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THE DEVELOPMENT OF THE KINETIC THEORY OF GASES
V. THE EQUATION OF STATE

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Lawrence Radiation Laboratory, University of California
Livermore, California

ABSTRACT

Some early attempts to explain deviations from the ideal gas laws are discussed. In 1846, Elie Ritter proposed the equation of state

$$p = a\rho(1 + \alpha t) - b\rho^2$$

(t = temperature in °C, ρ = density) where the first term represents the pressure of the caloric fluid (which was believed to behave like an ideal gas) and the second term is a small correction due to interatomic attractive forces. The constant b was to be calculated from the virial of the forces, assuming the atoms to be fixed in space.

After the establishment of the kinetic theory of gases, Clausius introduced the virial theorem which, together with the Maxwell-Boltzmann distribution law, made it possible to calculate low-density corrections to the ideal gas law for almost any force law. In general these corrections have the form suggested by Ritter, but the correction would be positive for repulsive forces, and b usually varies with temperature. The special case of hard spheres was first treated correctly by van der Waals (1873), who showed that the "excluded volume" is approximately four times the atomic volume; Lorentz later derived the same result by a direct application of the virial theorem. Second virial coefficients for more general force laws were calculated by Boltzmann (1896), Keesom (1912), and others.

While Ritter's equation is valid over a certain range of densities and temperatures, and his expression for b is similar to that obtained from the kinetic theory, his theory was based on incorrect physical assumptions and would not have survived comparison with more accurate experimental data.

1. INTRODUCTION

Among the natural phenomena in the domain of physics, the mechanical and thermal properties of gases under ordinary conditions are perhaps the best understood. By assuming a gas to be composed of many small particles obeying Newtonian mechanics, colliding with the walls of the container but occupying a negligible fraction of the total volume, one can easily deduce the "ideal gas" laws; a few refinements enable one to explain transport properties and the equation of state at low densities. The mysterious phenomena of condensation and the critical point are interpreted by means of a cubic equation, derived from a model of attracting but impenetrable spheres. Thus an impressive range of observations can be explained in terms of "atoms" without having to worry about the messy details of atomic structure, and without recourse to elaborate mathematics. In short, gas theory is the showpiece of classical physics.

In order to find an era when the situation was not so satisfactory -- and to understand how our present ideas were developed -- one must go back at least a century. With the exception of Bernoulli's work (1738) most of the theory was developed during the nineteenth century. In the previous articles in this series we have discussed the work of John Herapath (1790-1868), J. J. Waterston (1811-1883), Rudolf Clausius (1822-1888), and James Clerk Maxwell (1831-1879).[1] The efforts of these scientists were mainly directed toward establishing the kinetic explanation of the ideal gas laws, although in the later work of

Clausius and Maxwell the idea of atoms as non-interacting point-masses had to be abandoned in order to account for transport properties.

In this paper we shall look at some of the early attempts to explain deviations from the ideal gas laws. The first attempts were made by scientists who believed that the pressure of an ideal gas is due, not to the collisions of atoms with the sides of the container, but to the action of a subtle fluid -- "caloric." However, they also realized that the pressure would be affected by interatomic forces, and they could calculate the pressure due to such forces by assuming the atoms to be fixed in space. In this way the Swiss physicist Elie Ritter (1801-1862) derived an equation of state of the form[2]

$$p = a\rho(1 + \alpha t) - b\rho^2 \tag{1}$$

where ρ is the density, t the temperature in degrees Centigrade, α the coefficient of expansion, and the constant b is essentially the virial of the interatomic forces.

Ritter's paper appeared in 1846; many years later the kinetic theorists arrived at a similar equation by different reasoning. During the period 1845-1855 the caloric theory was overthrown and heat was shown to be, not a fluid, but simply a form of energy which could be converted into other forms of energy. Many scientists thought that thermodynamics, which described these energy transformations on a macroscopic basis, was sufficient for all practical purposes, and refused to entertain speculations about invisible atoms. But after Krönig, in 1856, revived the old idea that heat is the kinetic energy of atomic motion, Clausius, Maxwell, and Boltzmann developed the kinetic theory in considerable detail. The starting point for later theories of the equation of state is the virial theorem, proved by Clausius in 1870, which relates the pressure to the velocities of the atoms, and the forces and distances between pairs of atoms. For actual calculations it is necessary to know something about the average spatial distribution of the atoms; as long as the density is low enough that interactions between pairs of atoms can be considered independent of the positions of other atoms, it is sufficient to use the Maxwell-Boltzmann distribution law (first given by Maxwell in 1873 and later proved more rigorously by Boltzmann). Thus the necessary mathematical apparatus had been developed by 1875, even though detailed calculations with realistic force laws were not begun until thirty years later when accurate experimental data on the equation of state became available. Equation (1) was then regarded as merely the beginning of a series in increasing powers of the density. The coefficients of higher powers could be related theoretically to simultaneous interactions of three or more atoms, although because of the mathematical difficulties involved it was rarely possible to calculate these coefficients exactly.

The special case of a gas of hard spheres had already been considered by Bernoulli, who argued that the volume, v, of the gas should be replaced in the equation of state by (v - b), where b is a constant representing the volume occupied by the atoms themselves.[3] It was not until 1873 that van der Waals showed that b should really be equal to approximately four times the atomic volume. Somewhat later Lorentz obtained a similar result by applying the virial theorem, and pointed out that the net result of this correction was an increase in the pressure proportional to the square of the density (neglecting higher powers of the density).

As in other parts of atomic theory, the basic physical principles of gas theory were stated long before they were proved; one must resist the temptation to glorify the isolated pioneer merely because subsequent work showed that he had guessed right. Thus a critical examination of Ritter's theory shows that by making several unjustified assumptions he was fortunate enough to arrive at an expression for the second virial coefficient very similar to the correct one;

but that his theory could not have survived comparison with more accurate experimental data, and did not provide a good theoretical basis for further developments. It must therefore be regarded as an interesting curiosity, but not an anticipation of the more solid achievements of the later kinetic theorists.

2. THE EQUATION OF STATE IN THE CALORIC THEORY

As Ritter's work is not generally known, and is not very accessible, it seems worthwhile to give a fairly complete account of it here. Ritter did not discuss the caloric theory in any detail, but merely accepted the current idea that caloric behaved like an ideal gas. He considered the pressure of a real gas to be the result of two causes: the repulsion due to caloric, and the attraction due to interatomic forces. He assumed in particular that the two effects could be treated independently and then added together; while this had no theoretical justification, it permitted him to calculate the contribution of the forces in a manner independent of the caloric theory.

Ritter borrowed from Poisson[4] the mathematical apparatus necessary for this calculation. The pressure of a gas is the force per unit area exerted on a surface in the gas; Poisson and Ritter assumed that the atoms are fixed in a cubic array in space, neighbouring atoms being a distance Δ apart. Poisson showed that the pressure is

$$p = (1/6\Delta^3) \; \Sigma \; rf(r) \qquad (2)$$

where f(r) denotes the force exerted by an atom at a distance r; the sum is to be computed by choosing some central atom and summing the contributions from all the others.[14] Assuming that a spherical shell at a distance r from the central atom contains $4\pi r^2/\Delta^2$ atoms, Poisson wrote Eq. (2) in the form

$$p = (2\pi/3\Delta^5) \sum_r r^3 f(r) \qquad (3)$$

where now the sum is simply over possible values of the magnitude of r: Δ, 2Δ, 3Δ, ... In order to evaluate this sum he used the formula[5]

$$\sum_{r=\Delta}^{\infty} F(r) = (1/\Delta) \int_{0}^{\infty} F(r)dr - (1/2)F(0) + (2/\Delta)\int_{0}^{\infty}\left[\sum_{i=1}^{\infty} \cos(2\pi ir/\Delta)\right] F(r)dr.$$

By successive integrations by parts the last term in this equation can be reduced to a power series in Δ, the coefficients being the derivatives of F(r) at the origin. In this case $F(r) = r^3 f(r)$; so F(0), and F'(0), and F''(0) were all set equal to zero. (Neither Poisson nor Ritter considered the possibility that f(r) might become infinite at r = 0, and their formulae are not very useful for calculations with singular forces.) The final result, obtained by Poisson and given again by Ritter, is that the contribution to the pressure is

$$p = (2\pi/3\Delta^6) \int_{0}^{\infty} r^3 f(r)dr + (\pi/180\Delta^2)f(0) - (\pi/756)f''(0) + \ldots . \qquad (4)$$

Since the density is proportional to $1/\Delta^3$, this could also be written as a series in descending powers of $\rho^{2/3}$:

$$p = b\rho^2 + c\rho^{2/3} + d + e\rho^{-2/3} + \ldots . \qquad (5)$$

Poisson thought this formula might represent the total pressure of a gas, though he found it difficult to reconcile this with the empirical fact that the pressure is approximately proportional to the density, and he did not make much use of the formula.[6] Ritter, on the other hand, treated this contribution as a small correction to the ideal gas law, obtaining Eq. (1) as a first approximation for attractive forces. It should be noted that b is a constant independent of temperature and density according to Ritter's theory.

In order to compare theory with experiment, Ritter derived expressions for the coefficients of expansion at constant pressure and volume. If the density at t = 0 °C is ρ, and one raises the temperature to 100°C, keeping the pressure constant, the density will then be $\rho(1 + 100\alpha')$. (This is Ritter's definition of α'.) Eliminating the pressure, he obtained

$$1 + 100\alpha' = \frac{1 + 100\alpha + \left[(1 + 100\alpha)^2 + (1-2\rho/a)^2 - 1\right]^{1/2}}{2(1-b\rho/a)}. \quad (6)$$

If instead the volume is kept constant, the pressure will increase from p to $p(1+100\alpha'')$; eliminating p, the coefficient of expansion at constant volume was found to be

$$\alpha'' = a\alpha/(a-b\rho). \quad (7)$$

Both α' and α'' reduce to α for ideal gases ($b = 0$). Regnault[7] had found that hydrogen obeys the ideal gas law at pressures from 1 to 3-1/2 atmospheres, and that α has the value 0.0036613.

Regnault's experiments on air[7] showed deviations from the ideal gas laws, though the deviations were so small that Regnault himself attributed them to errors of observation. Ritter calculated the values of a and b in Eq. (7) for three observations and obtained the results: (1) a = 761.4714, b = 1.4714; (2) a = 760.2864, b = 0.2864; (3) a = 760.1865, b = 0.1865, where the pressure is measured in millimetres of mercury. Taking a = 761 and b = 1, he then calculated α' and α'' for several pressures with the following results:

Pressure (atmospheres)	α'		α''	
	theory	expt.	theory	expt.
1	.0036716	.0036706	.0036661	.0036650
3	.0036865	.0036944	.0036758	.0036894
5	.0037038		.0036856	

Regnault's observations on carbon dioxide could be represented, according to Ritter, by the formula

$$p = 500.5522\rho^2 - 2.3230\rho^2,$$

and the coefficients of expansion were as follows:

Pressure (mm mercury)	a''		Pressure (mm mercury)	a'	
	theory	expt.		theory	expt.
758.47	.0036874	.0036856	760	.00370685	.0037099
901.09	.0036924	.0036943	2520	.00381886	.0038455
1742.73	.0037225	.0037523			
3589.07	.0037920	.0038598			

Ritter concluded that his theory gave the correct explanation for deviations from the ideal gas laws, although further observations at higher pressures would be desirable.

3. THE EQUATION OF STATE IN THE KINETIC THEORY

During the next thirty years little progress was made in understanding deviations from the ideal gas laws, although it was well known that such deviations existed, and several empirical equations of state were suggested. The attention of theoretical physicists was occupied instead with establishing the principles of macroscopic thermodynamics and applying the kinetic theory to ideal gases. As early as 1853 the Joule-Thomson experiment[8] had shown that interatomic forces have a measurable effect on the thermal properties of gases, but it was some time before these forces were taken into account theoretically. Furthermore, little information was yet available about the precise nature of these forces, aside from the fact that they must reduce to inverse-square gravitational forces at large distances. A very elaborate hypothesis about the nature of interatomic forces had been proposed by Roger Boscovich (1711-1787), who regarded atoms as points, no two of which can ever coincide; the force between two atoms is a continuously changing function of their distance, beginning with infinite repulsion at very short distances, probably alternating several times between attraction and repulsion, and finally ending as gravitational attraction at large distances.[9] Although Boscovich's ideas remained popular for a long time, they were condemned by many nineteenth-century scientists, who thought it inconceivable that point atoms could have such properties. Indeed, any kind of action at a distance was somewhat suspect, and was usually explained as due to the action of the aether.[10]

Nevertheless, two simple models were proposed during the late nineteenth century before much was known about atomic structure, and both are still often used in calculations although they are now known to be incorrect. Maxwell[11] considered repulsives forces of the form r^{-n} in his work on the theory of viscosity, and found that by setting n equal to 5 the calculation was greatly simplified, and the result agreed with experimental data available at the time. Though later experiments showed that this force law could not be correct, a Maxwellian model is often assumed for transport-theory calculations for reasons of mathematical convenience.

A somewhat more realistic model was proposed by William Sutherland (1859-1912): a hard sphere with a fourth-power attractive force at greater distances, going over eventually to the inverse-square gravitational force at very large distances.[12] He thought that the "ultimate law of action of one particle on another" could be expanded in powers of $1/r^2$, the first term being the law of gravitation, the second being the law of molecular force,

> "....with $G/r^2 + M/r^4$ to express the law of molic force thru the whole range of distances from molecular up to astronomical, one is tempted to speculate whether the law of the terms representing atomic or chemic force may not be expressed by one or more higher powers of $1/r^2$, representing a force insensible at molecular distances as the molecular term of molic force is insensible at astronomical distances, but sensible at

atomic distances, with the associated idea that atomic distances are exceedingly small compared to molecular. This conception would (speaking in a purely relative manner) reduce the molecules almost to mathematical points, and would almost remove the difficulty as to collisions of molecules. In this manner we can endeavour to realize all the actions of matter on matter as pure attractions."

Having decided on some particular force law, one then has to calculate the effect on the pressure. The starting point for most modern work on the equation of state is the virial theorem of Clausius.[13] The theorem states that the mean value of the kinetic energy in a system of material points is equal to the mean value of a quantity called the virial:

$$\sum (m/2)\, \overline{V^2} = -(1/2) \sum \overline{(Xx + Yy + Zz)}, \tag{8}$$

where x, y, and z represent the rectangular coordinates of the points, X, Y, and Z the respective components of the force acting on each point; the average value is taken over a time, in the case of a periodic motion, equal to a complete period, or, in the case of irregular motion, sufficiently long that the mean value becomes constant. It is further assumed that the system is in "stationary motion," i.e., that the points move within a limited space and the velocities do not change continuously in any particular direction.

The total virial may be divided into two parts: (1) the internal virial, which results simply from the forces which the points exert on each other; and (2) the external virial, resulting from external forces acting on the system. If we let f(r) represent the force between two points at a distance r, the internal virial is the sum of $(-\frac{1}{2} r f(r))$ for each pair of points; and if the only external force is a pressure p confining the system to a volume v, the external virial is simply 3pv/2. In this way Clausius arrived at the equation

$$E = (1/2) \sum rf(r) + (3/2)pv \tag{9}$$

where E denotes the mean vis viva (kinetic energy) of the internal motions. This is essentially the same as the equation used by Ritter, except that Ritter used for E an empirical value derived from the ideal gas law, instead of setting it equal to the kinetic energy of atomic motion.[14]

Clausius gave the following proof of this theorem:

"The equations of the motion of a material point are:

$$m\left(\frac{d^2x}{dt^2}\right) = X; \qquad m\left(\frac{d^2y}{dt^2}\right) = Y; \qquad m\left(\frac{d^2z}{dt^2}\right) = Z.$$

But we have

$$\frac{d^2(x^2)}{dt^2} = 2\frac{d}{dx}\left(x\frac{dx}{dt}\right) = 2\left(\frac{dx}{dt}\right)^2 + 2x\frac{d^2x}{dt^2}$$

or, differently arranged,

$$2\,(dx/dt)^2 = -2x\frac{d^2x}{dt^2} + \frac{d^2(x^2)}{dt^2}. \tag{10}$$

Multiplying this equation by (m/4), and putting the magnitude X for $m(d^2x/dt^2)$, we obtain

$$\frac{m}{2}\left(\frac{dx}{dt}\right)^2 = -\frac{Xx}{2} + \frac{m}{4}\frac{d^2(x^2)}{dt^2}.$$

The terms of this equation may now be integrated for the time from 0 to t, and the integral divided by t; we thereby obtain

$$\frac{m}{2t}\int_o^t\left(\frac{dx}{dt}\right)^2 dt = -\frac{1}{2t}\int_o^t Xx\,dt + \frac{m}{4t}\left[\frac{d(x^2)}{dt} - \left(\frac{d(x^2)}{dt}\right)_o\right]$$

where $\left(\frac{d(x^2)}{dt}\right)_o$ denotes the initial value of $\frac{d(x^2)}{dt}$ ....

> "The last term of the equation, which has its factor included in the square brackets, becomes, when the motion is periodic, = 0 at the end of each period, as at the end of the period $d(x^2)/dt$ resumes the initial value $\left(\frac{d(x^2)}{dt}\right)_0$. When the motion is not periodic, but irregularly varying, the factor in brackets does not so regularly become = 0; yet its value cannot continually increase with the time, but can only fluctuate within certain limits; and the divisor, t, by which that term is affected, must accordingly cause the term to become vanishingly small with very great values of t. Hence, omitting it, we may write
>
> $$\frac{m}{2}\overline{\left(\frac{dx}{dt}\right)^2} = -\frac{\overline{Xx}}{2}$$
>
> As the same equation is valid also for the remaining coordinates .... and for a system of any number of points we have ....
>
> $$\sum \frac{m}{2}\overline{v^2} = -\frac{1}{2}\sum \overline{(Xx + Yy + Zz)} \text{ ."}$$

It should be noted that the important contribution of Clausius was the elimination of the last term in Eq. (10), since that equation itself was already well known in classical mechanics.[15]

The first attempt to apply the virial theorem was the famous equation of state of van der Waals (1837-1923), proposed in his Leiden thesis in 1873. Van der Waals did not make any special assumptions about the form of the force law, but he tried to draw some general conclusions about the effects of such forces. Although his discussion of these forces pertained mainly to liquids, it was reasonable to expect the same equation to apply to gases where the correction to the ideal gas law would be small anyway.

> He assumed that such forces have a very short range, so that "... we need only take account (in considering the force on any given particle) those other particles which are within a sphere of very small radius having the particle as centre, and termed the 'sphere of action,' the forces themselves becoming insensible at distances greater than the radius of the sphere."[17]

If the density is constant throughout,

> "... it follows that all those points will be in equilibrium about which we can describe a sphere of action without encroaching on the boundary. By this of course is meant that the particles will be in equilibrium as far as attraction alone is concerned; not necessarily so when the molecular motion is also taken into account -- though this will actually be the case for the mass taken as a whole. In other words, the forces X, Y, and Z are zero for all points within the mass. Consequently the expression $\sum(Xx + Yy + Zz)$ vanishes .... The particles for which the forces may be put equal to zero constitute a priori by far the greater part of the mass, leaving only a comparatively small number on which uncompensated forces act. These last lie on the boundary and form a layer whose thickness is the radius of the sphere of action; and the forces on these particles are directed inwards. If about one such particle we describe the sphere of action, part of this sphere will be external to the liquid, and this part will represent the space which would be occupied by the particles which would if present annul the forces. So the

> remaining force acting inwards is equal in magnitude to the attraction which the particle in question would have experienced from the action of the particles which are absent."[18]

The equation of state, including this additional pressure, may thus be written

$$(p + p')v = \sum mV^2/2 \qquad (11)$$

where p is the total pressure exerted by the boundary, and p' is the molecular pressure at the surface. Van der Waals believed that p would be much greater than p' in gases, but p' would be greater in liquids.

In order to determine how p' depends on density, van der Waals appealed to the hypothesis of molecular motion:

> "... consider an infinitely thin column in the boundary layer, and imagine a part of space below this layer, within the body, containing every molecule that could attract the column. If in this space there were a molecule at rest, we should require to know the law of force to be able to estimate its attraction on the column. But if this molecule is in motion, and can occupy any part of the space indifferently, the above difficulty for the most part disappears; and we can take the attraction exerted by the molecule to be the mean of the attractions which it would exert in its different possible positions in the space. The same consideration applies to a second molecule which may be within the space at the same time as the first. In short, the attraction exerted by the matter in the space mentioned is proportional to the quantity of matter, or to the density. The same holds for the molecules within the column, so that the attraction is proportional

> to the square of the density, or inversely proportional to the square of the volume."[19]

In order to take into account the influence of finite molecular extension, van der Waals used a different method; here he avoided a mistake which had been made by his predecessors.

> "Of course the effect of the extension will be to make the volume within which the motion takes place smaller than it seems to be. At first I considered that the difference between the external volume and the volume taken up by the molecules was the space within which the motion takes place. But I trust to be able to prove, by further considerations, that up to a certain degree of condensation of matter the external volume must be diminished by four times the volume of the molecules, and for greater condensation that it must be diminished by a continuously diminishing multiple of this volume."[20]

The factor of four was deduced by considering the mean free path of an atom. Clausius had taken into account, in his derivation of the mean free path formula (see the third paper of this series), the extension of the molecules in a plane perpendicular to the direction of motion, but not in the direction of motion itself, and hence his result was too large:

> "... just as if the free path of a ball thrown against a wall were said to be the distance of the centre of the ball from the wall when the motion began; whereas the free path is that distance minus the radius of the ball. Thus, considering the diameter of the molecule we get a shorter free path, and consequently a proportionately greater number of encounters. But then the opposing pressure must be greater in proportion."[21]

If λ is the mean distance of the molecules, supposed to be arranged in cubical order, and each molecule is regarded as a sphere of diameter σ, then according to Clausius the mean free path of a single moving molecule is

$$\ell = \lambda^3/\pi\sigma^2$$

when all the others are assumed at rest, or

$$\ell_1 = 3\lambda^3/4\pi\sigma^2$$

when the others are moving with the same velocity.

> "We must now find how much the diameter of the molecules diminishes the path. If all the impulses were in the motion joining the centres of the molecules considered as spheres, then ℓ_1 would have to be diminished by the distance between the centres when impact occurs. For half the diameter of the molecules must be subtracted at the beginning as well as at the end of the free path. Thus
>
> $$\ell_2 = \ell_1 - \sigma$$
>
> or $$\ell_2 = \frac{\lambda^3 - 4\pi\sigma^3/3}{4\pi\sigma^3/3}; \qquad \frac{\ell_2}{\ell_1} = \frac{\lambda^3 - 4\pi\sigma^3/3}{\lambda^3}$$
>
> Considering that $(\sigma/2)$ is the radius of the molecule here regarded as a sphere, and that $n\lambda^3$ is equal to the unit volume here taken as v; also that $(4\pi n\sigma^3/3)$ is eight times the volume of the molecules themselves; we get
>
> $$\frac{\ell_2}{\ell_1} = \frac{v - 8b_1}{v}$$
>
> where b_1 is the volume of the molecules.
>
> " The encounters, however, are only central exceptionally; and therefore, in the mean, ℓ_1 must be diminished by less

than σ. From the following considerations we can find what fraction of σ is to be subtracted from ℓ_1. At the instant of impact the centre of the moving molecule lies on a sphere of radius σ described about the centre of the second molecule. Consider this sphere bisected by a plane perpendicular to the direction of motion. For central impact the centre of the moving molecule has its greatest distance from this plane, and for intermediate cases the centre is at other points of the hemispherical surface. The diminution of the path is the distance at impact of the centre of the moving molecule from the plane, and hence the mean diminution of the mean path is the mean ordinate of the hemisphere. But since the centre is equally likely to fall on any point of the hemisphere, we must take the mean ordinate for equal elements of the hemispherical surface, and not, as might easily be thought, for equal elements of the plane. We have to find

$$\int Z\, d\omega \Big/ \int d\omega$$

where $d\omega$ is the element of surface. This is the ordinate of the centre of gravity of a hemispherical surface, and is known to be half the radius. Hence from ℓ_1 we must subtract $(\sigma/2)$ and not σ. Putting $\ell_1 - (\sigma/2) = \ell_3$ we get

$$\frac{\ell_3}{\ell_1} = \frac{v - 4b_1}{v} \text{."} \quad \text{(See ref. 22)}$$

If one takes into account the fact that the molecules have a Maxwellian distribution of velocities, the factor (4/3) in the above formula for ℓ_1 must be replaced[23] by $\sqrt{2}$, but this does not change the final result: the volume available to the molecules is to be written as v − b, where b is equal, as a first approximation, to four times the volume of the molecules themselves. Thus van der Waals derived his equation of state

$$(p + a/v^2)(v - b) = \sum mV^2/3 = R(1 + \alpha t). \qquad (12)$$

This equation has been very useful in correlating and interpreting the properties of gases, and its success may probably be attributed to the addition of the term (a/v^2) to represent the effect of interatomic forces. (The constant b was at this stage simply an adjustable parameter, chosen to fit experimental data, and therefore making it equal to <u>four</u> times the volume of the molecules had little practical significance.) However, the derivation of the equation is not very satisfactory from a theoretical point of view,[24] and since it is discussed quite thoroughly in most textbooks on the kinetic theory it does not seem necessary to go into the subject here. Later work, based on more direct application of the virial theorem, is of more interest than empirical modifications of the van der Waals equation, and has given more information about interatomic forces than can be obtained from such empirical equations of state.

A better deduction of the equation of state for hard spheres was given by H. A. Lorentz (1853-1928) in 1881.[25] Lorentz started by writing the contribution to the virial from collisions of spheres of diameter σ as

$$A = -(1/2) \sum (K\sigma)$$

where K is the repulsive force which the spheres exert on each other at a distance σ, and the sum is over all pairs of molecules which collide at a particular time. Actually K is zero except at the instants when collisions occur, and then it is infinite. To evaluate the sum it is more convenient to average over a time interval τ, and then interchange the order of summation and integration:[25]

$$A = -(1/2\tau) \int \sum (K\sigma) d\tau = -(\sigma/2\tau) \int \sum (K) d\tau = -(\sigma/2\tau) \sum \left[\int K d\tau \right].$$

The quantity $\left[\int K d\tau\right]$ is just the momentum change in a collision, so we have

$$A = -(m\sigma/2\tau) \sum U_n$$

where U_n is the relative velocity measured along the line of centres. This expression can then be written in terms of the velocity-distribution function f(u): the number of collisions during the time τ between two molecules with velocities lying in the ranges (u, u + du) and (u', u' + du'), such that the angle between u and u' is between ϕ and $\phi + d\phi$, and the angle between the relative velocity U and the line of centres is between χ and $\chi + d\chi$ (thus $U_n = U\cos\chi$), is

$$(\pi \sigma^2 \tau/v) f(u) f(u') U \sin\phi \sin\chi \cos\chi \; du\, du' \; d\phi \; d\chi .$$

Now substituting $U^2 = u^2 + u'^2 - 2uu' \cos\phi$ and integrating over all the variables, Lorentz obtained the result

$$A = -(\pi m\sigma^3/4v) \int_0^\infty \int_0^\infty \int_0^\pi \int_0^{\pi/2} f(u) f(u')(u^2 + u'^2 - 2uu' \cos\phi) \sin\phi \sin\chi \cos^2\chi \, du du' \, d\phi \, d\chi$$

$$= -(\pi m\sigma^3/6v) \int_0^\infty \int_0^\infty (u^2 + u'^2) f(u) f(u') \, du\, du' .$$

It is not actually necessary to know what f(u) is, since it is sufficient to express the answer in terms of N and the mean square velocity:

$$\int_0^\infty f(u) du = \int_0^\infty f(u') du' = N,$$

$$\int_0^\infty u^2 f(u) du = \int_0^\infty u'^2 f(u') du' = N \overline{u^2}.$$

Hence

$$A = (\pi m\sigma^3/3v) N^2 \overline{u^2}$$

and using the virial theorem we find for the equation of state

$$pv = (mN/3) \overline{u^2} (1 - b/v)^{-1}, \tag{13}$$

where b has the same meaning as in van der Waals's equation. Equation (13) agrees with Eq. (12) to first order in (b/v), if we set a = 0 (no attractive forces).

In order to calculate the contribution to the pressure of forces which are continuous functions of the distance, it is necessary to know something about the spatial distribution of molecules in the gas; Poisson's static model is clearly inadequate if the forces become strong when two molecules get close to each other. The required formula is of course the Maxwell-Boltzmann distribution law,[26] which states that the relative probability of a molecular configuration with potential energy V is $e^{-V/kT}$ (T = absolute temperature in °K and k = Boltzmann's constant). For the calculation of the second virial coefficient it is sufficiently accurate to assume that this formula can be applied to a pair of molecules, neglecting their interactions with other molecules in the gas.

This method was used by Boltzmann[27] to calculate the second virial coefficient for molecules interacting with a force law $f(r) = Kr^{-5}$ (Maxwellian molecules). The potential energy V(r) is then $\int_r^\infty f(r)dr = K/4r^4$, and the contribution to the virial is

$$\sum rf(r) = 3NB = (2\pi N^2/v) \int_0^\infty r^3 f(r) e^{-V(r)/kT}\, dr \qquad (14)$$

$$= (2\pi N^2 K/v) \int_0^\infty r^{-2}\, e^{-K/4r^4 kT}\, dr.$$

Evaluating the integral, Boltzmann obtained the result

$$pv = RT(1 + B/v) = RT(1 + a(N/v)(K/kT)^{3/4})$$

where a is a constant which has the value (not given explicitly by Boltzmann) of $(\pi/3\sqrt{2})\ \Gamma(1/4)$.[28]

Equation (14) is in principle the solution of the problem considered in this paper, in the sense that it permits one to calculate the first-order correction to the ideal gas law whenever the force law is given -- provided the integral converges. (The method does not work, for example, when the force is a Coulomb attraction, $V(r) = e^2/r$, and therefore ionized gases cannot be described in this way.) There is also a clearly defined procedure for calculating higher virial coefficients, even though the calculation may not be practical for most force laws. The main practical difference between Boltzmann's method and Ritter's method is that the former gives a temperature-dependent virial coefficient, so that by comparing theoretical formulae with observations one can obtain information about the force law which operates.

We conclude this account by giving Keesom's calculation of the second virial coefficient for the Sutherland model, which illustrates the procedure for a "realistic" potential. The integral is a sum of two terms,[29]

$$B = (N/2)\left\{e^{\mu/kT}(4\pi\sigma^3/3) + (1/kT)\int_{\sigma}^{\infty} e^{-V(r)/kT}(dV(r)/dr)(4\pi r^3/3)dr\right\} ;$$

the first term is the "collision virial," Lorentz's value multiplied by $e^{-\mu/kT}$ where $\mu = -V(\sigma)$.[30] The second integral may be evaluated at high temperatures by expanding the exponential function; for $V(r) = -cr^{-n}$ $(n > 3)$ Keesom obtained

$$B = \frac{2\pi N\sigma^3}{3}\left\{1 - \frac{3}{n-3}\left(\frac{\mu}{kT}\right) - \frac{1}{2!}\,\frac{3}{2n-3}\left(\frac{\mu}{kT}\right)^2 - \frac{1}{3!}\,\frac{3}{3n-3}\left(\frac{\mu}{kT}\right)^3 + \dots\right\}$$

where $\mu = c\sigma^{-n}$. Other calculations are discussed in the treatise by Hirschfelder et al.[31]

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FOOTNOTES

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