10.34, Numerical Methods Applied to Chemical Engineering
Professor William H. Green
Lecture #28: Guest lecture on Monte Carlo / MD.

Intro to MC Methods

- stochastic – element of randomness
- contrast with standard integration algorithms
- when is MC useful?

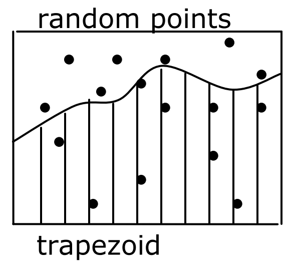


Figure 1. Trapezoidal rule versus Monte Carlo integration.

From Friday $< f >= \int f(x)p(x)dx$

point in curve = 1
point out curve = 0

- integral of p(q)f(q)dq where p(q) is probability distribution
- could do by sampling

Comparison of Accuracy

MC – accuracy ~ $N^{-0.5}$
Other methods – accuracy ~ $N^{\sim 1/d}$

effect of dimension on accuracy

Random States

- calculation of area of hyper-sphere for calculation of Pi
  - chance of hit → 0
- Importance sampling – concentrates sampling in regions of higher probability

$$\int f(x)p(x)dx \Rightarrow \left[\frac{f(x)}{p(x)}\right]p(x)p(x)dx$$

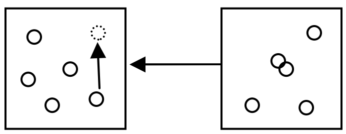
Ergodicity

- MC often used to simulate time-dependent processes, although there is no "time" in MC simulations
- Ergodic Theorem: Phase space average is identical to the time average

$$< f >= \int f\left(x(t)\right)dt$$

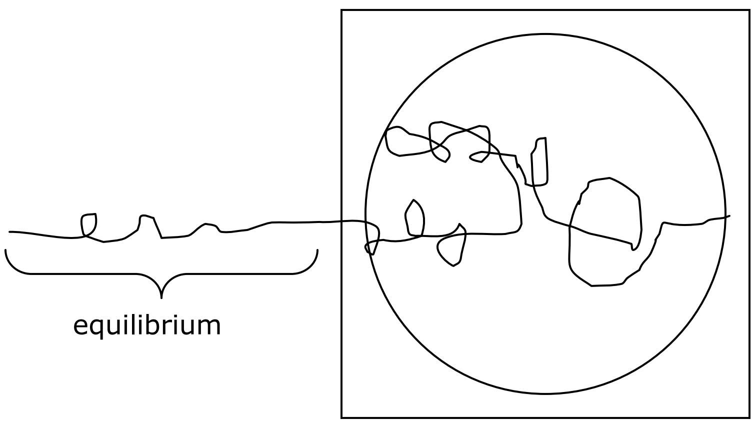
Metropolis Method

- if attempted move lowers the energy, it is automatically accepted
- if attempted move increases the energy, it is accepted with:
    - $p(x) = \exp(^{\Delta E}/_{RT})$
- Only need relative probabilities



$$p \sim \exp\left(\frac{-(E_2 - E_1)}{kT}\right)$$

Figure 2. Two configurations.



- attempted configuration represents a deviation from previous configuration
- Important: If move is rejected, the "old" state is counted again

Figure 3. Representation of an attempted configuration.

MC vs. MD

Equilibrium vs. Dynamics

Orientation of Polymers using MC

MD cannot probe large (ms) time scales

MC can find equilibrium sets of configurations

- typically shorter correlations because probability of impossible moves

EXAMPLE – evolution of torsions

- statistically sample phase space

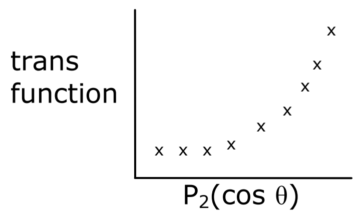


Figure 4. Evolution of torsional angles.