# Feynman's ratchet and timecrystalline molecular motors

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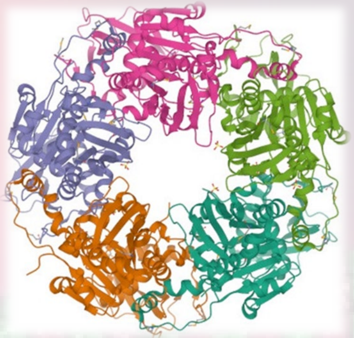
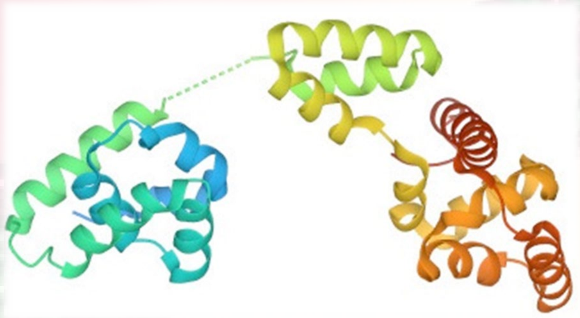
# (Bio)molecular motors:

- Sustainable and often highly sophisticated performance
- Move autonomously and continuously often without external control
- Harvest resources directly from environment

- Stability often poor
- Motion often maintained under narrowly defined conditions

<u>Challenge</u> to design synthetic and artificial molecular machines with a comparable control of motion and function





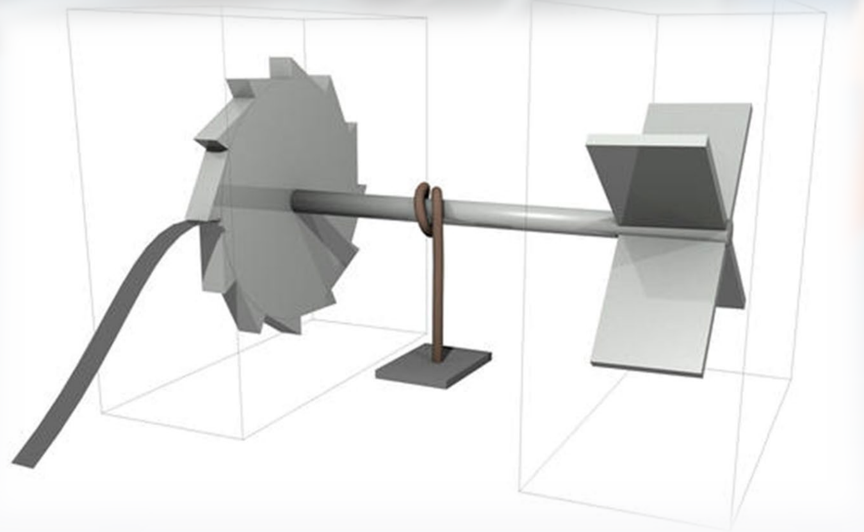
Maxwell's Demon, Schrödinger's Cat …

# Feynman's ratchet-and-pawl:

Gold Standard

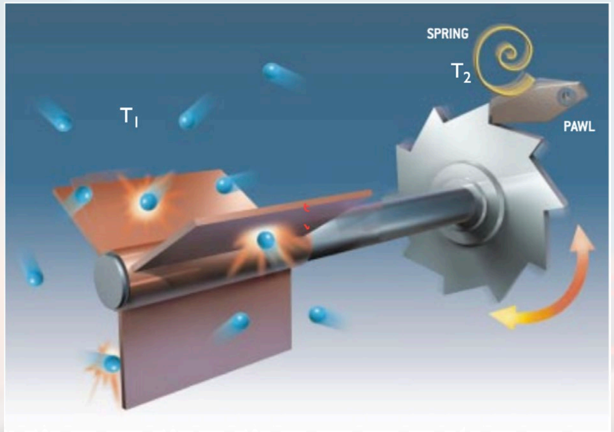
## Underlying assumptions:

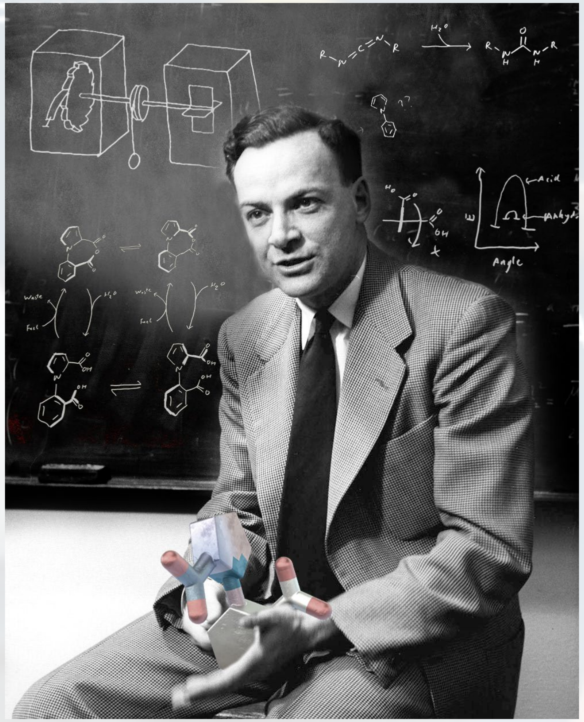
- Rigid body
- External torque
- Non-equilibrium   ($T_1 \neq T_2$)
- Broken symmetry (chirality)
- Driven by Brownian motion



# Paradigm:

A functional molecular motor must know how to go around Feynman’s No-Go arguments



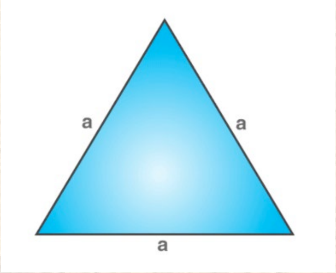
# What Feynman did not consider:

- Deformable bodies can have rotational motion - even with no angular momentum
- Energy conserving system can be in motion - even in the minimum of free energy

# Going around Feynman:

- ~~Rigid body~~
- ~~External torque~~
- ~~Non-equilibrium ($T_1 \neq T_2$)~~
- Broken symmetry (chirality)
- Driven by Brownian motion

Initially equilateral triangle with harmonically oscillating bond lengths



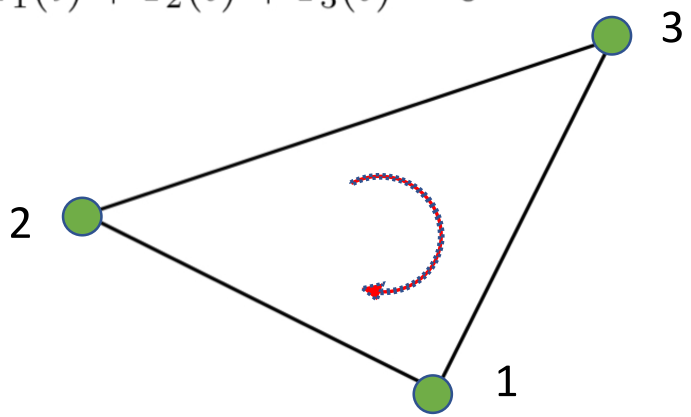

$$\mathcal{L} = \sum_{a=2,3} \left\{ \frac{1}{2} \left( \frac{dD_{1a}}{dt} \right)^2 - \frac{1}{2} \left( \frac{2\pi}{T_a} \right)^2 (D_{1a} - 1)^2 \right\}$$

$$D_{1a}(t) \;=\; 1 + a_{1a} \sin\left( \frac{2\pi}{T_a} t \right) \qquad (a = 2, 3) \qquad \& \qquad D_{23} \equiv 1$$

# rotational motion from change of shape:

Ambient

$$\mathbf{r}_1(t) + \mathbf{r}_2(t) + \mathbf{r}_3(t) = 0$$



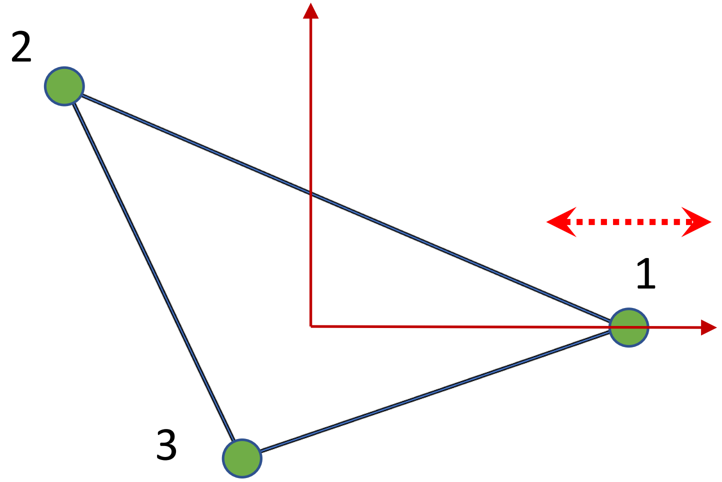

"gauge fixing"

$$s_{1x} > 0,\ s_{1y} = 0 \text{ and } s_{2y} > 0.$$

$$\mathbf{r}_i(t) \;=\; \mathcal{O}(t)\mathbf{s}_i(t)$$

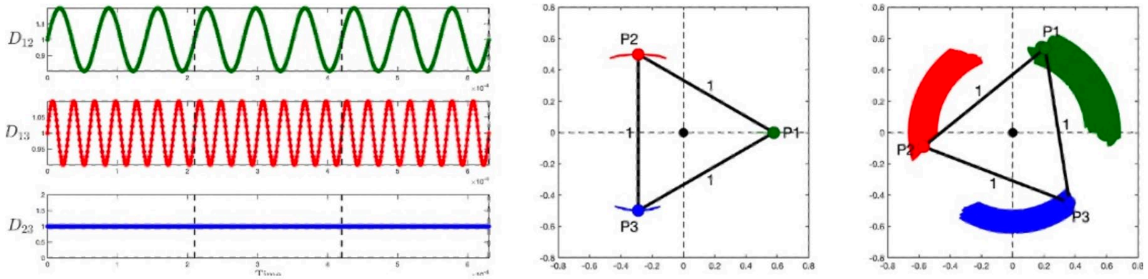
$$\mathcal{O}(t) \;=\; \begin{pmatrix} \cos\theta(t) & -\sin\theta(t) \\ \sin\theta(t) & \cos\theta(t) \end{pmatrix}$$

Internal




$$\boxed{\mathbf{L} \;=\; \mathbf{r}_1 \wedge \dot{\mathbf{r}}_1 + \mathbf{r}_2 \wedge \dot{\mathbf{r}}_2 + \mathbf{r}_3 \wedge \dot{\mathbf{r}}_3 \;=\; 0}$$

$$\theta(t) \;=\; \int_0^t dt' \, \frac{\sum_{a=1}^{3} \left(s_{ay}\dot{s}_{ax} - s_{ax}\dot{s}_{ay}\right)}{\sum_{i=1}^{3} \mathbf{s}_i^2}$$



$$\Delta\theta = \theta(T) - \theta(0) \;=\; \int_0^T dt\, \frac{\sum_{i=1}^{3}\{s_{iy}\dot{s}_{ix} - s_{ix}\dot{s}_{iy}\}}{\sum_{i=1}^{3}\mathbf{s}_i^2} \;\equiv\; \int_\Gamma d\mathbf{l}\cdot\mathbf{A}$$

= Connection in the shape space

Three-body problem – Jacobi coordinates

$$\begin{aligned}
\mathbf{s}_1 &= \frac{1}{\sqrt{2}}\boldsymbol{\rho}_1 - \frac{1}{\sqrt{6}}\boldsymbol{\rho}_2 \\
\mathbf{s}_2 &= \sqrt{\frac{2}{3}}\boldsymbol{\rho}_2 \\
\mathbf{s}_3 &= -\frac{1}{\sqrt{2}}\boldsymbol{\rho}_1 - \frac{1}{\sqrt{6}}\boldsymbol{\rho}_2
\end{aligned}$$

$$\boldsymbol{\rho}_1 = r\cos\frac{\vartheta}{2}\begin{pmatrix}\cos\phi_1\\ \sin\phi_1\end{pmatrix} \quad \& \quad \boldsymbol{\rho}_2 = r\sin\frac{\vartheta}{2}\begin{pmatrix}\cos\phi_2\\ \sin\phi_2\end{pmatrix}$$

$$\begin{aligned}
x &= r\sin\vartheta\cos\phi_- \\
y &= r\sin\vartheta\sin\phi_- \\
z &= r\cos\vartheta
\end{aligned}$$

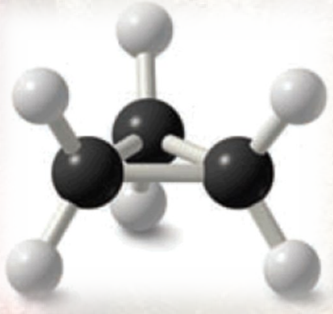
Dirac monopole in space of shapes

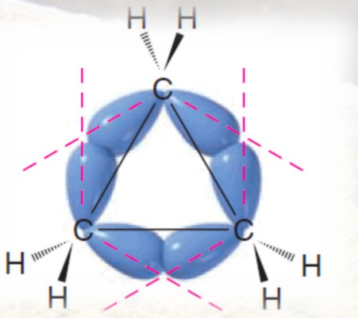
$$\mathbf{A} \;=\; \frac{1}{2}\cos\vartheta d\phi_- - \frac{1}{2}d\phi_- \;=\; \frac{1}{2}\frac{xdy - ydx}{r(r+z)}$$

# Physical example: cyclopropane

The CHARMM22 force field has the following potential energy function:[7]

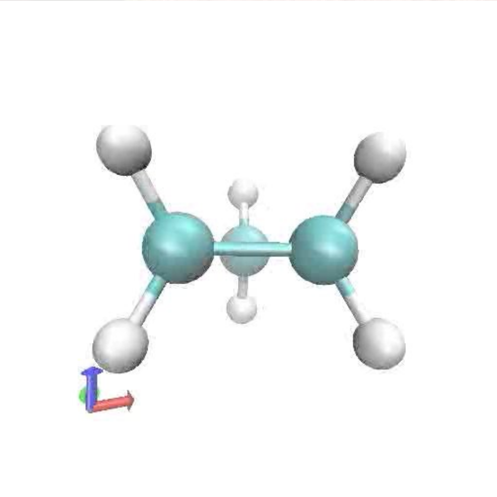
$$V = \sum_{bonds} k_b(b-b_0)^2 + \sum_{angles} k_\theta(\theta-\theta_0)^2 + \sum_{dihedrals} k_\phi[1+cos(n\phi-\delta)]$$
$$+ \sum_{impropers} k_\omega(\omega-\omega_0)^2 + \sum_{Urey-Bradley} k_u(u-u_0)^2$$
$$+ \sum_{nonbonded} \left(\epsilon\left[\left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{12} - \left(\frac{R_{min_{ij}}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{\epsilon r_{ij}}\right)$$

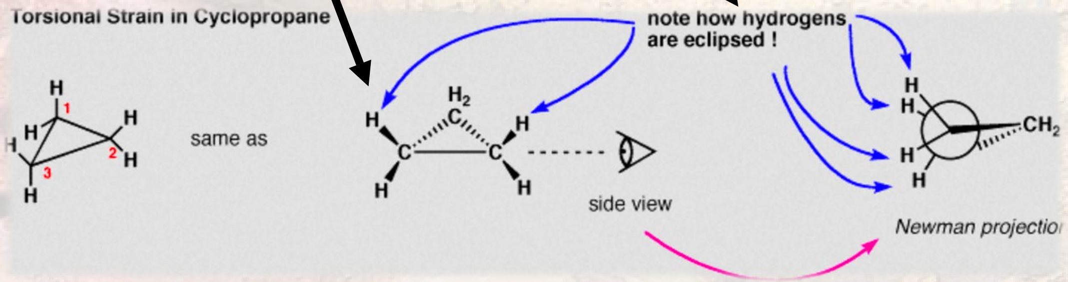




broken symmetry

10 microsecond trajectory:



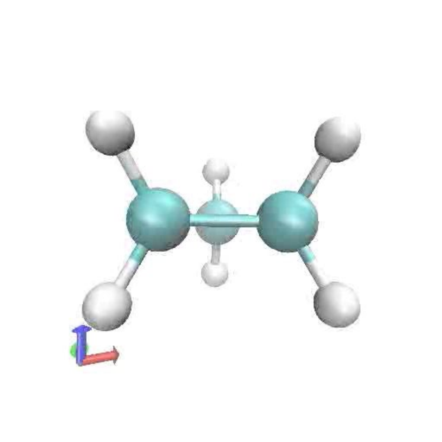



Microcanonical – no pawl
It still appears to rotate

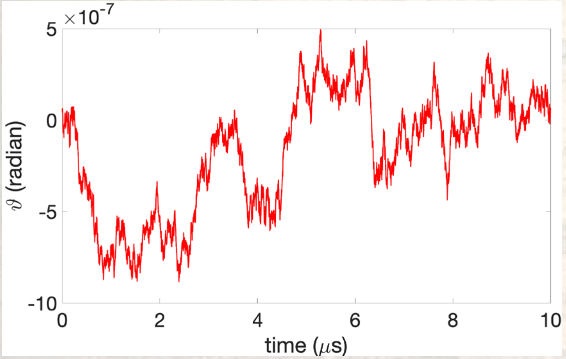
- Constructed as minimum of free energy
- Rotates with no angular momentum

$$\omega(n) = L_z(n)/I(n)$$

$$\vartheta(n) = \omega(n)\Delta\tau + \vartheta(n-1) = \sum_{i=1}^{n} \frac{L_z(i)}{I(i)}\Delta\tau$$



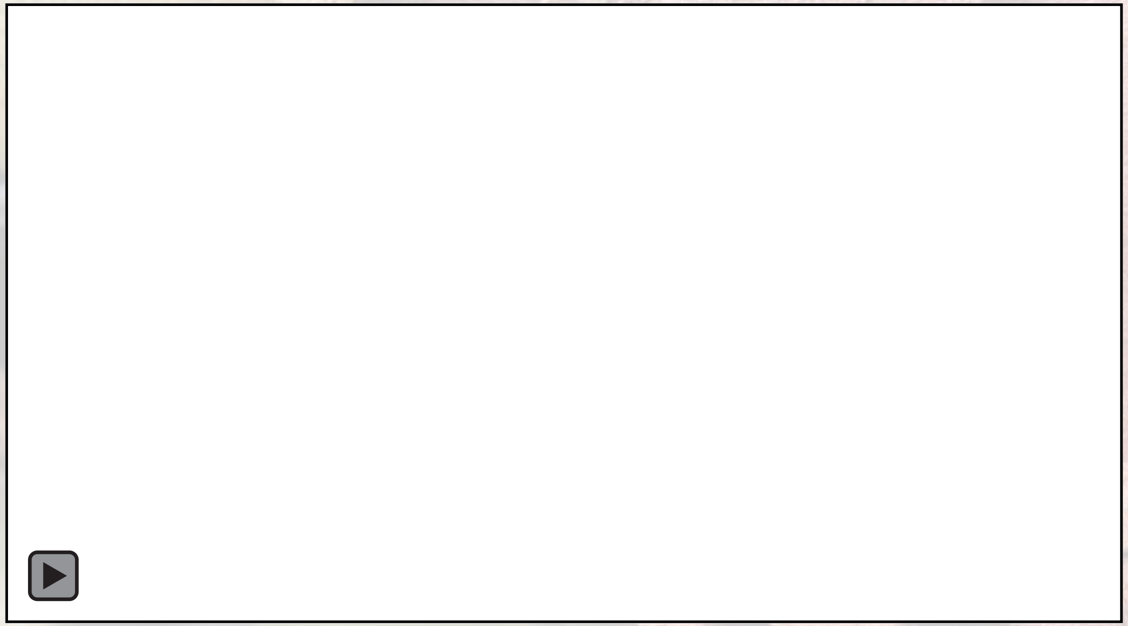
**L=0 !!**




- ➢ Rotational motion with no angular momentum
- ➢ Rotational motion even in lowest energy ground state
- ➢ Role of broken symmetry – broken parity

*After Feynman …*

# Rotation without angular momentum:



*Guichardet 1984:*
For three or more point-like particles, vibrations are continuously connected to rotations

*Shapere & Wilczek 1987:*
Connection in the space of shapes governs parallel transport: Periodic shape oscillation = closed trajectory

"Berry's phase"

Propose:

Connection in shape space combines and organizes individual atom thermal oscillations into a collective rotational motion of the entire molecule

# Universality:

The CHARMM22 force field has the following potential energy function:[7]

$$V = \sum_{bonds} k_b(b-b_0)^2 + \sum_{angles} k_\theta(\theta-\theta_0)^2 + \sum_{dihedrals} k_\phi[1+cos(n\phi-\delta)]$$
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$$\mathcal{L} = \sum_{a=2,3} \left\{ \frac{1}{2}\left(\frac{dD_{1a}}{dt}\right)^2 - \frac{1}{2}\left(\frac{2\pi}{T_a}\right)^2 (D_{1a}-1)^2 \right\}$$

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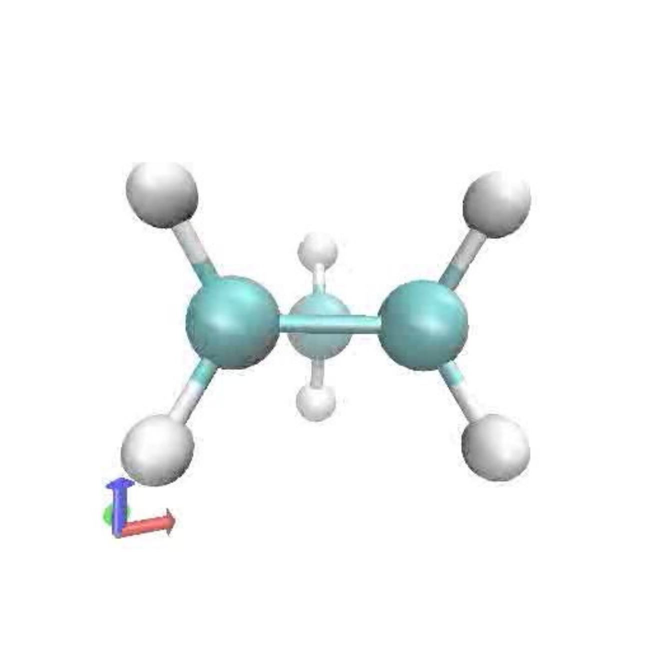
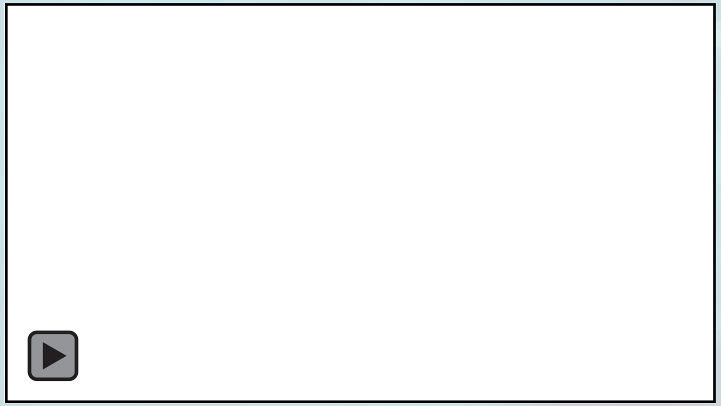


*After Feynman …*

***" Bizarre forms of matter called time crystals were supposed to be physically impossible. Now they're not."***

definition:

A material system is in a time crystal state when at the minimum of its free energy it can not be at rest but moves periodically.

propose:

Time crystal dynamics explains the impressive effectiveness of (bio)molecular motors, why they rotate apparently effortlessly even in highly viscous ambient water.

WIKIPEDIA
The Free Encyclopedia

## PARADIGM:

“A time crystal never reaches thermal equilibrium, as it is a type of nonequilibrium matter, a form of matter proposed in 2012, and first observed in 2017. This state of matter cannot be isolated from its environment—it is an open system in nonequilibrium.”

$$\dot{p}_i = \frac{\partial H}{\partial q_i} = 0$$

$$\dot{q}_i = -\frac{\partial H}{\partial p_i} = 0$$

$\Rightarrow$

Energy minimum is critical point
There are no hamiltonian time crystals

Counterexample:
*Hamiltonian with condition*

# Critical point: Constrained optimization:

- Energy $H$
- Minimize energy

$\Longrightarrow$ critical point of $H$

Hamilton's equation:

$$\delta H = 0 \quad \Leftrightarrow$$

$$\begin{cases} \partial H / \partial p^i = -\dot{q}^i = 0 \\ \partial H / \partial q^i = \dot{p}^i = 0 \end{cases}$$

No "time crystal"

- Energy $H$ and set of *conditions* $G^a = 0$
- Minimize energy $H$ subject to *conditions*

$$\Rightarrow \quad \text{Critical point of } H + \lambda^a G^a$$

$$\boxed{\begin{aligned} -\partial H / \partial p^i &= \lambda^a \partial G^a / \partial p^i \\ -\partial H / \partial q^i &= \lambda^a \partial G^a / \partial q^i \\ G^a &= 0 \end{aligned}} \quad \begin{aligned} &\equiv \lambda^a \{G^a, q^i\} = \dot{q}^i \\ &\equiv \lambda^a \{G^a, p^i\} = -\dot{p}^i \end{aligned}$$

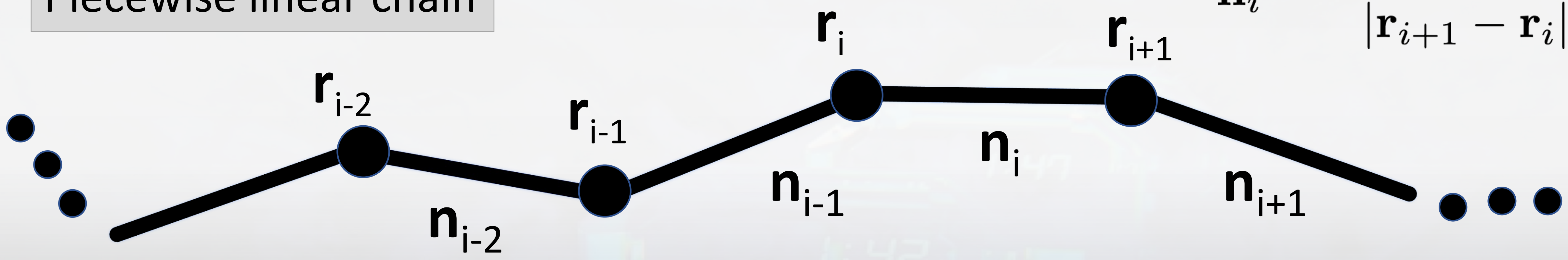
$$\text{Solution } (p^\star, q^\star, \lambda^\star)$$

$\lambda^\star \neq 0 \quad \Rightarrow$ time crystal

$$\text{Time evolution} = \text{symmetry transformation}$$

## Piecewise linear chain

$$\mathbf{n}_i = \frac{\mathbf{r}_{i+1} - \mathbf{r}_i}{|\mathbf{r}_{i+1} - \mathbf{r}_i|}$$




“all possible molecular motions  except bond stretching – shrinking“

Lie-Poisson bracket:

$$\boxed{\{n_i^a, n_j^b\} = \pm\epsilon^{abc}\delta_{ij}n_i^c}$$

$$\mathbf{n} = \begin{pmatrix} \cos\varphi\sin\theta \\ \sin\varphi\sin\theta \\ \cos\theta \end{pmatrix} \Rightarrow \{\cos\theta, \varphi\} = 1$$

Kirchhoff: Elastic rod in viscous fluid

Preserves bond length:

$$\{\mathbf{n}_i, \mathbf{n}_j \cdot \mathbf{n}_j\} = 0 \quad (\text{for all} \quad i, j)$$

# Examples of Hamiltonian time crystal:

$$\boxed{\{t_i^a, t_j^b\} = \epsilon^{abc}\delta_{ij}t_i^c}$$

*... when the equation*

$$\boxed{\dot{\mathbf{t}}_i = \mathbf{t}_i \times \frac{\partial H}{\partial \mathbf{t}_i}}$$

*has no time independent minimum energy solution*

**Condition:**

$$\frac{d}{dt}\left(\sum_{i=1}^{N}\mathbf{t}_i\right) = \left(\sum_{i=1}^{N}\mathbf{t}_i \times \frac{\partial}{\partial \mathbf{t}_i}\right) H \;\Rightarrow\; \boxed{\mathbf{G} \equiv \sum_{i=1}^{N}\mathbf{t}_i = 0}$$

An initially closed chain remains closed provided Hamiltonian rotation invariant

Examples:

$$H = \sum_{i=1}^{N} a_i\,\mathbf{t}_i \cdot \mathbf{t}_{i+1}$$

$$H = \sum_{i=2}^{N} b_i\,\mathbf{t}_i \cdot (\mathbf{t}_{i-1} \times \mathbf{t}_{i+1})$$

CONDITION

$$\{n_i^a, n_j^b\} = \epsilon^{abc}\delta_{ij}n_i^c$$

$$H = \sum_{i=1}^{N} a_i\, \mathbf{n}_i \cdot \mathbf{n}_{i+1}$$

Conserved: $\{H, \sum_{i=1}^{N} \mathbf{n}_i\} = 0$

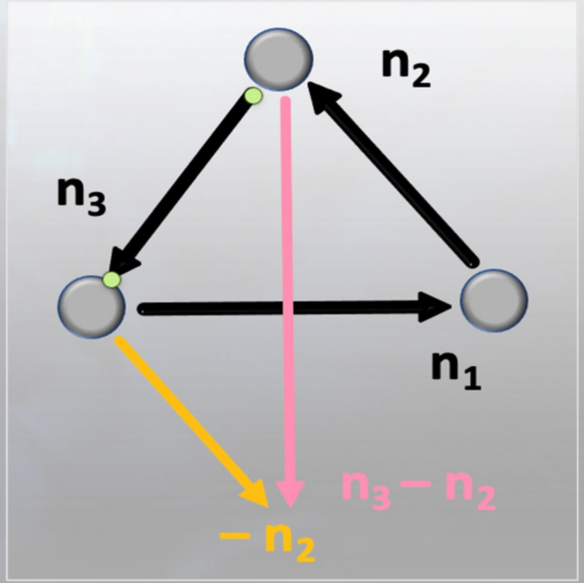
$\boxed{\text{Condition:}}$ $\sum_{i=1}^{N} \mathbf{n}_i = 0$ closed chain

$$\mathbf{n}_{N+1} = \mathbf{n}_1$$

N=3: Equilateral triangle

$$H = \mathbf{n}_1 \cdot \mathbf{n}_2 + \mathbf{n}_2 \cdot \mathbf{n}_3 - \mathbf{n}_3 \cdot \mathbf{n}_1$$

$$\begin{cases} \dfrac{d\mathbf{n}_1}{dt} = \mathbf{n}_1 \times (\mathbf{n}_2 - \mathbf{n}_3) \neq 0 \\ \dfrac{d\mathbf{n}_2}{dt} = \mathbf{n}_2 \times (\mathbf{n}_3 + \mathbf{n}_1) = 0 \\ \dfrac{d\mathbf{n}_3}{dt} = \mathbf{n}_3 \times (-\mathbf{n}_1 + \mathbf{n}_2) \neq 0 \end{cases}$$



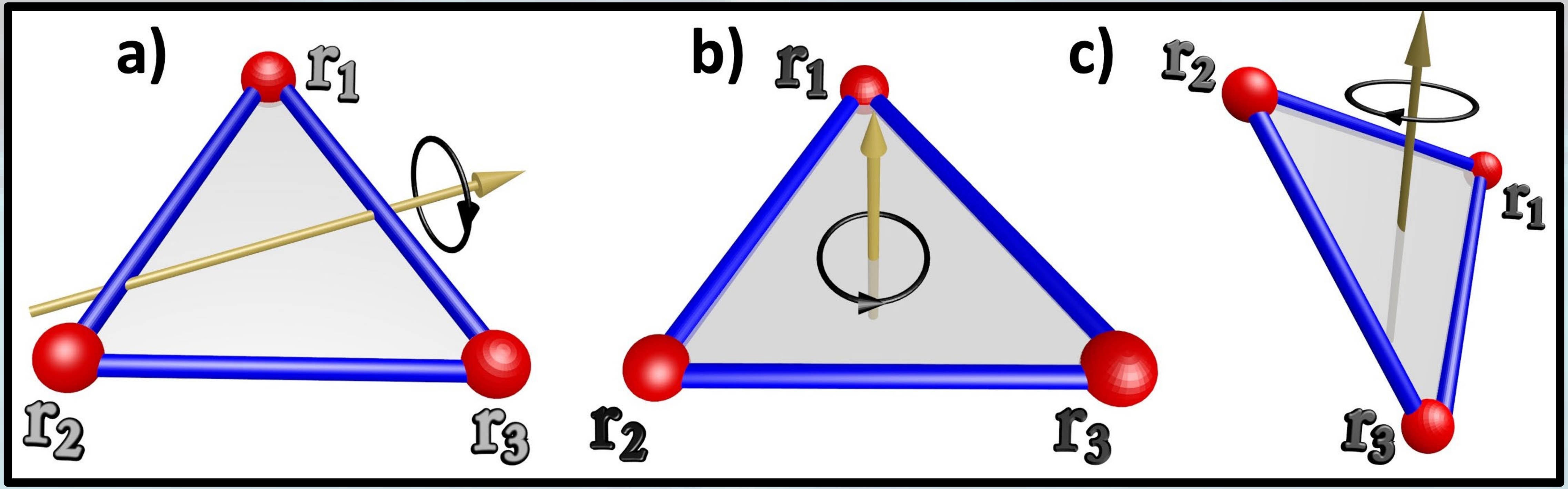

$\boxed{\text{Time crystal}}$

$$\text{sum up}: \quad \frac{d}{dt}(\mathbf{n}_1 + \mathbf{n}_2 + \mathbf{n}_3) = 0$$

$$H_1 = \sum_{i=1}^{3} a_i \mathbf{n}_i \cdot \mathbf{n}_{i+1}$$

$$H_2 = b\mathbf{n}_1 \cdot \mathbf{n}_2 \times \mathbf{n}_3$$

$$H_1 + H_2$$

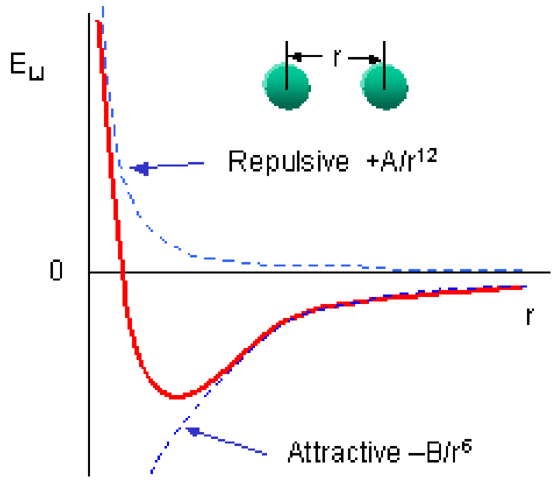


# Long range interactions

$$\mathbf{r}_i - \mathbf{r}_j = \mathbf{n}_i + \ldots + \mathbf{n}_{j-1}$$

Distance preserves chain closure: $\left\{\sum_{k=1}^{N} \mathbf{n}_k, |\mathbf{r}_i - \mathbf{r}_j|\right\} = 0$

Lennard-Jones

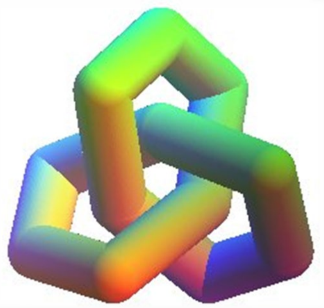



$$V_{long} = \sum_{\substack{i=1 \\ j\neq i}}^{N} V(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{\substack{i=1 \\ j\neq i}}^{N} \left( \frac{r_{min}}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12}$$

Pauli repulsion

$$H(\mathbf{n}) = H_0(\mathbf{n}) + V_{long}(\mathbf{n})$$

# Trefoil knot as a Hamiltonian time crystal- part 1



$$H = \sum_{i=1}^{12} \vec{t}_i \cdot \vec{t}_{i+1} + \sum_{\substack{i=1 \\ j\neq i}}^{12} \left( \frac{1/2}{|\mathbf{r}_i - \mathbf{r}_j|} \right)^{12}$$

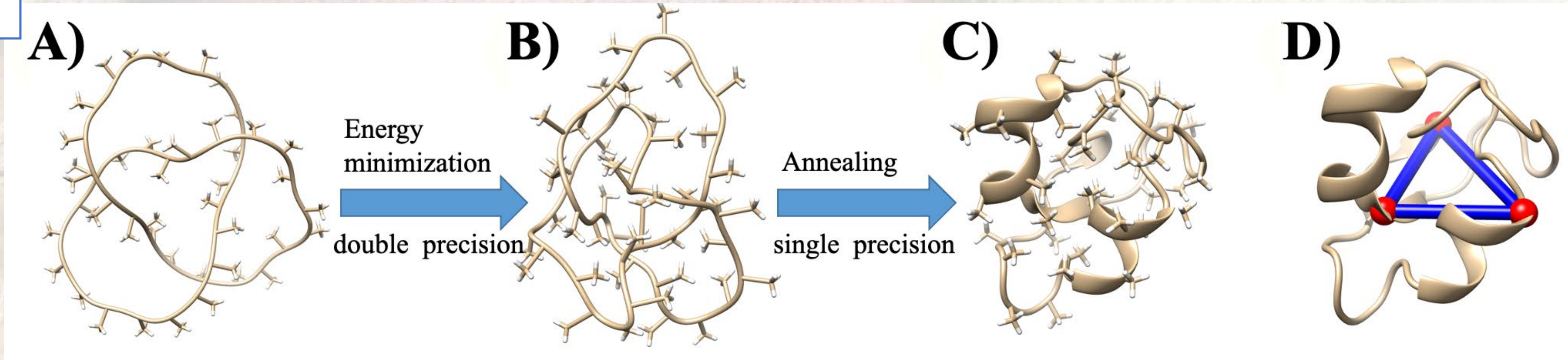
Example:

# Long Range Interactions

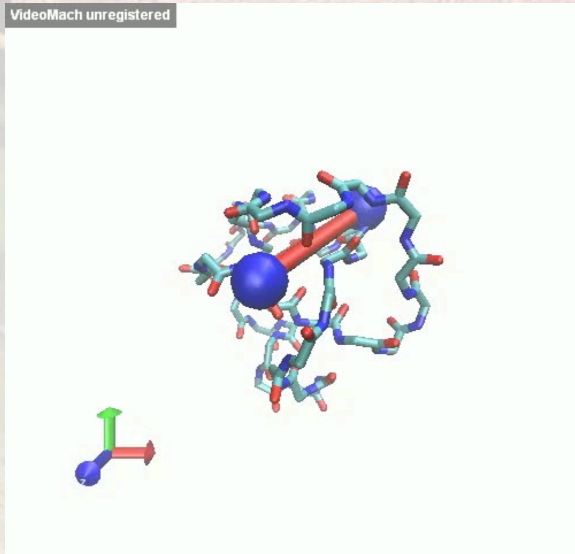
$$U(\mathbf{x}_1, \dots, \mathbf{x}_{12}) = \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{12} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{12} \left( \frac{3/4}{|\mathbf{x}_i - \mathbf{x}_j|} \right)^{12}$$

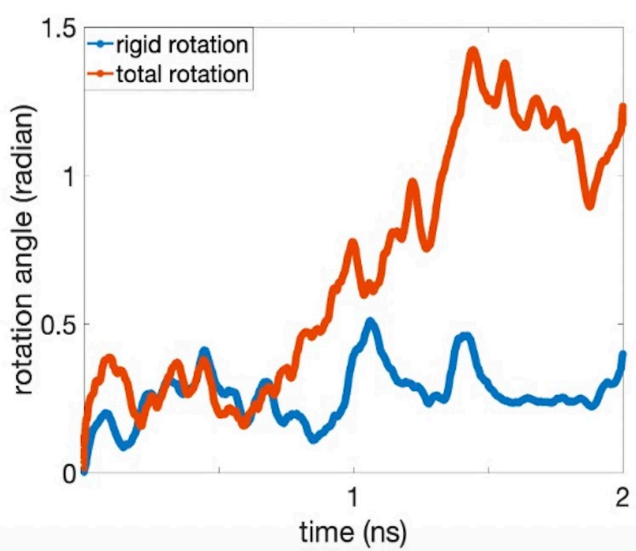
# Polyalanine trefoil with 42 amino acids in water at 310K

minimization



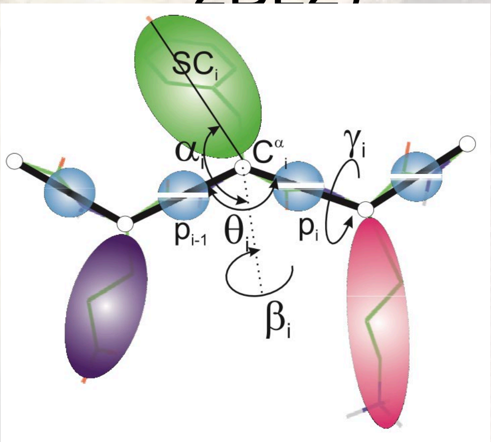

result:

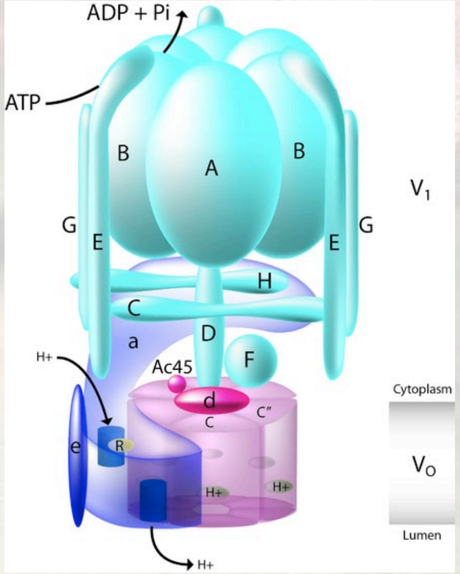


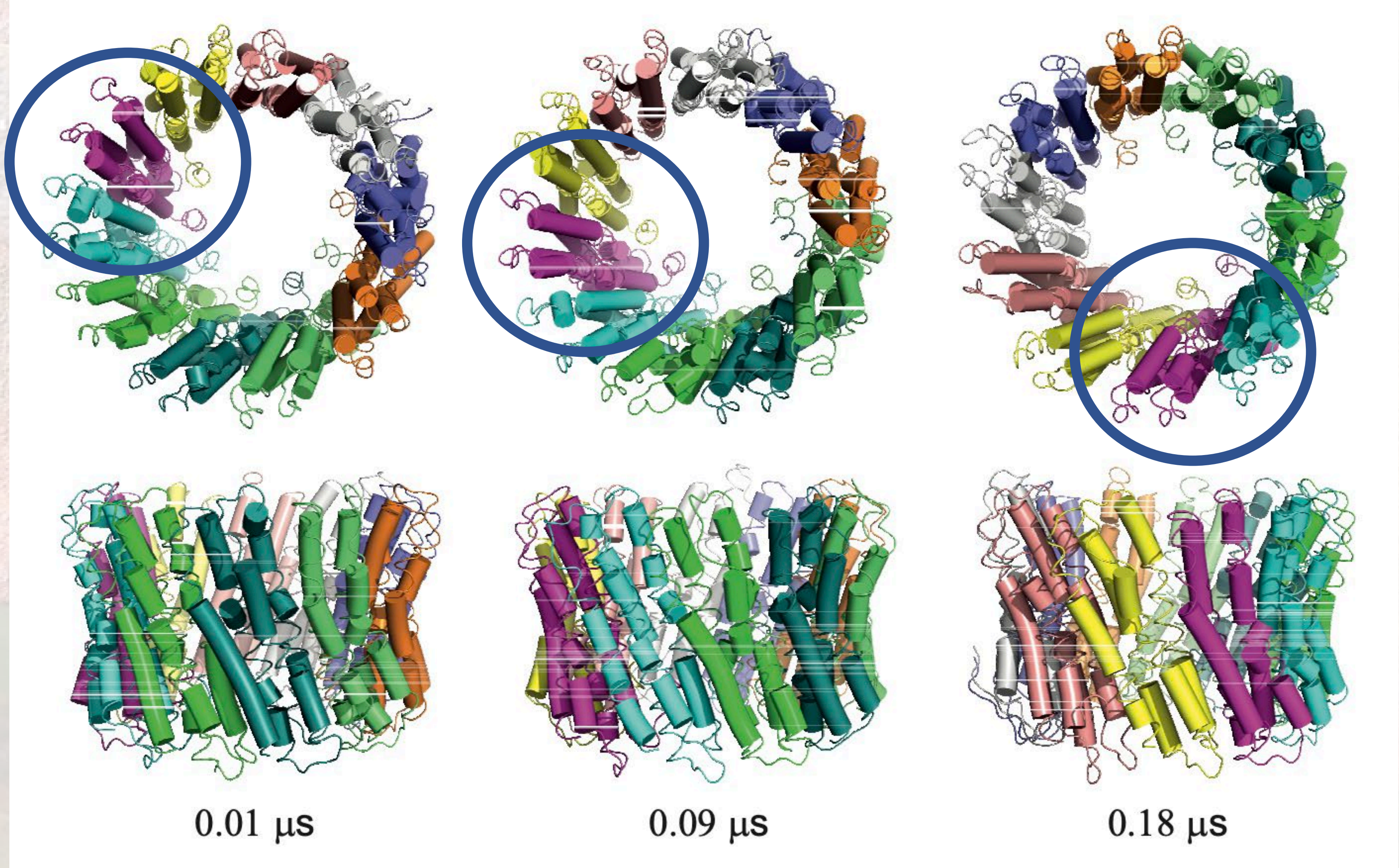



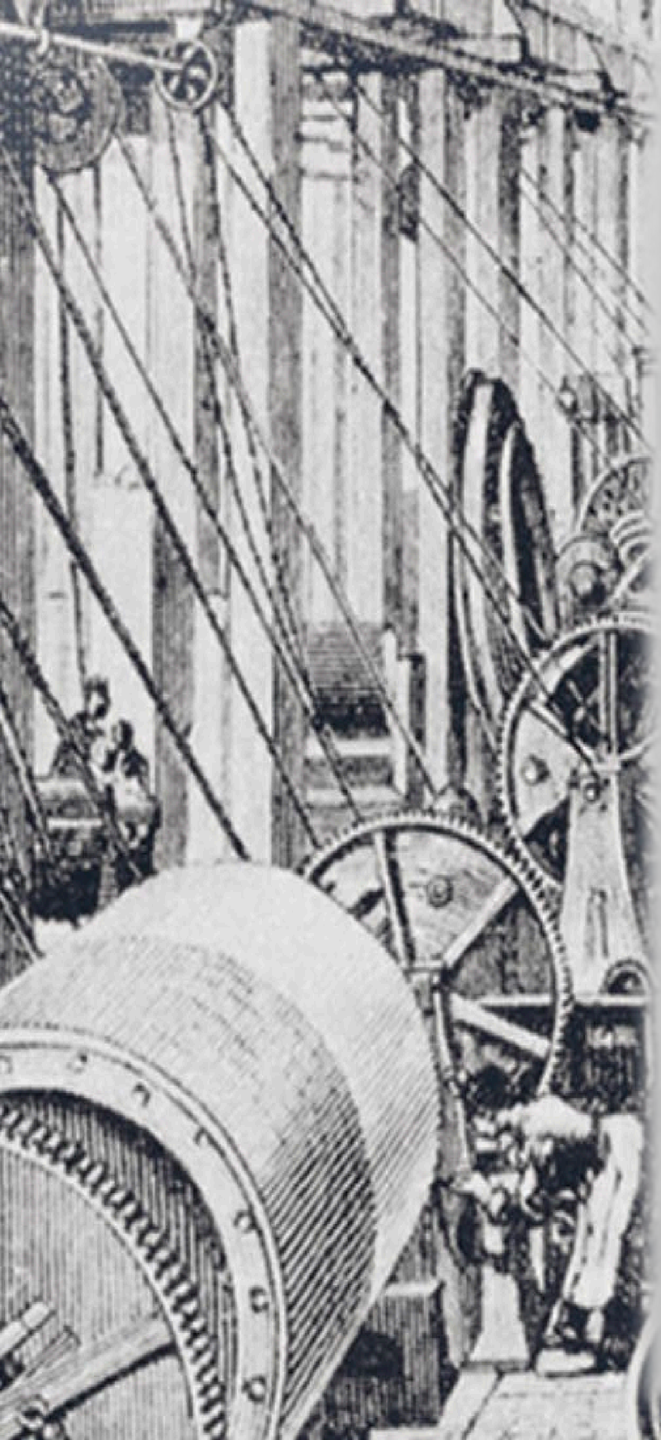

Rotational motion due to shape changes driven by thermal vibrations and water collisions

# UNRES simulation of V-ATPase rotor in *Enterococcus hirae* (PDB: 2BL2)





# Summary:

- Deformable bodies can rotate without angular momentum*
- Deformable bodies can display timecrystalline dynamics even in lowest energy ground state*
- Simulations show promise for molecular motor function

*Chirality*

*Feynman did not know