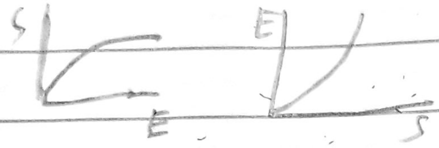
Lecture 20 review:

- The macrostate of an isolated system characterized by extensive variables E(energy), V(volume), etc.... has a partition function $W(E,V,N...)$ such that each microstate has equal probability $p_i = \frac{1}{W}$.
- ex. particles in a box $W = \left(\frac{V}{V_0 N}\right)^N$ if $M = \frac{V}{V_0 N} \gg N$, $W \gg 1$
- $W = 1$ when $E \to 0$ ($W \uparrow$ with $E$)


- When particles are free to move, the isolated system goes to the macrostate with largest W: $W(t>0) > W(t=0)$
- We define $S = k_B \ln W$, so $S = S_1 + S_2$, extensive like $E, V, N...$ ($E = E_1 + E_2$)

Lecture 21: Properties of S & E and intensive variables T, P, ...

- S increases with E → E increases with S




in an equation $\left(\frac{\partial E}{\partial S}\right)_{V,N} > 0$ (V,N held constant)

- $S(t>0) > S(t=0)$ → $\Delta S > 0$ for an isolated system (2nd Law)
- $\lim_{E \to 0} S = 0$ (3rd Law)

- Derivation of energy & entropy:

ex. $y = x^2 z$ $\left(\frac{\partial y}{\partial x}\right)_z = 2xz$ or $dy = 2xz\,dx$

$E(S,V,N..) \to dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_S dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN ...$

define these derivatives $dE = T\,dS + -P\,dV + \mu\,dN$

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

$dS = \left(\frac{1}{T_1}\right) dE_1 + \left(\frac{1}{T_2}\right) dE_2$

$dS = \left(\frac{1}{T_1}\right) dE_1 - \left(\frac{1}{T_2}\right) dE_1$

$dS = 0$ when equilibrium has been reached

$0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1$

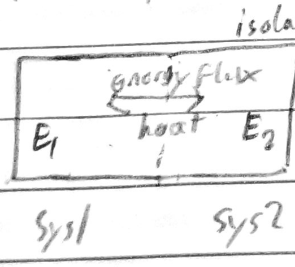
$T = \left(\frac{dE}{dS}\right)_{V,N} > 0$ $\quad \frac{1}{T_1} = \frac{1}{T_2} \to T_1 = T_2$ at equilibrium

"Temperature is the quantity equalized when heat is allowed to flow between systems."

- What is T?

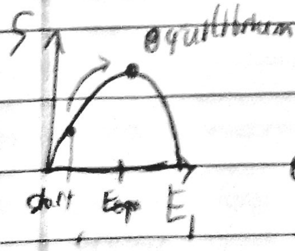
use trick of composite system

isolated system




$E_{tot}$ is constant, $dE_{tot} = 0$

- analogous derivation for pressure & volume, particle # and chemical potential.




$dE_1 = -dE_2$ (energy conservation)

once E stops flowing (W & S have reached the biggest possible value)

$dS = 0 = \left(\frac{\partial S}{\partial E_1}\right) dE_1 + \left(\frac{\partial S}{\partial E_2}\right) dE_2$