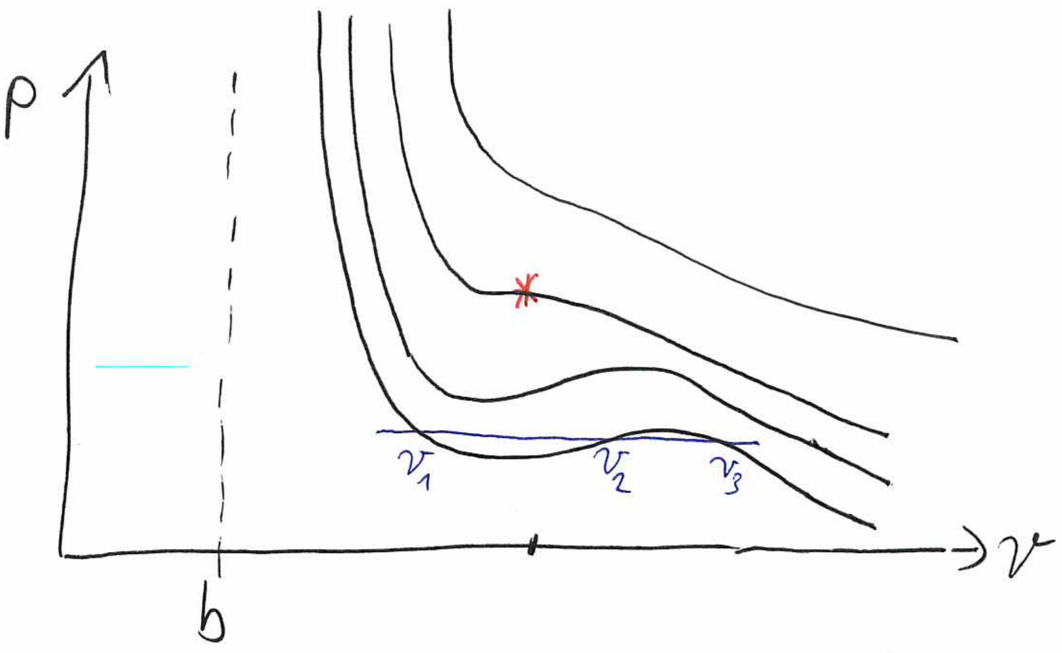
Behavior of the van der Waals Equation of State

(1873) $\boxed{\left(p+\frac{a}{v^2}\right)(v-b)=k_B T}$ or $p=\frac{k_B T}{v-b}-\frac{a}{v^2}$

derivatives

$$\frac{dp}{dv}=-\frac{k_B T}{(v-b)^2}+\frac{2a}{v^3}\overset{!}{=}0 \Leftrightarrow k_B T=\frac{2a(v-b)^2}{v^3}$$

$$\frac{d^2p}{dv^2}=\frac{2k_B T}{(v-b)^3}-\frac{6a}{v^4}\overset{!}{=}0 \Leftrightarrow k_B T=\frac{3a(v-b)^3}{v^4}$$



critical point $\frac{dp}{dv}=0=\frac{d^2p}{dv^2}$

$$\frac{2a(v-b)^2}{v^3}=\frac{3a(v-b)^3}{v^4} \quad \Big|\Big| \cdot \frac{v^4}{a(v-b)^2},\ a>0,\ v>b$$

$$2v=3v-3b \Rightarrow \boxed{v_c=3b,\ k_B T_c=\frac{8a}{27b}}$$

$$p_c=\frac{8a}{27b(3b-b)}-\frac{3a}{27b^2}=\boxed{p_c=\frac{a}{27b^2}} \qquad \boxed{\frac{p_c v_c}{k_B T_c}=\frac{3}{8}}$$

$T > T_c$: behavior similar to ideal gas

$T < T_c$: three solution v_1, v_2, v_3 for same p

isothermal compressibility $\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial p}$

for v_1, $p(v)$ very steep, κ_T small

↳ liquid, densly packed as $v \approx b$

for v_2, positive slope of $p(v)$, $\kappa_T < 0$

↳ system would be unstable ↯

for v_3, $p(v)$ comparably shallow

↳ gas, dilute as $v \gg b$

vdW EOS describes liquid-gas transition, however, with deficiencies

phase equilibrium requires

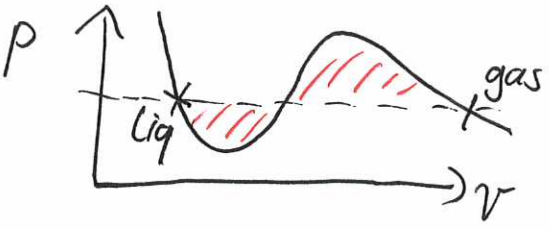
- mechanical equilibrium, $p_{gas} = p_{liq}$
- thermal equilibrium, $T_{gas} = T_{liq}$
- chemical equilibrium, $\mu_{gas} = \mu_{liq}$

already fullfilled are mechanical and thermal equilibrium, now impose chemical equilibrium:

$\mu = \mu(p, T)$, again $\left.\frac{\partial \mu}{\partial p}\right|_T = v$

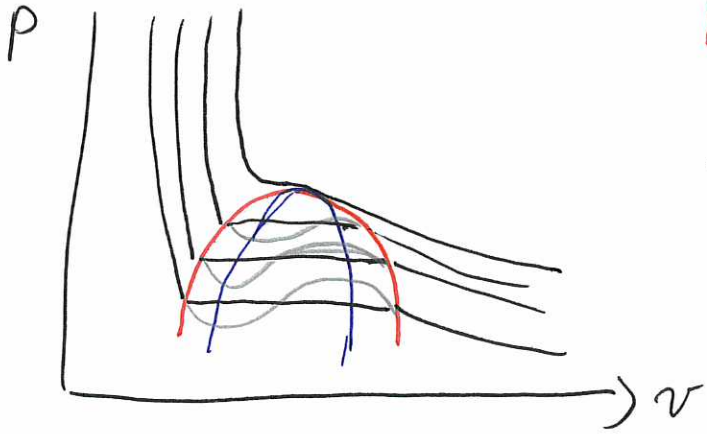
and integration along the isotherms

$$\mu(p,T) = \mu_{Liq} + \int_{p_{Liq}}^{p} dp'\, v(p',T) \stackrel{!}{=} \mu_{gas}$$



Maxwell construction (1875)

replace coexistence region by horizontal line



binodal curve

spinodal curve

inconsistency: integration over mechanically unstable branch of isotherms, lines of instability called spinodal: $\frac{\partial p}{\partial v} = 0$ → inserted back into EOS

$$p_S = \frac{2a(v-b)^2}{v^3(v-b)} - \frac{a}{v^2} = \frac{a}{v^2} - \frac{2ab}{v^3}$$

relative units

$$\tilde{p} = p/p_c\,, \quad \tilde{v} = v/v_c\,, \quad \tilde{T} = \frac{k_B T}{k_B T_c}$$

$$\tilde{p}\,\frac{a}{27b^2} = \tilde{p}\,p_c = p = \frac{\tilde{T}\,k_B T_c}{\tilde{v} v_c - b} - \frac{a}{\tilde{v}^2 v_c^2} = \frac{\tilde{T}\,\frac{8a}{27b}}{\tilde{v}\,3b - b} - \frac{a}{\tilde{v}^2\, 9b^2}$$

$$\boxed{\tilde{p} = \frac{8\tilde{T}}{3\tilde{v}-1} - \frac{3}{\tilde{v}^2}}$$

EOS vdW, Law of Corresponding States

$$p_s = \tilde{p}_s p_c = \tilde{p}_s \frac{a}{27b^2} = \frac{3a}{27b^2 \tilde{v}^2} - \frac{2}{\tilde{v}^3} \frac{ab}{27b^3}$$

$$\boxed{\tilde{p}_s(\tilde{v}) = \frac{3}{\tilde{v}^2} - \frac{2}{\tilde{v}^3}}$$

Spinodal curve

E. A. Guggenheim, The Principle of Corresponding States, Journal of Chemical Physics **13**, 253 (1945).

Same behavior for large number of different substances: monoatomic noble gases Ne, Ar, Kr, Xe

air molecules N_2, O_2, diatomic

other linear molecule CO

and methane CH_4

existence of critical points allow for analytical calculations in their vicinity: distance to critical point as small parameter

$$t := \frac{T - T_c}{T_c} = \tilde{T} - 1$$

critical exponent β:

$$\boxed{(\rho_{liq} - \rho_{gas}) \propto (-t)^{\beta}}$$

vdW for both liquid and gas branch emanating from $T = T_c$:

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v}_{liq} - 1} - \frac{3}{\tilde{v}_{liq}^2} = \frac{8\tilde{T}}{3\tilde{v}_{gas} - 1} - \frac{3}{\tilde{v}_{gas}^3}$$

$$\Rightarrow \tilde{T} = \frac{(3\tilde{v}_{liq} - 1)(3\tilde{v}_{gas} - 1)(\tilde{v}_{liq} + \tilde{v}_{gas})}{8\,\tilde{v}_{liq}^2\,\tilde{v}_{gas}^2}$$

$$\underset{\varepsilon}{\overset{\parallel}{\Delta\tilde{v}}} = \tilde{v}_{gas} - \tilde{v}_{liq}\ , \quad \text{Symmetry: } \tilde{v}_{gas} = 1 + \frac{\Delta\tilde{v}}{2}, \quad \tilde{v}_{liq} = 1 - \frac{\Delta\tilde{v}}{2}$$

$$\tilde{T} = \frac{(2 - 3\frac{\varepsilon}{2})(2 + 3\frac{\varepsilon}{2})}{4\left(1 - \frac{\varepsilon^2}{4}\right)^2} = \frac{16 - 9\varepsilon^2}{4 - 2\varepsilon^2 + \frac{\varepsilon^4}{4}} = \frac{16 - 9\varepsilon^2}{(4 - \varepsilon^2)^2}$$

Taylor-Expansion $\tilde{T}$ for $\varepsilon \approx 0$

$$\tilde{T} \approx 1 - \frac{1}{16}\varepsilon^2 + \mathcal{O}(\varepsilon^4) \Rightarrow v_{gas} - v_{liq} \propto (-t)^{1/2}$$

$$\boxed{\beta_{vdW} = \frac{1}{2}}$$

critical exponent δ

$$\boxed{(p-p_c) \propto |\rho_{liq}-\rho_{gas}|^{\delta} \, \mathrm{sgn}(\rho_{liq}-\rho_{gas})}$$

at T_c, $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0 \rightsquigarrow$ Taylor expansion starts with cubic term

$$(p-p_c) \propto (v-v_c)^3 \qquad \boxed{\delta_{vdW}=3}$$

critical exponent γ for isothermal compressibility

$$\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial p}\Big|_T \, , \quad \boxed{\kappa_T \propto |t|^{-\gamma}}$$

at T_c, $\frac{\partial p}{\partial v} = 0$ so varying T for $v = v_c$

$$\frac{\partial p}{\partial v} \approx -a(T-T_c) + \ldots \Rightarrow \kappa_T \propto \frac{1}{T-T_c}$$

$$\boxed{\gamma_{vdW}=1}$$