Lecture 5
CH-4114
Molecular Simulation

"Everything that living things do can be understood in terms of the jigglings and wigglings of atoms."
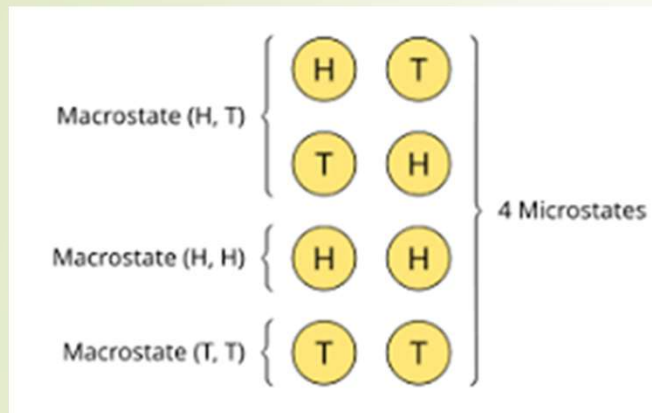
- Richard P. Feynman

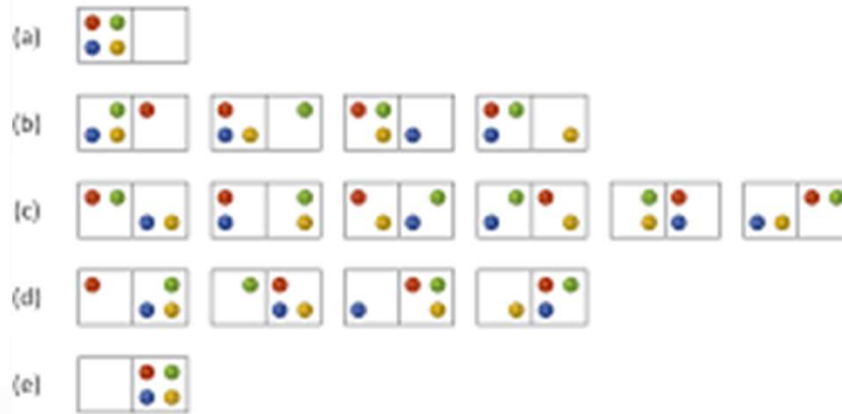**By**
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How do we define microstate?

2 **A state that describe microscopic length scale configuration of a system and the interaction.**

Four particles/atoms in **two** energy states

How to Calculate the Number of Microstates

Total Outcome=16

Number of Microstates:

for $N = 4$ $N_1 = 3$ $w_2 = ?$ (# of microstates in the 2nd macrostate)

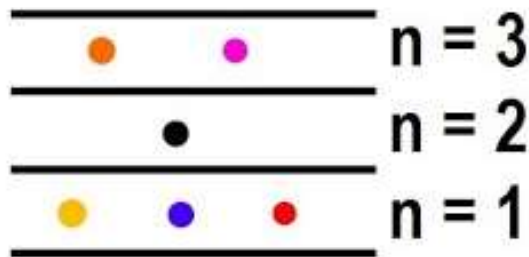$$w_k = \binom{N}{N_1} = \frac{N!}{N_1!\,(N - N_1)!}$$

$N = 10$ 5H, 5T $N_1 = 5$ $w = ?$

macro-state	macro-state specs.		microstates				thermo prob.	math prob.
k	N_1	N_2	coin1	2	3	4	w_k	$P_k = \frac{w_k}{\Omega}$
1	4	0	H	H	H	H	1	1/16
2	3	1	H H	H H	H T	T T	4	4/16
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮

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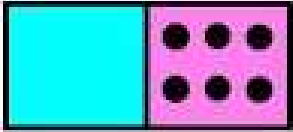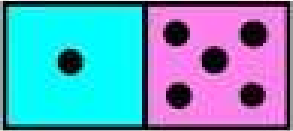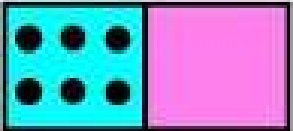## General Counting Method for w

$n = 3$

$n = 2$

$n = 1$

Assume there are n energy levels and N distinguisable particles N_1, N_2, N_3, ..., N_n are the outcomes of the occupation numbers for each energy level

$$w = \frac{N!}{N_1!\, N_2!\, N_3!\, \cdots\, N_n!} = \frac{N!}{\displaystyle\prod_{j=1}^{n} N_j!}$$

Statistical Mechanical Hypothesis

The Boltzmann hypothesis fundamentally links entropy, a measure of disorder or randomness in a system, to the number of ways the system's microscopic components (atoms, molecules, etc.) can be arranged while maintaining the same macroscopic properties.

6 Molecules in a Box (Divided in 2 Halves) and Entropy

Ensemble Concept

A system of an ensemble is a collection of microstates that are possible under a given thermodynamic condition.
For canonical onset, ensembles are very well distinguished by their partition function (PF). PF describes statistical properties of a system in their thermodynamic equilibrium.

Summary of Ensembles us in statistical mechanics	Ensembles		
	Micro canonical	Canonical	Grand Canonical
Constant Variable	E, N, V	T, N, V	T, μ, V
Microscopic Features	Number of Microstates Ω	Canonical Partition Function $Z = \sum_K e^{-\beta \epsilon_K}$	Grand Canonical Partition Function $\equiv = \sum_k e^{-\beta(\epsilon_K - \mu N_K)}$
Macroscopic Function	$S = K_\beta \ln \Omega$	$F = -K_\beta T \ln Z$	$F - G = -Pv$ $= -K_\beta T \ln \equiv$

Rationale Behind Statistical Mechanical Postulates:

6   What is the relationship between such a microscopic trajectory of a system and the experimental observables, or measured macroscopic properties?

For example, the temperature of a system is given by the mean square velocity (see Equipartition Theorem). Let us consider a one component system of N-molecules. Temperature will now be determined by performing average over time trajectory of each particle, and then average over all the particles

$$T = \frac{m}{3k_B} < v^2 > = \frac{m}{3k_B} \frac{1}{N} \sum_{i=1}^{N} \lim_{T \to \infty} \frac{1}{T} \int_0^T ds \, v_i^2(s)$$

But here we note that any experimental observable can be defined as an average over a time trajectory of the system whose property is being measured. One condition for a reliable average is that the trajectory must be long!
From a theoretical point of view, it is, however, practically impossible to generate a long time trajectory of a macroscopic system consisting of a large number of interacting atoms or molecules (our many-body system!), even with the help of the fastest computers.

Postulates of Statistical Mechanics

The First Postulate: Time Average Equals Ensemble Average

Experimentally we mostly measure the time average of a physical quantity. Time average of any property X is defined as an average over a long trajectory. Mathematically

$$\bar{X} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0 + \tau} ds\, X(s)$$

That is, we evaluate the value of the property X along a trajectory of the system in its phase space, add them up and then divide the sum by the total time spent.

The ensemble average is a simple average over all the members of the ensemble.

$$\langle X \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} p_i\, X_i$$

where p_i is the probability of a member of the ensemble to be in the ith microscopic state.

The first postulate of Statistical Mechanics says that *the time average is equal to the ensemble average*, that is,

$$\bar{X} = \langle X \rangle$$

The motivation behind this hypothesis is obvious. Left to itself, a system will go through all the microscopic states of the system which are also represented in the ensemble. This condition requires that both N and τ must be very large!

Ergodic Hypothesis

➤ The Ergodic Hypothesis states that during its trajectory in phase space a system is free to explore all the microscopic states of the system and given a sufficiently long period of time, spends time in a state that is proportional to the volume of the state in phase space.

➤ This hypothesis can break down if the system gets trapped or localized in a region of phase space (like in glass or supercooled liquids). In such a case, the ensemble average does not equal time average, leading to the violation of the first postulate of Statistical Mechanics.
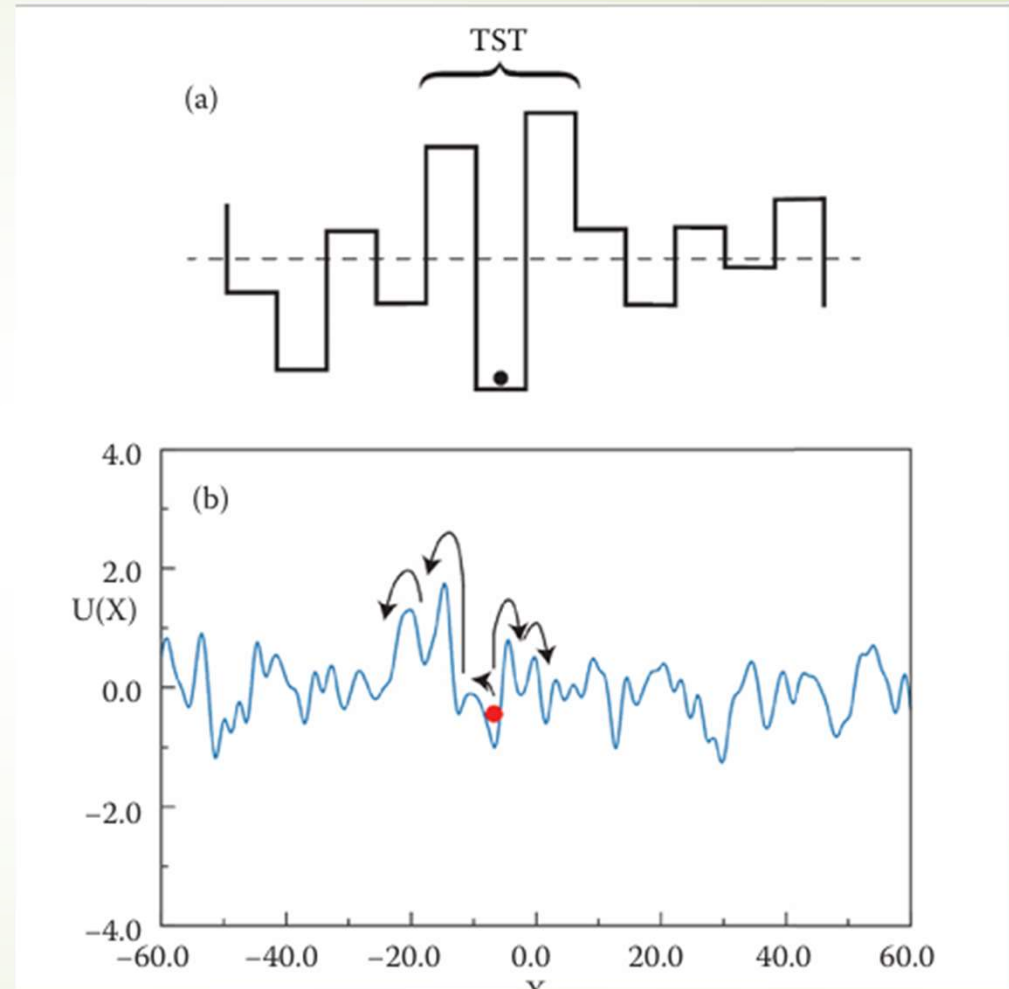
Ref: Statistical Mechanics for Chemistry and Materials Science, Biman Bagchi

The Second Postulate: Equal A Priori Probability

We now need to specify the probability of finding the ensemble in the ith microscopic state. Consider N non-interacting, distinguishable particles, each of which can be in one of two single-particle states: A or B.

Multiplicity of a macrostate

For fixed n, the number of microstates (multiplicity) is

$$\Omega(N, n) = \binom{N}{n} = \frac{N!}{n!(N-n)!}.$$

Probability of a macrostate

Because particles are independent, any given microstate with exactly n particles in A has probability $p^n q^{N-n}$.

All microstates that realize the same macrostate have the same probability, and there are $\binom{N}{n}$ of them, so

$$\boxed{P(N, n) = \binom{N}{n} p^n q^{N-n}}$$

The 2nd postulate tells all the microscopic states of an NVE system are equally likely as they all have the same energy! In the language of quantum mechanics, all the microstates are degenerate.

Solve Factorial of a large number using Stirling's approximation

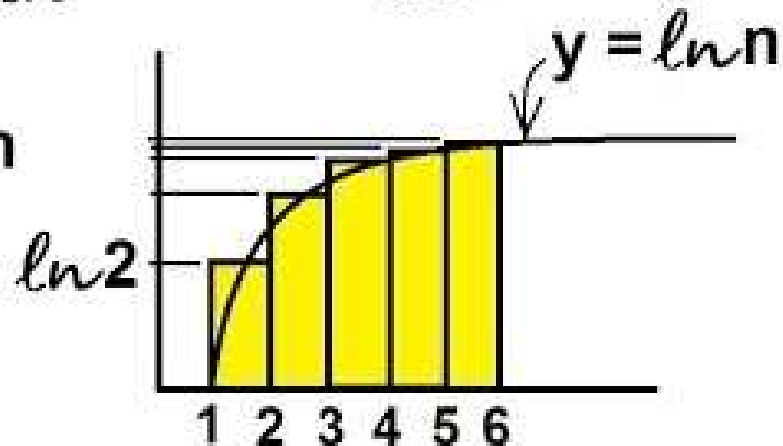## Stirling's Approximation (Explained and Example)

$100! = 100 \cdot 99 \cdot 98 \cdots 2 \cdot 1 = ?$ $N! = ?$ when N is large

$\ln n! = \ln 1 + \ln 2 + \ln 3 + \ln 4 + \cdots + \ln n$

$\ln n! = \sum_{i=1}^{n} \ln n_i = \int_{1}^{n} \ln n \, dn$

$\boxed{\ln n! = n \ln n - n + 1}$

$y = \ln n$

$\ln 2$

1 2 3 4 5 6

Home work:

Implement factorials (either via math.factorial or their own loop).
Implement Stirling's formula.

(a) Compute and print the exact factorial and Stirling's approximation for n=5,10,50,100.
(b) Calculate the relative error between the two for each n.
(c) Plot the relative error as a function of n for n=1 to 100.
(d) Comment on how the error changes with increasing n.