Lecture 23 review:

1. Find one of $S, E, F, G, H, \ldots$ for your system
2. Combine with eqns. from postulates, which always hold.

ex: Particles in a box

$W = \frac{M!}{(M-N)!N!} \rightarrow S = nR\ln(V_0 N) + nR\ln V$ $\rightarrow \frac{\partial S}{\partial V} = \frac{R}{V}$ } $PV = nRT$

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

$\leftarrow dS = \frac{1}{T}dE + \frac{P}{T}dV, \ldots$

~~V dependent concentration:~~ $nR(-\ln(\frac{n}{V}) + \ldots)$

$S = nR\,E(\ln(V_0 A n) + \ln V) = \ldots E\ln(V_0 A)$

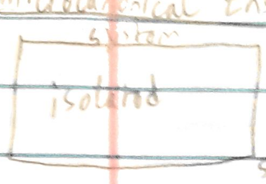
ex. Heat capacity

• At constant V, n: $dE = dq = C_V dT$, $dS = \frac{dE}{T} = \frac{C_V dT}{T}$ $\quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

• At constant p, n: $dH = dq = C_p dT$, $dS = \frac{dH}{T} = \frac{C_p dT}{T}$ $\quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$

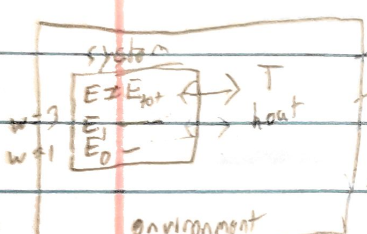
Lecture 24: systems at constant T, the Boltzmann factor $e^{-E/RT}$

• Microcanonical Ensemble (constant E)



E_{tot} = constant $\quad E = E_{tot}$ $\quad p = \frac{1}{W(E)}$

• Canonical Ensemble (constant T)



$\langle E_j \rangle = E = \sum_j p_j E_j$

• Derivation of p_j on pg. 17 of textbook

$E = \text{const.} \rightarrow p = \frac{1}{W} \quad W = e^{-TS/k_B T}$ (from $S = k_B \ln W$)

$T = \text{const.} \rightarrow p_j = \frac{W_j e^{-E/kT}}{Z}, \quad Z = e^{-F/kT} \quad (F = E - TS)$

$\sum p_j = 1 \rightarrow \sum_j e^{-E_j/kT} = Z$

$\rightarrow p_j = \frac{e^{-E_j/kT}}{Z} \leq 1$

(Note: $k_B T$ vs RT — units of E; units of E per mole)

• Note: if a bunch of microstates have the same E, can group them.

$p_j = \frac{W_j e^{-E_j/kT}}{Z}$

$Z = \sum W_j e^{-E_j/kT}$ ← microstates with different E

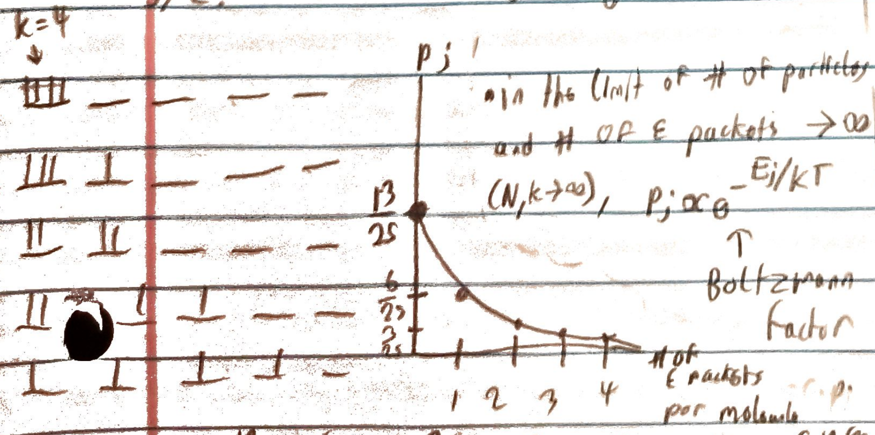
$Z = e^{-F/RT} = \sum W_j e^{-E_j/RT}$

↑ canonical partition function } counts microstates of system (like W at const. E) but difference is that at const. T all microstates (especially high E) have $p_j < 1$.

• Illustrate with example:

• system with $N = 5$ identical molecules. $K = 4$ energy packets of energy ε.

• if T is the average energy per degree of freedom, $\langle E_j \rangle = k_B T$



$\langle E_j \rangle = \sum p_j E_j = \frac{13}{25} \cdot 0 + \frac{6}{25} \cdot \varepsilon + \frac{3}{25} \cdot 2\varepsilon + \frac{2}{25} \cdot 3\varepsilon + \frac{1}{25} \cdot 4\varepsilon = \frac{22\varepsilon}{25}$ (need to normalize)