Lecture 22 review:

$W(E,V\ldots) \xrightarrow{\ln} S(E,V\ldots)$ (solve)

$dE = TdS - PdV + \ldots$

$T = \left(\frac{\partial E}{\partial S}\right)_V$ $\leftarrow E(S,V\ldots)$

$P = \left(\frac{\partial E}{\partial V}\right)_S$

~~Note on derivatives:~~

$H = E + PV \rightarrow dH = dE + PdV + VdP$

~~$dH = TdS - PdV + PdV + VdP$~~ $\leftarrow dE$

$dH = TdS + VdP$ (variables now S, P)

$T = \left(\frac{\partial H}{\partial S}\right)_P \quad V = \left(\frac{\partial H}{\partial P}\right)_S$

Heat flow & heat capacity (C)

$\boxed{dV_1 = 0 \mid 0 = dV_2 \quad \xleftrightarrow{\text{heat}} \quad dE_1 = -dE_2}$ if V and n const.,

$dE = TdS$

$= dq_{V,n\ldots}$

$dS = \frac{dq_{V,n\ldots}}{T}$

impossible to reach $T=0$

HWK 3.4

$\boxed{dV_1 \neq 0 \mid dV_2 \neq 0 \quad \xleftrightarrow{\text{heat}} \quad dH_1 \stackrel{?}{=} -dH_2}$

V = const

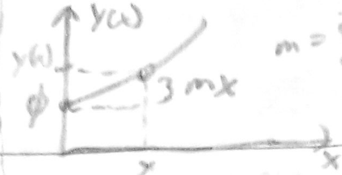
E = const

$dH = TdS + VdP$

$dS = \frac{dH}{T} = \frac{dq_{P,n\ldots}}{T}$

But what if we want variables in $E(S,V\ldots)$ to be $T, P\ldots$?

can't solve $E(T,P)$!



$m = \frac{\partial y}{\partial x}$

$\phi(m) = y(x(m))$ keeps all info in $y(x)$

$E(S,V) \xrightarrow[T = \frac{\partial E}{\partial S}]{S \rightarrow} F(T,V) = E - TS$

$V \rightarrow \downarrow \frac{\partial E}{\partial V} = -p \qquad V \rightarrow \downarrow -p$

$H(S,P) = E + PV \xrightarrow[T]{S \rightarrow} G(T,P) = F + PV$

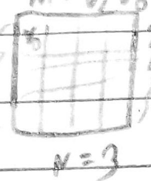
$= H - TS$

Lecture 23: Using stat mech to derive useful relationship

Ex: Gas in a box (in-class exercise)

1. Specify general properties (W or S, E, or H...)
2. Use eqs. derived from postulates.

1.



$M = V/V_0$

$N = 3$

$W = \frac{M!}{(M-N)!N!} = \left(\frac{V}{V_0 N}\right)^N$

$Nk_B = nN_A k_B = nR$

$S = k_B \ln W = N \ln\left(\frac{V}{V_0 N}\right) k_B$

$= nR \ln\left(\frac{V}{V_0 N}\right)$

$= nR \ln V - nR \ln V_0 N$

1+2: $\frac{\partial S}{\partial V} = \frac{nR}{V} = \frac{P}{T}$

2. ~~$dE = TdS - PdV\ldots$~~

$dS = \frac{1}{T}dE - \frac{P}{T}dV$

~~$PV = nRT$~~

E is not an explicit function of T (it is for S) but it certainly changes with T.

$\left(\frac{\partial E}{\partial T}\right)_{V,n} = \left(\frac{\partial E}{\partial S}\right)\left(\frac{\partial S}{\partial T}\right) = T\left(\frac{\partial S}{\partial T}\right)_V = C_V$ (heat capacity at constant V)

$\left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial H}{\partial S}\right)\left(\frac{\partial S}{\partial T}\right) = T\left(\frac{\partial S}{\partial T}\right)_P = C_P$ $\uparrow$ at constant P