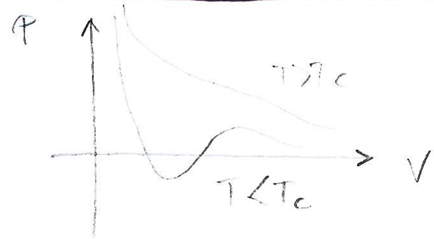
Van der Waals / critical exponents



At the critical point: $\dfrac{\partial P}{\partial V} = \dfrac{\partial^2 P}{\partial V^2} = 0$

$$P = \frac{NkT}{V-Nb} - a\frac{N^2}{V^2}$$

$$\frac{\partial P}{\partial V} = -\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0 \Rightarrow \frac{NkT}{(V-Nb)^2} = \frac{2aN^2}{V^3}$$

$$\frac{\partial^2 P}{\partial V^2} = +2\frac{NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \Rightarrow \frac{NkT}{(V-Nb)^3} = \frac{3aN^2}{V^4}$$

$$\frac{NkT}{(V-Nb)^2} = \frac{2aN^2}{V^3} = \frac{3aN^2}{V^4}(V-N\ldots$$

$$\Rightarrow 3(V-Nb) = 2V \Rightarrow \boxed{V_c = 3Nb} \; ; \; NkT_c = \frac{2aN^2}{V_c^3}(V_c-Nb)^2 = \frac{2aN^2}{27N^3b^3}4N^2b^2$$

$$\boxed{kT_c = \frac{8a}{27b}}$$

Finally, $P_c = \dfrac{NkT_c}{V_c-Nb} - a\dfrac{N^2}{V_c^2}$

$$= \frac{N\,8a}{27b}\frac{1}{2Nb} - a\frac{N^2}{9N^2b^2} \Rightarrow \boxed{P_c = \frac{a}{27b^2}}$$

Introducing reduced variables $p = \dfrac{P}{P_c}$, $t = \dfrac{T}{T_c}$, $v = \dfrac{V}{V_c}$:

$$\left(P_c p + a\frac{N^2}{V_c^2 v^2}\right)\left(vV_c - Nb\right) = Nk\,t\,T_c$$

$$\left(p\frac{a}{27b^2} + a\frac{\cancel{N^2}}{v^2 9b^2\cancel{N^2}}\right)\left(v3Nb - Nb\right) = Nt\frac{8a}{27b}$$

$$\frac{a}{27b^2}\left(p + \frac{3}{v^2}\right)(3v-1)\cancel{Nb} = \frac{\cancel{Nb}\,a}{27b^2}8t \Rightarrow \boxed{\left(p+\frac{3}{v^2}\right)(3v-1) = 8t}$$

Exponent δ: $|P-P_c| \propto |\rho-\rho_c|^\delta$ at T_c, meaning $|p-1| \propto |v-1|^\delta$ for $t=1$.

At $t=1$, we have $p = \dfrac{8}{3v-1} - \dfrac{3}{v^2}$; $p = 1+\delta p$; $v = 1+\delta v$

$$1+\delta p = \frac{8}{3\delta v+2} - \frac{3}{(1+\delta v)^2} = \frac{4}{1+\frac{3}{2}\delta v} - 3\frac{1}{1+2\delta v+(\delta v)^2}$$

$$\sim 4\left(1 - \frac{3}{2}\delta v + \frac{9}{4}(\delta v)^2 - \frac{27}{8}(\delta v)^3\right) - 3\left(1 - 2\delta v - (\delta v)^2 + 4(\delta v)^2 + 4(\delta v)^3 - 8(\delta v)^3\right)$$

$$\sim 1 - \frac{27}{2}(\delta v)^3 + 12(\delta v)^3 \sim 1 - \frac{3}{2}(\delta v)^3 \Rightarrow \boxed{\delta = 3}$$

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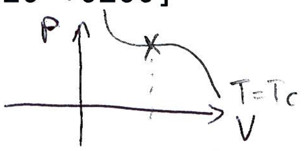
Note that $\delta = 3$ is graphically obvious:



inflection point, cubic behavior.

Exponent γ for the compressibility

$$\chi = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T \quad ; \quad p = \frac{8t}{3v-1} - \frac{3}{v^2} \Rightarrow \frac{\partial p}{\partial v} = \frac{8t\cdot 3}{(3v-1)^2} - \frac{6}{v^3} = 6(t-1) \text{ for } v=1$$

$$\text{with } t = 1+\delta t : \quad |\chi| \propto \frac{\partial v}{\partial p}\Big|_{v=1} \propto \frac{1}{|\delta t|} \Rightarrow \boxed{\gamma = 1}$$

Exponent β for the order parameter

$$p_\ell(T) - p_g(T) \propto (T_c - T)^\beta, \quad t = 1-x \; ; \; v = 1+y$$

Expand to order ~~x~~ 3: $\frac{1}{1+x} = x - x^2 + x^3 + \dots \Rightarrow \frac{1}{(1+x)^2} = 1 - 2x + 3x^2 - 4x^3$

$$p = \frac{8(1-x)}{3y+2} - \frac{3}{(1+y)^2} = 4(1-x)\frac{1}{1+\frac{3}{2}y} - 3(1 - 2y + 3y^2 - 4y^3)$$

$$\sim 4(1-x)\left(1 - \frac{3}{2}y + \frac{9}{4}y^2 - \frac{27}{8}y^3\right) - 3 + 6y - 9y^2 + 12y^3$$

$$\sim 4 - \cancel{6y} + \cancel{9y^2} - \frac{27}{2}y^3 - 4x + 6xy - 9xy^2 - 3 + \cancel{6y} - \cancel{9y^2} + 12y^3$$

$$\sim 1 - 4x + 6xy - \frac{3}{2}y^3 - 9xy^2 + \mathcal{O}(\text{four})$$

We expect $\beta < 1$, where $y \propto x^\beta$; keep y^3 but not xy^2 since $3\beta < 1 + 2\beta$

Take $\boxed{p = 1 - 4x + 6xy - \frac{3}{2}y^3}$ Note that $T = T_c \Rightarrow x = 0 \Rightarrow p \propto y^3$ i.e. $\delta = 3$.

Next: x is given (T); find y_ℓ and y_g ($y_\ell < y_g$) such that $p(y_\ell) = p(y_g)$ (*)

+ Maxwell construction: $p(y_\ell)(y_g - y_\ell) = \int_{y_\ell}^{y_g} p(y)\,dy$ (**)

Trick:

(*) $\Rightarrow 6x = \frac{3}{2}y_\ell^2 = \frac{3}{2}y_g^2 \Rightarrow y_g - y_\ell \propto \sqrt{x}$

$\Rightarrow \boxed{\beta = 1/2}$

Cubic in $y \Rightarrow \boxed{y_\ell = -y_g}$ and Maxwell rule (**) is obeyed automatically.