

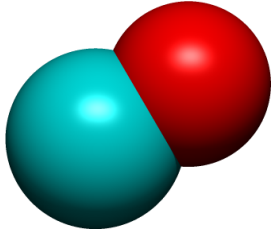
- Small molecules may be rigid (nitrogen, water, methane)
- Large molecules must be flexible ... except (some) bonds

## Vibrating (classical) bonds:

- ⊕ simplicity and consistency of the model
- ⊕ code simplicity
- ⊕ more realistic description of flexibility
- ⊖ technical problems with too stiff springs (short timestep in v MD, short trial moves in MC)
- ⊖ vibrational frequencies (esp. for hydrogens) are so high that cannot be treated by classical mechanics anyway
- ⊖ transfer of energy between the fast vibrations and slow degrees of freedom is slow (they are decoupled), unless a stochastic thermostat is used
- ⊖ flexible models are more complicated theoretically

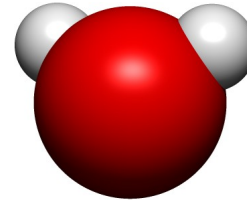
**Fixed (constrained) bonds:** just opposite

Example of a wrong algorithm for a linear molecule with axis  $(\theta, \phi)$ :



$$\begin{aligned}\theta^{\text{tr}} &= \theta + \Delta\theta u_{[-1,1]} \\ \phi^{\text{tr}} &= \phi + \Delta\phi u_{[-1,1]}\end{aligned}$$

Example of a correct algorithm for a general body:

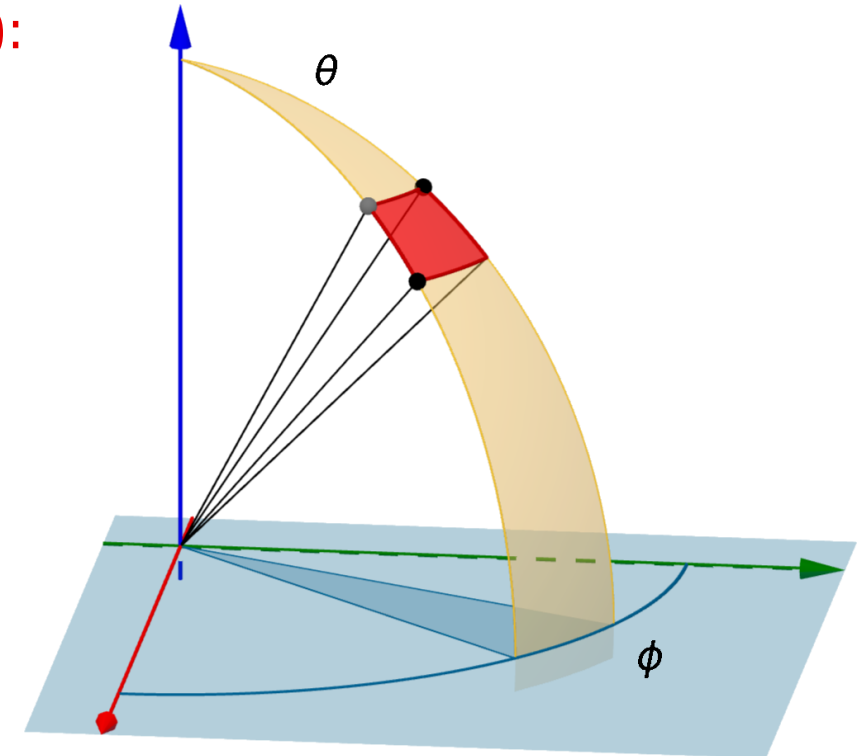


- choose an axis randomly:
  - any of  $\hat{x}, \hat{y}, \hat{z}$  in the body frame
  - any of  $\hat{x}, \hat{y}, \hat{z}$  Cartesian coordinates in 3D space
  - any random vector

- rotate by angle  $\Delta\alpha u_{[-1,1]}$ , where  $u_{[-1,1]}$  is a random number uniformly distributed in  $[-1, 1]$

Rotation by  $\Delta\alpha$  around  $\hat{z}$ -axis:

$$\begin{pmatrix} \cos \Delta\alpha & -\sin \Delta\alpha & 0 \\ \sin \Delta\alpha & \cos \Delta\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$



Integration of the equations of motion for systems with fixed bond lengths or angles is not the same as the infinitely-large force constant limit of the corresponding flexible system.

## What to fix:

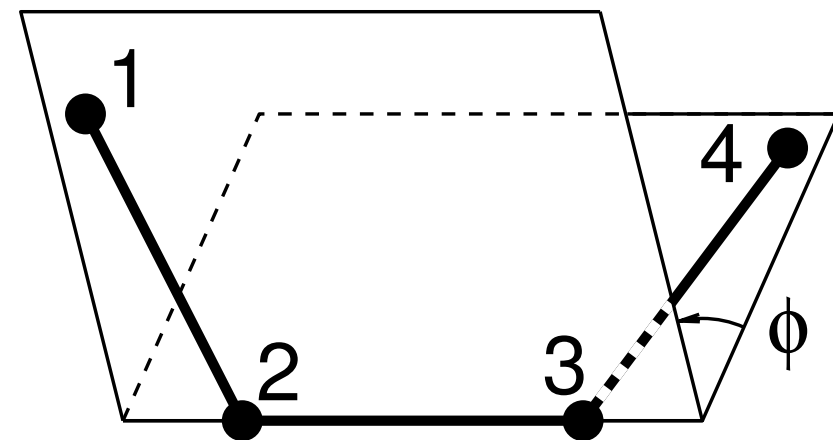
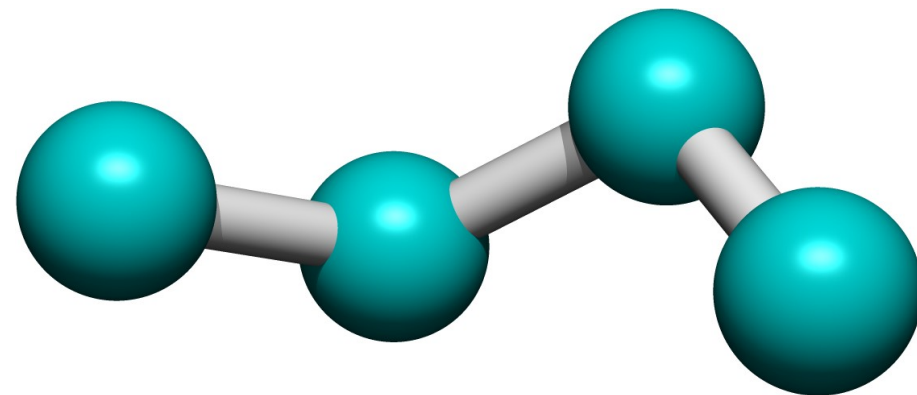
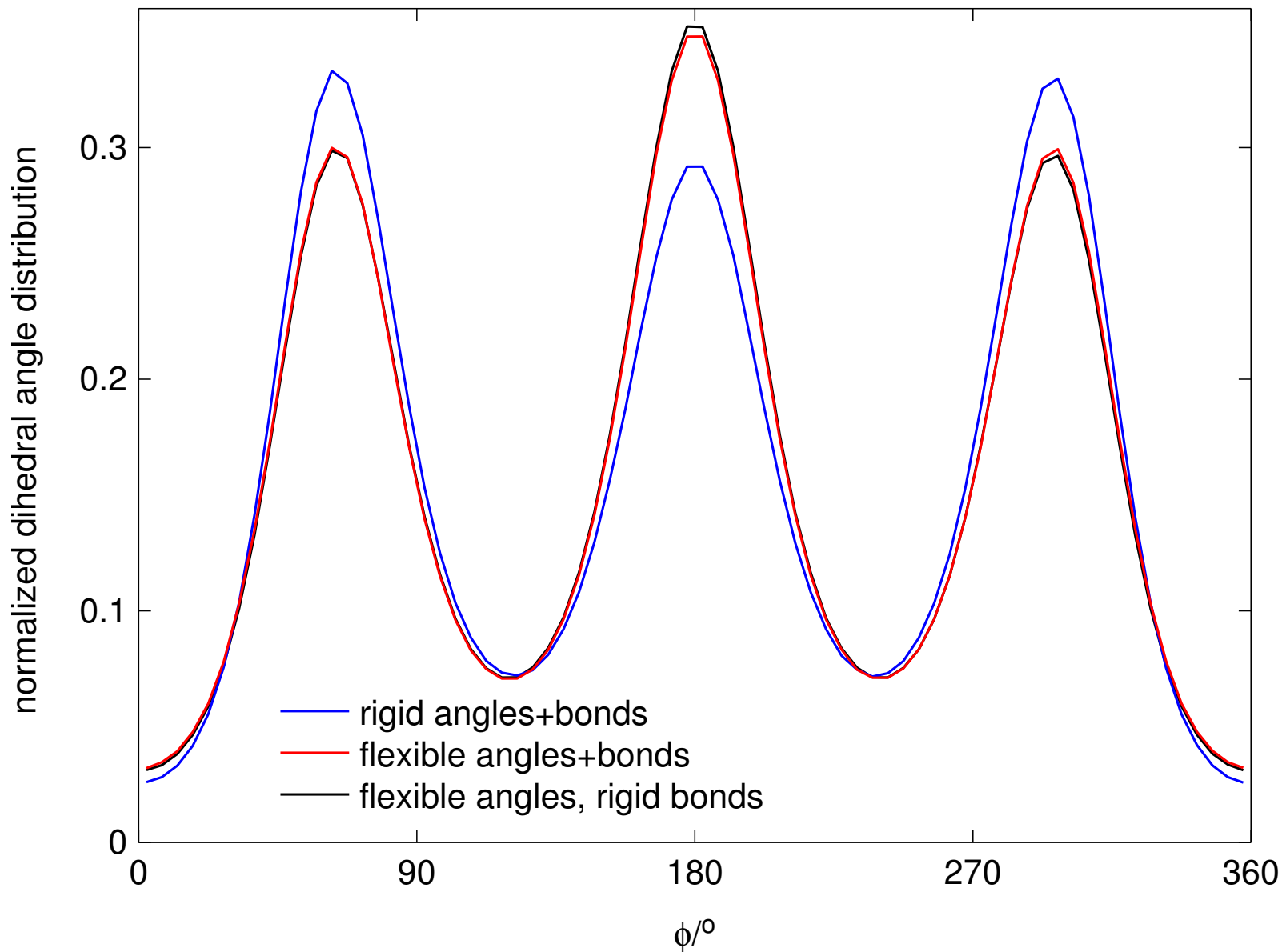
- nothing – short timestep, bad equipartition (convergence of different degrees of freedom)
- bonds with hydrogen only – longer timestep allowed, better (but not the best) equipartition  
GROMACS: special algorithm for H,  $h = 4$  ps
- all bond lengths – larger systematic errors, not good for rigid geometries (fullerene) and heavy atoms
- all bond lengths + angles with hydrogens – cheap and less precise, but longer timestep allowed + good equipartition
- all bond lengths + all angles – WRONG except small molecules

## Methods:

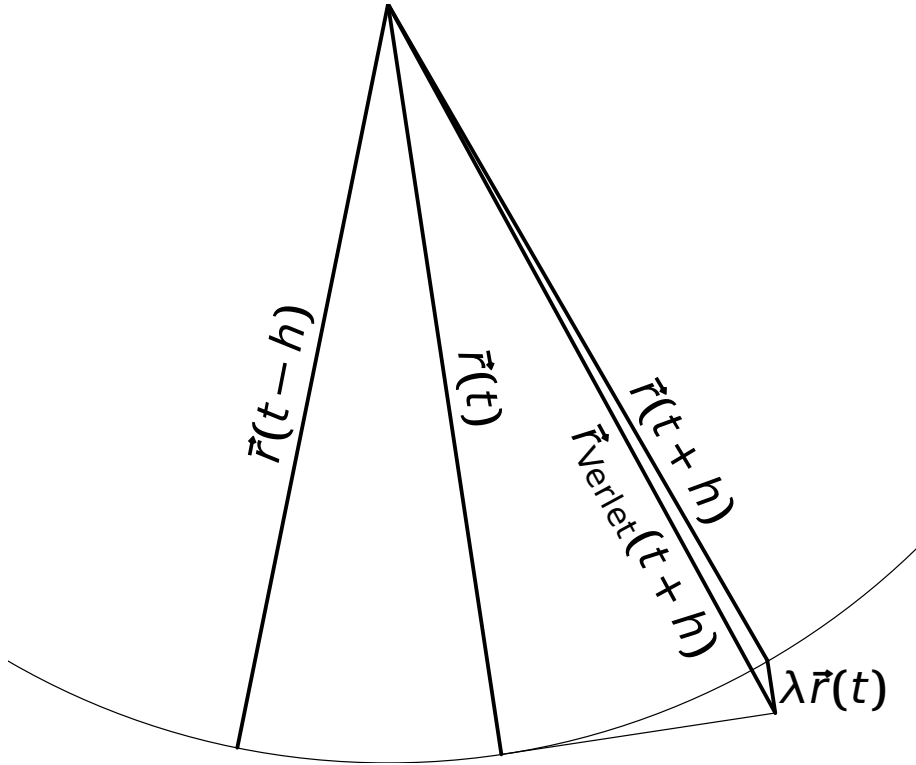
- SHAKE (+Verlet)
- Lagrangian constraint dynamics

# Dihedral angle distribution of butane

United-atom model (CHARMM19) of butane



## Mathematical pendulum:



$$\begin{aligned}\vec{r}(t+h) &= \vec{r}_{\text{Verlet}}(t+h) - \frac{h^2}{m} \vec{f}_c(t) \\ &= 2\vec{r}(t) - \vec{r}(t-h) + h^2 \frac{\vec{f}(t) - \vec{f}_c(t)}{m}\end{aligned}$$

$$\frac{h^2 \vec{f}_c(t)}{m} = \lambda \vec{r}(t)$$

$$|\vec{r}(t+h)|^2 = |\vec{r}(t)|^2 = l^2$$

$$[\vec{r}_{\text{Verlet}}(t+h) - \lambda \vec{r}(t)]^2 = \vec{r}(t)^2$$

$$\vec{r}_{\text{Verlet}}(t+h)^2 - 2\lambda \vec{r}_{\text{Verlet}}(t+h) \cdot \vec{r}(t) + \lambda^2 \vec{r}(t)^2 = \vec{r}(t)^2$$

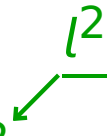
$$\lambda \approx \frac{|\vec{r}_{\text{Verlet}}(t+h)|^2 - |\vec{r}(t)|^2}{2\vec{r}_{\text{Verlet}}(t+h) \cdot \vec{r}(t)} = \frac{|\vec{r}_{\text{Verlet}}(t+h)|^2 - l^2}{2\vec{r}_{\text{Verlet}}(t+h) \cdot \vec{r}(t)}$$

**General atom-atom bond:**

$$\vec{r}_i(t+h) = \vec{r}_{\text{Verlet},i}(t+h) + \lambda \frac{1/m_i}{1/m_i + 1/m_j} \vec{r}_{ij}$$

$$\vec{r}_j(t+h) = \vec{r}_{\text{Verlet},j}(t+h) - \lambda \frac{1/m_j}{1/m_i + 1/m_j} \vec{r}_{ij}$$

where

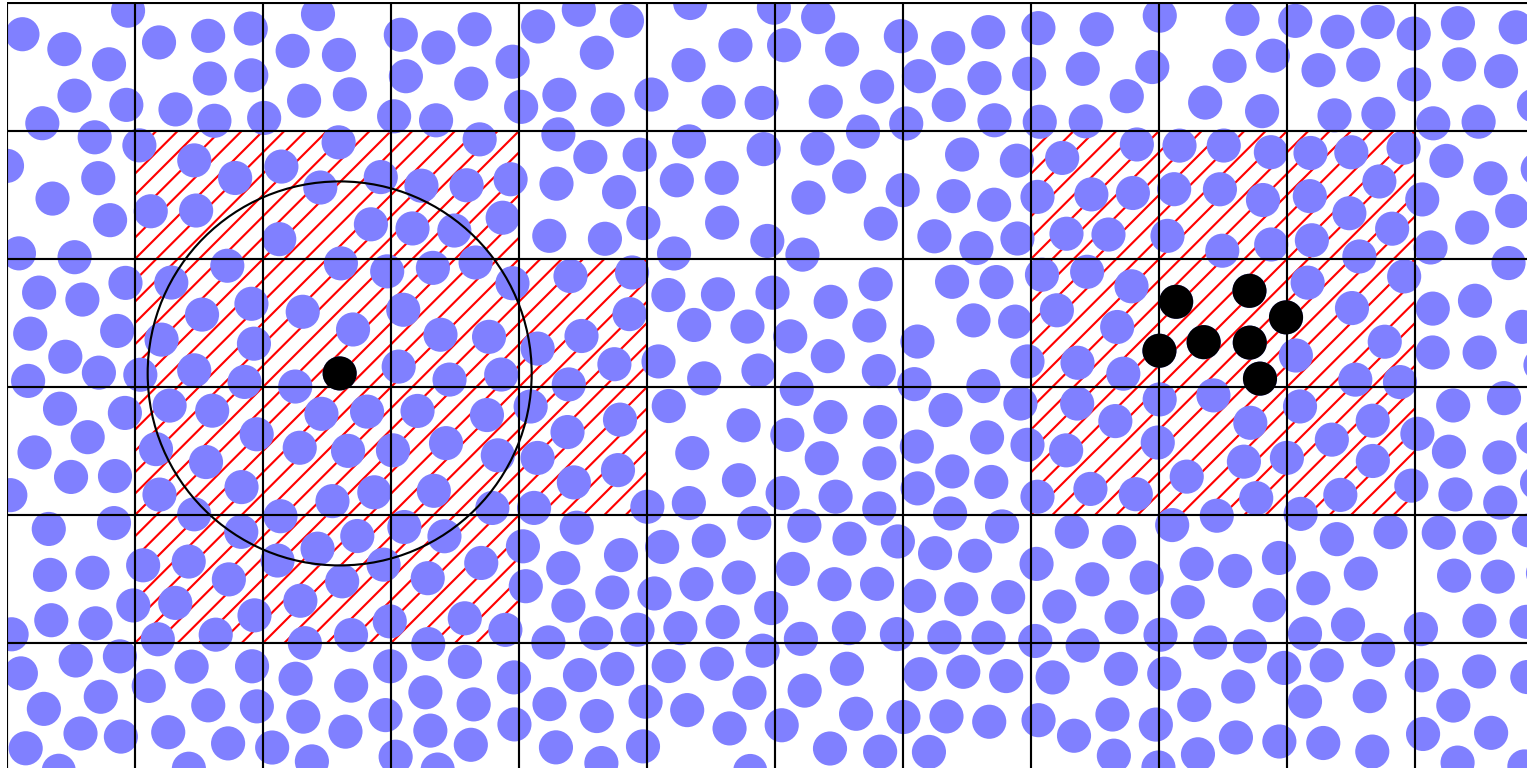
$$\lambda = \frac{|\vec{r}_{\text{Verlet},ij}(t+h)|^2 - |\vec{r}_{ij}(t)|^2}{2\vec{r}_{\text{Verlet},ij}(t+h) \cdot \vec{r}_{ij}(t)}$$


- Based on the Verlet method
- Center-of-mass is conserved (integral of motion)!
- Complex molecules: repeat iteratively until converged
- Speed up: superrelaxation
- Velocity version: RATTLE, more variants
- For  $m_i = \infty$ ,  $\vec{r}_i = (0, 0, 0)$ ,  $\vec{r} = \vec{r}_j = \vec{r}_{ij} \Rightarrow$  mathematical pendulum

$$\vec{r}_{ij} = \vec{r}_j - \vec{r}_i, \quad r_{ij} = |\vec{r}_{ij}|$$

For short-ranged pair potentials (also r-space Ewald):

- all pairs ( $N < 300$ )
- neighbor list ( $N \approx 1000$ )
- domain-decomposition algorithms: linked-cell list method



## A couple of tricks:

- MD: multiple timestep MD
- MC: multimoves (near the critical point – critical slowing-down)
- MC: identity change, non-Boltzmann sampling, ...
- hybrid MC/MD (not very good)

## Programming tricks:

- cache
- nearest neighbors in periodic boundary conditions
- tables: pair potential calculated by splines

## Parallel code:

- usually based on domain decomposition (linked-cell list)
- standard computers 4–32 cores
- Graphics Processing Units: thousands of processors, more difficult to program



# Kinetic quantities: EMD vs. NEMD

**Kinetic quantities:** diffusivity, electric conductivity, viscosity, heat conductivity

## Nonequilibrium molecular dynamics (NEMD)

- as in “real experiment” – field or perturbation added (electric field, thermal gradient, shear stress)
- dissipation – heat is generated  $\Rightarrow$  good thermostat needed
- dissipation extrapolation to zero perturbation
- SLODD

## Equilibrium molecular dynamics (EMD)

- one equilibrium simulation enough
- based on the Linear Response Theory – Green–Kubo:  $D = \frac{1}{3} \int_0^\infty \langle \dot{\vec{r}}_i(t) \cdot \dot{\vec{r}}_i(0) \rangle dt$

$$\text{Einstein: } 2tD = \frac{1}{3} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$$

