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 by Johannes Diderik van der Waals in 1873, 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.

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### Equation

The first form of this equation is

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

where

- \( p \) is the pressure of the fluid
- \( v \) is the volume of the container holding the particles divided by the total number of particles
- \( k \) is Boltzmann's constant
- \( T \) is the absolute temperature
- \( a' \) is a measure for the attraction between the particles
- \( b' \) is the average volume excluded from \( v \) by a particle

Upon introduction of the Avogadro constant \( N_A \), the number of moles \( n \), and the total number of particles \( nN_A \), the equation can be cast into the second (better known) form

\[
\left( p + \frac{a}{v^2} \right) (v - b) = \frac{RT}{v}
\]

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

where

- \( p \) is the pressure of the fluid
- \( V \) is the total volume of the container containing the fluid
- \( a \) is a measure of the attraction between the particles \( a = N_A^2 a' \)
- \( b \) is the volume excluded by a mole of particles \( b = N_A b' \)
- \( n \) is the number of moles
- \( R \) is the universal gas constant
- \( T \) is the absolute temperature

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 \( V = n b \).

**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 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 excluded volume per particle is \( 4\pi r^3/3 \approx 8 \times (4\pi r^3/3) \), which we must divide by two to avoid overcounting, so that the excluded volume \( b' \) is \( 4\times (4\pi r^3/3) \), which is four times the proper volume of the particle. It was a point of concern to van der Waals that the factor four yields actually an upper bound, empirical values for \( b' \) are usually lower. Of course, molecules are not infinitely hard, as van der Waals thought, but are often fairly soft.
Next, we introduce a pairwise attractive force between the particles. Van der Waals assumed that, notwithstanding 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 the particles do not notice that they 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

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

so that

\[
p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \implies (p + \frac{a}{V_m^2})(V_m - b) = RT.
\]

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

\[
(p + \frac{n^2a}{V_m^2})(V - nb) = nRT.
\]

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.

**Conventional derivation**

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

\[
p = \frac{RT}{V_m}.
\]

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

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

**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 \( \Lambda \) is the thermal de Broglie wavelength,

\[
\Lambda = \sqrt[3]{\frac{\hbar^2}{2\pi mkT}}
\]

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

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

\( r \) 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 \( \epsilon \).

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 \( \exp[-\varphi/(2kT)] \) 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

\[q = \frac{(V - Nb') e^{-\varphi/(2kT)}}{\Lambda^3}.
\]

The total attraction felt by a single particle is

\[
\phi = \int_d^\infty u(r) \frac{N}{V} \frac{4\pi r^2}{dr},
\]
where we assumed that in a shell of thickness $dr$ there are $\frac{N}{V} 4\pi r^2 dr$ 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

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

Hence, we obtain,

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

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

$$
p = \frac{NkT}{V - Nb'} - \frac{N^2 a'}{V^2} \implies \left( p + \frac{N^2 a'}{V^2} \right)(V - Nb') = NkT \implies \left( p + \frac{N^2 a'}{V^2} \right)(V - nT)
$$

**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

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

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

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 potentials 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),

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

where

\[
p_C = \frac{a'}{27b'^2}, \quad v_C = 3b', \quad \text{and} \quad kT_C = \frac{8a'}{27b'} \text{ as shown by Salzman.}^{[2]}
\]

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

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

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:

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

At the critical temperature, where \( T_R = p_R = 1 \) we get as expected

\[ v_R^3 - 3 v_R^2 + 3 v_R - 1 = (v_R - 1)^3 = 0 \quad v_R = 1 \]

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
- \( A, B \) and \( C \) are parameters.

Maxwell equal area rule

Below the critical temperature \( (T^* < 1) \) an isotherm of the Van der Waals equation oscillates as shown.

Along the red portion of the isotherm \( \left( \frac{\partial P'}{\partial V'} \right)_T > 0 \) which is unstable; the Van der Waals equation fails to describe real substances in this region. 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. \[3\]

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 \( b \). (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 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 be derived from an assumption of equal chemical potential $\mu$ of coexisting liquid and vapour phases[5].

See also

- Equation of state
- Gas laws
- Ideal gas
- Van der Waals constants (data page)
- Theorem of corresponding states
- Inversion temperature
- Maxwell construction
- Iteration To solve implicit equations like Van der Waals

References

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

External links

- Some values of a and b in the 2nd equation
  (http://faculty.wwu.edu/vawter/PhysicsNet/Topics/Thermal/vdWaalEquatOfState.html)

Categories: Fundamental physics concepts | Gases | Gas laws | Fluid dynamics | Equations | Chemical engineering

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