The van der Waals Fluid: A Renaissance

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The search for equations of state capable of describing accurately the properties of liquids and dense gases has been long and extensive. The literature abounds with examples of equations of widely varying complexity and having from two to eight disposable parameters. That this should be so is an inevitable consequence of the need of chemists and chemical engineers for a reliable basis for the calculation of thermodynamic data of great economic importance. It is, however, unfortunate that in some cases the desire to improve agreement with experimental data has rendered the physical basis of the equations less clear. Recent theoretical developments in the theory of dense fluids have shown the importance of a firm physical basis and have, perhaps surprisingly, led to a revival of interest in one of the oldest and surely the best known of such models, that of van der Waals.

The appearance, in 1873, of the dissertation 'On the continuity of the gas and liquid phases' by J. D. van der Waals[1] in which the equation of state

$$[P + a(N/V)^2][V - Nb] = NkT \tag{1}$$

was introduced provoked considerable discussion amongst such distinguished scientists as Maxwell and Lord Rayleigh.[2] The columns of 'Nature' in the following two decades carried several letters in which the merits and basis of the equation were discussed. This was perhaps not surprising for it has been remarked, 'the results of van der Waals do not appear to be due to any exact mathematical development of his physical ideas, but rather, as some German writers have commented, to inspiration.'[3] The resort to inspiration was not universally acceptable as may be seen from Maxwell's review of the dissertation.[4]

It was, however, a necessary procedure in view of the complexity of the problem, and in the light of contemporary knowledge. Before considering the nature of van der Waals' approach it will be useful to consider in general terms the basic difficulties involved in any attempt to describe the properties of matter in terms of molecular behaviour.

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[1] J. D. van der Waals, Dissertation, Leiden 1873; English translation, Threlfall and Adair, *Physical Memoirs*, 1890, **1**, 333.

[2] An extensive list of references may be found in J. R. Partington, 'An Advanced Treatise on Physical Chemistry', Longmans, Green and Co., London, 1949, vol. 1, 660.

[3] F. G. Keyes and W. A. Felsing, *J. Amer. Chem. Soc.*, 1919, **41**, 589.

[4] J. C. Maxwell, *Nature*, 1874, **10**, 477.

1 Intermolecular Forces and Structure

There are two essentially different aspects of this problem which must be considered. In the first place, the nature of intermolecular interactions must be understood. For an isolated pair of spherically symmetric molecules the intermolecular potential energy is a function of the separation of the molecular centres which may be represented as u(r), and has the approximate form illustrated in Figure 1. For non-spherical molecules the potential energy depends also on the relative orientation of the molecules, but this discussion will not be concerned with such cases. The *forces* between the molecules may be obtained from the gradient of the potential energy curve, and we see from Figure 1 that for small separations the forces are repulsive, and for larger separations they are attractive.

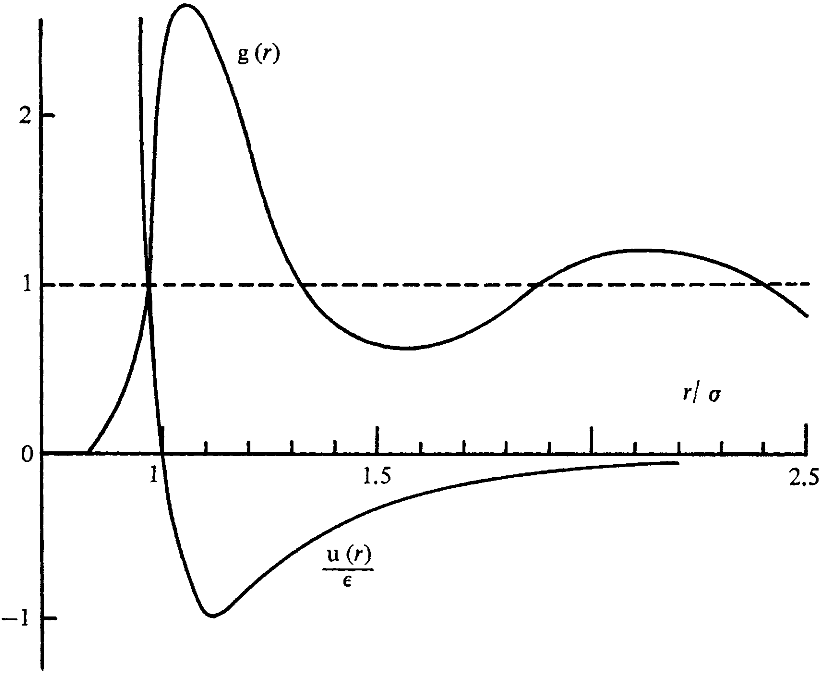

Figure 1 *An intermolecular pair potential energy function,* u(r), *and a typical liquid radial distribution function* g(r)

Information about the pair potential curve may be derived from studies of the properties of dilute gases, although it is not in general possible to obtain the potential curve directly in this way. When studying the properties of solids, liquids, or dense gases it is often necessary to calculate the potential energy associated with several molecules which are simultaneously close together. A fairly accurate estimate may be obtained by assuming that the total energy of such an assembly is equal to the sum of the energies of each pair of molecules.

One consequence of using this approximation is that a pair potential energy function which gives satisfactory results for dense matter may not yield good results when applied to dilute gas properties. In particular, the Lennard-Jones 12—6 potential function

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

where $u(\sigma) = 0$ and ϵ is the depth of the potential well, appears to give rise to a satisfactory description of the liquid inert gases but is not appropriate to the dilute gas properties.

The second problem which must be overcome is that of relating the bulk properties of a system to the properties of the constituent molecules. For this we use the methods of statistical mechanics. In general, we may calculate the thermodynamic properties of a system provided that we know both the appropriate potential energy function and the structure of the system.[5] It is a fairly easy matter to visualise the nature of a solid or dilute gas, but the liquid and dense gas states differ from these cases in that no simple model is available to describe their structures. Although the density of a liquid may approach that of a solid, the molecules are not localised and there is no regular lattice. The structure of a liquid or dense gas is best described in terms of molecular distribution functions, the most important of which, the pair distribution function, $g(r)$, defines the number density of molecular centres at a distance r from the centre of a given molecule. When N molecules are present in a total volume, V, the number of molecular centres in a volume element of size $4\pi r^2 dr$ at a distance r from the reference molecule is defined as $4\pi r^2(N/V)g(r)dr$, and the total number of molecular pairs separated by a distance r is then given by $4\pi r^2 N^2 g(r)dr/2V$. The mean number density of the fluid is N/V and $g(r)$, which is in general a function of both temperature and density, thus defines the microscopic deviations from the mean density due to the presence of neighbouring molecules. Values of $g(r)$ may be obtained experimentally from X-ray diffraction studies. A typical pair distribution function for a liquid is shown in Figure 1. It is seen that at separations less than the collision diameter, σ, $g(r)$ is very small. This is due to the effect of repulsive intermolecular forces, which effectively prevent molecules from approaching to very short distances. At slightly greater values of r the distribution function rises to a maximum which indicates that the likelihood of finding a molecule at these separations is considerably greater (two or three times) than would be expected on the basis of a completely uniform distribution [for which $g(r) = 1$]. At still greater separations, the value of $g(r)$ stays fairly close to the value of 1 appropriate to a uniform distribution, although small oscillations (which decrease with increasing r) occur as a result chiefly of packing requirements in the second and subsequent shells of neighbours. This overall situation is commonly summarised in the statement that liquids possess short-range order combined with long-range disorder, and it is this combination which causes considerable difficulty in the description of the liquid state.

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[5] J. S. Rowlinson, 'The Structure of Liquids' in 'Essays in Chemistry', ed. J. N. Bradley, Academic Press, London, 1970, **1**, 1.

If the pair distribution function is known, a rather obvious route to some of the bulk thermodynamic properties is available. Since the distribution function enables us to calculate the number of molecular pairs having a given separation, *r*, then knowing the potential energy function u(*r*) the calculation of that part of the internal energy which is derived from the intermolecular forces follows directly.

$$U' = \frac{N^2}{2V}\int_0^\infty 4\pi r^2 \mathrm{g}(r)\,.\,\mathrm{u}(r)\mathrm{d}r \qquad (3)$$

For monatomic systems, the total internal energy is the sum of U' (the configurational internal energy) and the ideal gas translational energy.

$$U = U' + 3\,NkT/2 \qquad (4)$$

The calculation of the pressure is less readily performed. It may be carried out by the use of a rigorous theorem, the virial theorem, developed in 1870 by Clausius, by means of which the average kinetic energy of a system may be related to its average potential energy. Using this theorem the following equation may be derived.

$$PV = NkT - \frac{N^2}{6V}\int_0^\infty 4\pi r^2 \mathrm{g}(r) r\frac{\mathrm{du}}{\mathrm{d}r}\,.\,\mathrm{d}r \qquad (5)$$

It is evident that if the intermolecular force, $-\mathrm{du}/\mathrm{d}r$, is zero for all values of *r* the ideal gas equation of state is recovered. The last term in equation (5) thus represents the corrections to the ideal gas equation resulting from intermolecular forces. It is possible to establish the overall effect of these forces by considering the deviations from ideal gas behaviour. For gases at low to moderate pressures and at temperatures below the Boyle temperature, the observed values of *PV* are less than *NkT*, and the predominant interaction between the molecules is thus an attractive force. In liquids, *PV* exceeds *NkT*, and the more important factor in this case is seen to be the repulsive forces.

2 The van der Waals Model

At the time of van der Waals' original work, little was known of the details of either the structure of liquids or of intermolecular forces. The formal relationship between the pressure and intermolecular forces had just been derived, but the information needed to make even a semi-quantitative evaluation of the terms involved was not available. The essence of van der Waals' derivation was thus the introduction of judicious approximations based on a physically reasonable model.

The most important approximation introduced was the separation of the effects of intermolecular repulsion and attraction. van der Waals believed that there were two essentially distinct corrections to the ideal gas laws, one resulting from the tendency of molecules to attract one another at moderate separations, and the other a consequence of the finite size of the molecules, associated with the short-range repulsive forces. He made the additional important assumption that the net force on a molecule in the body of a dense fluid resulting from the summed attractions of all its neighbours was zero. Thus, although the potential energy of the molecule was lowered as a result of the intermolecular energy, the overall potential field in which the molecule moved was regarded as essentially uniform. Since there were no potential gradients, the resultant force was zero. However, when a molecule was close to the walls of the containing vessel, its neighbours could no longer be symmetrically disposed about it, and the molecule was subjected to a resultant force directed away from the wall. The velocity of the molecule as it approached the wall was therefore reduced to a value somewhat less than its simple kinetic theory value, and the observed pressure was therefore less than the ideal gas value. van der Waals estimated the correction in a manner described by Maxwell[4] as 'ingenious and on the whole satisfactory' and suggested that the term $P + a(N/V)^2$ should replace the pressure in the ideal gas equation of state. The empirical constant a was a measure of the strength of the attractive forces and was assumed to be independent of temperature. van der Waals treated the repulsive forces by considering each molecule to have a hard core of diameter σ, so that it was not possible for the centres of a pair of molecules to approach to a distance less than σ. Thus each molecule was surrounded by a sphere of radius σ from which the centres of all other molecules were excluded. van der Waals attempted to calculate the extent to which the total volume V available to the molecular centres was reduced in this way, and concluded that the available volume was $V - Nb$, where $b = 2\pi\sigma^3/3$, four times the volume of a hard core. He admitted that this was an approximation, valid only at low densities. Replacing the total volume by this estimate of the available volume, we obtain van der Waals' equation of state in its familiar form

$$[P + a(N/V)^2]\,[V - Nb] = NkT \tag{6}$$

which may be written alternatively

$$P = \frac{NkT}{V - Nb} - a\left(\frac{N}{V}\right)^2 \tag{7}$$

in which the effect of each correction term on the pressure is more clearly shown.

A. The Generalised van der Waals Equations.—It is important to recognise that the van der Waals equation is just one of a general class of equations of state[3] which may be represented

$$P = \frac{NkT}{V}\beta\left(\frac{N}{V}\right) - \alpha\left(\frac{N}{V}\right) \tag{8}$$

where β and α are functions of the density, N/V, but are temperature independent. We shall describe equations of this type as generalised van der Waals equations. The function β represents the effects of molecular size and α relates to the effects of intermolecular attraction. The specific van der Waals form is obtained by the use of the approximate relations

$$\beta = \frac{V}{V - Nb} \text{ and } \alpha = a\left(\frac{N}{V}\right)^2 \tag{9}$$

We must distinguish between results following from the general form of equation (8) and those dependent on particular choices for the functions α and β.

An interesting comparison may be made between equation (8) and the thermodynamic equation of state

$$P = T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}} - \left(\frac{\partial U}{\partial V}\right)_{\mathrm{T}} \tag{10}$$

It is immediately seen that the generalised van der Waals equation requires that the thermal pressure coefficient, $\left(\frac{\partial P}{\partial T}\right)_{\mathrm{V}}$, be a function only of the molar volume, and consequently that at constant volume the pressure should increase linearly with temperature. For a wide range of liquids the observed behaviour closely approximates to this.[6]

Perhaps the most important consequence of equation (8) is that the entropy is determined solely by the term $\beta(N/V)$ and is thus governed only by considerations of molecular size. The structure, and hence the disorder, of the fluid is therefore independent of the attractive forces, and is identical with that of a system of molecules having the same repulsive forces, but no intermolecular attraction. This result is fundamental to the generalised van der Waals equations and greatly simplifies the treatment of attractive forces. If the structure due to repulsive interactions can be determined, the thermodynamic properties of any fluid with an arbitrary attractive potential, $\mathrm{u}(r)$, may be readily calculated. Defining properties of the fluid without attractive forces by the superscript $^{\mathrm{o}}$, we may write

$$U = U^{\mathrm{o}} + \frac{N^2}{2V}\int_0^\infty 4\pi r^2 \mathrm{g}^{\mathrm{o}}(r) \,.\, \mathrm{u}(r)\mathrm{d}r \tag{11}$$

and since $S = S^{\mathrm{o}}$, the Helmholtz free energy is given by

$$A = A^{\mathrm{o}} + \frac{N^2}{2V}\int_0^\infty 4\pi r^2 \mathrm{g}^{\mathrm{o}}(r)\, \mathrm{u}(r)\mathrm{d}r \tag{12}$$

If, following van der Waals, we associate the fluid without attractive forces with the hard sphere fluid, these equations permit us to calculate the properties of any fluid provided the distribution function for hard sphere systems is known.

B. Comparison with Experimental Data.—As is well known the original van der Waals equation gives a qualitatively correct description of the critical properties of fluids. The critical properties may be expressed in terms of the constants *a*

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[6] J. S. Rowlinson, 'Liquids and Liquid Mixtures', Butterworths Scientific Publications, London, 2nd edn., 1969.

and b of equations (6) and (7), and experimental values of two of the critical temperature, pressure, and volume may be used to derive characteristic values of these constants for specific substances. Below the critical temperature the van der Waals isotherms do not have the experimentally observed horizontal portion in the two-phase region, but are sinuous curves. These may be reinterpreted using the equal areas rule of Maxwell. A horizontal line is drawn intersecting the isotherm at three points and defining regions of equal area above and below the line. The extreme intersections correspond to liquid and vapour states of equal free energy and the modified isotherms then give a description of a liquid in equilibrium with its vapour. To this extent it may be said that van der Waals achieved his objective. However, a closer study of the predicted critical behaviour shows considerable disagreement with the experimental results. In particular, the form of the critical isotherm and of the coexistence curve near to the critical point are badly at variance with the data. This disagreement appears to be of a fundamental nature, and recent theoretical studies[7] have shown that correlations resulting from short-range attractive forces are of major importance in determining properties in the critical region. The van der Waals model, with its assumption of a uniform attractive potential field, cannot reproduce this behaviour correctly.

The use of van der Waals equation to calculate PVT data for simple systems leads to results which are qualitatively in agreement with experimental values, but which are inadequate for accurate work. One important factor is that the pressure calculated from equation (7) is the difference of two terms of similar size and a relatively small error in either term may have a large effect on the final result. This cancellation does not always occur in the estimation of other properties, such as the internal energy, for which the van der Waals theory is generally much more accurate. One apparently gross inadequacy of van der Waals equation is its failure to predict the existence of a solid phase. It is true that van der Waals was not attempting to account for the solid, but it does not seem an unreasonable expectation if the physical basis of the equation is sound.

The origins of these discrepancies may best be investigated by considering separately the approximations used for the functions α and β of equation (9). The van der Waals approximation for α implies that the configurational energy of the fluid is a linear function of the density and is independent of temperature. Experimental values of the configurational energy of liquid argon may be obtained from known thermodynamic data, and reveal that this approximation is remarkably accurate. The only significant deviations occur near to the critical point. For other substances the detailed data needed for the calculation are not available. However, values of the van der Waals 'constant' a may be derived for a number of simple liquids. From equations (8), (9), and (10) we see that

$$a = \left(\frac{V}{N}\right)^2 \left(\frac{\partial U}{\partial V}\right)_T \tag{13}$$

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[7] B. Widom, *Science*, 1967, **157**, 375.

For several simple liquids the values of a calculated using equation (13) and known experimental data are found to vary only slightly over the whole liquid range.[6] These results suggest that the approximation for α is quite accurate and that the use of refined versions cannot be expected to improve significantly the overall quality of the equation of state. The function β describes the behaviour of molecules which have finite size but no attractive forces. They are thus regarded as hard spheres, and the equation

$$\frac{PV}{NkT} = \frac{V}{V - Nb} \tag{14}$$

should reproduce the hard-sphere equation of state. Although the hard-sphere model is not a very realistic physical model for real molecules it has been extensively studied in the development of theories of fluids, and the equation of state is well established. Equation (14) is not a good approximation to the true equation of state at other than very low densities. The explanation of this failure is that the excluded volume is not simply proportional to the number of molecules in a given volume. The true excluded volume is less than the van der Waals value, because the 'excluded volume per molecule' relates to the exclusion of a molecular centre, and it is possible for the excluded volumes to overlap to a certain extent, in such a way that the volume excluded by a pair of molecules which are close together is less than the sum of the two separate excluded volumes per molecule. The van der Waals approximation thus overestimates the size of the correction for the molecular size, and the pressures calculated from equation (14) are greater than the true values. The exact hard-sphere equation of state is compared with the van der Waals form in Figure 2, and it is seen that although the approximate form is correct at low densities it is badly in error at higher densities, and indeed gives rise to an infinite pressure at about one-third of the close packed density. It is largely in the treatment of the effects of molecular size that the van der Waals equation is inadequate, and we shall now consider in more detail the properties of the hard-sphere fluid.

3 The Hard-sphere Fluid

A great deal of work has been done in the past thirty years on the development of theories of fluids expressed in terms of distribution functions. These theories provide a complete formal basis for the description of the liquid state, but it is not possible to calculate the values of the distribution functions from first principles. In order to obtain values of $g(r)$ it is necessary to introduce approximations into the theory. Much effort has been expended in attempts to devise satisfactory approximations, but in no case have completely satisfactory solutions been obtained. In order to test the various approximations, it is desirable to compare the theoretical results with those found experimentally from X-ray diffraction studies. However, a direct comparison is not simple, since a knowledge of the pair potential energy function is a prerequisite for the calculation of distribution functions and our present knowledge of these functions is incomplete. To some extent these problems may be overcome by the use of

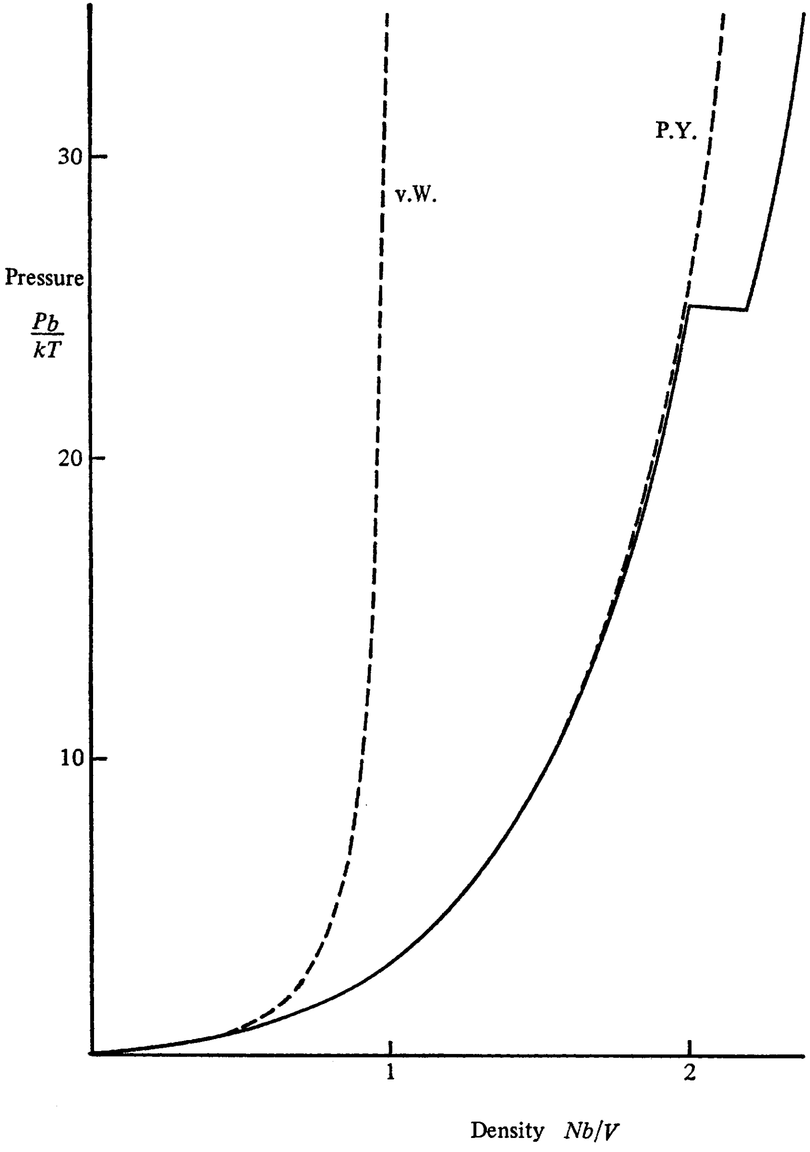

Figure 2 *The hard-sphere equation of state. The solid curve shows the results of computer studies and includes the solid–fluid phase transition. The dashed curves show the approximate equations of state based on the van der Waals (equation* 14) *and Percus–Yevick (equation* 15) *approximations*

simulation studies. By use of the Monte Carlo and Molecular Dynamics methods with fast electronic computers,[8] it is possible to study the behaviour of an imaginary model fluid in which the potential energy function is specified by the investigator. The results obtained are essentially exact, and are commonly regarded as pseudo-experimental data for the purpose of comparison with theory. Because of the considerable simplifications afforded by its use, the hard sphere model has been very extensively studied in this way, and the equation of state has been firmly established. The most striking result of these simulation studies was the discovery[9] that at certain densities the system may exist in two different states, one of which has the long-range order characteristic of a solid, and the other, which is associated with a higher pressure, having no long-range order. The latter is believed to correspond to a metastable fluid state, and the phenomenon is thought to be associated with a solid–fluid phase transition. Considerations of molecular size, without any attractive forces, thus lead to the existence of two states of matter.

Some pair distribution functions have been derived from simulation studies, and may be compared with the predictions of the various approximate theories. In general however, comparisons have been made with the calculated equation of state, which is determined (for hard-sphere systems only) by the value of the pair distribution function at the point of contact, g(σ). One theory in particular has been found to yield good solutions for the hard-sphere systems over the whole liquid range. This theory, due to Percus and Yevick,[10] leads to an equation of state which may be written in the form

$$\frac{PV}{NkT} = \frac{1 + \xi + \xi^2}{(1 - \xi)^3} \text{ where } \xi = \frac{Nb}{4V} \tag{15}$$

However, it does not predict the observed phase transition, and its application to systems having more realistic pair potentials is often difficult.

It is now possible to replace the approximate hard-sphere term in the van der Waals equation by the exact result. Since the hard-sphere system can exist in both solid and fluid forms, and the simple van der Waals theory shows both the liquid and gaseous phases, this corrected equation may reasonably be expected to show the existence of all three possible states of matter, and this expectation is realised. One major failure of the van der Waals equation is therefore removed, and is shown to be a consequence of the inaccurate description of the hard-sphere equation of state.

4 Perturbation Theory

We may now consider also the re-derivation of the term describing the effects of the attractive forces. van der Waals made the assumption that the distribution of the molecules was uniform, *i.e.*, that $g(r) = 1$ for all $r > \sigma$. It is evident from Figure 1 that this is not a good approximation for values of r between

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[8] M. A. D. Fluendy and E. B. Smith, *Quart. Rev.*, 1962, **16**, 241.

[9] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1960, **33**, 1439.

[10] J. K. Percus and G. J. Yevick, *Phys. Rev.*, 1958, **110**, 1.

about σ and 2σ, although it becomes better for larger separations. The van der Waals arguments will lead to a good approximation if the potential function is long ranged. In this case, the bulk of the configurational energy will arise from interactions between molecules which are far apart, and for which $g(r) \simeq 1$. Indeed it has been shown by rigorous methods[11] that the van der Waals attractive term will arise as an exact result in the case of molecules which consist of a hard core together with an attractive energy term of infinite range and vanishingly small magnitude.

However, we know that these conditions are not satisfied for real molecules and are led to consider an alternative approach to the problem. Zwanzig[12] showed that the hard-sphere fluid may be used as the basis of a perturbation expansion, the physical basis of which is that of the generalised van der Waals equation, namely that the geometrical distribution of real molecules is determined by the repulsive intermolecular forces and may be regarded as identical to that of a hard-sphere fluid of a suitably chosen density. The attractive forces act as a source of internal energy which maintains the high density of the liquid, but do not otherwise significantly affect the distribution of the molecules.

The first-order perturbation theory leads to equation (12), when $g^0(r)$ is the pair distribution function of the hard sphere system and $u(r)$ is the difference between the potential energy function of the perturbed system and the hard-sphere potential. It is possible to write formal expressions for the second-order perturbation contributions, but these involve higher order distribution functions about which very little is known. If only the first-order term is obtained the perturbation theory has the characteristics of the generalised van der Waals equation mentioned earlier. The neglect of higher order perturbation terms may be shown to be formally acceptable at high temperatures, and early applications of the theory were concerned with the development of a high-temperature equation of state for dense gases.

We have not so far considered the basis for the selection of the hard-sphere diameter. Since this value determines both the hard-sphere contribution to the pressure and also the size of the correction terms, it is evident that a reliable basis for its estimation is essential. It is possible to make a qualitative assessment of the hard-sphere diameter on the basis of simple physical arguments. The true pair potential rises rapidly as the separation of a pair of molecules is decreased from the collision diameter σ. The hard-sphere potential becomes infinite for pair separations less than its collision diameter, and such a situation has zero probability. In real systems, the molecules may approach to separations less than σ and their closest distance of approach will be reached when the potential energy is equal to the kinetic energy which was possessed at large separations. At higher temperatures the average kinetic energy is higher, and the average value of the distance of closest approach would be expected to be smaller. The effective hard-sphere diameter would thus be expected to decrease with rise in temperature.

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[11] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.*, 1963, **4**, 216.

[12] R. W. Zwanzig, *J. Chem. Phys.*, 1954, **22**, 1420.

In the earlier calculations[13] made using the first-order perturbation theory a rather arbitrary choice of hard-sphere diameter was made. Although the emphasis in this work was on the development of a high-temperature equation of state for gases, the use of a Lennard-Jones 12—6 potential as the perturbing potential led to a reasonably good estimation of the critical temperature of the inert gases. The hard-sphere distribution functions used in this work were calculated from exact analytic expressions appropriate only to fairly low densities. With the development of the Percus–Yevick approximation reliable estimates of the hard-sphere distribution functions over a wide density range became available, and further calculations[14] were made, again using the 12—6 potential. These calculations revealed the great sensitivity of the theory to the choice of the hard-sphere diameter, but after some slight adjustment of parameters, an equation of state was developed which was in good agreement with the data for gaseous argon at high densities.

The applicability of the perturbation theory to liquids was demonstrated by Smith,[15] who pointed out that the experimental data for many liquids were consistent with an equation of state of the form of equation (8) and showed that the function β could be derived from experimental thermal pressure coefficients and agreed closely with the hard-sphere equation of state.

The most successful extension of the perturbation theories has been due to Barker and Henderson,[16] who have considered both the choice of hard-sphere diameters and the development of approximate methods for the estimation of the second-order perturbation term. By a suitable definition of the perturbing intermolecular potential, these authors were able to develop a theory which dealt separately with the attractive forces and the slightly soft nature of the repulsive energy. The treatment of the repulsive forces was based on a method due to Rowlinson,[17] and provided a means of defining an effective hard-sphere diameter which was independent of density and decreased with increasing temperature. The first-order correction for the attractive forces was essentially that of Zwanzig, and in addition Barker and Henderson were able to approximate the second-order attractive term using accessible functions. By use of this theory, the equation of state was calculated for the Lennard-Jones potential, and the results compared with those obtained from Monte Carlo and Molecular Dynamics studies. These are shown in Figure 3. The agreement is seen to be excellent over a wide range of temperature and density, and this success may be seen as a strong justification of the basic validity of the approach. It seems that the effect of neglecting the higher order terms is negligible, except perhaps at the lowest temperature shown, which corresponds roughly to the triple point temperature of the inert gases. The critical constants obtained from this model are in excellent agreement with those obtained from computer studies. In addition,

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[13] E. B. Smith and B. J. Alder, *J. Chem. Phys.*, 1959, **30**, 1190.

[14] H. L. Frisch, J. L. Katz, E. Praestgaard, and J. L. Lebowitz, *J. Phys. Chem.*, 1966, **70**, 2016.

[15] E. B. Smith, *J. Chem. Phys.*, 1962, **36**, 1404.

[16] J. A. Barker and D. Henderson, *J. Chem. Educ.*, 1968, **45**, 2; J. A. Barker and D. Henderson, *J. Chem. Phys.*, 1967, **47**, 4714.

[17] J. S. Rowlinson, *Mol. Phys.*, 1964, **8**, 107.

the densities and pressures of the coexisting gas and liquid phases were calculated using the Maxwell equal area rule, and the derived coexistence and vapour pressure curves were found to be in good agreement with the experimental data

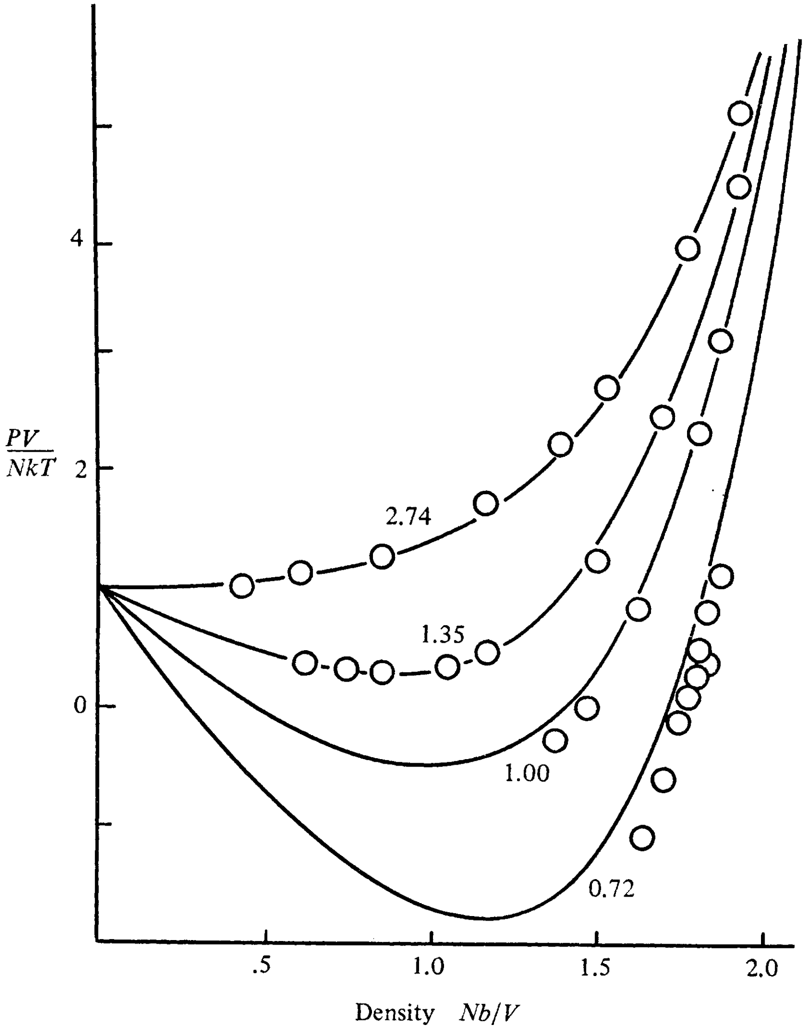

Figure 3 *The equation of state of a fluid of Lennard-Jones molecules. The compressibility factor,* PV/NkT, *is shown as a function of the density at four values of the reduced temperature* kT/ε. *The curves are based on the perturbation theory and are labelled with the value of the reduced temperature. The critical isotherm corresponds to a reduced temperature of ca.* 1·35. *The points show the results of computer calculations.* (W. W. Wood and F. R. Parker, *J. Chem. Phys.*, 1957, **27**, 720; I. R. Macdonald and K. Singer, *Discuss. Faraday Soc.*, 1967, **43**, 40; L. Verlet, *Phys. Rev.*, 1967, **159**, 98.)

for argon. We should note that this appears to be the first theory of liquids capable of describing the vapour pressure curve correctly, and may infer from this that the approach leads to an accurate description of the entropy of a liquid.

5 Applications of the van der Waals Concepts

It would be inappropriate to describe in detail the numerous applications of the van der Waals model. Instead three examples have been selected which emphasise the basic simplicity of this approach and the insight which it can provide.

A. Phase Changes.—The identification of the entropy of a fluid with that of an appropriately chosen hard-sphere system provides a simple basis for calculating entropies of vaporisation and fusion. For example, the entropy of vaporisation of a fluid at the normal boiling point is equal to the difference between the entropy of the hard-sphere gas at one atmosphere pressure and that of the hard-sphere fluid at the liquid molar volume. This difference may be readily calculated if the hard-sphere equation of state is known. Yosim and Owens[18] used the hard-sphere equation of state of equation (15) and took values of the collision diameters derived from studies of dilute gas properties. They were then able to calculate entropies of vaporisation for a large number of non-ionic liquids and obtained results which were in very good agreement with the experimental values in almost all cases. These authors also applied a similar approach to the calculation of entropies of fusion of the inert gases, and obtained results in fair agreement with experiment.

An alternative approach to melting phenomena was investigated by Widom and Longuet-Higgins,[19] who used a generalised van der Waals equation consisting of the exact hard-sphere results, including the solid–fluid phase transition, and the original form of the function α.

$$\frac{PV}{NkT} = \left(\frac{PV}{NkT}\right)_{\text{hard sphere}} - \frac{a}{kT}\left(\frac{N}{V}\right) \tag{16}$$

The use of this equation leads to isotherms which have a zig-zag portion in the density region near the hard-sphere melting transition. These may be reinterpreted using the Maxwell equal area rule and the equation then describes the temperature dependence of the melting density for a system of hard spheres immersed in a uniform potential field. Widom and Longuet-Higgins were able to establish the value of a/kT corresponding to the triple point, by using the criterion that the activities of the solid, liquid, and gas phases should be equal. They then evaluated such properties as the ratio of the liquid and solid molar volumes and the entropy of fusion at the triple point, and obtained values in good agreement with the experimental data for argon. These calculations were made without the introduction of any arbitrary parameters, and the success of this approach gives a striking confirmation of the validity of the physical model.

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[18] S. J. Yosim and B. B. Owens, *J. Chem. Phys.*, 1963, **39**, 2222.
[19] H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, 1964, **8**, 549.

B. Thermodynamic Properties of Mixtures.—Until recently the study of liquid mixtures has been dominated by a number of related theories which were based on the assumption that the distribution of different types of molecule within the liquid was random. The possibility of preferential packing arrangements resulting from differences in the intermolecular forces associated with the various types of pair interactions were neglected in the simplest forms of these theories. Although they have been successfully applied to simple mixtures of components similar in molecular size, the application of these theories to mixtures in which there is a large size difference has not proved satisfactory. In such cases large positive values of the excess free energy G^E are predicted, and these are not observed experimentally. Mixture theories based on the van der Waals concepts have proved much better able to take account of the effects of size differences and seem likely to provide the basis for future work in this field.

The van der Waals picture of a liquid mixture is again based on the assumption that the structure is determined largely by the repulsive intermolecular forces and may be closely approximated by the use of a hard-sphere model. However, the different species in a mixture will in general have different repulsive forces and will be represented by hard spheres of different sizes. The overall picture is thus of a hard-sphere mixture immersed in a uniform field due to the attractive intermolecular forces.

There have been several computer studies[20] of the properties of hard-sphere mixtures and the Percus–Yevick theory has also been successfully applied to these systems.[21] Calculations of the thermodynamic mixing functions[22] have shown that hard spheres mix at constant pressure with a small decrease in volume and a small negative excess free energy G^E. The decrease in volume occurs because it is possible to pack spheres of different sizes more efficiently than those of a single size, and the structure of the mixture is therefore rather different from that of a pure hard-sphere fluid. The van der Waals theory suggests that this structural change will also occur when real molecules are mixed and it now appears that it was the failure of earlier theories to take account of this effect which was responsible for their inability to describe mixtures whose components differed significantly in size.

Two different methods of applying the van der Waals model to mixtures have been described. Snider and Herrington[23] used a generalised form of equation (16) to describe the equation of state of a mixture. Leland, Rowlinson, and Sather[24] avoided the choice of an explicit equation of state by using an approach based on the principle of corresponding states which gave accurate results when applied to hard sphere mixtures. In both cases the calculated values of the thermodynamic properties of simple binary mixtures were in considerably better agreement with the experimental data than those based on earlier theories.

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[20] E. B. Smith and K. R. Lee, *Trans. Faraday Soc.*, 1963, **59**, 1535; B. J. Alder, *J. Chem. Phys.*, 1964, **40**, 2724.

[21] J. L. Lebowitz, *Phys. Rev.*, 1964, **133**, A895.

[22] J. L. Lebowitz and J. S. Rowlinson, *J. Chem. Phys.*, 1964, **41**, 133.

[23] N. S. Snider and T. M. Herrington, *J. Chem. Phys.*, 1967, **47**, 2248.

[24] T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.*, 1968, **64**, 1447.

C. Transport Properties of Dense Gases and Liquids.—Although the dilute gas transport properties of simple substances may generally be calculated, the extension to higher densities is very complex, owing to the possibility of many-body collisions. For hard spheres this problem does not arise since the potential is not long ranged and the theoretical treatment is less difficult. Enskog[25] developed an approximate theory in which it was assumed that a dense hard-sphere system behaves like a dilute hard-sphere system, with the modification that the collision rate is higher in the dense system. If the ratio of the collision rate at high density to that at low density is Y, the Enskog theory gives values of the transport properties of the dense hard-sphere fluids in terms of their low density values and the factor Y. Values of Y may be obtained from the hard-sphere equation of state and the transport properties of dense hard-sphere systems may then be calculated, using the known results for the low density coefficients.

The extension of these results to real molecules is based on the van der Waals concept of a uniform potential field in dense fluids. If this were exact, molecules would travel in straight lines between collisions. Although this is undoubtedly an approximation the successful application of the van der Waals model to equilibrium properties has suggested that the true situation is probably close to this. In order to use the Enskog equations for real systems, effective hard-sphere diameters for the molecules are needed. Dymond and Alder[26] obtained these from experimental compressibility data and calculated the coefficients of viscosity and thermal conductivity for the heavier inert gases at several temperatures and densities above the critical, obtaining results in good agreement with the available experimental data.

This approach has also been successfully applied to the calculation of the viscosity of liquid mixtures of argon and krypton[27] and to the study of gaseous diffusion in liquids.[28]

6 Conclusion

Almost a century has passed since the van der Waals equation of state was first proposed. After a period in which it was extensively used in early studies of phase equilibria and the properties of liquid mixtures it passed into disuse as its inadequacies were revealed. Only in recent years has it become apparent that these were due to an inadequate treatment of the physical model on which the equation was based rather than to weaknesses in the model itself. There is now much evidence that the structure of a liquid or dense gas is determined almost entirely by repulsive intermolecular forces and may be accurately reproduced by the use of a hard-sphere model. The attractive intermolecular forces give rise to an essentially uniform potential field and maintain the high density. Equations of state which accurately embody this picture of a liquid have proved remarkably

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[25] See S. Chapman and T. G. Cowling, 'The Mathematical Theory of Non-Uniform Gases', Cambridge University Press, Cambridge, 2nd edn.

[26] J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, 1966, **45**, 2061.

[27] N. Jhunjhunwala, J. P. Boon, H. L. Frisch, and J. L. Lebowitz, *Physica*, 1969, **41**, 536.

[28] E. McLaughlin, *J. Chem. Phys.*, 1969, **50**, 1254.

accurate and the use of this model has led to important advances in a number of fields.

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