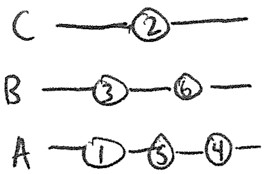
Statistical Mechanics * (Do counting problem first!)

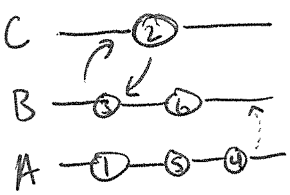
* Stat mech is all about counting <u>states</u> (ways of organizing things)

Ex: 

1 2 3 4 5 6
A C B A A B ← <u>micro</u>state (most information)

A B C
{3 2 1} ← <u>macro</u> state ("relevant" information)

* think about energy levels if it helps



swap two; what changes? <u>microstate only</u>

move one to a different level? micro <u>and</u> 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 <u>accessible</u> microstates are equally likely.

A measure of the # of (micro)states is Ω. This can be related to the ~~[illegible]~~ 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 # states $\Omega = 0$
(A) means # states doesn't change
what about (D) and (E)?

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

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

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

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

To count states, need to know constraints on the system. These constraints define the ensemble. For GRE, NVT (canonical) is the most common. Sometimes NVE (microcanonical) comes up too.

NVT constrains average 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

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

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

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

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 $\binom{4}{1} = \frac{4!}{1!\cdot 3!} = 4$ $\to 60$ $\boxed{E}$

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

$-\epsilon \to 0$
$2\epsilon \to 3\epsilon$

(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!

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

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