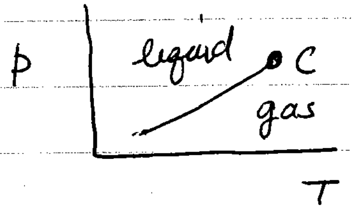
van der Waals Theory of Liquid-Gas phase transition

phase diagram



Liquid-Gas phase transition

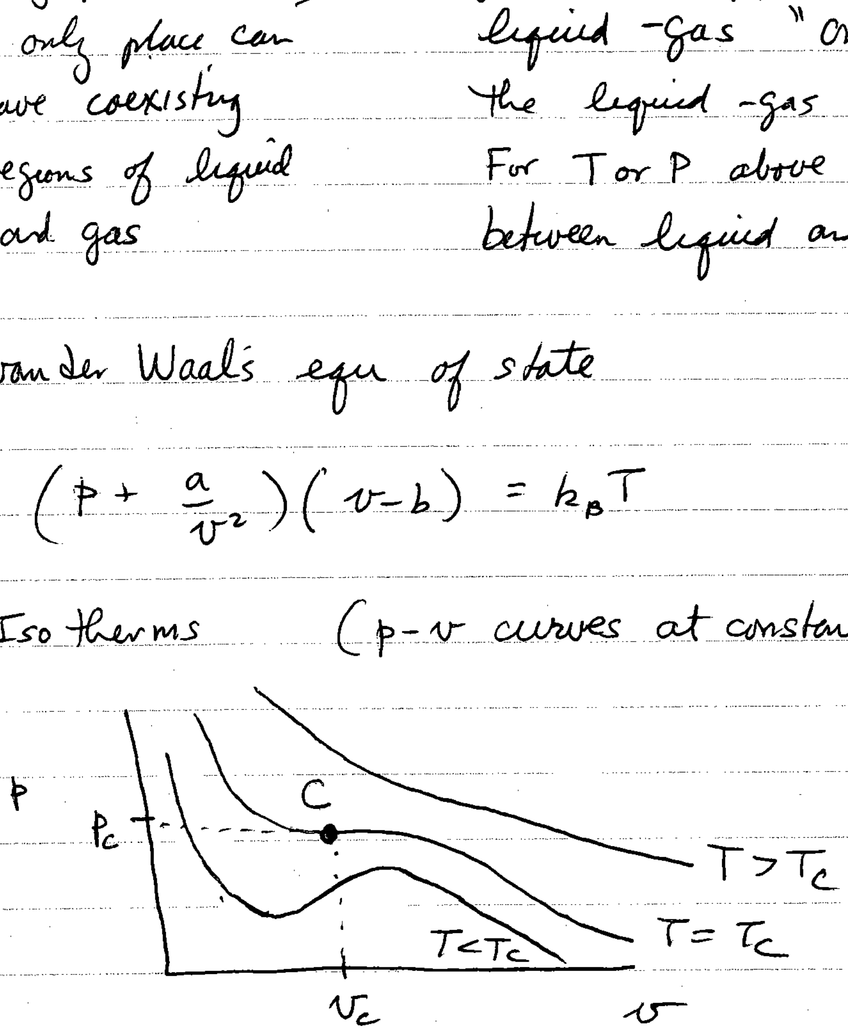
if one crosses the liquid-gas phase boundary, there is a discontinuous change in particle density. This change in density vanishes continuously as the point C is approached. C is called the liquid-gas "critical end point". The liquid-gas phase boundary ends at C. For T or P above C, there is no distinction between liquid and gas.

along phase boundary is only place can have coexisting regions of liquid and gas

van der Waal's equ of state

$$\left(p + \frac{a}{v^2}\right)(v-b) = k_B T \qquad a, b > 0$$

Isotherms (p-v curves at constant T) look like



There exists a critical isotherm T_c such that

For $T>T_c$, $dp/dv < 0$ monotonic decreasing $p(v)$

At $T=T_c$ first appearence of a point on isotherm with $\left(\frac{\partial p}{\partial v}\right)_T = 0$. this will turn out to be the critical point.

For $T<T_c$ isotherms are <u>not</u> monotonic – there is a region where $\left(\frac{\partial p}{\partial v}\right)_T > 0$.

Recall: isothermal compressibility

$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{-1}{v}\,\frac{1}{(\partial p/\partial v)_T}$$

For $T>T_c$, $\kappa_T > 0$ everywhere

For $T=T_c$, $\kappa_T \to \infty$ at the point C

For $T<T_c$, $\kappa_T < 0$ when $\frac{\partial p}{\partial v} > 0$ this is unphysical region – leads to thermodynamically unstable system. we will see that this is region of phase coexistence between liquid and gas

For $T<T_c$ the van der Waals isotherm when viewed as giving $v(p,T)$ becomes multi valued – ie three values of v for fixed p and T within some region of p. We will see that the physical system follows an isotherm that is given by the dashed line. It jumps from v_l to v_g at a given pressure $p^*(T)$. This $p^*(T)$

will be the location of the liquid gas phase boundary, $\frac{1}{v_\ell} - \frac{1}{v_g}$ gives the discontinuity in density at $p^*(T)$. The flat line between v_ℓ and v_g is coexistence region where system can be a mixture of both liquid and gas phases, with average specific volume v s.t. $v_\ell < v < v_g$.

As $T \to T_c^-$, $\left(\frac{1}{v_\ell} - \frac{1}{v_g}\right) \to 0$, $v_\ell, v_g \to v_c$ and $p^*(T) \to p_c$

$\Rightarrow$ C is the critical end point of the liquid-gas phase boundary.

For $T < T_c$ as $T \to T_c^-$ we see that the local max and local min of $p(v,T)$ both merge to the common pt C. $\Rightarrow$ C is an inflection point. $\frac{\partial^2 p}{\partial v^2} = 0$ at C.

Use $\left(\frac{\partial p}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$ to determine the location of C.

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

$$\left.\begin{array}{l} \frac{dp}{dv} = \frac{-k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow k_B T_c = 2a\,\frac{(v_c - b)^2}{v_c^3} \\ \frac{d^2 p}{dv^2} = \frac{2 k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow k_B T_c = 3a\,\frac{(v_c - b)^3}{v_c^4} \end{array}\right\} 2a = 3a\,\frac{(v_c - b)}{v_c}$$

$$2 v_c = 3 v_c - 3b \Rightarrow \boxed{v_c = 3b}$$ critical specific volume

$$\Rightarrow k_B T_c = 2a\frac{(v_c-b)^2}{v_c^3} = 2a\frac{(3b-b)^2}{(3b)^3} = \frac{2a(4b^2)}{27b^3}$$

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

$$p_c = \frac{k_B T_c}{v_c-b} - \frac{a}{v_c^2} = \frac{8}{27}\frac{a}{b}\left(\frac{1}{3b-b}\right) - \frac{a}{(3b)^2}$$

$$= \frac{8}{27}\frac{a}{b}\frac{1}{2b} - \frac{a}{9b} = \left(\frac{4}{27}-\frac{1}{9}\right)\frac{a}{b^2}$$

$$\boxed{p_c = \frac{1}{27}\frac{a}{b^2}}$$

Define $\bar{p} = \frac{p}{p_c}$, $\bar{T} = \frac{T}{T_c}$, $\bar{v} = \frac{v}{v_c}$

Then

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

$$\Rightarrow \left(p_c\bar{p} + \frac{a}{v_c^2\bar{v}^2}\right)(v_c\bar{v}-b) = k_B T_c \bar{T}$$

$$\left(\frac{1}{27}\frac{a}{b^2}\bar{p} + \frac{a}{9b^2\bar{v}^2}\right)(3b\bar{v}-b) = \left(\frac{8}{27}\frac{a}{b}\right)\bar{T}$$

$$\frac{1}{27}\frac{a}{b^2}\left(\bar{p} + \frac{3}{\bar{v}^2}\right)(3b)\left(\bar{v}-\frac{1}{3}\right) = \frac{8}{27}\frac{a}{b}\bar{T}$$

$$\Rightarrow \boxed{\left(\bar{p} + \frac{3}{\bar{v}^2}\right)\left(\bar{v}-\frac{1}{3}\right) = \frac{8}{3}\bar{T}}$$ Law of Corresponding states.

Also:
$$\frac{P_c v_c}{k_B T_c} = \frac{1}{27}\frac{a}{b^2}\frac{3b}{\left(\frac{8}{27}\right)\left(\frac{a}{b}\right)} = \frac{3}{8} = 0.375$$

universal # for all gases obeying van der Waals eqn of state

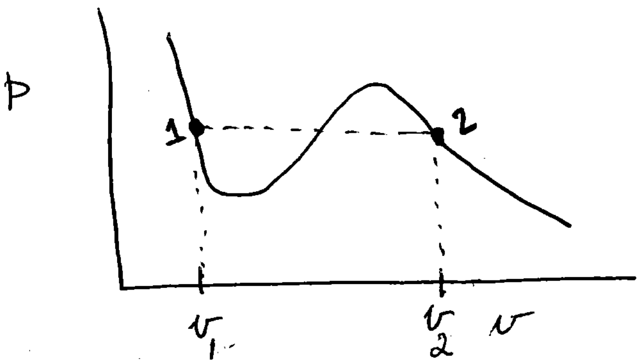
gas	T_c (K)	$\frac{P_c v_c}{k_B T_c}$
Ne	44.8	0.305
Ar	150.7	0.292
Kr	209.4	0.290
Xe	289.8	0.288
N_2	126.0	0.292
O_2	154.3	0.292
CO	133.0	0.294
CH_4	190.3	0.289

Law of corresponding states: If scale p, v, T by values at critical point to get $\bar{p}, \bar{v}, \bar{T}$, then isotherms in terms of $\bar{p}, \bar{v}, \bar{T}$ are independent of a and b - will be the same for any gas.

Now consider $T < T_c$ we want to determine the coexisting values of v_e and v_g that the physical system will have.

Two ways to do this

① Maxwell Construction



Gibbs free energy $G(T,p,N) = \mu N$

$$dG = -SdT + Vdp + \mu dN$$
$$= \mu dN + N d\mu$$
$$\Rightarrow d\mu = -\left(\frac{S}{N}\right)dT + v\,dp$$

↖ Gibbs-Duhem relation

along isotherm $dT = 0$

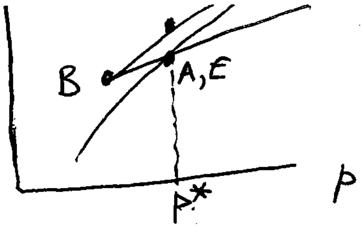
$$\Rightarrow d\mu = v\,dp$$

Now at liquid-gas coexistence, the condition for chemical equilib $\Rightarrow \mu_\ell = \mu_g$

$$\Rightarrow \int_1^2 d\mu = \mu_2 - \mu_1 = \int_1^2 v\,dp = 0 \quad \text{if}$$

v_1 is v_ℓ and v_2 is v_g for coexisting v_ℓ and v_g

graph of $\int v\,dp \rightarrow \mu = \frac{G}{N}$



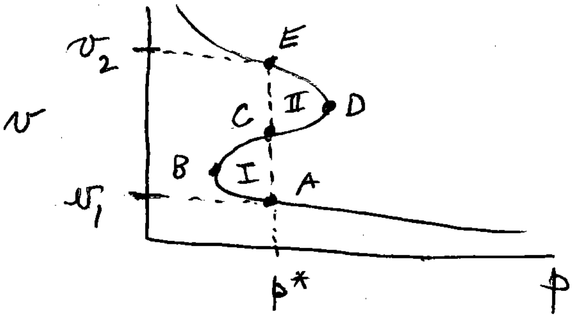
$\frac{G}{N}$ has cusp at p^*

$\frac{d\,G/N}{dp} = v$ is discontinuous at p^*

physical G/N is concave envelope

So $\int_1^2 v\,dp = 0$ determines $v_\ell = v_1$, $v_g = v_2$

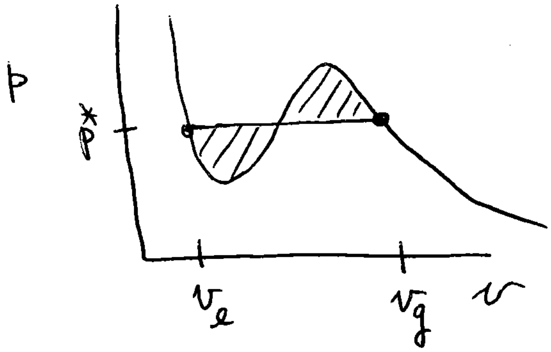
To see the geometric meaning of this



$$\int_1^2 v\,dp = \int_A^B v\,dp + \int_B^C v\,dp + \int_C^D v\,dp + \int_D^E v\,dp$$

$$= \text{area}_{I} - \text{area}_{II}$$

So we get condition of "equal areas"



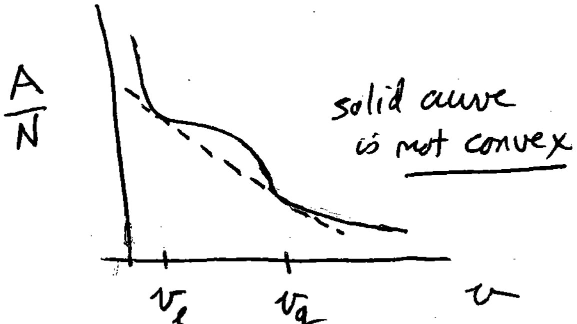
v_ℓ and v_g determined by the cord at constant p^* such that area above cord = area below cord

② Consider Helmholtz free energy $A(T,V)$ fixed N

$$dA = -s\,dT - p\,dV$$

$$A = -\int p\,dV \text{ along isotherm}$$

$$A/N = -\int p\,dv$$



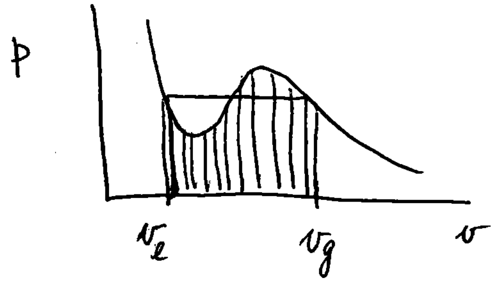
$$p = -\frac{\partial A}{\partial V} = -\frac{\partial A}{N\,\partial v}$$

p must be const from v_ℓ to v_g and A should be convex

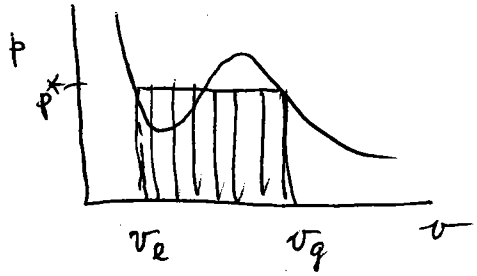
⇒ coexistence is given by dashed line

$$p^* = -\frac{\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_\ell\right]}{(v_g - v_\ell)}$$ coexistence pressure is slope of dashed line

$$p^*(v_g - v_\ell) = -\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_\ell\right] = +\int_\ell^g p\,dv$$

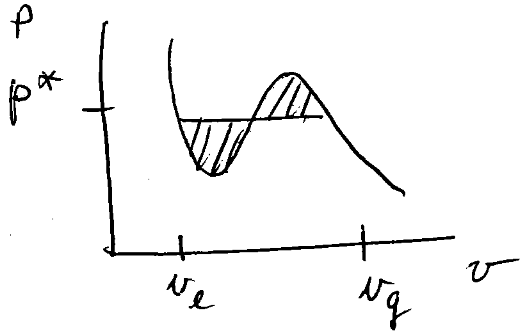


Shaded area is $\int_\ell^g p\,dv$



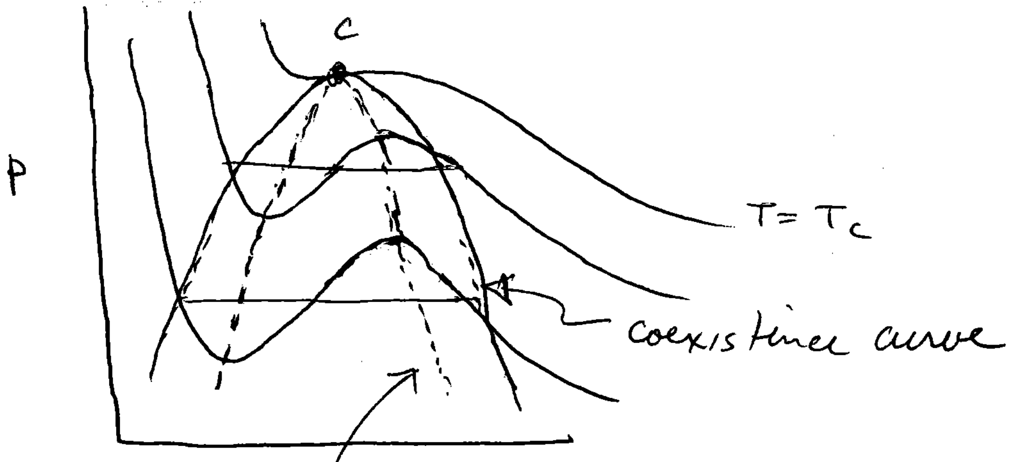
shaded area is $p^*(v_g - v_\ell)$

The two areas are equal only if



the shaded area above p^* equals shaded area below p^*

The locus of points $v_\ell(T)$, $v_g(T)$ in p-v plane as T varies is called the <u>coexistence curve</u>.



"Spinodal" line – locus of pts where $\frac{dp}{dv} = 0$

van der Waals suggested that states between coexistence curve ad spinodal line are metastable single phase regions

Law of corresponding states ⇒ when expressed in the scaled variables $\bar{p}, \bar{v}, \bar{T}$, the coexistence curves of all gases should collapse to a universal curve. Expt results give a good agreement with this prediction, but near C the coexistence curve does not agree too well with the van der Waals prediction

see Fig 3.20 of Plischke + Bergersen

from Huang

Table 16.2 Critical Exponents[a, b]

Exponent	*TH*	*EXPT*	*MFT*	*ISING2*	*ISING3*	*HEIS3*
α		0–0.14	0	0	0.12	−0.14
β		0.32–0.39	1/2	1/8	0.31	0.3
γ		1.3–1.4	1	7/4	1.25	1.4
δ		4–5	3	15	5	
ν		0.6–0.7	1/2	1	0.64	0.7
η		0.05	0	1/4	0.05	0.04
$\alpha + 2\beta + \gamma$	2	2.00 ±0.01	2	2	2	2
$(\beta\delta - \gamma)/\beta$	1	0.93 ±0.08	1	1	1	
$(2 - \eta)\nu/\gamma$	1	1.02 ±0.05	1	1	1	1
$(2 - \alpha)/\nu d$	1		$4/d$	1	1	1

[a] TH, theoretical values (from scaling laws); EXPT, experimental values (from a variety of systems); MFT, mean field theory; ISING*d*, Ising model in *d* dimension; HEIS3, classical Heisenberg model, $d = 3$.

[b] For more details and documentation see A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuation Theory of Phase Transitions* (Pergamon, Oxford, 1979), Table 3, pp. 42–43.

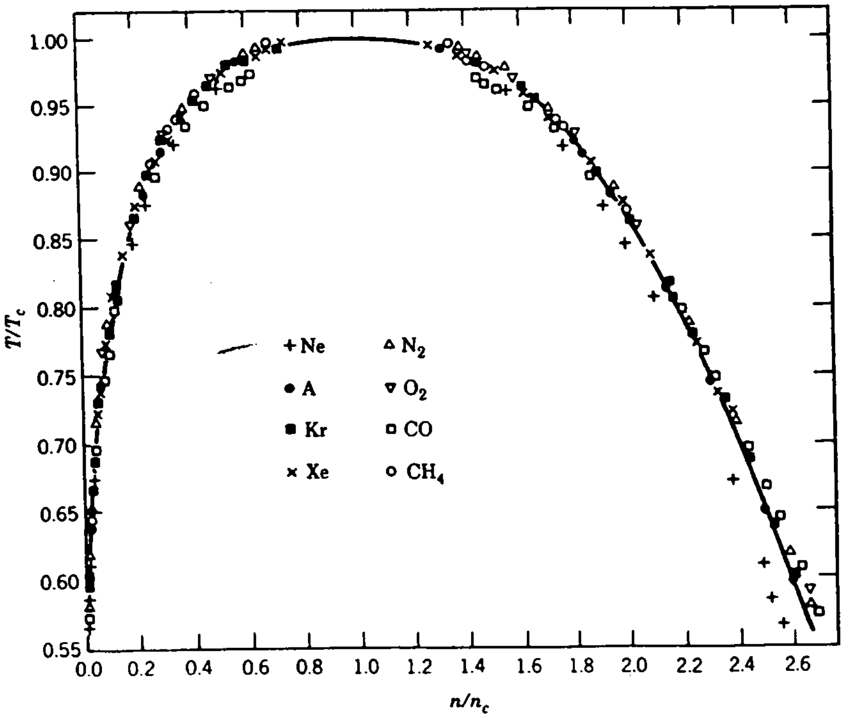
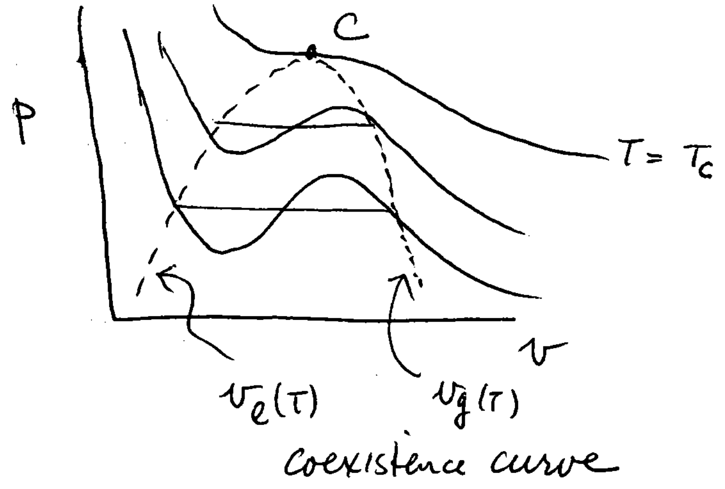


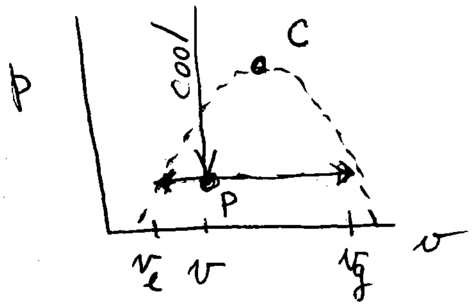
Fig. 16.2 Reduced temperature vs. reduced density in the gas-liquid coexistence region, for eight different substances.



Region of p-v plane under coexistence curve is the coexistence region.

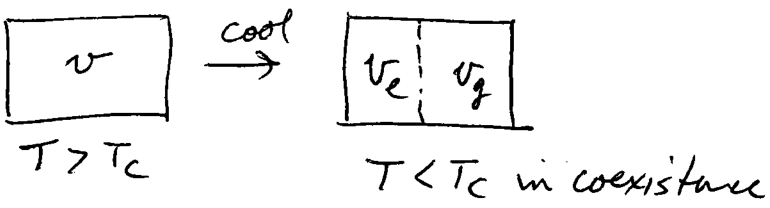
Region in which system can coexist as both liquid and gas

coexistence region is also called the phase separation region. If sit at a fixed density $n = 1/v$ that lies within coexistence region for some range of $T < T_c$, then cool system into coexistence region to point P,



the system can no longer exist at a uniform density $1/v$. It will split up in a part with density $1/v_\ell$ and a part with density $1/v_g$ such that average density remains $1/v$

The minimum energy state will be one in which the domain wall separating the liquid + gas is minimum, so one gets



the system "phase separates" into a region of liquid and a region of gas

Behavior near the critical point

To examine behavior near the critical point C, we can expand the equation of state about C.

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

critical point is at $\bar{p}=\bar{v}=\bar{T}=1$

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

$\bar{p}=1+\delta p$, $\bar{v}=1+\delta v$, $\bar{T}=1+\delta t$

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

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

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

expand to $O(\delta v^3)$ to get ∿ behavior in p vs v curves

$$1+\delta p=4(1+\delta t)\left[1-\frac{3}{2}\delta v+\frac{9}{4}\delta v^2-\frac{27}{8}\delta v^3\right]$$

$$-3\left[1-2\delta v-\delta v^2+4\delta v^2+4\delta v^3-8\delta v^3\right]$$

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

$$-\frac{27}{2}\delta t\,\delta v^3-3+6\delta v+3\delta v^2-12\delta v^2-12\delta v^3$$

$$+24\delta v^3$$

$$\delta p = -\tfrac{3}{2}\delta v^3 + \delta t\left[4 - 6\delta v + \underline{9\delta v^2} - \underline{\tfrac{27}{2}\delta v^3}\right]$$

as $\delta t \to 0$ it is sufficient to keep only

$$\delta p = -\tfrac{3}{2}\delta v^3 + \delta t\left[4 - 6\delta v\right] + \cdots$$

$$= -\tfrac{3}{2}\delta v^3 - (6\delta t)\,\delta v + 4\delta t$$

① critical isotherm is $\delta t = 0 \Rightarrow \delta p = -\frac{3}{2}\delta v^3$

$\propto \delta v^{\delta}$ critical exponent $\delta = 3$

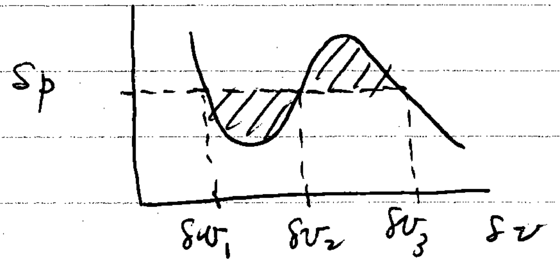
isothermal compressibility at T_c

$$\kappa_T = -\frac{1}{\bar v}\left(\frac{\partial \bar v}{\partial \bar p}\right)_{T,N} \doteq -\frac{1}{\bar v}\frac{1}{\left(\frac{\partial \bar p}{\partial \bar v}\right)_{T,N}} = -\frac{2}{9}\frac{1}{\delta v^2} \propto \frac{1}{\delta v^2}$$

on critical isotherm, $\delta v \propto (\delta p)^{1/3} \Rightarrow \boxed{\kappa_T \propto \frac{1}{\delta p^{2/3}}}$

as vary p through p_c on critical isotherm $T = T_c$

② coexistence curve



By Maxwell construction, coexistence determined as v_1 and v_3 such that shaded areas are equal.

$\delta v_1, \delta v_2, \delta v_3$ must solve

For $\delta p = -a\,\delta v^3 - b\,\delta v + 4\delta t$ $\quad a = 3/2,\ b \equiv 6\delta t$

coexistence is determined to be

$\boxed{\delta p = 4\delta t}$ ← coexistence curve in p–T plane

$$\Rightarrow -a\delta v^3 - b\delta v = 0 \Rightarrow \delta v_2 = 0,\ \delta v_{1,3} = \pm\sqrt{\frac{-b}{a}} = \pm\sqrt{\frac{2}{3}\cdot(-6\delta t)}$$

for $\delta t < 0$ (no coexistence for $\delta t > 0$)

$$\delta v_1 = \boxed{\delta v_\ell = -2\sqrt{|\delta t|}}$$

$$\delta v_3 = \boxed{\delta v_g = +2\sqrt{|\delta t|}}$$

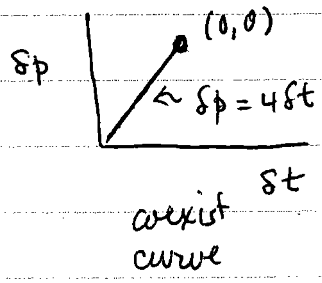
Jump in specific volume at coexistence curve

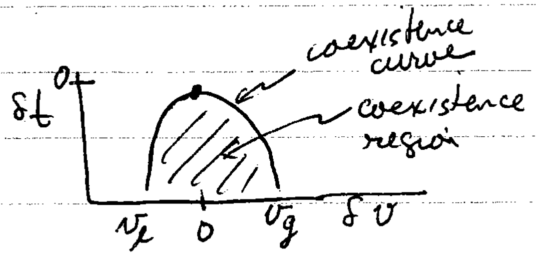
$$\Delta v = \delta v_g - \delta v_\ell = 4|\delta t|^{1/2} \propto |\delta t|^\beta \quad \beta = 1/2$$

<u>Note:</u> ~~if had kept the higher order terms in eqn of state, ie $(\delta t\, \delta v^2)$ and $(\delta t\, \delta v^3)$ terms, this would only lead to higher order corrects to above results ie~~

~~$\delta p = 4\delta t + o(\delta t)^2$~~

$$\delta v_{\ell,g} \sim \mp\sqrt{4|\delta t|(1+o(\delta t))}$$





Isothermal compressibility at fixed p_c as vary T.

$$\delta p = -\tfrac{3}{2}\delta v^3 + \delta t\,[4 - 6\delta v] \Rightarrow \frac{\partial p}{\partial v} = -\tfrac{9}{2}\delta v^2 - 6\delta t$$

$$\kappa_T = \frac{1}{\tfrac{9}{2}\delta v^2 + 6\delta t}$$

for $p = p_c$, ie $\delta p = 0$, equ of state gives

$$\delta p = 0 = -\frac{3}{2}\delta v^3 + \delta t\,[4 - 6\delta v]$$

$$\Rightarrow \quad \delta t = \frac{\frac{3}{2}\delta v^3}{4 - 6\delta v} \sim \frac{3}{8}\delta v^3 \Rightarrow \left(\frac{8}{3}\delta t\right)^{1/3} = \delta v$$

$$\kappa_T = \frac{1}{\frac{9}{2}\left(\frac{8}{3}\delta t\right)^{2/3} + 6\delta t} \approx \frac{1}{(\delta t)^{2/3}}$$

But if compute κ_T along critical isochore $\delta v = 0$ for $T > T_c$

then $\kappa_T = \dfrac{1}{6\,\delta t}$

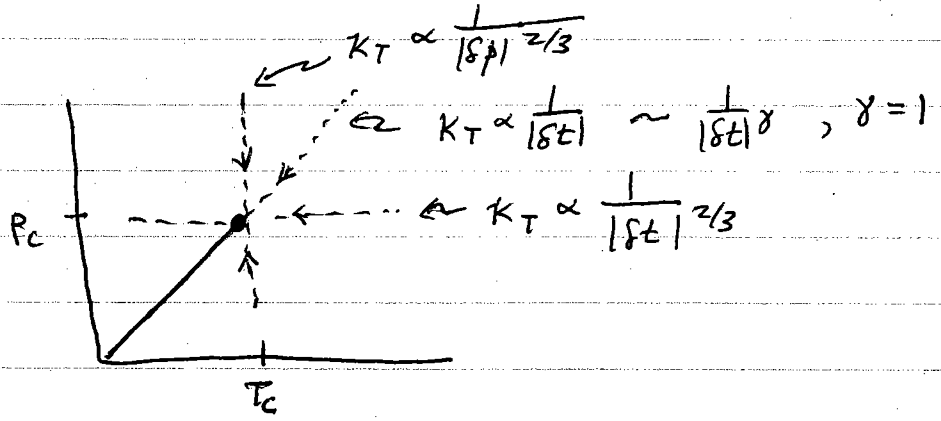
If compute along coexistence curve for $T < T_c$, then $\delta v^2 = 4|\delta t|$

$$\kappa_T = \frac{1}{\frac{9}{2}\cdot 4|\delta t| - 6|\delta t|} \qquad \text{since } \delta t = -|\delta t|$$

$$\kappa_T = \frac{1}{12\,|\delta t|}$$

amplitude ratio:

$$\lim_{\delta t \to 0} \frac{\kappa_T^+}{\kappa_T^-} = \frac{12\,\delta t}{6\,\delta t} = 2$$



How does specific heat C_v diverge? see homework problem!