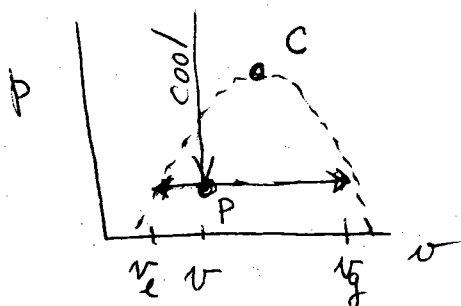


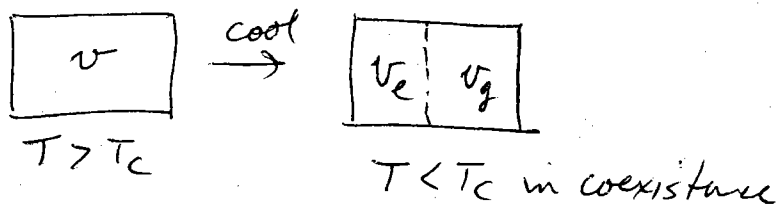
Region of p - v plane under coexistence curve is the coexistence region.
 Region in which system can coexist as both liquid and gas

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

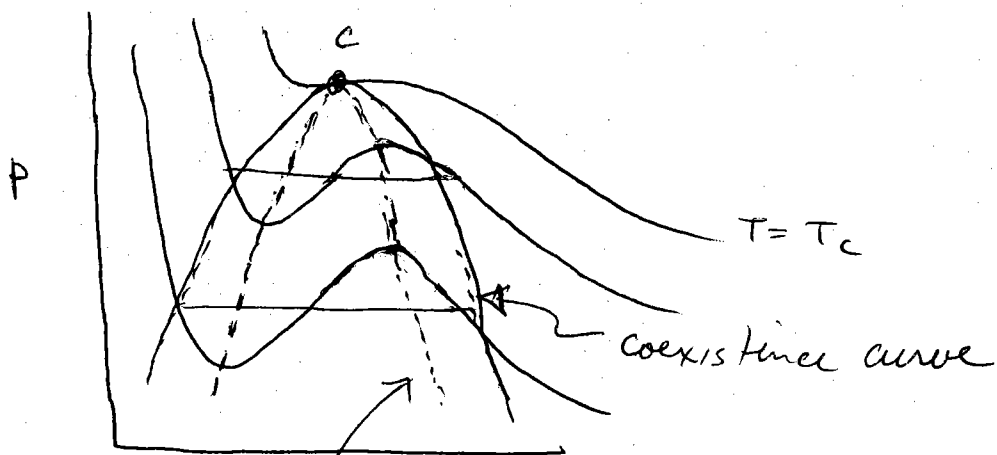


the system can no longer exist at a uniform density $1/v$. It will split up in a part with density $1/v_l$ and a part with density $1/v_g$ such that average density remains $1/v$.

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



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

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

Law of corresponding states \Rightarrow 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

Behavior near the critical point

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

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

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

critical point is at

$$\bar{P} = \bar{v} = \bar{T} = 1$$

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

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

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

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

expand to $o(\delta v^3)$
to get \searrow behavior
in pos v curves

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

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

$$= 4 - 6\delta v + 9\delta v^2 - \frac{27}{2}\delta v^3 + 4\delta t - 6\delta t\delta v + 9\delta t\delta v^2 \\ - \frac{27}{2}\delta t\delta v^3 - 3 + 6\delta v + 3\delta v^2 - 12\delta v^2 - 12\delta v^3 \\ + 24\delta v^3$$

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

at $\delta t \rightarrow 0$ it is sufficient to keep only

$$s_p = -\frac{3}{2} \delta v^3 + \delta t [4 - 6\delta v] + \dots$$

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

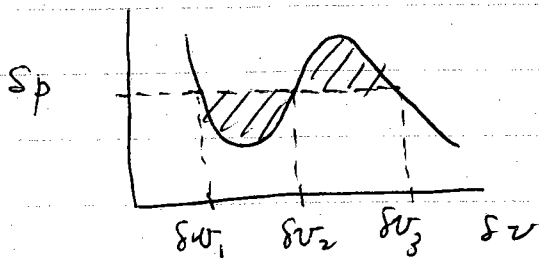
① critical isotherm in $\delta t = 0 \rightarrow s_p = -\frac{3}{2} \delta v^3$
 $\propto \delta v^{\delta}$ critical exponent $\delta = 3$

isothermal compressibility at T_c

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

on critical isotherm, $\delta v \propto (s_p)^{1/3} \rightarrow \boxed{\kappa_T \propto \frac{1}{s_p^{2/3}}}$
 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 $s_p = -a \delta v^3 - b \delta v + 4\delta t$ \leftarrow $a = 3/2, b = 6\delta t$

coexistence is determined to be

$\boxed{s_p = 4\delta t}$ \leftarrow 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 $\delta t > 0$)

$$\delta v_l = \delta v_e = -2\sqrt{|\delta t|}$$

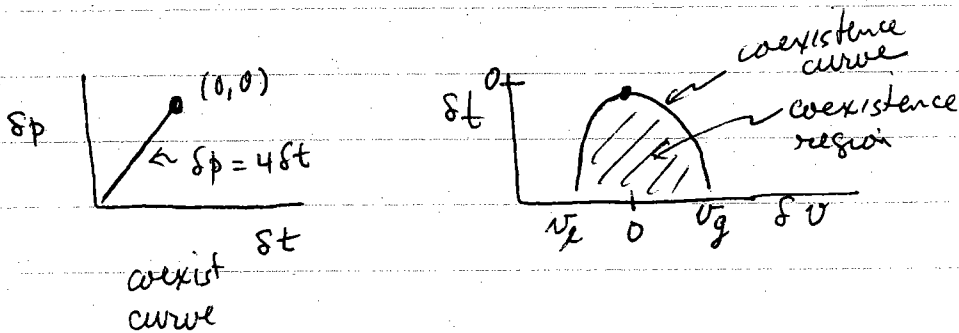
$$\delta v_g = \delta v_g = +2\sqrt{|\delta t|}$$

Jump in specific volume at coexistence curve

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

Note: ~~if had kept the higher order terms in expansion of state, i.e. $(\delta t \delta v^2)$ and $(\delta t \delta v^3)$ terms, this would only lead to higher order corrections to above result i.e.~~

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

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


isothermal compressibility at fixed p_c as vary T .

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

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

for $p = p_c$, i.e. $\delta p = 0$, eqn of state gives

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

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

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

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

$$\text{then } k_T = \frac{1}{6\delta t}$$

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

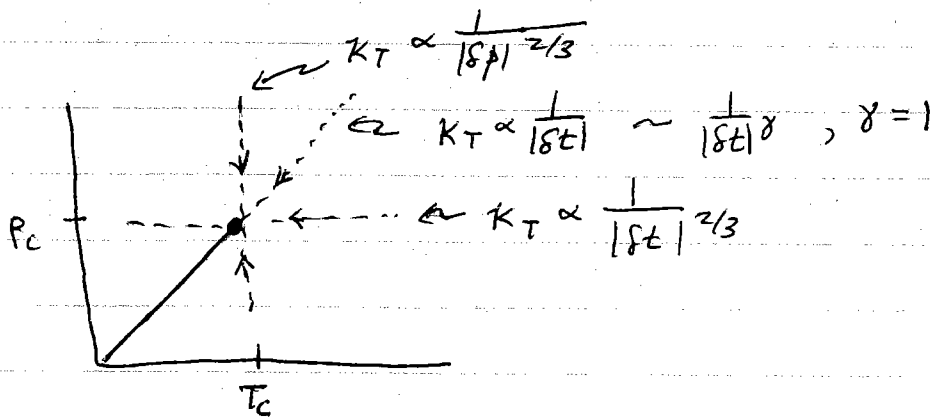
$$k_T = \frac{1}{\frac{9}{2} \cdot 4|\delta t| - 6|\delta t|}$$

$$\text{since } \delta t = -|\delta t|$$

amplitude ratio:

$$\lim_{\delta t \rightarrow 0} \frac{k_T^+}{k_T^-} = \frac{12\delta t}{6\delta t} = 2$$

$$k_T = \frac{1}{12|\delta t|}$$



How does specific heat C_v diverge? see homework problem!

Coexistence curve using more complete equation of state

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

$$\delta p = -a \delta v^3 + b \delta v^2 + \underset{\uparrow}{c \delta v} + 4 \delta t \quad \begin{cases} a = \frac{3}{2} + \frac{27}{2} \delta t \\ b = 9 \delta t \\ c = 6 \delta t \end{cases}$$

transform to $\delta v = \delta v_0 + u$

$$\delta p = -a (\delta v_0^3 + 3 \delta v_0^2 u + 3 \delta v_0 u^2 + u^3) + b (\delta v_0^2 + 2 \delta v_0 u + u^2) - c (\delta v_0 + u) + 4 \delta t$$

$$\delta p = -a u^3 + (b - 3a \delta v_0) u^2 - (c - 2b \delta v_0 + 3a \delta v_0^2) u + (4 \delta t - c \delta v_0 + b \delta v_0^2 - a \delta v_0^3)$$

Choose δv_0 to make the u^2 term vanish

$$b = 3a \delta v_0 \Rightarrow \delta v_0 = \frac{b}{3a} = \frac{9 \delta t}{3 \left(\frac{3}{2} + \frac{27}{2} \delta t \right)} = \frac{2t}{1 + 9 \delta t}$$

$$\delta v_0 \approx 2 \delta t - 18 \delta t^2$$

$$\delta p = -a u^3 - c' u + f(t)$$

$$\text{where } c' = c - 2b \delta v_0 + 3a \delta v_0^2$$

$$= 6 \delta t - 2(9 \delta t)(2 \delta t - 18 \delta t^2) + 3 \left(\frac{3}{2} + \frac{27}{2} \delta t \right) (2 \delta t - 18 \delta t^2)$$

$$= 6 \delta t - 36 \delta t^2 + 18^2 \delta t^3 + \left(\frac{9}{2} + \frac{3}{2} \cdot 27 \delta t \right) (4 \delta t^2 - 4 \cdot 18 \delta t^3)$$

$$= 6 \delta t - 36 \delta t^2 + 18 \delta t^3 + 18 \delta t^2 + (6)(27) \delta t^3 - (2)(9)(18) (\delta t^3)$$

$$= 6 \delta t - 18 \delta t^2 + (18 + 162 - 324) \delta t^3$$

$$c' = 6 \delta t - 18 \delta t^2 - 144 \delta t^3$$

$$\begin{aligned}
 f(t) &= 48t - c\delta v_0 + 6\delta v_0^2 - a\delta v_0^3 \\
 &= 48t - (6\delta t)(2\delta t - 18\delta t^2) + (9\delta t)(2\delta t - 18\delta t^2)^2 \\
 &\quad \left(\frac{3}{2} + \frac{27}{2}\delta t\right)(2\delta t - 18\delta t^2)^3 \\
 &= 48t - 12\delta t^2 + (6)(18)\delta t^3 + 36\delta t^3 - 12\delta t^3 \\
 &= 48t - 12\delta t^2 + 132\delta t^3 \dots
 \end{aligned}$$

$$\delta p = -a u^3 - c' u + f(t)$$

By the same arguments of symmetry used earlier, we see that the phase boundary is now given by

$$\boxed{\delta p = f(t) = 48t - 12\delta t^2 + o(\delta t^3)}$$

same result as earlier, but with higher order corrections

The coexistence curve densities are given by

$$-a u^3 - c' u = 0 \Rightarrow u_{l,g} = \pm \sqrt{-\frac{c'}{a}} = \pm \sqrt{\frac{-6\delta t + 18\delta t^2 + 144\delta t^3}{\frac{3}{2}(1+9\delta t)}}$$

$$u_{l,g} = \pm \sqrt{\frac{-48t + 12\delta t^2 + 96\delta t^3}{1+9\delta t}}$$

$$= \pm \sqrt{-48t + 12\delta t^2 + 36\delta t^2 + o(\delta t^3)}$$

$$u_{l,g} = \pm \sqrt{-48t(1-12\delta t)}$$

$$\delta v_{l,g} = \delta v_0 + u_{l,g} = 2\delta t - 18\delta t^2 \pm \sqrt{-48t(1-12\delta t)}$$

to lowest order

$$\delta v_{l,g} = \pm \sqrt{-4st} + 2st + o(st^{3/2})$$

$$= \pm 2\sqrt{|st|} + 2st$$

$$\delta v_{l,g} = \pm 2\sqrt{|st|} (1 \mp \sqrt{|st|})$$

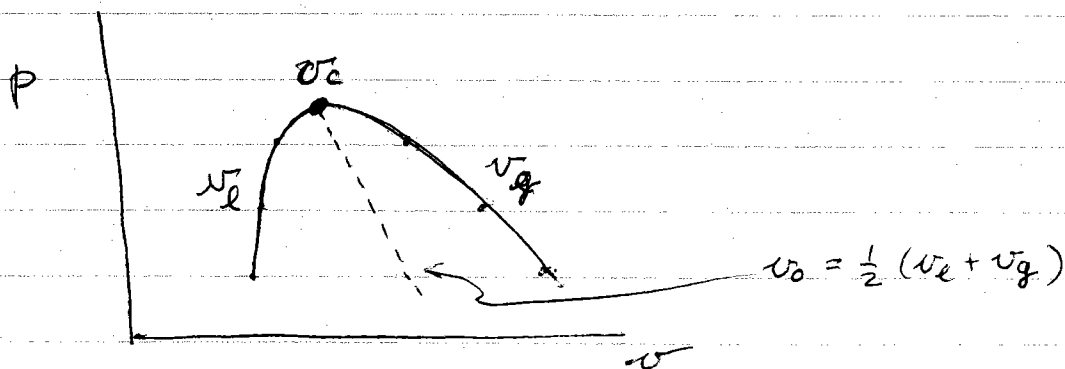
leading term higher order correction

to leading order we have the same result as before

$$\text{with } \Delta v = 4\sqrt{|st|} = \delta v_g - \delta v_l \text{ along phase boundary}$$

The main difference is that the coexistence curve is now not symmetric about the critical specific volume $\delta v_c = 0$ but rather about $\delta v_0 \approx 2st$

$$v_{l,g} \approx 2(st \pm \sqrt{|st|})$$



in experimental data one clearly sees this asymmetry

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

^aTH, 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, $d = 3$.

^bFor 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.

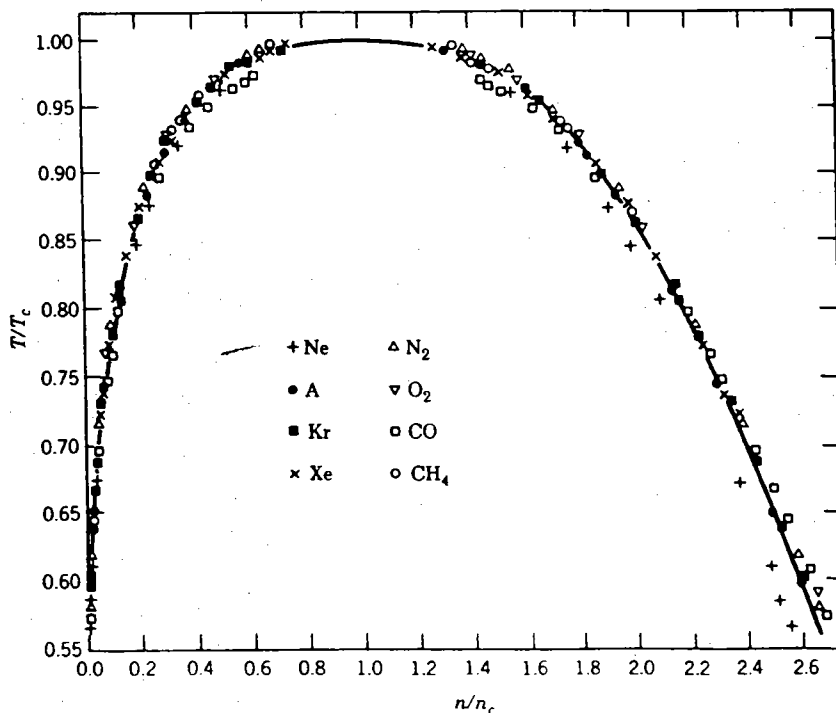


Fig. 16.2 Reduced temperature vs. reduced density in the gas-liquid coexistence region, for eight different substances.

Finally considers the free energy

$$\delta p = -a u^3 - c' u + f(t)$$

where $f(t) = \delta p^*(t)$ is the coexistence phase boundary

$$\begin{aligned} \frac{A}{N}(u, t) &= - \int_{u_{\text{ref}}}^u p \, dV + \frac{A_{\text{ref}}}{N} \\ &= - \int_{u_{\text{ref}}}^u \delta p \, du + \frac{A_{\text{ref}}}{N} \end{aligned}$$

$$\frac{A}{N}(u, t) = \frac{a}{4} u^4 + \frac{c'}{2} u^2 - \delta p^*(u - u_{\text{ref}}) + \frac{A_{\text{ref}}}{N}$$

$$\frac{A}{N}(u, t) + \delta p^* u = \left[\frac{c'}{2} u^2 + \frac{a}{4} u^4 \right] + \frac{A_{\text{ref}}}{N} + \delta p^* u_{\text{ref}}$$

Now $\frac{G}{N}(p, T) = \min_u \left(\frac{A}{N}(u, t) + \delta p u \right)$ Legendre transf

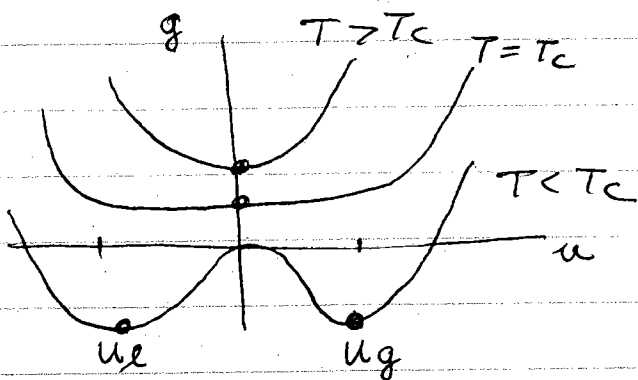
So along the phase boundary $\delta p^*(T)$

$$\frac{G}{N}(p^*, T) = \min_u \left[\frac{c'}{2} u^2 + \frac{a}{4} u^4 \right] + \frac{A_{\text{ref}} + \delta p^* u_{\text{ref}}}{N}$$

|||
 $g(u)$

indep of u

plot $g(u) = \frac{c'}{2}u^2 + \frac{a}{4}u^4$ for $T > T_c$, $T = T_c$, $T < T_c$



$$T > T_c, c' > 0, g(u) \sim u^2$$

$$T = T_c, c' = 0, g(u) \sim u^4$$

$$T < T_c, c' < 0, g(u) \sim -u^2$$

For $T \geq T_c$, the minimizing $u = 0$

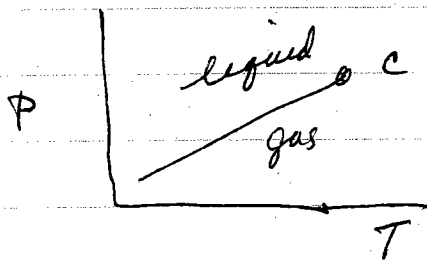
For $T < T_c$, the minimizing $u = \pm \sqrt{\frac{-c'}{a}} \propto \pm \sqrt{|8t|}$

So the transition occurs when the coefficient of the quadratic u^2 term vanishes. Above T_c

this coefficient is positive, the function is everywhere convex, the minimum is the single point $u = 0$.

Below T_c , this coefficient is negative, the minima move to two non zero values $\pm u_{\min}$ which increase in magnitude as $T - T_c$ increases. The two non zero values $\pm u_{\min}$ are the values in the two coexisting phases.

Liquid gas phase boundary



along phase boundary

$$\mu_l(T, p) = \mu_g(T, p) = \text{gibbs free energy per particle}$$

one constraint on two thermodynamic variables T, p determines the coexistence region in the p - T plane to be a line $p(T)$.

Gibbs - Duhem relation

$$d\mu_l = -s_l dT + v_l dp$$

$$d\mu_g = -s_g dT + v_g dp$$

where $s = \frac{S}{N}$

entropy per particle

along phase boundary

$$d\mu_l = d\mu_g$$

since $\mu_l = \mu_g$

$$\Rightarrow -s_l dT + v_l dp = -s_g dT + v_g dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{s_g - s_l}{v_g - v_l} = \frac{\Delta s}{\Delta v} \equiv \frac{L}{T \Delta v}$$

where $L \equiv T \Delta s$ is the latent heat of the transition.

= heat that must be absorbed to turn one particle of liquid

into gas. For system with fixed total V and total N , then change in total energy is $dE = T ds \Rightarrow dE/N = T ds \Rightarrow \Delta E = T \Delta s = L$

$$\boxed{\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{L}{T \Delta v}}$$

← Clausius Clapeyron relation

relates slope of phase boundary to discontinuities in entropy and density upon crossing phase boundary

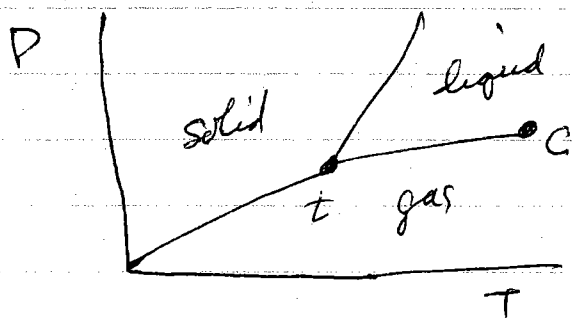
Note: Since $\frac{dp}{dT}$ is in general finite, and we know ΔV is finite but with $\Delta V \rightarrow 0$ as one approaches the critical pt C, then similarly it must be that ΔS is finite upon crossing the phase boundary, but with $\Delta S \rightarrow 0$ as one approaches C.

$\Rightarrow L$ is finite along phase boundary, but $L \rightarrow 0$ at C.

one often says that a phase transition is 1st order if there is a finite latent heat L . A phase transition is 2nd order if $L=0$. Liquid-gas phase boundary is a 1st order phase transition that ends a 2nd order phase transition at the critical point C.

Gibbs phase rule

phase boundary line in p - T plane is a locus of points where two phases coexist in equilibrium.
Can three phases coexist together?



3-phase coexistence at "triple point" t .

at 3-phase coexistence

$$\mu_s(T, p) = \mu_l(T, p) = \mu_g(T, p)$$

two thermodynamic variables T, p

two equations of constraint $\mu_s = \mu_l, \mu_l = \mu_g \Rightarrow$ there is a unique solution (p_t, T_t) is the locus of point where

3 phase may coexist at an isolated point (in contrast to 2-phase coexistence which is a line!). This is called the triple point.

Can 4 phases coexist together?

This would require $\mu_1(T, p) = \mu_2(T, p) = \mu_3(T, p) = \mu_4(T, p)$

two thermodynamic variables + 3 constraints

\Rightarrow solution is in general over specified - more constraints than variables \Rightarrow no solution.

So max number of coexisting phases is three, unless there are other thermodynamic variables besides p , and T .

Suppose one has a multicomponent system where

c_{ij} , $i=1, 2, \dots, r$ is the fraction of constituent i in thermodynamic phase j . $\sum_{i=1}^r c_{ij} = 1$

Suppose there are s coexisting phases

Then there are $p, T, c_{ij} = 2 + rs$ degrees of freedom

and $\sum_{i=1}^r c_{ij} = 1$, $\mu_{ij} = \mu_{i,j+1}$ for $\left. \begin{matrix} j=1 \text{ to } s-1 \\ i=1 \text{ to } r \end{matrix} \right\}$ gives

$s + r(s-1)$ constraints

\Rightarrow number of "free" variables is $(2 + rs) - (s + r(s-1))$

$$= 2 + rs - s - rs + r = 2 + r - s$$

this must be ≥ 0 to have a solution

\Rightarrow $s \leq r + 2$ maximum number of coexisting phases for an r -component system is $r + 2$