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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

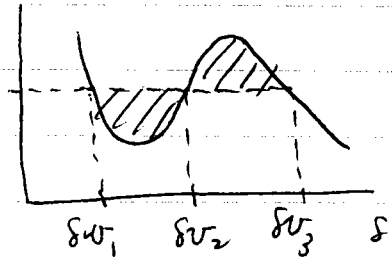
isothermal compressibility at T_c

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

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

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

coexistence is determined to be

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

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

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

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

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

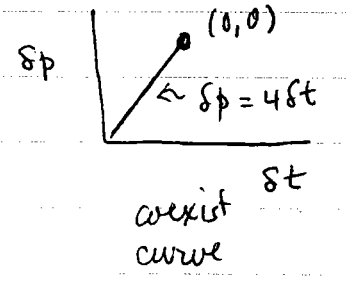
Jump in specific volume at coexistence curve

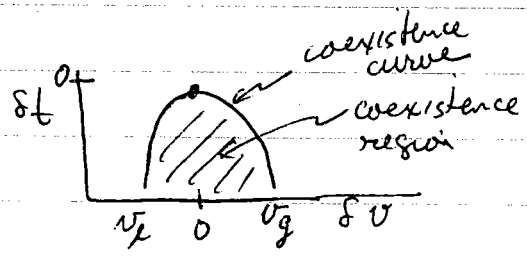
$$\Delta v = \delta v_g - \delta v_\ell = 4|\delta t|^{1/2} \propto |\delta t|^{\beta} \quad \beta = 1/2$$

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

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

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

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

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

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

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

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 $\delta v^2 = 4|\delta t|$

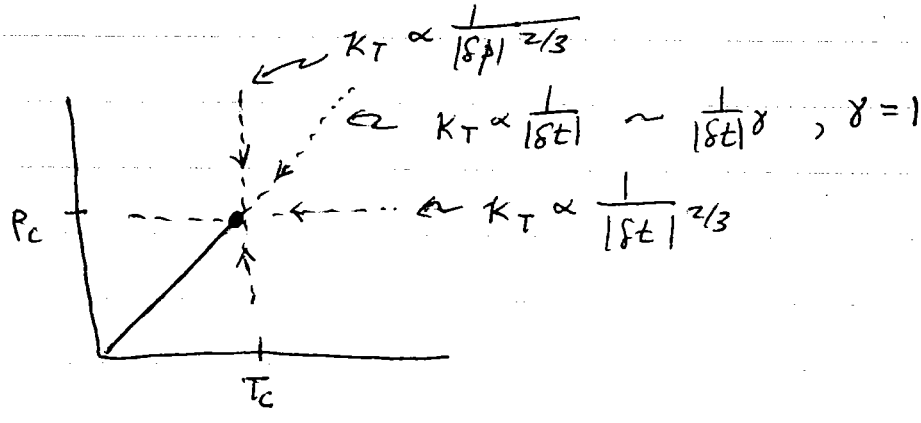
$$\kappa_T = \frac{1}{\frac{9}{2}\cdot 4|\delta t| - 6|\delta t|}$$

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!

Coexistence curve using more complete equation of state

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

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

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

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

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

Choose δv_0 to make the u^2 term vanish

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

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

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

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

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

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

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

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

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

$$f(t) = 4\delta t - c\delta v_0 + 6\delta v_0^2 - a\delta v_0^3$$

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

$$= 4\delta t - 12\delta t^2 + (6)(18)\delta t^3 + 36\delta t^3 - 12\delta t^3$$

$$= 4\delta t - 12\delta t^2 + 132\delta t^3 \ldots\ldots$$

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

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

$$\boxed{\delta p = f(t) = 4\delta t - 12\delta t^2 + o(\delta t^3)}$$

same result as earlier, but with higher order correction

The coexistence curve densities are given by

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

$$u_{l,g} = \pm\sqrt{\frac{-4\delta t + 12\delta t^2 + 96\delta t^3}{1 + 9\delta t}}$$

$$= \pm\sqrt{-4\delta t + 12\delta t^2 + 36\delta t^2 + o(\delta t^3)}$$

$$u_{l,g} = \pm\sqrt{-4\delta t\,(1 - 12\delta t)}$$

$$\delta v_{l,g} = \delta v_0 + u_{l,g} = 2\delta t - 18\delta t^2 \pm \sqrt{-4\delta t\,(1 - 12\delta t)}$$

to lowest order

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

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

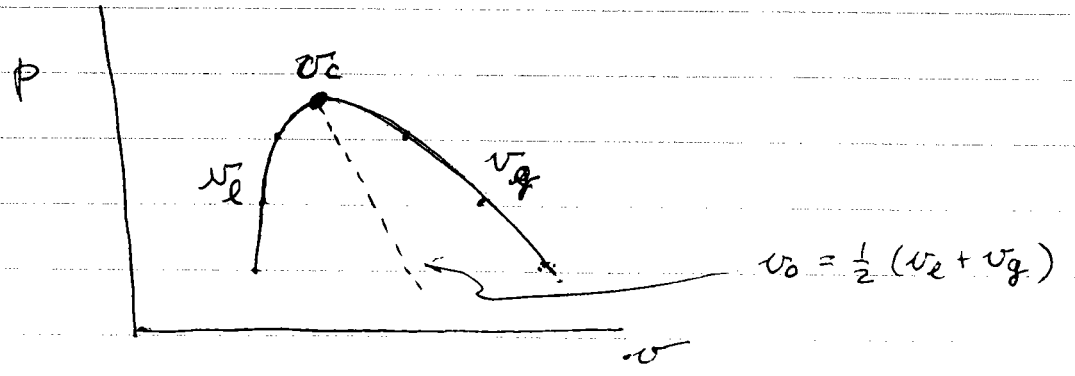
$$\boxed{\delta v_{l,g} = \pm 2\sqrt{|\delta t|}\left(1 \mp \sqrt{|\delta t|}\right)}$$

leading term higher order correction

to leading order we have the same result as before,
with $\Delta v = 4\sqrt{|\delta t|} = \delta v_g - \delta v_l$ along phase boundary

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

$$v_{l,g} \approx 2\left(\delta t \pm \sqrt{|\delta t|}\right)$$



in experimental data one clearly sees this asymmetry

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; ISINGd, 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.

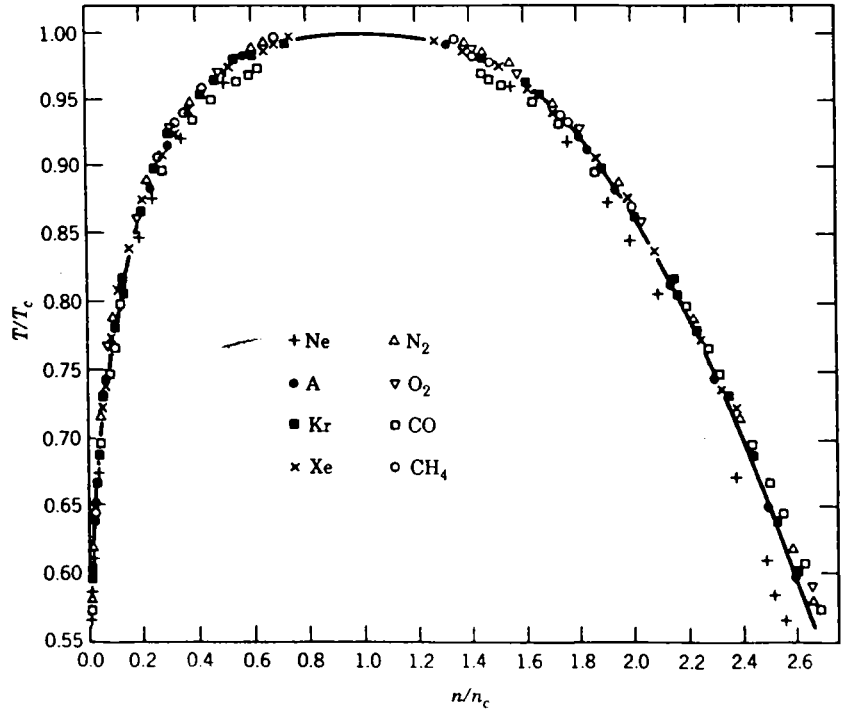


Fig. 16.2 Reduced temperature vs. reduced density in the gas-liquid coexistence region, for eight different substances.

Finally consider the free energy

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

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

$$\frac{A}{N}(u,t) = -\int_{v_{ref}}^{v} p\,dv + \frac{A_{ref}}{N}$$

$$= -\int_{u_{ref}}^{u} \delta p\,du + \frac{A_{ref}}{N}$$

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

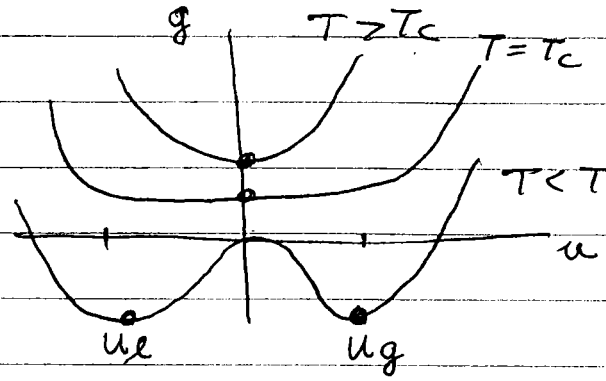
$$\frac{A}{N}(u,t) + \delta p^* u = \left[\frac{c'}{2}u^2 + \frac{a}{4}u^4\right] + \frac{A_{ref}}{N} + \delta p^* u_{ref}$$

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 $\delta p^*(T)$

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

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



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

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

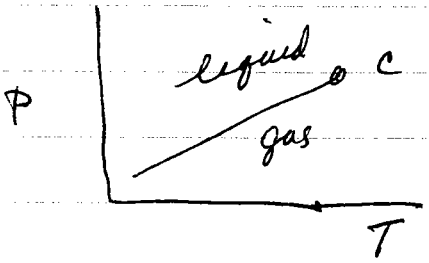
$T < T_c$, $c' < 0$, $g(u) \sim -u^2$

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

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

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

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

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

$$d\mu_\ell = -s_\ell\, dT + v_\ell\, dp$$

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

where $s = \frac{S}{N}$ entropy per particle

along phase boundary $d\mu_\ell = d\mu_g$ since $\mu_\ell = \mu_g$

$$\Rightarrow -s_\ell\, dT + v_\ell\, dp = -s_g\, dT + v_g\, dp$$

$$\Rightarrow \frac{dp}{dT} = \frac{s_g - s_\ell}{v_g - v_\ell} = \frac{\Delta s}{\Delta v} \equiv \frac{L}{T\Delta v}$$

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 $dE = TdS \Rightarrow dE/N = Tds \Rightarrow \Delta E = T\Delta s = L$

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

← Clausius Clapeyron relation relates slope of phase boundary to discontinuities in entropy and density upon crossing phase boundary

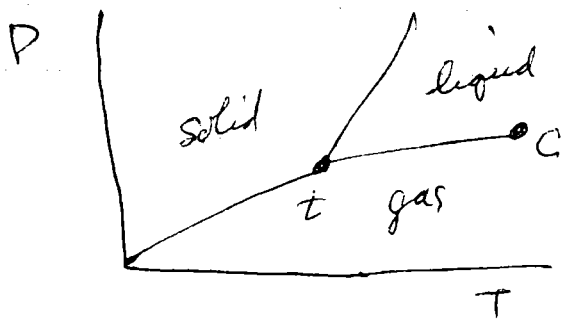
Note: since $\frac{dp}{dT}$ is in general finite, and we know Δv is finite but with $\Delta v \to 0$ as one approaches the critical pt C, then similarly it must be that Δs is finite upon crossing the phase boundary, but with $\Delta s \to 0$ as one approaches C.

$\Rightarrow$ L is finite along phase boundary, but $L \to 0$ 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 at 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

$$\mu_s(T,p) = \mu_\ell(T,p) = \mu_g(T,p)$$

two thermodynamic variables T, p

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

3 phases may coexist @ 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}, $i = 1, 2, \ldots, r$ 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 $\sum_{i=1}^{r} c_{ij} = 1$, $\mu_{ij} = \mu_{ij+1}$ for $\begin{cases} j = 1 \text{ to } s-1 \\ i = 1 \text{ to } r \end{cases}$ 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

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