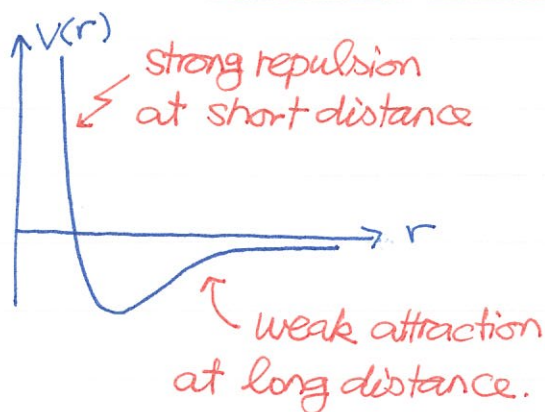


HH0030 van der Waals Equation of state

For an ideal gas, the equation of state is $PV = N\tau$. To describe a realistic gas, van der Waals introduces two approximations:

- (1) Finite volume of a molecule.
- (2) Long-ranged attraction between molecules



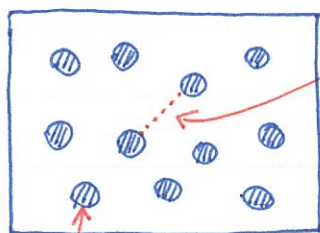
Based on the inter-molecular interaction profile, the strong repulsion can be approximated as "finite (hard-core) volume of a molecule". And, the weak attraction at long distance will be treated in "mean-field" approximation.

Taking both factors into account, van der Waals derives the equation of state for a realistic gas:

$$\left(p + a \frac{N^2}{V^2}\right)(V - Nb) = N\tau \quad \rightarrow \quad p = \frac{N\tau}{V - Nb} - a \frac{N^2}{V^2}$$

more suggestive form ↗

① Derivation of van der Waals equation.



inter-molecular attraction.

Inclusion of finite volume b is simple to Replacing the volume V by $V - Nb$ will do the work.

$$F = -N\tau \left\{ \log \left[\frac{N\tau(V - Nb)}{N} \right] + 1 \right\}$$

The corresponding pressure can be computed by $p = -(\partial F / \partial V)_{\tau, N}$

$$p = \frac{N\tau}{V - Nb} > \frac{N\tau}{V}$$

↖ pressure gets larger because of short-ranged repulsion!

Now we need to include the effect of inter-molecular attraction.

Suppose the 1st gas molecule sit at the origin, $\vec{R}_1 = 0$. The potential energy from attraction can be computed.

$$\Delta U_1 = \varphi(\vec{R}_2) + \varphi(\vec{R}_3) + \dots + \varphi(\vec{R}_N) = \sum_{i \neq 1} \varphi(\vec{R}_i)$$

How to express it in terms of $n(\vec{r})$?

Here I would like to show you an important trick to transform from "particles" to "field". The particle density for other molecules can be written as

$$n(\vec{r}) = \sum_{i \neq 1} \delta(\vec{r} - \vec{R}_i)$$

particles \rightarrow field.

$$\rightarrow \int_b^\infty d^3\vec{r} n(\vec{r}) \varphi(\vec{r}) = \sum_{i \neq 1} \int_b^\infty d^3\vec{r} \delta(\vec{r} - \vec{R}_i) \varphi(\vec{r}) = \sum_{i \neq 1} \varphi(\vec{R}_i)$$

This is just the potential energy we tried to compute!

$$\Delta U_1 = \sum_{i \neq 1} \varphi(\vec{R}_i) = \int_b^\infty d^3\vec{r} n(\vec{r}) \varphi(\vec{r})$$

Very important transform!

Assuming the particle density is uniform $n(\vec{r}) \approx n$,

$$\Delta U_1 \cong n \int_b^\infty d^3\vec{r} \varphi(\vec{r}) \cong -2na$$

a is positive and the minus sign for attraction. The factor of 2 is just for convenience.

Now we turn to the change of the internal energy U . The calculation is much more difficult than computing ΔU_1 for one molecule. However, within "mean-field" approximation, we assume ΔU can be computed by adding up ΔU_1

$$\Delta U = (\Delta U_1 + \Delta U_2 + \dots + \Delta U_N) \cdot \frac{1}{2} = \frac{1}{2} N \Delta U_1 \rightarrow \Delta U = -Nna$$

The $\frac{1}{2}$ factor is to remove the double counting of the pairwise interactions. Because $F = U - \tau \sigma$, the free energy becomes

$$F = -N\tau \left\{ \log \left[\frac{n_0}{N} (V - Nb) \right] + 1 \right\} - \frac{N^2 a}{V}$$

finite volume

attraction

The pressure can be computed, $p = -(\partial F / \partial V)_{\tau, N}$.

$$p = \frac{N\tau}{V - Nb} - \frac{N^2}{V^2} a$$

attraction reduces the pressure as expected ☹

The van der Waals equation gives better description for realistic gases. In addition, it also explains the liquid-gas transition!

Introduce the following quantities: $p_c = \frac{a}{27b^2}$, $V_c = 3Nb$, $\tau_c = \frac{8a}{27b}$

The van der Waals equation is made dimensionless:

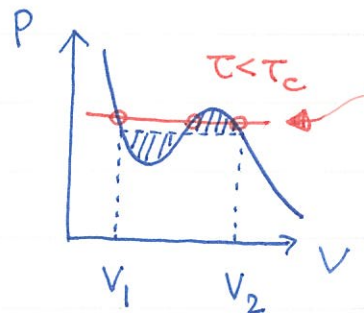
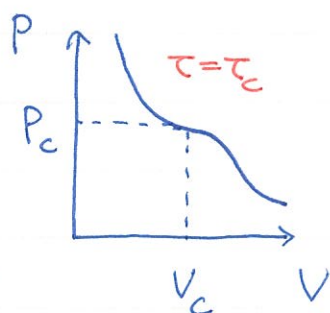
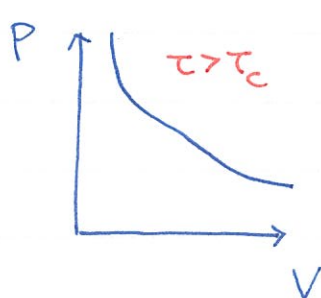
$$\hat{p} = \frac{\frac{8}{3}\hat{\tau}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}$$

Law of corresponding states

$$\hat{x} \equiv \frac{x}{x_c}$$

① Liquid-gas phase transition:

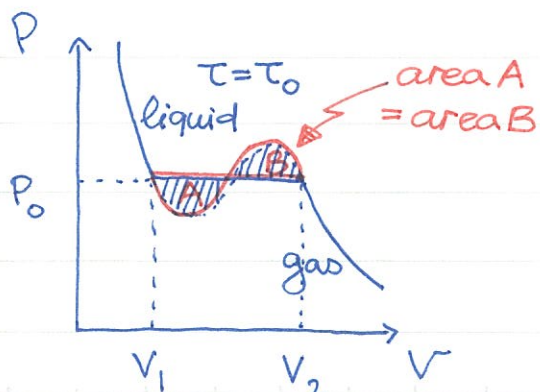
Let us plot the p - V curve at different temperatures.



Something strange when $\tau < \tau_c$
1 pressure, 3 volumes?

When $\tau < \tau_c$, the system may have three different values of volumes according to van der Waals equation. This doesn't make any sense

The correct answer is already shown in the previous notes.



The pressure between V_1 and V_2 remains constant. The flexible volume change is due to the coexistence of liquid and gas as discussed before.

We are going to show why this is the case.

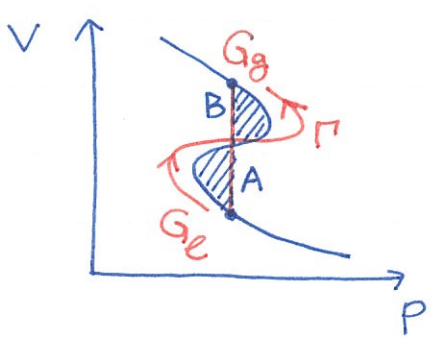
Write down the total differential for the Gibbs free energy,

$dG = -\sigma d\tau + V dp + \mu dN,$

at const τ with particle number held fixed, $d\tau=0, dN=0.$

Thus, $dG = V dp.$ Coexistence

requires $\tau_e = \tau_g, p_e = p_g, \mu_e = \mu_g.$ Thus, the p - V curve should be a horizontal line as shown before. Meanwhile, $G = \mu N,$ it also implies $G_e = G_g$ on the coexistence curve.



$G_g - G_e = \Delta G = \int_{\Gamma} V dp = \text{area A} - \text{area B}$

Since $G_g = G_e,$ the integral vanishes

$\text{area A} = \text{area B}$

Starting from the van der Waals equation, when $\tau < \tau_c,$ one can plot $p = p(V)$ isothermal curve. The trick to determine the coexistence pressure p_0 (and thus V_1 and V_2) is the criterion of equal areas above and below $p = p_0.$



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