

Simulations of molecular systems

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- 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

MC: molecules

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



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

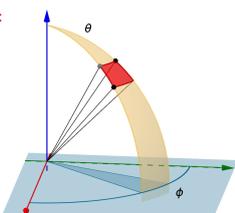
Example of a correct algorithm for a general body:

- choose an axis randomly:
 - any of $\hat{x}, \hat{y}, \hat{z}$ in the body frame
 - any of $\hat{x}, \hat{y}, \hat{z}$ 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:

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



SHAKE

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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

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

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

- 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

MD: bonds

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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:

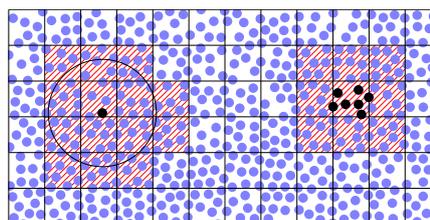
- SHAKE (+Verlet)
- Lagrangian constraint dynamics

Optimization I

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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



Optimization II

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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

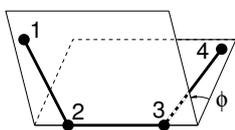
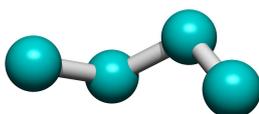
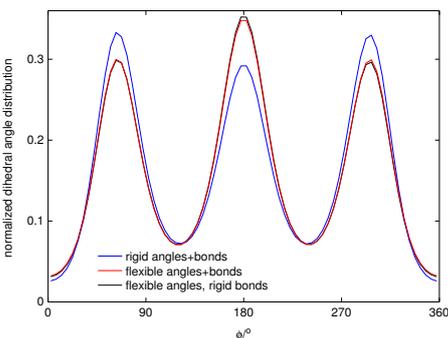
Parallel code:

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

Dihedral angle distribution of butane

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United-atom model (CHARMM19) of butane



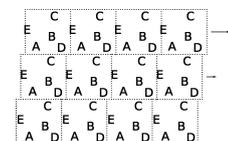
Kinetic quantities: EMD vs. NEMD

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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

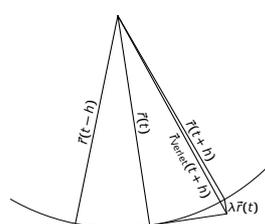
based on the Linear Response Theory – Green-Kubo: $D = \frac{1}{3} \int_0^\infty \langle \vec{r}_i(t) \cdot \vec{r}_i(0) \rangle dt$

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

Fixed constraints in MD: SHAKE

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Mathematical pendulum:



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

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

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

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

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

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