

The van der Waals equation of state

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Abstract

This lecture deals with a more general form of the equation of state, called van der Waals equation, which gives a better description of reality both under the conceptual and numerical point of view. The distinction from gas and vapour naturally springs out from this equation as well as the existence of an unstable region of the P - V diagram, nor foreseen neither described by the classical ideal gas law. Even if this unstable region is not correctly described by the van der Waals equation under the analytical point of view, with added assumptions (conceptual patch) it is possible to give at least a qualitative description of reality. Last but not least the van der Waals equation foreseen the existence of negative pressures. These negative pressures exist in nature (even if they are unstable) and are fundamental for some biotic mechanisms

How to obtain the van der Waals (1873)

An equation of state is a relationship between the thermodynamic variables that fully define the state of a system. If the system is air (that is essentially a mixture of nitrogen and oxygen) or water vapour, four thermodynamic variables are enough to determine the state of the system and they can be a combination of pressure, volume, mass (or number of moles) and temperature. In the atmospheric physics the equation of state usually used is the well known

$$pV = nRT$$

where p is pressure n is the number of moles, T is the absolute temperature and R is the ideal gas constant ($R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$).

Another form, even more used in meteorology, is the following

$$p = \rho R_a T$$

where ρ is the ideal gas density and R_a is the gas constant (i.e., the ideal gas constant R divided by the molar weight of the specific gas) that, for dry air, is $R_a = 287.04 \text{ J K}^{-1}$.

Both the above equations have essentially the same physical meaning and the same physical troubles.

The first of these troubles is the fact that when temperature decreases, keeping constant pressure and number of moles, the volume occupied by the gas tends to zero as well. Of course this cannot be physically true because, being material, the gas constituents cannot disappear. This means that both the above equations of state cannot be used at extremely low temperatures. However, this trouble can be easily solved in an heuristic way using a slightly different form for the equation of state, that is

$$p(V - V_0) = nRT$$

The advantage of this form of the equation of state is that when T tends toward zero at constant pressure and number of moles the gas volume tends toward V_0 . Then the gas constituents (atoms or molecules) do not disappear, i.e., they still occupy the portion of space V_0 . If V_0 is enough small for $T \gg 0$ the modified equation of state has almost the same behaviour of the previous forms.

Another trouble of the ideal gas law, neither solved by the above modified form, is that when the number of moles increases at constant volume and temperature, it is quite natural to assume that the gas pressure might not increase as expected (i.e., linearly with the number of moles) because of the mutual attraction between the gas constituents. In other words the pressure exerted by the gas on an virtual container is lower than that exerted by an ideal gas. This can be taken into account modifying the above equation of state in the following form

$$p = \frac{nRT}{(V - V_0)} - p_n$$

The quantity p_n is function of the number of atoms and/or molecules per unit volume as well as from the average force exerted by two atoms and/or molecules. By simple inductive description of the interaction between the gas constituents described in the below figure, assuming as φ the average force exerted by the gas constituents within a radius of influence λ , it is possible to give an analytic description of the term p_n , that is

$$p_n = \frac{F}{S} = \left(\frac{N}{2}\right)^2 \frac{\varphi}{S}$$

where N is the number of gas constituents contained in the sphere of λ diameter and F is the average force exerted on the surface S that divides the sphere of influence in two equivalent hemispheres.

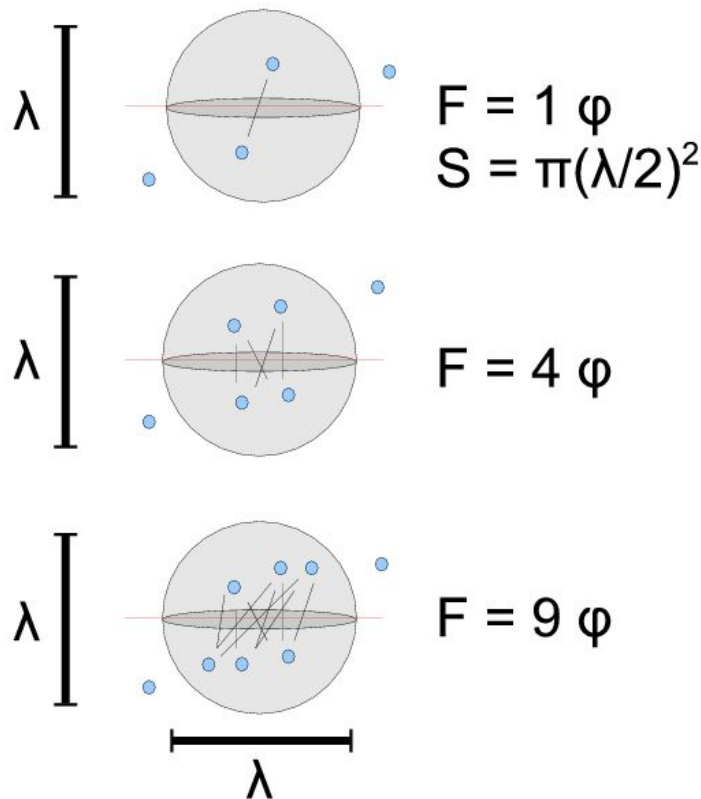


Figure: Inductive determination of the average force F exerted over the surface S with the increasing of the number of gas constituents N into the sphere of influence.

Introducing the Avogadro number A and the total gas volume V , the number of gas constituents N inside the sphere of influence becomes

$$N = \frac{nA}{V} \cdot \frac{4}{3} \pi \left(\frac{\lambda}{2}\right)^3$$

and the above expression for the pressure correction assumes the form

$$p_n = \left[\frac{\frac{nA}{V} \cdot \frac{4}{3} \pi \left(\frac{\lambda}{2}\right)^3}{2} \right]^2 \frac{\varphi}{\pi \left(\frac{\lambda}{2}\right)^2} .$$

Now, defining the molar specific volume as $v_m = (V/nA)$, with some algebra we can write the pressure correction as

$$p_n = \frac{\pi}{36} \frac{\lambda^4}{v_m^2} \varphi$$

which, even through this simple analytical approach, underlines the strong dependence of the correction factor by the radius of influence (fourth power of λ) and by the constituents density (second power of $1/v_m$). If density is low as well as the radius of influence, no matter the strength of the average force φ , the correction term becomes negligible. That is the reason why many gases at standard atmospheric conditions can be considered as ideal.

Using the above pressure correction term in the modified version of the ideal gas law we obtain the following “real” gas law, usually called van der Waals equation of state,

$$p = \frac{RT}{(v_m - a)} - \frac{b}{v_m^2}$$

where a and b are two positive defined constants that depends from the particular gas or vapour we are dealing with. In particular the a constant is related to the volume occupied by the gas constituents while b is essentially related to the radius of influence for the intra-molecular interaction.

The ideal gas law can be considered as a special case of the van der Waals equation of state, in fact when both a and b go to zero the van der Waals equation becomes the ideal gas one. Apart from this the above equation can give some useful theoretical hints on the behaviour of gases and vapours.

Critical temperatures (1861)

The first interesting theoretical aspect is that in the p - V (or equivalently p - v_m) diagram the “real” gas isotherms are no more hyperbolas, but they can have minima and maxima as can be seen by simply deriving the van der Waals equation with respect to molar specific volume and imposing null derivatives, obtaining.

$$\frac{\partial p}{\partial v_m} = -\frac{RT}{(v_m - a)^2} + 2\frac{b}{v_m^3} = 0 \quad \text{and} \quad \frac{\partial^2 p}{\partial v_m^2} = +2\frac{RT}{(v_m - a)^3} - 6\frac{b}{v_m^4} = 0 .$$

But it is much more useful to go a step further in the theoretical approach and consider the two null derivatives together with the van der Waals equation as a closed system of equations that can be solved. In particular what is usually done is to take the Van der Waals equation in conjunction with its null-imposed derivatives to obtain a closed system of three equations in the three variables p , v_m and T . The solutions of this system are

$$p = \frac{b}{27a^2} \equiv p_c, \quad T = \frac{8b}{27Ra} \equiv T_c \quad \text{and} \quad v = 3a \equiv v_c.$$

These solutions are called the “critical values” of the system for reasons that will appear clear (hopefully) later.

These three pressure, temperature and specific molar value can be used to express the free variables of the van der Waals equation in their “natural” form, that is with their typical units. This is done simply retrieving the parameters a , b and R (remember that a and b different for different gases and vapours) as function of the pressure, volume and temperature critical values, that is

$$R = \frac{3}{8} \frac{p_c}{v_c T_c}, \quad a = \frac{1}{3} v_c \quad \text{and} \quad b = \frac{27}{64} p_c.$$

Substituting the above values into the van der Waals equation we obtain a much simpler and general form of the equation of state, which is called *law of corresponding states*, that is

$$\frac{p}{p_c} = \frac{8 \frac{T}{T_c}}{3 \frac{v}{v_c} - 1} - \frac{3}{\left(\frac{v}{v_c}\right)^2}$$

always written in the more elegant form

$$p_r = \frac{8 T_r}{3 v_r - 1} - \frac{3}{v_r^2}$$

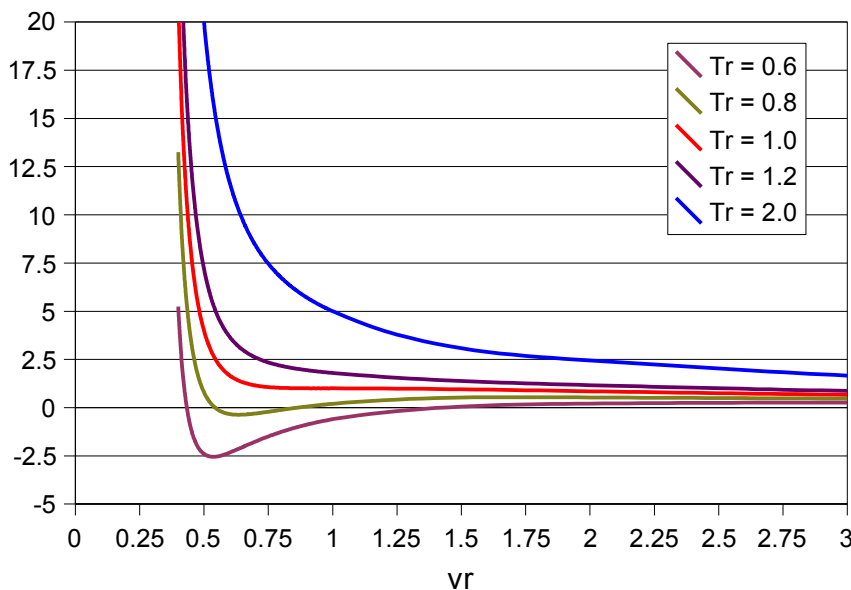
This equation can represent, in principle, the relationship between pressure, temperature and molar specific volume for all the substances when measured in units of specific pressure, temperature and molar specific volume. Just to have a look to the specific variables for real substances you can use the table below.

<i>Substance</i>	<i>T_c (°C)</i>	<i>p_c (hPa)</i>
N ₂	-122	34037
O ₂	-119	50346
H ₂ O	374	220834
CO ₂	31	733000

Of course when T_c and p_c are fixed, its molar specific value (density) is fixed as well by the simple relationship

$$\frac{p_c}{T_c} = \frac{3}{8} \frac{R}{v_c} = \frac{3}{8} R_{gas} \rho_c$$

What can be noticed from the above table is that critical pressures have high values, far beyond the classical atmospheric values (1013 hPa). On the contrary, critical temperatures show a different behaviour for carbon dioxide and water and for oxygen. But what is the meaning of the critical temperature? It can be shown by quite simple algebra (compute the derivative of the law of corresponding states) the mathematical constraint to admit minima and maxima is that of $T_r < 1$, that is $T < T_c$. This means that for typical atmospheric conditions only water and carbon dioxide may have minima and maxima. Just to have a naive description of what said, above take a look to the figure below. But what does it mean for the van der Waals equation (i.e., the law of corresponding states) the possibility to have a minimum or maximum? This means that between the minimum and maximum pressures decreases with molar specific volume (i.e., with increasing density). This situation is completely new when compared for the behaviour of ideal gases, for which pressure increases with the decreasing of volume. This behaviour is essentially unstable, in fact in this range of the PV diagram small compressions (expansions) of a system initially in equilibrium with the environment grow. This non linear behaviour stands for an extremely important process that takes place in atmosphere for some substances that is the change of phase.



Real isotherms (1873)

The behaviour of real isotherms is quite different for molar specific volumes (densities) in the unstable range, in particular what empirically observed is that for decreasing molar specific volume (i.e., increasing of density) “real” isotherms reach a point where pressure does not increase any more and stays constant up to a specific volume (density) where pressures starts to (quickly) grow again. Even this behaviour does not springs out naturally from the van der Waals equation it is possible to use its form at least to find the point in which reality starts to differ from theory. This was done by James Maxwell a few years after the publication of the van der Waals work with semi-heuristic considerations. In fact, if pressure remains constant after a certain point (during phase transition) and if the van der Waals equation gives a real description away from phase transition, we can use it to find at least the value of the pressure where phase transition

takes place. In particular we are pretty sure that the total energy should remain constant (first law of thermodynamics), then for a cyclic process (see figure below) that moves from the point A (beginning of phase transition) to the point E (ending of phase transition) along a real isotherm and comes back to the initial point A along a van der Waals isotherm, we should have

$$\oint dq = \oint du + \oint p dv .$$

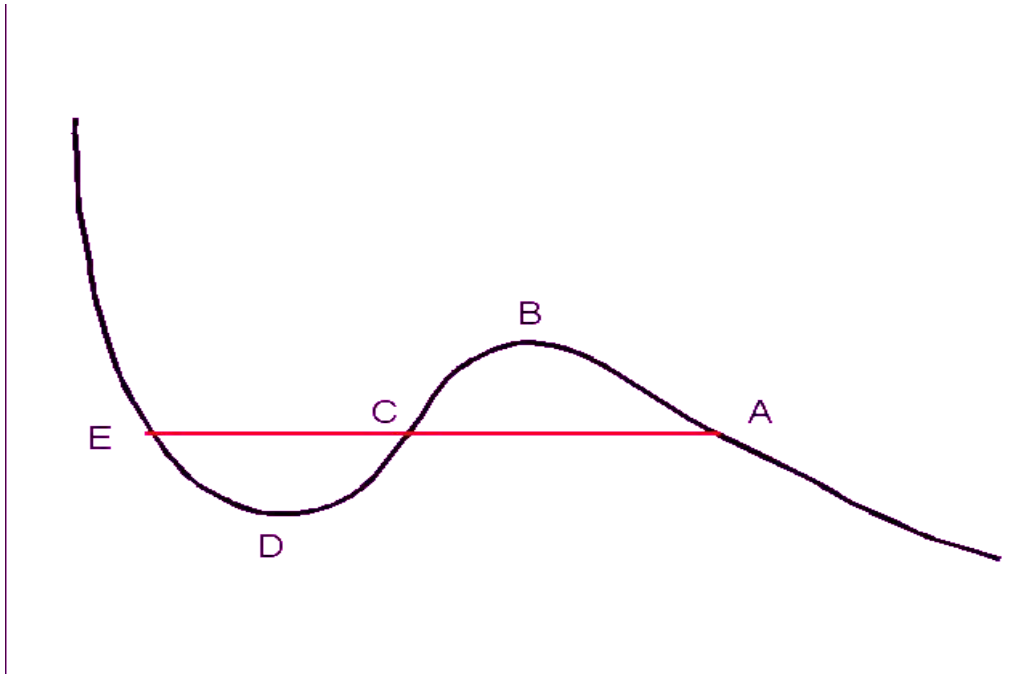


Figure. An ideal van der Waals isotherm (black line) and a real isotherm (red line). A represents the beginning of phase transition, E the end of phase transition, the segment ACE represents the real isotherm, the line ABCDE the van der Waals one.

Since the initial and final point are the same we are sure that

$$\oint du = 0 \text{ and } \oint ds = 0$$

where s is the system entropy (reversible process). Using the definition of entropy, remembering that temperature is constant (isotherm), we are sure that

$$\oint ds = \oint \frac{1}{T} dq = \frac{1}{T} \oint dq = 0$$

then the first law of thermodynamics states that

$$\oint p dv = \int_{ABCA} p dv + \int_{CDEC} p dv = 0 \text{ then } \int_{ABCA} p dv = - \int_{CDEC} p dv$$

These simple considerations give us an easy rule to graphically evaluate (not easy task) or numerically evaluate the value of pressure that makes equal the two integrals.

Negative pressures?

One interesting aspect that surely readers already noticed is the existence of negative pressures. This is another interesting aspect of van der Waals equation. Far beyond to be a failure of the van der Waals equation these are an important predictive aspect. To understand, or at least to create

an habit in our minds to this concept, we can think to negative pressures as “tension” or “tensile” pressures instead of “compression” pressures. This can be easily understood remembering recalling the stress tensor, which needs, to be defined, a surface and a force. If forces and surfaces have opposite verses pressure is negative. Experimentally it is possible to obtain extremely low (high in absolute value) negative pressures up to 300 000 hPa for water. Significantly low levels of negative pressure are currently occurring in trees. In fact, if you just try to compute the hydrostatic pressure at the roots of the trees exerted by the vertical amount of water that goes from the bottom up to the top of the leaves, you will find unsuspectedly high values. In spite of these high pressure values water reaches even the upper part of the tallest sequoia. This is possible thanks to the negative pressure. Negative pressures can be reached, as well foreseen by the van der Waals equation, only during phase transition, then negative pressures are unstable. Nevertheless this unstable situation is maintained by trees through transpiration. In other words they transpire to maintain a net flux from the roots up to the leaves, bringing nutrients with the fluid as well. This is the reason why plants do not need an earth to survive.

Do we really need van der Waals?

The answer to this question can be given only fixing correctly the problem. We can compare ideal gas law with van der Waals law only fixing two of the tree variables. So far we choosed to fix temperature and pressure to determine what happens to density (molar specific volume).

Above critical temperature we do not care about the difference between ideal and van der Waals aeriforms.

At the critical temperature we already found that

$$\frac{p_c}{T_c} = \frac{3}{8} \frac{R}{v_c} = \frac{3}{8} R_{gas} \rho_c$$

Since we know that for ideal gases

$$\frac{p}{T} = R_{gas} \rho_c$$

we can easily obtain the following relationship, remembering that pressure and temperature are the same.

$$\frac{\rho_c}{\rho} = \frac{p_c}{T_c} = \frac{p}{T} \frac{T_c}{p_c} \frac{8}{3} = \frac{8}{3}$$

Then at critical pressure and temperature van der Waals density is higher than ideal one. Under the naïve point of view we can say that van der Waals gas needs an higher density (higher frequency of bumps) to counteract the intra molecular attraction to reach the same pressure and temperature.

For lower temperatures we can use the already obtained relationships

$$a = \frac{1}{3} v_c \quad \text{and} \quad b = \frac{27}{64} p_c .$$

into the van der Waals equation, that is

$$p = \frac{R}{v_m} \left[\frac{T}{1 - \frac{v_c}{3v_m}} - \frac{9}{8} T_c \frac{v_c}{v_m} \right]$$

if we are far from the critical point (case already studied) we can consider $v_m \gg v_c$ and collecting T we obtain

$$p \sim \frac{RT}{v_m} \left[1 + \frac{v_c}{v_m} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) \right]$$

substituting specific molar volume with density $\rho = M/v_m$ where M is the molar weight we obtain

$$p \sim R_{gas} T \rho \left[1 + \frac{\rho}{\rho_c} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) \right]$$

then

$$\frac{p}{R_{gas} T \rho} \sim \left[1 + \frac{\rho}{\rho_c} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) \right]$$

that is

$$\frac{\rho_{ideal}}{\rho} \sim \left[1 + \frac{\rho}{\rho_c} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) \right]$$

If, with a further approximation, we substitute densities with pressures (e.g., $p \sim \rho$ for both ideal and van der Waals) we obtain

$$\frac{\rho_{ideal}}{\rho} \sim \left[1 + \frac{p}{p_c} \left(\frac{1}{3} - \frac{9}{8} \frac{T_c}{T} \right) \right]$$

This equation gives the van der Waals density departures from ideal gas density and, using the above critical values (see the table) you can decide if for the peculiar range of temperatures and pressure you are in an ideal or van der Waals situation.

Choosing the standard atmospheric partial pressures and 0 Celsius as a referring temperature you will obtain the following values

θ °C	CO_2	N_2	O_2	H_2O
$\rho_{vdwaals}/\rho_{ideal}$	1.0011	1.0009	1.0013	1.0001

That is, even if van der Waals gases and vapours are slightly denser than the ideal case the mistake committed is of the order of the 0.001 or lower.

References and notes

If we do not pay sufficient attention to the problem of physical reality , we can get trapped in paradoxes

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