Class H Statistical Mechanics

H1. Combinatorics Video Homework Pascal Triangle

H2. The Statistical Problem

N particles n_1 in energy ε_1
n_2 " " ε_2

Maximize $\to$ $\Omega = \dfrac{N!}{n_1!\,n_2!\,n_3!}$
\# Ways

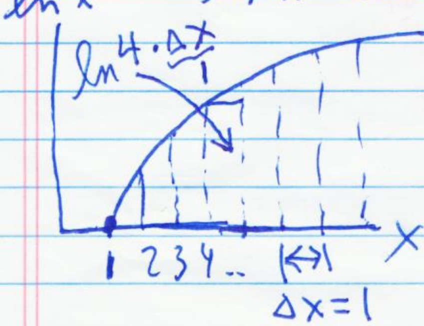
Maximize Ω with the constraints N fixed and E fixed (E = total energy)

By maximizing $\ln\Omega$ Easier

$$N = n_1 + n_2 + n_3 + \dots$$
$$E = n_1\varepsilon_1 + n_2\varepsilon_2 + n_3\varepsilon_3 + \dots$$

We will maximize $\ln\Omega = \ln N! - \ln n_1! - \ln n_2! - \dots$

$\ln n! = \ln 1 + \ln 2 + \dots \ln n$ In general N is super large, n_i are large



$$\ln n! \approx \int_1^n \ln x\,dx$$

Integrate by parts $d(x\ln x) = \ln x\,dx + \frac{1}{x}x\,dx$

$$\ln n! = \int_1^n d(x\ln x) - \int_1^n dx = n\ln n - (n-1)$$

$$x\ln x\Big|_1^n - x\Big|_1^n$$
$$n\ln n - 1\ln 1 - (n-1)$$

Note $\ln 1 = 0$

$\ln n! \approx n\ln n - n$ Throw away the 1 for large n

H3. Undetermined Multipliers Video Homework

Approximation $\boxed{\ln n! \approx n\ln n - n}$

H4. Maximize Ω

$$\ln\Omega = N\ln N - N - n_1\ln n_1 + n_1 + \dots$$
$$\ln\Omega \approx N\ln N - n_1\ln n_1 - n_2\ln n_2 - \dots$$

$-N$ cancels with $n_1 + n_2 + \dots$

So Can't do $\dfrac{\partial\Omega}{\partial n_1} = 0$ etc. since dn_i are not all independent

But $dN = dn_1 + dn_2 + \dots = 0$
$dE = \varepsilon_1\,dn_1 + \varepsilon_2\,dn_2 + \dots = 0$

So we set $d(\ln\Omega) - \alpha\,dN - \beta\,dE = 0$
The constants $\alpha + \beta$ will enable us to consider dn_i independent

$$\sum_i \underbrace{\left[\frac{\partial\ln\Omega}{\partial n_i} - \alpha\overbrace{\frac{\partial N}{\partial n_i}}^{1} - \beta\overbrace{\frac{\partial E}{\partial n_i}}^{\varepsilon_i}\right]}_{\text{zero}} dn_i = 0$$

I can consider independent since $\alpha + \beta$ are set to make it work

$$\frac{\partial\ln\Omega}{\partial n_1} = \overbrace{\frac{\partial N}{\partial n_1}}^{1}\ln N + N\frac{1}{N}\overbrace{\frac{\partial N}{\partial n_1}}^{1} - \ln n_1 - n_1\frac{1}{n_1}\underbrace{\frac{\partial n_1}{\partial n_1}}_{1}$$

Cancel

$$\frac{\partial\ln\Omega}{\partial n_1} = \ln N - \ln n_1$$

Macrostates have variables P, V, T, S

$S = k \ln \Omega$ ← Microstates #ways to place particles in energy levels

(Shown on this page) Connects Macrostate to Microstates

$$\frac{\partial \ln \Omega}{\partial n_1} = \ln N - \ln n_1$$ True for each n_i ← i^{th} case

$$\ln N - \ln n_i - \alpha - \beta \varepsilon_i = 0$$

$$\ln \frac{N}{n_i} = \alpha + \beta \varepsilon_i \qquad \ln \frac{n_i}{N} = -\alpha - \beta \varepsilon_i$$

$$\frac{n_i}{N} = e^{-\alpha - \beta \varepsilon_i}$$

H5. Evaluating α and β

$$n_i = N e^{-\alpha - \beta \varepsilon_i}$$

Find α $\quad N = \sum_i n_i = e^{-\alpha} N \sum_i e^{-\beta \varepsilon_i} \Rightarrow e^{-\alpha} = \frac{1}{\sum_i e^{-\beta \varepsilon_i}}$

Partition function $Z \equiv \sum_i e^{-\beta \varepsilon_i}$

$$n_i = N \frac{e^{-\beta \varepsilon_i}}{Z}$$ The α is gone.

Find β Video Homework Pascal's Law is used $\longrightarrow \beta = \frac{1}{kT}$

H6. Entropy $\quad \Delta U = \Delta Q - \Delta W$ is the 1st Law of Thermodynamics

$$\Delta Q = \Delta U + P \Delta V$$

P, V, T have meaning for the state of the gas

$$\Delta Q = \frac{3}{2} nR \Delta T + \frac{nRT}{V} \Delta V$$

$\Delta W \Rightarrow W$ doesn't. It depends on path.

Divide by T makes $\Delta Q/T$ good

$$\frac{\Delta Q}{T} = \frac{3}{2} nR \frac{\Delta T}{T} + \frac{nR}{V} \Delta V$$

All good variables on right side

$T \Delta S$

$$\Delta S \equiv \frac{\Delta Q}{T}$$ Entropy S good macroscopic variable.

$$dU = T\,dS - P\,dV \qquad \boxed{\frac{\partial U}{\partial S} = T}$$

But $\quad d(\ln \Omega) - \alpha\, dN - \beta\, dE = 0$

$$dE = \frac{1}{\beta} d(\ln \Omega) - \frac{\alpha}{\beta} dN$$

from before $\boxed{\frac{\partial E}{\partial \ln \Omega} = \frac{1}{\beta} = kT}$

But $U = E$

Therefore $\boxed{S = k \ln \Omega}$ Disorder

Since logs add → Note Entropies add combining 2 systems $\Omega = \Omega_1 \cdot \Omega_2$ (#ways multiply)