Monte Carlo and Molecular Dynamics: basic methods

Pascal Viot

September 12, 2020
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- To investigate equilibrium properties by calculating the fluctuations and higher moments of thermodynamic quantities, ...
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- For off-lattice systems, solve the Hamiltonian equations (or more generally the dynamical equations)
- 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)
Markov chain for sampling an equilibrium system

Thermal average of an observable $A$

$$\langle A \rangle = \frac{\sum_i A_i \exp(-\beta U_i)}{Z}.$$ 

where $i$ runs over configurations
Monte Carlo methods

Markov chain for sampling an equilibrium system

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defines the probability of having the configuration $i$ (at equilibrium).
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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

\[ x_{n+1} = (ax_n + c) \mod m \] (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.

\[ x_n = x_{n-103} \oplus x_{n-250} \]  
\[ (2) \]
**Inverse transformation**

If $f(x)$ denotes the probability distribution on the "interval" $I$, one defines the cumulative distribution $F$ as

$$F(x) = \int_0^x f(t) dt$$
Inverse transformation

If \( f(x) \) denotes the probability distribution on the ”interval” \( I \), one defines the cumulative distribution \( F \) as

\[
F(x) = \int_{-\infty}^{x} f(t) \, dt
\]

If there exists an inverse function \( F^{-1} \), then \( u = F^{-1}(x) \) define a cumulative distribution for random numbers with a uniform distribution on the interval \([0, 1]\).
Non uniform numbers

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Exponential distribution

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

$$F(x) = \int_{0}^{x} dt \lambda e^{-\lambda t} = 1 - e^{-\lambda x}$$ (3)
If $f(x) \sim e^{-x^2/2}$ then $F(x)$ is the error function which is not invertible.
Non uniform numbers

Box Müller Method

If $f(x) \sim e^{-x^2/2}$ then $F(x)$ is the error function which is not invertible. A couple of independent random variables $(x, y)$
Non uniform numbers

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If $f(x) \sim e^{-x^2/2}$ then $F(x)$ is the error function which is not invertible. A couple of independent random variables $(x, y)$ the joint probability distribution is $f(x, y) = \exp(-(x^2 + y^2)/2)/(2\pi)$. 

\[ x = \sqrt{-2 \ln(u)} \cos(2\pi v) \] 
\[ y = \sqrt{-2 \ln(u)} \sin(2\pi v) \] 
which are independent random variables with a Gaussian distribution.
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\[
f(x, y) \, dx \, dy = f(r^2) \, r \, dr \, d\theta = \exp\left(-\frac{r^2}{2}\right) \frac{dr}{2} \frac{d\theta}{2\pi}.
\] (4)
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\( r^2 \) is a random variable with a exponential probability \( e^{-r^2/2} \) and \( \theta \) is a random variable with a uniform probability distribution on the interval \([0, 2\pi]\).
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f(x, y) \, dx \, dy = f(r^2) \, r \, dr \, d\theta = \exp(-\frac{r^2}{2}) \frac{dr^2}{2} \frac{d\theta}{2\pi}.
\] (4)

\( r^2 \) is a random variable with an exponential probability \( e^{-r^2/2} \) and \( \theta \) 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 \( U_{[0,1]} \), one has

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

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

which are independent random variables with a Gaussian distribution.
For a system with equilibrium configurations, the thermal average of $A$ should be given by

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

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

Markov chain for sampling an equilibrium system

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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

\[
p(i, t + dt) = p(i, t) + \sum_j (W(j \rightarrow i)p(j, t) - W(i \rightarrow j)p(i, t)) \, dt
\]

i.e

\[
\frac{dp(i, t)}{dt} = \sum_j W(j \rightarrow i)p(j, t) - \sum_j W(i \rightarrow j)p(i, t)
\]

- \(dt\) 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

\[
\sum_j W(j \rightarrow i)p_j = \sum_j W(i \rightarrow j)p_i
\]
Monte Carlo method

Markov chain for sampling an equilibrium system

- At equilibrium
  \[ p_i = \frac{e^{-\beta E_i}}{Z} \]

- Balance equation
  \[ \sum_j W(j \rightarrow i)e^{-\beta E_j} = \sum_j W(i \rightarrow j)e^{-\beta E_i} \]

1. Infinite number of equations!
Monte Carlo method

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1. Infinite number of equations!
2. Infinite number of solutions!
3. At least, how to find one solution
Metropolis, Rosenbuth and Teller solution

- Detailed balance equation

\[ W(j \rightarrow i)e^{-\beta E_j} = W(i \rightarrow j)e^{-\beta E_i} \]
Metropolis, Rosenbuth and Teller solution

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- Detailed balance equation yields balance equation

\[ W(i \rightarrow j) \] is the probability of changing a configuration from \( i \) to \( j \). In practice, \( W(i \rightarrow j) \) is uniform.
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- Still a very large number of solutions!
Basic methods

Metropolis, Rosenbuth and Teller solution

- Detailed balance equation
  \[ W(j \rightarrow i)e^{-\beta E_j} = W(i \rightarrow j)e^{-\beta E_i} \]

- Detailed balance equation yields balance equation
- Still a very large number of solutions!
- Split the transition matrix element as
  \[ W(i \rightarrow j) = \alpha(i \rightarrow j)\Pi(i \rightarrow j) \]

where \( \alpha(i \rightarrow j) \) is the probability of changing a configuration \( i \) to \( j \). In practice, \( \alpha \) is uniform.
The choice introduced by Metropolis et al. is

\[
\Pi(i \rightarrow 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

\[
\Pi(i \rightarrow j) = \text{Min}(1, \exp(-\beta(E(j) - E(i))))
\]
Implemention method

- Periodic boundary conditions:

Compared to open boundaries, suppress the surface effect. For $10^3$ particles in three dimensions, 600 particles are located on boundaries. How to build an infinite system: Replicate the box in $d$ directions. If the range of interaction is less than the box linear size, the minimum image convention can be used. It not (Coulombic or gravitational forces), Ewald sums.

The thermodynamic quantities keep a finite size dependence, but not related to surface effects! Two regimes: the warm up regime and the equilibrium regime.
Periodic boundary conditions:

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Metropolis, Rosenbuth and Teller solution: examples

**Implementation method**

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- Two regimes: the warm up regime and the equilibrium regime.
## Ising model

- **Lattice model**: Hamiltonian

\[
H = -J \sum_{\langle i,j \rangle} S_i S_j
\]
Ising model

- Lattice model: Hamiltonian

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

1. Select a site is selected by choosing at random an integer \( i \) between 1 and \( N \) (\( \alpha(i \rightarrow j) = 1/N \)).
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.

(9x252) Metropolis, Rosenbuth and Teller solution: examples

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Ising model

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Ising model

- How to estimate the warm up regime. Determine the relaxation time (roughly!)
Metropolis, Rosenbuth and Teller solution: examples

Ising model

- How to estimate the warm up regime. Determine the relaxation time (roughly!)
- Thermodynamic quantities: energy, specific heat, magnetization "On the fly" method:

\[ \langle A \rangle \simeq \frac{1}{N_r} \sum_i A_i \]

\[ C_v \sim \langle E^2 \rangle - \langle E \rangle^2 \]
Ising model

- How to estimate the warm up regime. Determine the relaxation time (roughly!)

- Thermodynamic quantities: energy, specific heat, magnetization "On the fly" method:

  \[ \langle A \rangle \approx \frac{1}{N_r} \sum_i A_i \]

  \[ C_v \sim \langle E^2 \rangle - \langle E \rangle^2 \]

- Histogram method

  \[ \langle A \rangle \approx \sum_i A_i H(i) \]
Simple Liquids

- Hamiltonian

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

- Hamiltonian

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

- Lennard-Jones potential

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

with \( \epsilon \) energy scale and \( \sigma \) effective diameter of particle
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Simple Liquids

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

\[ x'_i \rightarrow x_i + \Delta (rand - 0.5) \]  
\[ y'_i \rightarrow y_i + \Delta (rand - 0.5) \]  
\[ z'_i \rightarrow z_i + \Delta (rand - 0.5) \]  

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

\[ v^{\text{trunc}}(r) = \begin{cases} 
  v(r) - v(r_c) & r \leq r_c, \\
  0 & r > r_c.
\end{cases} \]
Simple Liquids

- Trial move of a particle chosen randomly

Compute the energy difference $\Delta E$. If $\Delta E < 0$ accept the move. If $\Delta E > 0$, select a random number between 0 and 1. If

$$\eta < \exp(-\beta \Delta E)$$

accept the move. If $\eta > \exp(-\beta \Delta E)$, do not move the particle, but the weight of the configuration increases.
Simple Liquids

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- 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 weight of the configuration increases.