

Large molecules **vs.** small molecules (rigid or almost rigid)

Vibrating (classical) bonds – pros:

- simplicity and consistency of the model
- code simplicity
- more realistic description of flexibility

Cons:

- 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

Example of a wrong algorithm for a linear molecule with axis (θ, ϕ) :

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

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 $\hat{x}, \hat{y}, \hat{z}$ 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 interval $[-1, 1]$

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:

- bonds with hydrogen only – longer timestep allowed, slightly worse equipartition
- all bond lengths – slightly larger systematic error, not good for rigid geometries (fullerene)
- 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

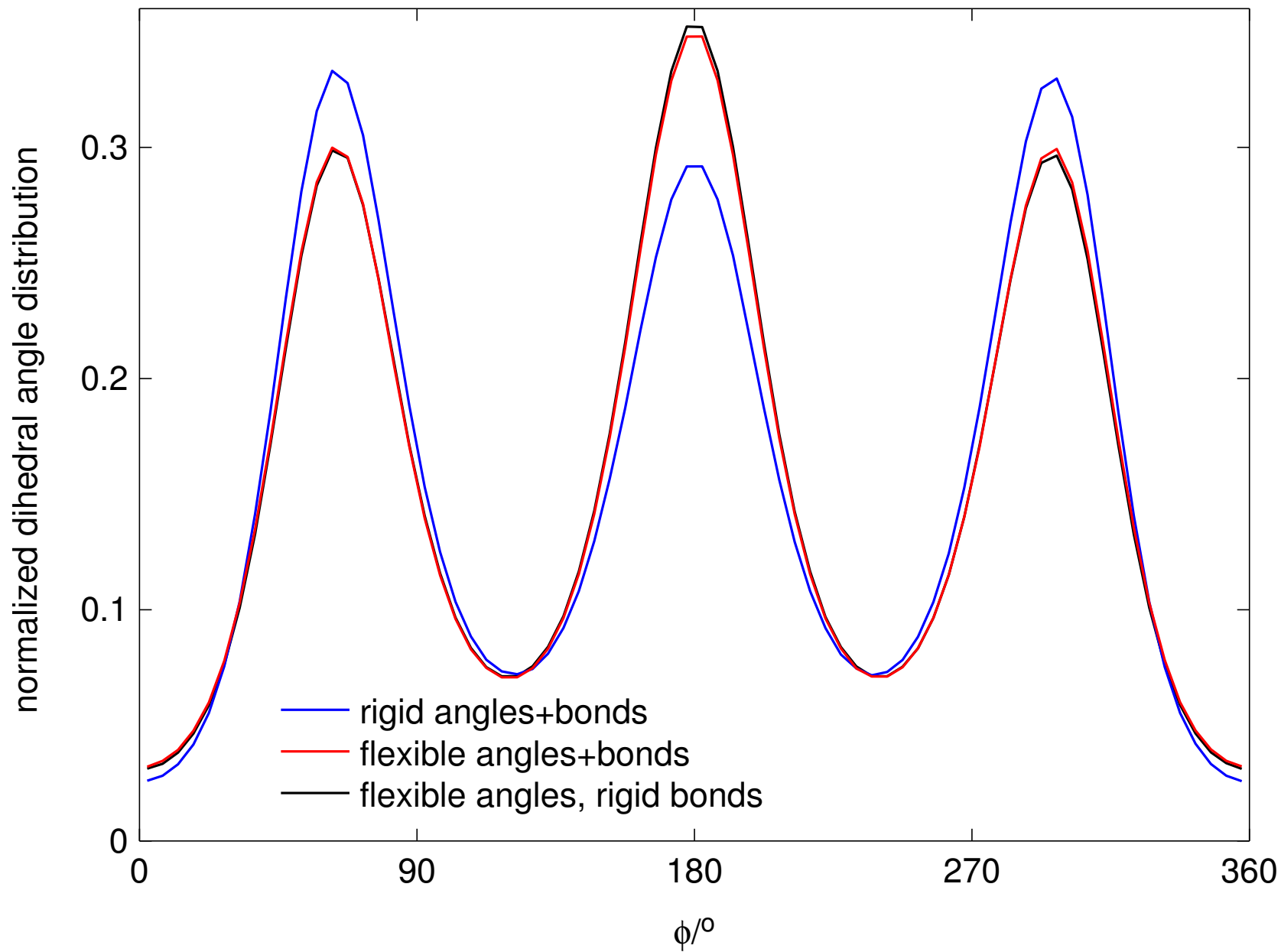
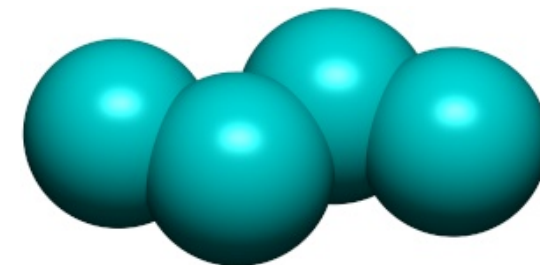
Methods:

- SHAKE (+Verlet)
- Lagrangian constraint dynamics

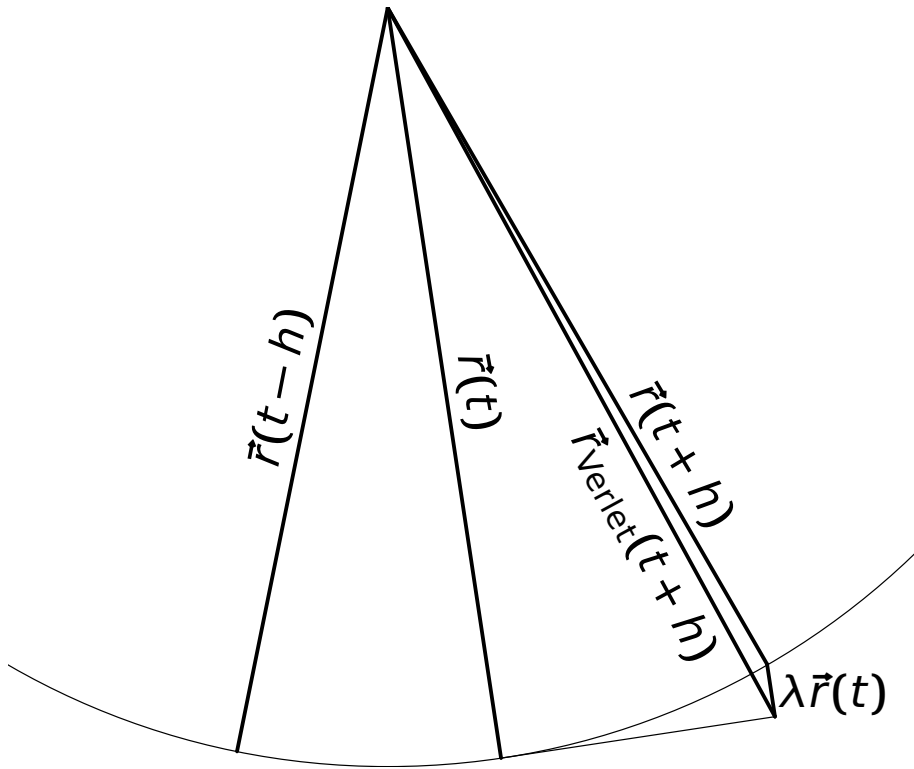
Dihedral angle distribution of butane

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United-atom model (CHARMM19) of butane



Mathematical pendulum:



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

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

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

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

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

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

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

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

Center-of-mass is conserved (integral of motion)!

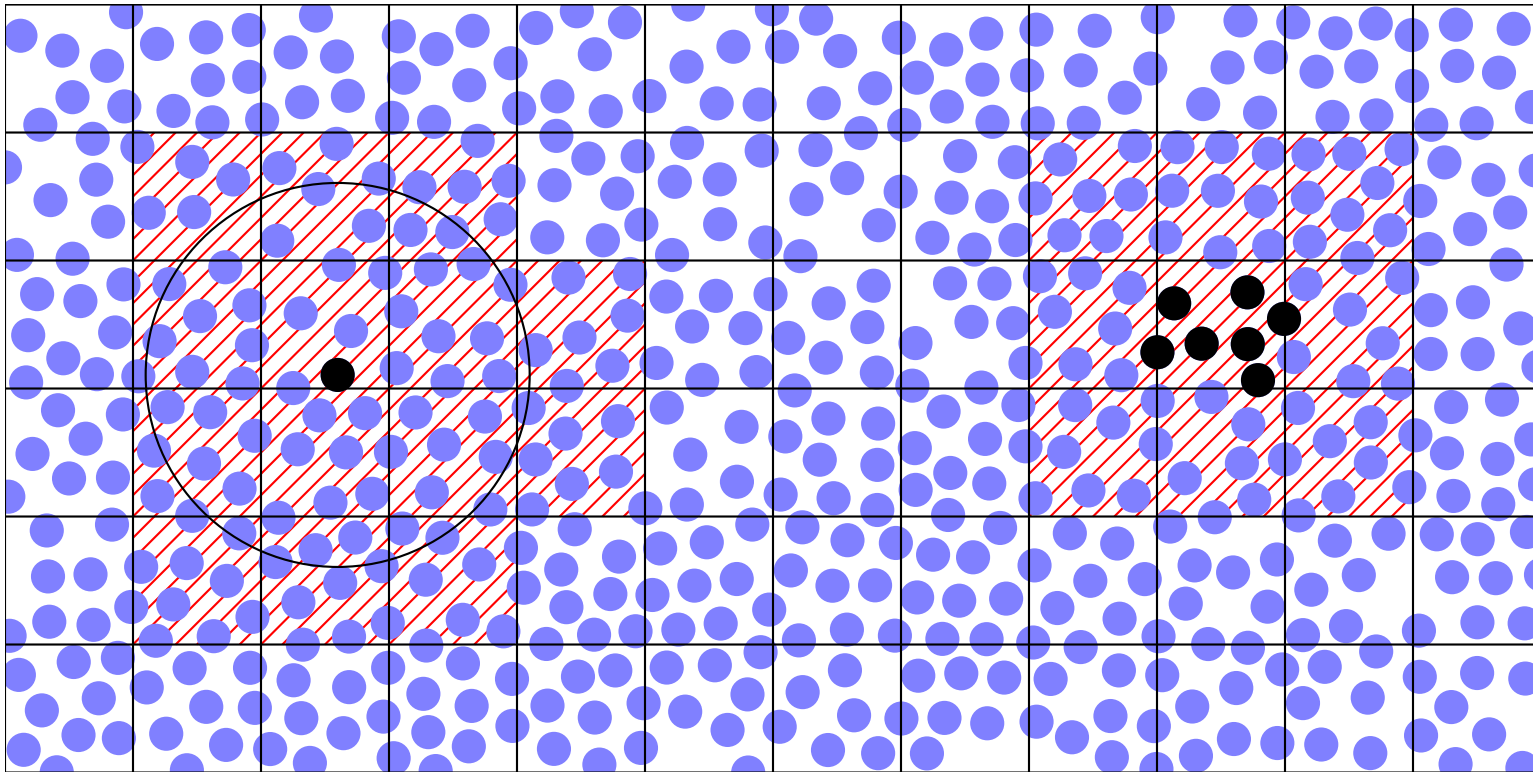
Complex molecules: repeat iteratively until converged

Superrelaxation

Optimization I

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

- all pairs ($N < 300$)
- neighbor list ($N \approx 1000$)
- linked-cell list method ($N > 1000$)



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 and 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: $D = \frac{1}{3} \int_0^\infty \langle \dot{\vec{r}}_i(t) \cdot \dot{\vec{r}}_i(0) \rangle dt$

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

