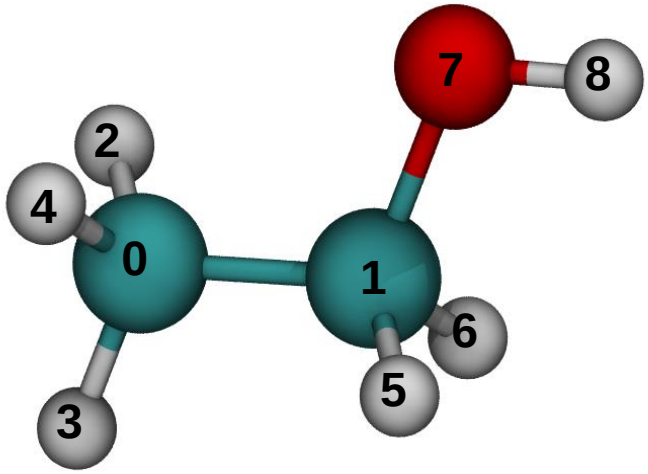
Topic: Force fields

Hands-on

- Using VMD software, load the given molecules. Define the potential energy surfaces (write all pairs of atoms contributing to each term).
  - Ethanol (C_2H_5OH)
  - Benzene (C_6H_6)
- Also, send me the following information for both molecules
  - Number of bonds _____
  - Number of angles _____
  - Number of Dihedrals _____
  - Number of Improper torsions _____
  - Number of non-bonded atom pairs _____

Topic: Force fields



- Number of bonds ____8____
- Number of angles ____13___
- Number of dihedrals ___12_____
- Number of improper torsions ___0____
- Number of non-bonded pairs ____3___

bonds

{0 1} {0 3} {0 4} {0 2} {1 5} {1 6} {1 7} {7 8}

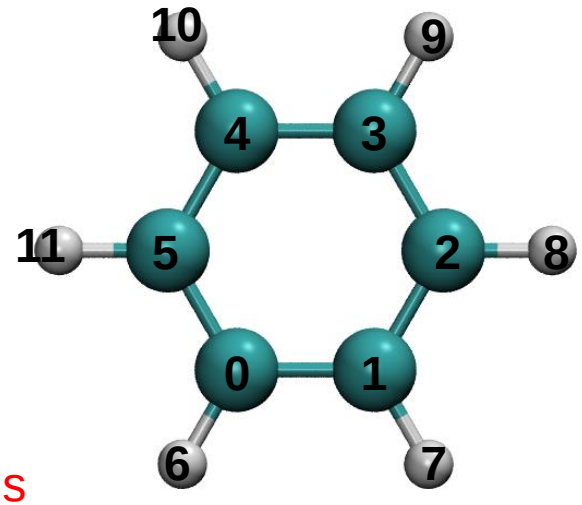
angles

{1 0 3} {1 0 4} {1 0 2} {3 0 4} {2 0 3} {2 0 4} {0 1 5} {0 1 6} {0 1 7} {5 1 6} {5 1 7} {6 1 7} {1 7 8}

dihedrals

{3 0 1 5} {3 0 1 6} {3 0 1 7} {4 0 1 5} {4 0 1 6} {4 0 1 7} {2 0 1 5} {2 0 1 6} {2 0 1 7} {0 1 7 8} {5 1 7 8} {6 1 7 8}

Topic: Force fields



- Number of bonds ___12_____
- Number of angles ____18____
- Number of dihedrals ___24_____
- Number of improper torsions ___6_____
- Number of non-bonded pairs ____24___

bonds

{0 6} {0 1} {0 5} {1 7} {1 2} {2 3} {2 8} {3 9} {3 4} {4 5} {4 10} {5 11}

angles

{1 0 6} {5 0 6} {1 0 5} {2 1 7} {0 1 7} {0 1 2} {3 2 8} {1 2 3} {1 2 8} {2 3 9} {2 3 4} {4 3 9} {3 4 5} {5 4 10} {3 4 10} {4 5 11} {0 5 4} {0 5 11}

dihedrals

{6 0 1 7} {6 0 1 2} {5 0 1 7} {5 0 1 2} {6 0 5 4} {6 0 5 11} {1 0 5 4} {1 0 5 11} {7 1 2 3} {7 1 2 8} {0 1 2 3} {0 1 2 8} {8 2 3 9} {8 2 3 4} {1 2 3 9} {1 2 3 4} {2 3 4 5} {2 3 4 10} {9 3 4 5} {9 3 4 10} {3 4 5 11} {3 4 5 0} {10 4 5 11} {10 4 5 0}

impropers

{6 0 5 1} {2 0 1 7} {3 1 2 8} {9 3 4 2} {5 3 4 10} {4 0 5 11}

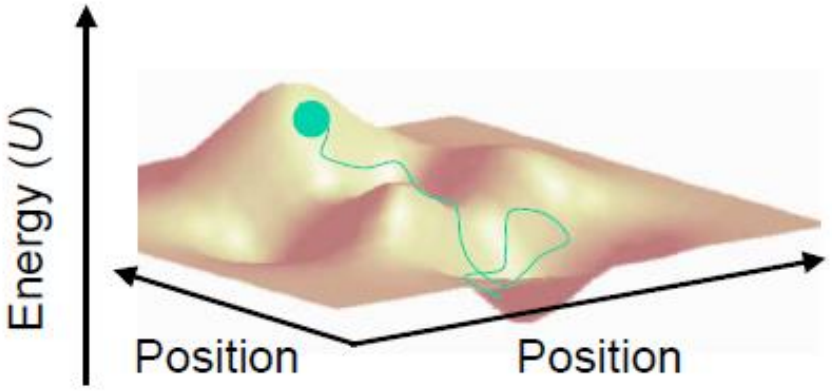
Topic: Molecular dynamics

Objective

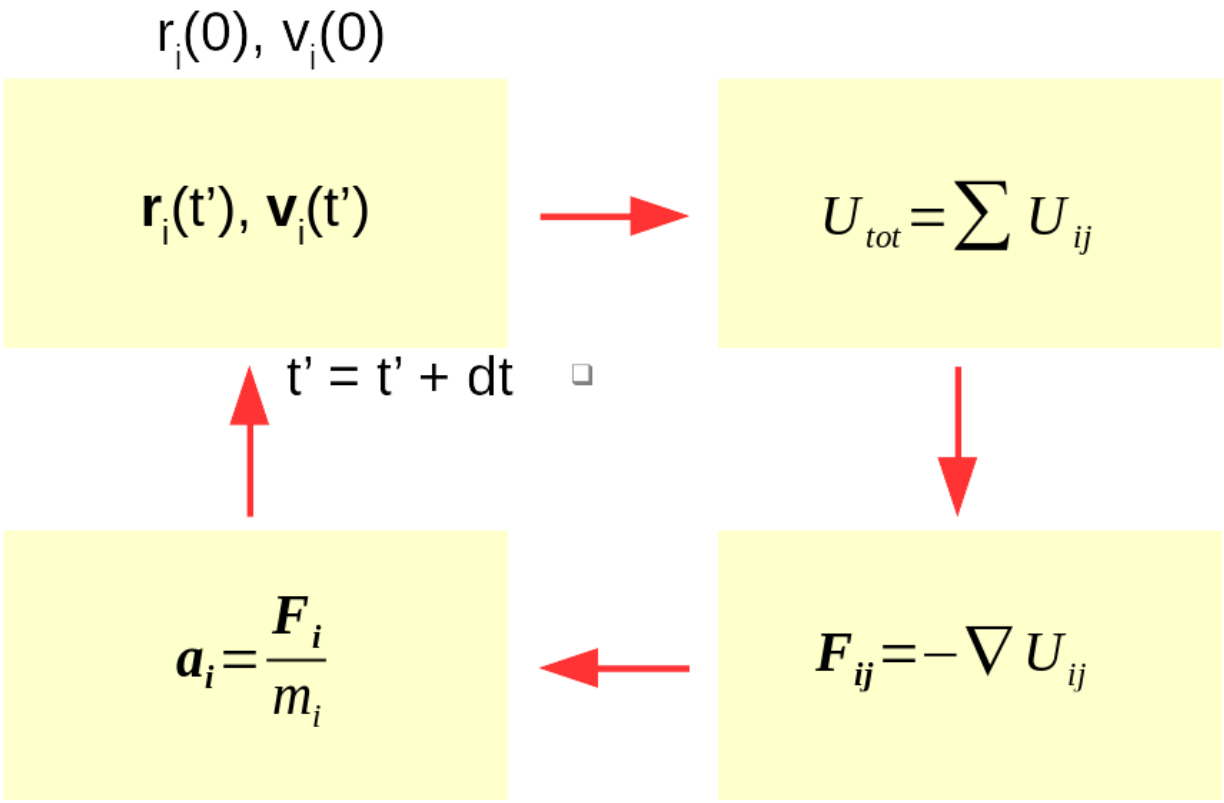
- Molecular dynamics (MD)
- Ingredients for running MD simulations
- Properties from MD simulations
- MD Fortran code for Argon
- Generate initial configurations
- Visualize the trajectory in VMD

Molecular dynamics (MD)

- Mimic the behavior of atoms in real systems.
- The potential energy function allows to calculate the force experienced by each atom due to the others
- Newton's law governs the motion of atoms



Molecular dynamics (MD)



Simple MD program

```
program MD
 call initialization
t=0
do while (t<tmax)
      call force
      call integrate
      t = t + delt
 enddo
stop
end program MD
```

Characteristics of good integrator

- Consumes little memory
- Allows a longer timestep
- Time-reversible and conserves energy

velocity-Verlet algorithm

$$\boldsymbol{r}(t+dt)=\boldsymbol{r}(t)+\boldsymbol{v}(t)dt+\frac{1}{2}\boldsymbol{a}(t)dt^2$$

$$\boldsymbol{v}(t+dt)=\boldsymbol{v}(t)+\frac{1}{2}\left[\boldsymbol{a}(t)+\boldsymbol{a}(t+dt)\right]dt$$

Properties from MD trajectories

- Potential energy
- density
- Temperature
- Pressure

$$P = \frac{Nk_BT}{V} + \frac{\sum_i^{N'} r_i \bullet f_i}{dV}$$

- Enthalpy of vaporization

$$\Delta H_{vap} = H_{gas} - H_{liquid} = U_{gas} - U_{liquid} + P(V_{gas} - V_{liquid})$$

- Isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

- Thermal expansion coefficient $\alpha_P = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$

Properties from MD trajectories

- Self-diffusion coefficient

$$D = \frac{1}{3}\int_0^\infty \langle v_i(t) v_i(0) \rangle \, dt$$

- Static dielectric constant

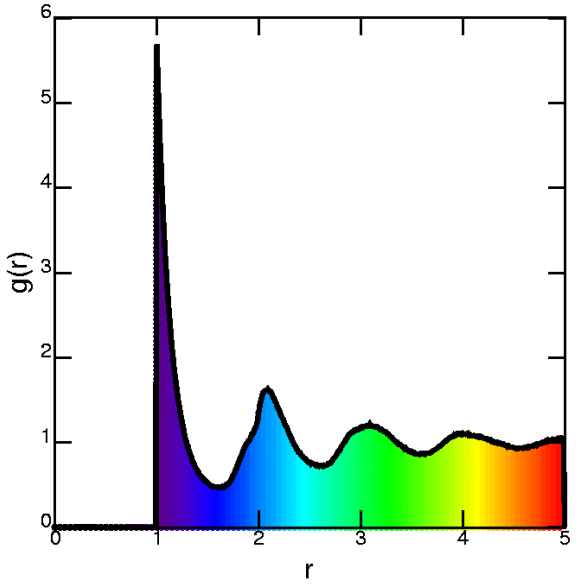
$$\epsilon = 1 + \frac{4\pi}{3Vk_B \langle T \rangle} \left(\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 \right)$$

- Surface tension

$$\gamma = \frac{1}{2} L_z \left\langle P_{zz} - \frac{1}{2}\left(P_{xx} + P_{yy}\right) \right\rangle$$

- Pair correlation function or

radial distribution function



http://www.physics.emory.edu/faculty/weeks//idl/gofr.html

Topic: Molecular dynamics

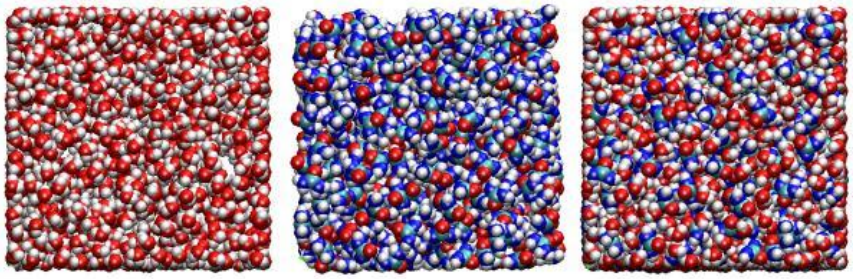
Steps in performing MD simulation

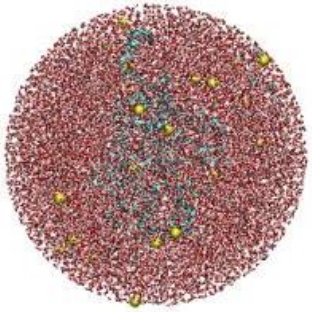
- Select interaction energy or molecular mechanics model
- Select boundary conditions, PBC?
- Select initial positions and velocities
- Select Ensemble (NVT, NVE, NPT, etc)
- Select target temperature, pressure, etc
- Select integrator, thermostat and barostat, etc
- Select timestep
- Perform equilibration
- Perform production simulation
- Analyze the results

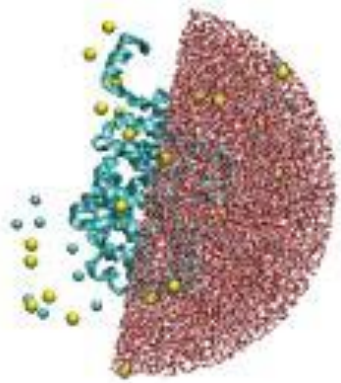
Topic: Molecular dynamics

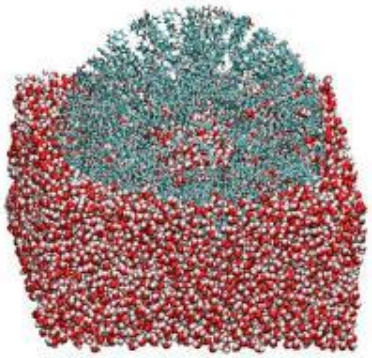
Initial configuration

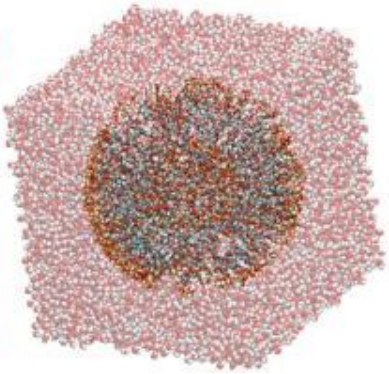
- Use packmol http://m3g.iqm.unicamp.br/packmol/











Initial velocities

- Assign velocities according to Boltzmann distribution:

$$\frac{1}{2}\sum m_i v_i^2 = \frac{3}{2} N k_B T$$

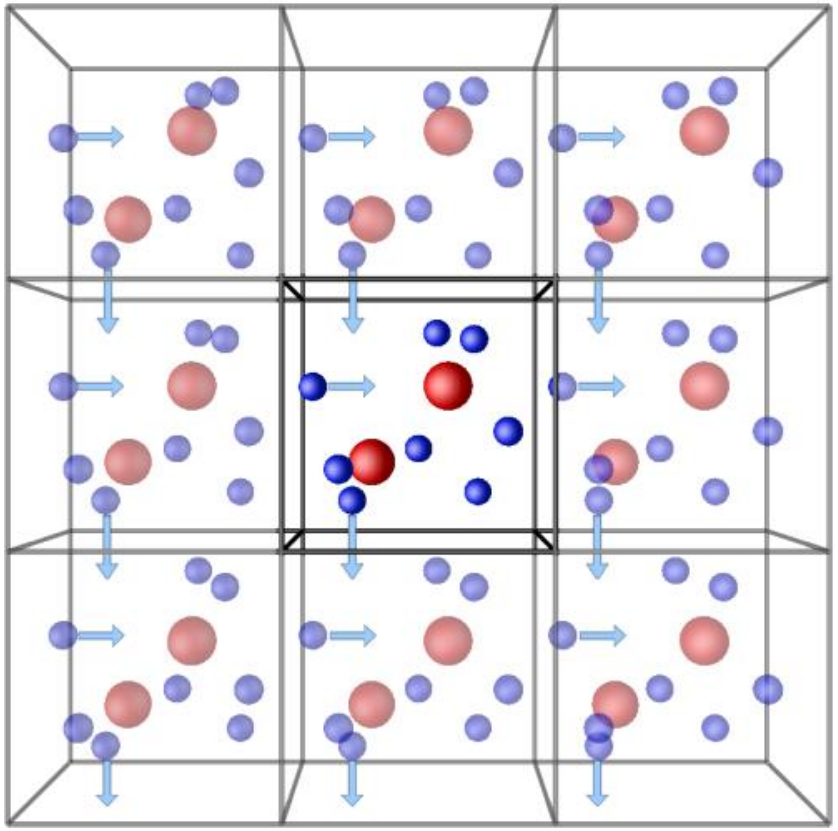
$$P(v_i) = \left(\frac{m_i}{2\pi k_B T} \right)^{1/2} \mathrm{e}^{\frac{-m_i v_i^2}{k_B T}}$$

Topic: Molecular dynamics

Benchmark

Potential	System	Atoms	Timestep	CPU	LJ Ratio
Granular	chute flow	32000	0.0001 tau	5.08e-7	0.34x
FENE bead/spring	polymer melt	32000	0.012 tau	5.32e-7	0.36x
Lennard-Jones	LJ liquid	32000	0.005 tau	1.48e-6	1.0x
DPD	pure solvent	32000	0.04 tau	2.16e-6	1.46x
EAM	bulk Cu	32000	5 fmsec	3.59e-6	2.4x
Tersoff	bulk Si	32000	1 fmsec	6.01e-6	4.1x
Stillinger-Weber	bulk Si	32000	1 fmsec	6.10e-6	4.1x
EIM	crystalline NaCl	32000	0.5 fmsec	9.69e-6	6.5x
SPC/E	liquid water	36000	2 fmsec	1.43e-5	9.7x
CHARMM + PPPM	solvated protein	32000	2 fmsec	2.01e-5	13.6x
MEAM	bulk Ni	32000	5 fmsec	2.31e-5	15.6x
Peridynamics	glass fracture	32000	22.2 nsec	2.42e-5	16.4x
Gay-Berne	ellipsoid mixture	32768	0.002 tau	4.09e-5	28.3x
AIREBO	polyethylene	32640	0.5 fmsec	8.09e-5	54.7x
COMB	crystalline SiO2	32400	0.2 fmsec	4.19e-4	284x
eFF	H plasma	32000	0.001 fmsec	4.52e-4	306x
ReaxFF	PETN crystal	16240	0.1 fmsec	4.99e-4	337x
ReaxFF/C	PETN crystal	32480	0.1 fmsec	2.73e-4	185x
VASP/small	water	192/512	0.3 fmsec	26.2	17.7e6
VASP/medium	CO2	192/1024	0.8 fmsec	252	170e6
VASP/large	Xe	432/3456	2.0 fmsec	1344	908e6

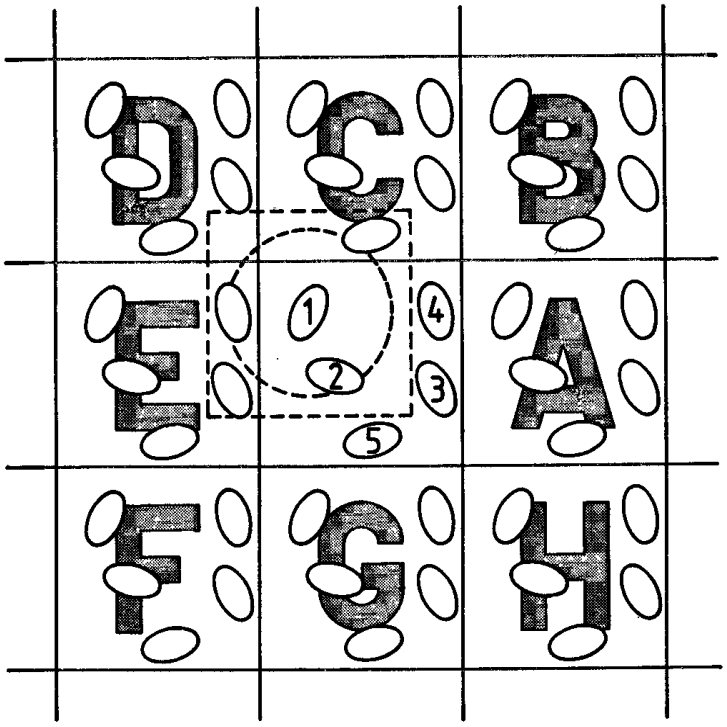
Periodic boundary conditions



No surface atoms !

Image coordinates:
x' = x + n1L
y' = y + n2L
z' = z + n3L

Minimum image convention



- Each i^{th} particle interacts with other as well as its images i_A, i_B..in neighboring boxes.
- Infinite no. of calculations
- Avoided: short-range forces
- Molecule 1 interacts with all those which lie within a certain radius, which is the closest periodic images of other N-1 molecules.

Computer simulations of liquids; Allen and Tildesley; Chapter 1

Topic:

Reading material

- Understanding Molecular Simulation. From Algorithms to Applications, Daan Frenkel and Berend Smit (Chapter 4. Read Chapter 1 and 2 as well)

- For packmol, See http://m3g.iqm.unicamp.br/packmol/home.shtml