Lecture 3:

Classical Mechanics and Microcanonical Ensemble

Last time - Hamilton's Eqns of Motion

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \qquad \dot{p} = -\frac{\partial \mathcal{H}}{\partial q_i}$$

Phase space is the coordinates describing everything about the system

so, $X(t) = \{q_1(t), q_2(t) \dots, q_{3N}(t), p_1(t), \dots p_{3N}(t)\}$

$\mathcal{H}(x)$ is one function of x, and we showed that $\frac{dH(x)}{dt} = 0$ if the system follows hamiltonian/newtonian dynamics

How do other quantities change with time? By the chain rule formula from last time:

$$da(x)/dt = \sum_{i=1}^{3N}\left(\frac{\partial a}{\partial q_i}\frac{\partial q_i}{\partial t} + \frac{\partial a}{\partial p_i}\frac{\partial p_i}{\partial t}\right) = \sum_{i=1}^{3N} \frac{\partial a}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}$$

if we define $\{a,b\} \equiv \sum_{i=1}^{3N} \frac{\partial a}{\partial q_i}\frac{\partial b}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial b}{\partial q_i}$ (Poisson Bracket)

then we see that $\boxed{\frac{da(x)}{\partial t} = \{a, H\}}$

A conserved quantity, one that doesn't depend on time i.e.

$da/dt = 0$, eg. we showed $\frac{dH}{dt} = 0$

so $\{H, H\} = 0$.

Another example, $a(\vec{X}) = \vec{P}_{tot} = \sum_{i=1}^{N} p_i$

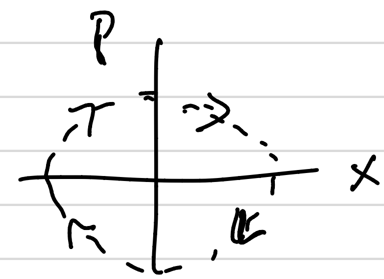
$$\frac{dp_i}{dt} = \{p_i, H\} = -\partial H/\partial q_i = F_i$$

$d\vec{P}_{tot}/dt = \sum \vec{F}_i$, so if net force is 0, momentum is conserved

A "microstate" of a system is one particular point in phase space $X(t)$ for our system

For a conservative system, $\mathcal{H}(x(t)) = \mathcal{E}$, const so the system must remain on some const $\mathcal{E}$ hypersurface.

Eg, if $\quad \mathcal{H}(x,p) = x^2/2 + p^2/2$



radius of this circle depends on initial total energy

An "ensemble" is a collection of microstates all with the same macroscopic characteristics

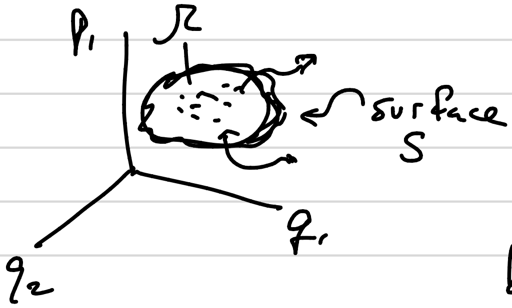
We can express the fraction of phase space points in the ensemble within a small volume $d\vec{x}$ of point $\vec{x}$ by the function $f(x,t)\,dx$

$\rightarrow \quad f(x,t) \geq 0 \quad$ and $\quad \int dx\, f(x,t) = 1$

We can assert that the total number of members of the ensemble stays fixed so that f stays normalized

If we draw a volume in phase space

no sources or sinks, # points in volume = flux through surface



fraction in $\Omega = \int_\Omega dx\, f(x,t)$

can see how f changes by equating flux out with $d\Omega/dt$

This turns out to reduce to (see Chapter 2.5)

$$\frac{\partial f(x(t),t)}{\partial t} + \underbrace{\frac{dx(t)}{dt}\cdot \nabla f(x(t),t)}_{\{\dot q_1, \dot q_2, \dots \dot q_{3N}, \dot p_1 \dots, \dot p_{3N}\}\cdot\{\frac{\partial f}{\partial q_1}, \dots, \frac{\partial f}{\partial q_{3N}}, \dots \frac{\partial f}{\partial p_{3N}}\}} = 0 = \frac{df}{dt}$$

$$+ \sum_{i=1}^{3N}\Big(\underbrace{\dot q_i}_{\frac{\partial H}{\partial p_i}} \frac{\partial f}{\partial q_i} + \underbrace{\dot p_i}_{-\frac{\partial H}{\partial q_i}} \frac{\partial f}{\partial p_i}\Big)$$

$$\boxed{\frac{\partial f}{\partial t} + \{f, H\} = 0}$$ Liouville equation

in analogy w/ QM, call $\{-, H\} \equiv iL$

such that $\frac{\partial f}{\partial t} + iLf = 0 \Rightarrow$ formally $f(t) = e^{-iLt} f(0)$

<u>Equilibrium</u> means f is const in time at every point in space, ie

$$\partial f/\partial t = 0 \Rightarrow \{f, H\} = 0$$

this means f is a function of the Hamiltonian

one way of restating this is if

$$f = \mathcal{F}(H) = \sum_{n=-\infty}^{\infty} c_n H^n \quad \text{(power series expansion)}$$

then $\{f, H\} = \{\sum_{n=-\infty}^{\infty} c_n H^n, H\} = \sum_{n=-\infty}^{\infty} c_n \{H^n, H\} = 0$ ← Exercise

$df/dt = 0$ only determines $\mathcal{F}$ up to a const factor

so $f(x,t) = \frac{1}{Z} \mathcal{F}(H(x))$

where $\boxed{Z = \int d\vec{x}\, \mathcal{F}(H(x))}$

This is called the partition function and it counts the total number of microstates accessible in the ensemble

Ensemble averaging if we knew Z (at Eq.)

$$\langle A \rangle = \int d\vec{x}\, A(x)\, \mathcal{F}(H(x)) / Z$$

The form of $\mathcal{F}$ will depend on the ensemble

Microcanonical Ensemble

For an isolated macroscopic system with a given set

all microstates with the same macroscopic properties are equally likely
(equal-a priori probabilities postulate)

If we have N particles in a box of volume V with no exchange of Energy, then it's a conservative system & dynamics will follow Ham. Eqns. of motion

Hence at equilibrium, $\mathcal{F}(H) = \delta(H(x) - E)$

where $\delta(x)$ is the dirac delta function, with the property $\int_{-\infty}^{\infty} dx\, \delta(x-a) f(x) = f(a)$

units of x^{-1}

The microcanonical partition function

$$\Omega(N, V, E) \propto \int d\vec{x}\, \delta(H(x) - E)$$

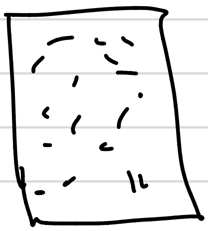
counting num points on hyper surface

The proportionality const can be set by comparison to expts, but here we will just note it should have a $1/N!$ in it since classical particles are indistinguishable

---

Connection to thermodynamics

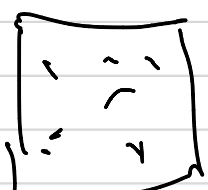
Suppose we have our system



N, V, E

with $\Omega(N,V,E)$ states

If we have 2 coppies of the system still in isolation, how many states are there



$\Omega(N,V,E)$

$\Omega(N,V,E)$

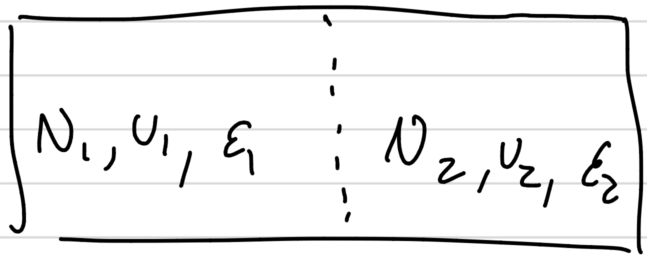
Total $\Omega(2N, 2V, 2E)$

$= \Omega(N,V,E) \cdot \Omega(N,V,E)$

Extensive functions double when the system size doubles, etc. What would an extensive function of Ω be?

$f(\Omega) \propto \log \Omega$ has this property

Suppose we take our two systems not exactly identical and let only $\mathcal{E}$ flow, whole system is isolated



$$\mathcal{E}_2 = \mathcal{E}_{tot} - \mathcal{E}_1$$

Since energy can move from one side to the other, $\mathcal{E}_1$ can be any value from 0 to $\mathcal{E}_{tot}$. Which value is most likely?

Same as saying which value of $\mathcal{E}_1$ maximizes $\Omega(\mathcal{E}_{tot}, N_1+N_2, V_1+V_2)$

To max/min Ω, we do $0 = \frac{d\Omega}{d\mathcal{E}_1}$, equivalently

$0 = d\log\Omega / d\mathcal{E}_1$, b/c $\log\Omega$ monotonically increasing

$$0 = \frac{d\log\Omega}{d\mathcal{E}_1} = \frac{d}{d\mathcal{E}_1}\left(\log(\Omega_1\Omega_2)\right) = \left(\frac{d\log\Omega(N_1,V_1,\mathcal{E}_1)}{d\mathcal{E}_1}\right)_{N_1,V_1} + \left(\frac{d\log\Omega(N_2,V_2,\mathcal{E}-\mathcal{E}_1)}{d\mathcal{E}_1}\right)_{N_2,V_2}$$

$$\Rightarrow \left(\frac{d\log\Omega(N_1,V_1,\mathcal{E}_1)}{d\mathcal{E}_1}\right)_{N_1,V_1} = -\left(\frac{d\log\Omega(N_2,V_2,\mathcal{E}-\mathcal{E}_1)}{d\mathcal{E}_1}\right)_{N_2,V_2} = \left(\frac{\partial\log\Omega(N_2,V_2,\mathcal{E}_2)}{\partial\mathcal{E}_2}\right)_{N_2,V_2}$$

Thermodynamics says heat will flow from one part to the other until the temperatures are equal

So somehow we expect $\left(\partial \log \Omega / \partial \varepsilon\right)_{N,V}$ to be related to the temperature

Basic thermo will tell us (next) that $\frac{1}{T} = \left(\frac{\partial S}{\partial \varepsilon}\right)_{N,V}$

hence if we associate $\boxed{S(N,V,\varepsilon) = k_B \log \Omega(N,V,\varepsilon)}$

we get that (1) 2 bodies in contact equalize $1/T \equiv \beta$

(2) Entropy is maximized for a closed system at equilibrium

This connects microscopic states to one macro observable (& others, see next)