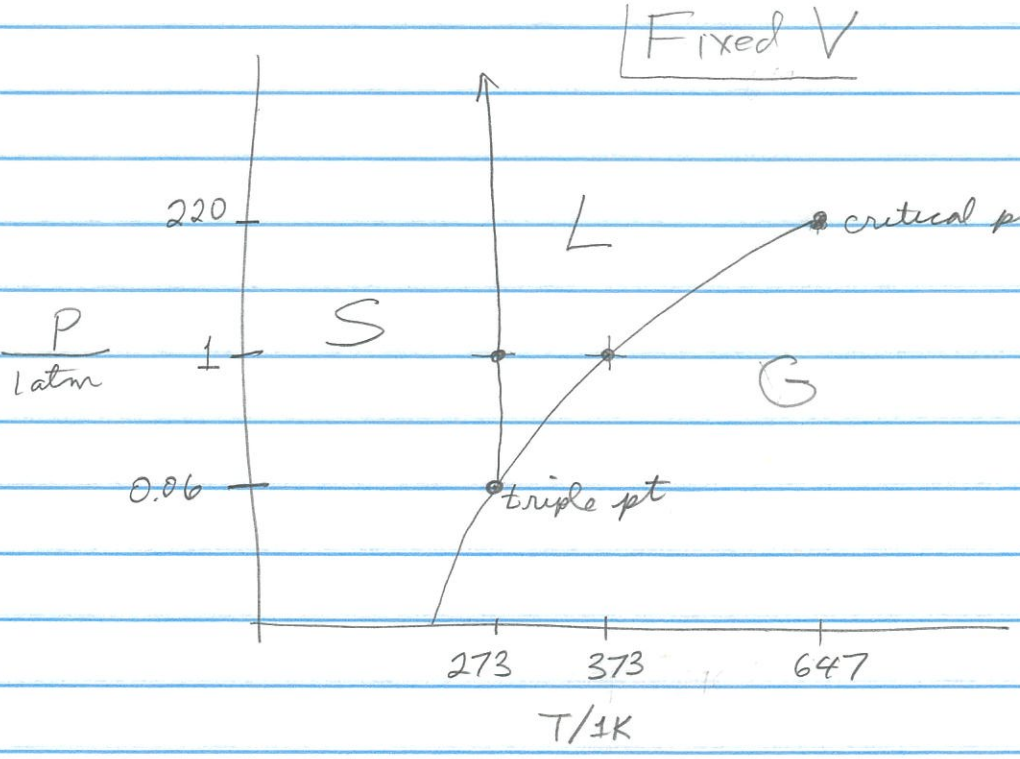
Phase Transitions

Thermodynamic functions are generally smooth (analytic) function of the independent thermodynamic variables.

However they can be discontinuous (nonanalytic) at a phase transition.

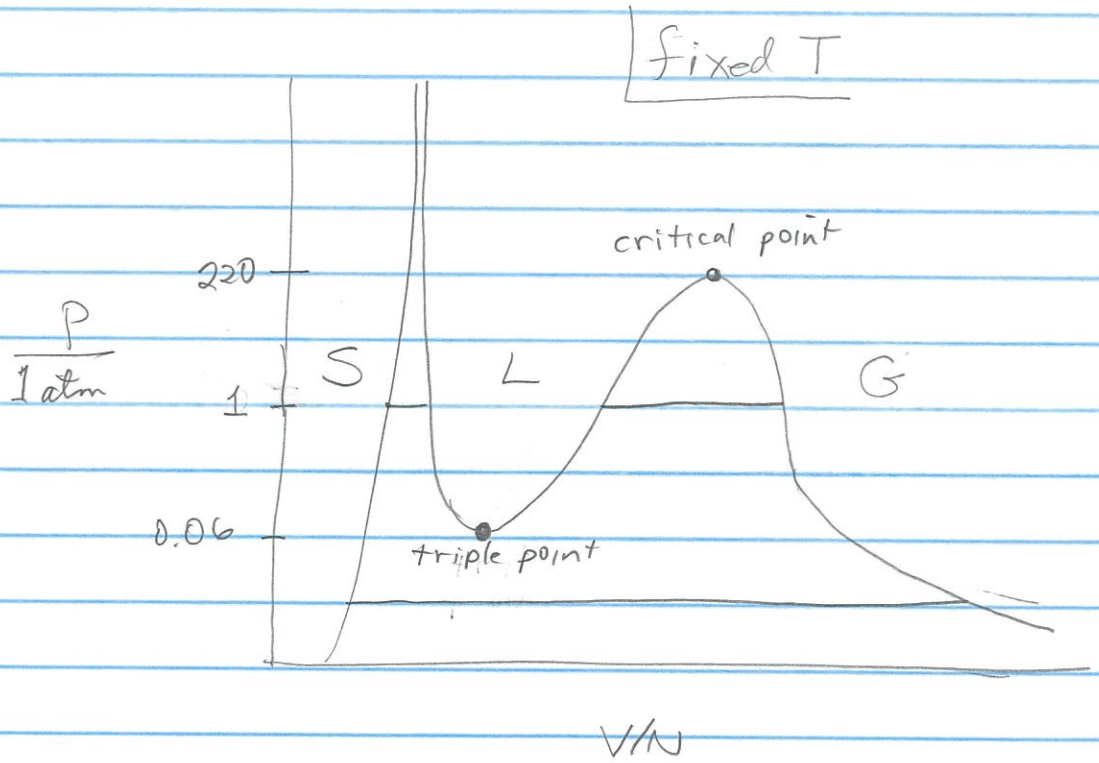
Water (H_2O) has 3 phases: Solid, Liquid, Gas
In the P-T plane, they are separated by phase transition lines



Two phases can coexist along the phase transition lines.
Specific volume per particle V/N is discontinuous across these lines
All three phases can coexist at the <u>triple point</u>.
The phase transition line between Liquid and Vapor ends at a <u>critical point</u>.

Along the transition line between phases A and B,
the macrostates are specified not only by P and T,
but also by the fraction x and 1-x
of the two phases

The macrostates can be specified by P and V/N.



Along the horizontal lines,
the fraction of the less dense phase varies from 0 to 1.

equilibrium between coexisting phases A and B
on a phase transition line

thermal: $T_A = T_B$

mechanical: $P_A = P_B$

chemical: $\mu_A = \mu_B$

Gibbs free energy: $G = U - TS + PV$

$$dG = -SdT + VdP + \mu dN$$

exactly intensive $\Longrightarrow$ $G(T,P,N) = N\mu(T,P)$

$$dG = Nd\mu + \mu dN$$

eliminate dG: $N d\mu = -SdT + VdP$

$$d\mu = -sdT + vdP$$

where $s = \frac{S}{N}$, $v = \frac{V}{N}$

$$\Longrightarrow \left(\frac{\partial \mu}{\partial T}\right)_P = -s, \quad \left(\frac{\partial \mu}{\partial P}\right)_T = v$$

Clausius-Clapeyron equation

phase transition line $P_{AB}(T)$ between phase A, B

chemical equilibrium:

$$\mu_A\left(T, P_{AB}(T)\right) = \mu_B\left(T, P_{AB}(T)\right)$$

differentiate with respect to T:

$$\left(\frac{\partial \mu_A}{\partial T}\right)_P + \left(\frac{\partial \mu_A}{\partial P}\right)_T \frac{d}{dT} P_{AB}(T) = \left(\frac{\partial \mu_B}{\partial T}\right)_P + \left(\frac{\partial \mu_B}{\partial P}\right)_T \frac{d}{dT} P_{AB}(T)$$

$$-s_A + v_A \frac{d}{dT} P_{AB}(T) = -s_B + v_B \frac{d}{dT} P_{AB}(T)$$

solve for $\frac{d}{dT} P_{AB}(T)$:

$$\frac{d}{dT} P_{AB}(T) = \frac{s_A - s_B}{v_A - v_B} = \frac{S_A - S_B}{V_A - V_B}$$

latent heat in transition from A to B at

$$L_{AB}(T) = \int_A^B T\,dS = T\int_A^B dS = T\left[S_B(T) - S_A(T)\right]$$

$$\boxed{\frac{d}{dT} P_{AB}(T) = \frac{L_{AB}(T)}{T\left[V_B(T) - V_A(T)\right]}} = \frac{l_{AB}}{T(v_B - v_A)}$$

l_{AB} = specific latent heat per particle

Liquid-Gas phase transition

using Clausius-Clapeyron equation

model for gas phase: ideal gas

$$PV = NkT$$

model for liquid phase: ??

except $V_L \ll V_G$

observation: latent heat $L(T)$
in transition from liquid to gas
does not depend strongly on T

Clausius-Clapeyron: $\frac{d}{dT} P_{coexist} \simeq \frac{L}{T V_G}$

$$= \frac{L}{T [NkT / P_{coexist}(T)]}$$

$$\frac{1}{P_{coexist}(T)} dP_{coexist}(T) = \frac{L}{Nk} \frac{dT}{T^2}$$

$$d \log P_{coexist}(T) = -\frac{L}{Nk} d\left(\frac{1}{kT}\right)$$

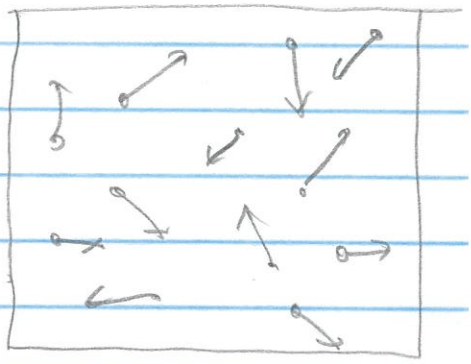
integrate from T_0 to T: $\log \frac{P_{coexist}(T)}{P_{coexist}(T_0)} = -\frac{L}{Nk}\left(\frac{1}{kT} - \frac{1}{kT_0}\right)$

$$P_{coexist}(T) = P_{coexist}(T_0) \exp\left(-\frac{L}{N}\left(\frac{1}{kT} - \frac{1}{kT_0}\right)\right)$$

Solid - Gas phase transition using microscopic models

model for gas phase:

classical monatomic ideal gas



Hamiltonian: $H = \sum_{n=1}^{N} \frac{1}{2m} \vec{p}_n^{\,2}$

use canonical ensemble

Helmholtz free energy:

$$F(T,V,N) = -NkT\left[\log\left(\frac{V}{N}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right) + 1\right]$$

pressure: $P = \left(\frac{\partial F}{\partial V}\right)_{TN} = \frac{NkT}{V}$

chemical potential: $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT\log\left(\frac{V}{N}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right)$

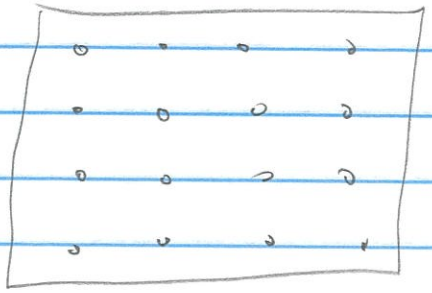
$$= -kT\log\left(\frac{kT}{P}\left(\frac{2\pi\hbar^2}{mkT}\right)^{3/2}\right)$$

"fugacity" $e^{\beta\mu} = \frac{P}{kT}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$

model for solid phase

Einstein solid (quantum harmonic oscillators about equilibrium positions in lattice)

Hamiltonian: $H = \sum_{n=1}^{N} \left[\frac{1}{2m} \vec{P}_n^2 + \frac{1}{2} m \omega^2 \left(\vec{X}_n - \vec{X}_{n,eq} \right)^2 - \epsilon \right]$



oscillator frequency ω
binding energy ϵ

cubic lattice with lattice spacing $a \Rightarrow V = N a^3$

use canonical ensemble

Helmholtz free energy:

$$F(T,N) = N\left[3kT \log\left(2 \sinh \frac{\hbar\omega}{kT} \right) - \epsilon \right]$$

chemical potential:

$$\mu = \frac{\partial F}{\partial N} = 3kT \log\left(2 \sinh \frac{\hbar\omega}{kT} \right) - \epsilon$$

fugacity: $e^{\beta\mu} = \left(2 \sinh \frac{\hbar\omega}{kT} \right)^3 e^{-\beta\epsilon}$

equilibrium between Solid and Gas

$$\left.\begin{aligned} T_S &= T_G \\ \mu_S &= \mu_G \end{aligned}\right\} \Rightarrow \left(e^{\beta\mu}\right)_S = \left(e^{\beta\mu}\right)_G$$

$$\left(2\sinh\frac{\hbar\omega}{kT}\right)^3 e^{-\beta E} = \frac{P}{kT}\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

coexistence pressure:

$$P_{coexist}(T) = \frac{kT}{(mkT/2\pi\hbar^2)^{3/2}}\left(2\sinh\frac{\hbar\omega}{kT}\right)^3 e^{-\epsilon/kT}$$