Lecture 5

Classical Monte Carlo simulation of Many body Systems

In this lecture we will see how to calculate properties of classical systems with detailed balance conditions using Metropolis algorithm.

Consider a system, which is essentially infinite in size, where we assume **periodic boundary conditions** and only account for the N particles inside the unit box. Generally, a **molecular model or force field** is assumed, for which several configurations are generated at random using a Metropolis algorithm.

The properties are calculated **within the framework of Statistical Physics**

Concepts from statistical mechanics

If a system in equilibrium can be in N states, the probability of the system having energy E_n is:

$$\frac{1}{Q}e^{-E_n/k_BT} \tag{5.1}$$

where Q is called the ***partition function***:

$$Q = \sum_{n=1}^{N} e^{-E_n/k_BT}$$

Then, we define the expected value of an observable A as

$$\langle A\rangle = \frac{1}{Q}\sum_{|i\rangle} e^{-E_i/k_BT}\,\langle i|A|i\rangle$$

The **classical expression** for the partition function of systems with N identical particles is

$$Q = \frac{1}{h^{3N}N!}\int d\vec{p}^N d\vec{r}^N e^{-H(\vec{r}^N,\vec{p}^N)/k_BT} \tag{5.2}$$

Here, $\vec{r}^N, \vec{p}^N$ stand for the coordinates andm omenta of all N particles and $H(\vec{r}^N, \vec{p}^N)$ is the Hamiltonian:

$$H(\vec{r}^N,\vec{p}^N) = \sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m} + U(\vec{r}^N)$$

The classical expression for $\langle A \rangle$ becomes

$$\langle A \rangle = \frac{\int d\vec{p}^N d\vec{r}^N A(\vec{p}^N, \vec{r}^N) e^{-\beta H(\vec{r}^N, \vec{p}^N)}}{\int d\vec{p}^N d\vec{r}^N e^{-\beta H(\vec{r}^N, \vec{p}^N)}} \tag{5.3}$$

with

$A(\vec{p}^N) \rightarrow$ easy analytical computation.

$A(\vec{r}^N) \rightarrow$ very difficult and costly, we have to compute it numerically.

As a result, we must then focus on the calculation of averages such as

$$\langle A \rangle = \frac{\int d\vec{r}^N A(\vec{r}^N) e^{-\beta U(\vec{r}^N)}}{\int d\vec{r}^N e^{-\beta U(\vec{r}^N)}} \tag{5.4}$$

with

$$\beta = \frac{1}{k_B T}$$
$$e^{-\beta U(\vec{r}^N)} \equiv \text{Boltzmann factor}$$

- We denote the configurational part of the partition function by Z:

$$Z \equiv \int d\vec{r}^N e^{-\beta U(\vec{r}^N)}$$

- The probability density of finding the system in a configuration around $\vec{r}^N$ is

$$\boxed{\mathcal{N}(\vec{r}^N) = \frac{e^{-\beta U(\vec{r}^N)}}{Z}}$$

The Metropolis method

Starting from the averages in Equation 5.4, we can see that this is in fact the ratio of two integrals. It is possible to devise an efficient Monte Carlo scheme to sample such a ratio.

Firstly, let us consider how to generate points in configuration space with a relative probability proportional to the Boltzmann factor:

- We prepare the system in a configuration $\vec{r}^N$, which we denote by R, that has a nonvanishing Boltzmann factor $e^{-\beta U(R)}$.
- Next, we generate a new trial configuration $\vec{r}'^N$, which we denote by R' by adding a small random displacement Δ.

  The Boltzmann factor in this trial configuration changes to $e^{-\beta U(R')}$
- We now decide whether we accept or reject the trial configuration.

Detailed balance condition

In equilibrium, the average number of accepted trial moves that result in leaving state $R \to R'$ must be exactly equal to the opposite number of moves from $R' \to R$. That is

$$\boxed{\mathcal{N}(R)\mathcal{P}(R \to R') = \mathcal{N}(R')\mathcal{P}(R' \to R)} \tag{5.5}$$

where

$$\begin{aligned} \mathcal{N}(R) &\equiv \text{Probability of being in configuration } R \\ \mathcal{P}(R \to R') &\equiv \text{Transition probability from configuration } R \to R' \end{aligned}$$

We can rewrite this transition probability as

$$\mathcal{P}(R \to R') = \alpha(R \to R') \times p_{\text{acc}}(R \to R')$$

the product of the transition matrix that determines the probability of performing a trial move from one state to the other and the probability of accepting said trial move.

If we assume that the transition matrix is **symmetric**, Equation 5.5 can be written as

$$\mathcal{N}(R)p_{\text{acc}}(R \to R') = \mathcal{N}(R')p_{\text{acc}}(R' \to R) \tag{5.6}$$

From this equation it follows that:

$$\frac{p_{\text{acc}}(R \to R')}{p_{\text{acc}}(R' \to R)} = \frac{\mathcal{N}(R')}{\mathcal{N}(R)} = e^{-\beta(U(R')-U(R))}$$

from which we can define our Metropolis acceptance rule:

$$\begin{cases} p_{\text{acc}(R\to R')} = \frac{\mathcal{N}(R')}{\mathcal{N}(R)} & \text{if } \mathcal{N}(R') < \mathcal{N}(R) \\ p_{\text{acc}(R\to R')} = 1 & \text{if } \mathcal{N}(R') \geq \mathcal{N}(R) \end{cases} \tag{5.7}$$

Basic Monte Carlo Algorithm

With our acceptance rule defined in eq.5.7, we can now describe the basic procedure to implement a Monte Carlo algorithm:

1. Select a particle at random, and calculate its energy $U(\vec{r}^N)$.
2. Give the particle a random displacement, $\vec{r}' = \vec{r} + \Delta$, and calculate its new energy $U(\vec{r}'^N)$.
3. Accept the move from $\vec{r}^N \to \vec{r}'^N$ with probability

$$p_{\text{acc}(R\to R')} = \min\left(1, e^{-\beta[U(\vec{r}'^N)-U(\vec{r}^N)]}\right)$$

Or in other words,

$$\begin{aligned} &U(\vec{r}'^N \leq U(\vec{r}^N)) \Rightarrow \text{We accept the trial} \\ &U(\vec{r}'^N > U(\vec{r}^N)) \Rightarrow \text{We generate a random number } u \text{ from a uniform distribution [0,1]} \\ &\qquad \Longrightarrow \begin{cases} \text{Accept} & \text{if } u < e^{-\beta[U(\vec{r}'^N)-U(\vec{r}^N)]} \\ \text{Reject} & \text{if } u > e^{-\beta[U(\vec{r}'^N)-U(\vec{r}^N)]} \end{cases} \end{aligned}$$

To generate a **trial displacement**, we can use for example:

$$x_i' \to x_i + \Delta(u_x - 0.5)$$
$$y_i' \to y_i + \Delta(u_y - 0.5)$$
$$z_i' \to z_i + \Delta(u_z - 0.5)$$

where u_x, u_y, u_z are random numbers generated from uniform distributions between [0,1]. The criterion to choose the value of Δ is to obtain an acceptance rate of the trial moves $\sim 50\%$.

5.1 Exercise 5: Simulating a Many Body system

The **radial distribution function (RDF)** describes how density varies as a function of distance from a reference particle. It is defined as

$$g(r) = \frac{1}{\rho}\frac{n(r)}{4\pi r^2 dr} = \frac{n(r)}{n_{id}(r)} \tag{5.8}$$

where $\rho = N/V$ is the average number density of particles, $n(r)$ is the mean number of particles within a distance of r and $r + dr$ away from a particle; and $n_{id}(r)$ is the mean number of particles for an ideal gas.

A useful way to calculate the RDF is to calculate the distance between all particle pairs and **binning them into a histogram**.

Lennard-Jones interaction potential

The Lennard-Jones (LJ) potential is an intermolecular pair potential. It describes electronically neutral atoms or molecules interactions and its expression is

$$U_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{5.9}$$

where r is the distance between two interacting particles, ε the depth of the potential well (also called the *dispersion energy*), and σ is the distance at which the particle-particle potential energy U is zero (also called the *size of the particle*).

In reduced units, the potential can be written as

$$U_{LJ}^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$

where $U_{LJ}^* = U_{LJ}/\varepsilon$ and $r^* = r/\sigma$.

Thermodynamic properties

We can calculate the energy of a many body system with the expression

$$E = \frac{3}{2}Nk_BT + \langle U_N \rangle$$

where $\langle U_N \rangle$ is the interaction energy (or potential energy):

$$\langle U_N \rangle = \langle U_N(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \rangle$$

If we assume pairwise interactions and truncate the potential at distances $r < r_c$, we obtain:

$$\langle U_N \rangle = \langle \sum_{i=1}^{N} \sum_{\substack{j>i, \\ r_{ij}<r_c}}^{N} U(r_{ij}) \rangle$$