The shortest way to calculate this correction by means of formula 11 is that which I followed l. c. § 61. If we substitute the expression D_4, which has now been found for the expression D, which has been used l. c. § 61 and has been represented by equation 173 there, we obtain

$$l\left[v - 2\,\nu\,m\,b + \frac{17}{16}\,\frac{\nu^2\,m^2\,b^2}{v} + \left(\frac{2357}{6720} - 2\,\beta\right)\frac{\nu^3\,m^3\,b^3}{v^2}\right] =$$

$$= l\,v - \frac{2\,\nu\,m\,b}{v} - \frac{15}{16}\,\frac{\nu^2\,m^2\,b^2}{v^2} - \left(\frac{1283}{6720} + 2\,\beta\right)\frac{\nu^3\,m^3\,b^3}{v^3}\,,$$

instead of the first formula on p. 174, and so instead of the formula which is found for S six lines lower

$$S = \frac{3\,n\,r}{2}\int(1+\beta)\frac{d\,T}{T} + r\left[l\,v - \frac{b}{v} - \frac{5}{16}\,\frac{b^2}{v^2} - \left(\frac{1283}{26880} + \frac{\beta}{2}\right)\frac{b^3}{v^3}\right].$$

The formula for

$$\frac{\partial\,(T\,S)}{\partial\,v}$$

which follows on this one in l. c. is changed to

$$\frac{\partial\,(T\,S)}{\partial\,v} = r\,T\left[\frac{1}{v} + \frac{b}{v^2} + \frac{5}{8}\,\frac{b^2}{v^3} + \left(\frac{1283}{8960} + \frac{3\,\beta}{2}\right)\frac{b^3}{v^4}\right]$$

so that the corrected equation of VAN DER WAALS would have the following form

$$p + \frac{a}{v^2} = r\,T\left[\frac{1}{v} + \frac{b}{v^2} + \frac{5}{8}\frac{b^2}{v^3} + \left(\frac{1283}{8960} + \frac{3\,\beta}{2}\right)\frac{b^3}{v^4}\right]$$

$$= \frac{r\,T}{v - b + \dfrac{3}{8}\dfrac{b^2}{v} + \left(\dfrac{957}{8960} - \dfrac{3\,\beta}{2}\right)\dfrac{b^3}{v^2}} \tag{12}$$

In this formula is according to Mr. VAN LAAR

$$\beta = \frac{73\sqrt{2} + 81.17\left(arc\,tg\sqrt{2} - \dfrac{\pi}{4}\right)}{32.35\,\pi} = 0.0958 \ .$$

Physics. — "*The galvano-magnetic and thermo-magnetic phenomena in bismuth*". (Second Communication.) By Dr. E. VAN EVERDINGEN JR. (Communication N°. 48 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES.)

1. In the Proceedings of the meeting of June 25th 1898 we have communicated the results of the observations of the four transverse galvano-magnetic and thermo-magnetic phenomena, all of them made in one and the same magnetic field with one and the same electrolytically prepared plate of bismuth. By means of the same plate of bismuth we have now observed the decrease of conductivity for electricity and heat and also the longitudinal thermomagnetic phenomenon. It has given us much trouble to measure the two last phenomena with sufficient accuracy, and the variation of the conductivity for heat can only approximately be deduced from the measurements. Yet I communicate the results for two reasons: in the first place, for a preliminary theory it is sufficient that the order of magnitude of the phenomena is known, and secondly in consequence of the small dimensions of the plate it is not probable that further measurements with the same plate would yield a much more exact result for the absolute value. Moreover the plate during one of the last experiments has developed a crack and this has put an end to all further observations under the same circumstances, even if we had wished to continue them.

These measurements having been finished we have obtained for