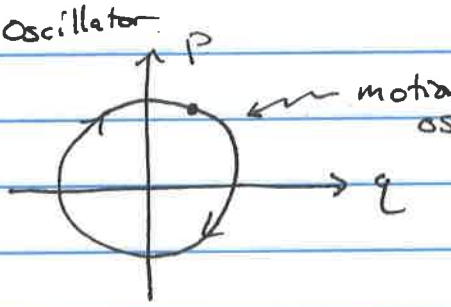
A very brief review of ensembles

Harmonic Oscillator

$V = \frac{1}{2} m\omega^2 q^2$

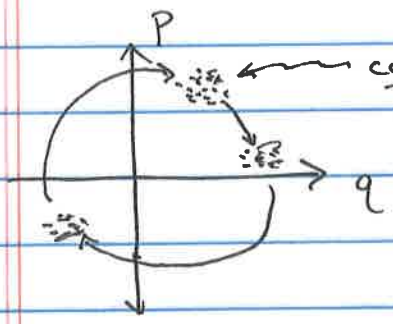
$T = \frac{1}{2m} p^2$

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



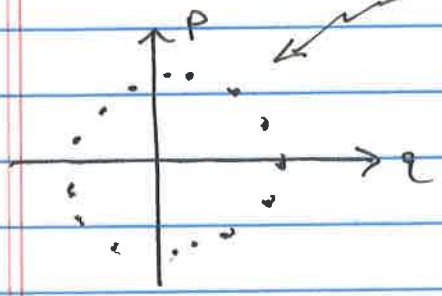
motion of one oscillator makes an orbit

(p, q) is the "phase-space" for this 1-D system.



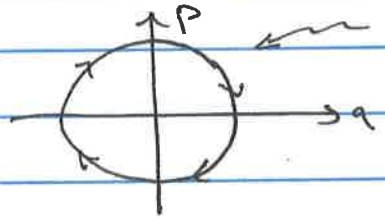
collection of oscillators (each represented by 1 point)

This collection is dynamic, it changes over time



This collection is stable, at any given time, the density $\rho(q,p)\,dq\,dp$ of points within dq, dp of q, p is fixed.

A stable collection of points is called an ensemble

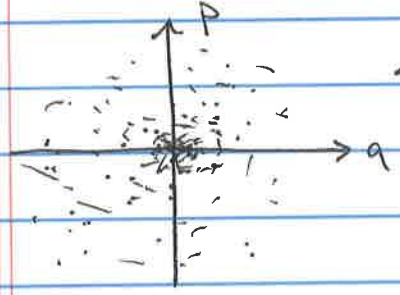


All of these points have the same total energy $E = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 q^2$

So the ensemble can be defined: $\rho(q,p) = \delta(\mathcal{H}(q,p) - E)$

only has value when $\mathcal{H}$ is equal to a fixed energy

This is called the Microcanonical Ensemble or NVE ← all members have same energy.



$\rho(q,p) \propto e^{-\mathcal{H}(q,p)/k_B T}$ ←

This ensemble says that lower energy states are more probable.

The <u>canonical ensemble</u> is characterized by a temperature, and not a single energy. We sometimes call this the NVT ensemble

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In general, we can obtain <u>static</u> properties by integrating over the density:

$$Q = \int\int \rho(q,p)\, dq\, dp$$ ← normalization or <u>partition function</u>

$$\langle A \rangle_{ens} = \frac{1}{Q} \int\int A(q,p)\, \rho(q,p)\, dq\, dp$$ ← ensemble average

<u>Newtonian</u> dynamics conserves total energy, so if a molecular system starts with one energy, it stays with it for all time.

Newtonian dynamics samples the <u>microcanonical</u> ensemble

Time Averages

$$\langle A \rangle_t = \frac{1}{\tau} \int_0^{\tau} A(q(t), p(t))\, dt$$

τ: total running time

$A(q(t), p(t))$: a property of the current state of the system

As long as the dynamics does a good enough job sampling the ensemble, the averages converge

$$\lim_{t \to \infty} \langle A \rangle_t = \langle A \rangle_{ensemble}$$

This is the ergodic hypothesis. If we wait long enough, a sufficiently chaotic system will sample all of the states in the ensemble in the right amount.

It is never really true, but sampling is usually good enough.

Temperature in MD

$$KE = \sum_{i=1}^{N} \frac{|\vec{P}_i|^2}{2m_i} = \overbrace{\frac{k_B T}{2}}^{\text{equipartition}} (3N) \leftarrow 3N \text{ degrees of freedom}$$

$$= \frac{k_B T}{2}(3N - N_c) \leftarrow \#\text{ of constraints}$$

(Standard MD is in the microcanonical ensemble, so total energy is conserved, as is total linear momentum $\vec{P} = \sum_{i=1}^{N} \vec{P}_i$. Angular momentum is also conserved, but not with periodic boundaries)

$$\therefore \quad T(t) = \sum_{i=1}^{N} \frac{P_i^2}{m_i k_B N_{df}} \qquad N_{df} = 3N - N_c$$

this defines an instantaneous temperature, which fluctuates.

Since most chemical experiments are done at constant T (& P) we'd like to sample members of the canonical (NVT) ensemble. Here's a simple approach:

$$T(t) = \sum_{i=1}^{N} \frac{m_i v_i^2}{k_B N_{df}}$$

$$T_{target} = \sum_{i=1}^{N} \frac{m_i \lambda^2 v_i^2}{k_B N_{df}} = \lambda^2 T(t)$$

$$\lambda^2 = \frac{T_{target}}{T(t)}$$

$$\lambda = \sqrt{T_{target}/T(t)}$$

at every step, rescale all the velocities by λ where $T(t)$ is the current temp.

- No fluctuations in T (not really sampling canonical dist)
- What if initial conditions have $T(0) = 0$?
- $\Delta T = T_{target} - T(t) = (\lambda^2 - 1) T(t)$

change in T in 1 step

Less-simple-minded thermostatting

Berendsen coupling:

$$\frac{dT(t)}{dt} = \frac{1}{\tau}\left[T_{target} - T(t)\right]$$

τ: coupling parameter or "thermostat" will give us exponential decay to desired temperature.

$$\Delta T = \frac{\delta t}{\tau}\left[T_{target} - T(t)\right] \leftarrow \text{one time step}$$

$$\lambda^2 = 1 + \frac{\delta t}{\tau}\left(\frac{T_{target}}{T(t+\delta t/2)} - 1\right)$$

$T(t+\delta t/2)$: using velocity verlet for velocities!

- In the $\tau \to \infty$ limit, this reverts to Newtonian MD
- In the $\tau \to 0$ limit, there are no velocity fluctuations
- When $\tau = \delta t$ this becomes the simple-minded scheme
- Typically $\tau \approx 100\,fs \to 10\,ps$
- How it works

move A:
- $V(t) \longrightarrow v(t+\delta t/2)$
- [illegible]
- scale all velocities by λ
- $r(t) \longrightarrow r(t+\delta t)$

do forces: $r(t+\delta t) \longrightarrow f(t+\delta t)$

move B:
- update $T(t+\delta t/2)$
- $v(t+\delta t/2) \longrightarrow v(t+\delta t)$
- scale all $v(t+\delta t)$

Sampling Canonical Ensemble with Nosé-Hoover

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\vec{q})$$

$$H_{Nose} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + V(\vec{q}) + \frac{p_s^2}{2Q} + g k_B T \ln s$$

2 new variables have been introduced:

s = "position" of a thermostat

p_s = "momentum" of the thermostat

The system ($\mathcal{H}$) can transfer & borrow energy from this extended system.

Q = fictitious mass that governs the speed of this transfer (Q small = quick transfer)

When $g = N_{df} + 1$, Nosé proved:

$$\int\int e^{-\beta \mathcal{H}} \, d\vec{q} \, d\vec{p} = \int\int\int\int \delta[\mathcal{H}_{Nosé} - E] \, d\vec{q} \, d\vec{p} \, ds \, dp_s$$

That is, microcanonical dynamics on $\mathcal{H}_{Nosé}$ samples canonical ensemble on $\mathcal{H}$!

This is Huge! We can do extended variables for very minimal additional expense!

One hitch: s = scaling factor for time and people tend to like even time steps, not fluctuating time intervals.

Nosé-Hoover:

$\zeta = p_\zeta / Q$ = thermodynamic "friction"

Hoover's equations of motion:

$$\dot{q}_i = \frac{p_i}{m_i}$$

$$\dot{p}_i = \frac{-\partial V}{\partial q_i} - \zeta p_i \quad \leftarrow \text{friction or drag}$$

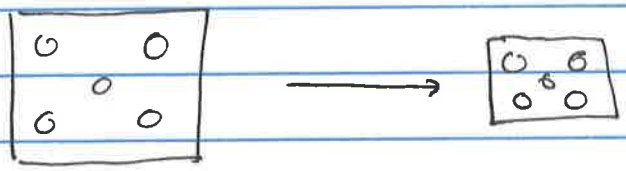
$$\dot{\zeta} = \frac{N_{df} k_B}{Q} \left(T(t) - T_{target} \right)$$

$$\frac{\dot{s}}{s} = \frac{d \ln s}{dt} = \zeta \quad \leftarrow \text{redundant}$$

$$\mathcal{H}_{Nosé} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(\vec{q}) + \frac{\zeta^2 Q}{2} + g s k_B T$$

Nosé-Hoover is guaranteed to sample canonical ensemble in $(\vec{q}, \vec{p})$ and uses fixed intervals in time. It is the standard NVT method today!

For constant pressure & temperature (NPT) we'll need a way to adjust the box volume as well as the particle velocities!



$P(t) < P_{target}$

$P(t) > P_{target}$

These transformations (where we scale all particle positions relative to the box size are called affine scalings.

Constant Pressure

Instantaneous Pressure: $P(t) = \frac{2}{3V}\sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{j\neq i}\vec{r}_{ij}\cdot\vec{f}_{ij}\right]$

Kinetic part — Virial (potential contribution to pressure)

Andersen's Method:

$$\dot{q}_i = \frac{p_i}{m_i} + \frac{1}{3}\left(\frac{\dot{V}}{V}\right)q_i$$ ← scales particle coordinates within the box by the same amount the box is being scaled

$$\dot{p}_i = -\frac{\partial V}{\partial q_i} - \frac{1}{3}\left(\frac{\dot{V}}{V}\right)p_i$$

$$\ddot{V} = \frac{1}{M_V}\left[P(t) - P_{target}\right]$$ ← Box volume is scaled to allow instantaneous pressure to approach target pressure

↑ fictitious mass controlling speed of box adjustments

This method samples the NPH ensemble (isobaric - isenthalpic)

Nosé-Hoover-Andersen (NPT)

A combination of NVT & NPH methods that samples isobaric - isothermal ensemble

- Box fluctuations governed by M_V or $\tau_{barostat}$
- Thermal reservoir governed by Q or $\tau_{thermostat}$
- Both mess up any timescales close to these τ values, so correlation functions need to be calculated with NVE dynamics ← IMPORTANT
- Static properties, e.g. $g(r)$ are safe in these ensembles.

Constraints

Sometimes we want to constrain objects in a simulation

Constrained systems are not the same as setting $k_{bond} \to \infty$ $\langle E_{bond} \rangle = k_B T$ for each bond no matter what k_{bond} is!

To constrain a bond length, we want to add an unknown bond force to $V(\vec{r})$ that has the effect of opposing all other interatomic forces:

$$V'(\vec{r}) = V(\vec{r}) + \lambda \sigma(\vec{r}_1, \vec{r}_2)$$

(λ: Lagrange Multiplier; σ: constraint equation that is 0 when constraint is satisfied)

$$\sigma(\vec{r}_1, \vec{r}_2) = r_{12}^2 - d^2$$

(d: constrained bond length)

As long as $\sigma = 0$, $V'(\vec{r}) = V(\vec{r})$

Notes: λ will change overtime to insure σ is kept @ 0

$$\dot{\sigma}(\vec{r}_1, \vec{r}_2) = \frac{d\sigma}{dt} = 2(\vec{r}_1 - \vec{r}_2) \cdot (\vec{v}_1 - \vec{v}_2) = 0$$

(satisfy this and σ stays put)

Force on atom 1:

$$\vec{f}_1' = \frac{-\partial V'}{\partial \vec{r}_1}$$

$$= \frac{-\partial V}{\partial \vec{r}_1} - \lambda \frac{d}{d\vec{r}_1} (r_{12}^2 - d^2) \qquad (r_{12}^2 = (\vec{r}_2 - \vec{r}_1)^2)$$

$$\boxed{\vec{f}_1' = \vec{f}_1 + 2\lambda(\vec{r}_1 - \vec{r}_2) = \vec{f}_1 + \vec{g}(t)}$$

($\vec{g}(t)$: constraint force)

If we put this force into verlet algorithm we get:

$$\vec{r}_1(t+\delta t) = \underbrace{2\vec{r}_1(t) - r_1(t-\delta t) + \frac{\vec{f}_1}{m_1}\delta t^2}_{\text{unperturbed by constraint}} + \underbrace{\frac{2\lambda}{m_1}\left[\vec{r}_1(t) - \vec{r}_2(t)\right]\delta t}_{\text{constraint force part}}$$

Like wise:

$$\vec{r}_2(t+\delta t) = 2\vec{r}_2(t) - r_2(t-\delta t) + \frac{\vec{f}_2}{m_2}\delta t^2 + \frac{2\lambda}{m_2}\left[\vec{r}_2 - \vec{r}_1\right]\delta t$$

The constraint would propagate:

$$\sigma = \left|\vec{r}_1(t+\delta t) - r_2(t+\delta t)\right|^2 - d^2 = 0$$

$$= \left|\vec{r}_1(t+\delta t) + \frac{2\lambda}{m_1}\left[\vec{r}_1(t) - r_2(t)\right] - \vec{r}_2(t+\delta t) - \frac{2\lambda}{m_2}\left[\vec{r}_2(t) - \vec{r}_1(t)\right]\right|^2 - d^2 = 0$$

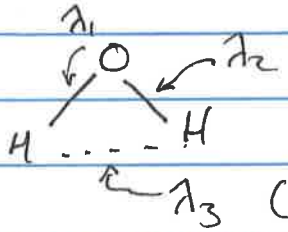
This is a quadratic equation for λ which can be solved to give a value. This modified value of λ will give us new position estimates in Verlet above which will satisfy the constraints.

SHAKE: Ryckaert, Ciccotti & Berendsen Verlet

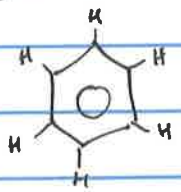
RATTLE: Andersen (velocity Verlet)

← Still in use today to freeze C-H bonds!

Multiple constraints



Rigid Bodies



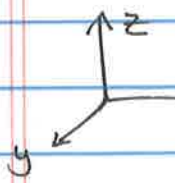
← Constrain all bonds?

or treat as a single moving object?

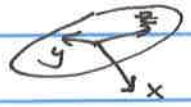
with coordinates:

X, y, Z (position of center of mass)

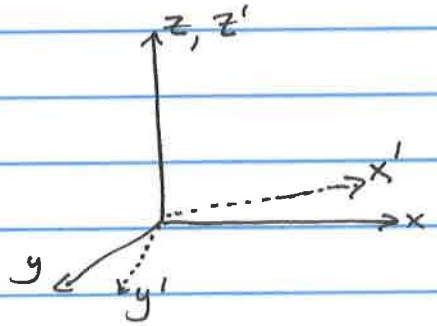
θ, ϕ, ψ ← orientation in Euler Angles



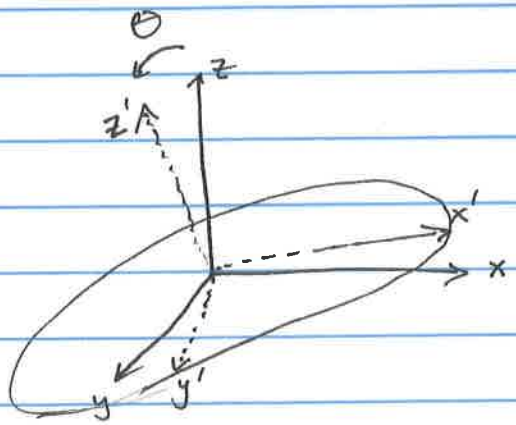
← lab-fixed frame



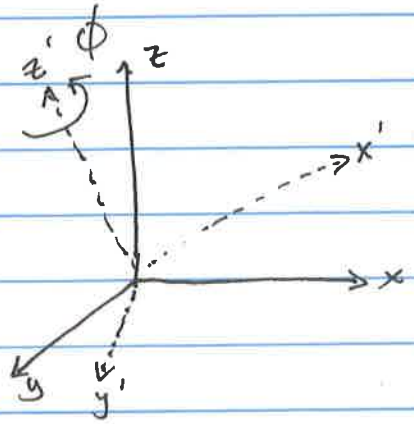
← Body-fixed frame



← first Euler Angle rotation around Z



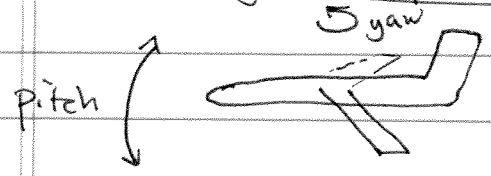
← second Euler Angle rotation of Z around y'



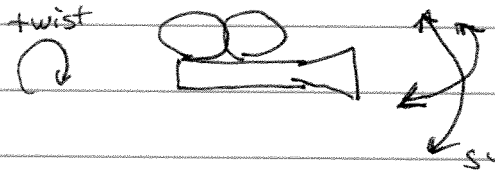
← 3rd Euler Angle rotation around Z' axis

(This is the Zyz convention)

Other Rigid Body formalisms



← Airplanes



← Movie Cameras

$$\underline{\underline{A}} = \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

rotation around z' — rotation around x' — rotation around z

ZXZ convention is most common

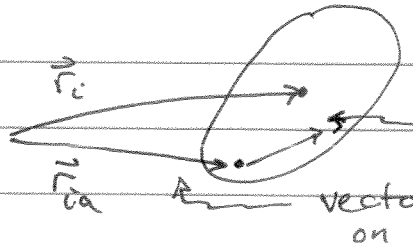
$$\vec{V}_{body} = \underline{\underline{A}} \cdot \vec{V}_{space} \qquad \vec{V}_{space} = \underline{\underline{A}}^T \cdot \vec{V}_{body}$$

$$\mathcal{H} = \sum_i \left(\frac{1}{2} m_i \vec{v}_i^{\,2} + \frac{1}{2} \vec{j}_i^{\,T} \cdot \underline{\underline{I}} \cdot \vec{j}_i \right) + V(\vec{r}, \{\underline{\underline{A}}\})$$

- m_i: mass of body
- $\vec{v}_i$: velocity of center of mass
- $\vec{j}_i$: angular momentum
- $\underline{\underline{I}}$: moment of inertia tensor

$$\vec{r}_i = \sum_a \vec{r}_{ia} m_a \Big/ \sum_a m_a$$

$\vec{r}_i$: center of mass



Torques

$$\vec{\tau}_i = \sum_a (\vec{r}_{ia} - \vec{r}_i) \times \vec{f}_{id}$$

$$= \sum_a \vec{d}_{ia} \times \vec{f}_{ia}$$

$\vec{d}_{ia}$ ← displacement from center of mass

$\vec{d}_{ia}$ are fixed in the body-fixed axes

$\vec{d}_{ia}$ change in the space-fixed axes

$$\vec{\tau}^b = \underline{\underline{A}} \cdot \vec{\tau}^s$$

$$\vec{\tau}^s = \underline{\underline{A}}^{-1} \cdot \vec{\tau}^b$$

Rotational Motion

Angular velocity $\vec{\omega}^s$ = rotational speed around space axes

Angular momentum $\vec{j}^b$ = around body-fixed axes

Newton's equation for rotational motion: $\dot{\vec{j}}^s = \vec{\tau}^s$

One odd consequence of this is that a vector in the space-frame may be moving only because the body frame is moving relative to fixed frame:

$$\dot{e}^s = \dot{e}^b + \vec{\omega}^s \times \vec{e}^s$$

($\vec{\omega}^s \times \vec{e}^s$ ← changes due solely to rotations)

So:

$$\dot{j}^b + \vec{\omega}^b \times \vec{j}^b = \vec{\tau}^b$$

← Newton, but now in body frame

$\vec{J}^b$ & $\vec{\omega}^b$ are related by $\overleftrightarrow{I}$ ← moment of inertia tensor

$$\overleftrightarrow{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

in the privileged body (or principal axis frame):

$$\overleftrightarrow{I} = \begin{pmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{pmatrix}$$

← The body frame where this is diagonal is the frame we want to use

In this frame:

$$\left.\begin{aligned} \dot{\omega}_x &= \frac{\tau_x^b}{I_1} + \left(\frac{I_2 - I_3}{I_1}\right) \omega_y^b \omega_z^b \\ \dot{\omega}_y &= \frac{\tau_y^b}{I_2} + \left(\frac{I_3 - I_1}{I_2}\right) \omega_z^b \omega_x^b \\ \dot{\omega}_z &= \frac{\tau_z^b}{I_3} + \left(\frac{I_1 - I_2}{I_3}\right) \omega_x^b \omega_y^b \end{aligned}\right\}$$ equations of motion in body frame for $\vec{\omega}$

These also give us equations of motion for the angles themselves:

$$\dot{\phi} = -\omega_x^s \frac{\sin\phi\cos\theta}{\sin\theta} + \omega_y^s \frac{\cos\phi\cos\theta}{\sin\theta} + \omega_z^s$$

$$\dot{\theta} = \omega_x^s \cos\phi + \omega_y^s \sin\phi$$

$$\dot{\psi} = \omega_x^s \frac{\sin\phi}{\sin\theta} - \omega_y^s \frac{\cos\phi}{\sin\theta}$$

So what happens when $\theta \to 0^a$ or $\theta \to 180^\circ$?

Euler angles are inherently prone to numerical instability

Alternatives to Euler Angle propagation:

1) quaternions (use 4 parameters to represent orientations)
   ↳ "QSHAKE"
2) Propagate entire rotation matrix (use 9 parameters to represent orientations)
   DLM integrator
3) Use Multiple sets of Euler angles (e.g. 4th gimbal in spacecraft to avoid gimbal lock)

All of these methods are used!