Monte Carlo and Molecular Dynamics: basic methods

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- To investigate equilibrium properties by calculating the fluctuations and higher moments of thermodynamic quantities, ...
- To imagine any kind of methods for solving this problem (Monte Carlo methods, Machine Learning,...)
- To benchmark the methods (efficiency, capabilities, resource requirement)

Monte Carlo methods

Markov chain for sampling an equilibrium system

Thermal average of an observable A

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$$\sum_i p_i = 1, \langle A \rangle = \sum_i A_i p_i$$

Generating non uniform random numbers

Linear congruence relation

$$x_{n+1} = (ax_n + c)\, mod\, m \tag{1}$$

where all variables are integers. This relation generates a sequence of pseudo-random integer numbers between 0 and $m-1$. MT19937 (Mersenne Twister generator). Its period is 10^{6000}! It uses 624 words and it is equidistributed in 623 dimensions!.

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Register shift

the logical operation "exclusive or". The Kirkpatrick and Stoll generator.

$$x_n = x_{n-103} \bigoplus x_{n-250} \tag{2}$$

Non uniform numbers

Inverse transformation

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Exponential distribution

Example: $f(x) = \lambda e^{-\lambda x}$

$$\begin{aligned} F(x) &= \int_0^x dt \lambda e^{-\lambda t} \\ &= 1 - e^{-\lambda x} \end{aligned} \tag{3}$$

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$$f(x, y)dxdy = f(r^2)rdrd\theta = \exp(-\frac{r^2}{2})\frac{dr^2}{2}\frac{d\theta}{2\pi}. \tag{4}$$

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r^2 is a random variable with a exponential probability $e^{-r^2/2}$ and θ is a random variable with a uniform probability distribution on the interval $[0, 2\pi]$. If u and v are two uniform random variables on the interval $[0, 1]$, or $\mathcal{U}_{[0,1]}$, one has

$$x = \sqrt{-2\ln(u)}\cos(2\pi v) \quad (5)$$

$$y = \sqrt{-2\ln(u)}\sin(2\pi v) \quad (6)$$

which are independent random variables with a Gaussian distribution.

Markov chain for sampling an equilibrium system

- For a system with equilibrium configurations , the thermal average of A should be given by

$$\langle A \rangle \simeq \frac{1}{N_r} \sum_{i}^{N_r} A_i$$

where N_r is the total number of configurations where A is evaluated. In this way, the thermal average becomes an arithmetic average

Monte Carlo methods

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- Metropolis, Rosenbluth and Teller in 1953 introduces a stochastic Markovian process between successive configurations, converging towards the equilibrium distribution p_{eq}.

Markov chain for sampling an equilibrium system

- Stochastic Marlovian Process

$$p(i, t + dt) = p(i, t) + \sum_j (W(j \to i)p(j, t) - W(i \to j)p(i, t))\, dt$$

i.e

$$\frac{dp(i, t)}{dt} = \sum_j W(j \to i)p(j, t) - \sum_j W(i \to j)p(i, t)$$

- dt corresponds to a timestep for a modification of the configuration denoted by i
- W transition matrix.
- At equilibrium, no further evolution of the probability distribution

$$\sum_j W(j \to i)p_j = \sum_j W(i \to j)p_i$$

Monte Carlo method

Markov chain for sampling an equilibrium system

- At equilibrium

$$p_i = \frac{e^{-\beta E_i}}{Z}$$

- Balance equation

$$\sum_j W(j \to i) e^{-\beta E_j} = \sum_j W(i \to j) e^{-\beta E_i}$$

1. Infinite number of equations!

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3. At least, how to find one solution

Basic methods

Metropolis, Rosenbuth and Teller solution

- Detailed balance equation

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- Still a very large number of solutions!
- Split the transition matrix element as

$$W(i \to j) = \alpha(i \to j)\Pi(i \to j)$$

where $\alpha(i \to j)$ is the probability of changing a configuration i to j. In practice, α is uniform.

Basic methods

Metropolis, Rosenbuth and Teller solution

- The choice introduced by Metropolis *et al.* is

$$\Pi(i \to j) = \begin{cases} \exp(-\beta(E(j) - E(i))) & \text{if } E(j) > E(i) \\ 1 & \text{if } E(j) \leq E(i) \end{cases}$$

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- In a concise manner

$$\Pi(i \to j) = Min(1, \exp(-\beta(E(j) - E(i))))$$

Metropolis, Rosenbuth and Teller solution: examples

Implemention method

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     It not (Coulombic or gravitational forces), Ewald sums.

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- Two regimes: the warmp up regime and the equilibrium regime.

Metropolis, Rosenbuth and Teller solution: examples

Ising model

- Lattice model: Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} S_i S_j$$

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1. Select a site is selected by choosing at random an integer i between 1 and N ($\alpha(i \to j) = 1/N$).
2. Compute the energy difference between the trial configuration (in which the spin i is flipped) and the old configuration.
3. If the trial configuration has a lower energy, the trial configuration is accepted. Otherwise, a uniform random number is chosen between 0 and 1 and if this number is less than $\exp(-\beta(E(j) - E(i)))$, the trial configuration is accepted. If not, the old configuration is kept and the configuration is counted again.

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$$C_v \sim \langle E^2 \rangle - \langle E \rangle^2$$

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- Histogram method

$$\langle A \rangle \simeq \sum_i A_i H(i)$$

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Simple Liquids

- Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} v(r_{ij})$$

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- Lennard-Jones potential

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

with ϵ enery scale and σ effective diameter of particle

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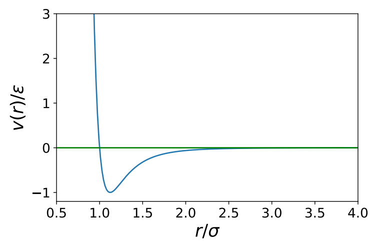

Metropolis, Rosenbuth and Teller solution: examples

Simple Liquids

- In a three-dimensional space a trial move is given by

$$x_i' \rightarrow x_i + \Delta(rand - 0.5) \tag{7}$$
$$y_i' \rightarrow y_i + \Delta(rand - 0.5) \tag{8}$$
$$z_i' \rightarrow z_i + \Delta(rand - 0.5) \tag{9}$$

with the condition that $(x_i' - x_i)^2 + (y_i' - y_i)^2 + (z_i' - z_i)^2 \leq \Delta^2/4$ (this condition corresponds to considering isotropic moves)

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- Compute the energy difference $\Delta E \sim N$
- Truncated Lennard-Jones potential

$$v^{trunc}(r) = \begin{cases} v(r) - v(r_c) & r \leq r_c, \\ 0 & r > r_c. \end{cases} \quad (10)$$

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- If $\Delta E < 0$ accept the move

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Simple Liquids

- Trial move of a particle chosen randomly
- Compute the energy difference ΔE
- If $\Delta E < 0$ accept the move
- If $\Delta E > 0$, select a random number between 0 and 1.
    1. If $\eta < \exp(-\beta \Delta E)$, accept the move
    2. If $\eta > \exp(-\beta \Delta E)$, do not move the particle , but the weitht of the configuration increases.