What is Statistical Mechanics?

1) Using microscopic principles to understand macroscopic phenomena:

Microscopic				Macroscopic
Particles wavefunctions States Quantum Mechanics Classical Mechanics	How do these →	SM	→ Become these?	Density Pressure Temperature Thermodynamics Rates Measurements

2) Studying emergent behavior of collections of microscopic systems.

What kind of limits should we set?

- Use the simplest model that exhibits a phenomenon, but no simpler.

  (Don't use quarks to study protein folding)
- Be sure to use a sufficiently elementary description of microscopic behavior or you'll be doing an exercise in curve fitting.

For Chemistry, the simplest nontrivial description of systems is atoms, molecules, and the states of these objects.

These things live at the boundary of Quantum & Classical mechanics.

Classical Mechanics

<u>The Big Idea</u>: The "state" of a system is completely defined by the <u>positions</u> and <u>velocities</u> of all the particles

N particles $\longrightarrow$ 3N positions $\begin{pmatrix} x \\ y \\ z \end{pmatrix}$ + $\left(\begin{array}{l} 3N \text{ velocities } \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \\ \underline{\underline{\text{or}}} \\ 3N \text{ momenta } \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \end{array} \right)$

$\longrightarrow$ 6N coordinates

$$\overset{\text{vector}}{\vec{q}} = (q_1, \ldots q_{3N}) \quad \longleftarrow \text{ vector of 3N positions}$$

$$\dot{\vec{q}} = (\dot{q}_1, \ldots \dot{q}_{3N}) \quad \longleftarrow \text{ vector of 3N velocities}$$

<u>dots</u> denote time derivatives: $\dot{a} = \frac{\partial}{\partial t} a$

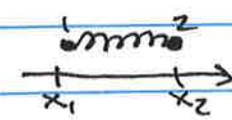
$$\ddot{a} = \frac{\partial}{\partial t} \dot{a} = \frac{\partial^2}{\partial t^2} a$$

<u>Kinetic energy</u> is a function of velocities (or momenta)

$$T(\dot{\vec{q}}) = \sum_{i=1}^{3N} \frac{1}{2} m_i \dot{q}_i^2 = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i}$$

<u>Potential energy</u> is usually a complicated function of positions $V(\vec{q})$:

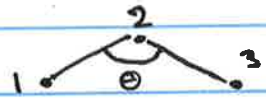
A "bond" between atoms:



$$V(x_1, x_2) = \underbrace{\tfrac{1}{2}k}_{\text{spring constant}} \big(\underbrace{|x_2 - x_1|}_{\text{distance}} - \underbrace{b}_{\text{equilibrium length}}\big)^2$$

$\longrightarrow$ In 3D: $V(\vec{q}) = \frac{1}{2}k\big(\underbrace{|\vec{q}_2 - \vec{q}_1|}_{\text{length of vector from } 2 \to 1} - b\big)^2$

Other more complicated potential energies



$$V(\vec{q}) = V(r_{21}, r_{32}, \theta_{123}) = \left.\begin{array}{l} \frac{1}{2}k\,(r_{21}-b)^2 \\ +\frac{1}{2}k\,(r_{32}-b)^2 \\ +\frac{1}{2}k_\theta\,(\theta-\theta_0)^2 \end{array}\right\} \text{internal coordinates}$$

$$\theta = \cos^{-1}\frac{\vec{r}_{32}\cdot\vec{r}_{21}}{|\vec{r}_{32}|\,|\vec{r}_{21}|} \longleftarrow \text{a bond angle}$$

Once we have a potential energy for our system, what do we <u>do</u> with it? We predict the future!

$\longleftarrow$ How do we get this?

The rules for generating a trajectory are called "equations of motion". There are 3 approaches we'll talk about:

1) <u>Newtonian</u> (familiar, easy for simple problems, <u>difficult</u> for complicated ones)

$$F = ma \Rightarrow -\frac{\partial V}{\partial q_i} = m_i \ddot{q}_i \quad \longleftarrow \text{creates a } 2^{nd} \text{ order diff EQ:}$$

$$\frac{\partial^2}{\partial t^2} q_i + \frac{1}{m_i}\frac{\partial V}{\partial q_i} = 0 \quad \text{solving <u>this</u> gives an equation of motion}$$

Can be impossible to work with for <u>non-conservative</u> problems: $V(\vec{q}, \dot{\vec{q}}) = \frac{1}{2}kq^2 - \gamma\dot{q}$ $\longleftarrow$ <u>friction</u>

2) <u>Lagrangian</u> (correct in all cases, sometimes the only way to solve a problem, conceptually harder)

3) <u>Hamiltonian</u> (a reworking of Lagrange to make it useful, particularly on computers)

Lagrangian Formulation

$$\boxed{L(\vec{q},\dot{\vec{q}}) = \underset{\uparrow\text{ kinetic}}{T(\dot{\vec{q}})} - \underset{\uparrow\text{ potential}}{V(\vec{q},\dot{\vec{q}})}}$$

The Lagrangian is a strange object — it is like an "excess" kinetic energy

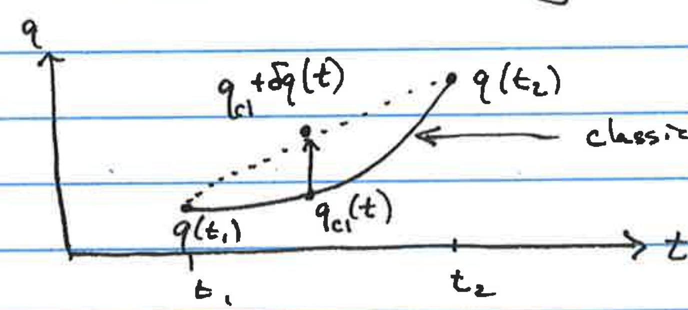
$$\boxed{S \equiv \text{the "action"} = \int_{t_1}^{t_2} L(\vec{q},\dot{\vec{q}})\,dt}$$

t_2 ← ending time

t_1 ← starting time

Hamilton's principle: Classical trajectories follow the path that extremizes the action.

$$\delta S\Big|_{q,\dot{q} = \text{classical trajectory}} = 0$$



classical path (why this path? what's so special about it?)

Hamilton tried to answer these things:

$$\delta S = \underbrace{S[\vec{q}+\delta\vec{q},\ \dot{\vec{q}} + \delta\dot{\vec{q}}] - S(\vec{q},\dot{\vec{q}})}_{\text{difference in action for small changes in } \vec{q},\,\dot{\vec{q}}}$$

$$= \int_{t_1}^{t_2} \delta L(\vec{q},\dot{\vec{q}})\,dt$$

$$= \sum_{i=1}^{3N} \int_{t_1}^{t_2} \left[\left(\frac{\partial L}{\partial q_i}\right)\delta q_i + \underbrace{\left(\frac{\partial L}{\partial \dot{q}_i}\right)\delta\dot{q}_i}_{\text{next time we'll start on this piece!}} \right] dt$$

2-1

Last time:

positions: $\vec{q} = (q_1 \dots q_{3N})$

velocities: $\dot{\vec{q}} = (\dot{q}_1 \dots \dot{q}_{3N})$ or momenta $\vec{p}$

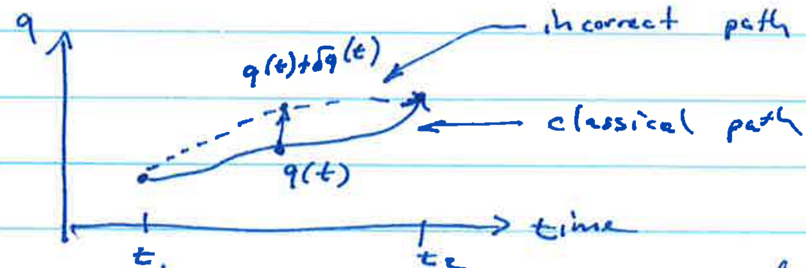
Kinetic $T(\dot{\vec{q}}) = \sum_{i=1}^{3N} \frac{1}{2} m_i \dot{q}_i^2$

Potential $V(\vec{q}, \dot{\vec{q}})$ [often $V(\vec{q})$] complicated function of positions

The Lagrangian:

$$L(\vec{q}, \dot{\vec{q}}) = T(\dot{\vec{q}}) - V(\vec{q}, \dot{\vec{q}})$$

Why one path instead of another



The "action" $S = \int_{t_1}^{t_2} L(\vec{q}, \dot{\vec{q}})\, dt$ depends on path we take

We want to minimize the action (this is the principle of least action

$$\delta S = \int_{t_1}^{t_2} \delta L(\vec{q}, \dot{\vec{q}})\, dt$$

$$\delta S = S[\vec{q} + \delta\vec{q}, \dot{\vec{q}} + \delta\dot{\vec{q}}] - S[\vec{q}, \dot{\vec{q}}]$$

difference in action for making small deviations in $\vec{q}$ and $\dot{\vec{q}}$.

$$\delta S = \sum_{i=1}^{3N} \int_{t_1}^{t_2} \frac{\partial L}{\partial q_i} \delta q_i + \underbrace{\frac{\partial L}{\partial \dot{q}_i} \delta \dot{q}_i}_{\text{do this piece}} \Big]\, dt$$

2-2

$$\int_{t_1}^{t_2} \frac{\partial L}{\partial \dot{q}_i}\, \delta \dot{q}_i \, dt = \int_{t_1}^{t_2} \underbrace{\frac{\partial L}{\partial \dot{q}_i}}_{u} \; \underbrace{\frac{\partial}{\partial t}(\delta q_i)\, dt}_{d\,v}$$

Integrate by parts

$$= uv\Big]_{t_1}^{t_2} - \int_{t_1}^{t_2} v\, du$$

$$= \frac{\partial L}{\partial \dot{q}_i}\, \delta q_i \Big]_{t_1}^{t_2} - \int_{t_1}^{t_2} \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) \delta q_i \, dt$$

$$= 0 \;\; \text{(endpoints fixed)} \; - \int_{t_1}^{t_2} \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) \delta q_i \, dt$$

Let's put this together:

$$\delta S = \sum_{i=1}^{3N} \int_{t_1}^{t_2} \left[\left\{ \frac{\partial L}{\partial q_i} - \frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{q}_i}\right) \right\} \delta q_i \, dt \right.$$

$= 0$ on the classical path

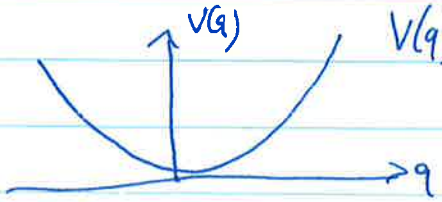
this is true for any variations along the path & even for a single coordinate:

$\therefore$

$$\boxed{\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \qquad i = (1 \dots 3N)}$$

Lagrange's equation $\Rightarrow$ equivalent, but more general than $F = ma$

Example Harmonic oscillator:



$V(q) = \frac{1}{2} k q^2$

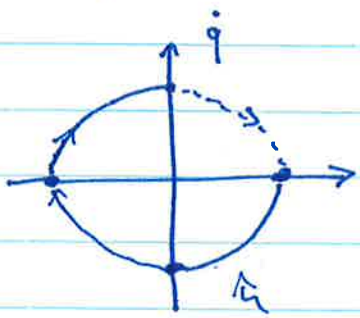
$T(\dot{q}) = \frac{1}{2} m \dot{q}^2$

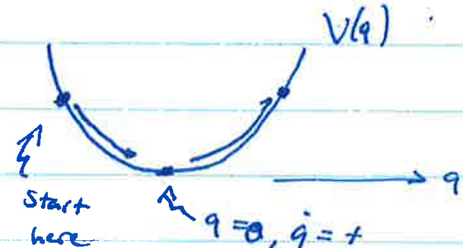
$V(q) = \frac{1}{2} k q^2$

$$L(q, \dot{q}) = T(\dot{q}) - V(q) = \frac{1}{2} m \dot{q}^2 - \frac{1}{2} k q^2$$

2-3

One way to think of harmonic motion:





an orbit
or trajectory that meets itself.

Now can we predict this motion

$$L(q,\dot{q}) = T(\dot{q}) - V(q) = \tfrac{1}{2}m\dot{q}^2 - \tfrac{1}{2}kq^2$$

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}}\right) - \frac{\partial L}{\partial q} = 0$$

So:

$$\frac{\partial L}{\partial \dot{q}} = m\dot{q} \qquad \frac{\partial L}{\partial q} = -kq$$

$\therefore$

$$\frac{d}{dt} m\dot{q} + kq = 0$$

$$m\ddot{q} + kq = 0$$

$$\ddot{q} + \frac{k}{m}q = 0$$

two constants can be replaced by $\omega = \sqrt{\frac{k}{m}}$

$$\ddot{q} + \omega^2 q = 0$$

$\longleftarrow$ 2^{nd} order Diff eq:

solution $\longrightarrow$

$$q(t) = A\cos\omega t + B\sin\omega t.$$

verify

$$\dot{q}(t) = -A\omega\sin\omega t + B\omega\cos\omega t$$

$$\ddot{q}(t) = -A\omega^2\cos\omega t - B\omega^2\sin\omega t = -\omega^2 q(t)$$

2-4

So:

$$-\omega^2 q + \omega^2 q = 0 \checkmark$$

So: $q(t) = A \cos \omega t + B \sin \omega t$ $\qquad \omega = \sqrt{\frac{k}{m}}$

what are these?

well, if initial conditions are:

$$\left.\begin{array}{l} q(0) = -q_0 \\ \dot{q}(0) = 0 \end{array}\right\} \Longrightarrow \left\{\begin{array}{l} A = -q_0 \\ B = 0 \end{array}\right.$$

Hamiltonian Dynamics:

$$\frac{\partial}{\partial t} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \qquad i = (1 \ldots 3N)$$

these are 3N 2^{nd} order differential equations

We can replace this with twice as many 1^{st} order equations:

$$\ddot{y} = f(y, \dot{y}) \longleftarrow 1 \ 2^{nd} \text{ order}$$

$$\left.\begin{array}{l} u = \dot{y} \\ \dot{u} = f(y, u) \end{array}\right\} 2 \ 1^{st} \text{ order}$$

Cheating right? Yes, but it amounts to treating velocity as a <u>separate</u> <u>object</u> from position.

2-5

We define the momentum

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

And a function called the Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{3N} p_i \dot{q}_i - L(\vec{q}, \dot{\vec{q}})$$

this is a Legendre transformation

The full differential:

$$dH = \sum_{i=1}^{3N} p_i \, d\dot{q}_i + \sum_{i=1}^{3N} \dot{q}_i \, dp_i - \sum_{i=1}^{N} \frac{\partial L}{\partial q_i} dq_i - \sum_{i=1}^{N} \frac{\partial L}{\partial \dot{q}_i} d\dot{q}_i$$

Since $p_i = \frac{\partial L}{\partial \dot{q}_i}$, we have

$$dH = \sum_{i=1}^{3N} \dot{q}_i \, dp_i - \sum_{i=1}^{3N} \frac{\partial L}{\partial q_i} dq_i$$

$\therefore$ $\mathcal{H}$ is a function only of $\vec{p}$ & $\vec{q}$

$$\mathcal{H} = \mathcal{H}(\vec{q}, \vec{p}) \quad \text{with} \quad \frac{\partial \mathcal{H}}{\partial p_i} = \dot{q}_i \quad \& \quad \frac{\partial \mathcal{H}}{\partial q_i} = -\frac{\partial L}{\partial q_i}$$

Lagrange's equation:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0$$

$$\frac{d}{dt} p_i - \frac{\partial L}{\partial q_i} = 0$$

$$\dot{p}_i = \frac{\partial L}{\partial q_i} = -\frac{\partial \mathcal{H}}{\partial q_i}$$

2-6

So:

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

Hamiltons equations are the foundation of modern classical mechanics

A brief aside on exact differentials

Suppose A is a function of only 2 variables, x & y:

$$A = A(x,y)$$

The exact differential tells us how much A will change upon changes to x & y:

$$dA = \left(\frac{\partial A}{\partial x}\right)dx + \left(\frac{\partial A}{\partial y}\right)dy$$

These get used all the time in thermodynamics:

$$G = G(N,T,P)$$

$$dG = \left(\frac{\partial G}{\partial N}\right)dN + \left(\frac{\partial G}{\partial T}\right)dT + \left(\frac{\partial G}{\partial P}\right)dP$$

These partial derivatives are also identified as important thermodynamic quantities!

Back to classical mechanics. Remember that we have:

1) $p_i \equiv \dfrac{\partial L}{\partial \dot{q}_i}$ ← definition of momentum

2) $L = T - V \implies L(\vec{q}, \dot{\vec{q}})$

3) $\underbrace{\dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \dot{q}_i}\right) - \dfrac{\partial L}{\partial q_i}}$ $= 0$ ← Lagrange's equation of motion

↑ this causes 2^{nd} ~~deg~~ order differential equations to appear.

4) We construct a Legendre transformation to make $\dot{q}_i$ go away:

$$\mathcal{H} = \sum_{i=1}^{3N} p_i \dot{q}_i - L(\vec{q}, \dot{\vec{q}})$$

Let's use the <u>exact</u> differential to find out things about $\mathcal{H}$:

$$d\mathcal{H} = \sum_{i=1}^{3N} \left(\frac{\partial \mathcal{H}}{\partial q_i}\right) dq_i + \left(\frac{\partial \mathcal{H}}{\partial \dot{q}_i}\right) d\dot{q}_i + \left(\frac{\partial \mathcal{H}}{\partial p_i}\right) dp_i$$

$$= \sum_{i=1}^{3N} -\left(\frac{\partial L}{\partial q_i}\right) dq_i + \underbrace{\left(p_i - \frac{\partial L}{\partial \dot{q}_i}\right)}_{\text{but } p_i \equiv \frac{\partial L}{\partial \dot{q}_i}\text{, so:}} d\dot{q}_i + \dot{q}_i\, dp_i$$

$$d\mathcal{H} = \sum_{i=1}^{3N} -\left(\frac{\partial L}{\partial q_i}\right) dq_i + \dot{q}_i\, dp_i$$

We now know: $\mathcal{H}(\vec{q}, \vec{p})$, <u>and</u> $\begin{cases} \left(\frac{\partial \mathcal{H}}{\partial q_i}\right) = -\left(\frac{\partial L}{\partial q_i}\right) \\ \left(\frac{\partial \mathcal{H}}{\partial p_i}\right) = \dot{q}_i \end{cases}$

Now, we can use Lagrange's equation:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_i}\right) - \frac{\partial L}{\partial q_i} = 0$$

$$\frac{d}{dt} p_i + \frac{\partial \mathcal{H}}{\partial q_i} = 0$$

$$\dot{p}_i = -\left(\frac{\partial \mathcal{H}}{\partial q_i}\right)$$

So: $\mathcal{H} = \mathcal{H}(\vec{q}, \vec{p}) \longrightarrow \boxed{\begin{aligned} \dot{q}_i &= \left(\frac{\partial \mathcal{H}}{\partial p_i}\right) \\ \dot{p}_i &= -\left(\frac{\partial \mathcal{H}}{\partial q_i}\right) \end{aligned}}$ ← These are Hamilton's Equations. This is what we <u>actually</u> use!

We now have $6N$ coupled 1^{st} order differential equations that can be solved numerically.

$$\dot{q} = \frac{dq}{dt} = \lim_{\Delta t \to 0} \frac{q(t+\Delta t) - q(t)}{\Delta t} = \left(\frac{\partial \mathcal{H}}{\partial p}\right)$$

We can generate <u>trajectories</u>

$$q(t+\Delta t) \approx q(t) + \Delta t \left(\frac{\partial \mathcal{H}}{\partial p}\right)$$

Now, we can ask what $\mathcal{H}$ is:

$$L = T(\dot{\vec{q}}) - V(\vec{q}) = \sum_{i=1}^{3N} \frac{m_i \dot{q}_i^2}{2} - V(\vec{q})$$

$$p_i \equiv \frac{\partial L}{\partial \dot{q}_i} = m_i \dot{q}_i \quad \text{in cartesian coordinates}$$

$$\mathcal{H} = \sum_{i=1}^{3N} p_i \dot{q}_i - L$$

$$= \sum_i p_i \dot{q}_i - \left[T(\dot{\vec{q}}) - V(\vec{q})\right]$$

$$= \sum_i m_i \dot{q}_i^2 - T(\dot{\vec{q}}) + V(\vec{q})$$

$$= 2T - T + V$$

$$\boxed{\mathcal{H} = T + V}$$

Questions to ponder:

Why bother with p_i? Doesn't mass scaling show that $p_i \propto \dot{q}_i$, so aren't they just the same coordinate?

In cartesian coordinates, yes they are.
In other coordinate systems with curvilinear degrees of freedom, they may not be!

Canonical Transformations

Suppose we have a system for which

$$\dot{p}_i = \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i} = 0$$

That is, $\mathcal{H} = \mathcal{H}(\vec{p}) \leftarrow$ no $\vec{q}$ dependence

We can integrate this easily:

$$\dot{p}_i = 0 \implies p_i = \alpha_i$$ (that is p_i is a constant, α_i)

q_i is the conjugate coordinate to p_i, and when p_i is constant, q_i is called a cyclic coordinate.

$$\dot{q}_i = \underset{\Uparrow \text{ constant}}{\frac{\partial \mathcal{H}}{\partial p_i}} = \frac{\partial \mathcal{H}}{\partial \alpha_i} = \omega_i = \underline{\text{constant}}$$

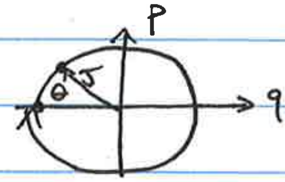
$\therefore$

$q_i(t) = \omega_i t + \beta_i$, so once we know α_i we know that

$$\mathcal{H} = \mathcal{H}(\{\alpha_i\}) \longleftarrow$$ If all coordinates are cyclic, All the time-dependence is known.

How do we find these cyclic coordinates?

Consider: $V = \frac{1}{2} m\omega^2 q^2 \qquad T = \frac{p^2}{2m}$



Suppose we have $q = \sqrt{\frac{2J}{m\omega}} \sin\theta$

$p = \sqrt{2mJ\omega} \cos\theta$

Then we have $\theta = m\omega \tan^{-1} \frac{q}{p}$

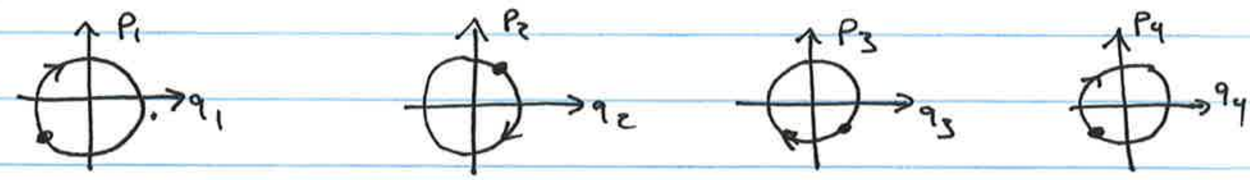
$$J = \frac{m\omega q^2}{2} + \frac{p^2}{2m\omega}$$

$$\mathcal{H} = T + V = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2 = \frac{2mJ\omega \cos^2\theta}{2m} + \frac{1}{2} m\omega^2 \frac{2J}{m\omega} \sin^2\theta$$

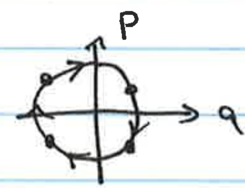
$$\mathcal{H} = J\omega(\cos^2\theta + \sin^2\theta) = J\omega \qquad \mathcal{H} = \mathcal{H}(J)$$

A short digression on <u>why</u> we're looking at phase space diagrams:

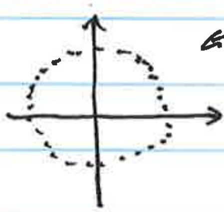
<u>One N_2 molecule</u> <u>another</u> <u>yet another</u> <u>and another</u>



all of these are in the <u>ground state</u> (i.e. with the same vibrational energy) We have a room full of these identical oscillators, and we might want to treat them all collectively on <u>one</u> diagram:

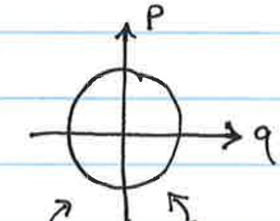


The <u>all</u> trace out a single circle in phase space, so if we have a <u>huge</u> number of identical systems:



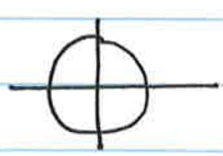
many

instead of talking about individual "dots", it makes more sense to talk about a distribution

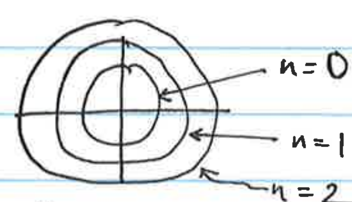


$\rho(q, p)$

A mixed QM / classical picture:



<u>all</u> in the ground state, everyone is on the same periodic orbit



after some collisions, some molecules might go up to a higher energy level

Canonical Transformations

(we did a simple example of this last time to get: $q, p \longrightarrow J, \theta$
Cartesian $\longrightarrow$ action-angle)

$$\left.\begin{aligned} Q_i &= Q_i(\vec{q}, \vec{p}, t) \\ P_i &= P_i(\vec{q}, \vec{p}, t) \end{aligned}\right\}$$

$\vec{Q}$ & $\vec{P}$ are new coordinates built out of the old ones.

We want to preserve Hamilton's equations, so we're only going to allow transformations that preserve:

$$\dot{Q}_i = \frac{\partial K}{\partial P_i} \qquad \dot{P}_i = -\frac{\partial K}{\partial Q_i}$$

Here $K(\vec{Q}, \vec{P})$ is a new Hamiltonian.

To do this, we preserve the principle of least action:

$$\delta \int_{t_1}^{t_2} \left[\sum_i P_i \dot{Q}_i - K(\vec{Q}, \vec{P}, t)\right] dt = 0$$

and

$$\delta \int_{t_1}^{t_2} \left[\sum_i p_i \dot{q}_i - \mathcal{H}(\vec{q}, \vec{p}, t)\right] dt = 0$$

How do we do this?

$$\boxed{\lambda \left(\sum_i p_i \dot{q}_i - \mathcal{H}\right) = \sum_i P_i \dot{Q}_i - K + \frac{dG}{dt}}$$

G is called a generating function, and there are 4 basic types:

1) $G_1 = G(\vec{q}, \vec{Q}, t)$ ← transforms $\vec{q} \to \vec{Q}$

2) $G_2 = G(\vec{q}, \vec{P}, t) - \sum_i Q_i P_i$

3) $G_3 = G(\vec{p}, \vec{Q}, t) + \sum_i q_i p_i$ ← does $\vec{p} \to \vec{Q}$

4) $G_4 = G(\vec{p}, \vec{P}, t) + \sum_i q_i p_i - \sum_i Q_i P_i$

In the 1^{st} case, the constrained minimization (boxed equation) takes the form:

$$\sum_i p_i \dot{q}_i - \mathcal{H} = \sum_i P_i \dot{Q}_i - K + \frac{\partial G}{\partial t} + \sum_i \left(\frac{\partial G}{\partial q_i}\right) \dot{q}_i + \sum_i \left(\frac{\partial G}{\partial Q_i}\right) \dot{Q}_i$$

This implies:

$$p_i = \left(\frac{\partial G}{\partial q_i}\right) \qquad P_i = -\left(\frac{\partial G}{\partial Q_i}\right)$$

$$K = \mathcal{H} + \frac{\partial G}{\partial t}$$

We need an example:

$$\mathcal{H} = \frac{1}{2m}\left(p^2 + m^2 \omega^2 q^2\right)$$

Last time, we postulated:

$$\left.\begin{aligned} p &= f(P) \cos Q \\ q &= \frac{f(P)}{m\omega} \sin Q \end{aligned}\right\} \quad \begin{aligned} p^2 &= f^2(P) \cos^2 Q \\ q^2 &= \frac{f^2(P)}{m^2 \omega^2} \sin^2 Q \end{aligned}$$

$$\mathcal{H} = \frac{1}{2m}\left(f^2(P) \cos^2 Q + f^2(P) \sin^2 Q\right) = \frac{f^2(P)}{2m}$$

This would make our new Hamiltonian:

$$\mathcal{H} \to K = \frac{f^2(P)}{2m}$$

but we don't yet <u>know</u> if Q & P are good conjugate coordinates!

If Q & P are good conjugate coordinates, we'll be able to use $K(P)$, which doesn't depend on Q, so Q is a cyclic (angle) coordinate.

That is, we want to be sure Hamilton's equations apply to $K(P)$: $\dot{Q} = \frac{\partial K}{\partial P}$, $\dot{P} = -\frac{\partial K}{\partial Q}$

If we want to guarantee Hamilton's equations work, we need to find the generating function. That is, find a G which gives:

$$p = \left(\frac{\partial G}{\partial q}\right), \quad P = -\left(\frac{\partial G}{\partial Q}\right), \quad K = \mathcal{H} + \frac{\partial G}{\partial t}$$

So far we have: $\left.\begin{array}{l} p = f(P)\cos Q \\ q = \frac{f(P)}{m\omega}\sin Q \end{array}\right] \longrightarrow \frac{p}{q} = m\omega \cot Q$

$p = m\omega q \cot Q$

So if $p = \left(\frac{\partial G}{\partial q}\right)$, G could be $\frac{1}{2} m\omega q^2 \cot Q$

What are the implications of $G_1 = \frac{1}{2} m\omega q^2 \cot Q$

$$P = -\left(\frac{\partial G}{\partial Q}\right) = + \frac{m\omega q^2}{2} \frac{1}{\sin^2 Q}$$

solve for q^2

$$q^2 = \frac{+2P\sin^2 Q}{m\omega}$$

solve for q

$$q = \sqrt{\frac{2P}{m\omega}} \sin Q$$

But we already postulated $q = \frac{f(P)}{m\omega}\sin Q \Longrightarrow f(P) = \sqrt{2m\omega P}$

This would make:

$$K = \frac{f^2(P)}{2m} = \frac{2m\omega P}{2m} = \omega P$$

OK, so if the generating function is

$$\boxed{G_1 = \frac{1}{2} m\omega q^2 \cot Q}$$

$$p = \left(\frac{\partial G}{\partial q}\right) = m\omega q \cot Q$$ ← matches our initial substitution

$$P = -\left(\frac{\partial G}{\partial Q}\right) = \frac{m\omega q^2}{2} \frac{1}{\sin^2 Q}$$

implies

$$q = \sqrt{\frac{2P}{m\omega}} \sin Q$$

$$p = \sqrt{2m\omega P} \cos Q$$

implies

$$K = \omega P$$

one last check

$$\mathcal{H} = K + \frac{\partial G_1}{\partial t}$$

$$\frac{1}{2m}\left(p^2 + m^2\omega^2 q^2\right) = \omega P + (0)$$

$$\frac{1}{2m}\left(2m\omega P \cos^2 Q + m^2\omega^2 \frac{2P}{m\omega} \sin^2 Q\right) = \omega P + 0$$

$$\frac{2m\omega P}{2m}\left(\cos^2 Q + \sin^2 Q\right) = \omega P + 0$$

$$\omega P = \omega P$$ ✓

So, this transformation is canonical.

So, we've transformed

<u>old cartesian coordinates</u> → <u>new action-angle coords</u>

$q \leftarrow$ position $\longrightarrow$ Q angle

$p \leftarrow$ momentum $\qquad P$ action

$\mathcal{H} = \frac{1}{2m}\left(p^2 + m^2\omega^2 q^2\right) \qquad K = \omega P$

$$\left.\begin{aligned} q(t) &= A\cos\omega t + B\sin\omega t \\ p(t) &= -\omega m A\sin\omega t + \omega m B\cos\omega t \end{aligned}\right\} \longrightarrow \left\{\begin{aligned} Q(t) &= (\omega t + \beta) \bmod 2\pi \\ P(t) &= \alpha \end{aligned}\right.$$

α, β, ω are <u>constants</u>

If you can find a generating function that maps old coordinates onto new ones, the transformation is <u>canonical</u> & <u>valid</u>.