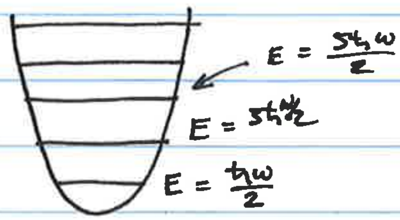
A simple Quantum View

The problem: States are quantized, but not all states are equally likely



These are the first 3 energy levels of the quantum mechanical harmonic oscillator

How do we get physical properties from an ensemble of molecules where each one might be in a different state?

$$\langle X \rangle = \sum_{molecules} X_{molecule}$$

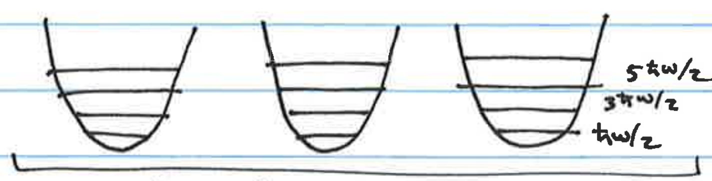
average of property X

Alternatively: $\langle X \rangle = \sum_{states} X_{state} P_{state}$

property X when a molecule is in a particular state

probability of that state

Consider:



3 identical harmonic oscillators

Suppose we have a total energy of $\frac{9}{2}\hbar\omega$ to distribute. Since the ground state is $\boxed{3 \times \frac{\hbar\omega}{2}}$, there are 3 quanta of energy to Distribute

Let's map out all possible ways of doing this:

System state	state of HO #1	state of HO #2	state of HO #3
a	3	0	0
b	0	3	0
c	0	0	3
d	2	1	0
e	2	0	1
f	1	2	0
g	0	2	1
h	1	0	2
i	0	1	2
j	1	1	1

There are 10 ways of dividing up the energy between these identical oscillators

$$C(N, n_0, n_1, n_2, n_3) = \frac{N!}{n_0!\,n_1!\,n_2!\,n_3!} = \text{count of configurations}$$

N: # of quanta to distribute

n_0: # of oscillators in the ground state

n_3: # of oscillators in state #3

$C(3, 2, 0, 0, 1)$ = states with 1 oscillator in $n=3$ and 2 oscillators in $n=0$ (system states a, b, and c)

$$= \frac{3!}{2!\,1!\,0!\,0!} = 3$$

$C(3, 1, 1, 1, 0)$ = states with 1 oscillator in each of $\begin{cases} n=0 \\ n=1 \\ n=2 \end{cases}$

= system states d, e, f, g, h, i

$$= \frac{3!}{1!\,1!\,1!\,0!} = 6$$

$C(3,0,3,0,0)$ = states with 3 oscillators in $n=1$ (system state j)

$$= \frac{3!}{0!\,3!\,0!\,0!} = 1$$

C is the number of ways of distributing objects between boxes:

$$W = \frac{N!}{\prod_{i=1}^{s} n_s!} = \text{permutations}$$

This turns out to be directly related to the entropy

$$S = k_B \ln W$$

W: indistinguishable permutations or microstates that contribute to that macrostate

S: entropy of a macrostate

k_B: Boltzman's Constant

Which arrangement has the largest entropy?

A review of basic probability theory:

If we carry out N trials with n_A trials resulting in outcome A:

$$P_A = \frac{n_A}{N}$$

Relationships between outcomes:

1) Mutually exclusive: Outcome A means B is not an outcome of this trial

2) Collectively exhaustive: Outcome must be A, B, C or D

$$P_A + P_B + P_C + P_D = 1$$

Rules

Mutually exclusive events

Will I see A or B ? $= P_A + P_B$

Independent outcomes

will I see A and B $= P_A * P_B$

Suppose there are only 2 car models: civic & camry
and only 2 possible car colors: red & blue

Will I see a red camry $= P_{r,cam} = \left(\frac{1}{2}\right)\left(\frac{1}{2}\right) = \frac{1}{4}$

Conditional Probabilities

$P(B|A)$ = probability of B given A

e.g.

It snows 10% of days in South Bend
It snows 50% of days with $T < 36°F$

$$P(\text{snow}) = 0.1$$
$$P(\text{snow} \mid T < 36°F) = 0.5$$

Joint Probabilities

$$p(AB) = p(B|A)\,p(A) = p(A|B)\,p(B)$$

snow and $T < 36°F = p(\text{snow} \mid T < 36°F) * p(T < 36°F)$

what we know:

$$p(B) = 0.1$$
$$p(B|A) = 0.5$$

we need at least 1 more piece of information

We need: $p(A)$ = probability that $T < 36°F$

or:

$P(A|B)$ ← probability of $T<36°F$, given snow

= 1 in this case

$$p(AB) = p(A|B)\,p(B) = 1 * 0.1$$

= probability of a cold, snowy day

Combinatorics

$$W = \frac{N!}{n_1!\,n_2!\,\ldots\,n_t!}$$

If there are only 2 outcomes (e.g. heads/tails)

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

N choose n

$P_H = p$
$P_T = 1-p$

suppose we do two trials:

$$P_{HH} = p^2$$
$$P_{HT} = p(1-p)$$
$$P_{TH} = (1-p)(p)$$
$$P_{TT} = (1-p)^2$$

different outcome, but same "macro" state (1 H and 1 T)

in any order

Binomial distribution

$$P(n_H, N) = p^{n_H}(1-p)^{N-n_H}\frac{N!}{n_H!\,(N-n_H)!}$$

$$P(n_1, n_2, \ldots n_t, N) = p_1^{n_1}\,p_2^{n_2}\,\cdots\,p_t^{n_t}\left(\frac{N!}{n_1!\,n_2!\,\ldots\,n_t!}\right)$$

Combinatorics

$$W = \frac{N!}{n_1!\, n_2! \dots n_t!} = \text{ways of putting } N \text{ indistinguishable objects into } t \text{ categories}$$

If there are only 2 categories (heads / tails ; yes / no)

N choose n

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

Probabilities are important: (consider a "cheater" coin that flips heads 60% of the time)

$P_H = p = 0.6$

$P_T = 1-p = 0.4$

2-flips:

			non-cheater
P_{HH}	$= p^2$	$= 0.36$	$= 0.25$
P_{HT}	$= p(1-p)$	$= 0.24$	0.25
P_{TH}	$= (1-p)p$	$= 0.24$	0.25
P_{TT}	$= (1-p)^2$	$= 0.16$	0.25

$$p(n_H, N) = p^{n_H}(1-p)^{N-n_H} \frac{N!}{n!\,(N-n_H)!}$$

in any order

Binomial Distribution

Multinomial:

$$p(n_1, n_2, \ldots n_t, N) = P_1^{n_1} P_2^{n_2} P_3^{n_3} \cdots P_t^{n_t} \left(\frac{N!}{n_1!\, n_2! \cdots n_t!} \right)$$

Continuous Distributions

$$p(x)dx = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2} \qquad -\infty \le x \le \infty$$

↑ probability of finding a value between x & $x+dx$

discrete: $$\langle i \rangle = \sum_{i=1}^{t} i\, p(i)$$ ← average of i over all t outcomes

continuous $$\langle x \rangle \quad \int x\, p(x)\, dx \Big/ \int p(x) dx$$ ← normalization

discrete $$\langle f(i) \rangle = \sum_{i=1}^{t} f(i)\, p(i)$$
← value of f in outcome i
← probability of outcome i

continuous: $$\langle f(x) \rangle = \int f(x)\, p(x)\, dx \Big/ \int p(x) dx$$

Central Limit Theorem

Consider rolling a die

Uniform Distribution in the integers between 1 & 6

What is $\langle n \rangle$

$$\langle n \rangle = \sum_{i=1}^{6} i\, p(i) = 1\left(\tfrac{1}{6}\right) + 2\left(\tfrac{1}{6}\right) + 3\left(\tfrac{1}{6}\right) + 4\left(\tfrac{1}{6}\right) + 5\left(\tfrac{1}{6}\right) + 6\left(1/6\right)$$

$$= 21/6 = 7/2 = 3.5$$ ← not an observed ~~result~~ outcome!

What is $\langle n^2 \rangle$

$$\langle n^2 \rangle = \sum_{i=1}^{6} i^2 p(i) = \frac{1+4+9+16+25+36}{6} = 15\,1/6$$

These are called the first and second moments of the distribution

$$\text{Variance} = \sigma^2 = \langle (x - \langle x \rangle)^2 \rangle$$ ← average square of deviation from the mean

$$= \langle (x - \langle x \rangle)(x - \langle x \rangle) \rangle$$

$$= \langle x^2 - 2\langle x \rangle x + \langle x \rangle^2 \rangle$$

$$= \langle x^2 \rangle - 2\langle x \rangle\langle x \rangle + \langle x \rangle^2$$

$$= \langle x^2 \rangle - \langle x \rangle^2 = 15\,1/6 - (3.5)^2$$

$$= 2.9166\ldots$$

Std. Dev:

$$\sigma = \sqrt{\sigma^2} = 1.7078\ldots$$

The Central Limit Theorem:

Let $n_1, n_2 \ldots$ be independent, identically distributed random variables having mean $\langle n \rangle$ and finite non-zero variance σ^2

Let $S_N = n_1 + n_2 + \ldots n_N$ ← the sum of N "trials"

Then

$$\lim_{N\to\infty} P\left(\frac{S_N - N\langle n\rangle}{\sigma\sqrt{N}} \le x\right) = \Phi(x)$$

where $\Phi(x)$ is the probability that a normal gaussian variable will be less than x

$$\Phi(x) = \int_{-\infty}^{x} \frac{1}{\sqrt{2\pi}} e^{-(x'-\langle n\rangle)^2/2\sigma^2} dx'$$

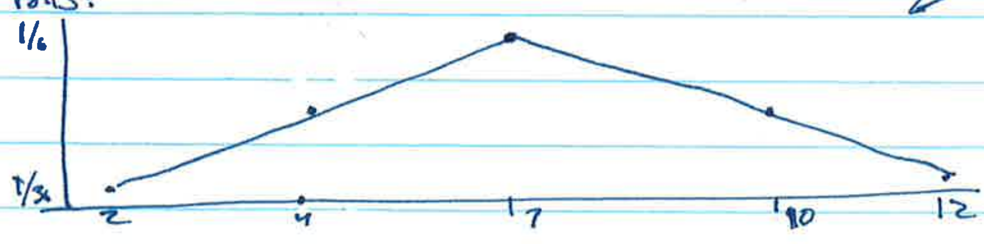
What does this mean? ~~Cons~~ Consider 2 dice:

what is n_{min}? 2 what is n_{max}? 12

There are 36 possible rolls:

	1	2	3	4	5	6
1	2	3	4	5	6	7
2	3	4	5	6	7	8
3	4	5	6	7	8	9
4	5	6	7	8	9	10
5	6	7	8	9	10	11
6	7	8	9	10	11	12

How Many rolls:



← flat 1/6 distribution goes to non-flat distribution

6-5

The CLT tells us that <u>summed</u> variables will approach the Gaussian distribution when the lengths of the sums (i.e. the number of dice) are large

---

The most important thing is that it doesn't matter if we have "cheater" dice: The distribution of sums will always be Gaussian distributed

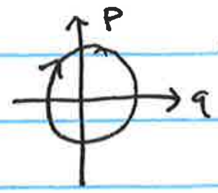
Probability and the connection to Classical Mechanics

$$\langle x \rangle = \frac{\int x\, P(x)\, dx}{\int P(x)\, dx} \qquad \langle f \rangle = \frac{\int f(x) P(x)\, dx}{\int P(x)\, dx}$$

average property of x

Probability density of x

Now let's look at a simple mechanical system:



say we wanted to know $\langle p^2 \rangle$ for this system

How would we do it?

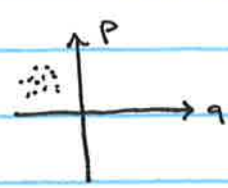
- watch for 1 orbit, or
- make <u>many</u> copies

$$\langle p^2 \rangle = \frac{\iint p^2\, P(q,p)\, dq\, dp}{\iint P(q,p)\, dq\, dp}$$

probability we'll find one copy with position in $[q, q+dq]$ and momentum in $[p, p+dp]$

Phase Space Density

ensemble of identical systems each with different initial conditions



the movement of this cloud of points describes the evolution of the ensemble

$$\rho(\vec{q}, \vec{p}, t)$$

The normalized density:

$$P(\vec{q},\vec{p},t) = \frac{\rho(\vec{q},\vec{p},t)}{\iint \rho(\vec{q},\vec{p},t)\, \underbrace{d^{3N}\vec{q}}_{= dq_1\, dq_2\, d\ldots\, dq_{3N}}\, d^{3N}\vec{p}}$$

An ensemble average:

$$\langle F(t)\rangle = \iint F(\vec{q},\vec{p})\, P(\vec{q},\vec{p},t)\, d^{3N}\vec{q}\, d^{3N}\vec{p}$$

this is an average over many members of the ensemble

Time average

$$\langle F\rangle_t = \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} F(\vec{q}(t),\vec{p}(t))\, dt$$

average one trajectory over a long time T

The Ergodic hypothesis

$$\langle F(t)\rangle = \langle F\rangle_t$$

the ensemble average is equal to the time average.

1) this holds for conservative, non-integrable systems

no friction or external pumping

no orbits which prohibit chaotic sampling

2) $T\to\infty$ is usually a challenge

Poisson Brackets

$$\{F, G\}_{\vec{q},\vec{p}} \equiv \sum_{i=1}^{3N}\left[\left(\frac{\partial F}{\partial q_i}\right)\left(\frac{\partial G}{\partial p_i}\right) - \left(\frac{\partial G}{\partial q_i}\right)\left(\frac{\partial F}{\partial p_i}\right)\right]$$

Suppose G is the Hamiltonian:

$$\left(\frac{\partial \mathcal{H}}{\partial p_i}\right) = \dot{q}_i = \frac{dq_i}{dt} \quad \text{and} \quad \left(\frac{\partial \mathcal{H}}{\partial q_i}\right) = -\dot{p}_i = -\frac{dp_i}{dt}$$

$\therefore$

$$\{F, \mathcal{H}\}_{\vec{q},\vec{p}} = \sum_{i=1}^{3N}\left[\left(\frac{\partial F}{\partial q_i}\right)\frac{dq_i}{dt} + \left(\frac{\partial F}{\partial p_i}\right)\frac{dp_i}{dt}\right]$$

$$= \frac{dF}{dt}$$

The Poisson bracket with $\mathcal{H}$ is one way of expressing how some observable F changes in time due to classical motion.

If $\frac{dA}{dt} = \{A, \mathcal{H}\}_{\vec{q},\vec{p}} = 0$ then A is called a constant of the motion.

Fundamental constants of the motion:

$\mathcal{H}$, $\vec{P}$ = total linear momentum, $\vec{L}$ = total angular momentum

usually taken to be 0, but this is not necessary.

Liouville's Theorem

If we follow a point in phase space, then the density of points in the neighborhood is constant,

$$\frac{d\rho(\vec{q},\vec{p},t)}{dt} = \left(\frac{\partial \rho}{\partial t}\right)_{\vec{q},\vec{p}} + \{\rho, \mathcal{H}\} = 0$$

explicit time dependence

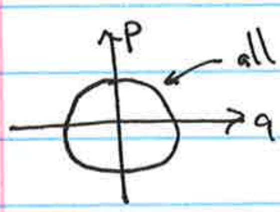
change in density due to normal motion

∴ density distribution is independent of time,

∴ Ergodic hypothesis is true!

Kinds of Ensembles

Microcanonical: $\rho(\vec{q},\vec{p}) \propto \delta\left(E - \mathcal{H}(\vec{q},\vec{p})\right)$



all points have same energy

only those points with energy $\mathcal{H}(\vec{q},\vec{p}) = E$ are allowed.

- All members of ensemble have the same energy. All are equally likely

Canonical – Stable ensemble that is

1) extensive, and
2) depends only on constants of the motion

$$\rho = \rho(E, \vec{P}, \vec{L}) = \rho\left(\mathcal{H}(\vec{q},\vec{p}), \vec{P}(\vec{q},\vec{p}), \vec{L}(\vec{q},\vec{p})\right)$$

Poisson Brackets

$$\{F, \mathcal{H}\}_{q,p} = \sum_{i=1}^{3N} \left\{ \left(\frac{\partial F}{\partial q_i}\right)\left(\frac{\partial \mathcal{H}}{\partial p_i}\right) - \left(\frac{\partial \mathcal{H}}{\partial q_i}\right)\left(\frac{\partial F}{\partial p_i}\right) \right\} \leftarrow F(\vec{q},\vec{p})$$

$$= \sum_{i=1}^{3N} \left\{ \left(\frac{\partial F}{\partial q_i}\right)\dot{q}_i + \left(\frac{\partial F}{\partial p_i}\right)\dot{p}_i \right\}$$

$$= \frac{dF}{dt} \longleftarrow$$ i.e. How does F change in time?

The Poisson Bracket with $\mathcal{H}$ is one way of expressing how some observables change in time due to classical motion:

if $\{A, \mathcal{H}\} = \frac{dA}{dt} = 0$, then A is called a constant of the motion:

Fundamental constants of the motion:

- $\mathcal{H}$ i.e. energy
- $\vec{P}$ i.e. total linear momentum
- $\vec{L}$ i.e. total angular momentum

(usually assumed to be $= 0$)

Liouville's theorem:

If we follow a point in phase space, then the density of local points is constant.

$$\frac{d\rho(\vec{q},\vec{p},t)}{dt} = \left(\frac{\partial \rho}{\partial t}\right) + \{\rho, \mathcal{H}\} = 0$$

explicit dependence on t (usually 0)

We'll eventually make a stab at proving this (so dust off your knowlege of the divergence theorem.)

$\therefore$ Density distribution is independent of time if ρ is a function of constants of the motion.

Ensembles (stable distributions in phase space)

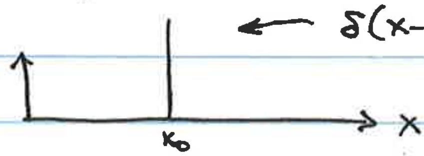
Microcanonical

$$\rho(\vec{q},\vec{p}) \propto \delta\left(E - \mathcal{H}(\vec{q},\vec{p})\right)$$

only those points in phase space where $\mathcal{H}(\vec{q},\vec{p}) = E$ are members of the ensemble

---

A brief note on the Dirac Delta function



$\leftarrow \delta(x-x_0)$ is infinitely thin, with an area of 1

$$\int \cos(x)\,\delta(x-x_0)\,dx = \cos(x_0)$$

But :

$$\int \delta(x-x_0)\,dx = 1$$

$$\delta(x-x_0) = \lim_{\sigma \to 0} \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(x-x_0)^2/2\sigma^2}$$

this is just one way of representing the δ function

Other Ensembles

Liouville's theorem tells us that $\{\rho, \mathcal{H}\} = 0$

so we can write ρ as if it depends only on other constants of the motion

$$\rho = \rho(E, \vec{P}, \vec{L})$$

$\leftarrow$ these are the only ones we're guaranteed to find.

$$\rho = \rho\left[\mathcal{H}(\vec{q},\vec{p}),\ \underbrace{\vec{P}(\vec{q},\vec{p}),\ L(\vec{q},\vec{p})}_{\text{these are usually set to } 0}\right]$$

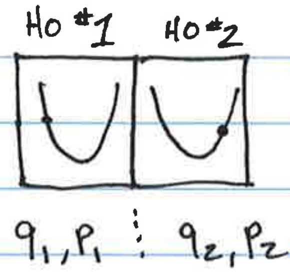
$$\rho = \rho\left[\mathcal{H}(\vec{q},\vec{p})\right]$$

Extensivity

ρ measures a joint probability. If we have two separate portions of our ensemble we can talk about their distributions independently

$$\rho(\vec{q},\vec{p}) = \rho_1(\vec{q},\vec{p})\,\rho_2(\vec{q},\vec{p})$$

Consider two independent harmonic oscillators



$$\rho(q_1,p_1,q_2,p_2) = \rho_1(q_1 p_1)\,\rho_2(q_2 p_2)$$

probability of finding HO1 at q_1, p_1 and HO2 at $q_2 p_2$

probability of finding HO1 at $q_1\ p_1$

$$= \rho_1(q_1 p_1, \underbrace{q_2 p_2}) \, \rho_2(\underbrace{q_1 p_1}, q_2, p_2)$$

these won't matter in the separate distributions

Now, most of the constants of the motion are extensive or additive, and we can try to figure out how ρ can be additive using logarithms:

$$\rho = \rho_1 \rho_2$$
$$\ln\rho = \ln\rho_1 + \ln\rho_2$$

If ρ is only a function of constants of the motion which are extensive:

$$\ln\rho(\vec{q},\vec{p}) = a + b\mathcal{H}(\vec{q},\vec{p}) + \vec{c}\cdot\vec{P} + \vec{d}\cdot\vec{L}$$

usually 0

$$\therefore \quad \rho \approx e^{a} e^{b\mathcal{H}(\vec{q},\vec{p})}$$

If $a=0$,

$$\rho \approx e^{bE(\vec{q},\vec{p})}$$

What we know so far:

ρ is independent of time $\frac{d\rho}{dt} = 0$

$\therefore$ ρ depends only on constants of motion e.g. $\rho(E)$

ρ is extensive measure of joint probability

$$\therefore \quad \rho = \rho_1 \rho_2$$

$$\ln\rho = \ln\rho_1 + \ln\rho_2$$

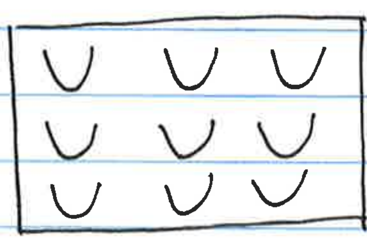
Energy is additive in the regions

$$E = E_1 + E_2$$

$$\therefore \quad \ln\rho = a + bE + \cancel{\vec{c}\cdot\vec{P}} + \cancel{\vec{d}\cdot\vec{L}}$$

$$\therefore \quad \rho = e^{bE(\vec{q},\vec{p})}$$

$\leftarrow$ ρ is an exponential function of the energy.



$\leftarrow$ An ensemble of oscillators make up our system $E_i = (n_i + \frac{1}{2})\hbar\omega$

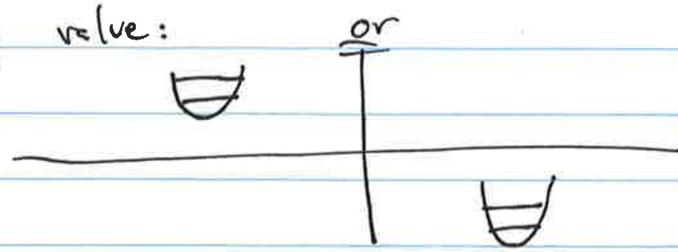
$\leftarrow$ A thermal reservoir at constant temperature, energy can be exchanged between oscillators, but no energy enters or leaves the ensemble

a_i = # of members of ensemble with energy E_i

$$\frac{a_2}{a_1} = f(E_1, E_2)$$

$\leftarrow$ relative populations depend on ρ which can only depend on E_i

Energy is <u>always</u> measured relative to a fixed arbitrary value:



If we move the zero bar up or down, the relative fraction, $\frac{a_1}{a_0}$, should not change

$\therefore$

$$\frac{a_2}{a_1} = f(E_1 - E_2)$$

$\therefore$ The importance of energy is in the <u>difference</u> between 2 states: