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Physics. "*On the variability of the quantity b in* VAN DER WAALS' *equation of state, also in connection with the critical quantities.*" III. By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

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The coefficients found in the preceding paper can be found by another way still. I will call this method the *symmetrical* method, because it is based on *two* logarithmic equations which are symmetrically constructed. We mean the relations

$$\left.\begin{aligned} \frac{8}{3}m\left[\frac{d'}{3(d-d')}\log\left(\frac{d}{d'}\frac{3-d'}{3-d}\right)-\frac{1}{3-d}\right] &= d'-d \\ \frac{8}{3}m\left[\frac{d}{3(d-d')}\log\left(\frac{d}{d'}\frac{3-d'}{3-d}\right)-\frac{1}{3-d'}\right] &= d-d' \end{aligned}\right\},$$

which have been formed by the combination of the two original equations (a). (see II p 432).

If again we put:

$$d = 1+2x+2y = 1+2p \; ; \; d' = 1-2x+2y = 1-2q,$$

in which $x = a\tau + c\tau^3 + \ldots$, $y = b\tau^2 + d\tau^4 + \ldots$, the two above equations become:

$$\left.\begin{aligned} \frac{2}{3}m\left[\frac{1-2q}{3(p+q)}\log\left(\frac{1+2p}{1-2q}\,\frac{1+q}{1-p}\right)-\frac{1}{1-p}\right] &= -(p+q) \\ \frac{2}{3}m\left[\frac{1+2p}{3(p+q)}\log\left(\frac{1+2p}{1-2q}\,\frac{1+q}{1-p}\right)-\frac{1}{1+q}\right] &= p+q \end{aligned}\right\}, \quad . \; (b),$$

because $3-d = 2(1-p)$, $3-d' = 2(1+q)$ and $d-d' = 2(p+q)$.

Now the logarithm gives (see II p. 440), after $p+q$ has been placed outside the parentheses:

$$3(p+q)\left[1-\frac{1}{2}(p-q)+(p^2-pq+q^2)-\frac{5}{4}(p^3-\ldots-q^3)+\right.$$
$$\left.+\frac{11}{5}(p^4-\ldots+q^4)-\frac{7}{2}(p^5-\ldots-q^5)+\frac{43}{7}(p^6-\ldots+q^6)\right].$$

After division of the *log* by $3(p+q)$, multiplication by $1-2q$, and subtraction of $1:(1-p) = 1+p+p^2+\ldots$ the former of the two above equations passes into

$$\frac{2}{3}m\left[-\frac{1}{2}.3(p+q)+\frac{1}{6}.0-\frac{1}{12}\,.\,9\,(3p^3+p^2q-pq^2+q^3)+\right.$$

$$+\frac{1}{20}.6(4p^4+p^3q-p^2q^2+pq^3-q^4)-\frac{1}{30}.27(5p^5+p^4q\ p^3q^2+p^2q^3-pq^4+q^5)+$$

$$+\frac{1}{42}\cdot 36[6p^6+p^5q-p^4q^2+p^3q^3-p^2q^4+pq^5-q^6)\Big]=-(p+q),$$

in which the coefficients 3, 0, 9, 6, 27, 36, etc. in general are represented by θ, $\theta(\theta-3)$, $\theta(\theta^2-4\theta+6)$, $\theta(\theta^3-5\theta^2+10\theta-10)$, $\theta(\theta^4-6\theta^3+15\theta^2-20\theta+15)$, $\theta(\theta^5-7\theta^4+21\theta^3-35\theta^2+35\theta-21)$, etc., where $\theta=3$.

The corresponding second equation is now evidently obtained by substituting $-q$ for p, and $-p$ for q, as is immediately seen by comparison of the above equations (b). If then the first equation is divided by $-(p+q)$, the second by $p+q$, we get:

$$\left.\begin{aligned}&m\Big[1+\frac{1}{2}(3p^2-2pq+q^2)-\frac{1}{5}(4p^3-3p^2q+2pq^2-q^3)+\\&+\frac{3}{5}(5p^4-4p^3q+3p^2q^2-2pq^3+q^4)-\frac{4}{7}(6p^5-5p^4q+4p^3q^2-3p^2q^3+2pq^4-q^5)\Big]=1\\&m\Big[1+\frac{1}{2}(p^2-2pq+3q^2)-\frac{1}{5}(p^3-2p^2q+3pq^2-4q^3)+\\&+\frac{3}{5}(p^4-2p^3q+3p^2q^2-4pq^3+5q^5)-\frac{4}{7}(p^5-2p^4q+3p^3q^2-4p^2q^3+5pq^4-6q^5)\Big]=1\end{aligned}\right\}.$$

Subtraction yields:

$$\frac{1}{2}(2p^2-2q^2)-\frac{1}{5}(3p^3-p^2q-pq^2+3q^3)+$$

$$+\frac{3}{5}(4p^4-2p^3q+2pq^3-4q^4)-\frac{4}{7}(5p^5-3p^4q+p^3q^2+p^2q^3-3pq^4+5q^5)=0,$$

or after division by $p+q$:

$$(p-q)-\frac{1}{5}(3p^2-4pq+3q^2)+$$

$$+\frac{3}{5}(4p^3-6p^2q+6pq^2-4q^3)-\frac{4}{7}(5p^4-8p^3q+9p^2q^2-8pq^3+5q^4)=0\quad.\quad(\alpha)$$

Addition, and division by $2m$ yields:

$$(p^2-pq+q^2)-\frac{1}{2}(p^3-p^2q+pq^2-q^3)+$$

$$+\frac{9}{5}(p^4-p^3q+p^2q^2-pq^3+q^4)-2(p^5-\ldots-q^5)=\tau^2+\tau^4+\ .\ ,\quad(\beta),$$

because $m=1-\tau^2$ and so $1:m=1+\tau^2+\tau^4+\ldots$

Re-substitution of $x+y$ for p, of $x-y$ for q (see above) transforms (α) and (β) into

$$\left.\begin{array}{l} 2y-\frac{1}{5}(2x^2+10y^2)+\frac{3}{5}.2y(6x^2+10y^2)-\frac{4}{7}(3x^4+42x^2y^2+35y^4)=0 \\ (x^2+3y^2)-\frac{1}{2}.2y(2x^2+2y^2)+\frac{9}{5}(x^4+10x^2y^2+5y^4)-2\,2y(3x^4+9x^2y^2+3y^4)=\tau^2+\tau^4 \end{array}\right\},$$

which is easily obtained when we consider that $4p^3-6p^2q+$ $+6pq^3-4q^3=(p-q)[4(p^2+q^2)-2pq]$; $5p^4-8p^3q+$ etc. $=5(p^4+q^4)-$ $-8pq(p^2+q^3)+9p^2q^2$; etc.

And if finally we substitute the values $a\tau+c\tau^3$ and $b\tau^2+d\tau^4$ for x and y, we get:

$$\left.\begin{array}{l} 2(b\tau^2+d\tau^4)-\frac{2}{5}\left(a^2\tau^2+(2ac+5b^2)\tau^4\right)+\frac{12}{5}b\tau^2(3a^2\tau^2)-\frac{4}{7}(3a^4\tau^4)=0 \\ \left(a^2\tau^2+(2ac+3b^2)\tau^4\right)-2b\tau^2(a^2\tau^2)+\frac{9}{5}(a^4\tau^4)=\tau^2+\tau^4 \end{array}\right\},$$

in which the development need not go any further than τ^4, whereas in the *asymmetrical* method (see the preceding paper) we had to go as far as τ^6. In consequence of this amongst others the whole last term of the first member of the second equation in x and y vanishes.

Summarizing this, we get finally:

$$\left.\begin{array}{l} \left(2b-\frac{2}{5}a^2\right)\tau^2+\left(2d-\frac{4}{5}ac-2b^2+\frac{36}{5}a^2b-\frac{12}{7}a^4\right)\tau^4=0 \\ a^2\tau^2+\left(2ac+3b^2-2a^2b+\frac{9}{5}a^4\right)\tau^4=\tau^2+\tau^4 \end{array}\right\},$$

from which follows:

$$\left.\begin{array}{ll} a^2=1\,; & 2ac+3b^2-2a^2b+\frac{9}{5}a^4=1 \\ 2b-\frac{2}{5}a^2=0\,; & 2d-\frac{4}{5}ac-2b^2+\frac{36}{5}a^2b-\frac{12}{7}a^4=0 \end{array}\right\},$$

and from this by successive substitution and solution:

$$\underline{a=1}\ ;\quad \underline{b=\frac{1}{5}}\ ;\quad \underline{c=-\frac{13}{50}}\ ;\quad \underline{d=\frac{64}{875}},$$

as in the first method. But here the coefficient e is not required to determine d, because they are not found in pairs together, — always from two equations with two unknown quantities — but *successively*, always from but one equation. It is again self-evident that if we only desire to know a and b, the above calculation is again considerably shortened, and the result is obtained almost immediately. For then only the terms with τ^2 are necessary.

Lastly we will also mention a *third* method, that of the *differential quotient*; the shortest method of all, but yet possibly slightly longer than the two discussed methods, because first the differential quotient must be derived. Let us start from the two equations (1^a) and (2) [See II, p. 432—433], viz.

$$(3-d)(3-d')(d+d') = 8m \quad ; \quad \log\left(\frac{d}{d'}\frac{3-d'}{3-d}\right) = \frac{3}{8}\,\frac{d-d'}{m}\left(6-(d+d')\right).$$

Now we differentiate with respect to τ ($m = 1-\tau^2$, so $\tau = \sqrt{1-m}$), and obtain in this way from the first equation, putting $\frac{dd}{d\tau} = x$ and $\frac{dd'}{d\tau} = y$:

$$-\frac{x}{3-d} - \frac{y}{3-d'} + \frac{x+y}{d+d'} = -\frac{2\tau}{1-\tau^2},$$

from which:

$$\frac{3-2d-d'}{3-d}\,x + \frac{3-d-2d'}{3-d'}\,y = -\frac{2\tau}{1-\tau^2}(d+d') \quad . \quad . \quad . \quad (\alpha)$$

The second equation yields:

$$\frac{x}{d} - \frac{y}{d'} - \frac{y}{3-d'} + \frac{x}{3-d} = -\frac{3}{8}\,\frac{d-d'}{m}(x+y) + \frac{3}{8}\,\frac{6-(d+d')}{m}(x-y) +$$
$$+\frac{3}{8}\,\frac{2\tau}{m^2}(d-d')\left(6-(d+d')\right),$$

i. e.

$$\left[\frac{1}{d} + \frac{1}{3-d} + \frac{3}{8m}(d-d') - \frac{3}{8m}\left(6-(d+d')\right)\right]x +$$
$$+\left[-\frac{1}{d'} - \frac{1}{3-d'} + \frac{3}{8m}(d-d') + \frac{3}{8m}\left(6-(d+d')\right)\right]y =$$
$$= \frac{3}{8}\,\frac{2\tau}{m^2}(d-d')\left(6-(d+d')\right),$$

or

$$\left[\frac{3}{d(3-d)} + \frac{3}{8m}(2d-6)\right]x + \left[-\frac{3}{d'(3-d')} + \frac{3}{8m}(6-2d')\right]y =$$
$$= \frac{3}{8}\,\frac{2\tau}{m^2}(d-d')\left(6-(d+d')\right).$$

If in this $(3-d)(3-d')(d+d')$ is substituted for $8m$, we get:

$$\left[\frac{1}{d(3-d)} - \frac{2}{(3-d')(d+d')}\right]x - \left[\frac{1}{d'(3-d')} - \frac{2}{(3-d)(d+d')}\right]y =$$
$$= \frac{2\tau}{8m^2}(d-d')\left(6-(d+d')\right),$$

or also

$$-\frac{(d-d')(3-2d-d')}{d(3-d)(3-d')(d+d')}x-\frac{(d-d')(3-d-2d')}{d'(3-d)(3-d')(d+d')}y=$$
$$=\frac{2\tau}{8m^2}(d-d')\Big(6-(d+d')\Big),$$

hence finally, writing again $8m$ for $(3-d)(3-d')(d+d')$:

$$\frac{3-2d-d'}{d}x+\frac{3-d-2d'}{d'}y=-\frac{2\tau}{1-\tau^2}\Big(6-(d+d')\Big) \quad . \quad . \quad (\beta)$$

We must now combine (α) and (β) to solve x and y. Elimination of y gives:

$$(3-2d-d')\left(\frac{d'}{d}-\frac{3-d'}{3-d}\right)x=-\frac{2\tau}{1-\tau^2}\left[d'\Big(6-(d+d')\Big)-(3-d')(d+d')\right],$$

or

$$\frac{3-2d-d'}{d(3-d)}\Big(-3(d-d')\Big)x=-\frac{2\tau}{1-\tau^2}\Big(-3(d-d')\Big),$$

so that we get:

$$\frac{dd}{d\tau}=x=-\frac{2\tau}{1-\tau^2}\,\frac{d(3-d)}{3-2d-d'}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and a similar expression for $y=\dfrac{dd'}{d\tau}$, which differs from the above only in this that d and d' are interchanged. It is this comparatively simple result, which makes us find the coefficients a, b, c, etc. pretty soon. Substitution, namely of $\left\{\begin{matrix} d \\ d' \end{matrix}\right. = 1 \pm 2a\tau + 2b\tau^2 \pm 2c\tau^3 + 2d^4$ immediately gives:

$$2a+4b\tau+6c\tau^2+8d\tau^3=-\frac{2\tau}{1-\tau^2}\,\frac{(1+2a\tau+2b\tau^2+..)\,2\,(1-a\tau-b\tau^2-..)}{-2a\tau-6b\tau^2-2c\tau^3-6d\tau^4-...}$$

i. e.

$$(a+2b\tau+3c\tau^2+4d\tau^3)(a+3b\tau+c\tau^2+3d\tau^3)=$$
$$=\frac{(1+2a\tau+2b\tau^2+2c\tau^3)(1-a\tau-b\tau^2-c\tau^3)}{1-\tau^2},$$

or

$$a^2+5ab\tau+(4ac+6b^2)\tau^2+(7ad+11bc)\tau^3=$$
$$=\frac{1+a\tau+(b-2a^2)\tau^2+(c-4ab)\tau^3}{1-\tau^2}=1+a\tau+(1+b-2a^2)\tau^2+(a+c-4ab)\tau^3.$$

And from this follows:

$a^2=1$; $5ab=a$; $4ac+6b^2=1+b-2a^2$; $7ad+11bc=a+c-4ab$,
i. e.

$$\underline{a=1}; \quad \underline{b=\frac{1}{5}}; \quad \underline{c=-\frac{13}{50}}; \quad \underline{d=\frac{64}{875}}.$$

For the knowledge of a and b only we should have to go no further than terms with τ, and so the calculation would then be very simple indeed.

8. After the above digressions, which have made us acquainted to a certain extent with the nature of the problem, and the results of which may later on be used for a comparison, we proceed: in the first place to derive the reduced equations for the case of *association* of the molecules, and in the second place to determine from this the coefficients a and b of the expansion into series:

$$d = 1 + a\tau + b\tau^2$$

in the neighbourhood of the critical point.

From the equation of state

$$p = \frac{\frac{1+x\beta}{1+x} RT}{v-b} - \frac{a}{v^2},$$

in which all the quantities are made to refer to single molecular quantities, and in which RT is therefore multiplied by $(1+x\beta):(1+x)$ instead of by $1+x\beta$, the equation

$$\frac{1}{27} f_2 \frac{a}{b_k^2} \varepsilon = \frac{\frac{1+x\beta}{1+x} \frac{8}{27} f_1 \frac{a}{b_k} m}{2{,}1\, b_k n - b_k \gamma} - \frac{a}{(2{,}1)^2 b_k^2 n^2},$$

or

$$\frac{f_2}{f_1} \varepsilon = \frac{8 \frac{1+x\beta}{1+x} m}{2{,}1\, n - \gamma} - \frac{27}{(2{,}1)^2 f_1 n^2}.$$

follows by substitution of

$$p = \varepsilon p_k, \quad T = mT_k, \quad v = nv_k, \quad b = \gamma b_k,$$

in which (see I, p. 296—297)

$$p_k = \frac{1}{27} f_2 \frac{a}{b_k^2}; \quad RT_k = \frac{8}{27} f_1 \frac{a}{b_k}; \quad v_k = 2{,}1\, b_k.$$

Hence, by equalisation of the expressions for $\frac{f_2}{f_1}\varepsilon$ for the two co-existing phases:

$$\frac{\frac{1+x\beta}{1+x} d}{2{,}1-\gamma d} - \frac{\frac{1+x\beta'}{1+x} d'}{2{,}1-\gamma' d'} = \frac{6}{8} \frac{d^2-d'^2}{m}, \quad . \quad . \quad . \quad (10)$$

when we again introduce the densities $d = 1:n$ and $d' = 1:n'$. For

$x=1$ ($\nu=2$) (association to double molecules) we have viz. (see I p. 297):

$$\frac{27}{(2,1)^2 f_1}=\frac{27}{(2,114)^2\times 1,004}=\frac{27}{4,469\times 1,004}=\frac{6,042}{1,0043}=6,016,$$

for which we have written 6 for brevity's sake. So in later calculations in (10) 2,1 must always be replaced by 2,114 and 6 by 6,016 — at least for $x=1$. At constant b this value 6 becomes $\frac{27}{3^2}=3$, while $\frac{1+x\beta}{1+x}$, γ etc. become all $=1$, so that then the original relation (1) is found back (see II, p. 432).

The former logarithmic relation, formed from $\int pdv$ must now be obtained in a somewhat different way, because the direct integration would become too intricate in consequence of the variability of β and b. The same result is, however, obtained by equalisation of the thermodynamic potentials of the two coexisting phases [1]), and the formula

$$(1+x)\,log\left[\frac{p+{}^{a}/_{v^2}}{p+{}^{a}/_{v'^2}}\,\frac{\beta}{1+x\beta}\,\frac{1+x\beta'}{\beta'}\right]=\frac{a}{RT}\left[2\left(\frac{1}{v}-\frac{1}{v'}\right)-(1+x)b_2\left(\frac{1}{v^2}-\frac{1}{v'^2}\right)\right]$$

is then found, as we derived before [see among others Solid State V p. 456 (These Proc. Nov. 1910) and VII p. 89 (June 1911). But as here everything refers to double molecular quantities, and in future everything will refer to single quantities, we must substitute $a:(1+x)^2$ for a, b_2 for $(1+x)\,b_2$, $v:(1+x)$ for v, and we get:

$$log\left(\frac{v'-b'}{v-b}\,\frac{\beta}{\beta'}\right)=\frac{a}{RT}\left[2\left(\frac{1}{v}-\frac{1}{v'}\right)-b_2\left(\frac{1}{v^2}-\frac{1}{v'^2}\right)\right], \quad . \quad (11)$$

when $p+{}^{a}/_{v^2}$ is replaced by $\frac{1+x\beta}{1+x}RT:(v-b)$ and $p+{}^{a}/_{v'^2}$ by the corresponding expression.

In this connection we will just show that equation (11) is identical with that which would follow from $p=\frac{1}{v'-v}\int_v^{v'} pdv$. Let us for this purpose write (11) in the form

$$RT\,log\left(\frac{v'-b'}{v-b}\,\frac{\beta}{\beta'}\right)=\left(\frac{a}{v}-\frac{a}{v}\right)+\left[\left(\frac{a}{v}-\frac{a}{v'}\right)-b_2\left(\frac{a}{v^2}-\frac{a}{v'^2}\right)\right],$$

in which the expression between [ ] can be written:

[1]) Cf. also Chemisch Weekblad 1909, N$^{\text{r}}$. 51.

$$\frac{a}{v^2}(v-b_2)-\frac{a}{v'^2}(v'-b_2)=\left(\frac{\frac{1+x\beta}{1+x}RT}{v-b}-p\right)(v-b_2)-\left(\frac{\frac{1+x\beta'}{1+x}RT}{v'-b'}-p\right)(v'-b_2),$$

or

$$RT\left[\frac{1+x\beta}{1+x}\,\frac{v-b_2}{v-b}-\frac{1+x\beta'}{1+x}\,\frac{v'-b_2}{v'-b'}\right]+p\,(v'-v).$$

Hence after substitution and solution of p:

$$p=\frac{RT}{v'-v}\log\left(\frac{v'-b'}{v-b}\,\frac{\beta}{\beta'}\right)-\frac{a}{vv'}+\frac{RT}{v'-v}\left[\frac{1+x\beta'}{1+x}\,\frac{v'-b_2}{v'-b'}-\frac{1+x\beta}{1+x}\,\frac{v-b_2}{v-b}\right]\quad . \quad (11^a)$$

And now it is immediately seen that in (11^a), for b constant — in which $b=b'=b_2$, while $(1+\beta):(1+x)$ and $(1+\beta'):(1+x)$ both become $=1$ — the last term disappears and the following equation remains:

$$p=\frac{RT}{v'-v}\log\frac{v'-b'}{v-b}-\frac{a}{vv'},$$

as before. So the second member of equation (11^a) can be considered as the value of the integral $\frac{1}{v'-v}\int_v^{v'} pdv$, but obtained by an indirect course by equalisation of the thermodynamic potentials.

Now, after this short digression, we return to (11). In consequence of the substitutions $v=nv_k$, etc. — to which $b_2=sb_k$ can be added, this equation reduces to

$$\log\left(\frac{2{,}1b_kn'-b_k\gamma'}{2{,}1b_kn-b_k\gamma}\,\frac{\beta}{\beta'}\right)=\frac{a}{\frac{8}{27}f_1\frac{a}{b_k}m}\left[\frac{2}{2{,}1b_k}\left(\frac{1}{n}-\frac{1}{n'}\right)-\frac{sb_k}{(2{,}1)^2b_k^2}\left(\frac{1}{n^2}-\frac{1}{n'^2}\right)\right],$$

or to

$$\log\left(\frac{d}{d'}\,\frac{2{,}1-\gamma'd'}{2{,}1-\gamma d}\,\frac{\beta}{\beta'}\right)=\frac{6}{8}\,\frac{d-d'}{m}\left[2\times 2{,}1-s\,(d+d')\right],\quad . \quad . \quad (12)$$

because $1:n=d$, etc. and (for $x=1$) 6 has been substituted for $27:(2{,}1)^2f_1=6{,}016$. Here too our former relation (2) for b constant (II, p. 433) is found back when we put β and β', γ and $\gamma'=1$, replace 6 by 3 (see above), 2,1 too by 3, while also s becomes $=1$.

Now it is the equations (10) and (12) that quite determine d and d' as functions of m. But the presence of β and γ now makes the problem much more intricate. We shall see that in the expression for the coefficient a of the expansion $d=1+a\tau+b\tau^2$ even the *third* differential quotient with respect to v of the quantity b of VAN

DER WAALS's equation of state occurs, whereas in the expression for the coefficient b even the *fifth* differential quotient $\frac{d^5 b}{dv^5}$ plays a part.

9. Of the different ways by which we can arrive at the knowledge of the coefficient a, the following one seems the simplest to me. As (see I p. 283)

$$b = b_2 - (1 - \beta)\,\Delta b,$$

b_k is also $= b_2 - (1 - \beta_k)\,\Delta b$, and we find by subtraction:

$$b - b_k = (\beta - \beta_k)\,\Delta b,$$

i.e. after division by b_k:

$$\beta - \beta_k = \frac{b_k}{\Delta b}(\gamma - 1),$$

because $b = \gamma b_k$. Now we put (see I, p. 283).

$$(1 + x\beta)\frac{\Delta b}{v-b} = \varphi,$$

hence we have also:

$$(1 + x\beta_k)\frac{\Delta b}{v_k - b_k} = \varphi_k,$$

and so we can substitute $\frac{v_k - b_k}{1 + x\beta_k}\varphi_k$ for Δb, so that we get:

$$\beta - \beta_k = \frac{b_k}{v_k - b_k}\,\frac{1 + x\beta_k}{\varphi_k}(\gamma - 1),$$

and hence, putting $(1 + x\beta) : (1 + x) = \alpha$:

$$\beta = \beta_k + \frac{(1+x)\,\alpha_k}{1{,}1\,\varphi_k}(\gamma - 1) \quad \ldots\ldots\ldots \quad (13)$$

because $v_k : b_k = 2{,}1$, so $(v_k - b_k) : b_k = 2{,}1 - 1 = 1{,}1$. (This value 1,1 is subjected to a slight modification, just as the other numerical values, when x is taken successively $=1$, 2, etc.). Now we have always:

$$b = b_k + b'_k(v - v_k) + \frac{1}{2}b_k''(v - v_k)^2 + \frac{1}{6}b_k'''(v - v_k)^3 + \text{etc.},$$

in which $b'_k = \left(\frac{db}{dv}\right)_k$, etc. Hence division by b_k gives:

$$\gamma = 1 + 2{,}1\,p'(n-1) + 2{,}1\,p''(n-1)^2 + 2{,}1\,p'''(n-1)^3 + \text{etc.}, \quad (14)$$

because $\frac{v-v_k}{b_k} = \frac{(n-1)\, v_k}{b_k} = 2{,}1\,(n-1)$; $\frac{(v-v_k)^2}{b_k} = \frac{(n-1)^2\, v_k^2}{b_k} =$

$$= 2{,}1\,(n-1)^2 \,.\, v_k \;;\quad \frac{(v-v_k)^3}{b_k} = \frac{(n-1)^3\, v_k^3}{b_k} = 2{,}1\,(n-1)^3 \,.\, v_k^2\,;$$

while

$$b'_k = p' \quad ; \quad \frac{1}{2}\, b_k''\, v_k = p'' \quad ; \quad \frac{1}{6}\, b_k'''\, v_k^2 = p'''$$

has been put.

In consequence of (14), (13) now reduces to

$$\beta = \beta_k + \frac{2{,}1}{1{,}1}\,\frac{(1+x)\alpha_k}{\varphi_k}\, p'\;(n-1) + \frac{2{,}1}{1{,}1}\,\frac{(1+x)\alpha_k}{\varphi_k}\, p''\,(n-1)^2 + \ldots \, , \quad (15)$$

and so also, because $\alpha = (1+x\beta):(1+x)$ (see above):

$$\alpha = \alpha_k \left[1 + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p'\,(n-1) + \frac{2{,}1}{1.1}\,\frac{x}{\varphi_k}\, p''\,(n-1)^2 + \ldots \right] . \quad (15a)$$

By the aid of the found expressions for γ and α we shall now calculate the fraction

$$\frac{\frac{1+x\beta}{1+x}\, d}{2{,}1 - \gamma d} = \frac{\alpha d}{2{,}1-\gamma d} = \frac{\alpha}{2{,}1\, n-\gamma}$$

in (10). We find for it:

$$\frac{\alpha}{2{,}1\, n-\gamma} = \frac{\alpha_k \left(1 + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p'\,(n-1) + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p''\,(n-1)^2 + \ldots\right)}{2{,}1\, n-1 - 2{,}1\, p'\,(n-1) - 2{,}1\, p''\,(n-1)^2 - \ldots} .$$

But as evidently $2{,}1\, n-1 = 1{,}1 + 2{,}1\,(n-1)$, this becomes:

$$\frac{\alpha}{2{,}1\, n - \gamma} = \frac{\alpha_k}{1{,}1}\; \frac{1 + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p'\,(n-1) + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p''(n-1)^2 + \ldots}{1 + \frac{2{,}1}{1{,}1}(1-p')(n-1) - \frac{2{,}1}{1{,}1}\, p''\,(n-1)^2 - \ldots} .$$

If now the second member is represented by

$$\frac{\alpha_k}{1{,}1}\left[1 - \frac{2{,}1}{1{,}1}\, A\,(n-1) + \frac{2{,}1}{1{,}1}\, B\,(n-1)^2 - \ldots\right],$$

the coefficients A, B, C, etc. may be determined from

$$1 + \frac{2{,}1}{1{,}1}\,\frac{x}{\varphi_k}\, p'\,(n-1) + \ldots =$$

$$= \left[1 - \frac{2{,}1}{1{,}1}\, A\,(n-1) + \ldots\right]\left[1 + \frac{2{,}1}{1{,}1}(1-p')\,(n-1) - \ldots\right].$$

In this we find by equalisation of the coefficients of the different powers of $n-1$:

$$\left.\begin{aligned}
A &= 1-p'\left(1+\frac{x}{\varphi_k}\right); \qquad B = \frac{2{,}1}{1{,}1} A\,(1-p') + p''\left(1+\frac{x}{\varphi_k}\right) \\
C &= \frac{2{,}1}{1{,}1} B\,(1-p') + \frac{2{,}1}{1{,}1} Ap'' - p'''\left(1+\frac{x}{\varphi_k}\right) \\
D &= \frac{2{,}1}{1{,}1} C\,(1-p') + \frac{2{,}1}{1{,}1} Bp'' - \frac{2{,}1}{1{,}1} Ap'' + p^{IV}\left(1+\frac{x}{\varphi_k}\right) \\
E &= \frac{2{,}1}{1{,}1} D\,(1-p') + \frac{2{,}1}{1{,}1} Cp'' - \frac{2{,}1}{1{,}1} Bp''' + \frac{2{,}1}{1{,}1} Ap^{IV} - p^{V}\left(1+\frac{x}{\varphi_k}\right)
\end{aligned}\right\} \quad (16)$$

Now equation (10) passes into

$$\frac{2.1\,a_k}{(1{,}1)^2}\Big[-A\left\{(n-1)-(n'-1)\right\} + B\left\{(n-1)^2-(n'-1)^2\right\} - \\ - C\left\{(n-1)^3-(n'-1)^3\right\} + \ldots\Big] = \frac{6\,(n'-n)\,(n'+n)}{8\,n^2n'^2 \, . \, m} \qquad (10a)$$

In this the coefficient $\frac{6}{8}$ may be replaced by another expression. We saw, namely (see above), that 6 is properly $= 27:(2{,}1)^2 f_1$, in which (see I, p. 297)

$$f_1 = \frac{1+x}{1+x\beta_k}\,\frac{n_k^2\,(3m_k^2-2n_k)}{m_k^5}.$$

In this m_k and n_k (given by (5) on p. 288 loc. cit.) have of course another meaning than the above m and n, so that we have marked them with the index k to distinguish them. Now we can also write for f_1:

$$f_1 = \frac{1}{a_k}\cdot\frac{9}{4}\left(\frac{v_k-b_k}{v_k}\right)^2 .\ 3\,\frac{b_k}{v_k} .\ m_k\,,$$

because $\frac{v_k-b_k}{v_k} = \frac{2n_k}{3m_k^2}$, and $\frac{b_k}{v_k} = \frac{3m_k^2-2n_k}{3\,m_k^2}$. (see I, p. 288). In consequence of this we obtain

$$f_1 = \frac{27}{4}\,\frac{(1{,}1)^2}{(2{,}1)^3}\,\frac{m_k}{a_k},$$

because $v_k : b_k = 2{,}1$ and $(v_k-b_k) : b_k = 1{,}1$. What we have represented by the figure 6 is therefore, properly speaking:

$$\frac{27}{(2{,}1)^2} \times \frac{4}{27}\,\frac{(2{,}1)^3}{(1{,}1)^2}\,\frac{a_k}{m_k} = 4\,\frac{2{,}1}{(1{,}1)^2}\,\frac{a_k}{m_k}.$$

So we get, dividing both members of (10a) by $\frac{2{,}1\,a_k}{(1{,}1)^2}\,(n'-n)$:

$$A - B \left\{ (n-1) + (n'-1) \right\} + C \left\{ (n-1)^2 + (n-1)(n'-1) + (n'-1)^2 \right\} + .. =$$

$$= \frac{1}{m_k} \frac{{}^1/_2 (n+n')}{n^2 n'^2 \, m}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10b)$$

in which m_k has been given by (see p. 288 loc. cit.)

$$m_k = 1 + \frac{1}{x+1} \beta_k (1-\beta_k)(x+\varphi_k)^2.$$

For $x = 1$ m_k is e. g. $= 1{,}107$ (see p. 297 loc. cit.). If we now put again, just as in the expansion of $d = 1 : n$ (the further developments confirm again that $1-n$ and $n'-1$ are really of the order of magnitude $\tau = \sqrt{1-m}$):

$$\left. \begin{array}{l} n = 1 - a'\tau + b'\tau^2 \ . \ . \ . \\ n' = 1 + a'\tau + b'\tau^2 \ . \ . \ . \end{array} \right\} \text{[1]}$$

we may write for the second member of (10b)

$$\frac{1}{m_k} \frac{1+b'\tau^2}{[(1+b'\tau^2)^2 - a'^2\tau^2]^2} \frac{1}{1-\tau^2} = \frac{1}{m_k} \frac{1+b'\tau^2}{[1-(2a'^2-4b')\tau^2](1-\tau^2)},$$

as $m = 1-\tau^2$, and because we shall for the present content ourselves with terms of the degree τ^2.

Now (10^b) passes into

$$A - B(2b'\tau^2) + C(a'^2\tau^2 - a'^2\tau^2 + a'^2\tau^2) = \frac{1}{m_k}\left(1 + (1+2a'^2-3b')\tau^2\right), (10c)$$

and it is only left to calculate A, B and C. For A we find from (16):

$$A = 1 - p'\left(1 + \frac{x}{\varphi_k}\right).$$

But we can easily show that this $= \frac{1}{m_k}$. For we found in I, p. 292:

$$b' = \frac{db}{dv} = \frac{\frac{1}{x+1}\beta(1-\beta)\varphi(x+\varphi)}{1 + \frac{1}{x+1}\beta(1-\beta)(x+\varphi)^2} = \frac{\varphi}{x+\varphi} \frac{m-1}{m}, \quad . \quad . \quad . \quad (a)$$

because m has been written for the denominator of the expression for $b' = \frac{db}{dv}$ (see above). Hence also, because $b'_k = p'$ has been put:

[1]) See for the equality of the numerical values of the coefficients a', b', etc. for n and n' the observations in II, p. 438—439.

$$A = 1 - \frac{m_k - 1}{m_k} = \frac{1}{m_k},$$

so that the equality of the terms with τ^0 identically has been fulfilled. So there remains:

$$-B(2b'\tau^2) + C(a'^2\tau^2) = \frac{1}{m_k}(1+2a'^2-3b')\tau^2. \quad . \quad . \quad (10d)$$

After substitution of $A = \frac{1}{m_k}$ we find for B from (16):

$$B = \frac{2,1}{1,1}\frac{1-p'}{m_k} + p''\left(1+\frac{x}{\varphi_k}\right).$$

In this $p''\left(1+\frac{x}{\varphi_k}\right)$ can be expressed in p' by the aid of a relation, holding between p' and p'' at the critical point. We have viz. (see I p. 285):

$$\frac{dp}{dv} = \frac{2a}{v^3} - \frac{RT}{\Delta b\,(v-b)}\frac{\varphi}{m},$$

and hence:

$$\frac{d^2p}{dv^2} = -\frac{6a}{v^4} + \frac{RT(1-b')}{\Delta b\,(v-b)^2}\frac{\varphi}{m} - \frac{RT}{\Delta b\,(v-b)}\frac{d}{dv}\left(\frac{\varphi}{m}\right).$$

At the critical point $\frac{dp}{dv} = 0$ and also $\frac{d^2p}{dv^2} = 0$, hence we have there:

$$\frac{\varphi}{m} = \frac{2a}{v^3} : \frac{RT}{\Delta b\,(v-b)}; \quad \frac{1-b'}{v-b}\frac{\varphi}{m} - \frac{d}{dv}\left(\frac{\varphi}{m}\right) = \frac{6a}{v^4} : \frac{RT}{\Delta b\,(v-b)}..$$

And from this follows:

$$\frac{1-b'}{v-b}\frac{\varphi}{m} - \frac{d}{dv}\left(\frac{\varphi}{m}\right) = \frac{3}{v}.\frac{\varphi}{m},$$

or

$$\frac{d}{dv}\left(\frac{\varphi}{m}\right)_k = \left(\frac{1-b'_k}{v_k-b_k} - \frac{3}{v_k}\right)\frac{\varphi_k}{m_k}, \quad . \quad . \quad . \quad . \quad . \quad (a)$$

in which we must bear in mind that this relation only holds for T_k, $\frac{dp}{dv}$ and $\frac{d^2p}{dv^2}$ being $= 0$ only there.

Now we saw above that $1 - b'\left(1+\frac{x}{\varphi}\right) = \frac{1}{m}$, so also:

$$\varphi - b'(x+\varphi) = \frac{\varphi}{m},$$

and hence

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$$(1-b')\frac{d\varphi}{dv} - b''(x+\varphi) = \frac{d}{dv}\left(\frac{\varphi}{m}\right), \quad . \quad . \quad . \quad . \quad . \quad (\beta)$$

which relation holds everywhere, and not only for T_k. But only *there* $\frac{d}{dv}\left(\frac{\varphi}{m}\right)$ may be replaced by its value from (α), and we get:

$$(1-b')\left(\frac{d\varphi}{dv}\right)_k - b''_k(x+\varphi_k) = \left(\frac{1-b'_k}{v_k-b_k} - \frac{3}{v_k}\right)\frac{\varphi_k}{m_k},$$

or after substitution of $\frac{1}{v-b}\frac{\varphi}{m}$ for $\frac{d\varphi}{dv}$ (see loc. cit. p. 285)

$$b''_k(x+\varphi_k) = \left[\frac{3}{v_k} - \frac{2(1-b'_k)}{v_k-b_k}\right]\frac{\varphi_k}{m_k},$$

i. e.

$$\frac{1}{2}b''_k v_k \frac{x+\varphi_k}{\varphi_k} = \frac{1}{m_k}\left[\frac{3}{2} - (1-b'_k)\frac{v_k}{v_k-b_k}\right],$$

or (see above)

$$p'\left(1+\frac{x}{\varphi_k}\right) = \frac{1}{m_k}\left[\frac{3}{2} - \frac{2{,}1}{1{,}1}(1-p')\right] \quad . \quad . \quad . \quad (17)$$

This is the required relation between p'' and p' at T_k, and in consequence of this the value of B (see above) passes into

$$B = \frac{2{,}1}{1{,}1}\frac{1-p'}{m_k} + \frac{1}{m_k}\left[\frac{3}{2} - \frac{2{,}1}{1{,}1}(1-p')\right] = \frac{3}{2}\frac{1}{m_k}.$$

Now our last equation (10d) becomes:

$$-\frac{3b'}{m_k}\tau^2 + Ca'^2\tau^2 = \frac{1}{m_k}(1+2a'^2)\tau^2 - \frac{3b'}{m_k}\tau^2,$$

so that also the terms with the coefficient b' are cancelled, and only

$$Ca'^2\tau^2 = \frac{1+2a'^2}{m_k}\tau^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10e)$$

is left, from which immediately

$$a'^2 = \frac{1}{Cm_k-2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

is found.

And now the coefficient a' is found, because C can easily be calculated. Also from the second equation, viz. (12), we might have calculated the value of a', but then the calculation would have been more lengthy, and the result quite the same, of which we have convinced ourselves for the greater security. For the calculation of the following coefficient b', however, we shall have to use the equation (12) by the side of (10).

By way of control the following remarks may serve. It follows from (16) for the case b constant, in which p', p'', p''', etc. are all $=0$, that $C=\frac{2,1}{1,1}B$, i. e. $Cm_k=\frac{3}{2}\cdot\frac{2,1}{1,1}$. But then $\frac{2,1}{1,1}$ passes into $\frac{3}{2}$ (since $v_k\ b_k$ is not $=2,1$ then, but $=3$), so that Cm_k becomes $=\frac{9}{4}$. Hence $a'^2=\frac{1}{2^1/_4-2}=4$, and so $\underline{a'=2}$ as it should be. (Before we put (see II, p. 438) $d=1+2a\tau$, whereas we now put $n=1:d=1-a'\tau$, so that $a'=2a$).

In the general case we find for C from (16):

$$C=\frac{2,1}{1,1}\frac{3}{2}\frac{1-p'}{m_k}+\frac{2}{1,1}\frac{1}{m_k}\frac{p''}{m_k}-p'''\left(1+\frac{x}{\varphi_k}\right),$$

so that we get:

$$a'^2=\frac{1}{\frac{2,1}{1,1}\left[\frac{3}{2}(1-p')+p''\right]-p'''m_k\left(1+\frac{x}{\varphi_k}\right)-2} \quad . \quad . \quad (18^a)$$

I will just call attention to this, that the value of a' has been derived by me in at least four different ways, and that always identical results were obtained. Moreover I have convinced myself that the coefficients in the development of n and n' have really the same numerical values; only with difference of sign for the odd powers of $\tau=\sqrt{1-m}$ (see also II, p. 438).

It also follows from the expression derived by us just now for the coefficient a' in the expansion into series $n=1-a'\tau+b'\tau^2$, that — for the determination of the relations at the critical point — it is *not sufficient* to know the differential quotients $b'_k=\left(\frac{db}{dv}\right)_k$ and $b''_k=\left(\frac{d^2b}{dv^2}\right)$, but that also the knowledge of the *third* differential quotient of b with respect to v, viz. $b'''_k=\left(\frac{d^3b}{dv^3}\right)_k$ at the critical point, is indispensable. And for the coefficient b' in the above expansion into series, which coefficient determines the *direction* of the "straight" diameter in T_k, the knowledge even of the *fourth* and *fifth* differential quotient will appear to be required.

Let us now proceed, therefore, to the calculation of the *third* differential quotient.

10. The third differential quotient. We start from the formula (11) for $b'=\frac{db}{dv}$ (see I, p. 292), viz.

$$b'=\frac{\frac{1}{x+1}\,\beta(1-\beta)\varphi(x+\varphi)}{1+\frac{1}{x+1}\,\beta(1-\beta)(x+\varphi)^2}\quad\text{of}\quad\frac{1}{b'}=\frac{1}{\frac{1}{x+1}\,\beta(1-\beta)\varphi(x+\varphi)}+\frac{x+\varphi}{\varphi}\;.\;(1)$$

From this follows $\left(\text{representing } \frac{1}{x+1}\,\beta\,(1-\beta)\,\varphi\,(x+\varphi) \text{ by } N, \text{ so that } b'=\frac{N}{m}\right)$:

$$-\frac{b''}{b'^2}=-\frac{1}{N^2}\left[\frac{1}{x+1}\,\beta\,(1-\beta)\,(x+2\varphi)\left(-\frac{1}{v-b}\,\frac{\varphi}{m}\right)+\right.$$
$$\left.+\frac{1}{x+1}\,\varphi\,(x+\varphi)\,(1-2\beta)\,.\,\frac{b'(1+x\beta)}{\varphi(v-b)}\right]-\frac{x}{\varphi^2}\left(-\frac{1}{v-b}\,\frac{\varphi}{m}\right).$$

taking the values found in I, p. 285 (formulae (δ) and (ε)) for $\frac{d\varphi}{dv}$ and $\frac{d\beta}{dv}$ into consideration, viz.

$$\frac{d\varphi}{dv}=-\frac{1}{v-b}\,\frac{\varphi}{m}\quad;\quad\frac{d\beta}{dv}=\frac{1+x\beta}{v-b}\,\frac{b'}{\varphi}\,,$$

bearing in mind that $1+\frac{1}{x+1}\,\beta\,(1-\beta)\,(x+\varphi)^2=m$ has been put, and the second member of (δ) is evidently $=\frac{b'}{\varphi}$. Hence:

$$\frac{b''}{b'^2}=\frac{1}{N^2(v-b)}\left[-\frac{\frac{1}{x+1}\,\beta(1-\beta)\varphi(x+2\varphi)}{m}+\right.$$
$$\left.+\frac{1}{x+1}\,(x+\varphi)\,(1+x\beta)\,(1-2\beta)\,b'\right]-\frac{1}{v-b}\,\frac{x}{\varphi m}.$$

Now N is evidently $=b'm$ (see above), and $\frac{1}{x+1}\,\beta(1-\beta)\,\varphi(x+2\varphi):m=$ $=\frac{x+2\varphi}{x+\varphi}\,b'$, so that we get:

$$(v-b)\,b''=\frac{b'}{m^2}\left[-\frac{x+2\varphi}{x+\varphi}-\frac{x+\varphi}{x+1}\,(1+x\beta)\,(2\beta-1)\right]-b'^2\,\frac{x}{\varphi m}\,,$$

i. e.

$$(v-b)\,b'' = -\frac{b'}{m^2}\left[\frac{x+2\varphi}{x+\varphi} + \frac{x+\varphi}{x+1}(1+x\beta)(2\beta-1) + x\frac{mb'}{\varphi}\right].$$

Replacing in this mb' by $\frac{1}{x+1}\beta(1-\beta)\varphi(x+\varphi)$ (see above), we get:

$$(v-b)\,b'' = -\frac{b'}{m^2}\left[\frac{x+2\varphi}{x+\varphi} + \frac{x+\varphi}{x+1}\Big\{(1+x\beta)(2\beta-1) + x\beta(1-\beta)\Big\}\right],$$

i. e.

$$(v-b)\,b'' = -\frac{b'}{m^2}\left[\frac{x+2\varphi}{x+\varphi} + \frac{x+\varphi}{x+1}(x\beta^2+2\beta-1)\right], \quad \ldots \quad (2)$$

identical with (12) in I, p. 293, paying attention to the above expression (1) for b'. This derivation seems somewhat shorter to me than that in I, p. 292—293, and besides confirms the validity of the result, so that we can calculate b''' from it with full assurance.

Clarens, Nov. 13, 1911.

(*To be concluded*).

Astronomy. — *"A photographical method of research into the structure of the galaxy."* By Dr. A. PANNEKOEK. (Communicated by E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of November 25, 1911).

In my paper: "Researches into the structure of the galaxy", published in the Proceedings of the Meeting of June 25, 1910, I have pointed out that the chief difficulty in this kind of researches consists in the lack of completeness and homogeneity in the material of star-countings that is at our disposal. HERSCHEL's and EPSTEIN's gauges and the countings on photographic and other stellar charts have relation to small, generally non-coincident parts of the examined galactic region. Owing to this the fluctuations of density, which may be considerable even in smaller regions (comp. MAX WOLF's and BARNARD's photographs of the Milky Way), appear with their full amount as errors of the function $N(m)$ (number of stars per square degree as function of the limiting magnitude m). At best we may only hope that in the mean of a great amount of countings these irregularities lose their influence. Still there always remains uncertainty and doubt justifying the question whether these drawbacks may not be avoided by another method.