The Van der Waals equation can be obtained considering the atoms of a gas as hard spheres. In this case, in fact, the mean field $\varphi$ has the form:

$$\varphi(\vec{r}) = \begin{cases} +\infty & |\vec{r}| < r_0 \\ u & |\vec{r}| \geq r_0 \end{cases}$$

with $u < 0$ a parameter that in general can depend on $N$ and $V$. In other words the particles are modelled as spheres of radius $r_0$: for large distances the potential is attractive, while for short distances it is repulsive and prevents the atoms from overlapping. Note also that this is a very rough first approximation: the potential, when attractive, does not depend on the distance between the atoms, and $\varphi$ is discontinuous. We will later see what happens when we make a more realistic approximation.

Therefore, we will have:

$$e^{-\beta \varphi(\vec{r})} = \begin{cases} 0 & |\vec{r}| < r_0 \\ e^{-\beta u} & |\vec{r}| \geq r_0 \end{cases}$$

and calling $V_{\text{exc}}$ the volume that must be excluded because the particles are hard spheres (namely the volume occupied by all the other atoms) the configurational partition function will be:

$$Q_N = [(V - V_{\text{exc}}) e^{-\beta u}]^N$$

The configurational part of the free energy is thus:

$$F_N^{\text{conf}} = -N k_B T \left[ \ln(V - V_{\text{exc}}) - \beta u \right]$$

We can determine the state equation of this system as usual (we derive only the configurational part of $F_N$ because the kinetic one does not contain terms depending on $V$):

$$P = -\frac{\partial F_N^{\text{conf}}}{\partial V} = \frac{N k_B T}{V - V_{\text{exc}}} - N \frac{\partial u}{\partial V}$$
Now, since $u$ is the attractive term between the particles we can suppose that it is proportional to the particle density (intuitively, if the system is dense the particles will be closer to each other and will interact strongly), and of course the excluded volume $V_{\text{exc}}$ will be proportional to the number of particles; therefore, setting:

$$u = -a \frac{N}{V} \quad V_{\text{exc}} = bN \quad a, b > 0$$

we have:

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

which is exactly Van der Waals equation. Defining $v = V/N$ we can rewrite it as:

$$P = \frac{k_BT}{v-b} - \frac{a}{v^2}$$

### 1 Critical point of Van der Waals equation

The behaviour of the Van der Waals isotherms is the following:

As we can see this changes with the temperature and resembles that of real isotherms (see Phase transitions and phase diagrams); however, Van der Waals isotherms are always analytic and have a non physical behaviour in certain regions of $(v, P)$ plane, called spinodal curves, if $T < T_c$ : for some values of $v$ we
have $\partial P/\partial v > 0$, which is physically impossible. This is a consequence of the roughness of the approximation we have made, since it can be shown that it doesn’t ensure that the equilibrium state of the system globally minimizes the Gibbs free energy. As we will shortly see, however, this problem can be solved “by hand” with Maxwell’s equal area rule, or Maxwell’s Construction.

Let us now see how to determine the critical point of a system obeying Van der Waals equation. First of all, from the representation of the isotherms we can see that the critical point is a flex for the critical isotherm (i.e. the one with $T = T_c$); in other words, we can determine the critical point from the equations:

$$\frac{\partial P}{\partial v} = 0 \quad \frac{\partial^2 P}{\partial v^2} = 0$$

Equivalently, we can note that the equation $P(v) = P = \text{const.}$ is cubic in $v$. In fact, we can rewrite the Van der Waals equation as:

$$v^3 - \left(b + \frac{k_BT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

For $T > T_c$ this equation has one real solution and two imaginary ones, and for $T < T_c$ three distinct real solutions; when $T = T_c$ the three solutions of the equation coincide. This means that at the critical point this last equation must be written in the form:

$$(v - v_c)^3 = v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0$$

Equating the coefficients we get:

$$3v_c = b + \frac{k_BT_c}{P_c} \quad 3v_c^2 = \frac{a}{P_c} \quad v_c^3 = \frac{ab}{P_c}$$

from which we have:

$$v_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{1}{k_B} \frac{8a}{27b}$$

We have found a very interesting result: in fact, if we can measure $a$ and $b$ at high temperatures then we are able to determine the critical point of the system.

This model has also an interesting property, since it predicts that:

$$\frac{P_c v_c}{k_BT_c} = \frac{3}{8} = 0.375$$

which is a universal number, independent of $a$ and $b$ and so of the particular fluid considered. Experimentally this ratio is approximately 0.29 for Argon, 0.23 for water and 0.31 for $^4\text{He}$. Therefore, even if it is very rough, this model leads to reasonable conclusions.
2 Law of corresponding states

We can also rewrite Van der Waals equation in a dimensionless form, rescaling the thermodynamic quantities of the system. In particular, defining:

\[ \pi := \frac{P}{P_c} = \frac{p}{27b^2/a} \quad \nu := \frac{v}{v_c} = \frac{v}{3b} \quad \tau := \frac{T}{T_c} = \frac{k_B T}{8a} \]

Van der Waals equation becomes:

\[ \left( \pi + \frac{3}{\nu^2} \right) (3\nu - 1) = 8\tau \]

We have found another very interesting result: when rescaled by their critical thermodynamic properties, all fluids obey the same state equation. This is the law of corresponding states that we have already encountered in Critical exponents and universality. This is a form of universality, but substantially different from the one we have seen until now, which applies only in the neighbourhood of a critical point: in fact, the law of corresponding states applies everywhere on the phase diagram. It can even be shown that this law is a consequence of dimensional analysis, and is more general than what might seem: experimentally the law of corresponding states is well satisfied also by fluids which do not obey Van der Waals equation.

3 Maxwell’s equal area rule

As we have previously anticipated, Maxwell’s equal area rule is a method to “manually” remove the unphysical regions of Van der Waals isotherms.

From Phase coexistence and general properties of phase transitions we know that at the coexistence of two phases the chemical potentials and the pressures of the two phases must be equal; furthermore, from Thermodynamic potentials we also know that the chemical potential is the Gibbs free energy per particle, namely \( G = \mu N \), and in general we have also:

\[ dG = -SdT + VdP + \mu dN \]
Now, differentiating $G = \mu N$ and subtracting this last equation we get:

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP$$

Therefore, since along an isotherm $dT = 0$, we will have:

$$\mu_{\text{gas}} - \mu_{\text{liq}} = \int_{\text{liq}}^{\text{gas}} d\mu = \frac{1}{N} \int_{\text{liq}}^{\text{gas}} V dP = 0$$

Looking also at the previous figure, we see that this means that the horizontal segment of the isotherm must be drawn so that regions $A$ and $B$ have the same area (from which the name of the method).

# 4 Critical behaviour

Let us now study the behaviour of systems obeying Van der Waals equations near the critical point, computing one of the critical exponents.

## 4.1 Exponent beta

This exponent $\beta$ can be computed from the shape of the coexistence curve for $T \to T_c$; this can be done using the law of corresponding states. In fact, defining:

$$t := \frac{T - T_c}{T_c} = \tau - 1 \quad \rho := \frac{V - V_c}{V_c} = \nu - 1$$

we can expand the law of corresponding states near $\tau = \nu = 1$, or equivalently $t = \rho = 0$ (namely in the neighbourhood of the critical point):

$$\pi = \frac{8\tau}{3\nu - 1} - \frac{3}{\nu^2} = \frac{8(1+t)}{3(1+\rho) - 1} - \frac{3}{(1+\rho)^2} =$$

$$= (1 + t) \left( 4 - 6\rho + 9\rho^2 - \frac{27}{2} \rho^3 + \cdots \right) - (3 - 6\rho + 9\rho^2 - 12\rho^3 + \cdots) \sim$$

$$\sim 1 + 4t - 6\rho t + 9t^2 \rho - \frac{3}{2} \rho^3 - \frac{27}{2} \rho^3 t + \cdots$$

Therefore:

$$\pi = 1 + 4t - 6\rho t - \frac{3}{2} \rho^3 + O(t^2 \rho^4)$$

where the terms we have neglected are justified a posteriori (i.e. we will see that $\rho \sim t^{1/2}$; we could have not neglected them, but the result of the computation doesn’t change). The strategy we want to apply is the following: since we want to determine how $\rho$ changes with $t$, we can determine the relation between the densities $\rho_g$ and $\rho_l$ in the gaseous and liquid phase from Maxwell’s equal area rule. This way, from the expression of $\pi$ we can determine the pressures in the
two phases and express them in terms of $\rho_g$ or $\rho_l$, and since $\pi_1 = \pi_g$ at the coexistence we can obtain from this equation the behaviour of $\rho$ in terms of $t$.

Therefore, from Maxwell’s equal area rule we have:

$$\int_{\text{liq.}}^{\text{gas}} v dP = \int_{\text{liq.}}^{\text{gas}} (\rho + 1) v_c P_c \, d\pi = 0$$

where we have used the definitions of $\pi$ and $\rho$. If we now set our system on an isotherm with $t < 0$ and $t$ small (so that the expansion of $\pi$ makes sense), the variation of $\pi$ in terms of $\rho$ is:

$$d\pi = -6td\rho - \frac{9}{2} \rho^2 d\rho$$

We thus have [2]:

$$\int \rho^2 \left( -6t - \frac{9}{2} \rho^2 \right) d\rho = 0 \quad \Rightarrow \quad 3\rho_g^2 \left( t + \frac{\rho_g^2}{8} \right) = 3\rho_l^2 \left( t + \frac{\rho_l^2}{8} \right)$$

Since $t$ is small we can neglect it, and so:

$$\rho_g^2 = \rho_l^2 \quad \Rightarrow \quad \rho_g = \pm \rho_l$$

Remembering that:

$$\rho_l = \frac{v_l - v_c}{v_c} \quad \rho_g = \frac{v_g - v_c}{v_c}$$

we see that the only acceptable solution is $\rho_g = -\rho_l$ (since the volume of a gas is larger than that of a liquid). Therefore, substituting $\rho_g$ and $\rho_l = -\rho_g$ into $\pi$ we get:

$$\pi_g = 1 + 4t - 6t\rho_g - \frac{3}{2} \rho_g^3 \quad \pi_1 = 1 + 4t + 6t\rho_g + \frac{3}{2} \rho_g^3$$

Since $\pi_g = \pi_1$ at the phase coexistence, we have:

$$3\rho_g \left( 4t + \rho_g^2 \right) = 0$$

and excluding of course the case $\rho_g = 0$, in the end:

$$\rho_g \sim t^{1/2}$$

Therefore:

$$\beta = \frac{1}{2}$$

which is what we could have expected from a mean field theory.

In fact, if we compute all the other critical exponent, we get exactly:
\[ \alpha = 0 \quad \beta = \frac{1}{2} \quad \gamma = 1 \quad \delta = 3 \]

5 A more precise approximation

We have seen that the problem of Van der Waals equation comes from the rough approximation that we have made in . A better formulation of Van der Waals mean field theory can be done using the potential:

\[ \varphi(\vec{r}) = \begin{cases} +\infty & |\vec{r}| < r_0 \\ -ke^{-k|\vec{r}|} & |\vec{r}| \geq r_0 \end{cases} \]

where \( k \) is a parameter that determines the range of the potential. In this case (we don’t do the computations, we just state the result) after having computed the partition function, in the limit \( k \to 0 \) the potential becomes infinitely ranged and weak. The interesting fact is that in this limit the theory becomes essentially the same that we have seen before, but with the exception that there are no unphysical regions and Maxwell’s rule is no longer necessary, since this model naturally predicts the existence of the “plateaux” relative to the liquid-gaseous phase transition in \( (v, P) \) plane.

1. Remember that by definition \( \beta \) describes the behaviour of the order parameter in the neighbourhood of the critical temperature, so we will have \( \varrho \sim |t|^\beta \).

2. If we didn’t neglected the term of the expansion of \( \pi \), we would have found:

\[ -3\varrho_g^2 \left( t - 2t\varrho_g + \frac{3}{8}\varrho_g^2 \right) = -3\varrho_l^2 \left( t - 2t\varrho_l + \frac{3}{8}\varrho_l^2 \right) \]

Again, the terms linear in \( t \) can be neglected since \( t \) is small (and \( \varrho_g \), \( \varrho_l \) are just numbers).
6 Text and image sources, contributors, and licenses

6.1 Text

- Course: Statistical Mechanics/Mean field theories/Van der Waals equation Source: https://en.wikitolearn.org/Course%3AStatistical_Mechanics/Mean_field_theories/Van_der_Waals_equation?oldid=12046 Contributors: Sofia, Leonardo Pacciani, WikiToBot and Hariseldon99

6.2 Images


6.3 Content license

- [Project:Copyright Creative Commons Attribution Share Alike 3.0 & GNU FDL]
- Creative Commons Attribution-Share Alike 3.0