Monte Carlo Simulations
II. Metropolis Monte Carlo Method

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Previously on ….

- We have covered basic concepts of Monte Carlo Simulations
- We have introduced ways of generating random numbers and sampling.

Course Structure

- Part A: Introduction to Modelling

- Part B: Monte Carlo Simulations
  - Basic Concepts
  - **Metropolis Monte Carlo Simulations**
  - Examples of MC in Materials Simulation

- Part C: Density Functional Theory (DFT) Calculations

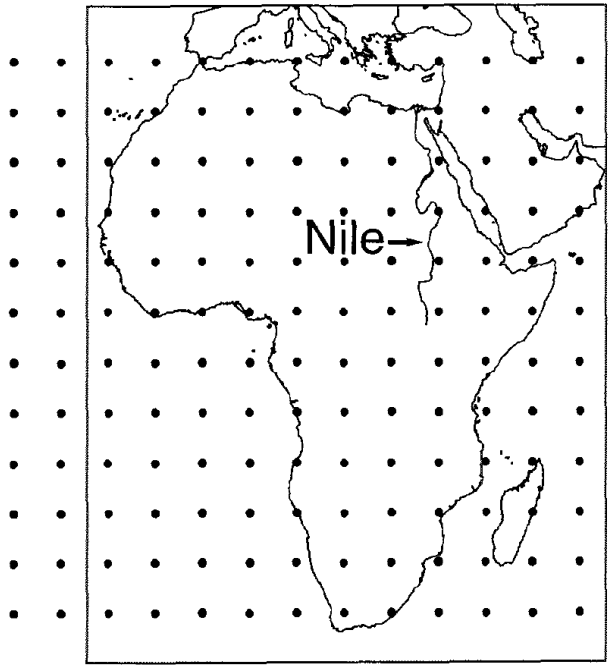
Measuring the depth of Nile

- Problem: Measure the averaged depth of rive Nile

Solution 1: (Conventional Quardrature)

- Prepare a set of point (randomly distributed on the map)
- measure depth at each point
- Take a integral over all points and get the averaged value

- **Problem**: many points are “wasted”.

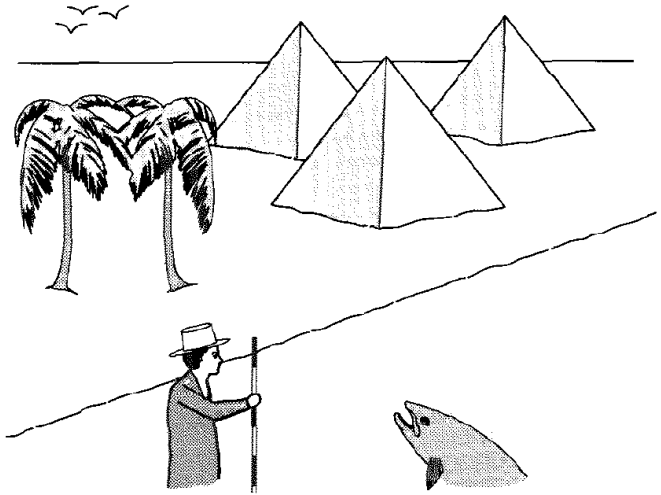


Measuring the depth of Nile

- Problem: Measure the averaged depth of rive Nile

Solution 2: (Metropolis Scheme)

- Random points are taken along the river ("a random walk").
- **During the random walk, if you walk out of the river, the move is rejected.**
- Measure depth at accepted points.
- Take average.



Nile

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*
- For example state A is a regular crystalline lattice, and State B is a slightly deformed state A.

- Thought experiment 1:

> The transition from A to B must satisfy one condition (called *detailed balance*):
>
> Transformation from A to B is reversible.

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

- Thought experiment 1:

This means, the probability of transition from A to B must be equal to the probability from B to A.

We can express this as:

P(A) T(A->B) =P(B) T(B->A)

P(A): probability density of finding a system in State A.

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

- Thought experiment 2:

Let's recall the concept of "random walk". We can pick a system with State A and make it transform to any random state (may not be B), this is called a "trial move". (**R(A->B)**)

If the trial move is made from A→B, we may or may not accept the move eventually. (**acc(A->B)**)

Then T(A->B) can be expressed by:
T(A->B) = R(A->B) acc(A->B)
Also, we have **T(B->A) = R(B->A) acc(B->A)**

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

Combine the results from thought experiment 1 and 2, we have:

P(A)R(A->B)acc(A->B)=P(B)R(B->A)acc(B->A)

acc(A->B)/acc(B->A)=(P(B)R(B->A)) / (P(A)R(A->B))

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

acc(A->B)/acc(B->A)=(P(B)R(B->A)) / (P(A)R(A->B))

Recall that “transformation from A to B is reversible”.
i.e. if A->B happens, then acc(B->A)=1. (if we want to know acc(B->A), we can assume acc(A->B)=1)

Applying this,

acc(A->B) = (P(B)R(B->A)) / (P(A)R(A->B))

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

acc(A->B) = (P(B)R(B->A)) / (P(A)R(A->B))

To satisfy this equation, the choice of Metropolis et al. is:

acc(A->B) = min [(P(B)R(B->A)) / (P(A)R(A->B)), 1]
if P(A)R(A->B)>0

= 1
otherwise

Metropolis Monte Carlo Method: A Simple Derivation

- *Determine the transition probability **T (A->B)** to go from State A to State B for a equilibrium system.*

Hence, **T(A->B)** is given by:

T(A->B) = R(A->B)
if P(B)R(B->A)>=P(A)R(A->B)

= R(A->B) (P(B)R(B->A)) / (P(A)R(A->B))
if P(B)R(B->A)<P(A)R(A->B)

To summarize…

- We have derived the transition probability from one state to another by satisfying the acceptance probability equation (acc(A->B)<=1) :
- **acc(A->B) = (P(B)R(B->A)) / (P(A)R(A->B))**
- This is a very general derivation of Metropolis Monte Carlo scheme. Now let's turn to a slight more specific case.

Metropolis Monte Carlo Simulations for *a Canonical Ensemble*

- Ensemble is first introduced in statistical mechanics to study the behavior of a microscopic system.
- Ensemble: assembly of a large number of virtual copies of a system, each of which represents a possible state that the real system might be in.
- Canonical Ensemble (most applied ensemble): Suppose we have N particles in a box of volume V, and we put the box in a heat bath of temperature T. The box keeps its thermal equilibrium by exchanging energy with external heat bath.

Metropolis Monte Carlo Simulations for *a Canonical Ensemble*

- *Determine if State A can transform to State B in a Canonical Ensemble.*

Here,

acc(A->B) = (P(B)R(B->A)) / (P(A)R(A->B))

can be expressed by a Boltzmann factor:

acc(A->B) = exp(kB/T*(E(B)-E(A))

E(A) : the potential energy of State A

Metropolis Monte Carlo Simulations for *a Canonical Ensemble*

- *Determine if State A can transform to State B in a Canonical Ensemble.*

acc(A->B) = exp(kB/T*(E(B)-E(A))

Under this equation, A->B is always accepted if E(B)<E(A)

If E(B)>E(A), A->B is accepted if **exp(kB/T*(E(B)-E(A))<1**

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i.e. if the energy of a system decreases from one state to another, the transition is always welcome, otherwise the transition can still proceed with a certain probability.

A General Algorithm for Metropolis MC

- 1. We start with a system of N particles and calculate its energy E.

- 2. Select one random particle and give it a random displacement, and calculate the energy of the system after the move, denoted as E'.

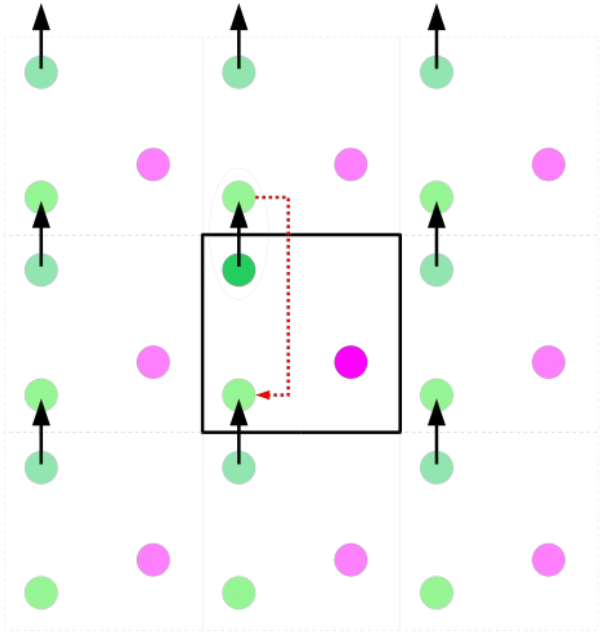
- 3. Accept the move if E'-E<0
- or exp(kB/T*(E'-E))<1 if E'-E>0

- 4. If accepted, use the new configuration as the base configuration and return to Step 1.
- If rejected, do nothing and return to Step 1.

- 5. The loop is stopped when a certain criterion is meet. Then we regard the system as "relaxed".

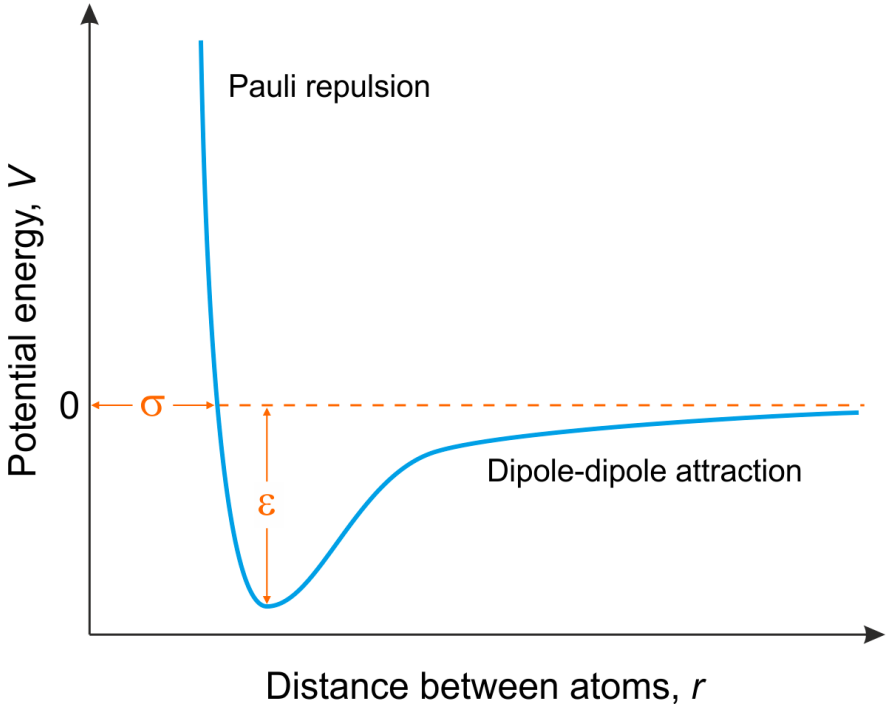
Technical Details: Boundary Conditions

- We usually apply periodic boundary conditions to our simulation box.
- The surface atoms only accounts for a small fraction of total atoms (for a simple cubic crystal of 1000000 atoms, the fraction of surface atoms is only ~6%).
- An effective method for simulating homogeneous bulk systems.



Technical Details: Truncation of Interactions

- Another way to reasonably reduce computational costs.
- Interatomic potentials are usually truncated beyond a critical distance (called cut-off distance), beyond which the interatomic potential is ignored (i.e. regarded as zero).



Summary

- Metropolis Monte Carlo Simulation:

acc(A->B) = min ((P(B)R(B->A)) / (P(A)R(A->B)),1)

- Algorithm of relaxing a microscopic system using Metropolis Monte Carlo simulations
- Always accept move when energy decrease. If energy increases, accept with probability

- In practice, we often use periodic box / truncation of potentials to save computational expenses.