

Lecture 1 - Foundations of Statistical Mechanics

02/02/16

"If today's lecture seems wishy-washy... good! That means you're following it. If it all makes sense, you weren't really paying attention!"

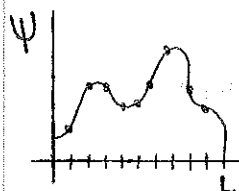
Estimating the amount of data needed for stat mech:

Consider a system of N non-relativistic, quantum mechanical particles

✓ God-given ground-state wavefunction

$$\Psi(\vec{r}_1, \dots, \vec{r}_N)$$

$3N$ variables for N particles



If for the first coordinate of the first particle, x_1 , we have a wavefunction of 10 pts

$\Rightarrow$ this corresponds to 10^{3N} points for N particles described by 3-dimensions

a box of dimension L

- Amount of memory required

$$\sim 10^{3N} \times 8 \text{ bytes} \times 2 \approx 10^{61} \text{ bytes}$$

for $N=20$ particles

to put this in more tangible values...

there are $\sim 10^{12}$ bytes / 0.4 kg

(or ~ 1 Tbyte / 1b)

$$\text{so } 10^{61} \text{ bytes} \approx 10^{49} \times 0.4 \text{ kg}$$

$\Rightarrow$ For just 20 particles, this data is heavier than the planet!

It should be impossible to describe this system!

But we know we can do statistical mechanics... So what's the trick?

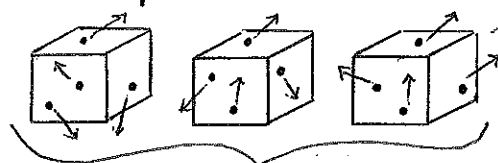
Two tricks to save the day!

① Constrain our interests to only macroscopic variables of large systems (e.g., E, V, N, M, S , etc.)

- We choose large systems because the more particles there are, the more microscopic variables that cancel out, and the less you have to worry about

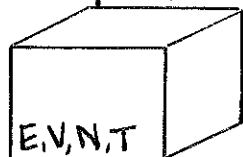
- for example: many microscopic states with the position and momentum of each particle may be described by a single macroscopic state

Microscopic states



specific position & momentum of each particle specified

Macroscopic state

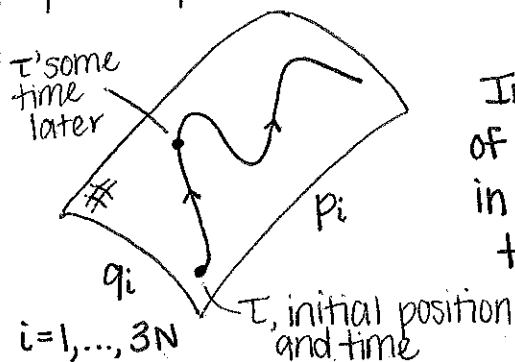


all of the above states can be described by the same Macroscopic state

② Study equilibrium states

- Once you stop shaking a system, the macroscopic states don't change very much

Let us consider a classical system using Hamiltonian Dynamics:
phase space - $6N$ dimensions



Instead of describing the position and momentum of every particle in this space, we use one particle in phase space as a macroscopic state to represent the entire system.

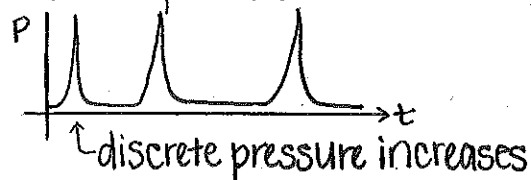
We let the particle go from its initial position at time τ and it evolves in a deterministic way (never self-intersects path)

how that single point evolves in time:

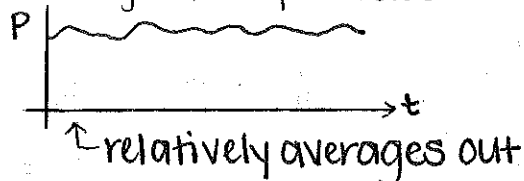
$$\left. \begin{aligned} \frac{\partial q_i}{\partial t} &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \frac{\partial p_i}{\partial t} &= -\frac{\partial \mathcal{H}}{\partial q_i} \end{aligned} \right\} \text{Hamilton's Equations}$$

→ Assuming the system is a gas in a glass...

We now measure pressure at a single point on the glass
for one particle:



for a gazillion particles:



Mathematically:

✓ what we're measuring; dependent on particle's location in phase space
 $f(q_i(t), p_i(t))$

but what we're actually measuring is some kind of average

$$\bar{f} = \frac{1}{T} \int_{\tau}^{\tau+T} dt f(q_i(t), p_i(t))$$

time-averaged integral

To describe all path possibilities mathematically, we take $\lim T \rightarrow \infty$
(where T is much longer than any macrostate system scale)

the quantity that results from a measurement

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{\tau}^{\tau+T} dt f(q_i(t), p_i(t))$$

initial time of measurement
duration of measurement

because $T \rightarrow \infty$, the result of the measurement is dependent only on the initial position of that macro point, because this determines the trajectory of the system.

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{\tau}^{\tau+T} dt f(q_i(t), p_i(t)) = \tilde{f}(q_i(0), p_i(0))$$

initial point in phase space

→ BUT NOT REALLY

A measurement beginning at τ is no different from a measurement beginning at τ' because the duration, T , is infinite!

f actually depends on the path (where the particle goes eventually), not the trajectory, which is very convoluted and of infinite length.

⇒ Ergodic Hypothesis: f is also independent of $q_i(0), p_i(0)$

Assume the path visits almost all[†] points in phase space. If we start anywhere and wait an infinite amount of time, we will end up anywhere else on the path, so it does not matter where on the path we started.

(in the subset of points that have a fixed energy and angular momentum)

[†] almost all = representative sample of the phase space (there is always a point infinitely close that is visited for every point that is not)

Ergodic Systems

* Note: The Ergodic Hypothesis only applies for non-integrable systems

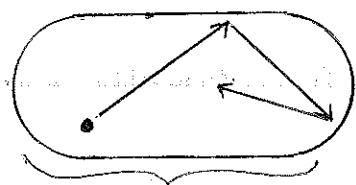
The Ergodic hypothesis asserts that the time-average of a function along a set of trajectories in phase space exists almost everywhere in phase space and is related to the space average. For Ergodic systems, this time-average is the same for almost all initial points.

- Statistically speaking, an Ergodic system that evolves for a long time "forgets" its initial state.

The underlying idea is that for certain systems, the time-average of their properties is equal to the average over the entire space. That is, over long periods of time, the time spent by an ergodic system in some region of the phase space of microstates with the same energy is proportional to the volume of this region (all accessible microstates are equiprobable over a long period of time)

→ Liouville's Theorem for Hamiltonian systems states that if the microstates are uniformly distributed in phase space initially, they will remain so at all times (Note that Liouville's theorem does NOT imply that the ergodic hypothesis holds for all Hamiltonian systems)

ex: Non-interacting gas in a non-square box



"Stadium"

* the only example ever successfully (mathematically) proven to be Ergodic

One particle in a stadium-shaped phase space will explore "almost all" states of

the same energy (assuming the walls are able to create perfectly elastic collisions and that the particle does not begin on a flat wall and follow a path directly aimed at the opposite flat wall)

ex: Non-interacting molecules in a perfect box

-- This system is non-Ergodic

Now, let the molecules interact even the tiniest bit...

→ The system is now Ergodic!

* It actually takes a very special system to be non-Ergodic!
With any interaction, almost all systems tend towards being Ergodic

Computing Observables

When making measurements, we can, by Ergodic Theory, average over phase space instead of time.

$$\bar{f} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_t^{t+T} dt f(q_i(t), p_i(t)) = \frac{\int dq_i dp_i f(q_i, p_i) \delta(\mathcal{H} - E)}{\int dq_i dp_i \delta(\mathcal{H} - E)}$$

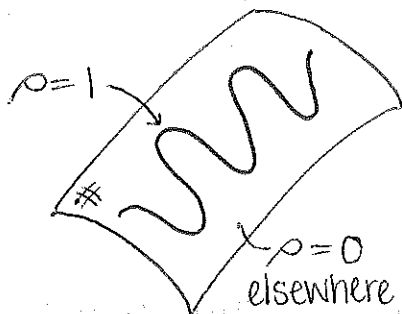
averaged by the volume of the phase space
for the Hamiltonian at a specific value of E

$= \int dq_i dp_i f(q_i, p_i) \rho(q_i, p_i)$, a $6N$ -dimensional integral

$$\rho(q_i, p_i) = \frac{\delta(\mathcal{H}(q, p) - E)}{\int dq_i dp_i \delta(\mathcal{H}(q, p) - E)}$$

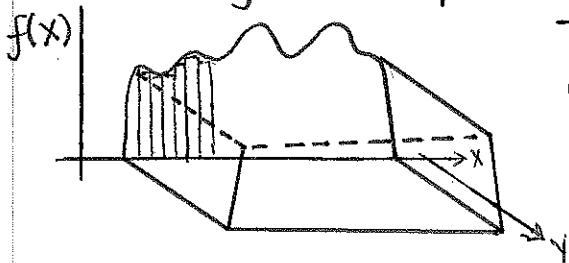
the microcanonical distribution function

* All statistical mechanics systems can be reduced to this integral!



To compute the observable, you don't need to compute the integral over all phase space, only where the microcanonical distribution function, ρ , equals 1.

Introducing Thermodynamics



The %-error we are willing to accept for an estimation determines the amount of points our estimation requires.

— in 1-D(x), we would need 100 points if we were willing to accept 1% error.

If we extended our wavefunction into 2-D(x&y), we would now need $100 \times 100 = 10,000$ points if we were willing to accept 1% error.

→

→ in phase space:

$$(100)^{60} \approx 10^{120} \text{ points}$$

another mathematical impossibility!

This is where thermodynamics comes in!

- not based on classical or quantum mechanics
- was developed before statistical mechanics

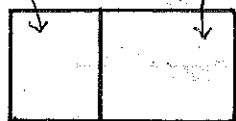
You can go very far in thermodynamics without using stat. mech.

(We can, but should we?)

⇒ We will work in parallel; some in thermodynamics, some in statistical mechanics

Claim: Every problem in thermodynamics can be reduced to the following...

E_1, V_1, N_1 E_2, V_2, N_2



Dividing the subsystems is a non-porous, rigid, non-conducting wall

→ system will remain in this equilibrium

Subsystems → energy, volume, and # molecules known

Now, let the wall change in some way



[interim non-equilibrium system]

E'_1, V'_1, N'_1



E'_2, V'_2, N'_2

The system will find a new equilibrium!
(which we will see may be expressed in terms of the initial values)