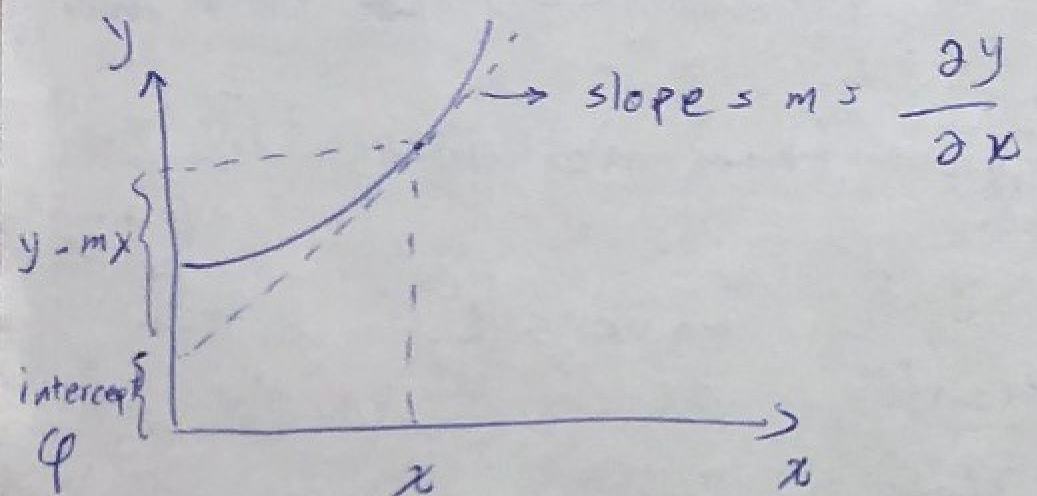
L23: review

$A = \sum_{j=1}^{W} P_j A_j$; $P_j = \frac{1}{W}$ at constant E

$\Rightarrow W(E) \xrightarrow{\ln} S(E) \xrightarrow{\text{invert}} E(S)$

because W & S monotonically increase with E.

Also, $T = \left(\frac{\partial E}{\partial S}\right)$, what is the analog $F(T)$ of $E(S)$?



$\Rightarrow \varphi(m) = y - mx \Rightarrow F(T) = E - TS$

Similarly $E \longrightarrow F \longrightarrow G \longrightarrow H$

$\uparrow$ (S, V) $\uparrow$ (T, V) $\uparrow$ (T, P) $\uparrow$ (S, P)

Today: { * How E, S, H change with T (heat capacity)

* How to derive "laws" about systems by using stat mech & thermo

Heat capacity:

F & G are explicit functions of T, but E, S & H are not but can still change if T changes:

$dE = TdS - PdV + \mu dn + \cdots$

V = const } let's assume no mechanical or

n = const } chemical work is done

$\Rightarrow dE = TdS = dq_{V,n}$

$\downarrow$

heat flow at const. V & n.

$dE = TdS = dq_{V,n} \Rightarrow dS = \frac{dq_{V,n}}{T}$

this is the reason why it's hard to cool system to ~~~~ zero kelvin; the smaller T the larger entropy loss (unfavorable) going to be.

$$\left(\frac{\partial E}{\partial T}\right)_{V,n} = T\left(\frac{\partial S}{\partial T}\right)_{V,n} \equiv \underbrace{C_V}_{V = \text{const.}}(T)$$

$\Downarrow$

$dE_{V,n} = C_V dT$; $dq_{V,n} = C_V dT$

$$dS_{V,n} = \frac{C_V dT}{T}$$

How to get C_V from postulate #1: $C_V = T\left(\frac{\partial S}{\partial T}\right) =$

$$\frac{T}{\left(\frac{\partial T}{\partial S}\right)} = \frac{(\partial E/\partial S)}{\left(\frac{\partial^2 E}{\partial S^2}\right)}$$

Using the above formula, once can calculate C_V if W, and therefore E & S, is known.

Calculation of "laws" for a system using

$W(E)$, $S(E)$, $E(S)$, ...

Example: box filled with randomly moving particles

Always same 2 steps:

1) Specify the basic properties of your system (e.g. $W(E)$) → "system specific"

2) Use eqs. from postulates 1 & 2 → "universal"

Answer: identical

(1) For particles in a box of volume V, where particles have volume V_0, and

$$M = \frac{V}{V_0} \gg N:$$

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

(2) From postulates, we proved:

$$dE = TdS - PdV + \mu dn$$

$$\Rightarrow dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn$$

let's calculate S from W: $S = k_B \ln W$

$$= k_B \ln\left(\frac{V/V_0}{N}\right)^N = -Nk_B \ln(V_0) + Nk_B \ln\left(\frac{V}{N}\right)$$

and $N = nA$, where A is $\sim 6 \times 10^{23}$

and $A k_B = 8.31\ J\ mol^{-1} K^{-1} \equiv R$

$$\Rightarrow S = n S_0 + nR \ln\left(\frac{V}{n}\right), \text{ where } S_0 \equiv R \ln V_0$$

let's take the derivative of S with respect to V and compare (1) & (2):

$$(1)\quad \frac{\partial S}{\partial V} = \frac{\partial}{\partial V}\left(nS_0 + nR\ln\frac{V}{n}\right) = \frac{nR}{V}$$

$$(2)\quad \frac{\partial S}{\partial V} = \frac{P}{T}$$

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