Van der Waals equation

The **van der Waals equation** is an equation of state for a fluid composed of particles that have a non-zero volume and a pairwise attractive inter-particle force (such as the van der Waals force). It was derived in 1873 by Johannes Diderik van der Waals, who received the Nobel prize in 1910 for "*his work on the equation of state for gases and liquids*". The equation is based on a modification of the ideal gas law and approximates the behavior of real fluids, taking into account the nonzero size of molecules and the attraction between them.

Equation

The equation uses the following state variables: the pressure of the fluid p, total volume of the container containing the fluid V, number of moles n, and absolute temperature of the system T.

One form of the equation is

$$\left(p + \frac{a'}{v^2}\right)(v - b') = kT$$

where

$$v = V/N$$

is the volume of the container shared between each particle (not the velocity of a particle),

$$N = N_A n$$

is the total number of particles, and

$$k = R/N_A$$

is Boltzmann's constant, given by the universal gas constant R and Avogadro's constant N_A.

Extra parameters are introduced: a is a measure for the attraction between the particles, and b is the average volume excluded from v by a particle.

The equation can be cast into the better known form

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where

$$a = N_A^2 a'$$

is a measure of the attraction between the particles,

$$b = N_A b'$$

is the volume excluded by a mole of particles.

The van der Waals isotherms: the model correctly predicts a mostly incompressible liquid phase, but the oscillations in the phase transition zone do not fit experimental data.

A careful distinction must be drawn between the volume *available to* a particle and the volume *of* a particle. In particular, in the first equation v refers to the empty space available per particle. That is, v is the volume V of the container divided by the total number nN_A of particles. The parameter b, on the other hand, is proportional to the proper volume of a single particle - the volume bounded by the atomic radius. This is the volume to be subtracted from v because of the space taken up by one particle. In Van der Waals' original derivation, given below, b is four times the proper volume of the particle. Observe further that the pressure p goes to infinity when the container is completely filled with particles so that there is no void space left for the particles to move. This occurs when $V = nb$.
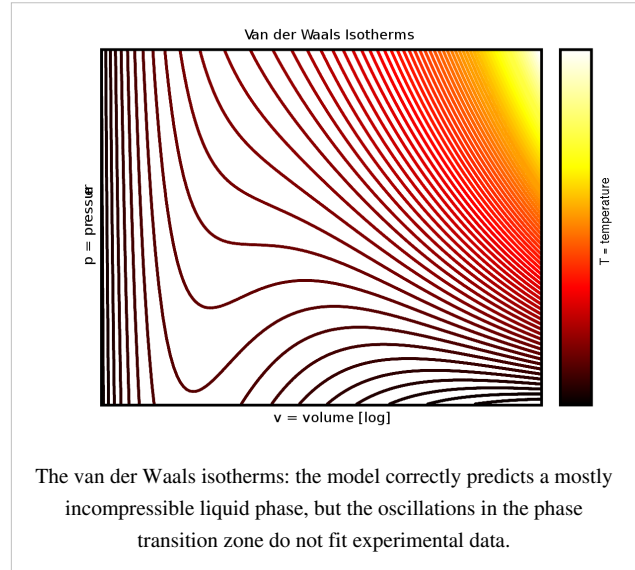
Validity

Above the critical temperature the van der Waals equation is an improvement of the ideal gas law, and for lower temperatures the equation is also qualitatively reasonable for the liquid state and the low-pressure gaseous state. However, the Van der Waals model is not appropriate for rigorous quantitative calculations, remaining useful only for teaching and qualitative purposes.[1]

In the first-order phase transition the range of (*P, V, T*), where the liquid phase and the gas phase are in equilibrium, it does not exhibit the empirical fact that p is constant as a function of *V* for a given temperature: although this behavior can be easily inserted into the van der Waals model (see Maxwell's correction below), the result is no longer a simple analytical model, and others (such as those based on the principle of corresponding states) achieve a better fit with roughly the same work.

Derivation

Most textbooks give two different derivations. One is the conventional derivation that goes back to van der Waals and the other is a statistical mechanics derivation. The latter has the major advantage that it makes explicit the intermolecular potential, which is neglected in the first derivation. The conventional Van der Waals equation is a mechanical equation of state, which cannot be used to specify all thermodynamic functions, while the statistical mechanical derivation yields the partition function for the system, which does allow all thermodynamic functions to be specified, including the mechanical equation of state.

Conventional derivation

Consider first one mole of gas which is composed of non-interacting point particles that satisfy the ideal gas law

$$p = \frac{RT}{V_{\mathrm{m}}}.$$

Next assume that all particles are hard spheres of the same finite radius *r* (the van der Waals radius). The effect of the finite volume of the particles is to decrease the available void space in which the particles are free to move. We must replace *V* by *V* − *b*, where *b* is called the *excluded volume*. The corrected equation becomes

$$p = \frac{RT}{V_{\mathrm{m}} - b}.$$

The excluded volume b is not just equal to the volume occupied by the solid, finite-sized particles, but actually four times that volume. To see this, we must realize that a particle is surrounded by a sphere of radius *r* = 2*r* (two times the original radius) that is forbidden for the centers of the other particles. If the distance between two particle centers were to be smaller than 2*r*, it would mean that the two particles penetrate each other, which, by definition, hard spheres are unable to do.

The excluded volume per particle (of average diameter *d* or radius *r*) is

$$b' = 4\pi d^3/3 = 8 \times (4\pi r^3/3) \quad \rightarrow \quad b' = 4 \times (4\pi r^3/3),$$

which was divided by 2 to prevent overcounting. So *b is four times the proper volume of the particle. It was a point of concern to Van der Waals that the factor four yields an upper bound; empirical values for* **b** are usually lower. Of course, molecules are not infinitely hard, as Van der Waals thought, and are often fairly soft.

Next, we introduce a pairwise attractive force between the particles. Van der Waal assumed that, not withstanding the existence of this force, the density of the fluid is homogeneous. Further he assumed that the range of the attractive force is so small that the great majority of the particles do not feel that the container is of finite size. That is, the bulk of them have more attracting particles to their right than to their left when they are relatively close to the left-hand wall of the container. The same statement holds with left and right interchanged. Given the homogeneity of the fluid, the bulk of the particles do not experience a net force pulling them to the right or to the left. This is

different for the particles in surface layers directly adjacent to the walls. They feel a net force from the bulk particles pulling them into the container, because this force is not compensated by particles on the side where the wall is (another assumption here is that there is no interaction between walls and particles, which is not true as can be seen from the phenomenon of droplet formation; most types of liquid show adhesion). This net force decreases the force exerted onto the wall by the particles in the surface layer. The net force on a surface particle, pulling it into the container, is proportional to the number density

$$C = N_A / V_m.$$

The number of particles in the surface layers is, again by assuming homogeneity, also proportional to the density. In total, the force on the walls is decreased by a factor proportional to the square of the density, and the pressure (force per unit surface) is decreased by

$$a' C^2 = a' \left(\frac{N_A}{V_m} \right)^2 = \frac{a}{V_m^2},$$

so that

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \Rightarrow \left(p + \frac{a}{V_m^2} \right) (V_m - b) = RT.$$

Upon writing n for the number of moles and $nV_m = V$, the equation obtains the second form given above,

$$\left(p + \frac{n^2 a}{V^2} \right) (V - nb) = nRT.$$

It is of some historical interest to point out that van der Waals in his Nobel prize lecture gave credit to Laplace for the argument that pressure is reduced proportional to the square of the density.

Statistical thermodynamics derivation

The canonical partition function Q of an ideal gas consisting of $N = nN_A$ identical particles, is

$$Q = \frac{q^N}{N!} \quad \text{with} \quad q = \frac{V}{\Lambda^3}$$

where Λ is the thermal de Broglie wavelength,

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k T}}$$

with the usual definitions: h is Planck's constant, m the mass of a particle, k Boltzmann's constant and T the absolute temperature. In an ideal gas q is the partition function of a single particle in a container of volume V. In order to derive the van der Waals equation we assume now that each particle moves independently in an average potential field offered by the other particles. The averaging over the particles is easy because we will assume that the particle density of the van der Waals fluid is homogeneous. The interaction between a pair of particles, which are hard spheres, is taken to be

$$u(r) = \begin{cases} \infty & \text{when} \quad r < d, \\ -\epsilon \left(\frac{d}{r} \right)^6 & \text{when} \quad r \geq d, \end{cases}$$

r is the distance between the centers of the spheres and d is the distance where the hard spheres touch each other (twice the van der Waals radius). The depth of the van der Waals well is ϵ.

Because the particles are independent, the total partition function still factorizes,

$$Q = q^N / N!,$$

but the intermolecular potential necessitates two modifications to q. First, because of the finite size of the particles, not all of V is available, but only $V - Nb'$, where (just as in the conventional derivation above)

$$b' = 2\pi d^3 / 3.$$

Second, we insert a Boltzmann factor exp[- $\phi/2kT$] to take care of the average intermolecular potential. We divide here the potential by two because this interaction energy is shared between two particles. Thus

$$q = \frac{(V - Nb')\, e^{-\phi/(2kT)}}{\Lambda^3}.$$

The total attraction felt by a single particle is

$$\phi = \int_d^\infty u(r) \frac{N}{V} 4\pi r^2 dr,$$

where we assumed that in a shell of thickness dr there are $N/V\, 4\pi\, r^2 dr$ particles. This is a mean field approximation; the position of the particles is averaged. In reality the density close to the particle is different than far away as can be described by a pair correlation function. Furthermore it is neglected that the fluid is enclosed between walls. Performing the integral we get

$$\phi = -2a'\frac{N}{V} \quad \text{with} \quad a' = \epsilon\frac{2\pi d^3}{3} = \epsilon b'.$$

Hence, we obtain,

$$\ln Q = N \ln (V - Nb') + \frac{N^2 a'}{VkT} - N \ln (\Lambda^3) - \ln N!$$

From statistical thermodynamics we know that

$$p = kT\frac{\partial \ln Q}{\partial V},$$

so that we only have to differentiate the terms containing V. We get

$$p = \frac{NkT}{V - Nb'} - \frac{N^2 a'}{V^2} \Rightarrow \left(p + \frac{N^2 a'}{V^2}\right)(V - Nb') = NkT \Rightarrow \left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT.$$

Other thermodynamic parameters

We reiterate that the extensive volume V is related to the volume per particle $v=V/N$ where $N = nN_A$ is the number of particles in the system.

The equation of state does not give us all the thermodynamic parameters of the system. We can take the equation for the Helmholtz energy A

$$A = -kT \ln Q.$$

From the equation derived above for ln$Q$, we find

$$A(T, V, N) = -NkT \left[1 + \ln\left(\frac{(V - Nb')T^{3/2}}{N\Phi}\right)\right] - \frac{a'N^2}{V}.$$

Where Φ is an undetermined constant, which may be taken from the Sackur-Tetrode equation for an ideal gas to be:

$$\Phi = T^{3/2}\Lambda^3 = \frac{h}{\sqrt{2\pi mk}}$$

This equation expresses A in terms of its natural variables V and T, and therefore gives us all thermodynamic information about the system. The mechanical equation of state was already derived above

$$p = -\left(\frac{\partial A}{\partial V}\right)_T = \frac{NkT}{V - Nb'} - \frac{a'N^2}{V^2}.$$

The entropy equation of state yields the entropy (S)

$$S = -\left(\frac{\partial A}{\partial T}\right)_V = Nk\left[\ln\left(\frac{(V - Nb')T^{3/2}}{N\Phi}\right) + \frac{5}{2}\right]$$

from which we can calculate the internal energy

$$U = A + TS = \frac{3}{2} NkT - \frac{a'N^2}{V}.$$

Similar equations can be written for the other thermodynamic potential and the chemical potential, but expressing any potential as a function of pressure p will require the solution of a third-order polynomial, which yields a complicated expression. Therefore, expressing the enthalpy and the Gibbs energy as functions of their natural variables will be complicated.

Reduced form

Although the material constants a and b in the usual form of the van der Waals equation differs for every single fluid considered, the equation can be recast into an invariant form applicable to *all* fluids.

Defining the following reduced variables (f_R, f_C is the reduced and critical variables version of f, respectively),

$$p_R = \frac{p}{p_C}, \qquad v_R = \frac{v}{v_C}, \quad \text{and} \quad T_R = \frac{T}{T_C},$$

where

$$p_C = \frac{a'}{27b'^2}, \qquad v_C = 3b', \quad \text{and} \quad kT_C = \frac{8a'}{27b'}$$

as shown by Salzman.[2]

The first form of the van der Waals equation of state given above can be recast in the following reduced form:

$$\left(p_R + \frac{3}{v_R^2}\right)(3v_R - 1) = 8T_R$$

This equation is *invariant* for all fluids; that is, the same reduced form equation of state applies, no matter what a and b may be for the particular fluid.

This invariance may also be understood in terms of the principle of corresponding states. If two fluids have the same reduced pressure, reduced volume, and reduced temperature, we say that their states are corresponding. The states of two fluids may be corresponding even if their measured pressure, volume, and temperature are very different. If the two fluids' states are corresponding, they exist in the same regime of the reduced form equation of state. Therefore, they will respond to changes in roughly the same way, even though their measurable physical characteristics may differ significantly.

Cubic equation

The van der Waals equation is a cubic equation of state. That is we can write the equation into a cubic form of the volume. In the reduced formulation the cubic equation is:

$$v_R^3 - \frac{1}{3}\left(1 + \frac{8T_R}{p_R}\right)v_R^2 + \frac{3}{p_R}v_R - \frac{1}{p_R} = 0$$

At the critical temperature, where $T_R = p_R = 1$ we get as expected

$$v_R^3 - 3v_R^2 + 3v_R - 1 = (v_R - 1)^3 = 0 \quad \Longleftrightarrow \quad v_R = 1$$

For $T_R < 1$, there are 3 values for v_R. For $T_R > 1$, there is 1 real value for v_R.

Application to compressible fluids

The equation is also usable as a PVT equation for compressible fluids (e.g. polymers). In this case specific volume changes are small and it can be written in a simplified form:
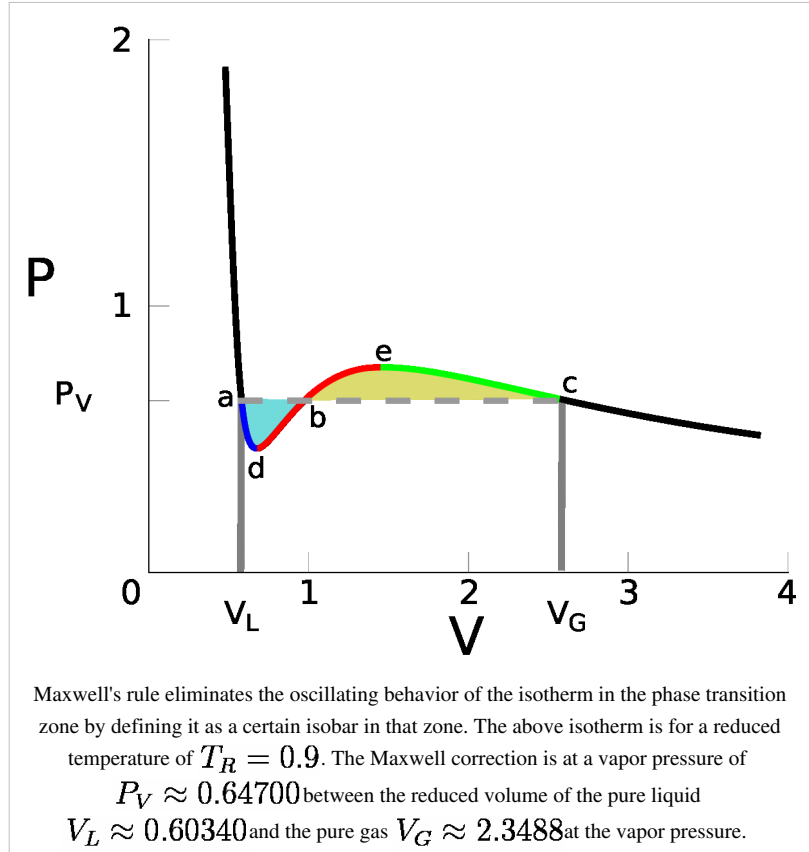
$$(p + A)(V - B) = CT,$$

where p is the pressure, V is specific volume, T is the temperature and A, B, C are parameters.

Maxwell equal area rule

Below the critical temperature $T_R < 1$ an isotherm of the Van der Waals equation oscillates as shown.

Along the red portion of the isotherm $(\partial P/\partial V)_{T,N} > 0$ which is unstable; the Van der Waals equation fails to describe real substances in this region because the equation always assumes that the fluid is uniform while between a and c on the isotherm it becomes more stable to be a coexistence of two different phases, a denser phase which we normally call *liquid* and a sparser phase which we normally call *gas*. To fix this problem James Clerk Maxwell (1875) replaced the isotherm between a and c with a horizontal line positioned so that the areas of the two hatched regions are equal. The flat line portion of the isotherm now corresponds to liquid-vapor equilibrium. The portions a–d and c–e are interpreted as metastable states of super-heated liquid and super-cooled vapor respectively.[3] The equal area rule can be expressed as:

Maxwell's rule eliminates the oscillating behavior of the isotherm in the phase transition zone by defining it as a certain isobar in that zone. The above isotherm is for a reduced temperature of $T_R = 0.9$. The Maxwell correction is at a vapor pressure of $P_V \approx 0.64700$ between the reduced volume of the pure liquid $V_L \approx 0.60340$ and the pure gas $V_G \approx 2.3488$ at the vapor pressure.

$$P_V(V_G - V_L) = \int_{V_L}^{V_G} P \, dV$$

where P_V is the vapor pressure (flat portion of the curve), V_L is the volume of the pure liquid phase at point a on the diagram, and V_G is the volume of the pure gas phase at point c on the diagram. The sum of these two volumes will equal the total volume V.

Maxwell justified the rule by saying that work done on the system in going from c to b should equal work released on going from a to b. (The area on a *PV* diagram corresponds to mechanical work). That's because the change in the free energy function $A(T,V)$ equals the work done during a reversible process, and the free energy function - being a state variable - should take on a unique value regardless of path. In particular, the value of A at point b should calculate the same regardless of whether the path came from left or right, or went straight across the horizontal isotherm or around the original Van der Waals isotherm. Maxwell's argument is not totally convincing since it requires a reversible path through a region of thermodynamic instability. Nevertheless, more subtle arguments based

on modern theories of phase equilibrium seem to confirm the Maxwell Equal Area construction and it remains a valid modification of the Van der Waals equation of state.[4]

The Maxwell equal area rule can also be derived from an assumption of equal chemical potential μ of coexisting liquid and vapour phases.[5] On the isotherm shown in the above plot, points a and c are the only pair of points which fulfill the equilibrium condition of having equal pressure, temperature and chemical potential. It follows that systems with volumes intermediate between these two points will consist of a mixture of the pure liquid and gas with specific volumes equal to the pure liquid and gas phases at points a and c.

The Van der Waals equation may be solved for V_G and V_L as functions of the temperature and the vapor pressure P_V. Since:

$$P = \left(\frac{\partial A}{\partial V} \right)_{T,N}$$

where A is the Helmholtz free energy, it follows that the equal area rule can be expressed as:

$$P_V = \frac{A(V_G, T, N) - A(V_L, T, N)}{V_G - V_L}$$

Since the gas and liquid volumes are functions of P_V and T only, this equation is then solved numerically to obtain P_V as a function of temperature (and number of particles N), which may then be used to determine the gas and liquid volumes.

References

[1] T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading (1960), p. 280

[2] W. R. Salzman, *Critical Constants of the van der Waals Gas*,http://www.chem.arizona.edu/~salzmanr/480a/480ants/vdwcrit/vdwcrit. html

[3] Maxwell,J.C. *The scientific papers of James Clerk Maxwell* Dover 1965(c1890) p424

[4] Cross, Michael *First Order Phase Transitions*,http://www.pma.caltech.edu/~mcc/Ph127/b/Lecture3.pdf

[5] A E Elhassan, R J B Craven, K M de Reuck, *The Area Method for pure fluids and an analysis of the two-phase region*, Fluid Phase Equilibria 130 (1997) 167-187.

External links

- Van der Waals Equation Solver (http://www.webqc.org/van_der_waals_gas_law.html)
- Some values of a and b in the 2nd equation (http://faculty.wwu.edu/vawter/PhysicsNet/Topics/Thermal/ vdWaalEquatOfState.html)

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