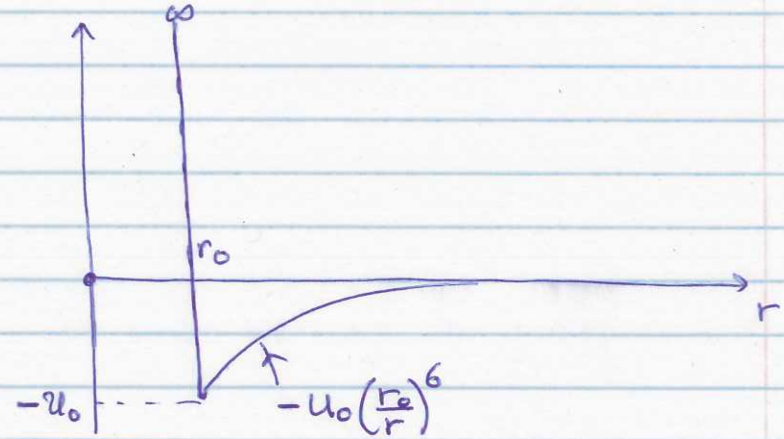
Van der Waals equation of state

2nd virial coefficient

$$B_2(T) = -\frac{1}{2}\tilde{b}_2 = -\frac{1}{2}\int d^3q\left(e^{-\beta v(q)} - 1\right)$$

Model potential



$$B_2(T) = \frac{1}{2}\left(\int_{|q|<r_0} d^3q - \int_{|q|>r_0} d^3q\,\underbrace{\left(e^{\beta u_0\left(\frac{r_0}{r}\right)^6} - 1\right)}_{\approx\, \beta u_0\left(\frac{r_0}{r}\right)^6}\right)$$

at large r, and use this as a model

$$= \frac{1}{2}\left(\frac{4\pi}{3}r_0^3 - \underbrace{\int_{r_0}^{\infty} 4\pi r^2 dr\; \beta u_0\left(\frac{r_0}{r}\right)^6}_{\beta u_0\, 4\pi r_0^6 \frac{-1}{3r^3}\Big|_{r_0}^{\infty} = \beta u_0\cdot\frac{4\pi r_0^3}{3}}\right) =$$

$$= \frac{1}{2}\cdot\frac{4\pi}{3}r_0^3\left(1 - \beta u_0\right) = \frac{1}{2}\Omega\left(1 - \beta u_0\right).$$

$$\frac{p}{k_BT} \approx n + B_2(T)n^2 = n\left(1 + \frac{1}{2}\Omega n\right) - n^2\frac{1}{2}\Omega\beta u_0$$

$$p + \frac{1}{2}\Omega u_0 n^2 = n k_B T \left(1 + \frac{1}{2}\Omega n\right)$$

$$n k_B T = \frac{\left(p + \frac{1}{2}\Omega u_0 n^2\right)}{1 + \frac{1}{2}\Omega n} \approx \left(p + \frac{1}{2}\Omega u_0 n^2\right)\left(1 - \frac{1}{2}\Omega n\right)$$

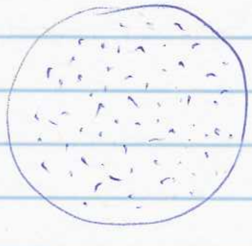
$$N k_B T = \left(p + \frac{1}{2}\Omega u_0 \left(\frac{N}{V}\right)^2\right)\left(V - \frac{1}{2}\Omega N\right)$$

$$\boxed{N k_B T = \left(p + a\left(\frac{N}{V}\right)^2\right)\left(V - Nb\right)}$$ – van der Waals equation of state

Physical ingredients:

- $b = \frac{1}{2}\Omega$ – "effective volume reduction per particle" because of mutual exclusion of hard cores
- $a = \frac{1}{2}\Omega u_0$ – writing $p = \frac{N k_B T}{V - Nb} - a\left(\frac{N}{V}\right)^2$,

  $a\left(\frac{N}{V}\right)^2$ is effective reduction in the pressure exerted on the outside walls



because of long-range van der Waals attraction between molecules

Remark

van der Waals equation can be viewed as approximate phenomenological equation of state. We motivated it from more microscopic treatment by truncating series, which is accurate at low density / high pressure.

With additional physical fixing (Maxwell construction), van der Waals equation can be also used to discuss liquid-gas transition (liquid – dense phase formed because of attractive forces between molecules).

Isotherms of the van der Waals gas

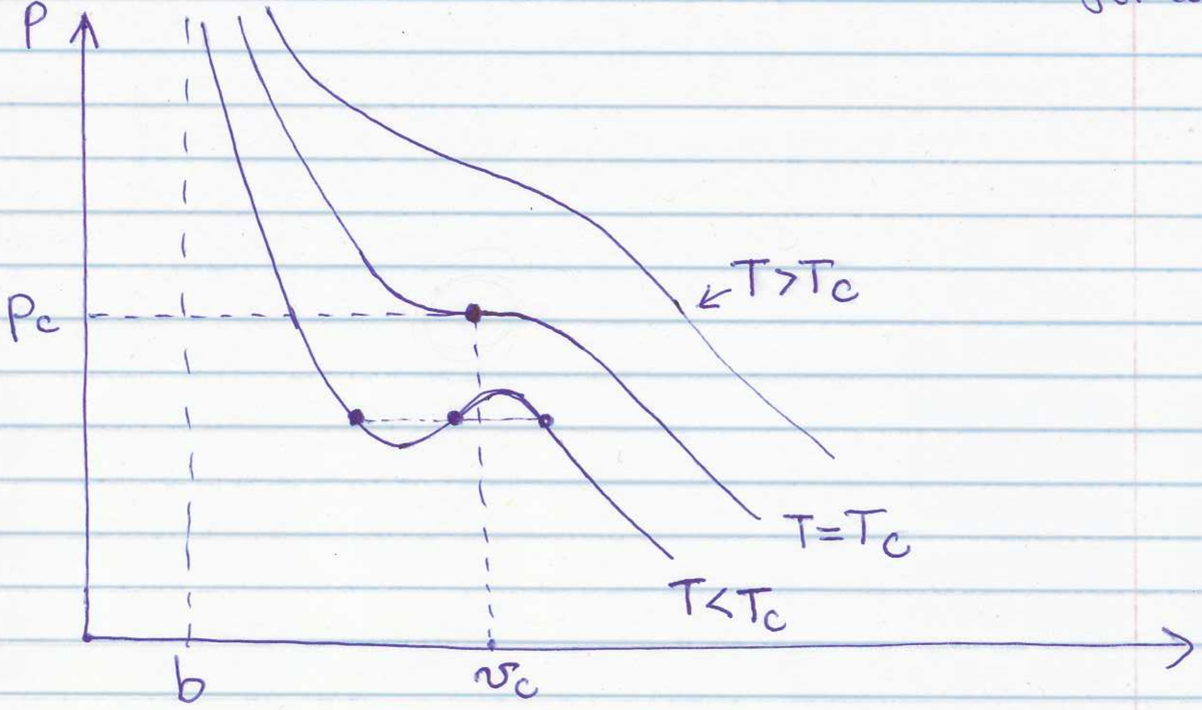
$$\boxed{p = \frac{N k_B T}{V - Nb} - a\left(\frac{N}{V}\right)^2 = \frac{k_B T}{v-b} - \frac{a}{v^2}},$$

$\boxed{v = \frac{V}{N}}$ – volume per particle ; assuming $v > b$

$$\frac{dp}{dv} = -\frac{k_B T}{(v-b)^2} + \frac{2a}{v^3} = -\frac{v^3 k_B T - 2a(v-b)^2}{v^3 (v-b)^2} =$$

$$= -\frac{1}{v^3}\left(v \cdot k_B T \cdot \left(\frac{v}{v-b}\right)^2 - 2a\right)$$

At high enough T, e.g. $b \cdot k_B T > 2a$, clearly $\frac{dp}{dv} < 0$ for all $v > b$



$$\boxed{\begin{aligned} &\frac{\partial p}{\partial v}(v_c, T_c) = 0 \\ &\frac{\partial^2 p}{\partial v^2}(v_c, T_c) = 0 \\ &p(v_c, T_c) = p_c \end{aligned}}$$

Critical point is given by

$$\boxed{\frac{\partial p}{\partial v} = -\frac{k_B T}{(v-b)^2} + \frac{2a}{v^3} \overset{!}{=} 0}$$ - when is it possible to satisfy this eq.?

Consider

$$f(v) = \frac{2a}{v^3} - \frac{k_B T}{(v-b)^2}$$

maximize $f(v)$:

$$\frac{\partial^2 p}{\partial v^2}$$

$$\boxed{f'(v) = -\frac{6a}{v^4} + \frac{2k_B T}{(v-b)^3} = 0}$$

$$\Rightarrow \frac{v^4}{(v-b)^3} = \frac{3a}{k_B T} \Rightarrow v = v(T).$$

If $f(v(T)) < 0$, then $\frac{\partial p}{\partial v} < 0$ for all v.

Critical T_c is when

$$f'(v_c, T_c) = 0$$

$$\frac{\partial p}{\partial v}(v_c, T_c) = 0$$

$$\frac{k_B T_c}{(v_c-b)^3} - \frac{3a}{v_c^4} = 0 \qquad \frac{k_B T_c}{(v_c-b)^3} = \frac{3a}{v_c^4}$$

$$-\frac{k_B T_c}{(v_c-b)^2} + \frac{2a}{v_c^3} = 0 \qquad \frac{k_B T_c}{(v_c-b)^2} = \frac{2a}{v_c^3}$$

$$\Rightarrow \quad v_c - b = \frac{2}{3} v_c, \quad \boxed{v_c = 3b}$$

$$\boxed{k_B T_c = \frac{8a}{27b}}$$

$$\boxed{p_c = \frac{\frac{8a}{27b}}{2b} - \frac{a}{9b^2} = \frac{a}{27b^2}}$$

Remarks (non-universal)

a, b – system-dependent parameters

* $\boxed{\dfrac{p_c v_c}{k_B T_c} = \dfrac{3}{8} = 0.375}$ – "universal number" (in the sense that all system-dep. parameters dropped out)

Experimentally, $\dfrac{p_c v_c}{k_B T_c}$ varies between 0.23 (H_2O) and 0.31 (He)

* Measure p, v, T in units of p_c, v_c, T_c:

$$\bar{p} \equiv \frac{p}{p_c}, \quad \bar{v} = \frac{v}{v_c}, \quad \bar{T} = \frac{T}{T_c}$$ – "reduced variables"

$$\bar{p} \cdot \frac{a}{27b^2} = \frac{\frac{8a}{27b}\bar{T}}{\bar{v}\cdot 3b - b} - \frac{a}{\bar{v}^2 \cdot 9b^2},$$

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2}, \qquad \boxed{\left(\bar{p} + \frac{3}{\bar{v}^2}\right)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{3}\bar{T}}$$

all material parameters dropped out

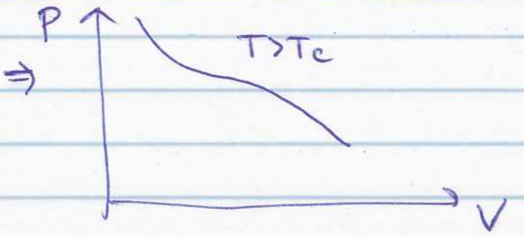
Van der Waals equation implies "law of corresponding states" – "universal equation of state".

This is special to the van der Waals equation and does not hold in general (e.g. equation of state of a gas depends on the details of the interatomic potential). Still, it is roughly satisfied and is useful for crude comparisons.

(Later will discuss different "true universality" in the vicinity of T_c)

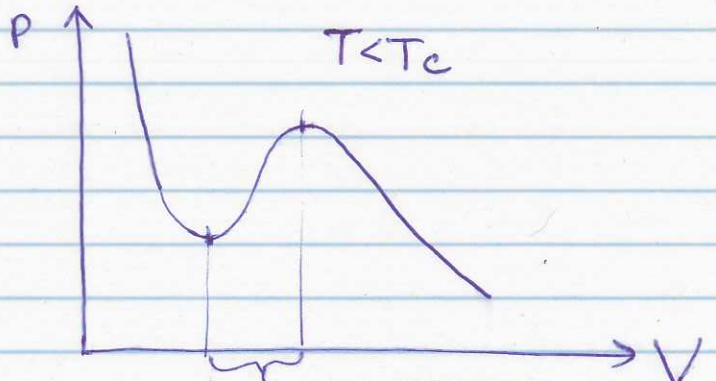
Liquid-gas transition in the van der Waals model

$\underline{T > T_c}$ $\Rightarrow$



van der Waals equation is physically sensible (does not violate any general thermodynamic laws and in principle there can be gases obeying precisely this equation of state)

$\underline{T < T_c}$



- there is a problem! At the very least in this region

$$\frac{\partial p}{\partial v} > 0 \Rightarrow \text{compressibility } \varkappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T < 0$$

Negative compressibility is thermodynamically unstable — from general arguments of stability in thermodynamics

$S = S(U,V)$ - concave fnctn of U,V $\Rightarrow \left(\frac{\partial^2 S}{\partial V^2}\right)_U \leq 0$

will argue for this physically below $\rightarrow$ $\left(\frac{\partial^2 F}{\partial V^2}\right)_T \geq 0$

not sure how to prove quickly, but this is correct (e.g. Landaufshitz)

$$F = U - TS$$

$$dF = -SdT - pdV$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V^2}\right)_T \leq 0$$

must be in thermodynamics

The breakdown of the van der Waals equation is not the problem of statistical mechanics. If we could calculate the partition sum exactly, the derived thermodynamics satisfies the stability conditions automatically. For example: in grand canonical ensemble

Suppose we calculate things exactly in the grand canonical ensemble

$$\langle N\rangle = \frac{1}{\beta}\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{T,V} = \frac{1}{\beta}\left(\frac{\partial}{\partial \mu}\left(+\frac{pV}{k_BT}\right)\right)_{T,V} =$$

$$= +V\left(\frac{\partial p}{\partial \mu}\right)_{T,V}$$

$$\langle N^2\rangle = \frac{1}{\beta^2}\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$

$$\langle N\rangle = \frac{1}{\beta}\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}$$

$$\langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta^2}\left(\frac{1}{\mathcal{Z}}\frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \left(\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \mu}\right)^2\right) = \frac{1}{\beta^2}\frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} =$$

$$= \frac{1}{\beta}\left(\frac{\partial}{\partial \mu}(\langle N\rangle)\right)_{T,V}$$

positive! →

$$\left\{\frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} = +\frac{k_BT}{V}\frac{\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V}}{\left(\frac{\partial p}{\partial \mu}\right)_{T,V}} = +\frac{k_BT}{V}\frac{1}{\left(\frac{\partial p}{\partial N}\right)_{T,V}} \Rightarrow\right.$$

Mathematics: [redacted]

$$p = p(N,T,V)$$

[redacted]

keep T fixed; $p = p(N,V)$

Chain rule $$\left(\frac{\partial p}{\partial N}\right)_V \left(\frac{\partial N}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_N = -1$$

from extensivity $n =$

$$\Rightarrow k_BT\boxed{\left(\frac{\partial N}{\partial V}\right)_{P,T}}\cdot\left(-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T}\right) = k_BT\cdot n\cdot \varkappa_T$$

$\Rightarrow \varkappa_T$ must be +ve.

Exact : $$\boxed{n k_B T \cdot \varkappa_T = \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle}} > 0$$

van der Waals equation is not an exact eq. of state – we made approximations and in the process we violated the above condition of thermodynamic stability. We will first try to [redacted] fix [redacted] things "by hand" appealing to thermodynamic arguments. Then we will motivate this "fix" also differently doing approximations in the microscopic calculation smwht differently ("mean field calculation")