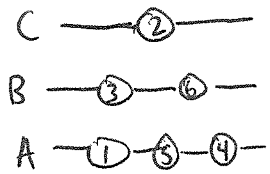
Statistical Mechanics * (Do counting problem first!)

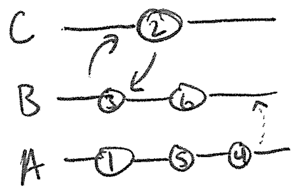
* Stat mech is all about counting states (ways of organizing things)

Ex: 

1	2	3	4	5	6	
A	C	B	A	A	B	← microstate (most information)

A B C
{3 2 1} ← macrostate ("relevant" information)

* think about energy levels if it helps



swap two; what changes? microstate only

move one to a different level? micro and macro!

* multiple microstates correspond to a given macrostate

~~Now, imagine a deck of cards. Probability of drawing~~

Now imagine two dice. The individual #s are the microstates; the sum is the macrostate. How many of each? (36, 11)

Which macrostate is most probable? $\boxed{7}$ Why?

What did you assume to get that? Dice are fair! All states are equally likely. This is known as the "principle of equal a priori probability". It is an unprovable assumption, but one that has not let us down. All accessible microstates are equally likely.

A measure of the # of (micro)states is Ω. This can be related to the ~~classical~~ thermodynamic concept of entropy by

$$S = k_B \ln \Omega$$

Maximizing this quantity gives the most likely (macro)state.

GRE Question: The 3D harmonic oscillator transitions from the $n=1$ state to the $n=2$ state. What is the change in entropy?

(A) 0
(B) $\hbar\omega$
(C) k_B
(D) $k_B \ln 2$
(E) $k_B \ln 3$

can rule out (B) for units, form
(C) implies ~~entropy~~ # states Ω ~~...~~ is non-integer
~~on~~ (A) means # states doesn't change
what about (D) and (E)?

$$\Delta S = k_B \ln \Omega_2 - k_B \ln \Omega_1 = k_B \ln \frac{\Omega_2}{\Omega_1}$$

$n=1$: $(1,0,0)$; $(0,1,0)$; $(0,0,1)$ $\quad \Omega_1 = 3$

$n=2$: $(2,0,0)$ ... $(1,1,0)$ .. $\quad \Omega_2 = 6$

$$\Delta S = k_B \ln\left(\frac{6}{3}\right) = \underline{k_B \ln 2} \quad \boxed{D}$$

To count states, need to know constraints on the system. These constraints define the <u>ensemble</u>. For GRE, $\underline{N}\,\underline{V}\,\underline{T}$ (canonical) is the most common. Sometimes $\underline{N}\,\underline{V}\,\underline{E}$ (microcanonical) comes up too.

$NV\underline{T}$ constrains <u>average</u> energy & $\langle E \rangle = \sum_{\text{microstates}} p_i E_i$; $\sum p_i = 1$

with these two constraints, maximizing S means (use Lagrange multiplie[rs])

$$p_i = \frac{e^{-\beta E_i}}{\sum e^{-\beta E_i}} \qquad \sum e^{-\beta E_i} = Z \text{ defined as the } \underline{\text{partition function}}$$

GRE Question: What is the partition function of a 1D harmonic oscillator?

(A) $e^{-\hbar\omega/kT}$
(B) $1 - e^{-\hbar\omega/kT}$
(C) $(1 - e^{-\hbar\omega/kT})^{-1}$
(D) $\left(2\cosh \frac{\hbar\omega}{2kT}\right)^{-1}$
(E) $\left(2\sinh \frac{\hbar\omega}{2kT}\right)^{-1}$

$$Z = \sum_i e^{-\beta E_i} \qquad E_i = \hbar\omega(n + 1/2)$$

$$Z = \sum_{n=0}^{\infty} e^{-\hbar\omega/kT\,(n+1/2)} = e^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} \left[e^{-\left(\frac{\hbar\omega}{kT}\right)}\right]^n$$

$$= e^{-\hbar\omega/2kT}\left(\frac{1}{1 - e^{-\hbar\omega/kT}}\right) = \left(\frac{1}{e^{\hbar\omega/2kT} - e^{-\hbar\omega/2kT}}\right)$$

$$= \left(2\sinh\frac{\hbar\omega}{2kT}\right)^{-1} \quad \boxed{E}$$

Partition Function contains all our knowledge of the system

Ex: $\langle E\rangle = \sum p_i E_i = \dfrac{\sum E_i e^{-\beta E_i}}{Z} = \frac{1}{Z}\sum\left(-\frac{\partial}{\partial\beta} e^{-\beta E_i}\right)$

$= \frac{1}{Z}\left(-\frac{\partial}{\partial\beta}\sum e^{-\beta E_i}\right) = \frac{1}{Z}\left(-\partial/\partial\beta\, Z\right) = \underline{-\frac{\partial}{\partial\beta}\ln Z}$

What is the average energy of a 1D harmonic oscillator?

$Z = \left(2\sinh\frac{\hbar\omega}{2kT}\right)^{-1} = \left(2\sinh\frac{\hbar\omega\beta}{2}\right)^{-1}$

$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left(-1\ln 2\sinh\left(\frac{\hbar\omega\beta}{2}\right)\right) = \frac{1}{2\sinh\frac{\hbar\omega}{2kT}}\cdot\cancel{2}\cosh\left(\frac{\hbar\omega}{2kT}\right)\cdot\frac{\hbar\omega}{\cancel{2}}$

$= \frac{\hbar\omega}{2}\coth\left(\frac{\hbar\omega}{2kT}\right) = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT}-1}\right)$

Do you know how to count? Are you sure?

GRE: Six cups #1–6 each can hold one marble. There are three red, one blue. How many ways to fill the cups with all four marbles?

(A) 6
(B) 12
(C) 24
(D) 30
(E) 60

Two solutions

#1) choose 4 cups $\binom{6}{4} = \frac{6!}{4!\cdot 2!} = \frac{6\cdot 5}{2} = 15$

then choose 1 for the blue marble $\binom{4}{1} = \frac{4!}{1!\cdot 3!} = 4$ $\boxed{E}$ $\rightarrow \underline{60}$

GRE: A system has two states with energies $-\epsilon$ and 2ϵ. What is the probability of the higher energy state?

$-\epsilon \rightarrow 0$

$2\epsilon \rightarrow 3\epsilon$

(A) 0
(B) $(1+e^{3\epsilon/kT})^{-1}$
(C) $(1-e^{3\epsilon/kT})^{-1}$
(D) $(e^{\epsilon/kT}+e^{-2\epsilon/kT})^{-1}$
(E) 1

A, E seem unlikely!

$p_i = \frac{e^{-\beta E_i}}{Z} = \frac{e^{-\beta\cdot 3\epsilon}}{\cancel{e^{\beta\cdot 0}}\,1 + e^{-3\beta\epsilon}} = \frac{1}{e^{3\beta\epsilon}+1}$

$= \left(1+e^{3\epsilon/kT}\right)^{-1}$ $\boxed{B}$