上海交通大學
材料科学与工程学院
School of Materials Science and Engineering, SJTU

MSE6701H Multiscale Materials Modeling and Simulation

Lecture 06

Molecular Dynamics Simulations

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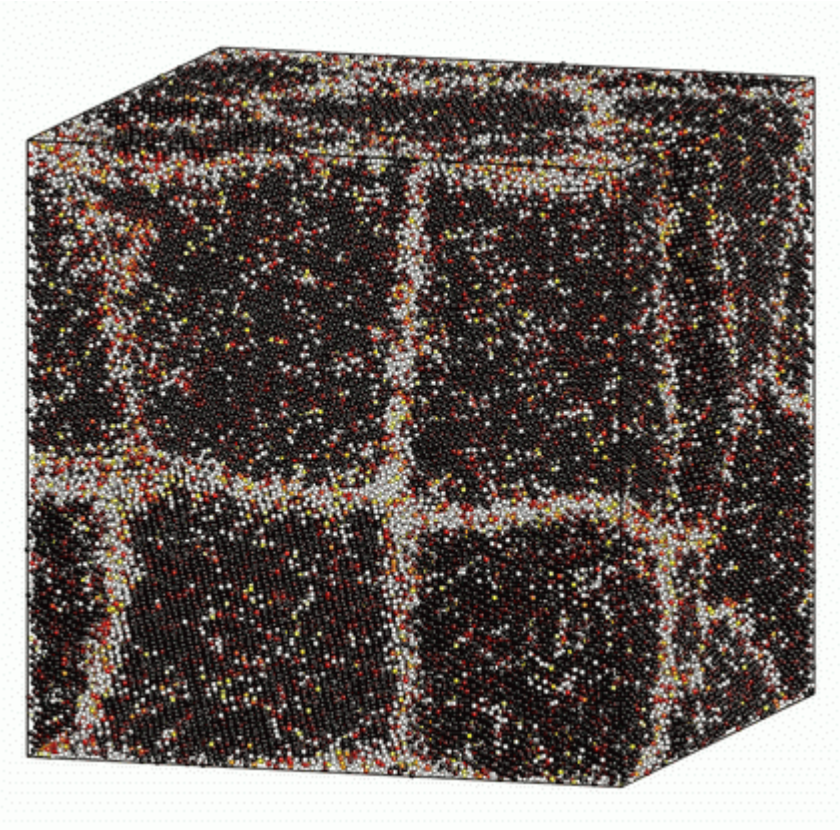
What is MD?

- Dynamics: a branch of mechanics that deals with forces and their relation primarily to the **motion** of bodies
- MD: Method that simulates the "real" dynamics of a collection of atoms, molecules, particles, or other objects.
- Method widely used in
  - Materials Science
  - Biological Sciences
  - Physics, Chemistry, Mechanics
- Method widely used for
  - Metal, ceramics, polymers, composites
  - Solids, liquids, gasses, and interfaces



MD: History

1953
- Metropolis et al.
- Metropolis Monte Carlo

1956
- Alder and Wainwright
- Molecular dynamics simulation of hard spheres

1964
- A Rahman
- MD for liquid Argon

1974
- Stillinger and Rahman,
- MD of liquid water

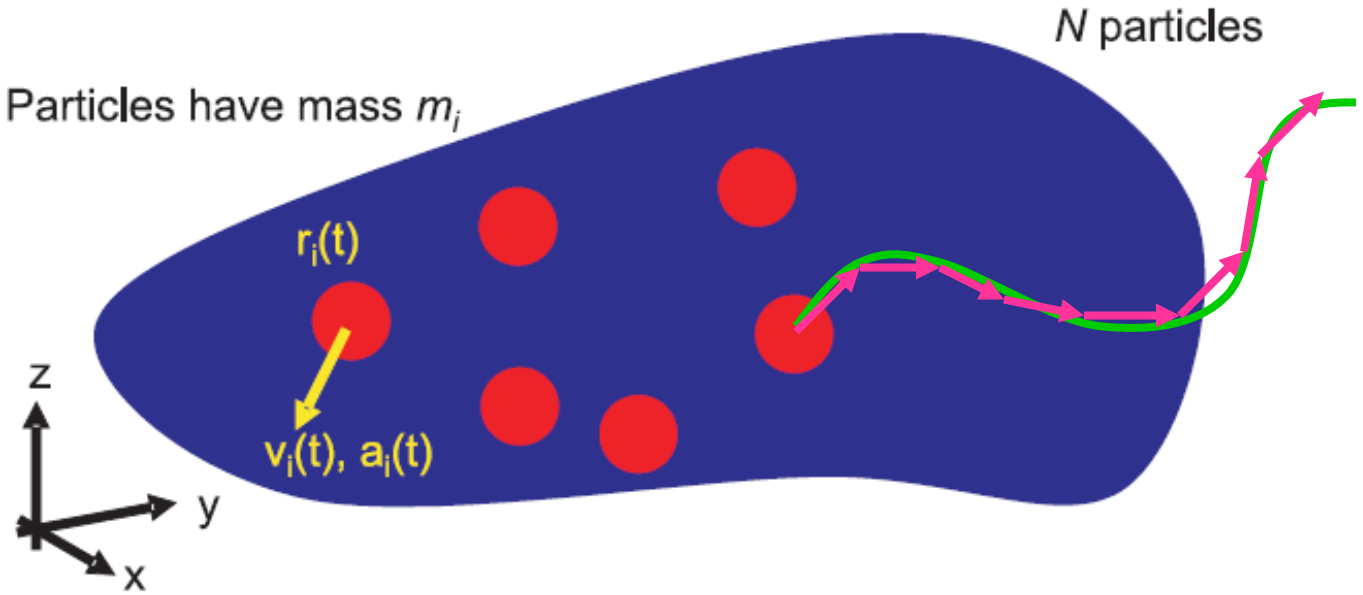
1980
- H. C. Andersen
- MD method for NPH, NVT, NPT ensembles

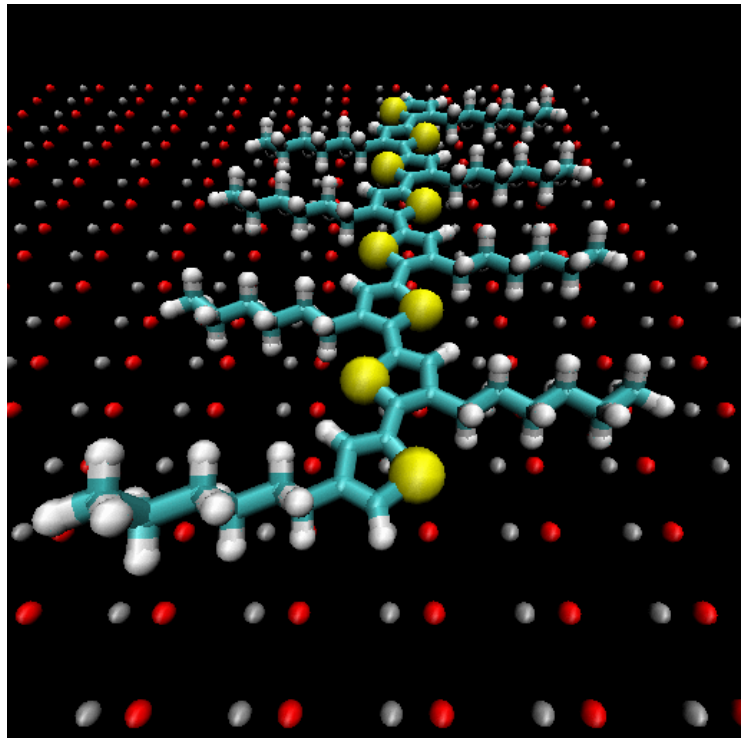
1986
- R. Car and M. Parrinello
- Ab initio MD

MD: Basic Idea

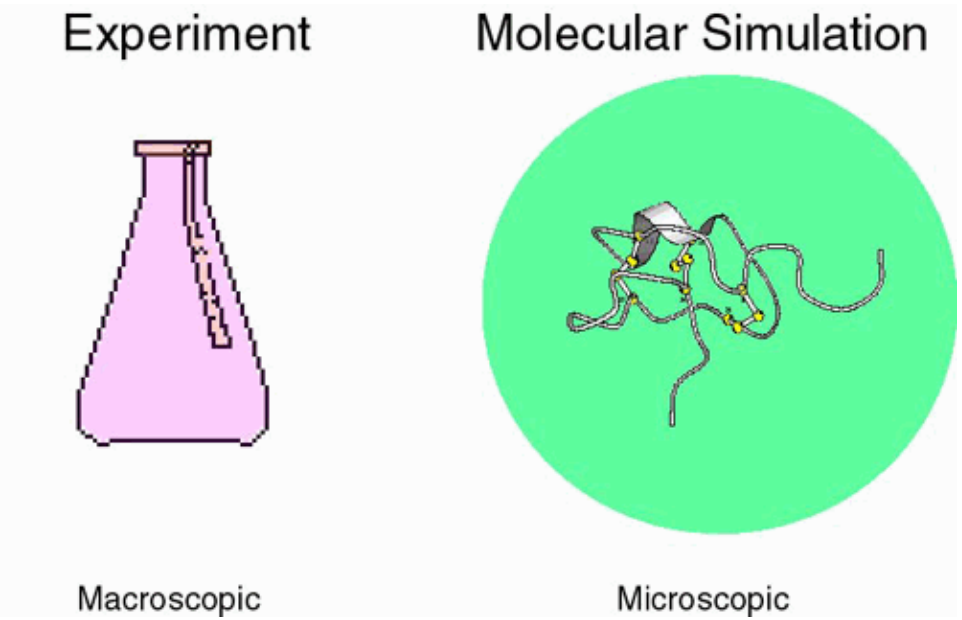
Solution of Newton's equations of motions for the particles

$$\boldsymbol{F = ma = m\ddot{r}}$$





MD: Basic Idea



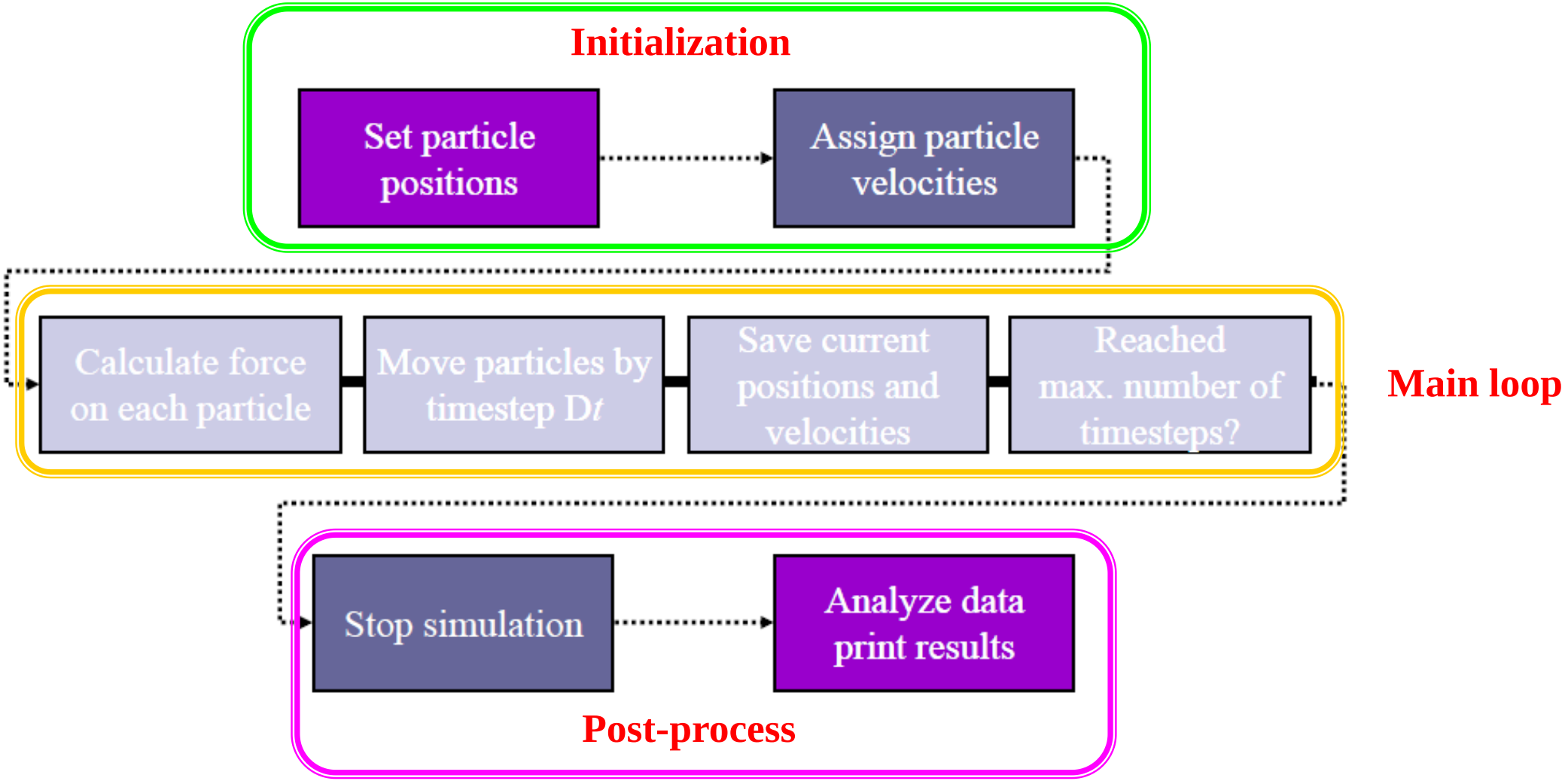
$$\langle A \rangle_{\text{ensemble}} = \int\int \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N A(\mathbf{p}^N, \mathbf{r}^N) \rho(\mathbf{p}^N, \mathbf{r}^N)$$

$$\rho(\mathbf{p}^N, \mathbf{r}^N) = \frac{1}{Q} \exp\left[-\frac{H(\mathbf{p}^N, \mathbf{r}^N)}{k_B T}\right]$$

$$Q = \int\int \mathrm{d}\mathbf{p}^N \mathrm{d}\mathbf{r}^N \exp\left[-\frac{H(\mathbf{p}^N, \mathbf{r}^N)}{k_B T}\right]$$

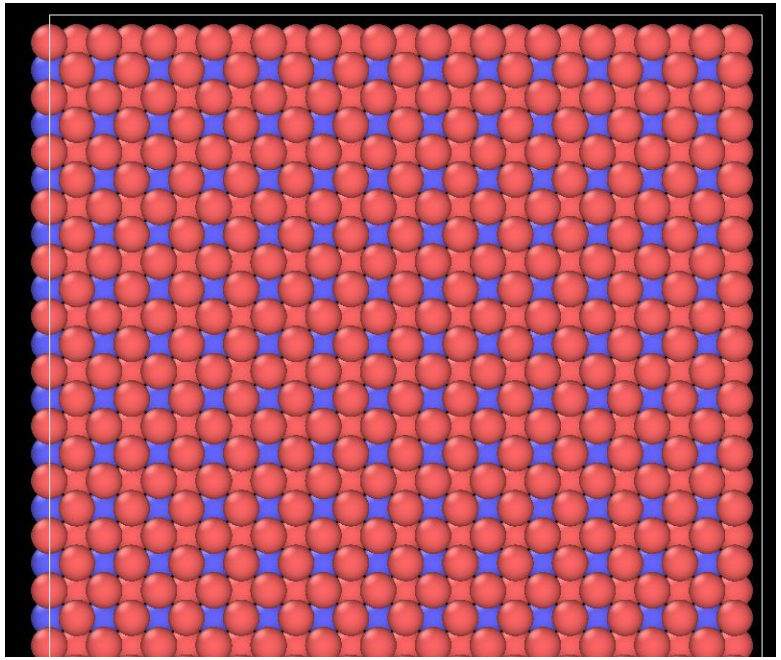
$$\langle A \rangle_{\text{time}} = \lim_{\tau\to\infty} \frac{1}{\tau} \int_{t=0}^{\tau} A\left(\mathbf{p}^N(t), \mathbf{r}^N(t)\right) \mathrm{d}t = \frac{1}{M} \sum_{t=1}^{M} A(\mathbf{p}^N, \mathbf{r}^N)$$

MD: General procedure



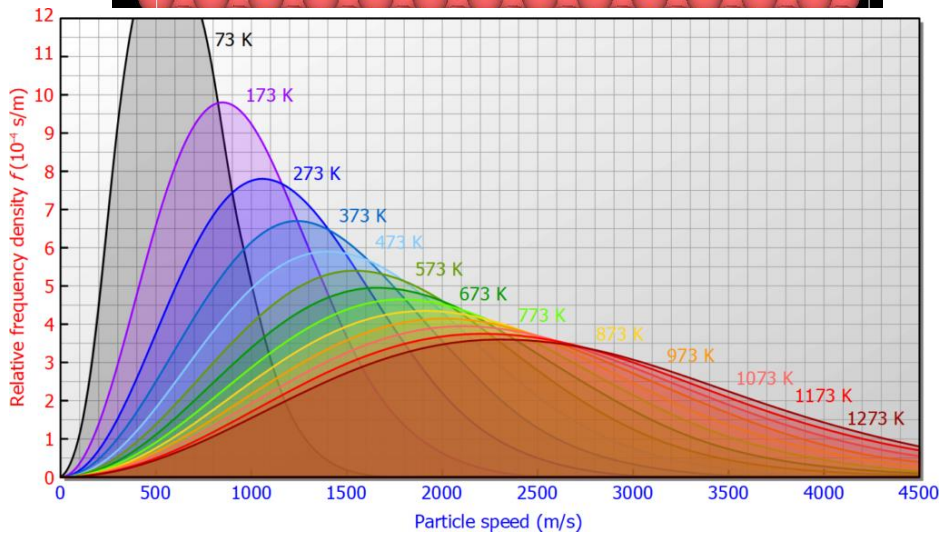
Initialization

- Initial atomic configuration
- Initial velocity (temperature)
- Boundary condition
- Controlling parameters



Maxwell-Boltzmann Distribution

$$p(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left[-\frac{1}{2}\frac{mv^2}{k_B T}\right]$$



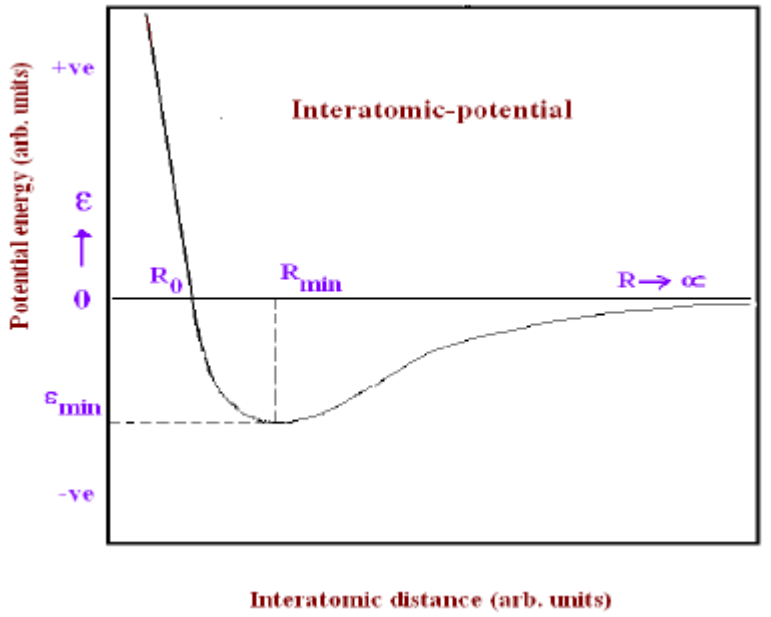
$$\sum_{i=1}^{N} m_i \mathbf{v}_i = 0 \qquad T = \frac{1}{3Nk_B}\sum_{i=1}^{N}\frac{|\mathbf{p}_i|^2}{2m_i}$$

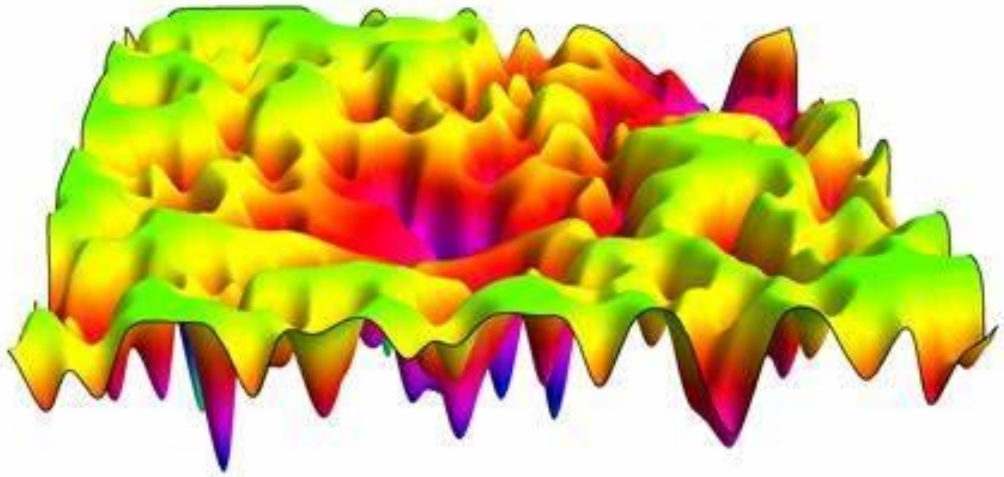
Force calculation

$$U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

$$\vec{f}_i = -\frac{\partial U}{\partial \vec{r}_i}$$

$$= -\sum_{j \neq i} \frac{\partial U}{\partial r_{ij}} \frac{\partial r_{ij}}{\partial \vec{r}_i}$$





Integration algorithm: Verlet algorithm

$$x = x_0 + v_0 t + \frac{1}{2} a t^2 + \frac{1}{6} b t^3 + \cdots$$

$$x(t + \Delta t) = x(t) + v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 + \frac{1}{6} b(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$$x(t - \Delta t) = x(t) - v(t)\Delta t + \frac{1}{2} a(t)\Delta t^2 - \frac{1}{6} b(t)\Delta t^3 + \mathcal{O}(\Delta t^4)$$

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t) + a(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

L. Verlet, *Computer experiments on classical fluids. I. Thermodynamical properties of Lennard-Jones molecules*, Physical Review **159**, 98 (1967)

Integration algorithm: Verlet algorithm

$$v(t) = \frac{x(t+\Delta t) - x(t-\Delta t)}{2\Delta t} + \mathcal{O}(\Delta t^2)$$

Disadvantages

$$v(t+\Delta t) = \frac{x(t+\Delta t) - x(t)}{\Delta t} + \mathcal{O}(\Delta t)$$

- **Error in velocity is $O(\Delta t^2)$**
- **Need $x(t+\Delta t)$ to get $v(t)$**
- **Numerical imprecision in adding small and big numbers**

$$x(t+\Delta t) - x(t) = x(t) - x(t-\Delta t) + a(t)\Delta t^2 + \mathcal{O}(\Delta t^4)$$

$O(\Delta t)$ $O(\Delta t)$ $O(\Delta t^2)$

Integration algorithm: velocity Verlet

$$x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2$$

$$a(t+\Delta t) = f(x(t+\Delta t))$$

$$v(t+\Delta t) = v(t) + \frac{1}{2}(a(t) + a(t+\Delta t))\Delta t$$

$$v(t+\frac{1}{2}\Delta t) = v(t) + \frac{1}{2}a(t)\Delta t$$

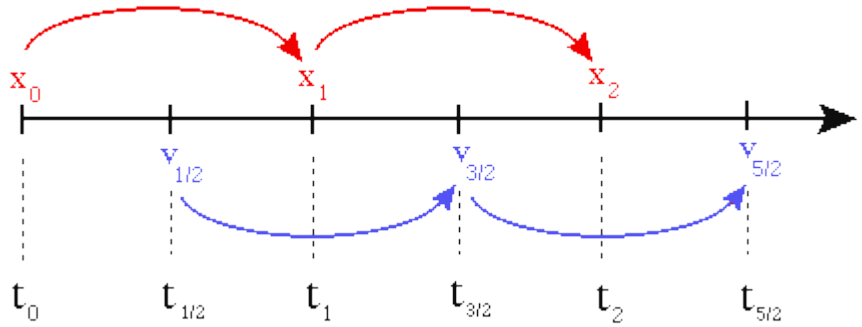
$$x(t+\Delta t) = x(t) + v(t+\frac{1}{2}\Delta t)\Delta t$$

$$a(t+\Delta t) = f(x(t+\Delta t))$$

$$v(t+\Delta t) = v(t+\frac{1}{2}\Delta t) + \frac{1}{2}a(t+\Delta t)\Delta t$$

Other integration algorithms

- Leap frog



- Beeman algorithm

$$x(t+\Delta t) = x(t) + v(t)\Delta t + \left(\frac{2}{3}a(t) - \frac{1}{6}a(t-\Delta t)\right)\Delta t^2 + O(\Delta t^4)$$

$$v(t+\Delta t) = v(t) + \left(\frac{1}{3}a(t+\Delta t) + \frac{5}{6}a(t) - \frac{1}{6}a(t-\Delta t)\right)\Delta t + O(\Delta t^3)$$

- Gear algorithm

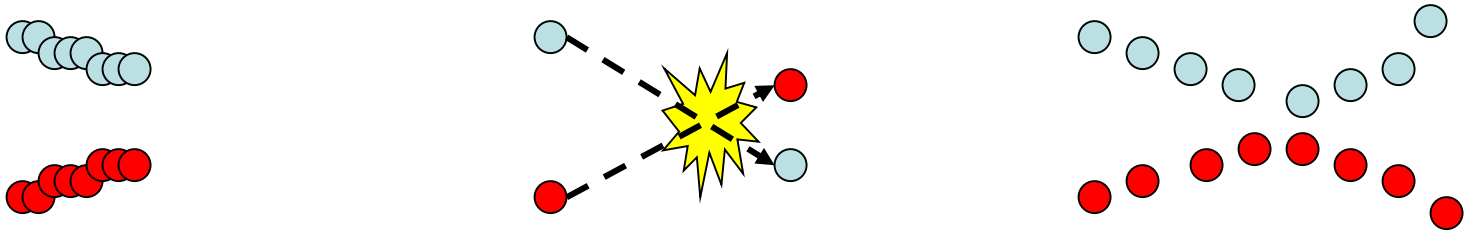
  Prediction → Correction

- Tuckerman, Berne and Martyna

  Reversible multiple time scale

Time step

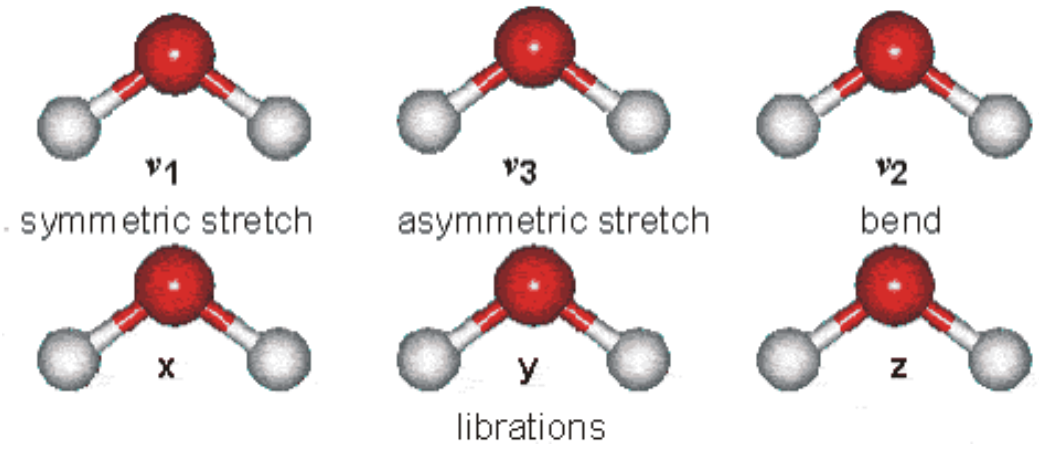
$$x(t+\Delta t) = x(t) + v(t)\Delta t + \frac{1}{2}a(t)\Delta t^2$$

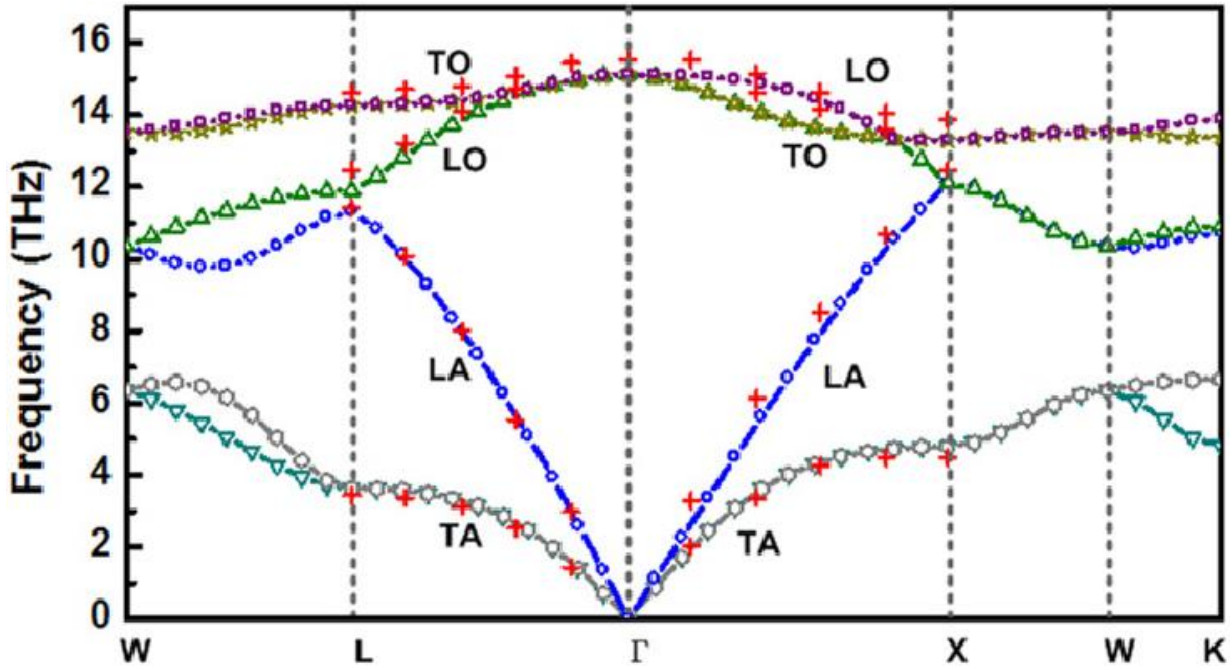


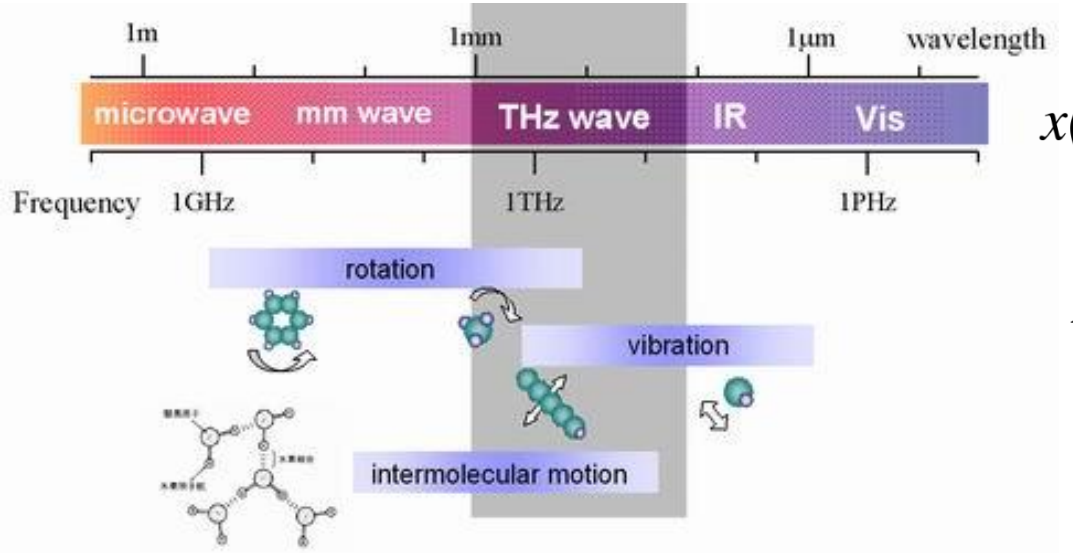
Too small　　Too large　　Just fine

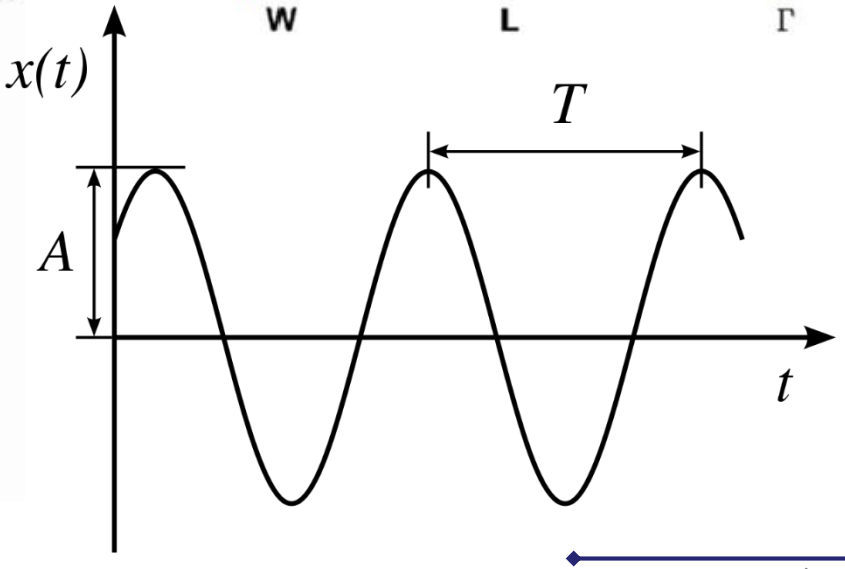
- As large as needed to generate trajectory sufficient long for problem
- Can’t be too large, otherwise inaccurate or unstable
- Must be smaller than the smallest time modeled

Time step



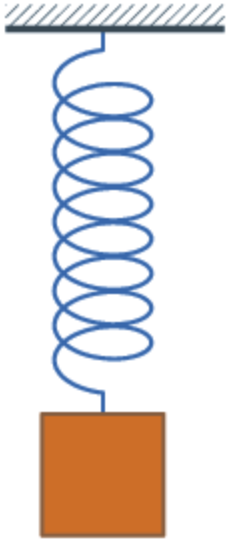






$$\Delta t \sim \frac{T_{\min}}{20\sim50}$$

First MD: harmonic oscillator



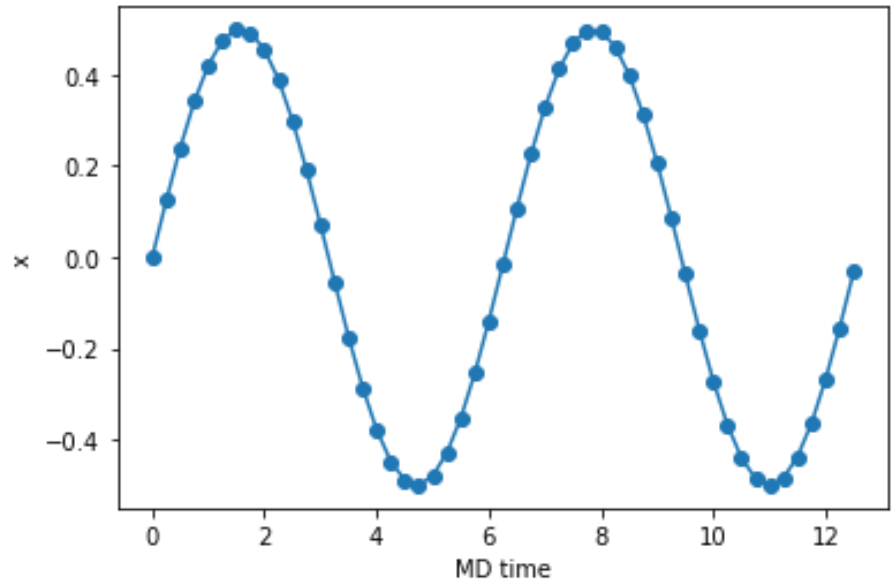
```python
def MD_Harmonic():
    mass = 1.
    k    = 1.
    x    = 0.
    f    = -k * x
    v    = 0.5
    a    = f / mass

    period = 2.*np.pi*np.sqrt(mass/k)
    dt   = 0.05
    half_dt = dt * 0.5
    nsteps = int(2.*period/dt)
    ioutput = 5

    thermo = list()
    Ep = 0.5*k*x*x
    Ek = 0.5*mass*v*v
    Et = Ep + Ek
    thermo.append([0, 0*dt, x, v, Ep, Ek, Et])

    for istep in range(1,nsteps+1):
        v = v + a * half_dt
        x = x + v * dt
        f = -k * x
        a = f / mass
        v = v + a * half_dt

        if istep%ioutput == 0:
            Ep = 0.5*k*x*x
            Ek = 0.5*mass*v*v
            Et = Ep + Ek

            thermo.append([istep, istep*dt, x, v, Ep, Ek, Et])
    return thermo
```

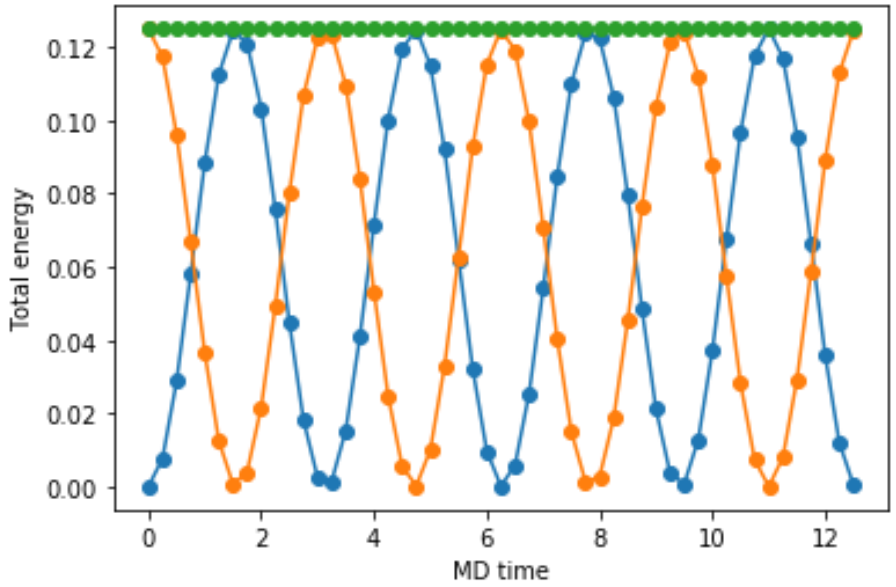
Initialization

Setup

Verlocity-verlet

Property

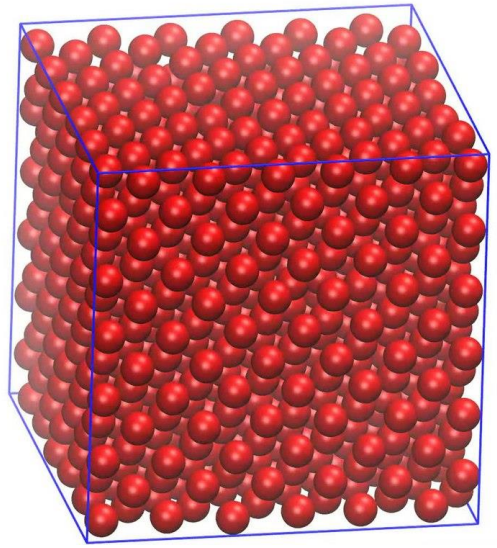




Boundary Conditions

Simulation cell: domain within which the simulation is carried out.

- **Frequently orthogonal**
- **Non-orthogonal also possible**

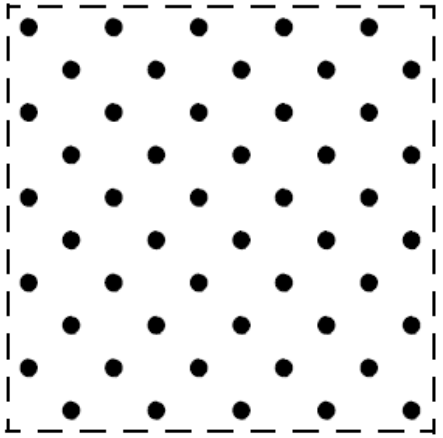


Problem: What to do with the atoms at the borders?

Option 1: free boundary

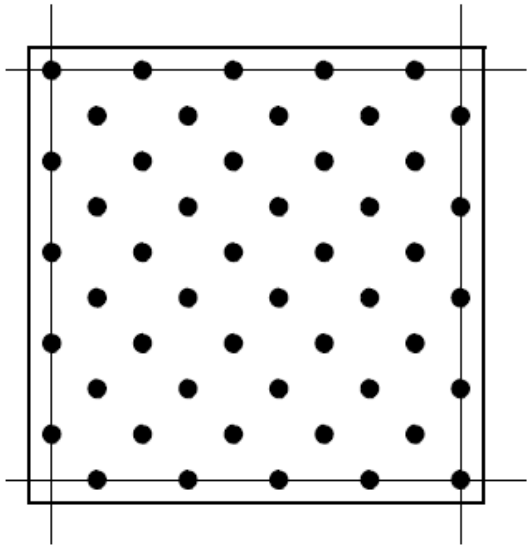
✓ **Suitable for single molecule, cluster, nanoparticle**

☐ **Does not work for bulk materials: dangling bonds**



Boundary Conditions

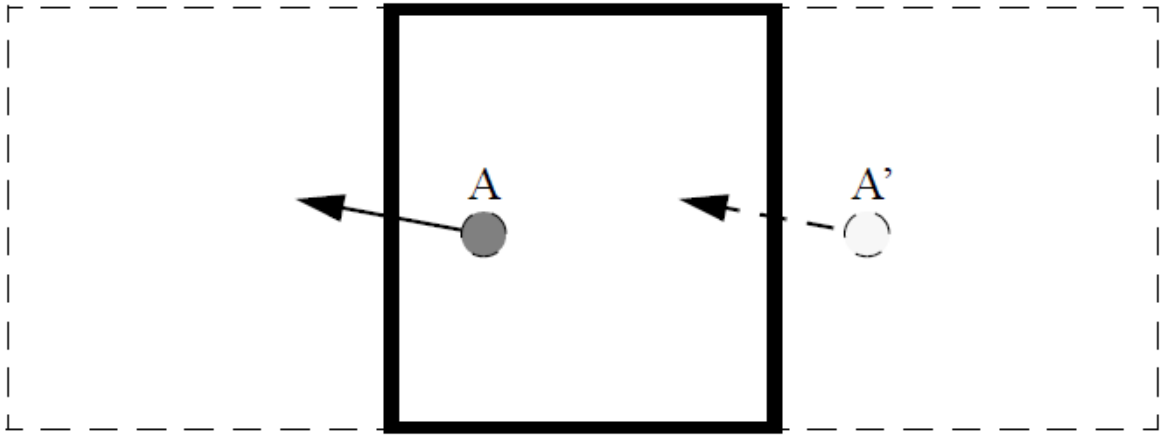
Option 2: fix the boundary atoms



- ✓ Completely unphysical, generally avoided
- ✓ Sometimes needed

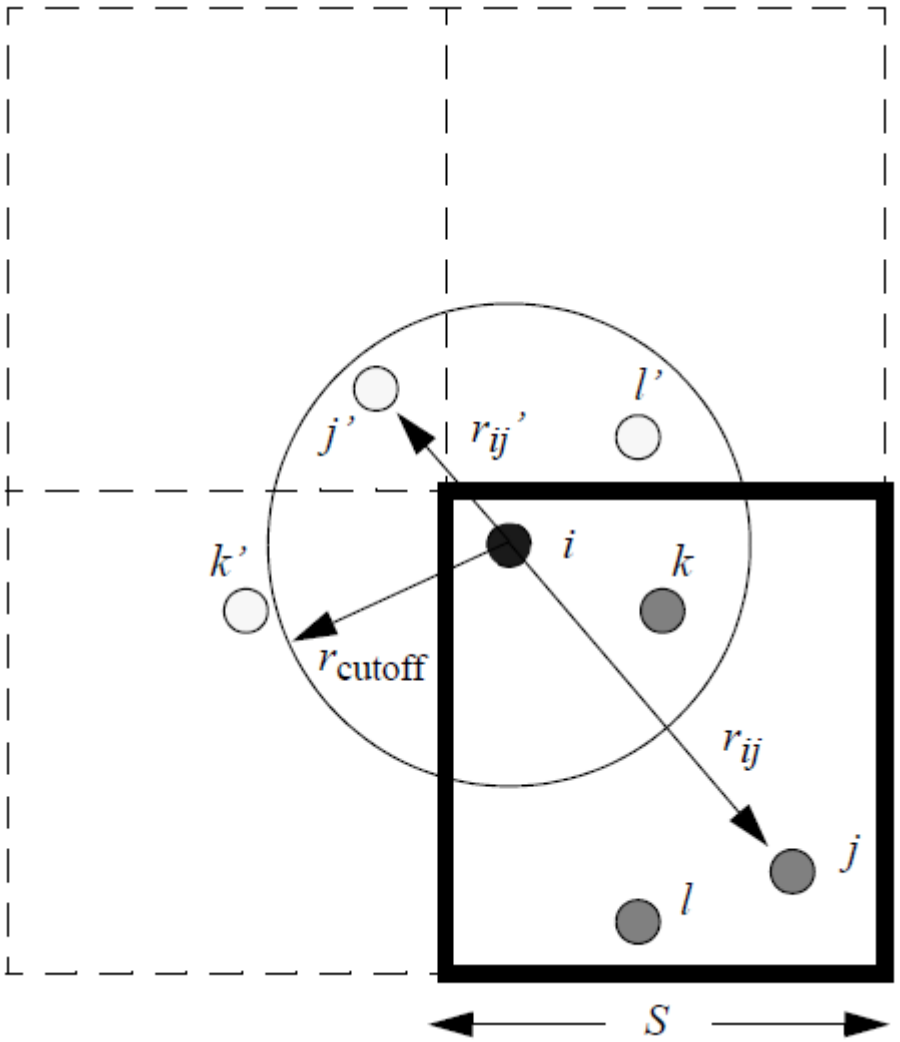
Option 3: Periodic boundary condition

- ✓ Atoms passing the boundary comes back on the other side
- ✓ PBC must be considered when evaluating distances



http://www.acclab.helsinki.fi/~knordlun/moldyn/

Periodic boundary condition



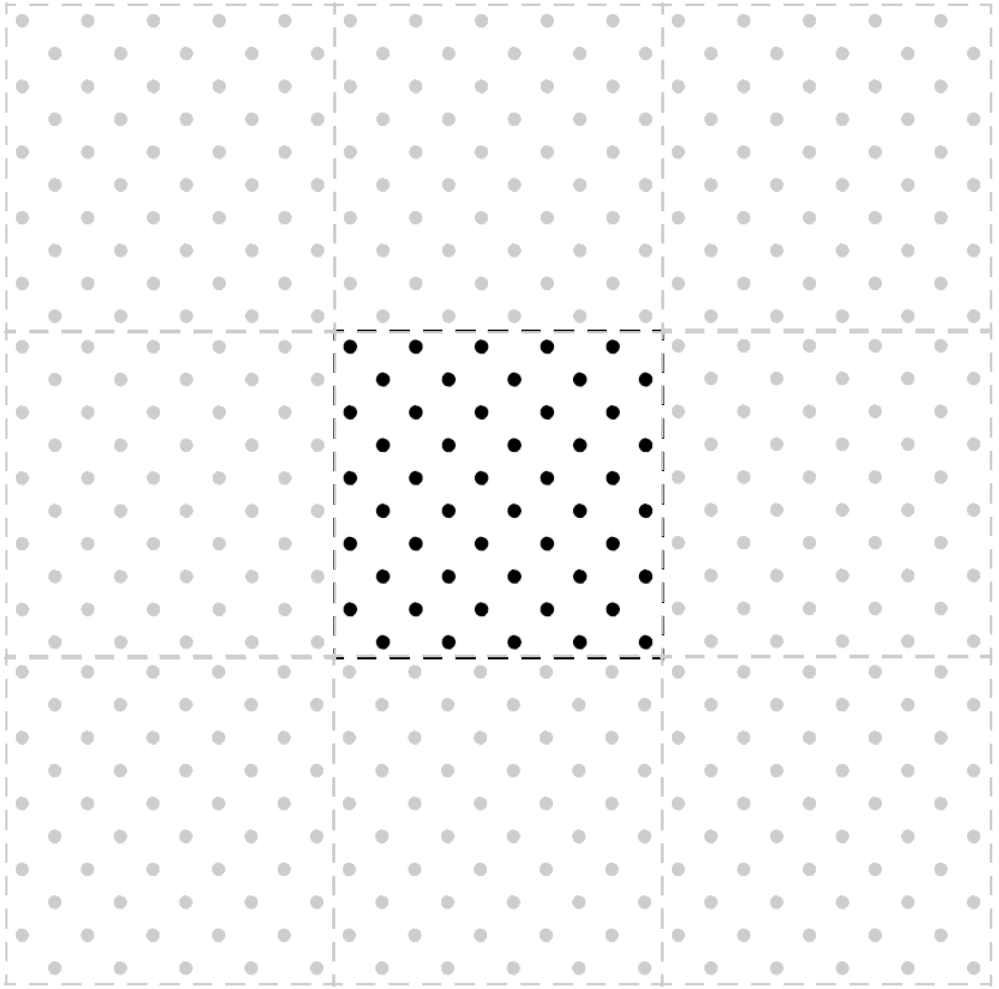
$$\vec{\mathbf{r}}_{ij} = x_{ij}\vec{\mathbf{x}} + y_{ij}\vec{\mathbf{y}} + z_{ij}\vec{\mathbf{z}}$$

$$x_{ij} = x_j - x_i$$

```
if pbc_x:
    while xij > 0.5*xbox:
        xij = xij - xbox
    while xij <= -0.5*xbox:
        xij = xij + xbox
```

http://www.acclab.helsinki.fi/~knordlun/moldyn/

Periodic boundary condition



Pro:

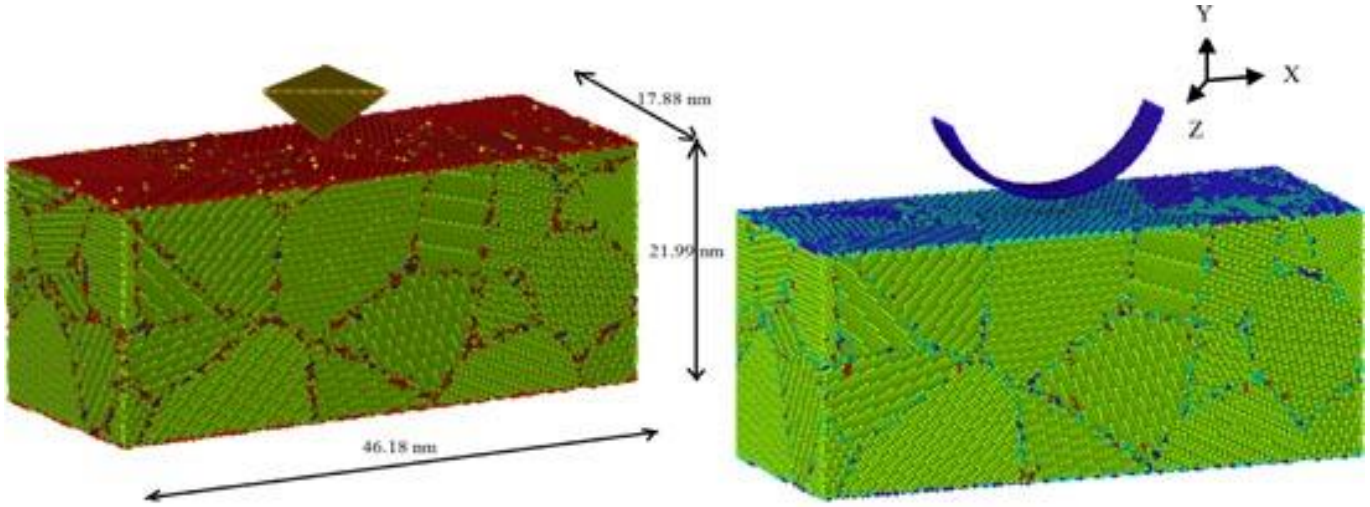
- ✓ Eliminate free surface
- ✓ Model infinite system

Con:

- ☐ Artificial interaction across boundary
- ☐ Upper limit for phonon wavelength
- ☐ Size scaling test generally required

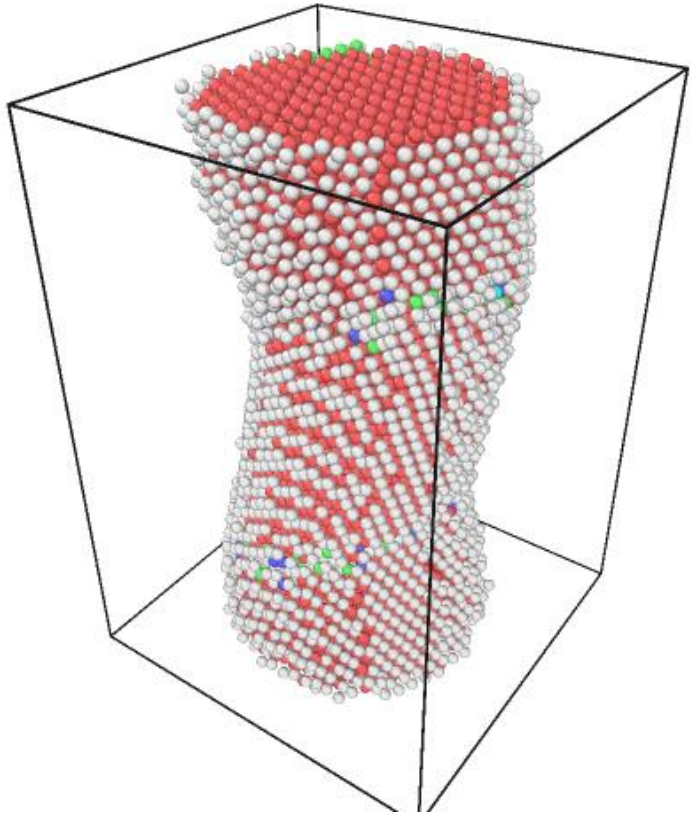
http://www.acclab.helsinki.fi/~knordlun/moldyn/

Mixed boundary conditions



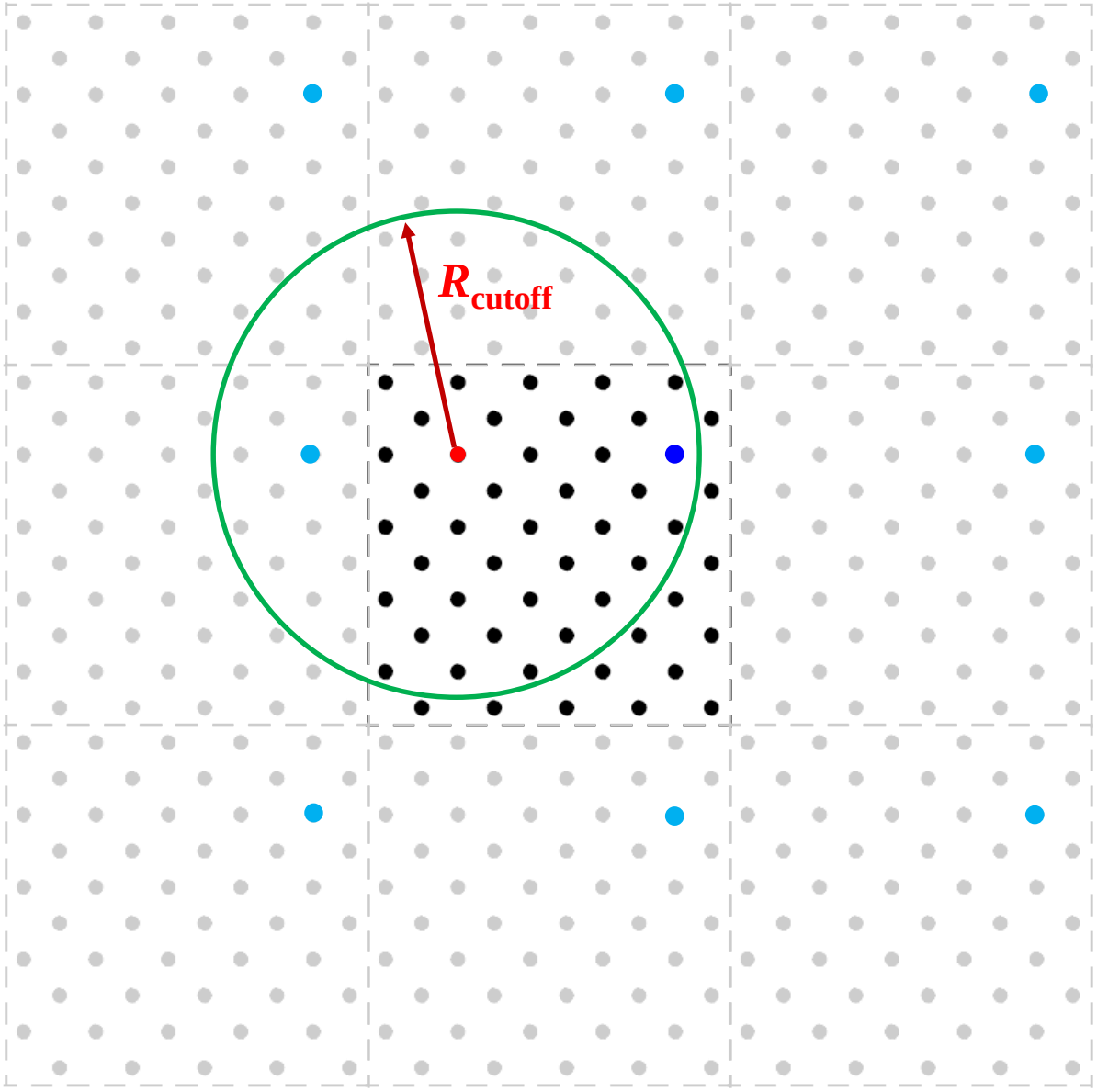
(a) Berkovich (pyramidal) indenter (b) Spherical (arc) indenter

Side	BC
Y+	Free
Y-	Fixed
X	Periodic
Z	Periodic



Side	BC
Axial	Periodic
Transverse	Free

Minimum Image Convention

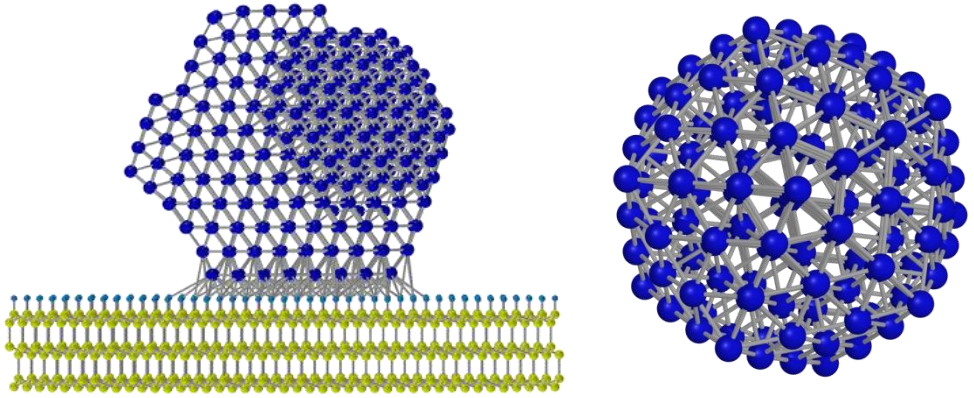


$$L > 2*R_{cutoff}$$

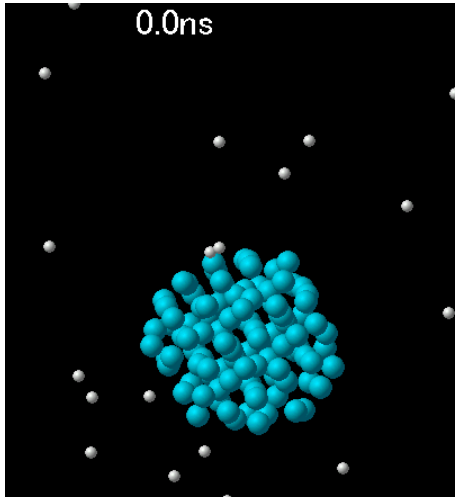
Guarantees that an atom interacts with at most one of the other atoms and its images.

Capability of MD

- ☑ **Structural**: crystal structure, defects (vacancies, interstitials, dislocations, grain boundaries, precipitates)
- ☑ **Thermodynamic**: equation of state, heat capacities, thermal expansion, free energies
- ☑ **Mechanical**: elastic constants, cohesive and shear strength, elastic and plastic deformation, fracture toughness
- ☑ **Vibrational** : phonon dispersion, vibration frequencies, molecular spectroscopy
- ☑ **Transport** : diffusion, viscous flow, thermal conduction



Ag on H-Si(111) *vs* free standing Ag particle

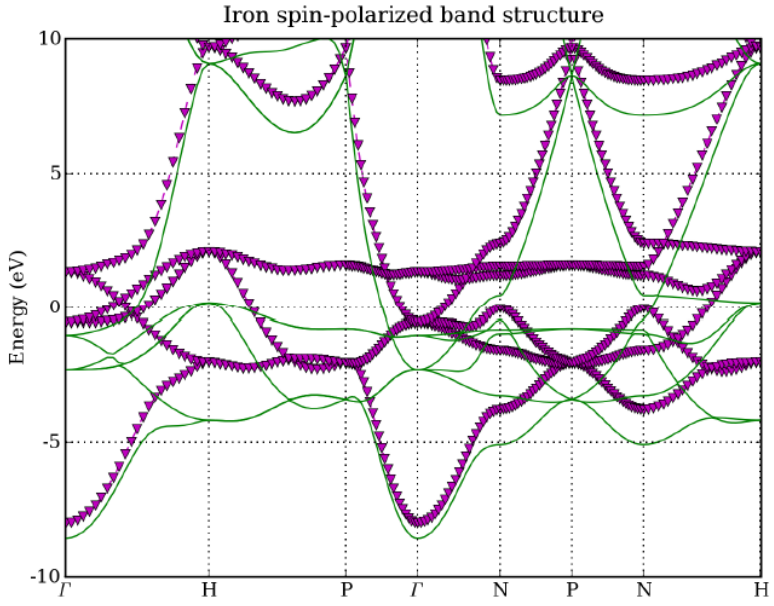


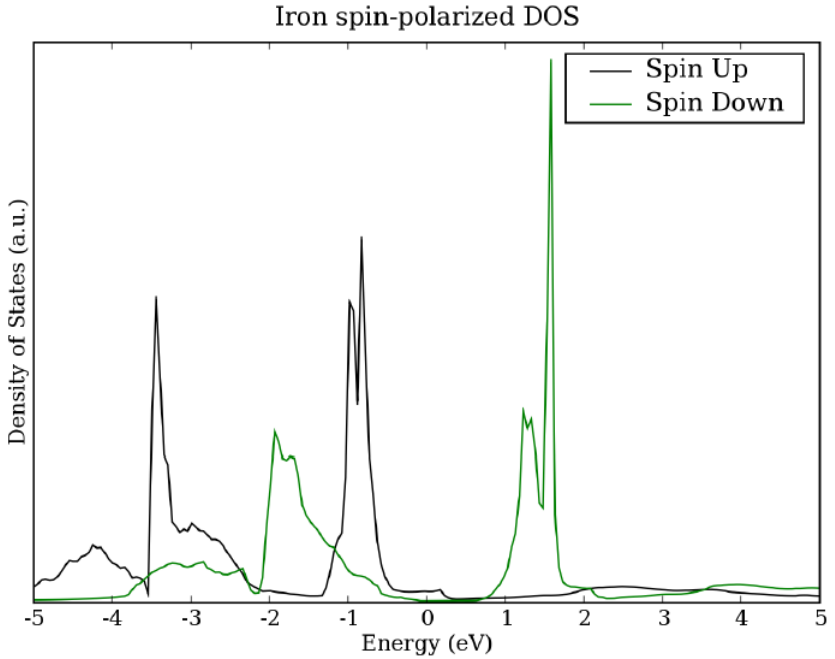
Growth of SWCNT via CVD

Limitation of MD

- There are properties which classical MD cannot calculate because electrons are involved.

- To treat electrons properly one needs quantum mechanics. In addition to electronic properties, optical and magnetic properties also require quantum mechanical (first principles or *ab initio*) treatments.



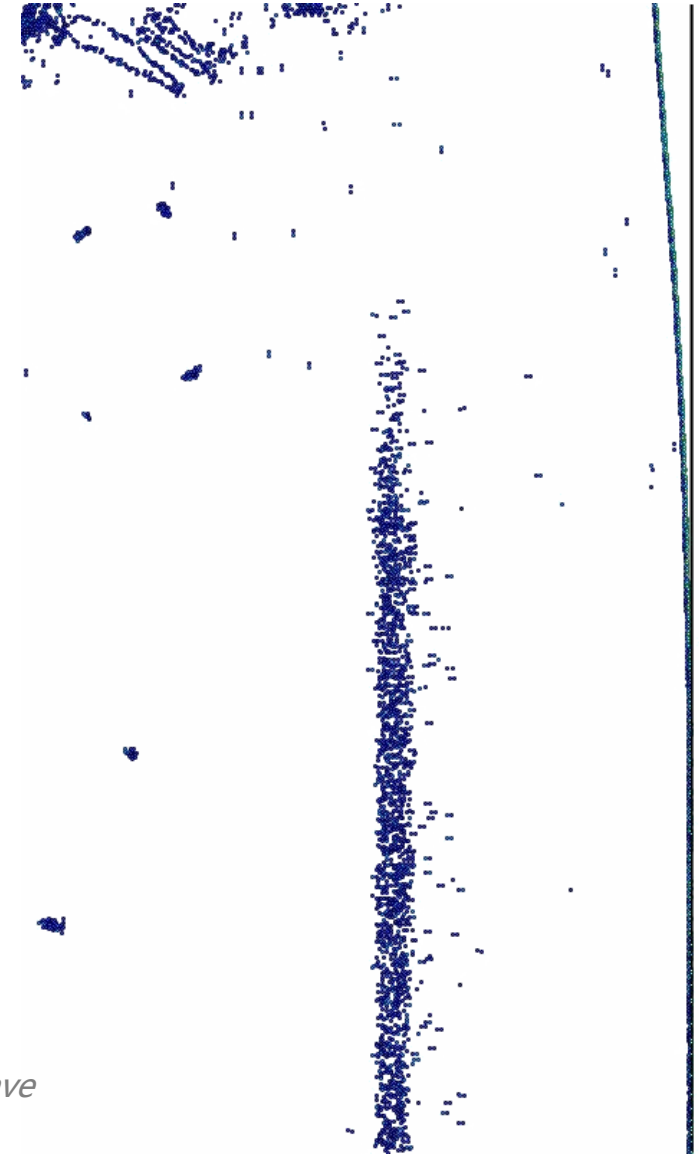


- **Time scale: *ns***
- **Length scale: *nm***

Yet MD is still a unique tool …

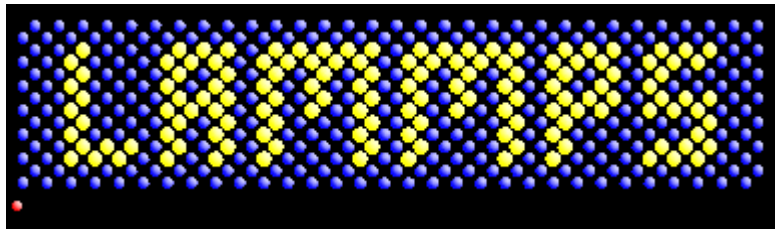
- **Unified study of all physical properties**
- **Several hundred particles are sufficient to simulate bulk matter**
- **Direct link between potential model and physical properties**
- **Complete control over input, initial and boundary conditions**
- **Detailed atomic trajectories**

(adapted from S. Yip, Nuclear Engrg./MIT.)



Video from: V. V. Stegailov and A. V. Yanilkin, *Structural transformations in single-crystal iron during shock-wave compression and tension: Molecular dynamics simulation*, J of Expt and Theoretical Physics, 104, 928-935 (2007).

Popular codes



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Discovery Studio Visualization tools you can to view molecular data

OVITO

Atomeye

VMD
Visual Molecular Dynamics

Home work

Extend the MD_Harmonic_Oscillator code to simulate a one-dimension periodic array of particles, where particles interact with their nearest neighbors only via a spring.

- You can use any programming language; (python, c++, fortran, perl, java, julia…)
- You would need to use arrays;
- You would need to write the thermal info to a file;
- You could visualize the output with gnuplot, matplotlib, xmgrace, origin…
- Due: Nov 10th, 2021

Next Lecture：

Interatomic Potentials