

Principles of Monte Carlo Simulation

What is Monte Carlo Simulation?

- MC is a stochastic simulation technique based on random numbers and probability.
- Widely used across various disciplines in Economics, Physics, Chemistry, Biophysics and Material Science.
- Typically used to solve complex many-body problems with different types of interactions.
- Classical Monte Carlo: Uses Boltzmann distribution for random sampling to calculate the thermodynamic properties
- Quantum Monte Carlo: Random walks are used to calculate energies and wavefunctions using Schrodinger's equation.

Why Monte Carlo Simulation?

- It is used for problems which are difficult to solve mathematically.
- Too many particles in the system.
- Complex interactions among particles and/or in presence of an external field.

Properties of MC Simulation

- Large number of inputs.
- The inputs should be random and uniformly distributed.

An Example of MC Simulation

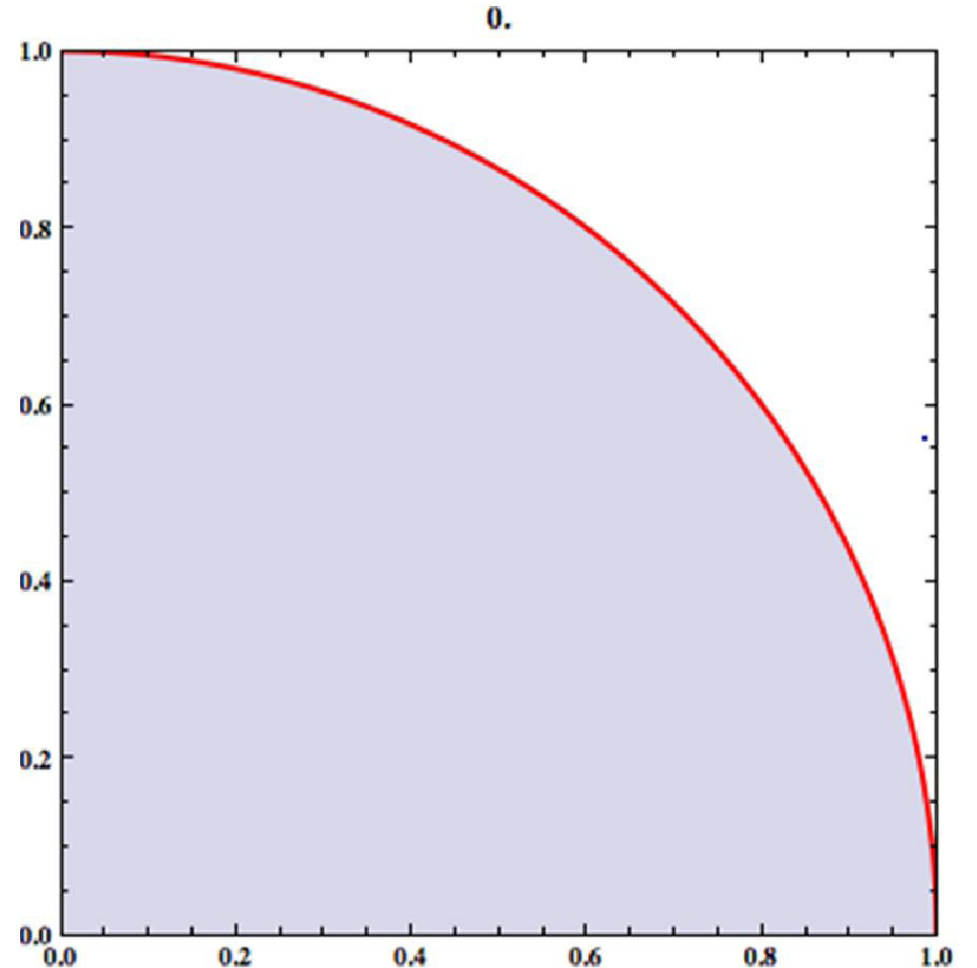
Value of π may be determined by MC simulation.

Inscribe a circle within a square.

Some trial shots are generated uniformly over the square.

The total number of trial shots inside the shaded area of the circle is N_{hit} and the total number of shots are N_{shot}

$$\pi \approx \frac{4N_{hit}}{N_{shot}}$$



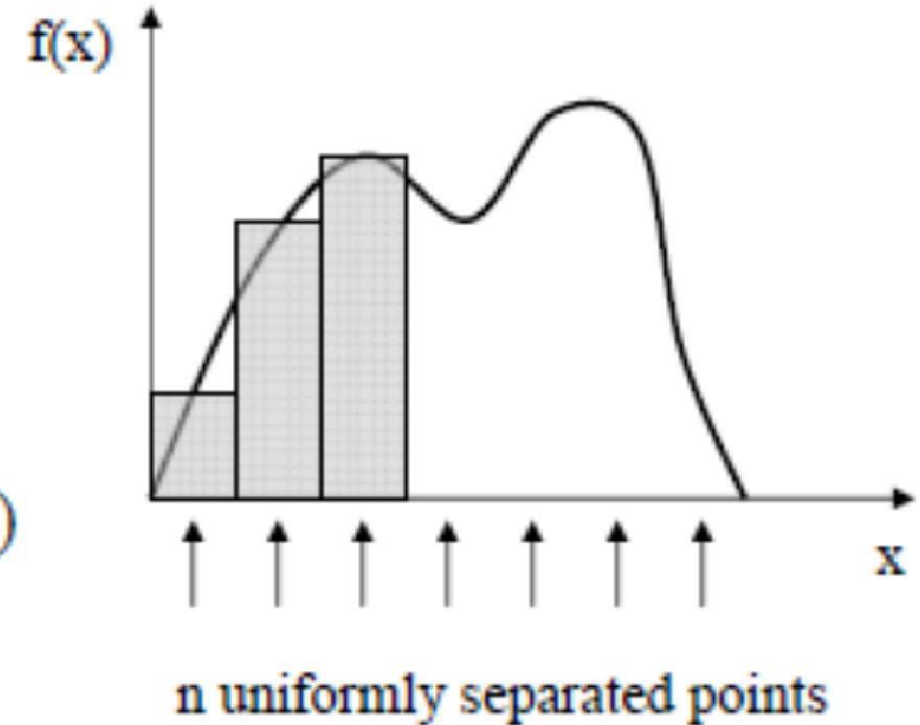
Calculation of Definite Integrals by Conventional Methods

Conventional approaches: rectangle, trapezoidal, Simpson's methods ...

$$I = \int_a^b f(x) dx$$

Quadrature formula:

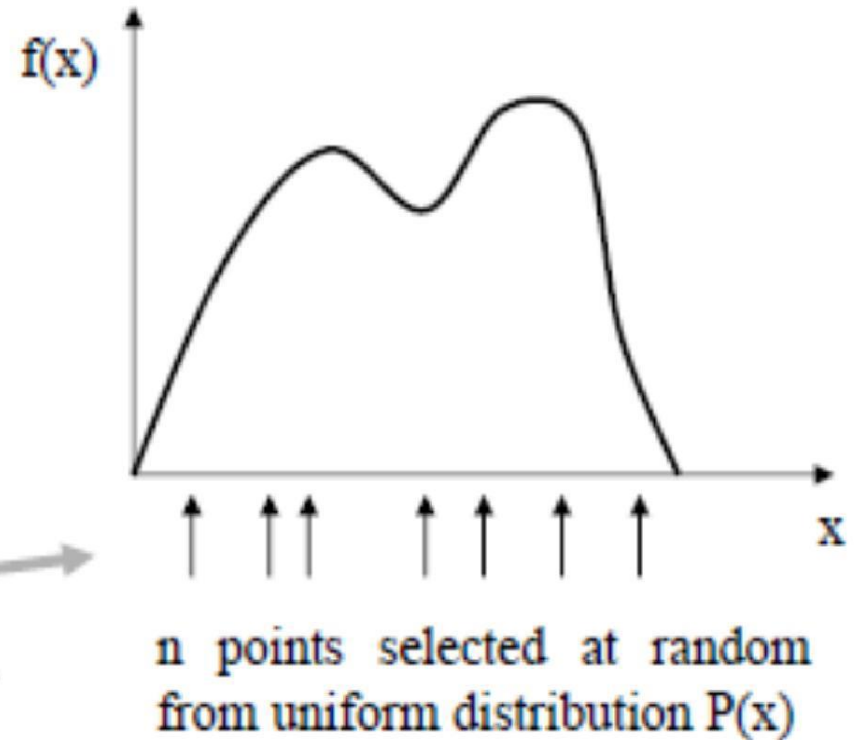
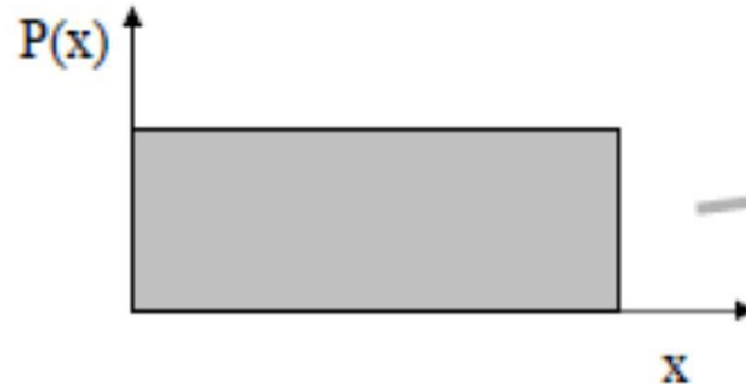
$$I \approx \Delta x \sum_{i=1}^n f(x_i) = \frac{b-a}{n} \sum_{i=1}^n f(x_i)$$



Calculation of Definite Integrals by Monte Carlo Method

Monte Carlo Integration: same quadrature formula, different selection of points

$$I \approx \frac{b-a}{n} \sum_{i=1}^n f(x_i)$$



Classical Monte Carlo Simulation

- The ensemble average of any physical quantity A is given by

$$\langle A \rangle = \frac{1}{Z} \iint dp dq A(p, q) \exp\{-\beta H(p, q)\}$$

where Z is defined as $Z = \frac{1}{h^{3N}} \iint dp dq \exp\{-\beta H(p, q)\}$, $H(p, q)$ is the Hamiltonian that describes the system and $\beta = 1/k_B T$.

An exact calculation of the partition function Z is not possible since it involves an integration over $6N$ dimensional phase space.

Calculation of the complex many-body interaction in the Hamiltonian is also difficult.

Monte Carlo Sampling

- It is difficult to compute the $6N$ dimensional integral for computing the ensemble average.
- Therefore average is calculated over a finite number of states, a subset of all possible states, with the correct Boltzmann weight. If a subset is chosen at random with a probability distribution p_x then

$$A_N = \frac{\sum_{x=1}^N A_x p_x^{-1} \exp(-\beta E_x)}{\sum_{x=1}^N p_x^{-1} \exp(-\beta E_x)} \quad N \rightarrow \infty, A_N \approx \langle A \rangle$$

Usually in MC simulation N is very large i.e., $10^6 - 10^{10}$

Simple Sampling

- To specify p_x such that the chosen N states will give correct $\langle A \rangle$
- A choice of $p_x = p$ gives

$$A_N = \frac{\sum_{x=1}^N A_x p^{-1} \exp(-\beta E_x)}{\sum_{x=1}^N p^{-1} \exp(-\beta E_x)} = \frac{\sum_{x=1}^N A_x \exp(-\beta E_x)}{\sum_{x=1}^N \exp(-\beta E_x)}$$

This average is valid for non-thermal and non-interacting systems of molecules.

For such systems, the temperature, T , is high

$$\langle A \rangle \approx A_N = \frac{1}{N} \sum_{x=1}^N A_x$$

Importance Sampling

- For discrete energy states, the ensemble average of A is given by

$$\langle A \rangle = \frac{1}{Z} \sum_{x=1}^N A_x \exp(-\beta E_x) \text{ where } Z = \sum_{x=1}^N \exp(-\beta E_x)$$

- At high temperature, the Boltzmann factor is unity which reduces to simple average.
- At low temperature, the system is in the ground state or one of the lowest energy states.
- A small fraction of the phase space only contributes to the average and hence this part of the phase space should be scanned.
- Random sampling of the phase space is therefore computationally inefficient.

Metropolis Monte Carlo

- An atom is chosen randomly and is subjected to a uniform random displacement along each of the spatial coordinates, x , y and z .
- Random number generator is used to generate the new position coordinate. This is a FORTRAN program that gives uniformly distributed random numbers between $[0,1]$.
- The size of the move is controlled by $\delta\mathbf{r}_{max}$.
- The transition between two states depends on the relative probabilities of the initial state m and the final state n which is given by

$$P_m = \frac{\exp(-\beta E_m)}{Z} \quad \text{and} \quad P_n = \frac{\exp(-\beta E_n)}{Z}$$

- The probabilities P_m and P_n cannot be determined exactly as it is difficult to calculate the canonical partition function.

- The ratio of the probabilities of the initial and final states is

$$\frac{P_m}{P_n} = \exp(-\beta E_{mn}) \quad \text{where} \quad E_{mn} = E_n - E_m$$

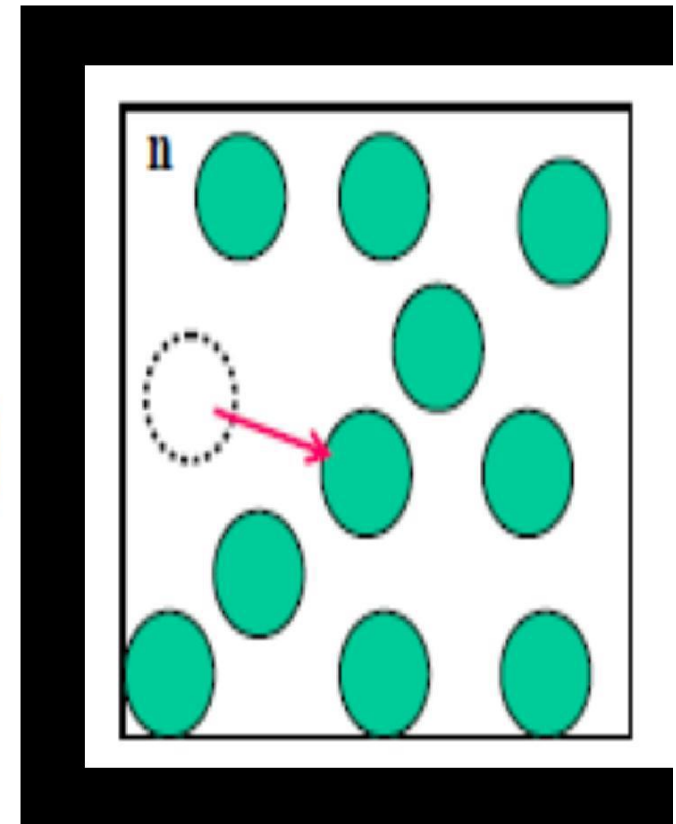
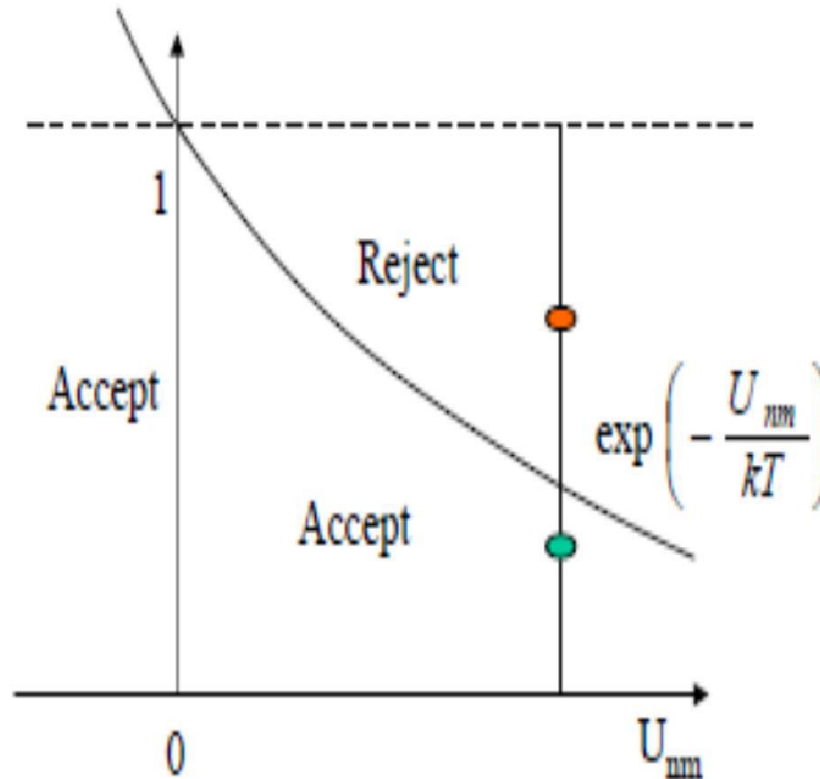
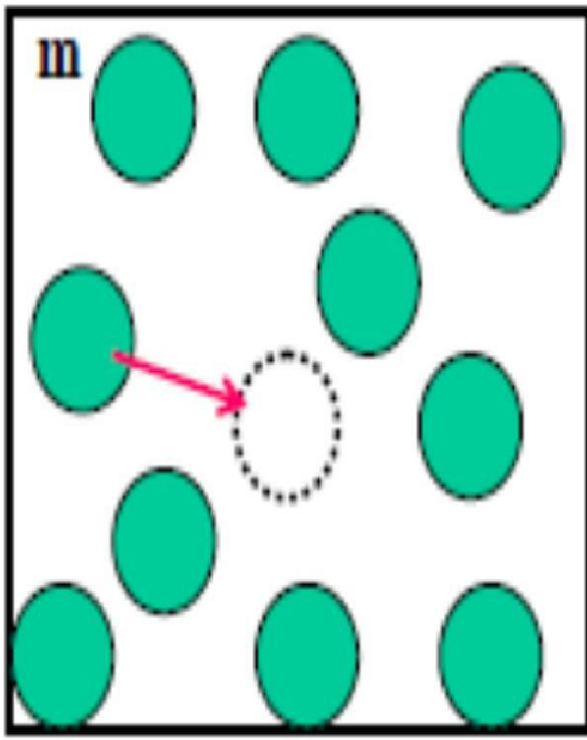
- Transition probability = $\frac{P_m}{P_n} = \exp(-\beta E_{mn})$ if $E_{mn} > 0$

$$\frac{P_m}{P_n} = 1 \quad \text{if} \quad E_{mn} \leq 0$$

Metropolis MC Method

Call a random number, $r = [0,1]$ uniformly distributed between 0 and 1.

If $r \leq \frac{P_m}{P_n}$, there is a change in state from m to n , otherwise the initial state is retained.



Application of Metropolis MC

Different conditions for the acceptance/rejection of moves

If $E_n < E_m$

The MC move is accepted and E_n becomes the energy of new conformation.

If $E_n > E_m$

The MC move is accepted conditionally
Transition probability is calculated
and compared with a random number
 r between 0 and 1.

If Transition probability $> r$

Then the MC move is accepted
and E_n becomes the energy of
the new conformation.

If Transition probability $< r$

Then the MC move is rejected and the
energy of the initial state E_m is
retained.

Choice of Potential

- Determination of the potential energy is an important step in MC and MD simulations.

- The change in potential energy is given by

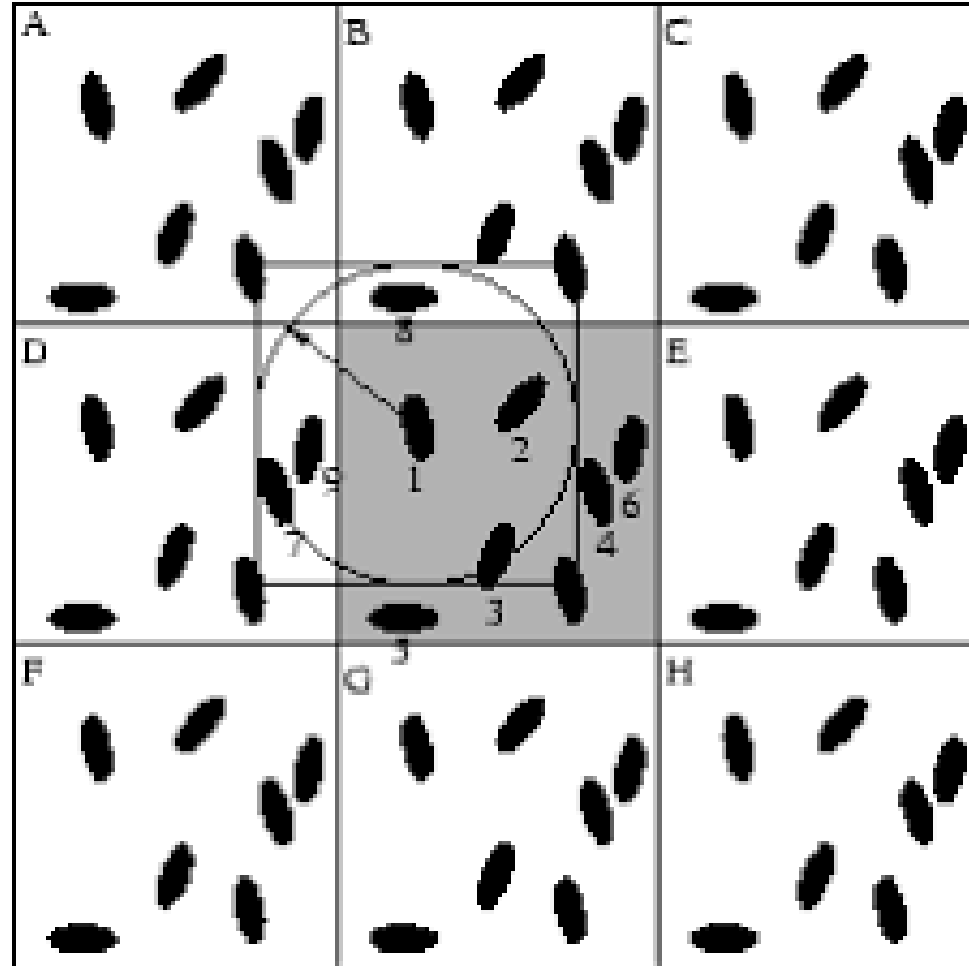
$$\delta E_{mn} = \sum_{j=1}^N E_{ij}^n - \sum_{j=1}^N E_{ij}^m$$

Sum over atoms excludes the i -th atom.

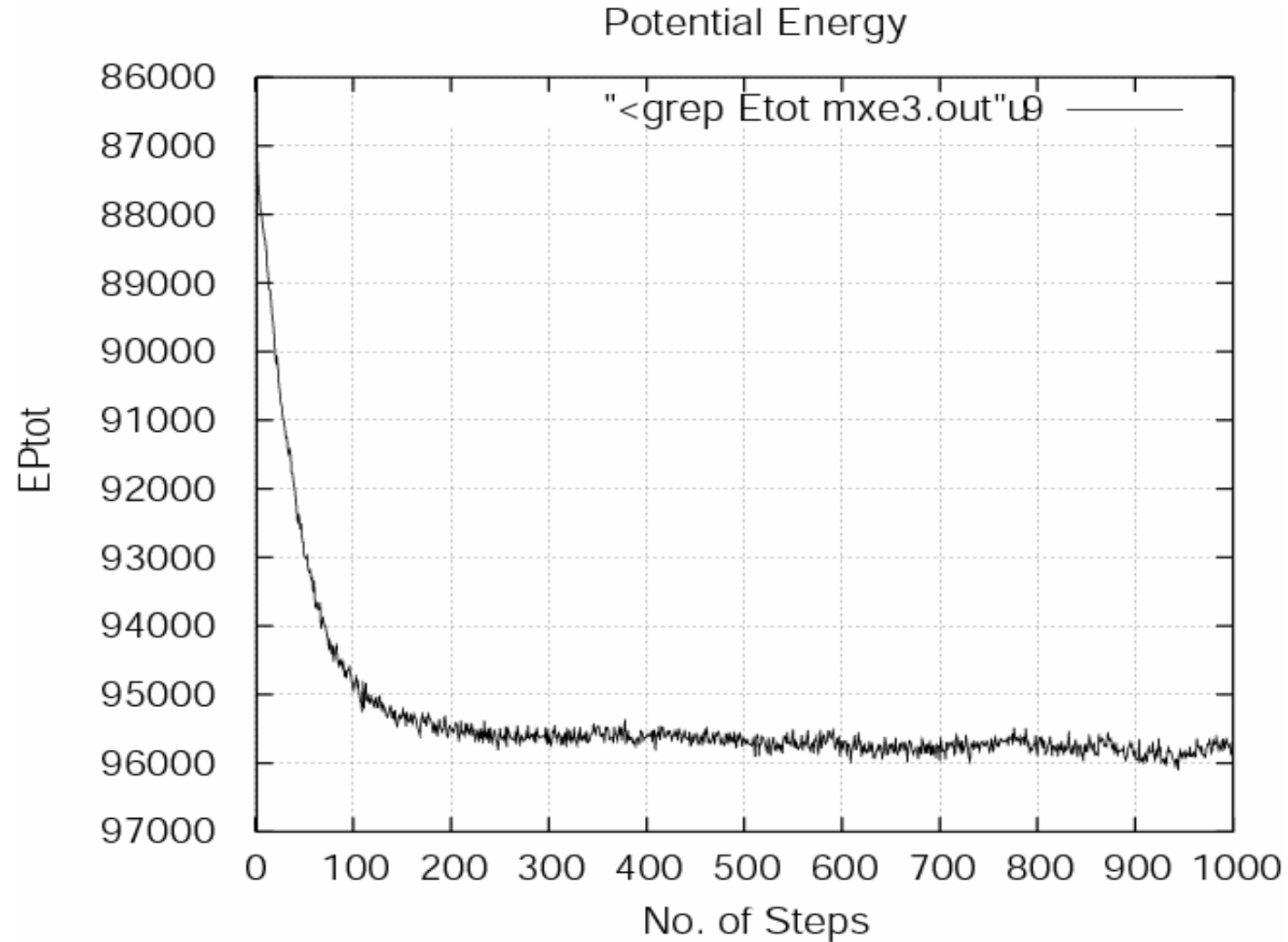
- The interaction of the atom i with its neighbours up to a certain cut-off distance R_c is considered.

Minimum Image Convention

- Potential energy is calculated using the pairwise additivity principle.
- For a short-ranged potential energy function, the interaction between an atom with other atoms and its closest periodic images that are within a cut-off distance R_C are only considered.
- Natural consequence of the periodic boundary condition.



Potential Energy Plot



Density Plot

