Kinetic Monte Carlo Notes

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Monte Carlo Methods

- Solve complex problems using random sampling from a probablity distribution (i.e. stochastic description).
- Useful to evolve a physical system to a new state from an esemble of potential future states.

Integrating a function MC sampling

- If we want to evaluate the integral of a function over some domain we can numerically approximate this using the midpoint rule:

$$\int_a^b f(x)dx = \frac{b-a}{N}\sum_{i=1}^{N} f(x_i) \tag{0.1}$$

- There is an alternative way to do this using probablity theory to determine the expectation value of a function $f(x)$ for random variable x:

$$\int_a^b p(x)f(x)dx = \frac{b-a}{N}\sum_{i=1}^{N} f(x_i) \tag{0.2}$$

  where $p(x)$ is a uniform probablity distribution over the interval $[a, b]$.

- The difference between numerically evaluating Equation 0.1 and Equation 0.2, is that Equation 0.1 is evaluated over a grid of points and Equation 0.2 is randomly sampled points.
- The error of MC integration is $\propto \frac{1}{\sqrt{N}}$ as a result of central limit theorem

Example integrating a function using MC sampling[1]

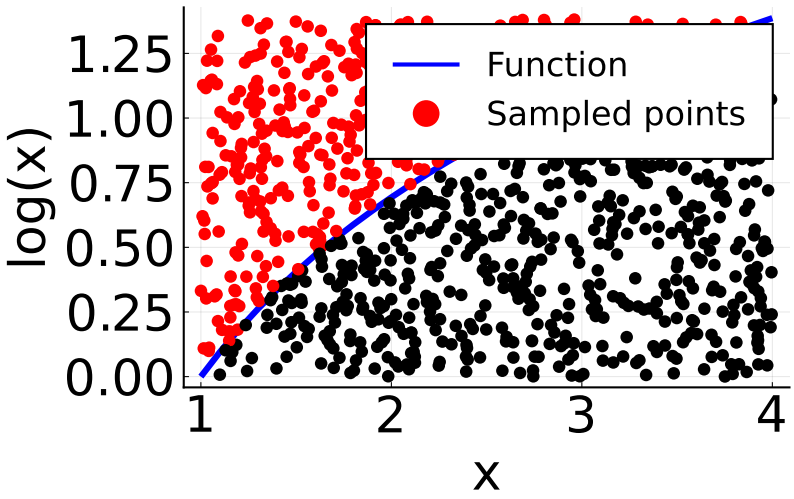

Figure 0.1: Random sampled points from uniform distribution over the interval $[1, 4]$. The black points are those that are accepted.

[1] A more detailed notebook implementing the code can be viewed here

Example integrating a function using MC sampling

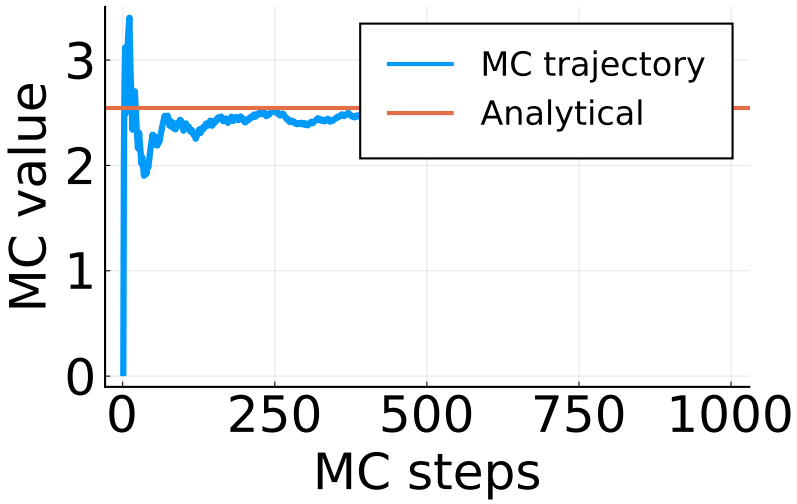

Figure 0.2: Integration of $log(x)$ using MC.

Statistical Thermodynamics & Ensemble Properties

- Microscopic → Macroscopic description
  - How positions and momenta of 10^{23} particles relates to bulk temperature, pressure, or volume.
- Ensembles use probablity of specific microstate. Probability theory provides average of a function or variable, $\langle X \rangle$:

$$\langle X \rangle = \frac{1}{N} \sum_{i=1}^{N} n_i \, X_i = \sum_{i=1}^{N} \underbrace{p_i}_{\text{PDF}} \, X_i \tag{0.3}$$

- If $\langle X \rangle$ is continous, Equation 0.3 is an integral.
- p_i is the probablity the system is in state i. The probablity density function (PDF) has the property that its normalized, i.e. $\sum_{i=1}^{N} p_i = 1$

Statistical Thermodynamics & Ensemble Properties

- The consqequence of Equation 0.3 is that microscopic collections (i.e. ensemble of systems) can be used to calculate macroscopic properties.
- Choice of $p_i = \frac{z_i}{Z}$ depends on macroscopic conditions which manifest through the partition function:

$$Z = \sum_i e^{-\beta X_i} \tag{0.4}$$

- For a macroscopic system that has constant particles, volume and temperature, i.e., canonical.
  - $\beta = \frac{1}{k_b T}$ and $X_i = E_i$ where Boltzmann factor is $z_i = e^{-\frac{E_i}{k_b T}}$

$$\langle E \rangle = \frac{1}{Z} \sum_i e^{-\frac{E_i}{k_b T}} E_i \tag{0.5}$$

Statistical Thermodynamics & Ensemble Properties

- The biggest challenge in evaluating Equation 0.5 is it requires knowledge of all possible configurations.
- If Z is a configurational integral, e.g., $Z = \int e^{-U(\mathbf{r}^N)/k_B T} d\mathbf{r}^N$, then there are $3N$ possible configs!
- The key insight is that most configurations are not probable:
  - If the two atoms are extremely close at moderate T, the term $U(\mathbf{r})$ is large an hence the probablity low.
- The question then becomes, can we determine $p_i = \frac{1}{Z} e^{-\frac{E_i}{k_B T}}$ efficiently, that is the states with highest probablity centered around $\langle E \rangle$ given that Z is not accessible.

$U(\mathbf{r})$ is the potential energy between pairs of atoms.

Metropolis Monte Carlo

- If we wanted to evaluate Equation 0.5 for an atomic system (i.e. the discrete states are replaced by continous atomic configurations), we could use the MC sampling as in Equation 0.2.
- However we need to integrate over $3N$ dimensions!
- This eliminates the feasability for determining the partition function Z which is required to know the probablity of any specific configuration p_i

Metropolis Monte Carlo

- The Metropolis algorithm is a process to sample states i with probablity p_i
- This is achieved by using relative probablities, i.e., $\frac{p_i}{p_j}$
- From this we get the correct average quantities.
- This works because, even though we don't know Z and can't determine p_i, the results of $\frac{p_i}{p_j}$ gives the correct distribution
- Relative probablities are given as:

$$\frac{p_i}{p_j} = \frac{e^{-E_i/k_B T}}{Z} \frac{Z}{e^{-E_j/k_B T}} = e^{-(E_i - E_j)/k_B T} \tag{0.6}$$

- Which only depends on energy difference between states as shown in graph

Metropolis Monte Carlo

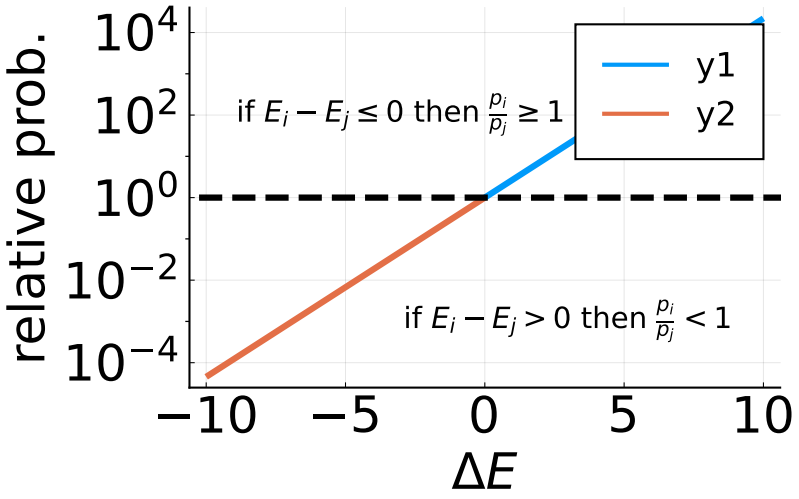

Figure 0.3: Relative probablity for two states.

Metropolis Monte Carlo

- In the metropolis MC approach we use the relations on Figure 0.3 to create a trajectory of states.
- The steps for MMC are:

  1. Generate configuration i with E_i
  2. Randomly trial configuration, $i+1$, and calculate E_{i+1}
  3. Get relative probablity via Equation 0.6.
  4. Use relations in Figure 0.3 to accept or accept with probability $\frac{p_i}{p_j} < 1$ given a randomly generated number betwen $(0, 1)$

Backmatter

Connect with me!

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> **Note**
>
> This presentation can be viewed online at https://stefanbringuier.github.io/KMCNotes. A report formated PDF of this presentation can be downloaded here.

> **Tip**
>
> To export `revealjs` presentations to pdf, press 'e' then 'ctrl-p' 'save as pdf'

References

Andersen, Mie, Chiara Panosetti, and Karsten Reuter. 2019. "A Practical Guide to Surface Kinetic Monte Carlo Simulations." *Frontiers in Chemistry* 7. https://doi.org/10.3389/fchem.2019.00202.

LeSar, R. 2013. *Introduction to Computational Materials Science: Fundamentals to Applications*. Cambridge University

Press. https://books.google.com/books?id=QzkhAwAAQBAJ.

"Numerical Integration - Midpoint, Trapezoid, Simpson's Rule." 2021.