XCI. Notes on the kinetic theory of gases. Sutherland's constant S and van der Waals' a and their relations to the intermolecular field

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XCI. *Notes on the Kinetic Theory of Gases. Sutherland's constant S and van der Waals' a and their relations to the intermolecular field.* By R. H. FOWLER, *Fellow and Lecturer of Trinity College, Cambridge* *.

§ (1). *INTRODUCTION AND SUMMARY.*—This paper consists of two somewhat loosely connected parts. In the first part, § 2, I point out the conditions under which a strict comparison may be made between the intermolecular fields deduced from Sutherland's constant S and from van der Waals' a . On comparing the numerical results I have then to point out a serious outstanding discrepancy between the values deduced in these two ways; I make a suggestion as to the probable source of this discrepancy, but have not yet resolved it in detail.

In the second part, §§ 3–11, I give two simple proofs of the exact formula for van der Waals' a as a function of the intermolecular field of force which I believe to be illuminating and new, or at least insufficiently known. The calculations are reduced to explicit formulæ for two particular molecular models:—

(1) Elastic spheres attracting according to an inverse n th power law.

(2) Elastic spheres surrounded by a limited spherical shell in which there is a *constant* attraction, with no forces at all outside.

* Communicated by C. G. Darwin, M.A.

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§ (2). *Sutherland's S and van der Waals' a.*—It is well known that both the constant *S* introduced by Sutherland* into the formula for the viscosity of a gas, and the constant *a* of van der Waals' or Dieterici's equations of state† express the effects of intermolecular attractions. On the assumption of "spherically symmetrical" molecules—i. e., that the molecules are spheres and that the attractive force $\phi(r)$ between two molecules depends only on the distance *r* between their centres and acts along the line joining them—Chapman‡ has shown how to obtain an exact expression for *S* in terms of $\phi(r)$ and known constants. The most complete determination of *a* in terms of $\phi(r)$ with which I am acquainted has been made by Keesom§, but no attempt appears to have been made to compare together both theoretical and experimental values of *a* and *S*. This is the more to be regretted as the quantities *a* and *S* may be taken to refer to gases in identical physical states. A strict comparison of theory with the experimental values of *a* and *S* is then legitimate, and should lead to results of interest as to the nature of the law of intermolecular attraction under these conditions.

When we come to compare *a* with experiment, we must remember that our theoretical calculations only apply to gases at reasonably large dilutions, that is to cases in which the departures from the perfect gas laws are moderately small. In order to make a reliable comparison between theory and experiment we must therefore be certain that the observations and calculations do actually apply strictly to one and the same state of the gas. The calculations used really always present the equation of state of a gas in the form

$$pv = NkT + \frac{1}{v}f(T) + O\left(\frac{1}{v^2}\right) \parallel, \dots \dots (1)$$

* Sutherland, *Phil. Mag.* ser. 5, vol. xxxvi. p. 507 (1893) and succeeding vols.

† Jeans, 'The Dynamical Theory of Gases,' ed. 3, chap. 6 (1921).

‡ Chapman, *Phil. Trans. A*, vol. 211. p. 460 (1912). The actual formula given by Chapman is affected by an algebraical slip. The correct expressions have been given by C. G. F. James, *Proc. Camb. Phil. Soc.* vol. xx. p. 447 (1921), and previously in part by D. Euskog, *Inaugural-Dissertation*, Uppsala 1917, p. 95.

§ Keesom, *Proc. Sect. of Sciences, Amsterdam*, vol. xv. (1) pp. 240, 256, 417, 643 (1912).

$\parallel O\left(\frac{1}{v^2}\right)$ is a convenient and comprehensive notation for "terms of order $1/v^2$, which may therefore be neglected for values of *v* which are sufficiently large." This is a satisfactory paraphrase of the strict mathematical definition of *O*, to which of course I adhere throughout.

where p is the pressure, v the volume, k the gas-constant for one molecule, N the number of molecules, and $f(T)$ is a function of the absolute temperature T which can be calculated exactly. Now it is precisely in this form that Kamerlingh Onnes has prepared his extensive data on the equations of state of the simpler gases. Actually * he assumes the form

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5}, \quad \dots \quad (2)$$

and determines $A, \dots, F$ as functions of T to fit the observations. The coefficients $A, \dots, F$ he calls the first, second, etc., *virial coefficients*. It is clear that when the observed second virial coefficient B is obtained in this way it is strictly comparable to the calculated $f(T)$ of equation (1). Moreover, it appears to me that nothing much less than the exhaustive numerical analysis of Kamerlingh Onnes allows a legitimate comparison between theory and experiment to be made.

Such comparisons have already been made in certain cases and on certain assumptions by Keesom (*loc. cit.*), but without consideration of the corresponding viscosity data. I hope to take up the question in detail in a future paper. For the present I must content myself with the following observations. Keesom finds that the observed and calculated second virial coefficients for Argon, between the absolute temperatures 123° and 293° on the centigrade scale, can be reconciled on the assumption that the argon atom behaves like a sphere of diameter, $\sigma = 3.29 \times 10^{-8}$ cm., surrounded by a field of force $\phi(r) = ar^{-5}$, of such intensity that the work $\Pi(\sigma)$ done in separating two molecules from contact ($r = \sigma$) to infinity is 1.63×10^{-14} erg †. The exponent 5 is a little doubtful, but is probably better than the exponents 4 or 6 and presumably better than any other integral exponent.

These values of σ and $\phi(r)$ correspond to definite values of b (van der Waals') and S , Sutherland's constant. The values of b and σ are related by the well-known formula

$$b = \frac{2}{3}\pi N\sigma^3, \quad \dots \quad (3)$$

* Kamerlingh Onnes, Proc. Sect. of Sciences, Amsterdam, vol. iv. p. 125 (1902), or Communications Phys. Lab. of Leiden, No. 71.

† Keesom (*loc. cit.* p. 646) gives 1.46×10^{-14} , but this is based on the incorrect value 6.85×10^{23} for Loschmidt's number. I have reworked the calculation with the more recent figure 6.66×10^{23} .

and S is given by Chapman's corrected formula *

$$S = 0.1956 \Pi(\sigma)/k. \quad (\text{Inverse 5th-power attractions.}) \quad (4)$$

The numerical values deduced from Keesom's figures are $b = 0.00201$ for 1 c.c. at normal pressure and temperature, and $S = 23.6$. But the viscosity data for ordinary temperatures should be fairly comparable with the preceding "compressibility" data, and should lead to the same values of b , σ , $\Pi(\sigma)$, and S . When analysed, however, by Chapman's formulæ, they lead unmistakably to the values $b = 0.00133$, $S = 162$. We may exhibit this significant discrepancy thus:—

Argon.

	$\Pi(\sigma) \times 10^{14}$.	S .	$b \times 10^3$.	$\sigma \times 10^8$.
Compressibility data...	1.63	23.6	2.01	3.29
Viscosity data	11.2	162	1.33	2.84

The disagreement, particularly in the values of S and $\Pi(\sigma)$, is striking; so far as I know at present similar discrepancies occur for other gases besides argon, but the available data are not generally so suitable for a direct comparison. This disagreement is all the more interesting in view of the close agreement between the two values of σ (or b) given by Chapman † himself. But the values of b from the compressibility data there given appear to be obtained from critical data, and must in my opinion give way to values calculated from Kamerlingh Onnes' second virial coefficient.

The discrepancy which thus remains seems to arise from the fact that whereas the theoretical formula for the second virial coefficient B is exact, the formula used for the viscosity is only correct so far as the first power of S/T . The agreement of this approximate viscosity theory with experiment is usually regarded as good, at least at ordinary temperatures, so that an exact formula including further powers of S/T is not likely to improve this fit. It may well, however, bring the facts of compressibility and viscosity into reasonable agreement—in particular at fairly high temperatures, and so enable a reliable picture to be formed of the range and intensity (under these conditions) of the intermolecular forces.

* Chapman gives $S = \Pi(\sigma)/3k$ in our notation for all power laws. The correction affects only the numerical coefficient which becomes a function of s the power law exponent (James, *loc. cit.*).

† Phil. Trans. A, vol. 216. Table VIII. p. 347 (1916).

The existing discrepancies in S and σ are qualitatively such as should be properly accountable for by such an extension of the theory; to this point I hope to return in a later paper.

Elementary calculations of van der Waals' a .

§ (3). My immediate object in the rest of this paper is to present two simple proofs of the exact formula for B , and so for van der Waals' a . Keesom has calculated B in terms of the intermolecular field by a somewhat elaborate method based on Boltzmann's expression for the entropy, a method which can be used when the molecules are not spherically symmetrical. But Keesom's own work shows that molecules with spherical symmetry give the best representation of experimental facts for the simplest (monatomic) gases. Such molecular models are therefore of the first importance, and for such it is possible to calculate B directly by very simple arguments—(1) By a direct calculation of the boundary field, measured by W , the work to be done in bringing a molecule from the interior to the boundary of the gas; or, (2) By a calculation of the Virial of Clausius.

Method (1) has moreover this advantage over all other methods, that it enables adequate account to be taken of surface effects, which is not possible, or at least far less simple, by the entropy and virial methods. In calculating B all the terms in $p v$ of order $1/v^2$ are of course to be omitted.

§ (4). *The meaning of a .*—The so-called constant a of van der Waals' or Dieterici's equation of state can be specified in various ways. The most satisfactory physical meaning can be attached to it, by first recognizing* that intermolecular attractions must result in the production of a permanent field of force near any boundary of a gas, and then connecting a to the work that must be done against this boundary field in bringing one molecule from the interior to the actual boundary of the gas. At sufficiently great dilutions this work W must obviously be proportional to the molecular density ν , and it is easily proved that†

$$a = N^2 W / \nu, \quad (5)$$

where N is the total number of molecules in the body of gas considered. Thus a will be independent of the volume.

* Jeans, *loc. cit.* p. 159.

† Jeans, *loc. cit.*

It appears, however, to be generally assumed * that under the same conditions W , and therefore a , is independent also of the temperature, and that a is therefore, theoretically at least, a true constant. When one looks into this assumption more closely it is easy to convince oneself that it has no justification whatever, however great the dilution. The ordinary kinetic theory of gases really demands an a which is a function of the temperature whose variations for most gases are appreciable at ordinary and even at fairly high temperatures. It is the more unfortunate that this theoretical result is so often overlooked, since the independence of a of the temperature is not borne out by experiment. In point of fact, both theory and experiment demand variations of a with the temperature which are, qualitatively at any rate, in full agreement with one another.

As we shall see directly in calculating a , the error arises from regarding the gas molecules in the interior of the gas as uniformly distributed through its volume. But if there are attractive forces sufficient to create a boundary field, these attractive forces must also make it correspondingly more probable that any pair of molecules will be close together than far apart. This alters the calculated value of W by an amount which may be called the *clustering correction*. It appears on calculation that this clustering correction depends on the temperature, and at ordinary temperatures is in fact of the same order as the whole boundary field itself.

§ (5). *The dependence of a on the nature of the intermolecular forces.*—We have stated above that a is independent of the volume in the circumstances we contemplate here. It seems necessary even now to insist that this independence holds good whatever the nature of the intermolecular forces, and is in no way dependent on obedience to any special law of variation with distance such as for example the inverse 4th power law. It is still frequently stated † that if van der Waals' a is to be independent of the volume the law of attraction must be the inverse 4th power. This is quite untrue. As we shall see, the law of variation with the distance affects and only affects the form of a as a function of the temperature.

In the case of spherically symmetrical attractions following inverse sth power laws generally we can go further, for we find that the integrals that occur do not converge unless $s > 4$. The physical meaning of this failure is easily seen to

* Jeans, *loc. cit.*

† *E. g.*, Lewis, 'A System of Physical Chemistry,' vol. i. p. 8 (1918), and many recent papers in the *Phil. Mag.*

be that if $s \leq 4$ the attractions of distant molecules in the gas will then be of equal or greater importance than those of the neighbouring molecules. In such a case the recorded pressure at any point would be affected or even dominated by the distant attractions and would depend on the general shape of the whole body of gas. This is of course directly contrary to experience, and no such attractions of sensible magnitude* can be admitted.

Finally, it is interesting to observe that we can obtain the case $s=4$ as a limiting case in which the intensity of the intermolecular attraction between any pair of molecules tends to zero as $s \rightarrow 4$ from above. In this limiting case and this only, we do in fact obtain a value of a which is a true constant *independent of the temperature*. This, however, can only be achieved at the price of a zero value for $\Pi(\sigma)$, and therefore for Sutherland's constant; this is inadmissible in the case of any actual gas.

§ (6). *The work done in bringing a molecule from the interior to the boundary of a gas.*—The molecular model that we consider is that of a hard elastic sphere of diameter σ , surrounded by a field of attractive force. Two molecules whose centres are distant r apart act on each other with an attraction $\phi(r)$ along their line of centres. It is this molecular model which is so successful in explaining the "transport phenomena" in gases and their variation with temperature at ordinary temperatures—in particular the coefficient of viscosity. When such fields of force are postulated, the distribution of molecules in the gas is not on the average uniform with reference to any selected molecule. If ν is the general molecular density in the gas, the molecular density at a distance r from the selected molecule is, not ν , but †

$$\nu e^{2j \int_r^\infty \phi(x) dx}, \quad \dots \quad (5a)$$

* Gravitational attractions are in this category, and are of course insensibly small. Electrostatic attractions are in the same category, but are so large that they entirely dominate the distribution of charged molecules or ions.

† See, e. g., Boltzmann, *Vorlesungen über Gastheorie*, vol. ii. p. 150 or Jeans, *loc. cit.* p. 132. Jeans' suggested correction of this formula is here insensible. Owing to the standardization of the use of h for Planck's constant, I believe that the time has come for the use of some letter other than h for the constant in Maxwell's Law for the distribution of velocities, and I propose to use j for this purpose. I believe, further, that it is desirable to use a notation distinguishing systematically between "the gas-constant for one gramme-molecule" and "the gas-constant for one molecule" (the constant k in $2j=1/kT$) and to conform to the continental notation of R and k respectively.

where $2j=1/kT$. Consider an infinite plane slab of thickness df , which is small compared with σ , and let us calculate the average attraction dF of all the molecules in this slab on a molecule distant z from the slab*. The calculation is a generalization of the classical calculation of Laplace's theory of surface tension†, generalized in such a way as to recognize the real molecular structure of the fluid.

Suppose first that the selected molecule is at P and that $z=\sigma$. Then the average number of molecules in the slab, per unit area of the slab at a distance r from P, is

$$vdf e^{2j\Pi(r)},$$

where we have written, for convenience,

$$\Pi(r) = \int_r^\infty \phi(x) dx. \quad . \quad . \quad . \quad (6)$$

Fig. 1.

The number in the annulus at distances between r and $r+dr$ from P is

$$2\pi r \sin \theta \cdot \frac{dr}{\sin \theta} \cdot vdf e^{2j\Pi(r)},$$

and their resultant attraction along PO is

$$2\pi v z df \phi(r) e^{2j\Pi(r)} dr. \quad . \quad . \quad . \quad (7)$$

To obtain the attraction of the whole slab, we must integrate the expression for values of r from z to infinity.

* For shortness a molecule is said to be in the slab or distant z from the slab, when its *centre* is in or distant z from the slab.

† See, *e. g.* Rayleigh, *Scientific Papers*, vol. iii. pp. 397, 513 (1890, 1892); 'The Theory of Surface Forces.'

Since $\phi(r) = -\Pi'(r)$, it can be integrated in finite terms, giving

$$dF = \frac{2\pi\nu z df}{2j} (e^{2j\Pi(z)} - 1), \quad (z \geq \sigma) \quad (8)$$

When $z \leq \sigma$ the conditions change, for now the body of the selected molecule prevents any attracting molecule from being present in the slab for values of r less than σ . The total attraction of the slab is therefore obtained by replacing z , the lower limit of integration, by σ , and we have

$$dF = \frac{2\pi\nu z df}{2j} (e^{2j\Pi(\sigma)} - 1), \quad (z \leq \sigma) \quad (9)$$

Formulæ (8) and (9) can be combined into the single formula

$$dF = \frac{2\pi\nu z df}{2j} (e^{2j\Pi(z)} - 1), \quad (10)$$

valid for all values of z , if we make the convention that

$$\Pi(z) = \Pi(\sigma), \quad (0 \leq z \leq \sigma) \quad (11)$$

As $\Pi(z)$ is meaningless so far as equation (6) is concerned for such values of z , there is no objection to this convention.

It follows at once that the work done by the attractions of the slab when the molecule is brought from infinity to z is

$$\frac{2\pi\nu df}{2j} \int_r^\infty u (e^{2j\Pi(u)} - 1) du;$$

it is convenient to have a notation for this expression, and we shall call it

$$2\pi\nu df \varpi(z).$$

It is obvious from the symmetry that we must have

$$\varpi(z) = \varpi(-z);$$

just as much work is done by the attractions when the molecule is brought from infinity to $+z$ as when it is brought right through the slab to $-z$.

Consider a boundary surface of a body of gas, which may be supposed to extend to infinity in the direction of the positive axis of z . When a boundary field exists, the general molecular density in any slab must be a function $\nu(f)$ of f the distance from the boundary. The boundary of any actual vessel may in general be regarded as plane since the curvature will be negligible compared with the scale of molecular sizes and distances with which we are concerned.

The total work $\chi(z)$ done by the attractions of all slabs when a molecule is brought from positive infinity in the gas to the distance z from the boundary of the gas, which may be supposed to be the plane $z=0$ *, is therefore given by the equation

$$\chi(z) = 2\pi \int_0^\infty \varpi(z-f) \nu(f) df. \quad . \quad . \quad (12)$$

§ (7). *The effect of variation of ν with f .*—So far our arguments are quite general, provided only that the molecular density in the neighbourhood of a selected molecule is adequately given by (5a). This expression must fail at sufficiently great concentrations, for the gas may for example be so dense that no excess concentration in the neighbourhood of any molecule is physically possible. It is easily seen that the necessary correction can be introduced in the usual way by taking account of the presence of one molecule in affecting the chances for the presence of a second etc., and that such corrections must result in terms of order $1/\nu$, $1/\nu^2$,, compared to the leading terms in W . They are therefore irrelevant in the calculation of B from equation (12).

To proceed further with (12) we require the molecular density $\nu(f)$ as a function of f the distance from the boundary. It turns out that the effect of this variation is also of order $1/\nu$ and irrelevant for our present purposes. This may be seen as follows. It is well known † that $\nu(f)$ depends on f (a) because of the existence of the field of force of potential $\chi(\infty) - \chi(f)$, and (b) because the molecules are of finite size. Jeans gives an expression for $\nu(0)$ which takes account of the first-order correction for the size of the molecules and of the complete effect of the field of force. It is easy to extend the method so as to calculate not only $\nu(0)$ but also $\nu(f)$ to the same order of accuracy.

Ignoring details we may write this expression for $\nu(f)$ in the form

$$\nu(f) = \nu e^{-2j(\chi(\infty) - \chi(f))} \{1 + \nu e^{-2j(\chi(\infty) - \chi(f))} \phi(f, j, \sigma)\}, \quad (13)$$

where the function ϕ depends only on those variables which are explicitly mentioned. If we combine together (12) and

* The strict meaning of this statement is that when the centre of the molecule lies in the plane $z=0$, the molecule is in contact with the rigid boundary of the vessel (supposed plane).

† Jeans, *loc. cit.* pp. 154–164. Jeans denotes our $\nu(0)$ by ν_δ .

(13) we obtain the following integral equation for $\chi(z)$, namely,

$$\frac{\chi(z)}{2\pi\nu} = \int_0^\infty \varpi(z-f) e^{-2j(\chi(\infty)-\chi(f))} \{1 + \nu e^{-2j(\chi(\infty)-\chi(f))} \phi(f, j, \sigma)\} df. \quad . . . (14)$$

Further corrections for the size of molecules beyond the first-order correction result in a series of similar terms $\nu^2, \nu^3, \dots$, on the right-hand side.

This is an integral equation of an unusual type. A formal proof that it has a unique solution would not (apparently) be particularly difficult. The relevant point at the moment is that the form of (14) shows that the first approximation to the solution (ν small, ν large) must be of the form

$$\frac{\chi(z)}{2\pi\nu} = \int_0^\infty \varpi(z-f) df + O\left(\frac{1}{\nu}\right), \quad . . . (15)$$

and therefore that in calculating B we should ignore all boundary variations of $\nu(f)$, and replace $\nu(f)$ by ν in equation (12).

§ (8). Continuing the calculations of § 6 in view of the discussion of § 7, we find that, to the required order,

$$\begin{aligned} \chi(z) &= 2\pi\nu \int_0^\infty \varpi(z-f) df, \\ &= 2\pi\nu \int_0^z \varpi(f) df + 2\pi\nu \int_0^\infty \varpi(f) df. \quad . . . (16) \end{aligned}$$

Using the definition of $\varpi(z)$ we obtain after reduction (integration by parts)

$$\begin{aligned} \chi(z) &= \frac{2\pi\nu}{2j} \left\{ \int_0^\infty (z+x)(e^{2j\Pi(x)}-1)x dx \right. \\ &\quad \left. - \int_0^z (z-x)(e^{2j\Pi(x)}-1)x dx \right\}. \quad . . . (17) \end{aligned}$$

From equation (17) it follows at once that

$$\chi(0) = \frac{1}{2}\chi(\infty) = \frac{2\pi\nu}{2j} \int_0^\infty x^2 (e^{2j\Pi(x)}-1) dx. \quad . (18)$$

One would expect *a priori* $\chi(\infty)$ to vanish. The fact that it does not do so is due to the artificial nature of the assumed infinity conditions. And in fact it does not matter, for $\chi(\infty)$ means the work done *by* the attractions when the molecule is brought from positive infinity (in the gas) to a

point in the gas which is still (practically) at an infinite distance from the boundary $z=0$. In the same way $\chi(0)$ means the work done *by* the attractions when the molecule is brought to the boundary itself. Whatever the infinity conditions, the work W done *against* the attractions when a molecule is brought to the boundary must be given by

$$W = \chi(\infty) - \chi(0) = \chi(0),$$

and we have from (5),

$$a = \frac{N^2 \chi(0)}{\nu} = \frac{2\pi N^2}{2j} \int_0^\infty x^2 (e^{2j\Pi(x)} - 1) dx. \quad (19)$$

From (19) we can calculate a without much trouble for any reasonable law of force.

§ (9). *The correct value of van der Waals' b .*—The correct value of the second virial coefficient is of course given by van der Waals' or Dieterici's equations of state in the form

$$NkTb - a,$$

provided correct values of a and b are used. The correct value of a is given by (19). It is usually assumed that $b = \frac{2}{3}\pi N\sigma^3$, but when intermolecular attractions exist, this is no longer correct, but we must have

$$b = \frac{2}{3}\pi N\sigma^3 e^{2j\Pi(\sigma)}, \quad (20)$$

a result which is often overlooked. Consider, for example, the proof of the usual formula for b given by Jeans*. He first obtains expressions for the excluded regions of the usual generalized space, and allows for them on the usual assumption that the *a priori* probability for the presence of a molecule in any element of generalized space is the same. To allow, for example, for the excluded region,

$$\Sigma (x_a - x_b)^2 < \sigma^2$$

on this assumption of the equal probability of all positions of the b -molecule, we must exclude a fraction $\frac{2}{3}\pi\sigma^3/\Omega$ of the total generalized space Ω^N . But when there are central forces acting between the molecules we are no longer at liberty to assume that this *a priori* equal probability for elements of *generalized* space implies equal probabilities for equal volume elements in *ordinary* space. The correcting term must be multiplied by the probability of another molecule being at a distance σ from the selected molecule—

* *Loc. cit.* p. 157.

that is to say by $e^{2j\Pi(\sigma)}$. Making this correction the value of b given by (20) follows at once by the usual arguments. Equations (19) and (20) used in the ordinary formula $NkTb - a$ must give the exact form for the second virial coefficient.

We may note here the differences between the usual values of a and b and the values given by (19) and (20). The usual values are really obtained on the assumption that $2j\Pi(\sigma)$ is small so that $e^{2j\Pi(\sigma)}$ is very nearly unity, and the effect of this factor on a and b negligible. The value of a so obtained is of course

$$a = 2\pi N^2 \int_0^\infty x^2 \Pi(x) dx.$$

It is most important to recognize that increasing the dilution has no effect whatever on the accuracy or inaccuracy of this approximation, for it does not affect $2j\Pi(\sigma)$. The approximation can only be justified if the temperature is sufficiently high. But by equation (4) $2j\Pi(\sigma)$ is of the order $5S/T$. For an ordinary monatomic or diatomic gas, whose viscosity is analysed by Sutherland's formula, $S > 100$. [The only exceptions are He, H₂, and Ne.] Analysed by a more exact formula, taking account of all powers of $1/T$, a considerably smaller value of S (perhaps 5–10 times smaller) might fit the observations, and agree with the compressibility data (see § 2). But even so, $2j\Pi(\sigma)$ is about unity at a temperature of 100° absolute, and can hardly be considered small at temperatures less than 1000° absolute. It is not till we reach these temperatures that the clustering effect can be ignored, and the gas regarded as genuinely of uniform density throughout.

§ (10). *The direct calculation of the Virial of Clausius.*—It is possible to calculate independently by this method the exact value of the coefficient of $1/v$ in the expression for pv , and so confirm the results of the last section. The virial method is, however, unsuitable for making allowance, when the need arises, for the effect of the boundary field.

We take a molecular model for which the law of repulsion $f(r)$ between a pair of molecules is

$$\begin{aligned} f(r) &= Q, & (\sigma - \epsilon \leq r < \sigma), \\ f(r) &= -\phi(r), & (r > \sigma). \end{aligned}$$

We obtain the elastic sphere model (diameter σ) with the

proper field of *attractive* force $\phi(r)$ by making $Q \rightarrow \infty$ and $\epsilon \rightarrow 0$ in a suitable manner. The virial argument starts from the formula *

$$\frac{2\pi N^2}{v} r^2 e^{-2j} \int_r^\infty f(x) dx \, dr$$

for the number of pairs of molecules in the gas whose centres are at a distance between r and $r + dr$. Then for the contribution $\frac{1}{3} \Sigma \Sigma r f(r)$ to the virial we have

$$\frac{1}{3} \Sigma \Sigma r f(r) = \frac{2\pi N^2}{3v} \int_0^\infty r^3 f(r) e^{-2j} \int_r^\infty f(x) dx \, dr. \quad (21)$$

We split this integral up into the two ranges $(\sigma - \epsilon, \sigma)$ and (σ, ∞) . In the former we can replace r^3 by σ^3 since eventually $\epsilon \rightarrow 0$. On evaluating $\int_r^\infty f(x) dx$ we get

$$\begin{aligned} \frac{1}{3} \Sigma \Sigma r f(r) = & \frac{2\pi N^2 \sigma^3}{3v} e^{2j\Pi(\sigma)} \int_{\sigma-\epsilon}^\sigma Q e^{-2jQ(\sigma-r)} dr \\ & - \frac{2\pi N^2}{3v} \int_\sigma^\infty r^3 \phi(r) e^{2j\Pi(r)} dr. \end{aligned}$$

The first integral can be evaluated; it is

$$\frac{1}{2j} (1 - e^{-2jQ\epsilon}).$$

If therefore we make $Q \rightarrow \infty$ and $\epsilon \rightarrow 0$ in such a way that $Q\epsilon \rightarrow \infty$ we may replace the first integral by $1/2j$, which must be its value appropriate to elastic spheres. We can write the second integral in the form

$$- \int_0^\infty r^3 \Pi'(r) e^{2j\Pi(r)} dr$$

with our previous conventions for $\Pi(r)$. This can be integrated by parts in the form

$$- \left[\frac{r^3}{2j} (e^{2j\Pi(r)} - 1) \right]_0^\infty + \frac{3}{2j} \int_0^\infty r^2 (e^{2j\Pi(r)} - 1) dr,$$

and the integrated part vanishes at both limits. Hence

$$\frac{1}{3} \Sigma \Sigma r f(r) = \frac{2\pi N^2 \sigma^3}{6jv} e^{2j\Pi(\sigma)} - \frac{2\pi N^2}{2jv} \int_0^\infty r^2 (e^{2j\Pi(r)} - 1) dr.$$

The complete virial equation is

$$pv = NkT + \frac{1}{3} \Sigma \Sigma r f(r),$$

* Jeans, *loc. cit.* p. 132.

so that in this case, with our previous notation,

$$pv = NkT + \frac{1}{v} \left\{ NkTb e^{2j\Pi(\sigma)} - \frac{N^2 \chi(0)}{v} \right\} + O\left(\frac{1}{v^2}\right), \quad (22)$$

which confirms equations (19) and (20). This result is in agreement with Keesom's*, obtained by yet another independent method—the calculation of the entropy.

§ (11). *Particular molecular models.*—The molecular models which are of interest are those in which the attraction (1) varies as the inverse s th power of the distance, $\phi(r) = \alpha r^{-s}$, and (2) is constant over a certain range and zero outside that range, $\phi(r) = A$, ($\sigma \leq r \leq d$); $\phi(r) = 0$, ($r > d$). The latter may be regarded as the natural successor of the model originally proposed by Young in his theory of capillary forces. In the first model it is essential for convergence to take $s > 4$; the physical meaning of this restriction has already been commented on in § 5.

(i.) *The inverse s^{th} -power law.*—If we take $\phi(r) = \alpha r^{-s}$ we have

$$\Pi(r) = \begin{cases} \frac{\alpha r^{1-s}}{s-1}, & (r > \sigma), \\ \frac{\alpha \sigma^{1-s}}{s-1}, & (r \leq \sigma). \end{cases} \quad \dots \quad (23)$$

For the second virial coefficient B we combine (19) and (20), expand $e^{2j\Pi(r)}$, and integrate term by term. We obtain after reduction

$$B = NkTb \left\{ 1 - 3 \sum_{n=1}^{\infty} \frac{(2j\Pi(\sigma))^n}{n! \{n(s-1) - 3\}} \right\}, \quad (24)$$

where $b = \frac{2}{3}\pi N\sigma^3$, its classical meaning.

(ii.) *Young's model.*—In this case we have

$$\Pi(r) = \begin{cases} 0, & (r > d), \\ A(d-r), & (d > r > \sigma), \\ A(d-\sigma), & (\sigma > r). \end{cases} \quad \dots \quad (25)$$

The integral for $\chi(0)$ can be evaluated in finite terms by integration by parts. We obtain after reduction,

$$\chi(0) = \frac{2\pi\nu}{2j} \left\{ \left(\frac{1}{3}\sigma^3 + \frac{\sigma^2}{2jA} + \frac{2\sigma}{(2jA)^2} + \frac{2}{(2jA)^3} \right) e^{2jA(d-\sigma)} - \left(\frac{1}{3}d^3 + \frac{d^2}{2jA} + \frac{2d}{(2jA)^2} + \frac{2}{(2jA)^3} \right) \right\}. \quad (26)$$

* *Loc. cit.* p. 264.

Equation (26) is suitable for use in computations for low temperatures. The expanded form for $\chi(0)$ analogous to (24) is suitable for use with high temperatures and is more immediately intelligible than (26). This form is

$$\chi(0) = 2\pi\nu\Pi(\sigma) \sum_{n=1}^{\infty} \frac{(2j\Pi(\sigma))^{n-1}}{n!} \\ \times \left\{ \frac{1}{3}\sigma^3 + \frac{(d-\sigma)d^2}{n+1} - \frac{2(d-\sigma)^2d}{n+2} + \frac{(d-\sigma)^3}{n+3} \right\}. \quad (27)$$

and the corresponding form of the second virial coefficient is

$$B = NkTb - 2\pi N^2\Pi(\sigma) \sum_{n=1}^{\infty} \frac{(2j\Pi(\sigma))^{n-1}}{n!} \\ \times \left\{ \frac{(d-\sigma)d^2}{n+1} - \frac{2(d-\sigma)^2d}{n+2} + \frac{(d-\sigma)^3}{n+3} \right\}. \quad (28)$$

XCII. The Reflexion of X-Rays from Imperfect Crystals.

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1. Introduction.

THE recent work of Bragg, James, and Bosanquet †, on the reflexion of X-rays from rock-salt crystals is of extreme importance in that it promises more directly than any other method to supply information about the actual positions which the electrons occupy in the atom. The method consists in a study of the intensity with which the various faces of the crystal reflect a given wave-length, and is based on the theoretical formulæ given by the present writer ‡. These formulæ showed that such experiments should determine a certain quantity, which is, roughly speaking, the amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. A study of the various faces of a crystal gives this amplitude as a function of the angle of scattering, and from that the positions of the electrons can be inferred—with this second half of the problem I shall not be here concerned. But the deduction of the amplitude from the experiments encountered certain peculiar difficulties; for the absorption

* Communicated by the Author.

† Bragg, James, and Bosanquet, *Phil. Mag.* vol. xli. p. 309, and vol. xlii. p. 1 (1921).

‡ Darwin, *Phil. Mag.* vol. xxvii. p. 315 and p. 675 (1914).