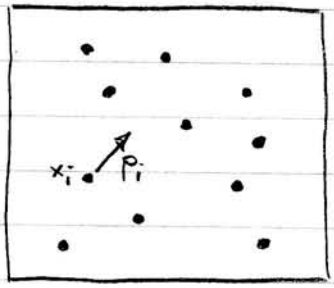
Lecture 1

Microscopic vs. macroscopic states

- Microscopic state (or "microstate") = complete description of each particle / configuration in a system
- Macroscopic state (or "macrostate") = description of a system in terms of a few (2) properties

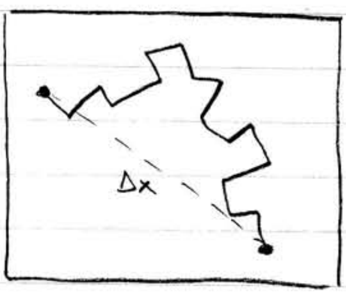
Ex: gas molecules in a box



Microstate = $\{x_i, p_i\}$ of all molecules in system

Macrostate = pressure of gas (for example)

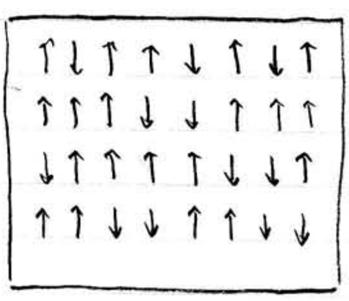
Ex: polymer



Microstate = configuration of every segment of polymer

Macrostate = end-to-end distance

Ex: magnet



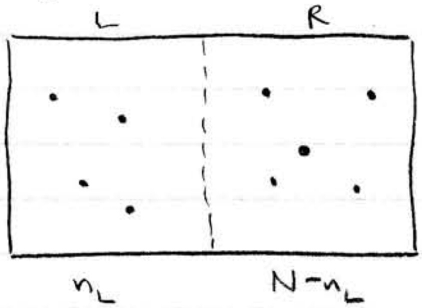
Microstate = configuration of every spin in system

Macrostate = average magnetization M of magnet

- Definition of microstate / macrostate is <u>not rigid</u>
  will depend on system and question being asked

- There are many more microstates than macrostates

Ex: gas molecules in a box split in 1/2

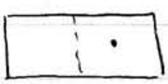
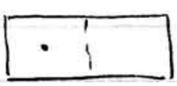


N molecules
n_L in left 1/2 = macrostate

microstate = configuration of N molecules

How many microstates (configurations) give the same macrostate (n_L molecules in left 1/2) $= \Omega(n_L, N)$?

<u>N = 1</u>

Microstate	Ω	Macrostate
	1	$n_L = 0$
	1	$= 1$
Total	2^1	2

This is called a <u>statistical ensemble</u>
- repeat experiment many times, get every possible configuration (microstate)

$N=2$

Microstate	Ω	Macrostate
[∣ 1 2]	1	$n_L = 0$
[1 ∣ 2]	2	$n_L = 1$
[2 ∣ 1]		
[1 2 ∣]	1	$n_L = 2$
total =	$2^2 = 4$	$2+1=3$

$N=3$

Microstate	Ω	Macrostate
[∣ 1 2 3]	1	$n_L = 0$
[1 ∣ 2 3]	3	$n_L = 1$
[2 ∣ 1 3]		
[3 ∣ 1 2]		
[1 2 ∣ 3]	3	$n_L = 2$
[1 3 ∣ 2]		
[2 3 ∣ 1]		
[1 2 3 ∣]	1	$n_L = 3$
total	$2^3 = 8$	$3+1 = 4$

And so on ...

total number of microstates $= 2^N$
total number of macrostates $= N+1$

There are $\Omega(n_L, N)$ ways of configuring N gas molecules so that n_L are in the left 1/2. $\underline{\Omega(n_L, N) = \text{multiplicity}}$

How do we get $\Omega(n_L, N)$ in general?
- Take N slots (represent N molecules)
- Distribute n_L molecules to the L ($N-n_L$ to the R)

L	R	R	L		R	L
1	2	3	4	...	N-1	N

N choices for 1st L molecule
N-1 " 2nd
N-2 " 3rd
⋮
$N-n_L+1$ " n_Lth

$$\therefore \quad N(N-1)(N-2)\cdots(N-n_L+1)$$

<u>But</u> molecules are <u>indistinguishable</u>. There are $n_L!$ identical ways to arrange L molecules so we divide by $n_L!$

$$\Omega(n_L, N) = \frac{N(N-1)(N-2)\cdots(N-n_L+1)}{n_L!}$$

$$= \frac{N!}{n_L!(N-n_L)!} \equiv \binom{N}{n_L} \qquad \text{"N choose } n_L\text{"}$$

This is called the <u>binomial coefficient</u>

Comes from binomial distribution :

$$(p+q)^N = \sum_{n_L=0}^{N} \binom{N}{n_L} p^{n_L} q^{N-n_L}$$

Note that $\quad 2^N = \sum_{n_L=0}^{N} \Omega(n_L, N) \quad$ as expected

<u>Fundamental assumption</u> – each microstate in system is <u>equally likely</u>

Prob. of 1 particular microstate $= \dfrac{1}{2^N}$

(Same as saying each molecule has prob. ½ of being to the left. $\therefore$ For N molecules $= \left(\frac{1}{2}\right)^N$)

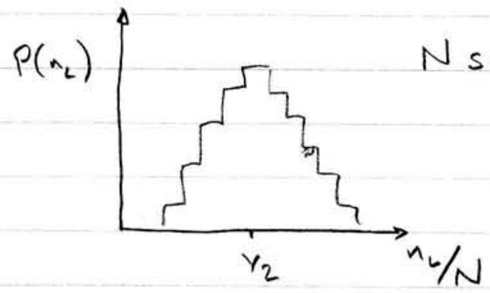
Although each <u>microstate</u> is equally likely, some <u>macrostates</u> are more likely than others (Ex: $N = 3$ $n_L = 1$ is 3x more likely than $N=3$, $n_L = 0$)

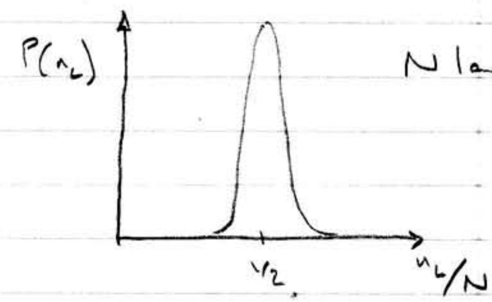
Probability that we get n_L out of N :

$$P(n_L) = \frac{\Omega(n_L)}{\Omega(0) + \Omega(1) \cdots \Omega(N)} = \frac{\Omega(n_L)}{2^N}$$

$$= \frac{N!}{n_L!\,(N-n_L)!} \left(\frac{1}{2}\right)^N$$

What does $P(n_L)$ look like?





$P(n_L)$ is peaked at $n_L = \frac{N}{2}$, <u>gets sharper</u> as $N >> 1$
Most likely macrostate is $1/2$ molecules L, $1/2$ R.
because most microstates have $n_L = \frac{N}{2}$.

Properties of probabilities

Normalization:

$$\sum_{n_L=0}^{N} P(n_L) = 1 \qquad \text{prob. of being in } \underline{\text{any}} \text{ macrostate} = 1$$

From binomial distribution

$$\left(\frac{1}{2}+\frac{1}{2}\right)^N = \sum_{n_L=0}^{N} \frac{N!}{n_L!(N-n_L)!}\left(\frac{1}{2}\right)^{n_L}\left(\frac{1}{2}\right)^{N-n_L}$$

$$1 = \sum_{n_L=0}^{N} P(n_L) \qquad \checkmark$$

Mean values:

$$\langle f(n_L)\rangle = \sum_{n_L=0}^{N} f(n_L)\, P(n_L)$$

Ex: $$\langle n_L\rangle = \sum_{n_L=0}^{N} n_L\, P(n_L)$$

$$\langle n_L^2\rangle = \sum_{n_L=0}^{\infty} n_L^2\, P(n_L) \qquad \ldots$$

Calculate $\langle n_L \rangle$ for $P(n_L)$

Math trick

Use : $P(n_L) = \sum_{n_L=0}^{N} \binom{N}{n_L} p^{n_L} q^{N-n_L}$ (with $p = q = \frac{1}{2}$)

$$\langle n_L \rangle = \sum_{n_L=0}^{N} n_L P(n_L) = \sum_{n_L=0}^{N} \binom{N}{n_L} n_L p^{n_L} q^{N-n_L}$$

$$n_L p^{n_L} = \left(p \frac{\partial}{\partial p} \right) p^{n_L}$$

$$\langle n_L \rangle = p \frac{\partial}{\partial p} \sum_{n_L=0}^{N} P(n_L) = p \frac{\partial}{\partial p} (p+q)^N$$

$$= N p (p+q)^{N-1} = \frac{N}{2}$$

The average # of L molecules is ½ the total #

Calculate the standard deviation δn_L

$$\delta n_L^2 \equiv \langle (n_L - \langle n_L \rangle)^2 \rangle = \langle n_L^2 \rangle - \langle n_L \rangle^2$$

$$\langle n_L^2 \rangle = \sum_{n_L=0}^{N} \binom{N}{n_L} n_L^2 p^{n_L} q^{N-n_L}$$

$$n_L^2 p^{n_L} = \left(p \frac{\partial}{\partial p} \right)^2 p^{n_L}$$

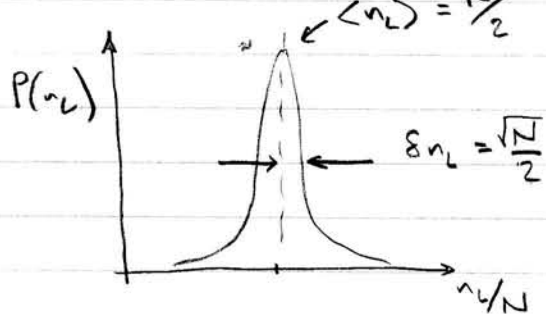
$$\langle n_L^2 \rangle = \left(p \frac{\partial}{\partial p} \right)^2 (p+q)^N = p \frac{\partial}{\partial p} \left[N p (p+q)^{N-1} \right]$$

$$= N p (p+q)^{N-1} + N(N-1) p^2 (p+q)^{N-2}$$

$$= \frac{N}{2} + \frac{N^2 - N}{4}$$

$$\delta n_L^2 = \langle n_L^2 \rangle - \langle n_L \rangle^2 = \frac{N}{2} + \frac{N^2 - N}{4} - \frac{N^2}{4}$$

$$= \frac{N}{4}$$



$$\frac{\delta n_L}{\langle n_L \rangle} = \frac{1}{\sqrt{N}}$$ for large system $N \sim 10^{20}$ $\frac{\delta n_L}{\langle n_L \rangle} \sim 10^{-10}$

i.e. width is 10^{-10} of total range of graph

Extremely sharp

In sum

- Most likely macrostate has $N/2$ to the L $N/2$ to the R
  This is because there are the most microstates with this property : Ω maximum

- When $N \gg 1$ any other macrostate is extremely unlikely to occur

- This applies to any binary system (see K+K Chapter 1)

Entropy

$\sigma \equiv \ln \Omega$ $\quad\quad\quad$ Ω = multiplicity function
# of microstates

σ is maximum when Ω is maximum

$\therefore$ System is in macrostate that maximizes entropy

Why define entropy as ln?

Take two systems A + B with Ω_A Ω_B

$$\Omega_{A+B} = \Omega_A \Omega_B$$

$$\therefore \quad \sigma_{A+B} = \sigma_A + \sigma_B$$

Entropies are additive, multiplicities are multiplicative

Entropy is an example of an extensive quantity – linear with system size
(Intensive quantities do not change with size)

σ depends on N, will see how it depends on E