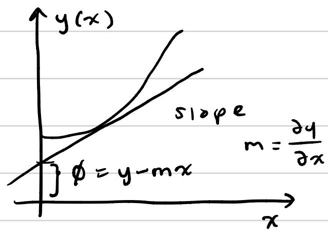
Lecture 23

Last Time: changing from functions of extensive variables $(S, V, \ldots)$ to functions of intensive variables $(T, P, \ldots)$



$$\begin{tikzcd}
E(S,V) \arrow[r, "S \to m = T"] \arrow[d, "V \to m = -P"] & F(T,V) = E - TS \arrow[d, "V \to m = -P"] \\
H(S,P) = E + PV \arrow[r, "S \to m = T"'] & G(T,P) = H - TS = E + PV - TS
\end{tikzcd}$$

$y(x)$ and $\phi(m)$ are unique functions

$dE = TdS - PdV + \mu dN + \ldots$ ⋮ $E = TS - PV + \mu n$

$dG = -SdT + VdP + \mu dN + \ldots$ ⋮ $G = E - TS + PV = \mu n$

(or $G = \sum \mu_i n_i$ for many compounds)

Today: ① Heat capacity (how E, S, H depend on T)

② Deriving "Laws" using stat mech

① Heat Capacity: how much does temperature have to go up or down to change E, S, H, etc. by a certain amount

$dE = TdS - PdV + \mu dn$

if V constant, n constant, then

$\Rightarrow dE = TdS$

$\Rightarrow dS = \dfrac{dE}{T} = \dfrac{\text{heat}}{T}$ can't get to 0K

$dH = TdS + VdP + \mu dn$

if P constant, n constant then

$\Rightarrow dH = TdS$

$\Rightarrow dS = \dfrac{dH}{T} = \dfrac{\text{heat}}{T}$

Similarly

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = C_v$$

$\Rightarrow dE = C_v \, dT$ (at const. volume)

$\Rightarrow dS = \frac{dE}{T} = \frac{C_v \, dT}{T}$

with H (P constant) $\Rightarrow dH = C_p \, dT$

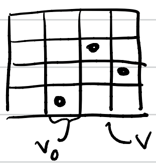
$\Rightarrow dS = \frac{dH}{T} = \frac{C_p \, dT}{T}$

② How to derive "laws" using stat mech

1) Find an equation for your system that relates the variables of interest
2) Find one of the general equations from postulates that relates the variables of interest
3) Combine the two equations

ex: law for gas in a box

1)



$M = \frac{V}{V_0}$

$N = \#$ of particles

$M >> N >> 1$

$$W = \frac{M!}{(M-N)!\,N!} \approx \left(\frac{M}{N}\right)^N$$

take log:

$$S = nR \log \frac{V}{N} - nR \log V_0$$

↑ extensive

$$\Rightarrow \frac{\partial S}{\partial V} = nR \frac{1}{(V/N)}\left(\frac{1}{N}\right)$$

$$= \frac{nR}{V}$$

2) From postulate 1 and 2, we derived for any system

$$dE = T\,dS - P\,dV + \mu\,dn$$

$$dS = \underbrace{\frac{1}{T}}_{\partial S/\partial E} dE + \underbrace{\frac{P}{T}}_{\partial S/\partial V} dV - \underbrace{\frac{\mu}{T}}_{\partial S/\partial n} dn$$

$$\frac{\partial S}{\partial V} = \frac{P}{T}$$

3) combine 1) and 2)

$$\frac{\partial S}{\partial V} = \frac{P}{T} = \frac{nR}{V} \Rightarrow PV = nRT$$

ex: if we used $W = \frac{M!}{(M-N)!\,N!}$

$$\Rightarrow P(V - NV_0) = nRT$$