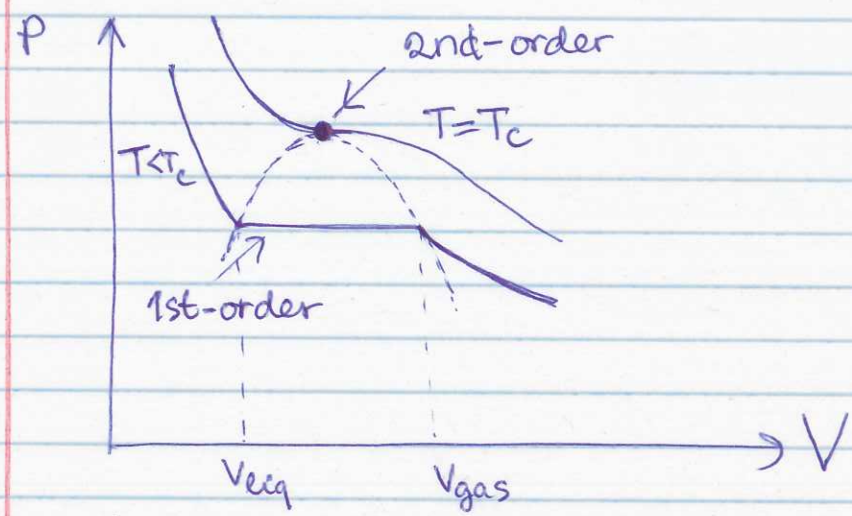
Critical point behavior



For any liquid/gas phase transition (1st, 2nd order)

for total system

$$\begin{cases} \alpha_p \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \infty & \text{(thermal expansion coeff.)} \\ \varkappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \infty & \text{(isothermal compressibility)} \\ c_p \equiv \left(\frac{\partial H}{\partial T}\right)_p = \infty & \text{(heat capacity at const } p\text{)} \\ C_V = \left(\frac{\partial U}{\partial T}\right)_V \leq \infty & \end{cases}$$

enthalpy

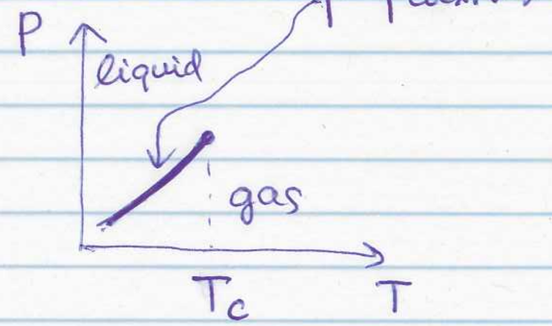
Proof: Along the horizontal (liquid-gas) coexistence segment, we have

$$\left.\Delta T = \Delta p = 0, \text{ while } \Delta V \neq 0 \right\} \Rightarrow \begin{array}{l} \alpha_p = \infty \\ \varkappa_T = \infty \end{array}$$

Also, we supply heat to convert liquid to gas while $\Delta T = 0$

$$C_p = \left(\frac{\delta Q}{\delta T}\right)_p = \infty .$$

For 2nd-order liquid-gas transition

Crit. exponents $\alpha, \beta, \gamma, \delta$ for $T \to T_c$	VdW	experiment
• $C_V \sim \lvert T-T_c\rvert^{-\alpha}$, $(V=V_c)$	$\alpha=0$	$0<\alpha<0.4$
• $n_{liq}-n_{gas} \sim (T_c-T)^{\beta}$, $T<T_c$, $p=p_{coex.}(T)$  "order parameter" exponent	$\beta=\frac{1}{2}$	$\beta=0.35$
• $\varkappa_T \sim \lvert T-T_c\rvert^{-\gamma}$, $V=V_c$ "susceptibility" exponent	$\gamma=1$	$\gamma=1.26$
• $\lvert p-p_c\rvert \sim \lvert n-n_c\rvert^{\delta}$, $T=T_c$ critical isotherm	$\delta=3$	$\delta=4.4$

Proof of VdW exponents β, γ, δ

VdW equation of state in reduced variables:

$$\bar{p} = \frac{8\bar{T}}{3\bar{v}-1} - \frac{3}{\bar{v}^2}, \qquad \bar{p}_c=\bar{T}_c=\bar{v}_c=1$$

Shifted variables $\quad \delta\bar{p} = \bar{p} - 1$

$$\delta\bar{v} = \bar{v} - 1$$

$$\delta\bar{T} = \bar{T} - 1$$

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

Drop bar "$\bar{*}$" from now on; expand rhs for small δT, δv:

$$\boxed{\delta p} \approx -1 + \frac{8(1+\delta T)}{2}\left(1 - \frac{3}{2}\delta v + \frac{9}{4}\delta v^2 - \frac{27}{8}\delta v^3 + \ldots\right)$$

$$-3\left(1 - (2\delta v + \delta v^2) + (2\delta v + \delta v^2)^2 - (2\delta v + \underbrace{\cancel{\delta v^2}}_{\text{drop}})^3\right) =$$

$$= \delta T\left(4 - 6\,\delta v + 9\,\delta v^2 - \frac{27}{2}\delta v^3\right)$$

$$- 6\delta v + 9\delta v^2 - \frac{27}{2}\delta v^3 + 6\delta v + 3\delta v^2 - 3\cdot 4\delta v^2 -$$

$$- 3\cdot 4\,\delta v^3 + 3\cdot 8\,\delta v^3 =$$

$$\boxed{= \delta T\cdot\left(4 - 6\delta v + 9\delta v^2 - \frac{27}{2}\delta v^3\right) - \frac{3}{2}\delta v^3}$$

Critical isotherm : $\delta T = 0$

$T = T_c$

quick proof: T_c, v_c was defined by $\frac{\partial p}{\partial v} = \frac{\partial^2 p}{\partial v^2} = 0$

$\Rightarrow p - p_c \sim \frac{1}{3!}\frac{\partial^3 p}{\partial v^3}(v - v_c)^3$

$$\delta\bar{p} \approx -\frac{3}{2}\delta\bar{v}^3$$

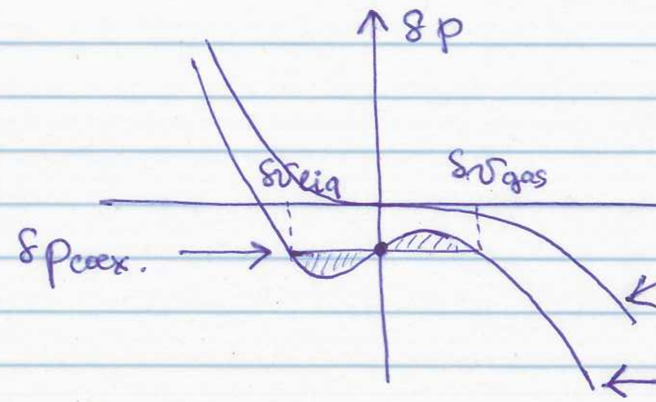
$$\boxed{\frac{p-p_c}{p_c}} \approx -\frac{3}{2}\left(\frac{v-v_c}{v_c}\right)^3 = -\frac{3}{2}\left(\frac{\frac{1}{\rho}-\frac{1}{\rho_c}}{1/\rho_c}\right)^3 =$$

$$= -\frac{3}{2}\left(\frac{\rho_c - \rho}{\rho}\right)^3 \approx \boxed{-\frac{3}{2}\left(\frac{\rho_c-\rho}{\rho_c}\right)^3}$$

$\Rightarrow$ exponent $\boxed{\delta = 3}$

Order parameter:

Maxwell construction near critical point



$-\frac{3}{2}\delta v^3$ (critical isotherm) $\delta T = 0$

$\approx 4\delta T - 6\delta T \cdot \delta v - \frac{3}{2}\delta v^3$ (sub-critical isotherm; $\delta T < 0$)

(if we ignore $\delta T \cdot \delta v^2$, etc., the subcrit isotherm is "odd" wrt point $(0, 4\delta T)$ and the Maxwell construction is trivial)

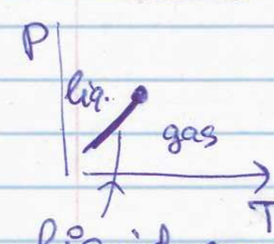
$$\Rightarrow \quad \delta p_{coex} = 4\delta T \stackrel{!}{=} 4\delta T - 6\delta T\, \delta v_{l/g} - \frac{3}{2}\delta v_{l/g}^3$$

$$\Rightarrow \boxed{\delta v_{liquid/gas} = \mp 2\sqrt{(-\delta T)}}$$

$$\Rightarrow \boxed{\frac{n_{liq} - n_{gas}}{n_c}} = \frac{1}{\bar{v}_{liq}} - \frac{1}{\bar{v}_{gas}} = \frac{1}{1+\delta\bar{v}_{liq}} - \frac{1}{1+\delta\bar{v}_{gas}} \approx$$

$$\approx \delta\bar{v}_{gas} - \delta\bar{v}_{liq} = 4\sqrt{-\delta\bar{T}} = \boxed{4\left(\frac{T_c - T}{T_c}\right)^{1/2}}$$

$\Rightarrow \boxed{\beta = \frac{1}{2}}$ – order parameter exponent



liquid-gas coexistence

$$-\frac{1}{p_c(1+\delta\bar v)}\cdot\left[-3\,\frac{8(1+\delta\bar T)}{(3\delta\bar v+2)^2}+\frac{6}{(1+\delta\bar v)^3}\right]^{-1}$$

$$\|$$

Compressibility

$$\varkappa_T = -\frac{1}{v}\left[\left(\frac{\partial p}{\partial v}\right)_T\right]^{-1} = -\frac{1}{(1+\delta\bar v)\,p_c}\left[\left(\frac{\partial \delta\bar p}{\partial \delta\bar v}\right)_{\delta\bar T}\right]^{-1}$$

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{p_c}{v_c}\left(\frac{\partial \bar p}{\partial \bar v}\right)_T = \frac{p_c}{v_c}\left(\frac{\partial \delta\bar p}{\partial \delta\bar v}\right)_{\delta\bar T}$$

$$v = v_c(1+\delta\bar v)$$

Above critical point, $\delta\bar T > 0$

at $v=v_c$, (point ⊠)

$$\left(\frac{\partial \delta\bar p}{\partial \delta\bar v}\right)_{\delta\bar T} = \delta\bar T\cdot(-6)$$

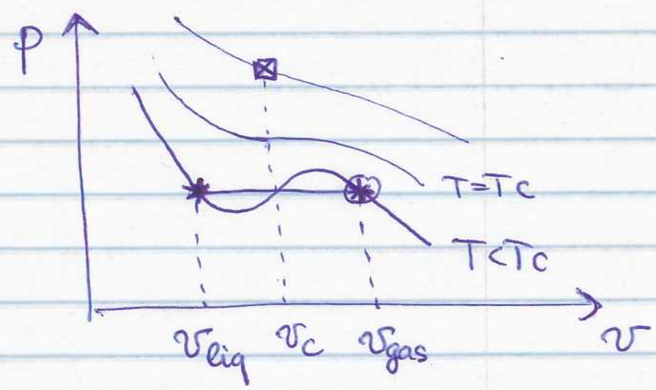
$$\boxed{\varkappa_T = -\frac{1}{p_c}\cdot\frac{1}{-6\delta\bar T} = \frac{1}{6p_c}\,\frac{1}{\delta\bar T} = \frac{1}{6p_c}\left(\frac{T-T_c}{T_c}\right)^{-1}}$$

$T > T_c$

$$\Rightarrow \gamma = 1,$$

Below the critical point

At points $*$, ⊛



$$\varkappa_{T,\,liq\ or\ gas} \approx -\frac{1}{p_c(1+\delta\bar v_{l/g})}\times$$

$$\times\frac{1}{6\left(\frac{1}{1+3\delta\bar v+3\delta\bar v^2+\delta\bar v^3}-\frac{1+\delta\bar T}{1+2\cdot\frac{3}{2}\delta\bar v+\left(\frac{3}{2}\delta\bar v\right)^2}\right)}$$

$$\approx -\frac{1}{6p_c}\times\frac{1}{1+3\delta v+\frac{9}{4}\delta v^2-\left(1+3\delta v+3\delta v^2+O(\delta v^3)\right)-\delta T-O(\delta T\cdot\delta v)}$$

$$= -\frac{1}{6p_c}\times\frac{1}{-\delta T-\frac{3}{4}\delta v^2_{liq/gas}} = -\frac{1}{6p_c}\times\frac{1}{-\delta T-3(-\delta T)} = \frac{1}{12p_c\cdot(-\delta T)}$$

$$\boxed{\varkappa_{T,\,\substack{\text{liq}\\ \text{or gas}}} \approx \frac{1}{12p_c}\left(\frac{T_c-T}{T}\right)^{-1}} \quad , \quad T<T_c$$

$\Rightarrow$ critical exponent for $\varkappa_T$ is the same above and below T_c ($\gamma=1$), but critical amplitude (prefactor $\frac{1}{6p_c}$ and $\frac{1}{12p_c}$) is not!

$\Rightarrow$ behavior of $\varkappa_{T,\text{gas}}$ is not symmetric wrt T_c, i.e. $\varkappa_{T,\text{gas}}$ is <u>not</u> only a fnctn of $|T-T_c|$.

Mnemonic
Terminology for result $\text{amplitude}_{\boxtimes} = 2\,\text{amplitude}_{\circledast}$:

$\boxtimes$ is twice as close to crit point as $\circledast$

$\boxtimes$ is removed from crit point only in temperature
$\circledast$ —〃— both in temperature and volume

<u>Remark</u>: General relations among critical exponents (valid for any system):

$$\left\{\begin{array}{ll} \gamma = \beta(\delta-1) & \text{Widom scaling law} \\ \alpha + 2\beta + \gamma = 2 & \text{Rushbrooke —〃—} \end{array}\right\} \text{satisfied by VdW exponents}$$

Will discuss later from scaling theory

VdW exponents = mean field exponents.