

Topic: Molecular dynamics

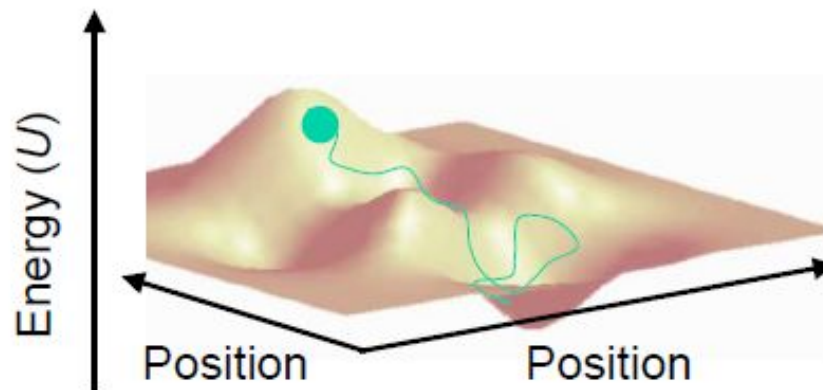
Objective

- 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

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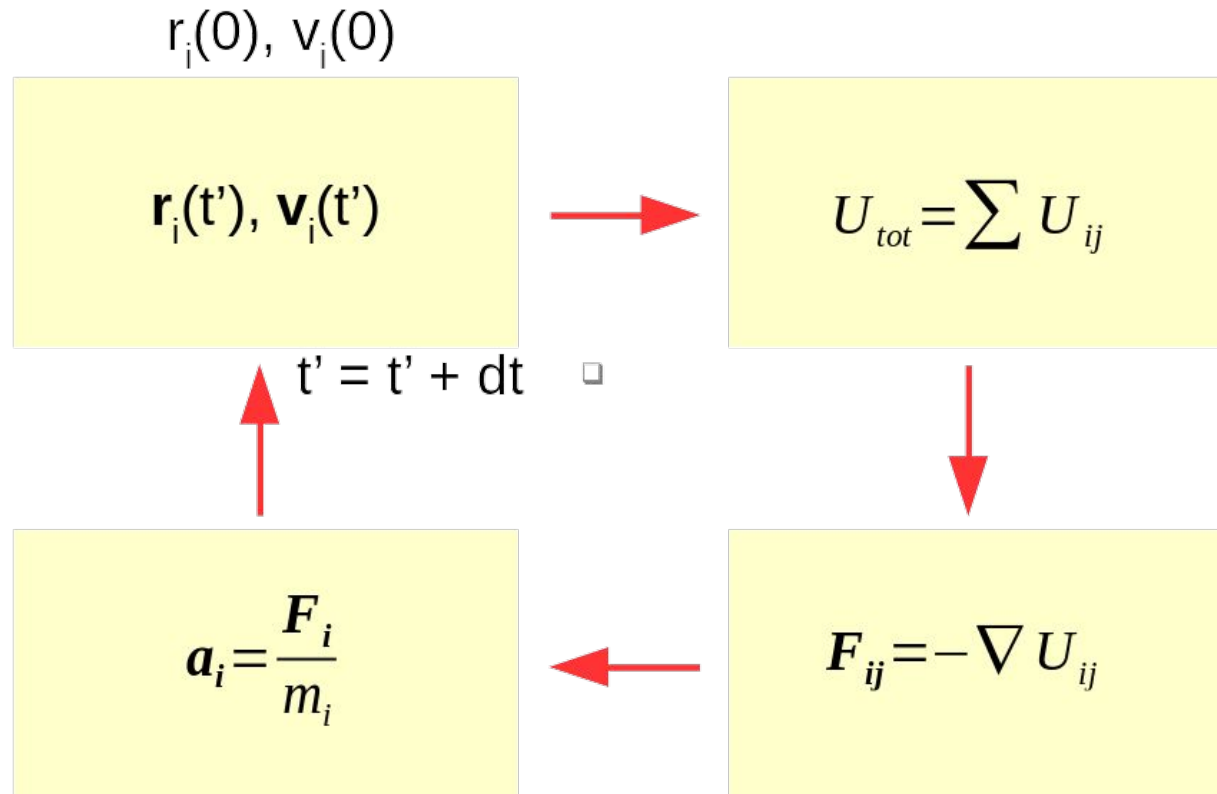
Molecular dynamics (MD)

- 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



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Molecular dynamics (MD)



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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
```

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Characteristics of good integrator

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

velocity-Verlet algorithm

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

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

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Properties from MD trajectories

- Potential energy
- density
- Temperature
- Pressure
- Enthalpy of vaporization

$$P = \frac{Nk_B T}{V} + \frac{\sum_i^{N'} r_i \bullet f_i}{dV}$$

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

- Isothermal compressibility

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

- Thermal expansion coefficient

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

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Properties from MD trajectories

- Self-diffusion coefficient

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

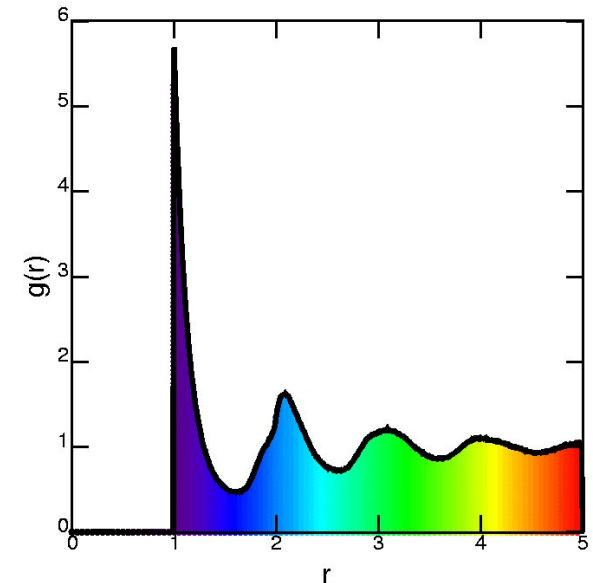
- Static dielectric constant

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

- Surface tension

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

- Pair correlation function or
radial distribution function



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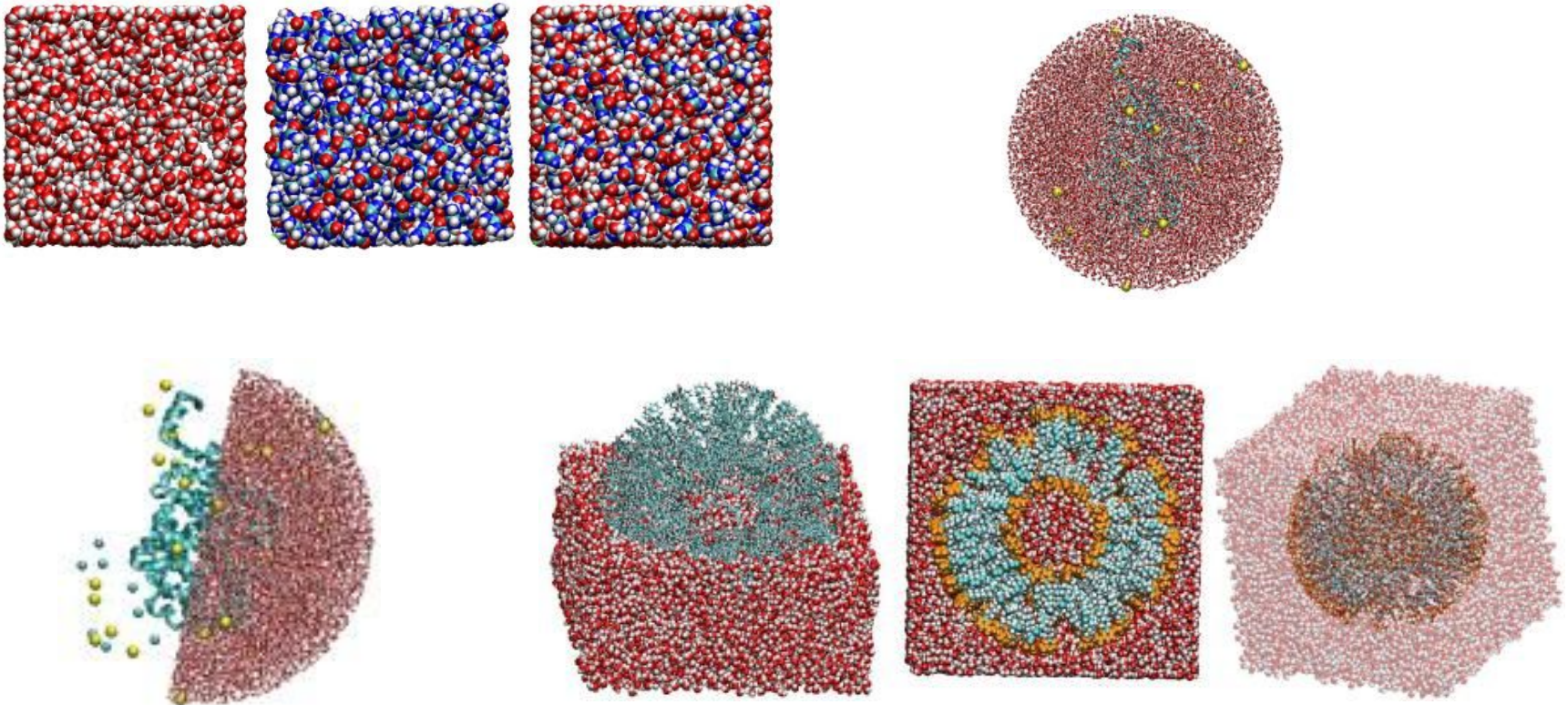
Steps in performing MD simulation

- 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

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Initial configuration

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



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Initial velocities

- Assign velocities according to Boltzmann distribution:

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

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

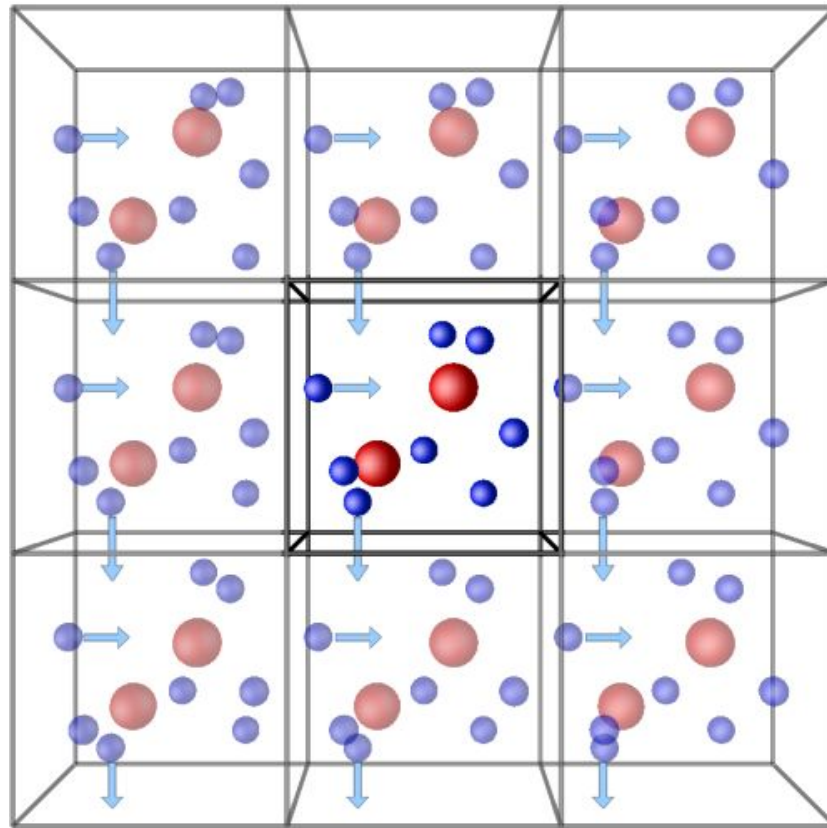
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Benchmark

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

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Periodic boundary conditions



No surface atoms !

Image coordinates:

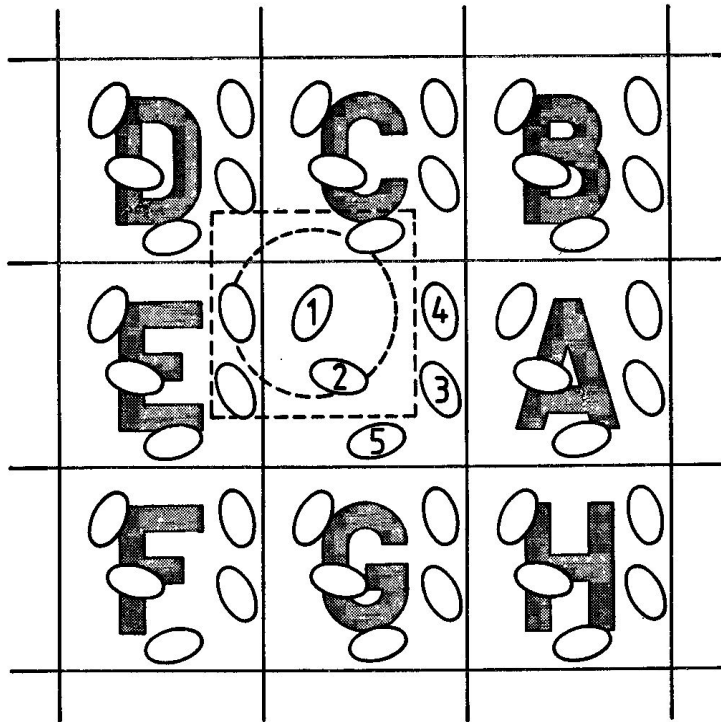
$$x' = x + n_1L$$

$$y' = y + n_2L$$

$$z' = z + n_3L$$

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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.

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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>