

Coexistence curve using more complete equation of state

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

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

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

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

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

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

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

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

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

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

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

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

$$\begin{aligned}
 f(t) &= 48t - c\delta v_0 + 6\delta v_0^2 - a\delta v_0^3 \\
 &= 48t - (68t)(28t - 188t^2) + (98t)(28t - 188t^2)^2 \\
 &\quad \left(\frac{3}{2} + \frac{27}{2}8t\right)(28t - 188t^2)^3 \\
 &= 48t - 128t^2 + (6)(18)8t^3 + 368t^3 - 128t^3 \\
 &= 48t - 128t^2 + 1328t^3 \dots
 \end{aligned}$$

$$s_p = -a u^3 - c'u + f(t)$$

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

$$s_p = f(t) = 48t - 128t^2 + o(8t^3)$$

same result as earlier, but with higher order corrections

The coexistence curve densities are given by

$$-a u^3 - c'u = 0 \Rightarrow u = \pm \sqrt{\frac{-c'}{a}} = \pm \sqrt{\frac{-68t + 188t^2 + 1448t^3}{\frac{3}{2}(1 + 98t)}}$$

$$u_{l,g} = \pm \sqrt{\frac{-48t + 128t^2 + 968t^3}{1 + 98t}}$$

$$= \pm \sqrt{-48t + 128t^2 + 368t^2 + o(8t^3)}$$

$$u_{l,g} = \pm \sqrt{-48t(1 - 128t)}$$

$$s_{v,l,g} = \delta v_0 + u_{l,g} = 28t - 188t^2 \pm \sqrt{-48t(1 - 128t)}$$

to lowest order

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

$$= \pm 2\sqrt{|8t|} + 2st$$

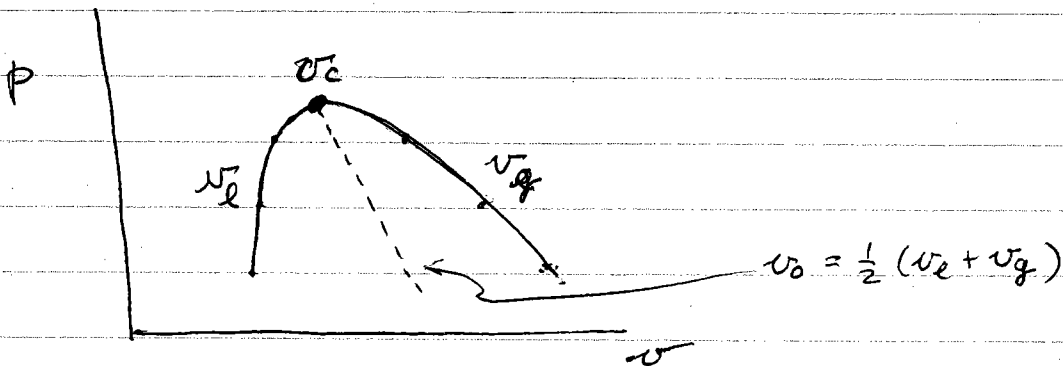
$$\delta v_{lg} = \pm 2\sqrt{|8t|} (1 \mp \sqrt{|8t|})$$

leading term high order correction

to leading order we have the same result as before
with $\Delta v = 4\sqrt{|8t|} = \delta v_g - \delta v_l$ 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 $\delta v_0 \approx 2st$

$$v_{lg} \approx 2(st \pm \sqrt{|8t|})$$



in experimental data one clearly sees this asymmetry

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

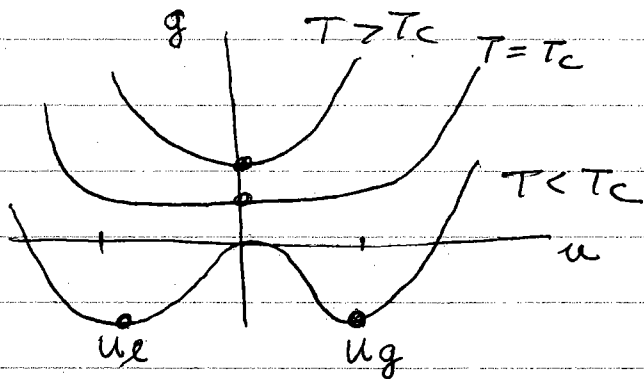
So along the phase boundary $\delta p^*(T)$

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

|||
 $g(u)$

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 $u = 0$

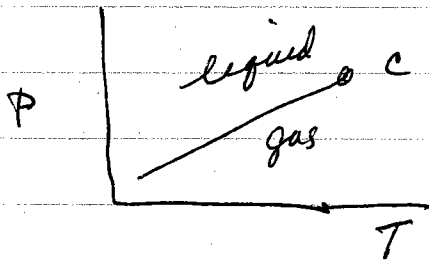
For $T < T_c$, the minimizing $u = \pm \sqrt{\frac{-c'}{a}} \propto \pm \sqrt{|8t|}$

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

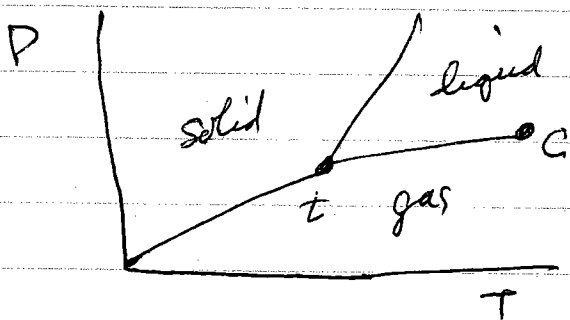
Note: Since $\frac{dp}{dT}$ is in general finite, and we know ΔU is finite but with $\Delta U \rightarrow 0$ as one approaches the critical pt C, then similarly it must be that ΔS is finite upon crossing the phase boundary, but with $\Delta S \rightarrow 0$ as one approaches C.

\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) i.e. 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 ϕ , 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 $\left. \begin{array}{l} j=1 \text{ to } s-1 \\ i=1 \text{ to } r \end{array} \right\}$ 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 $r + 2$