Computational Material Science
Part I

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➢ Simulation conditions

NVT : constant N, V, T (number of particles, volume, temperature)
- the so-called canonical ensemble (often used in MC)

NVE : constant N, V, E (number of particles, volume, energy)
- the so-called microcanonical ensemble (often used in MD)

NPT : constant N, P, T (number of particles, pressure, temperature)
- the so-called isothermal-isobaric ensemble

μVT : constant μ, V, T (chemical potential, volume, temperature)
- the so-called grand canonical ensemble

What is chemical potential , μ ?

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}$$

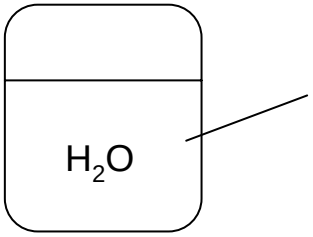
Under the condition of constant T and V, chemical potential is the partial derivative of Helmholtz free energy

- Potential energy surface can be based on
  - empirical energy function (MM)
  - quantum mechanical energy function (QM)
  - combined (QM/MM)
- Initial configuration: from experimental and/or optimized

  Note: MD and MC are time-consuming when hundreds to thousands of atoms are handled. Do not start from a configuration that is far from your interested target.
- Equilibration phase: enable the system to evolve from the starting configuration to reach equilibrium (monitored by quantities such as E, T, P).
- Averaging phase: at this stage, data are accumulated for the calculation of interested quantities. (E.g., energy, heat capacity, free energy, radial distribution function, correlation function, diffusion constant, etc…)

- Boundaries

How to simulate the bulk with efficiency?



1 liter of water = 3.3×10^{25} molecules

The molecular diameter of water is 2.8 Å
If interactions with the walls extend up to 10 molecular diameters,
Only 2×10^{19} molecules are interacting with the wall. (one in 1.5 million)

$\therefore$ Simulate bulk without considering the wall

$\Rightarrow$Periodic boundary condition
Examples: surfaces, bulk materials

$\Rightarrow$Non-periodic boundary condition
Examples: hydrated enzyme, conformation analysis of a molecule
or a molecular complex

⇒Periodic boundary condition (PBC) : enable a simulation to be performed using a relatively small number of particles, in such a way that the particles experience forces as if they were in bulk fluid.

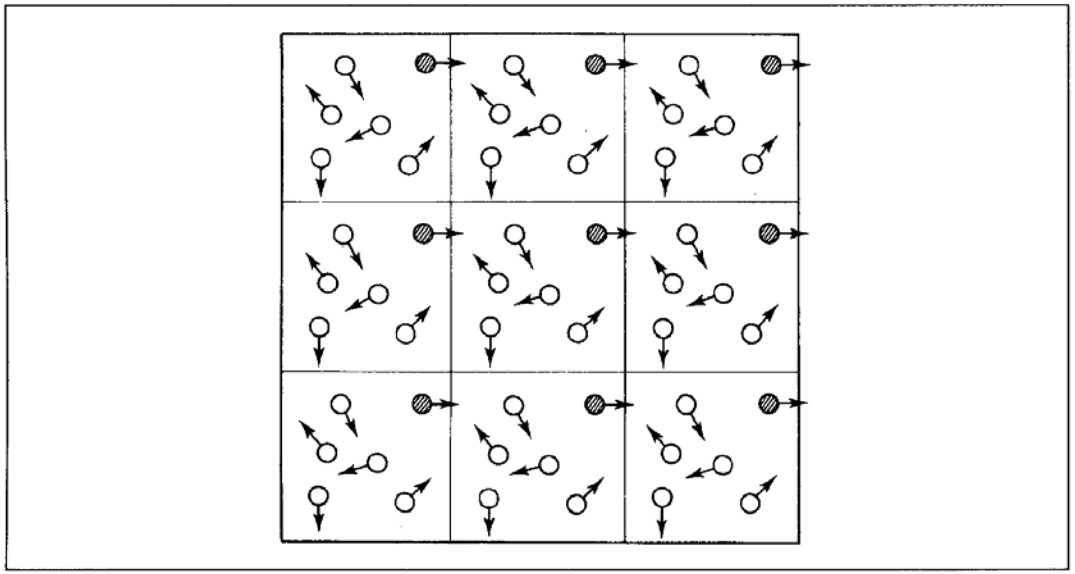


Fig. 6.4: Periodic boundary conditions in two dimensions.

Note: other shapes are possible in PBC

In 2-dimensional case, each box is surrounded by 8 neighbours;
3-dimensional 26

• Coordinates of the particles in the image boxed can be computed by adding or subtracting integral multiples of the box sides.

• A particle leaving the box is replaced by an image particl that enters from the opposite side (so N is constant).

- Cutoff distances and the minimum image convention

In MM force fields, the numbers of bond-stretching, angle-bending, and torsion are proportional *N* (the number of atoms), but the number of non-bonded terms increase as N^2 in a pairwise model.

$\therefore$ calc. of nonbonded => time consuming! => beyond a cutoff distance the energy is set to zero or calculated differently

The Lennard-Jones potential (for vdW interaction) falls off very rapidly with distance

$\Rightarrow$ at 2.5σ, the Lennard-Jones potential has just 1% of its value at σ!

The electrostatic interaction (1/r) falls off far less rapidly than Lennard-Jones interaction

$\Rightarrow$ larger cutoff distance is needed or special treatment

(for details, see chap 6.8 of Molecular Modelling: Principles and Applications)

Rule of thumb for cutoff distance?

- At least 10 Å
- The minimum image convention: each atom "sees" at most just one image of every other atom in the system; that is, should not see its own image or the same atom twice. => the cutoff distance cannot be larger than half of the cell length

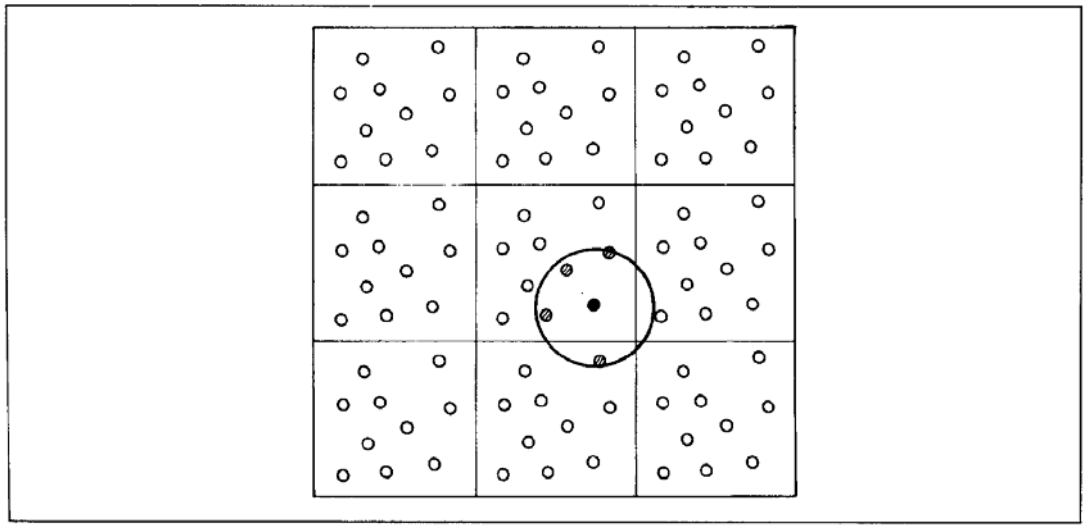
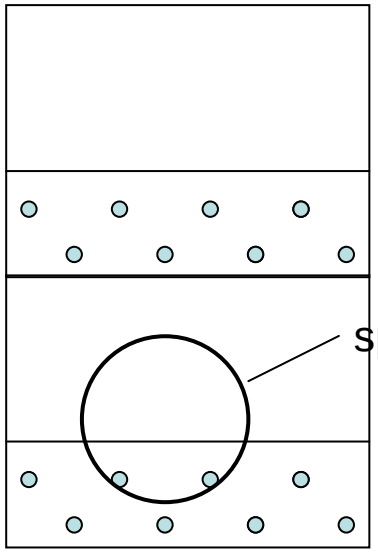


Fig. 6.11: The spherical cutoff and the minimum image convention.

PBC conditions are normally 3D. *How to model surface?*

- Increase the cell dimension for the direction perpendicular to the surface
- Choose a cell length that is longer than the cutoff distance, so one slab do not see the next slab



- Structure analysis : Radial distribution function (rdf)

Consider a spherical shell of thickness δr at a distance r from a chosen atom, the pair distribution function, $g(r)$, gives the probability of finding an atom in that shell compared to the ideal gas distribution.

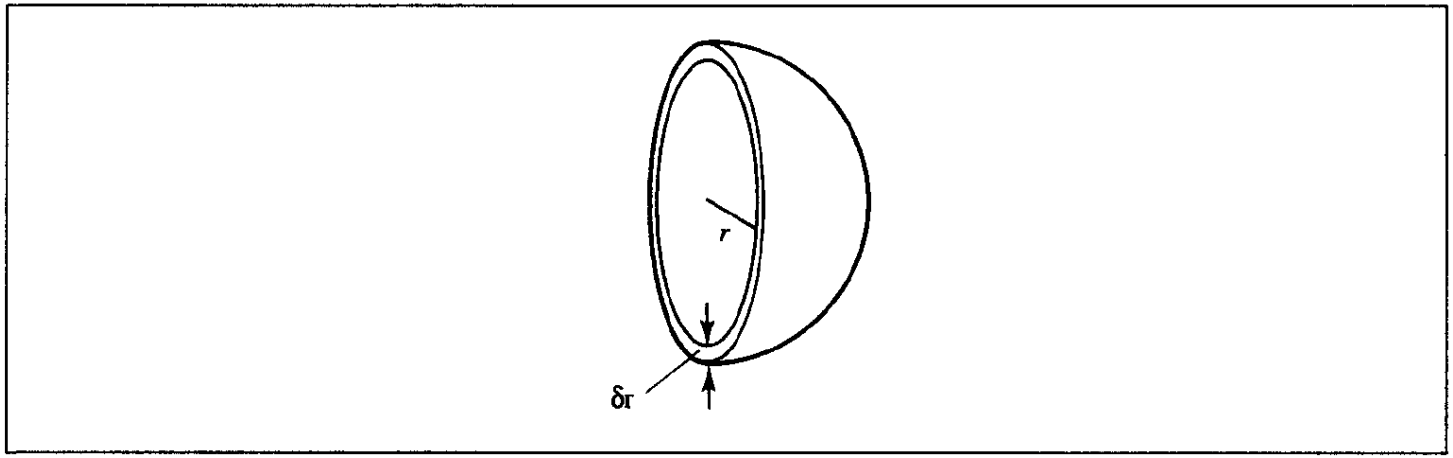


Fig. 6.1: Radial distribution functions use a spherical shell of thickness δr.

$$V = \tfrac{4}{3}\pi(r+\delta r)^3 - \tfrac{4}{3}\pi r^3$$

$$= 4\pi r^2\delta r + 4\pi r\delta r^2 + \tfrac{4}{3}\pi\delta r^3 \approx 4\pi r^2\delta r$$

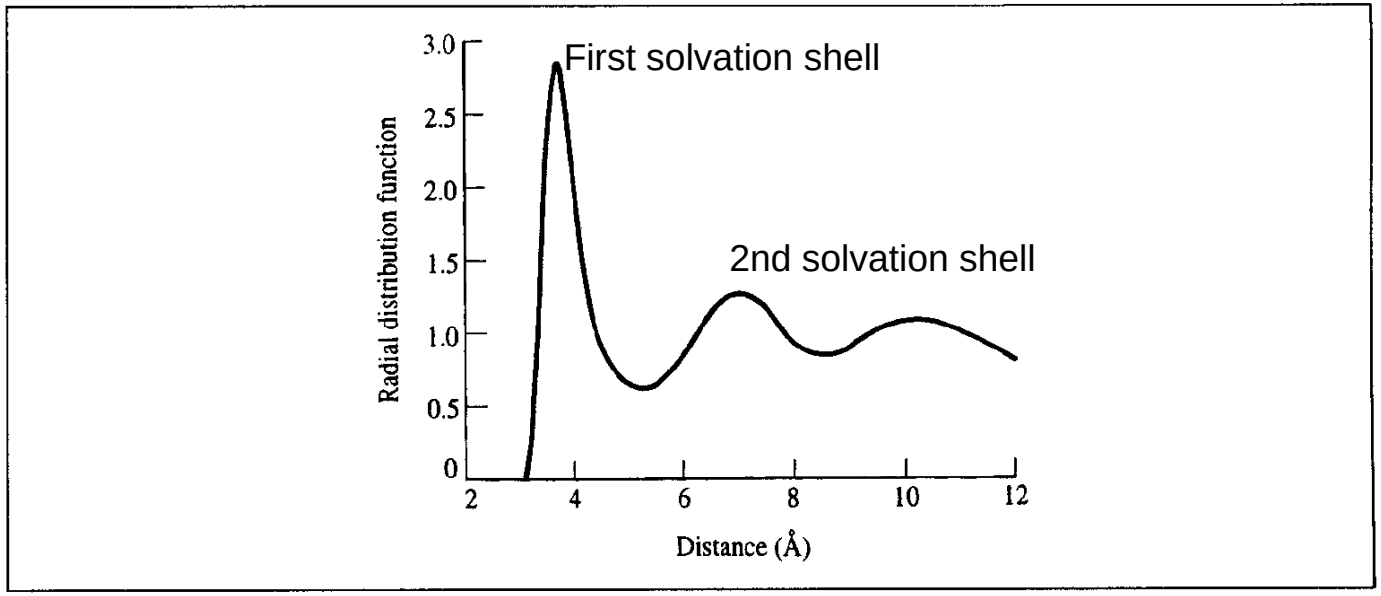


Fig. 6.2: Radial distribution function determined from a 100 ps molecular dynamics simulation of liquid argon at a temperature of 100 K and a density of 1.396 g cm^{-3}.

Experimentally, radial distribution functions can be measured using X-ray diffraction. So, experimental and theoretical results can be compared to know the quality of a simulation