Chapter 3:

Monte Carlo Simulations

1

Evaluation of Ensemble Properties

Properties of thermodynamic ensembles: $\langle A \rangle = \sum_{i=1}^{N_{tot}} w_i A_i$

w_i: probability of finding system in configuration I

$w_i = N_i / N_{tot}$

All possible classical configurations defined by the phase space ($\mathbf{r}^N$, $\mathbf{p}^N$) with $\mathbf{r}^N$: $\mathbf{r}_1 \ldots \mathbf{r}_N$, $\mathbf{p}^N$: $\mathbf{p}_1 .. \mathbf{p}_N$ => evaluate phase space integrals

$$\langle A \rangle = \int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, w(\vec{r}^{\,N}, \vec{p}^{\,N}) A(\vec{r}^{\,N}, \vec{p}^{\,N})$$

For the **canonical** ((NVT) ensemble:

$$w\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) = \frac{e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}$$

Boltzmann factor

Partition function

$$\langle A \rangle = \frac{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, A\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, d\vec{p}^{\,N}\, e^{-E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right)/k_B T}}$$

$$E_{tot}\left(\vec{r}^{\,N}, \vec{p}^{\,N}\right) = E_{pot}\left(\vec{r}^{\,N}\right) + E_{kin}\left(\vec{p}^{\,N}\right)$$

6N dimensional integral

Momentum part simple quadratic dependence => analytic evaluation possible

Potential energy part more complex => evaluated numerically

=> Configurational space integral

$$\langle A \rangle = \frac{\int \ldots \int d\vec{r}^{\,N}\, A\left(\vec{r}^{\,N}\right) e^{-E_{pot}\left(\vec{r}^{\,N}\right)/k_B T}}{\int \ldots \int d\vec{r}^{\,N}\, e^{-E_{pot}\left(\vec{r}^{\,N}\right)/k_B T}}$$

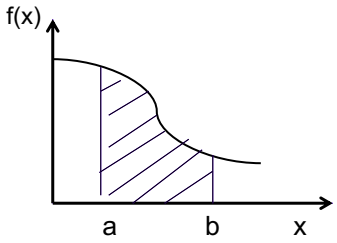
QM analogon:

$$\langle A \rangle = \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\int \ldots \int d\vec{r}^{\,N} \Psi^* A \Psi}{\int \ldots \int d\vec{r}^{\,N} \Psi^* \Psi}$$

2

Quiz IV: Numerical Integration

1) Which algorithms do you know to perform a numerical integration of a function?

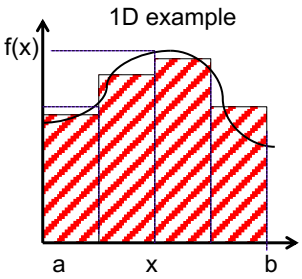


$$\int_a^b f(x)dx \approx \sum_i w_i f(x_i)$$

3

Numerical Evaluation of Configurational Space Integrals

1) By Numerical quadrature



e.g. with:
- trapezoidal rule
- Simpson's rule
- Etc.

$$\int_a^b f(x)dx \approx \frac{(b-a)}{M}\sum_{i=1}^{M-1}\frac{f(x_{i+1})-f(x_i)}{2}$$

uniform grid of M points with grid spacing $\Delta x = \frac{b-a}{M}$

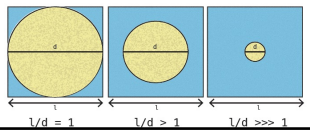
To evaluate 3N dimensional integral => M^{3N} points
e.g. M=100 => 100^{3N} grid points with N=1000-100'000

2) By Monte Carlo sampling

$$\int_a^b f(x)dx \approx (b-a)\langle f(x)\rangle = \frac{(b-a)}{M}\sum_{i=1}^{M} f_i(x_i)$$

Still high-dimensional (3N) integral
x_i randomly chosen e.g. equal probability [0,1] => uniform sampling?

Computer exercise 1: Determination of π via Monte Carlo sampling



⇒ Uniform sampling becomes inefficient when function is very inhomogeneous!!!
⇒ Statistically important parts of configurational space often highly inhomogeneously distributed!

5

Previous exercise: Derivation of the Maxwell-Boltzmann Distribution

What is the probability $P(\vec{p})$ to find a particle with momentum $\vec{p}$ in a system of classical particles (no quantum effects) with only kinetic energy (E_{pot} = 0) at temperature T (canonical ensemble)? b = $1/k_BT$

$$P(\vec{p}) = \frac{e^{-\frac{\beta\vec{p}\bullet\vec{p}}{2m}}}{\int_{-\infty}^{+\infty} d\vec{p} e^{-\frac{\beta\vec{p}\bullet\vec{p}}{2m}}} = P(p_x, p_y, p_z) = \frac{e^{-\frac{\beta(p_x^2+p_y^2+p_z^2)}{2m}}}{\int_{-\infty}^{+\infty} dp_x e^{-\frac{\beta p_x^2}{2m}} \int_{-\infty}^{+\infty} dp_y e^{-\frac{\beta p_y^2}{2m}} \int_{-\infty}^{+\infty} dp_z e^{-\frac{\beta p_z^2}{2m}}}$$

$$\int_{-\infty}^{+\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \qquad a = \frac{\beta}{2m} = \frac{1}{2mk_BT}$$

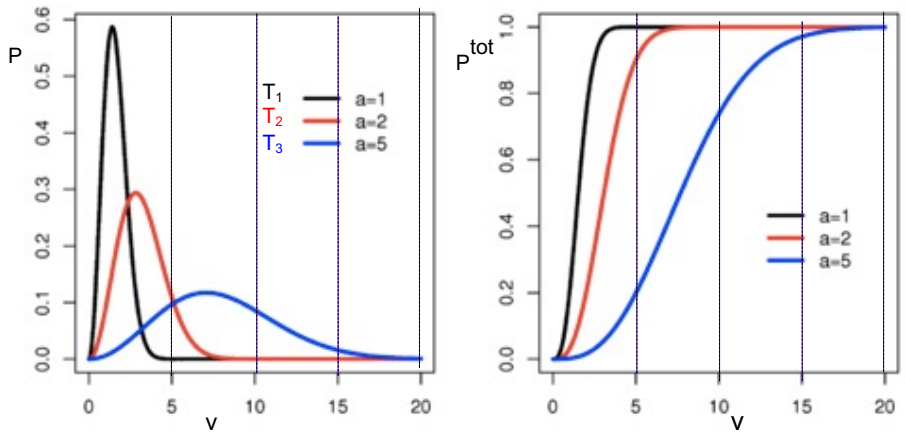
$$P(\vec{p}) = (2\pi mk_BT)^{-3/2} e^{-\frac{\beta p^2}{2m}}$$

$$P(v) = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{k_BT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_BT}}$$

6

Homogeneous Sampling versus Importance Sampling

Example: Maxwell-Boltzmann Distribution



-> most regions: zero contribution!
Uniform random sampling is not efficient!

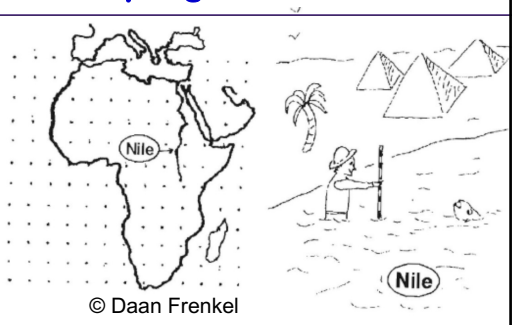
7

Importance Sampling

Evaluate ensemble averages via MC sampling

$$\langle A \rangle = \sum_{i=1}^{N_{tot}} w_i A_i$$

Ideally:
choose sampling points/configurations with important contributions =>
importance sampling
e.g. thermal averages in canonical ensemble =>generate sampling points according to their Boltzmann weights!



© Daan Frenkel

$$w(\vec{r}^N) = \frac{e^{-E_{tot}(\vec{r}^N)/k_B T}}{\int \ldots \int d\vec{r}^N e^{-E_{tot}(\vec{r}^N)/k_B T}}$$

Partition function Q
=> Again 3N dimensional integral!

Idea: cannot evaluate absolute probabilities but can calculate relative probabilities!

$$\frac{P_i}{P_j} = \frac{\frac{e^{-E_{tot}(\vec{r}_i^N)/k_B T}}{Q}}{\frac{e^{-E_{tot}(\vec{r}_j^N)/k_B T}}{Q}} = e^{-\left(E_{tot}(\vec{r}_i^N) - E_{tot}(\vec{r}_j^N)\right)/k_B T}$$

Relative probability of configurations i and j

8

Metropolis algorithm

N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller J .Chem. Phys. ***21****, 1087 (1953)*


Nicholas Metropolis (1915-1999)


Arianna Rosenbluth (1927-2020)


Marshall Rosenbluth (1927-2003)


Augusta H. Teller (1909-2000)


Edward Teller (1908-2003)

1. Choose initial configuration $\mathbf{r}_{old}$ with finite Boltzmann weight
2. Generate new configuration $\mathbf{r}_{new}$ from $\mathbf{r}_{old}$ via random move with probability α_{on}
3. Accept/reject new configuration $\mathbf{r}_{new}$ with relative Boltzmann probability

$$acc(\vec{r}_{old} \rightarrow \vec{r}_{new}) = \min\left(1, e^{-(E(\vec{r}_{new}) - E(\vec{r}_{old}))/k_B T}\right)$$

- If $E_{new} < E_{old}$ => accept
- If $E_{new} > E_{old}$ -> accept with relative Boltzmann probability

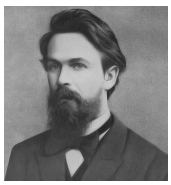
4. If $\mathbf{r}_{new}$ is accepted set $r_{old} = r_{new}$ and goto 2
   if $\mathbf{r}_{new}$ is not accepted goto 2

⇒ Generates random walk through configuration space where every configuration is visited with a Boltzmann probability

⇒ Probability of accessing new configuration $\mathbf{r}_{new}$ only depends on current configuration $\mathbf{r}_{old}$ (and not on previously visited points, no memory effect)

⇒ **Markov process, Markov chain**

1. How do we choose the initial configuration?
   - start from low T in e.g known crystal structure and heat system up to T
   - distribute molecules on a uniform grid
   - etc..


Andrey Andrejevich Markov (1856-1922)

9

Quiz V: Random Process with Given Probability

1) Hypothetical* case:

In the beginning of the semester, you have decided that you will attend the lectures/exercises of the MD/MC course with a probability of 5/6.
Every Tuesday morning, you decide if you will attend or not. How can you make sure that the probability is 5/6?

** This is a purely hypothetical case since, fascinated by the subject, you have of course decided to come to the course 100% of the time!*

10

Metropolis algorithm

1. Choose initial configuration $\mathbf{r}_{old}$ with finite Boltzmann weight
2. Generate new configuration $\mathbf{r}_{new}$ from $\mathbf{r}_{old}$ via random move with probability α_{on}
3. Accept/reject new configuration $\mathbf{r}_{new}$ with relative Boltzmann probability

$$acc(\vec{r}_{old} \rightarrow \vec{r}_{new}) = \min\left(1, e^{-(E(\vec{r}_{new})-E(\vec{r}_{old}))/k_B T}\right)$$

- If $E_{new} < E_{old}$ => accept
- If $E_{new} > E_{old}$ -> accept with relative Boltzmann probability

4. If $\mathbf{r}_{new}$ is accepted set $r_{old} = r_{new}$ and goto 2
   if $\mathbf{r}_{new}$ is not accepted goto 2

⇒ Generates random walk through configuration space where every configuration is visited with a Boltzmann probability
⇒ Probability of accessing new configuration $\mathbf{r}_{new}$ only depends on current configuration $\mathbf{r}_{old}$ (and not on previously visited points, no memory effect)
⇒ **Markov process, Markov chain**

1. How do we choose the initial configuration?
   - start from low T in e.g .known crystal structure and heat system up to T
   - distribute molecules on a uniform grid
   - etc..
3. How do we accept/reject with a given probability acc_{on}?

⇒ Compare with known random process! Generate random number ranf [0,1]
⇒ if acc_{on} > ranf => accept, otherwise reject

12

DEMO

Monte Carlo Simulation of methane/water

https://youtu.be/78tzIwqd4f8

13

Metropolis algorithm

1. Choose initial configuration $\mathbf{r}_{old}$ with finite Boltzmann weight
2. Generate new configuration $\mathbf{r}_{new}$ from $\mathbf{r}_{old}$ via random move with probability α_{on}
3. Accept/reject new configuration $\mathbf{r}_{new}$ with relative Boltzmann probability

$$acc(\vec{r}_{old} \rightarrow \vec{r}_{new}) = \min\left(1, e^{-(E(\vec{r}_{new})-E(\vec{r}_{old}))/k_B T}\right)$$

- If $E_{new} < E_{old}$ => accept
- If $E_{new} > E_{old}$ -> accept with relative Boltzmann probability

4. If $\mathbf{r}_{new}$ is accepted set $r_{old} = r_{new}$ and goto 2
   if $\mathbf{r}_{new}$ is not accepted goto 2

⇒ Generates random walk through configuration space where every configuration is visited with a Boltzmann probability

⇒ Probability of accessing new configuration $\mathbf{r}_{new}$ only depends on current configuration $\mathbf{r}_{old}$ (and not on previously visited points, no memory effect)

⇒ **Markov process, Markov chain**

1. How do we choose the initial configuration?
   - start from low T in e.g .known crystal structure and heat system up to T
   - distribute molecules on a uniform grid
   - etc..
3. How do we accept/reject with a given probability acc_{on}?

⇒ Compare with known random process! Generate random number ranf [0,1]

⇒ if acc_{on} > ranf => accept, otherwise reject

14

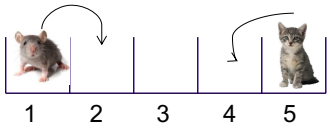
Stochastic Matrix A_{on}

Stochastic matrix, transition matrix, underlying matrix of Markov process:
Square matrix that gives transition probability α_{on} to go from any state o to any state n

$$A = \begin{pmatrix} \alpha_{11} & \cdots & \alpha_{1N} \\ \vdots & & \\ \alpha_{N1} & \cdots & \alpha_{NN} \end{pmatrix}$$

Any conditions for A?

Example of a stochastic matrix of a Markov process (wikipedia): Cat & mouse



5 states:

State 1: (1,3)
State 2: (1,5)
State 3: (2,4)
State 4: (3,5)
State 5: (2,2)(3,3),(4,4)

What is the average life time of the mouse?

$$A = \begin{pmatrix} 0 & 0 & 1/2 & 0 & 1/2 \\ 0 & 0 & 1 & 0 & 0 \\ 1/4 & 1/4 & 0 & 1/4 & 1/4 \\ 0 & 0 & 1/2 & 0 & 1/2 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

- A asymmetric
- has an absorbing state

15

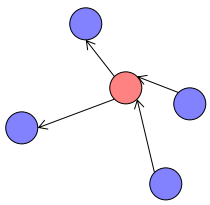
Stochastic Matrices for Ensemble Sampling: Detailed Balance

For MC sampling: considerable freedom to choose random moves, matrix A but some important conditions should be fulfilled: detailed balance ((microscopic reversibility)

Once systems has reached thermodynamic equilibrium with correct statistical weights, these weights should not change anymore

Only possible if total probability to generate $\mathbf{r}_{new}$ from all possible states $\mathbf{r}_{old}$ is equal to the probability of leaving $\mathbf{r}_{new}$

Like dynamic equilibrium in chemical reactions $A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} B$ $k_{AB}[A] = k_{BA}[B]$ $K = \frac{[B]}{[A]} = \frac{k_{AB}}{k_{BA}}$



Overall probability to reach $\mathbf{r}_{new}$: $\pi_{on} = \alpha_{on}\, acc_{on}$

In equilibrium: $N(\mathbf{r}_{old})\pi_{on} = N(\mathbf{r}_{new})\pi_{no}$

$$\frac{N(\vec{r}_{new})}{N(\vec{r}_{old})} = \frac{\pi_{on}}{\pi_{no}} = \frac{\alpha_{on} acc_{on}}{\alpha_{no} acc_{no}} = \frac{\alpha_{on} acc_{on}}{\alpha_{no} acc_{no}} = e^{-(E_{new}-E_{old})/k_B T}$$

=> $\alpha_{on} = \alpha_{no}$ => A symmetric!

microscopic reversibility - detailed balance

16

Metropolis algorithm

1. Choose initial configuration $\mathbf{r}_{old}$ with finite Boltzmann weight
2. Generate new configuration $\mathbf{r}_{new}$ from $\mathbf{r}_{old}$ via random move with probability α_{on}
3. Accept/reject new configuration $\mathbf{r}_{new}$ with relative Boltzmann probability

$$acc(\vec{r}_{old} \rightarrow \vec{r}_{new}) = \min\left(1, e^{-(E(\vec{r}_{new})-E(\vec{r}_{old}))/k_B T}\right)$$

- If $E_{new} < E_{old}$ => accept
- If $E_{new} > E_{old}$ -> accept with relative Boltzmann probability

4. If $\mathbf{r}_{new}$ is accepted set $r_{old} = r_{new}$ and goto 2
   if $\mathbf{r}_{new}$ is not accepted goto 2

⇒ Generates random walk through configuration space where every configuration is visited with a Boltzmann probability

⇒ Probability of accessing new configuration $\mathbf{r}_{new}$ only depends on current configuration $\mathbf{r}_{old}$ (and not on previously visited points, no memory effect)

⇒ **Markov process, Markov chain**

1. How do we choose the initial configuration?
   - start from low T in e.g .known crystal structure and heat system up to T
   - distribute molecules on a uniform grid
   - etc..

3. How do we accept/reject with a given probability acc_{on}?

⇒ Compare with known random process! Generate random number ranf [0,1]

⇒ if acc_{on} > ranf => accept, otherwise reject

17

Trial Moves

Ideal Properties:

- Should not violate detailed balance
- Should generate all possible thermally accessible configurations (ergodicity)
- Should be efficient: minimum number of necessary moves for maximal accuracy
- Generate next configuration with high acceptance probability and at the same time moving widely in configurational space

=> Often trade-off between acceptance ratio (percentage of successful moves) and ergodicity

18

Trial Moves

Translational Moves:
x => x + Δx (ranf -0.5)
y
z…

- To centre of mass or to particle coordinates?
- Move one particle or all at the same time?

Orientational Moves

θ => θ + $\Delta\theta$ (ranf -0.5) (rigid body rotation)

- Cartesian unit vector
- In Euler angles
- In quaternions

Flexible molecules

Random moves of Cartesian coordinates => not a good idea for chemically bonded systems

Random changes in internal coordinates e.g. dihedral angles

⇒ Gets more and more difficult for large molecules (e.g. biomacromolecules proteins DNA), dense systems, low T

⇒ Smart moves necessary!

Different thermodynamic ensembles

Isothermal-isobaric: also variations of volume!
Grand canonical: particle insertions/deletions

19

More Sophisticated Trial Moves

Possible Trial Moves

20