

# Lecture 1

- Movies of protein, H<sub>2</sub>O Molecular Dynamics trajectories
  - Lots of dynamics
  - Lots of fluctuations

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?

- Glass of H<sub>2</sub>O (big)  $\Rightarrow$  Boring and placid

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

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

heat capacity  
(how hard it is to heat  
the H<sub>2</sub>O by one degree)  
Thermodynamics world

fluctuations  
in energy  
(statistical mechanics world)

But we're getting way ahead of ourselves! The point for now is that microscopic systems fluctuate. These fluctuations are interesting for their own sake but they also determine material properties.

We will seek to describe the likelihood of the various possible fluctuations with a probability distribution.

Ultimately the fluctuations come about because the chemical degrees of freedom move. How should one model that motion?

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

"Useful" depends on your goals and on the scale of the phenomena you seek 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	$\{q, p\}$	$\begin{cases} \frac{\partial q}{\partial t} = \frac{\partial H}{\partial p} \\ \frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q} \end{cases}$ <p style="text-align: right;">Hamilton's Equations (a fancy way of writing Newton's laws)</p>
$H(q, p) = T(p) + V(q)$		
↑ Hamiltonian		
↑ Kinetic energy		
↑ Potential energy		

Up to this point, evolution of the state has occurred deterministically, and Physics teaches us that energy <sup>(of a closed, isolated system)</sup> is conserved, so though  $|\psi(t)\rangle, \rho, q, p$  can all move around, the total energy is fixed at its initial value.

The starting point:

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

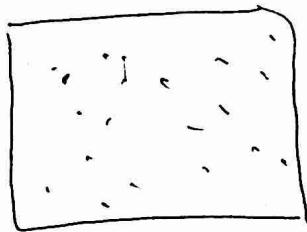
"Microstate" specifies all possible microscopic details  $\checkmark$

"equally probable" - dynamics generates a statistical distribution independent of detailed preparation (hist sensitive to global constraints on  $N, V, E$ )

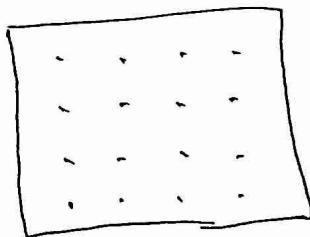
Ergodic Hypothesis

- ① Is this really true?  
② Why?

① This should seem surprising. Ex: dilute solution



$v_1$



$v_2$

$$P(v_1) \stackrel{?}{=} P(v_2)$$

Ex: Coin flipping

HTTHHTHHTT

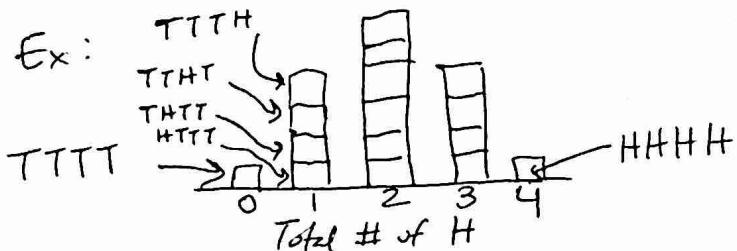
$v_1$

HHHHHHHHHH

$v_2$

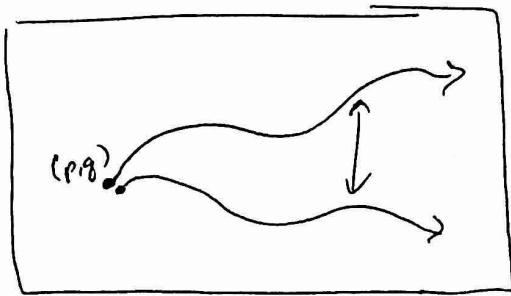
$$P(v_1) \stackrel{?}{=} P(v_2)$$

Resolution: Equal probability of microstates does not imply an equal probability of macrostate.



Uniform distribution over 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 rate of divergence is exponential in time.

If you prepare a sample then wait a while to measure it, it will have effectively forgotten where it started (except for the constants of motion) so we model our ignorance by the assumption that it is equally likely to be in all of the accessible configurations.

Mathematically, at fixed  $E, V, N$ :

$$P(\mathcal{V}) = \begin{cases} \frac{1}{\Omega(E, V, N)}, & \text{if } E_v = E, N_v = N, V_v = V \\ 0, & \text{otherwise} \end{cases}$$

$$\Omega = \sum_{\text{allowed}} (1) = \# \text{ of allowed microstates}$$

How big is  $\Omega$ ?

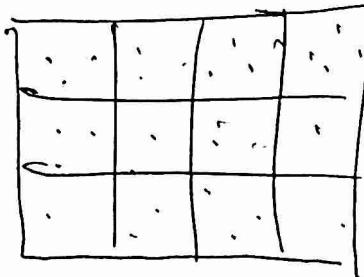
First consider microstates with completely ~~independent~~ independent components

$$\Omega = 6^1 ; \quad \Omega = 6^2 ; \quad \dots ; \quad \Omega = 6^n$$

Equivalently  $\exp[n \ln 6] \leftarrow \text{exponential growth}$

What about if statistical independence is less clear...

Ex: Dilute solution



Volume  $v$  - large enough that the state of one cell cannot significantly influence the others making them independent

$$M \equiv \# \text{ of cells} = \frac{V}{v} \quad \text{density } \rho = \frac{N}{V}$$

$M$  independent subsystems

$$\Omega = \tilde{\omega}^M = [\tilde{\omega}^{1/v}]^N = \omega^N$$

# of configurations  
for one cell

What does  $\omega$  depend on?  $v, \rho, \frac{E}{N} \in \epsilon \Leftarrow$  Intensive things

$$\Omega = [\omega(\epsilon)]^N = \exp [N \ln \omega(\epsilon)]$$

"large deviation form"