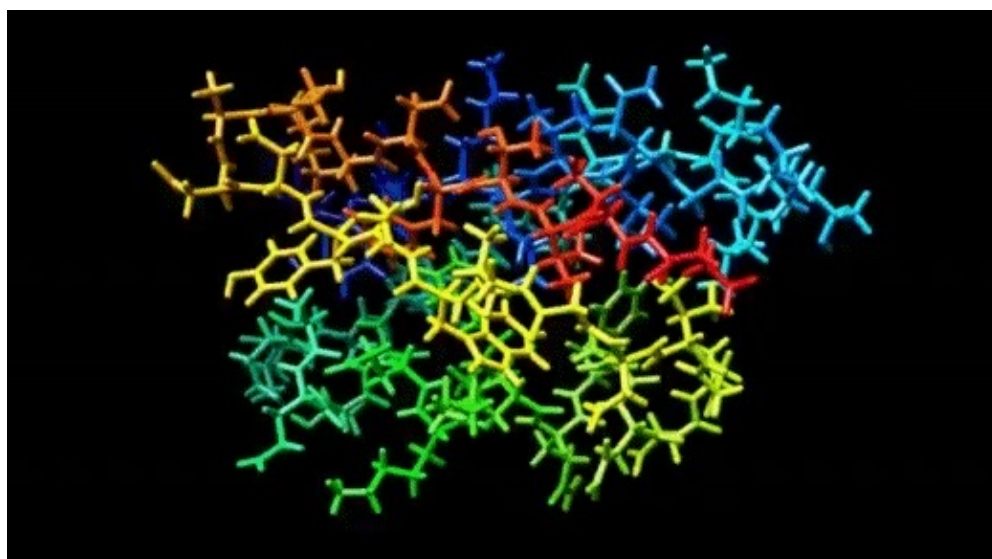
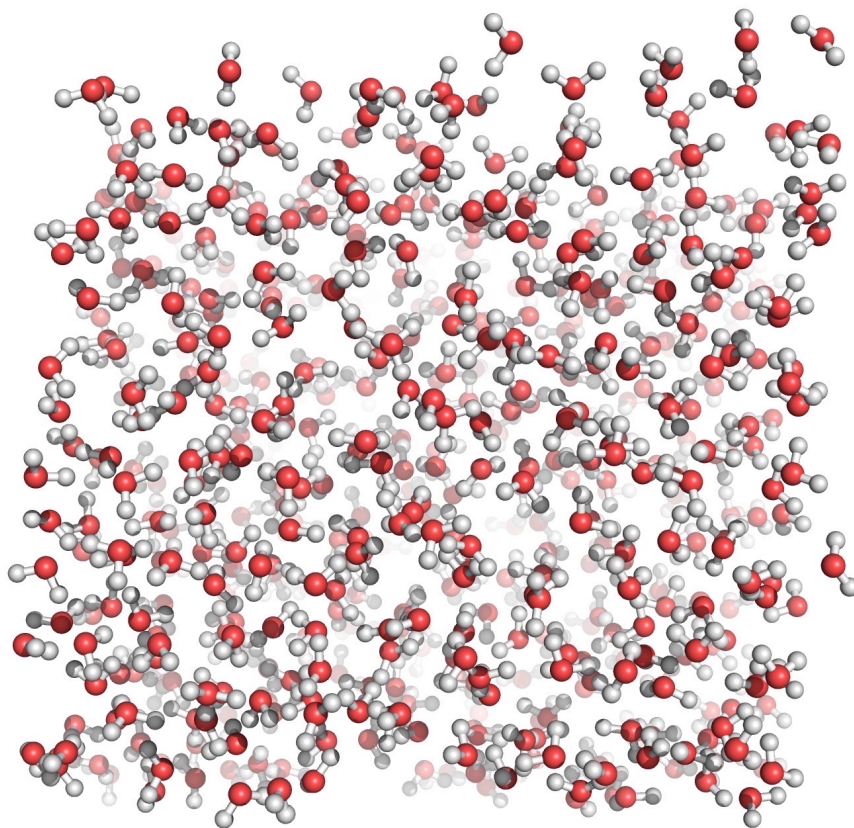


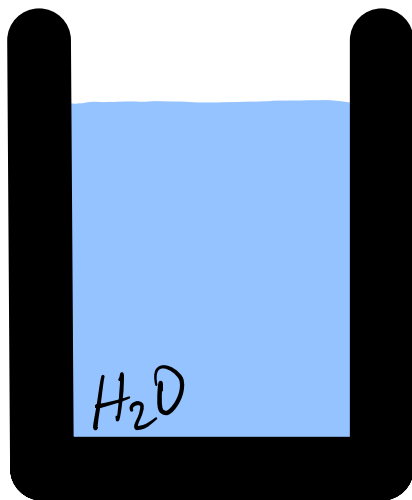
Lecture 1



Major Thematic Questions:

- What is typical?
- How improbable are atypical occurrences?
- How much work is required to make the improbable probable?
- How does all of this depend on system size?

A big glass of water:



Boring and placid

Remarkably, the fluctuations of the small, dynamic system determine how the big, boring system responds to change!

$$\text{Thermodynamics } C = \frac{\langle (E - \langle E \rangle)^2 \rangle}{k_B T^2} \text{ Statistical Mechanics}$$

Heat Capacity

How hard it is to heat the H_2O by one degree

Fluctuations in Energy

But we're getting way ahead of ourselves!

For now:

- Microscopic systems fluctuate.
- Those fluctuations are interesting for their own sake but also because they determine bulk material properties.

Ultimately, the fluctuations come about because the chemical degrees of freedom move.

How should we model that motion?

"All models are wrong. Some models are useful."

Useful depends on what your goals are, and it depends on the scale of the phenomena you hope to understand.

What is changing in time?	How do we denote the state space?	How does an element in that state space evolve?
Pure Quantum State	$ \Psi(t)\rangle$	$\frac{\partial}{\partial t} \Psi(t)\rangle = -\frac{i}{\hbar} H \Psi(t)\rangle$
Mixed Quantum State	$\rho = \sum_n C_n n\rangle \langle n $	$\frac{\partial \rho}{\partial t} = -\frac{i}{\hbar} [H, \rho]$
Classical Phase Space Distribution	$\rho(q, p)$ [Effectively the likelihood of finding a classical system with positions q and momenta p .]	$\frac{\partial \rho}{\partial t} = -\{ \rho, H \}$
A Point in Classical Phase Space	$\{q, p\}$	$\begin{cases} \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p} \\ \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q} \end{cases}$ [Hamilton's Equations - A fancy way of writing Newton's laws.]

$$H(q, p) = T(p) + V(q)$$

$\uparrow$
Hamiltonian
 $\uparrow$
Kinetic Energy
 $\uparrow$
Potential Energy

In all four of these cases, we are talking about a closed and isolated system.

Physics teaches us that the states $(|\Psi(t)\rangle, \rho, q, p)$ evolve deterministically with an energy equal to its initial value. (A conservation law)

Our Starting Point:

In an isolated system (fixed N, V, E), all microstates are equally probable.

"microstate"?

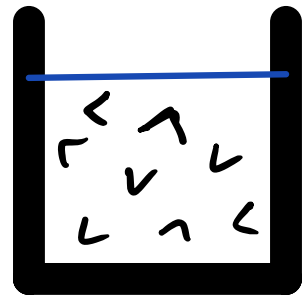
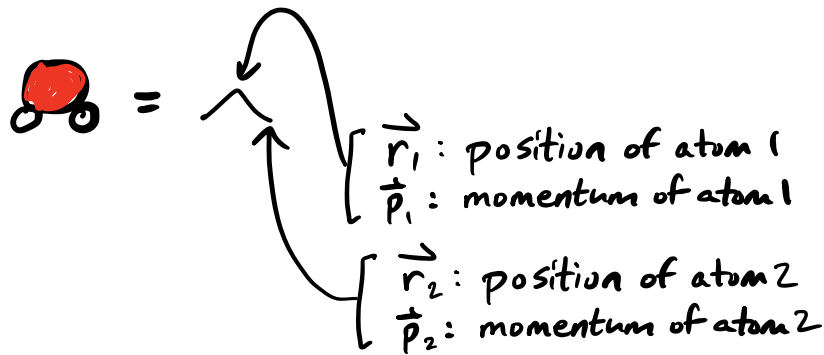
"equally probable"?

A microstate specifies all microscopic details
(of the model)

✓
(nu, not vee)

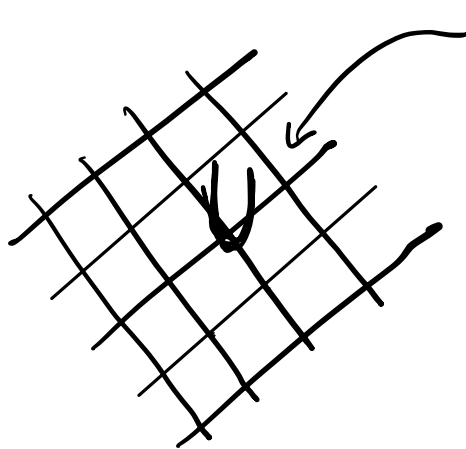
Examples:

Classical World:



The microstate $\vec{X} \equiv (\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \dots, \vec{r}_N, \vec{p}_N)$

Quantum Mechanical World:



Quantum Harmonic Oscillator @ each lattice site

$$|0\rangle_{(0,0)} \otimes |2\rangle_{(1,0)} \otimes |1\rangle_{(0,1)} \dots$$

Ground State
at $(0,0)$

"equally probable"?

Dynamics generates a statistical distribution
independent of detailed preparation
(just sensitive to global constraints — N, V, E)

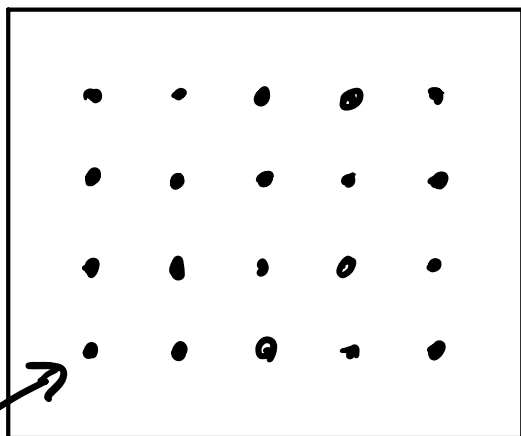
Ergodic Hypothesis

① Is this really true?!

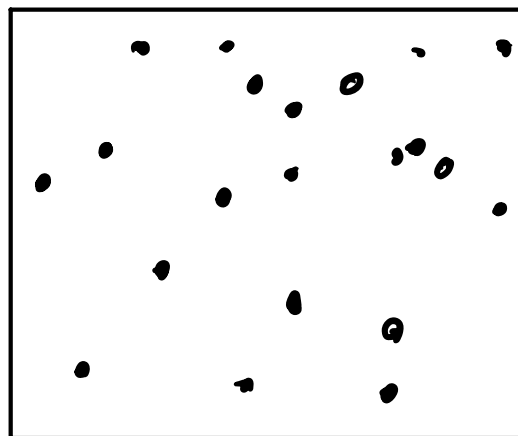
② Why?

① This claim should seem surprising.
Ex: dilute solution...

ν_1



ν_2



solutes

$$P(\nu_1) \stackrel{?}{=} P(\nu_2)$$

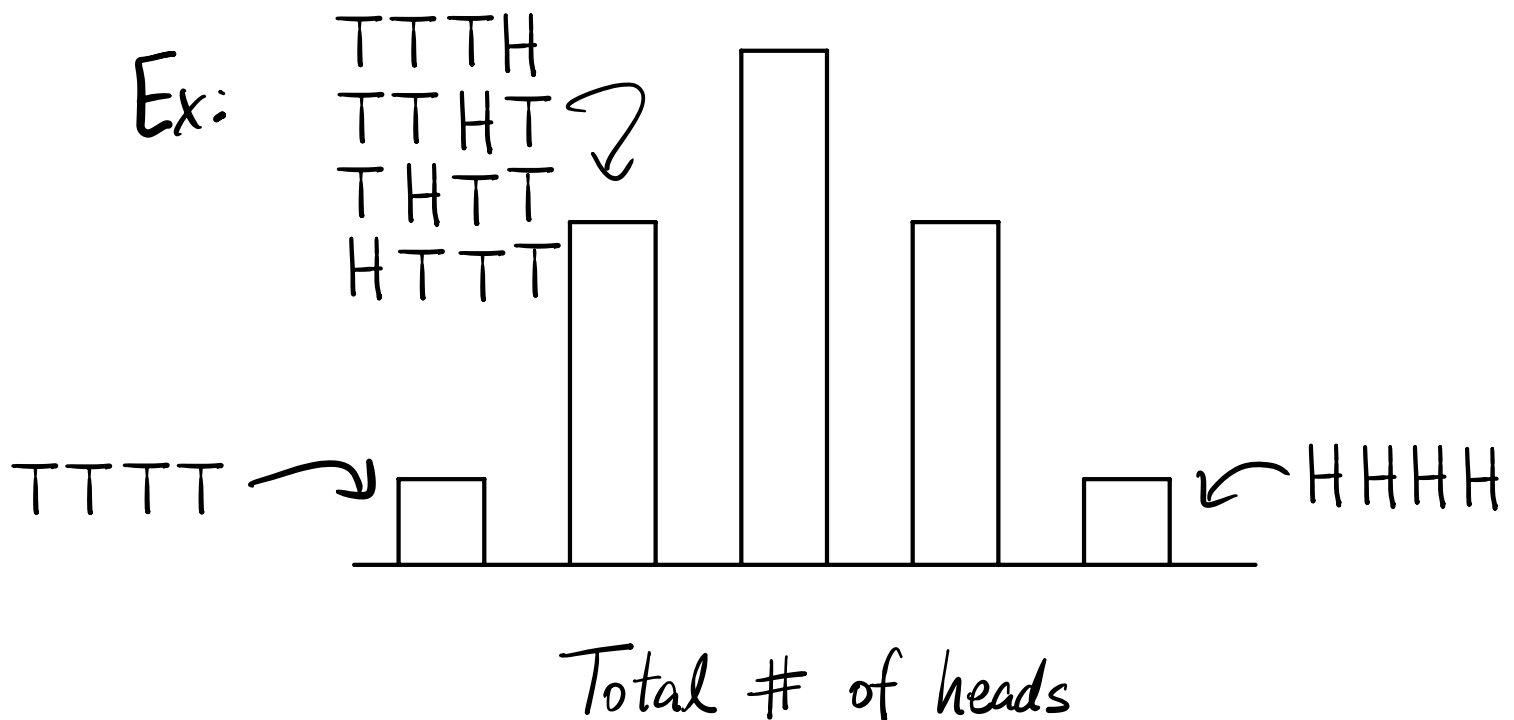
Ex: Coin flips

HTHTTHTTTHH

H H H H H H H H H H

$$P(v_1) = P(v_2)$$

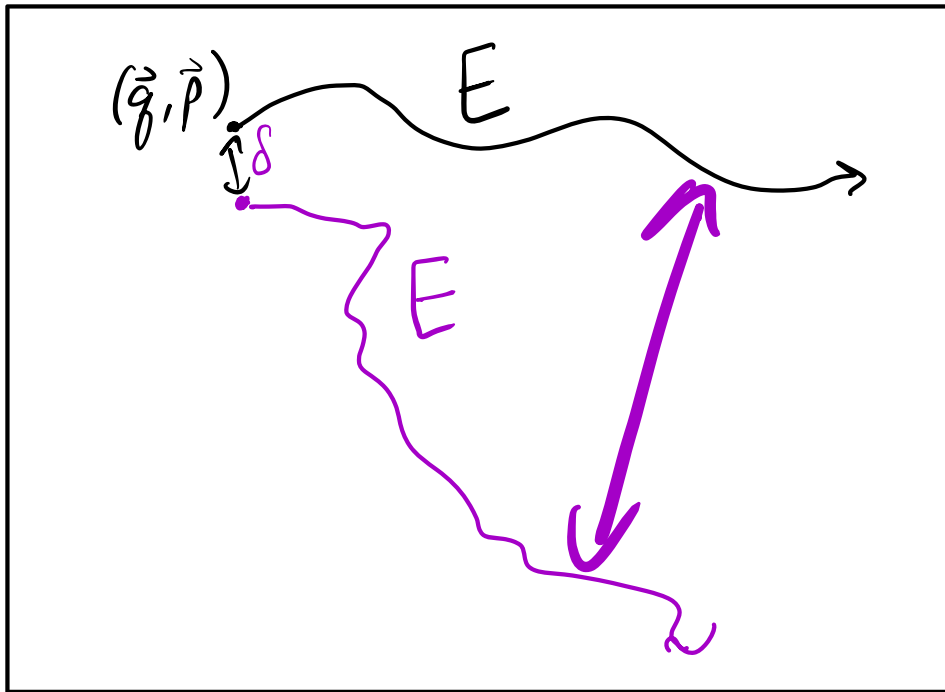
Resolution: An equal probability of microstates
does not imply an equal probability
of macrostates



Uniform distribution of microstates

⇒ Nonuniform distribution over macrostates!

② Why? Chaos.



Trajectories which start very close together lose memory and end up very far apart. In fact, the divergence is exponential in time.

If you prepare a sample then wait a while to measure it, the system will have effectively forgotten where it started. (Though it will not forget the constants of motion.)

We model our ignorance by the assumption that all accessible configurations are equally likely.