

THE LEGACY OF VAN DER WAALS

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Abstract

The physical implications of the form and nature of the van der Waals equation of state are explained. The relation of this equation to so-called van der Waals forces and radii is discussed. The conclusion is drawn that the van der Waals equation of state is practically worthless and its use should be abandoned.

Resumen

Se explican las implicaciones físicas de la forma y la naturaleza de la ecuación de estado de van der Waals. Además, se discute la relación entre esta ecuación y las llamadas fuerzas y radios van der Waals. Se llega a la conclusión de que la ecuación de estado de van der Waals no es útil y que no debería utilizarse.

Key words: equation of state, corresponding states, intermolecular forces, weakly bound molecules, van der Waals.

Palabras claves: ecuación de estado, fuerzas intermoleculares, van der Waals.

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On the occasion in 2010 of the centenary of Johannes Diderik van der Waals (1837-1923) being awarded Nobel laureate in physics, Tang and Toennies published a paean of praise [1] that astonishingly proclaimed that Dutchman's achievement of allegedly "triggering a revolution in the understanding of the molecular physics of liquids, gases and their mixtures, and laying the foundations of modern thermodynamics and statistical mechanics". Although van der Waals might certainly have exerted a formative influence on Dutch science and scientists during his life, and is undoubtedly mildly important as an historical figure in physics, the validity of association of some concepts with his name must be challenged: that objective, a critique of his equation of state and the validity of the term 'van der Waals molecule' constitute the purpose of this essay.

Despite the cautions that from time to time appear in the literature emphasizing not to attach too great significance to conclusions drawn from its application, the van der Waals equation of state maintains a remarkably resilient position in many textbooks of general and physical chemistry. In part following Duclaux [2], we present here some considerations of this equation and its implications, after reviewing the historical development and related background.

One seeks to specify completely the state of unit quantity (one mole) of a fluid according to some characteristic equation,

$$f(p, V_m, T) = 0, \quad (1)$$

in which p = pressure, V_m = volume per mole and T = absolute temperature. According to the kinetic-molecular theory of gases, the ideal gas law,

$$p V_m / T = \text{constant} = R, \quad (2)$$

is derivable. To the extent – considerable excepting extreme conditions of pressure and temperature – that a real gas has properties resembling those of an ideal gas, this equation is useful. One pursues, however, a more accurate representation of the properties of real fluids to take account of the possibility of universal liquefaction at sufficiently small temperatures, and other deviations at large pressures. The first attempt to allow for non-ideal behaviour was made by Hirn (1867) who wrote

$$p (V_m - b) = R T, \quad (3)$$

in which b is a characteristic parameter called the covolume. In his dissertation at the University of Leyden (1873), van der Waals introduced a second correction to obtain

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$$(p + a/V_m^2)(V_m - b) = R T \quad (4)$$

The correction a/V_m^2 was intended to allow for attractive forces between molecules in the gaseous sample. Direct experimental evidence of such attractive forces between gaseous molecules had been previously obtained and recognised by Joule and Thomson (Lord Kelvin) as a result of their 'porous-plug' experiment, 1853.

Interactions of three classes – electrostatic, inductive and dispersive – arise between simple molecules at sufficiently large separations [3]; orientational factors are neglected. The Keesom interaction, an attraction that arises between two molecules of separation R each having permanent electric dipolar moment μ , has this energy,

$$E_K = - 2 \mu^4 / (4\pi \epsilon_0)^2 (3 R^6 k T) \quad (5)$$

A molecule with a permanent electric dipolar moment invariably induces an electric dipolar moment in a neighbouring non-polar molecule of polarizability α , producing an attraction known as the Debye interaction, equal to

$$E_D = - \alpha \mu^2 / (4 \pi \epsilon_0)^2 R^6 \quad (6)$$

Another interaction, which arises from fluctuating instantaneous dipoles in otherwise non-polar molecules, has the London energy,

$$E_L = - 3 I \alpha^2 / (4 \pi \epsilon_0)^4 (4 R^6) \quad (7)$$

in which the like molecules have first ionization energy I and polarizability α . All these interactions have energies that signify attraction by their negative signs, and that are of appreciable magnitude for only small separations, as indicated by the dependence R^{-6} on separation. At even smaller separations, repulsion becomes more important. These two effects are taken into account in a model function for potential energy associated with Lennard-Jones,

$$V(R) = 4 \epsilon [(\sigma/R)^{12} - (\sigma/R)^6]; \quad (8)$$

in this equation ϵ is the binding energy or depth of the well of potential energy, and σ is the distance of closest approach or molecular diameter. As force is the gradient of energy, the force of attraction has then a dependence R^{-7} appropriate to the attraction energy as R^{-6} . With this background, we proceed to explore the implications of the van der Waals equation of state.

We examine first the pressure term. The correction a/V^2 is obtainable [2] on being guided by no theory whatsoever, but merely on developing a series in negative powers of V_m and terminating with V_m^{-2} ,

$$p = R T / (V_m - b) - a / V_m^2 \quad (9)$$

What is the physical significance of a ? As expressed by Moelwyn-Hughes [4] on the basis of a dimensional argument, "the molecular model with which the equation of van der Waals is consistent is that of a system of incompressible spheres, of diameter σ , which attract each other with a force varying inversely as the fourth power of their distance apart". As we see above, the various interactions as forces that arise between non-polar or weakly polar molecules all have dependences according to R^{-7} , not R^{-4} , on separation. As attractive forces were not discovered by van der Waals, and as these forces according to his equation lack the correct dependence upon R , it consequently seems inappropriate to associate collectively the Keesom, Debye and London interactions with van der Waals. We can, for the same reason, expect correction term a/V_m^2 to yield inaccurate results of calculations. The typical quasi-derivation of this correction is, in any case, most dissatisfying, as the derivation implies that the pressure near a boundary of the gas is less than in the bulk because of unbalanced forces tending to pull back the molecule from the boundary [5]. In any real situation, the boundary is constituted of a dense material, on the surface of which there are invariably adsorbed layers of molecules of the gas providing that sufficient sample is available; in that case the pressure must increase toward the boundary, relative to the bulk gas. The adsorption of part of the gas would cause a bulk pressure decreased by comparison with an hypothetical ideal gas that were not adsorbed. This effect might perhaps be encompassed, or avoided, in an alternative derivation of the corrective term for pressure, but its presence until that achievement makes the offered derivations seem spurious.

Regarding covolume parameter b , its significance is that it represents the average forbidden molar volume [4] of molecules for which only binary collisions are important. The magnitude of b is thus four times the intrinsic volume of a mole of incompressible spheres. The circumscribed volume of a collection of close-packed spheres is, however, 1.350 times the intrinsic volume of the spheres. It is thus entirely feasible for the volume of a fluid during compression to approach, to become equal to, and then to become less than b that is almost three times the minimum attainable volume, i.e. the circumscribed volume of close-packed spheres. Under these conditions, it would be necessary to admit of negative pressures, positive and negative infinities of pressure, and even zero pressure during compression, as Duclaux has deduced [2]. van der Waals, apparently aware of the first consequence, above, of his equation, justified it by stating that a liquid

can support a negative pressure: this phenomenon has never been observed. These difficulties, and others, arise because of the nature of the subtractive correction b , the covolume, which really regresses to Hirn's formulation. A covolume is a common feature of three state equations containing two parameters, those of van der Waals, Berthelot and Dieterici. To prevent absurd consequences resulting from the covolume correction, it is merely necessary to define b to be the circumscribed volume of the close-packed collection of molecules, in which case for pressure to tend to infinity when V_m approaches b is physically acceptable. The effects of ternary collisions, which become significant at large pressures, and consequently the effects of conditions at large pressures or densities, are formally neglected in these equations of state.

The attraction of the van der Waals theory is such that the magnitudes of parameters a and b of his equation of state are considered constant, even though that at least a varies with temperature has been long known (Clausius, 1880). To test the constancy by numerical calculation is easy: Duclaux [2] presented data that indicate that both a and b for non-polar molecules dinitrogen and dioxygen vary by about a factor two for a temperature range of a similar factor up to 300 K; a and b thus vary in inverse proportion to the absolute temperature. This effect is expected as the resemblance of these gases to an hypothetical ideal gas must increase as the temperature increases far above the critical temperature. In compilations of quantities a and b for various substances, for instance in editions of standard handbooks [6], there is indication of neither the temperature for which the stated values are appropriate, nor even that a dependence on temperature exists; users are thus exposed to significant error. For instance, for dioxygen at 15 MPa and 423 K -- neither extreme conditions nor near the critical point, with standard values of a and b the correction, relative to an ideal gas, for pressure even has an incorrect sign.

As the covolume parameter is generally taken to be related to molecular size, further complications appear. According to certain questionable assumptions, one can pragmatically derive molecular radii, or radii of atoms or groups of atoms in molecules; compilations of so-called van der Waals radii exist [7]. In the singular, the specifying term implies an effective radius constituting half the distance of closest approach between like atoms deemed not covalently bonded. One might attempt formally to calculate these radii from covolume parameter b , but to consider molecules to become smaller as temperature increases would be then necessary. In fact, just the reverse occurs, as molecules enlarge slightly with increasing temperature because the occupancy of excited vibrational states becomes thermally enhanced, with correspondingly increased mean amplitudes of oscillation. Above the dissociation limit of a diatomic molecule, the effective radius of each separate atomic fragment decreases with increasing temperature, but, for two interacting strongly bound diatomic

molecules within a weakly bound tetratomic molecule, the effective radius of each fragment again increases with increasing temperature. The association of van der Waals with these non-bonded radii is hence unjustified; neither his equation of state nor the principle of corresponding states provides direct evidence for the existence of weakly bound molecules, which are adequately characterised in contemporary spectrometric experiments. The association of van der Waals with these radii because of the attractive (and repulsive) forces, which are responsible for the proximity with which molecules can approach one another, is equally spurious. Various weakly bound molecules are characterised, with ${}^4\text{He}_2$ and Ar_2 as diatomic instances involving atomic fragments, and $(\text{HF})_2$ involving diatomic fragments; their properties and characteristics are so diverse as to lack much in common other than their small energies of dissociation into either atoms or strongly bound molecules. As the energies of dissociation of the strongest 'hydrogen bonds' are not much less than those of bonds considered ordinary, such as that of diiodine, I_2 , in its electronic ground state, there is nearly a continuous gradation of bonds from the weakest, in ${}^4\text{He}_2$, to the strongest, in CO, for diatomic molecules for instance. There has been proffered no suggestion that van der Waals ever discussed such a diversity, nor that his understanding of their molecular physics exceeded that of Joule and Kelvin who originated an experimental proof of the existence of intermolecular forces in a gaseous context; it is significant that the Joule-Thomson coefficient, $(\partial T/\partial p)_H$, is the only thermodynamic function of a real gas that fails to approach the corresponding function of an ideal gas as the gaseous density approaches zero.

Rowlinson stated [2] in 1958, "The best known equation of state ... is that of van der Waals, and for many years the principle [of corresponding states] was associated solely with this equation". According to this principle, pressure, volume and temperature are expressed in terms of ratios with their respective values at the critical point, so $p_r = p / p_c$, $V_r = V_m / V_{m,c}$ and $T_r = T / T_c$, and the compression factor $Z = P V_m / RT$ is the same for all gases, but differing markedly from unity – becoming as small as 0.2 near the critical temperature [8]. Guggenheim stated [2] in 1945, "The principle of corresponding states may safely be regarded as the most useful by-product of the van der Waals equation of state. Whereas this equation of state is nowadays recognised to be of little or no value, the principle of corresponding states, correctly applied, is extremely useful and remarkably accurate". Contrary to popular belief, the van der Waals equation of state fails to establish the physical reality of corresponding states [2], because it leads to invalid mathematical definitions instead of physical definitions. The mathematical definitions are contained in these well known relations for the critical parameters, obtained on differentiation:

$$V_{m,c} = 3b, \tag{10}$$

$$T_c = 8 a / (27 b R),$$
$$p_c = a / (27 b^2)$$

Here is exposed an internal contradiction of the van der Waals equation: whereas the minimum circumscribed volume of a collection of spheres is $0.337 b$, the critical volume is nine times as great, an unreasonably large factor. These relations would be acceptable if parameters a and b were independent of temperature. Even when a and b for a temperature slightly greater than the critical point are inserted into these relations, the resulting critical parameters for dinitrogen are inaccurate [2]. If this 'law' were true, the critical ratio,

$$p_c V_{m c} / R T_c = 3/8 \quad (11)$$

would be the same for all gases, whereas this ratio varies between $1/5$ and $1/3$ for common gases [8]. In any case, all equations of third degree in V , as is that of van der Waals, yield, if they deviate not too severely from experience, a mathematical critical point. All equations with two parameters, such as a and b , yield reduced variables and corresponding states. There is hence no special virtue of the van der Waals equation as far as corresponding states are concerned: it leads to nonsensical situations because of the abstract nature of critical parameters determined from a and b .

Barker and Henderson stated [9], "It is a tribute to the insight of van der Waals that, in the nineteenth century, he was able to give an essentially correct physical description of the liquid state, and that much of the recent progress has been to put his ideas on a rigorous mathematical basis". They then proceeded to derive some useful results with which to prove their point [9], but they achieved these results by imposing on their systems the 6-12 potential-energy function of Lennard-Jones, as in formula 8 above, whereas the van der Waals equation is consistent with an inverse fourth-power attractive force [4]. This approach seems to be an instance of what Duclaux [2] contended when he stated that a mystical atmosphere surrounds the van der Waals theory such that men's eyes are closed to the manifest errors and inadequacies of this equation of state. As it expresses or verifies no single theory, but is instead consistent with many theories, it is possible to read into this equation diverse properties and hence to be misled as to its significance.

In summary, because of its demonstrated faults, the van der Waals equation of state, for both practical and pedagogical purposes, "is of little or no use", after Guggenheim. It can of course be used merely as an interpolation formula for moderately accurate calculations of pressure within a limited range at a particular temperature for which parameters a and b are optimal, but, for this purpose, other

empirical equations of state yield superior results; for instance in the vicinity of the critical point, the Dieterici equation of state is remarkably accurate and “is the best all-round analytic two-constant equation of state” [3]. Never having had any sound theoretical foundation, the van der Waals equation must be considered only an historical relic. In agreement with Duclaux [2], we conclude that this equation of state can be entirely abandoned, without regret. During the past sixty years, numerous papers on the van der Waals equation of state, mostly alleging some pedagogical significance, appeared but can likewise be ignored as mere distraction. The association of weakly bound molecules and of forces with dependence R^{-7} on intermolecular distance with the name van der Waals is equally unjustifiable and worthy of abandon. Tang and Toennies [1] noted that the number of publications that mention the name van der Waals in the title, abstract or key words is currently about 2000 per annum; in their vast majority these papers refer not to the worthless equation of state nor even to the separate and worthy principle of corresponding states, but rather to van der Waals forces or molecules for which there is at most only a superficial basis to associate with van der Waals the physicist.

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