PART 1

Classical Monte Carlo Methods
Outline

1. Statistical thermodynamics, ensembles
2. Numerical evaluation of integrals, crude Monte Carlo (MC)
3. MC methods for statistical thermodynamics, Markov chains
4. Variants of MC methods
Statistical thermodynamics

**microscopic description**
(positions, momenta, interactions)
Statistical thermodynamics

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macroscopic description
(pressure, density, temperature)
Statistical thermodynamics

**Microscopic description**
(positions, momenta, interactions)

**Macroscopic description**
(pressure, density, temperature)

Statistical Thermodynamics
Statistical thermodynamics

time averages → Molecular Dynamics methods

\[ B = \bar{b} \equiv \lim_{\tau \to +\infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} b(\vec{r}_k(t), \vec{p}_k(t)) \, dt \]
Statistical thermodynamics

ensemble averages $\rightarrow$ Monte Carlo methods

$$B(A_1,\ldots,A_n) = \langle b \rangle = \frac{\int b(\vec{r}_k,\vec{p}_k)\rho(\vec{r}_k,\vec{p}_k;A_1,\ldots,A_n)\,d\Gamma}{\int\rho(\vec{r}_k,\vec{p}_k;A_1,\ldots,A_n)\,d\Gamma}$$
Statistical thermodynamics

Statistical (Gibbs) ensembles

✓ microstate (μ-state): positions and momenta
✓ macrostate (m-state): macroscopic variables \( (A_1, \ldots) \)
✓ 1 m-state = many μ-states → Gibbs ensemble
✓ probability distribution in system’s phase space, \( \rho(\vec{r}_k, \vec{p}_k; A_1, \ldots, A_n) \)
Examples of statistical (Gibbs) ensembles

- micro-canonical: $N, V, E$
- canonical: $N, V, T$
- grand-canonical: $\mu, V, T$
- isobaric-isothermic: $N, P, T$
- etc.
Statistical thermodynamics

Canonical Gibbs ensemble

\[
\rho(\vec{r}_K, \vec{p}_K; N, V, T) \propto \exp \left[ - \frac{H_N(\vec{r}_K, \vec{p}_K; V)}{k_B T} \right]
\]

\[
H_N(\vec{r}_K, \vec{p}_K; V) = \sum_{K=1}^{N} \frac{\vec{p}_K^2}{2M_K} + W(\vec{r}_K; V)
\]
Statistical thermodynamics as a mathematical problem

\[ B(A_1, \ldots, A_n) = \langle b \rangle = \frac{\int b(\vec{r}_K, \vec{p}_K) \rho(\vec{r}_K, \vec{p}_K; A_1, \ldots, A_n) \, d\Gamma}{\int \rho(\vec{r}_K, \vec{p}_K; A_1, \ldots, A_n) \, d\Gamma} \]

\[ d\Gamma = \frac{1}{N!h^{3N}} \, d^3\vec{r}_1 \, d^3\vec{p}_1 \ldots d^3\vec{r}_N \, d^3\vec{p}_N \]
Statistical thermodynamics

Statistical thermodynamics as a mathematical problem

\[ B(\mathbf{A}_1, \ldots, \mathbf{A}_n) = B_{\text{kin}} + \frac{\int b_{\text{con}}(\mathbf{r}_K) \rho_{\text{con}}(\mathbf{r}_K; \mathbf{A}_1, \ldots, \mathbf{A}_n) \, d\mathbf{r}_1 \ldots d\mathbf{r}_N}{\int \rho_{\text{con}}(\mathbf{r}_K; \mathbf{A}_1, \ldots, \mathbf{A}_n) \, d\mathbf{r}_1 \ldots d\mathbf{r}_N} \]

Canonical ensemble

\[ \rho_{\text{con}}(\mathbf{r}_K; N, V, T) \propto \exp\left[-\frac{W_N(\mathbf{r}_K; V)}{k_b T}\right] \]
Numerical evaluation of integrals

1D – rectangular, trapezoid, Simpsonian, …

\[ \int_{a}^{b} f(x) \, dx \approx \frac{b - a}{n} \sum_{j=1}^{n} f(a + \frac{b - a}{n} \cdot j) = \frac{b - a}{n} \sum_{j=1}^{n} f(x_j) \]
Numerical evaluation of integrals

1D – **rectangular**, trapezoid, Simpsonian, ...

\[
\int_a^b f(x) \, dx \approx \frac{b-a}{n} \sum_{j=1}^{n} f(a + \frac{b-a}{n} \cdot j) = \frac{b-a}{n} \sum_{j=1}^{n} f(x_j)
\]

1D – **crude Monte Carlo**

\[
\int_a^b f(x) \, dx \approx \frac{b-a}{n} \sum_{j=1}^{n} f(x_j)
\]

\(x_j\) randomly distributed over \([a,b]\)
Numerical evaluation of integrals

Example
\[ \int_0^\pi \sin x \, dx \]
Numerical evaluation of integrals

Localized functions

\[ \int_{a}^{b} f(x) \rho(x) \, dx \]
Numerical evaluation of integrals

Localized functions

\[ \int_a^b f(x) \rho(x) \, dx \]

Solution: Sampling from \( \rho(x) \).
Numerical evaluation of integrals

Localized functions

\[
\int_{a}^{b} f(x) \rho(x) \, dx
\]

Solution: Sampling from \( \rho(x) \).

Markov chains

**Simplified example – finite number of microstates**

- microstates: \(s_1, \ldots, s_n\)
- probability distribution: \(\rho_1 = \rho(s_1), \ldots, \rho_n = \rho(s_n)\)
- equilibrium PD: \(\rho_1^{(e)}, \ldots, \rho_n^{(e)}\)
Simplified example – finite number of microstates

✓ Markov chain:

\[ s^{(1)} \rightarrow s^{(2)} \rightarrow \ldots \rightarrow s^{(N)} \rightarrow \ldots \]

\( s^{(K)} \) is from \( \{s_1, \ldots, s_n\} \)

✓ transition probabilities:

(stochastic matrix)

\[ \pi_{ik} = \pi_{i \rightarrow k} \]

\[ 0 \leq \pi_{ik} \leq 1 \]

\[ \sum_{k=1}^{n} \pi_{ik} = 1 \]
Markov chains

Simplified example – finite number of microstates

✓ PD function evolution:

\[ \rho_k^{(N+1)} = \sum_{j=1}^{n} \rho_j^{(N)} \pi_{ik} \quad \quad \quad \bar{\rho}^{(N+1)} = \bar{\rho}^{(N)} \bar{\pi} \]

✓ equilibrium PD function:

\[ \rho_k^{(e)} = \sum_{j=1}^{n} \rho_j^{(e)} \pi_{ik} \quad \quad \quad \bar{\rho}^{(e)} = \bar{\rho}^{(e)} \cdot \bar{\pi} \]
Markov chains

**Simplified example – finite number of microstates**

**Theorem:**

Let \( s^{(1)}, s^{(2)}, ..., s^{(N)}, ... \) be an infinite Markov chain of microstates generated using a stochastic matrix \( \pi_{ik} \). Then the generated microstates are distributed over the state space of the system in congruence with the equilibrium PD function of the used stochastic matrix.

**Remarks:**

The Markov chain does not represent any physical time evolution.

From the statistical thermodynamics point of view, only the equilibrium PD function is physically relevant. (Not, *e. g.*, the stochastic matrix.)
Markov chains

Construction of an appropriate stochastic matrix

\[ \rho_k^{(e)} = \sum_{j=1}^{n} \rho_j^{(e)} \pi_{jk}, \quad \sum_{k=1}^{n} \pi_{jk} = 1 \]

Mathematically

- 2n linear algebraic equations for \( n^2 \) variables
- many (infinite number of) solutions
Markov chains

Construction of an appropriate stochastic matrix

\[ \rho_k^{(e)} = \sum_{j=1}^{n} \rho_j^{(e)} \pi_{jk}, \quad \sum_{k=1}^{n} \pi_{jk} = 1 \]

Mathematically

✓ 2n linear algebraic equations for \( n^2 \) variables
✓ many (infinite number of) solutions

Detailed balance

\[ \rho_k^{(e)} \pi_{kj} = \rho_j^{(e)} \pi_{jk} \]
Markov chains

Decomposition of the stochastic matrix

\[ \pi_{ik} = p_{ik} a_{ik} \]

\( p_{ik} \) ... probability of proposing a particular transition

\( a_{ik} \) ... probability of accepting the proposed transition

Metropolis solution [1]

\[ \rho_k^{(e)} p_{ki} a_{ki} = \rho_i^{(e)} p_{ik} a_{ik} \implies a_{ik} = \min \left\{ 1, \frac{\rho_k^{(e)}}{\rho_i^{(e)}} \frac{p_{ki}}{p_{ik}} \right\} \implies a_{ik} = \min \left\{ 1, \frac{\rho_k^{(e)}}{\rho_i^{(e)}} \right\} \]

Markov chains

**Decomposition of the stochastic matrix**

\[ \pi_{ik} = p_{ik} a_{ik} \]

\( p_{ik} \) ... probability of **proposing** a particular transition

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**Metropolis solution** [1]

\[ \rho_k^{(e)} p_{ki} a_{ki} = \rho_i^{(e)} p_{ik} a_{ik} \implies a_{ik} = \min \left\{ 1, \frac{\rho_k^{(e)}}{\rho_i^{(e)}} \frac{p_{ki}}{p_{ik}} \right\} \]

\[ p_{ki} = p_{ik} \]

\[ a_{ik} = \min \left\{ 1, \frac{\rho_k^{(e)}}{\rho_i^{(e)}} \right\} \]

Notice that the PD function need not be normalized!

Metropolis algorithm

... for evaluating configuration integrals of statistical thermodynamics (canonical ensemble)

\[ B = B_{\text{kin}} + \int b_{\text{con}}(\vec{r}_K) e^{-\frac{W(\vec{r}_K)}{k_B T}} d\vec{r}_1 ... d\vec{r}_N \]

\[ \int e^{-\frac{W(\vec{r}_K)}{k_B T}} d\vec{r}_1 ... d\vec{r}_N \]

and, consequently,

\[ \rho_i^{(e)} \land e^{-\frac{W(\vec{r}_{(i)}^{(j)})}{k_B T}} \equiv e^{\frac{W(i)}{k_B T}} \Rightarrow \frac{\rho_k^{(e)}}{\rho_i^{(e)}} = e^{\frac{(W(k)-W(i))}{k_B T}} = e^{\frac{\Delta W(i\rightarrow k)}{k_B T}} \]
Metropolis algorithm

✓ from the configuration generated in the preceding step, \( r(i) \), generate a new one using an algorithm obeying that the probability for old \( \rightarrow \) new is the same as for new \( \rightarrow \) old (usually isotropic translation and/or rotation)

✓ if \( W^{(\text{new})} < W(i) \) then \( r(i+1) = r^{(\text{new})} \)

✓ if \( W^{(\text{new})} > W(i) \) then
  ✓ \( r(i+1) = r^{(\text{new})} \) with probability \( \frac{e^{-\Delta W(i \rightarrow \text{new}) / k_B T}}{1 - e^{-\Delta W(i \rightarrow \text{new}) / k_B T}} \)
  ✓ \( r(i+1) = r(i) \) with probability

✓ repeat until “infinity” (convergence)
Metropolis algorithm

Then

\[
\int b_{\text{con}}(\vec{r}_K) \frac{W(\vec{r}_K)}{k_b T} \, d\vec{r}_1 \ldots d\vec{r}_N = \lim_{n \to +\infty} \frac{1}{n} \sum_{i=1}^{n} b_{\text{con}}(\vec{r}_K^{(i)})
\]
Metropolis algorithm

Then

\[ \int b_{\text{con}}(\vec{r}_K) e^{\frac{-W(\vec{r}_K)}{k_B T}} d\vec{r}_1 ... d\vec{r}_N = \lim_{n \to +\infty} \frac{1}{n} \sum_{i=1}^{n} b_{\text{con}}(\vec{r}_K^{(i)}) \]

Canonical (or NVT or isochoric-isothermic) Monte Carlo
A general sketch of an MC simulation

- propose an initial configuration
- employ the Metropolis algorithm to generate as many as possible further configurations
- collect necessary data along the MC path to evaluate ensemble averages
- calculate the averages as simple arithmetic means of the collected data
Troublesomes

Periodic boundary conditions - example

Diagram showing a grid with black and white circles.
Literature


Appendix

Simulated annealing [1] and basin hopping [2]

MC simulation at a high temperature

$T \rightarrow 0$ K

simulated annealing

gradient optimization

basin hopping

equilibrium structure for $T = 0$ K

Example 2

Simulated annealing of small water clusters.
PART 2

Wang-Landau algorithm
Problem: low temperatures

- Simulation at low temperatures – combination of integration and optimization
- Molecular clusters, biomolecules:
- Complicated energy landscapes
- A lot of minims separated by large energy barriers
Mean value of variable $B$

$$B(A_1,\ldots,A_n) = B_{\text{kin}} + \int \frac{b_{\text{con}}(\vec{r}_K)\rho_{\text{con}}(\vec{r}_K;A_1,\ldots,A_n)}{\rho_{\text{con}}(\vec{r}_K;A_1,\ldots,A_n)} \, d\vec{r}_1 \ldots d\vec{r}_N$$

**IF** $b_{\text{con}}(\vec{r}_K) \equiv b(W(\vec{r}_K))$, then mean value of $B$ can be expressed as a 1D integral

$$B(A_1,\ldots,A_n) = B_{\text{kin}} + \frac{\int_{W_{\text{min}}}^{\infty} b_{\text{con}}(W)\rho_{\text{con}}(W;A_1,\ldots,A_n) \, \Omega(W) \, dW}{\int_{W_{\text{min}}}^{\infty} \rho_{\text{con}}(W;A_1,\ldots,A_n) \, \Omega(W) \, dW}$$

where $\Omega(W)$ is classical density of states

$$\Omega(W) = \lim_{\Delta W \to 0} \frac{\int_{\bar{W}_1,\ldots,\bar{W}_N;W(\bar{r}_1,\ldots,\bar{r}_N)\in(W,W+\Delta W)} 1 \, d\bar{r}_1 \ldots d\bar{r}_N}{\int_{\bar{r}_1,\ldots,\bar{r}_N} 1 \, d\bar{r}_1 \ldots d\bar{r}_N}$$

How to calculate $\Omega(W)$? Wang-Landau algorithm
Calculation of $\Omega$ Wang-Landau algorithm – basic idea

- Compleatly random walk in configuration space $\Rightarrow$ energy histogram $h(W) \sim \Omega(W)$, but low energy configurations will not be visited

- Metropolis algorithm: configurations are sampled by $\rho(E_{i}(r))$, $\Rightarrow$ energy histogram $h(W) \sim \Omega(W) \times \rho(W(r))$

- If we use $\rho(W_{i}(r)) = 1/\Omega(W)$, then energy histogram will be constant function
Wang-Landau algorithm – calculation of density of states

- Start of simulation: $\Omega(W)$ is unknown, we start with constant $\Omega(W) = 1$ and from random initial configuration $r$
- Following configuration $r_2$ created by small random change of foregoing configuration $r_1$ is accepted with probability
  \[
  \min \left\{ 1, \frac{\rho(W_{\text{new}} (r_{\text{new}}))}{\rho(W_{\text{old}} (r_{\text{old}}))} \right\} = \left\{ 1, \frac{\Omega(W_{\text{old}})}{\Omega(W_{\text{new}})} \right\}
  \]
- Visiting of energy $W_i$: change of $\Omega(W_i) \rightarrow \Omega(W_i) \times k_0$, where modification factor $k_0 > 1$.
- e. g., $k_0 = 2$, big $k \rightarrow$ big statistical errors, small $k \rightarrow$ long simulation
- After reaching of flat energy histogram $h(W)$, modification factor is changed e.g. by rule $k_{j+1} = \sqrt{k_j}$, energy histogram is deleted (density of states isn't deleted!) and we start a new simulation
- Computations is finished, when $k$ reaches predetermined value (e. g. 1,000 001)
Wang-Landau algorithm – accuracy of results depends on:

- Final value of modification factor $k_{\text{final}}$
- Softness of deals of energy
- Criterion of flatness of histogram
- Complexity of simulated system
- Details of implemented algorithm
Wangův-Landau algorithm: parallelization

- MPI, each core has one own walker, all cores share actual density of states and actual energy histogram

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**Fig. 1.** Schematic plot of a four GPU implementation of the parallel Wang-Landau algorithm, where $H(E)$ is the energy histogram and $g(E)$ is the density of states. Each rectangle stands for a GPU card which contains thousands of threads.
W-L algorithm-example:

Fig. 6. Specific heat curve for (H₂O)₆₀. Two snapshots (with pointing arrow) are taken at the average energy for corresponding temperatures, respectively, and another snapshot (leftmost) is for the ground state structure after quenching. The red ball stands for an Oxygen atom, the white ball for a Hydrogen atom, and the dash line for the hydrogen bonding.
Thank you for your attention