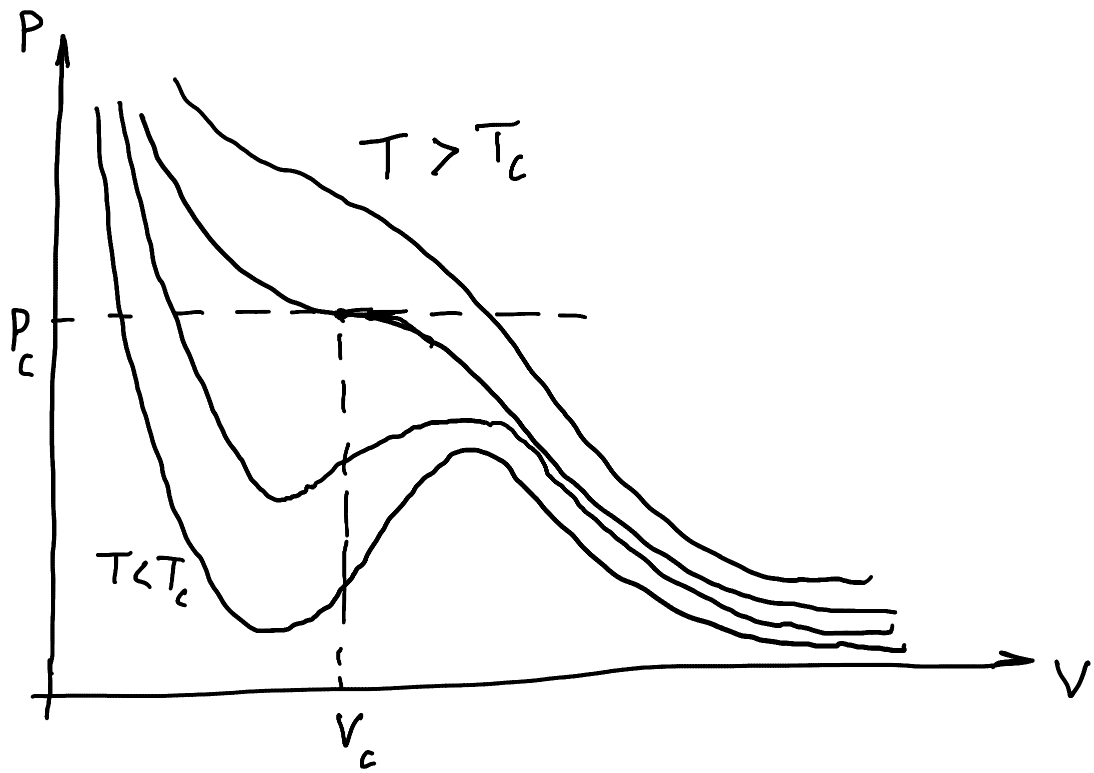
Phase transition liquid-gas

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = NT$$ – the Van der Waals equation

Rewrite it in the form

$$P = \frac{NT}{V - Nb} - \frac{N^2 a}{V^2}$$ and plot it in coords. P, V

isotherms



T_c – critical temperature; below it the isotherms have a maximum and a minimum

Found from the conditions $\begin{cases} \frac{\partial P}{\partial V} = 0 \\ \frac{\partial^2 P}{\partial V^2} = 0 \end{cases}$

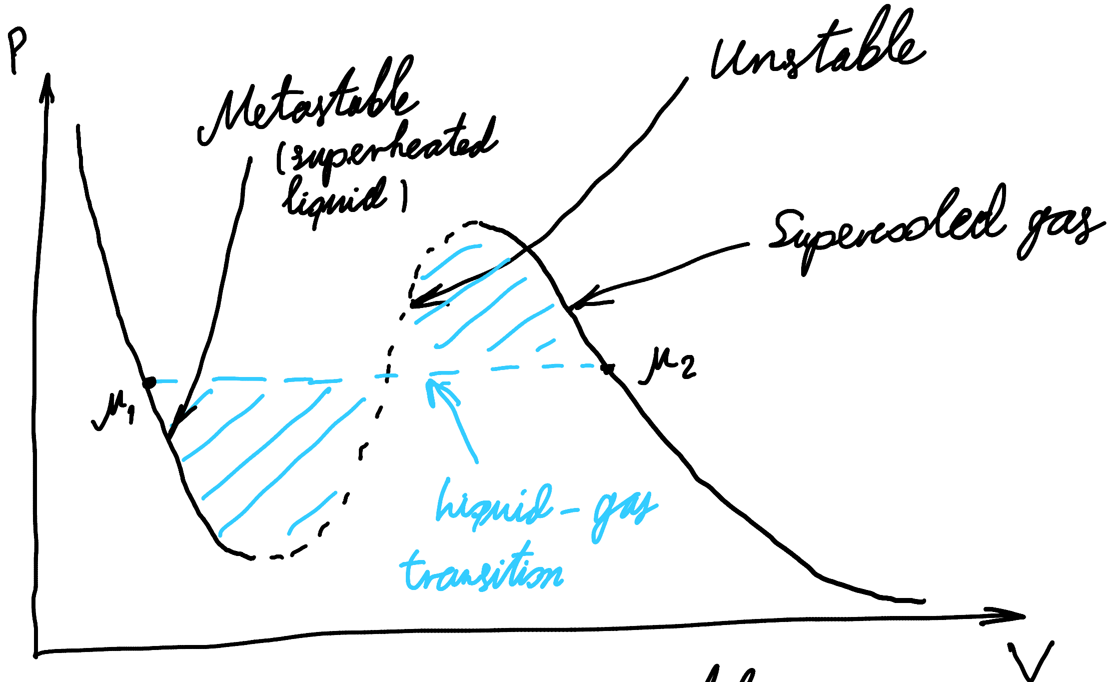
$$\begin{cases} \frac{\partial P}{\partial V} = -\frac{NT}{(V - Nb)^2} + \frac{2N^2 a}{V^3} = 0 \\ \frac{\partial^2 P}{\partial V^2} = \frac{2NT}{(V - Nb)^3} - \frac{6N^2 a}{V^4} = 0 \end{cases}$$

$$\begin{cases} \dfrac{\partial^2 P}{\partial V^2} = \dfrac{2NT}{(V-Nb)^3} - \dfrac{6N^2 a}{V^4} = 0 \end{cases}$$

$$\boxed{V_c = 3Nb\,, \quad T_c = \frac{8}{27}\frac{a}{b}\,, \quad P_c = \frac{1}{27}\frac{a}{b^2}}$$

The meaning of the critical temperature will be clear from below

Let's have a more careful look at one isotherm at $T < T_c$. The system is stable at $\boxed{\left(\frac{\partial P}{\partial V}\right)_T < 0}$



Another condition of equilibrium is $\mu_1 = \mu_2$ (at constant P and T, for example, that follows from minimising Φ wrt the # of particles in one of the wrt the # of particles in the

phases ; $\frac{\partial \varphi}{\partial N_1} = \frac{\partial \varphi_1}{\partial N_1} - \frac{\partial \varphi_2}{\partial N_2} = \mu_1 - \mu_2$)

There is one point there where μ_1 and μ_2 are the same.

On this curve then $\int_1^2 d\mu = 0$

Along the isotherm $d\mu = v\, dP$, which follows from the differential for the thermodynamic potential.

volume per particle

Then the position of the line is determined by $\int_1^2 V\, dP = 0$