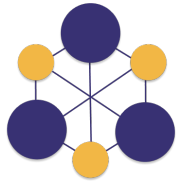


Monte Carlo of Molecular Systems

MSSE Bootcamp

August 13, 2020

Berkeley
UNIVERSITY OF CALIFORNIA
College of Chemistry
College of Engineering

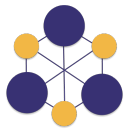
Monte Carlo Connection to Molecular Systems

According to **statistical mechanics**

We can use MC to evaluate this integral!

$$\langle Q \rangle = \int_V Q(r^N)\rho(r^N)dr^N$$

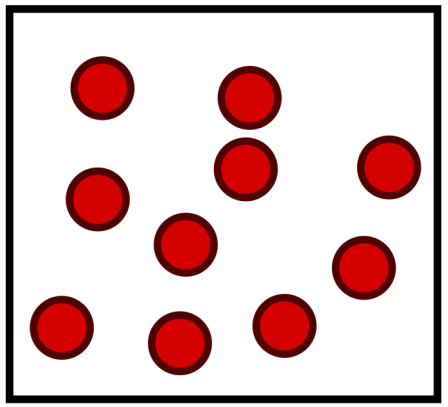
Q	quantity which depends on atomic coordinates (r^N)
$\langle Q \rangle$	average value of quantity Q (square brackets denote average)
r^N	atomic coordinates with N dimensions
$\rho(r^N)$	probability density based on thermodynamic properties (beyond scope of this course)



Monte Carlo Connection to Molecular Systems

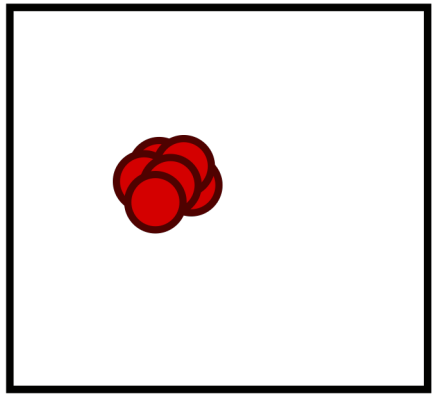
In order to evaluate this integral we have some special considerations

$$\langle Q \rangle = \int_V Q(r^N)\rho(r^N)dr^N$$



Consider our 10 particles in a box.

Because we have so many possible states, it is not effective to sample points with a uniform distribution.



This configuration (particles stacked) is high energy and not likely to occur

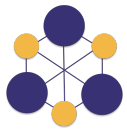
The Metropolis Monte Carlo Method

- No longer using a uniform distribution for coordinate generation.

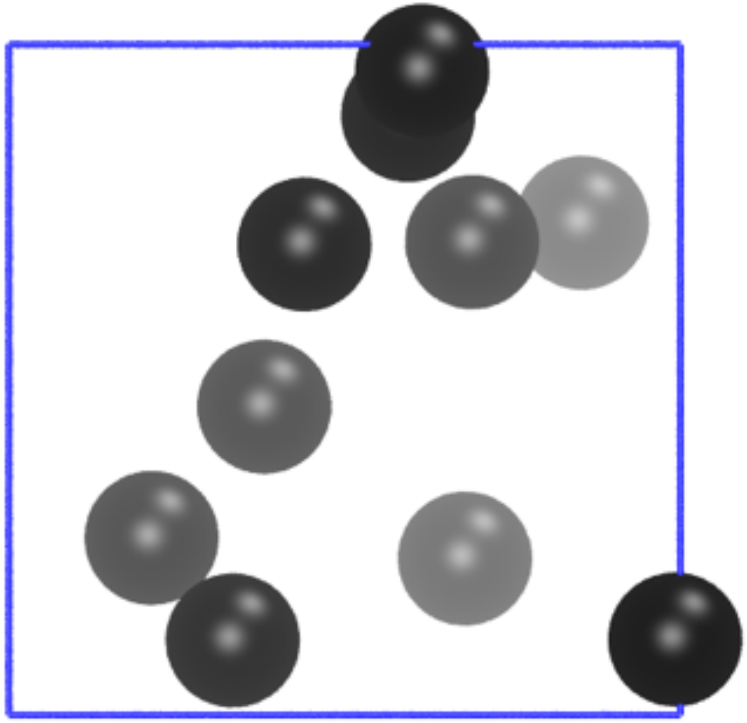
- Instead, generate configurations with distribution - $\boldsymbol{\rho}\left(\boldsymbol{r}^{\boldsymbol{N}}\right)$ - the probability density based on thermodynamic properties.

Then, we can evaluate the integral as the average of the generated configurations:

$$\langle Q \rangle = \frac{1}{N} \sum_{i=1}^{N} Q(r_i^N)$$

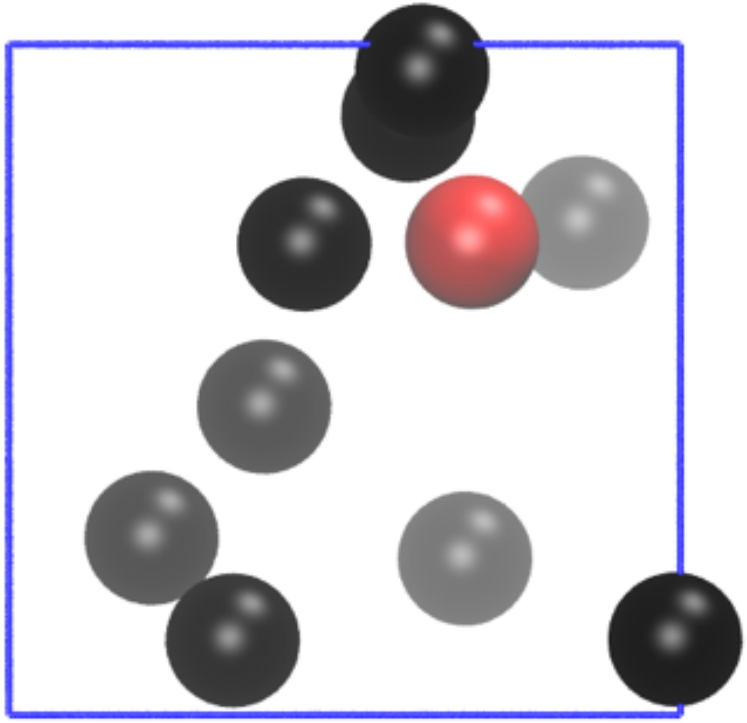


The Metropolis Monte Carlo Recipe

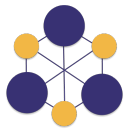


Generate an initial state *m* and calculate its energy.

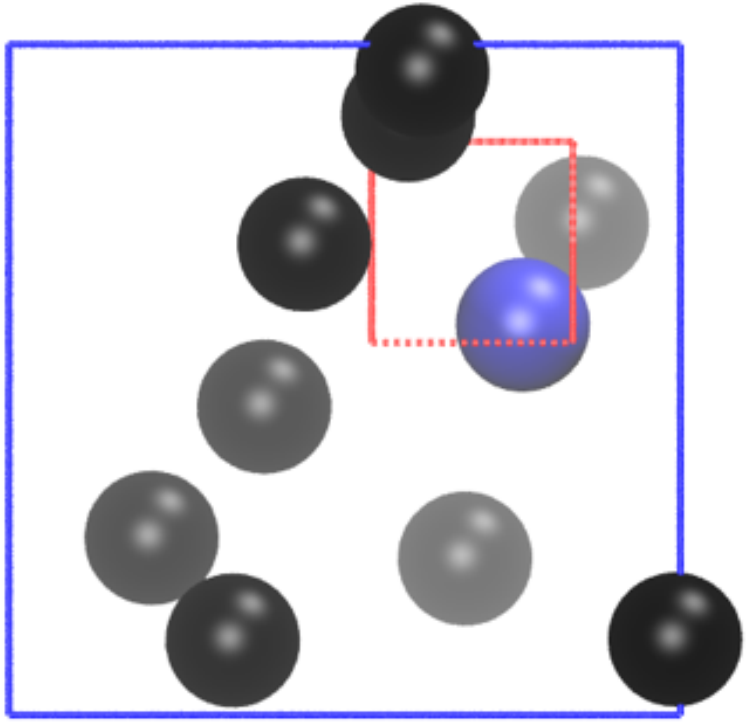
The Metropolis Monte Carlo Recipe



Choose an atom with uniform probability



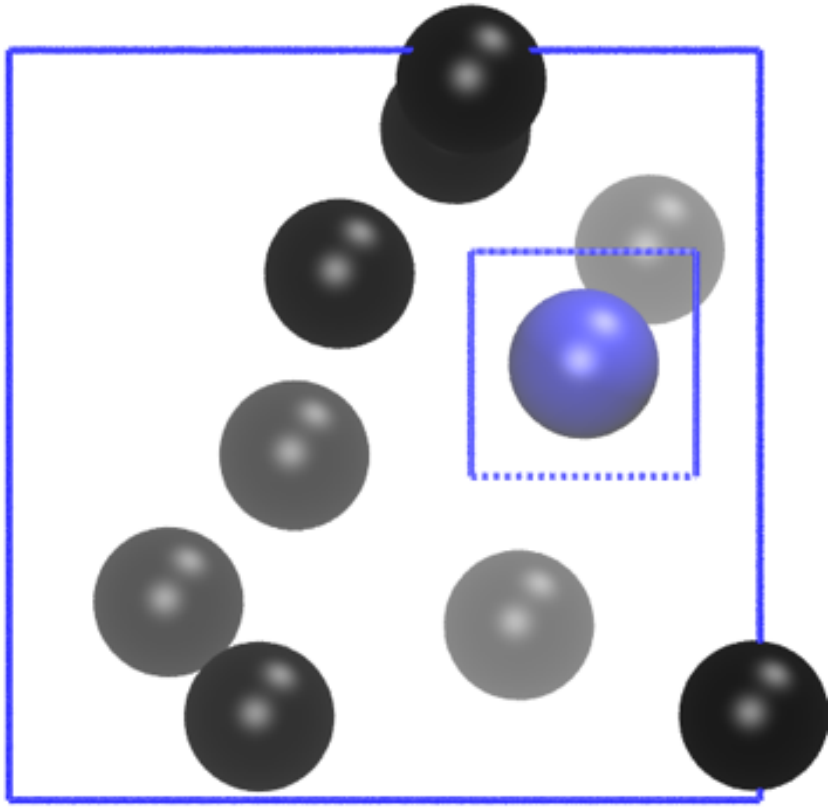
The Metropolis Monte Carlo Recipe



Attempt a random translation within a maximum distance.

Calculate the energy of the new state, n.

The Metropolis Monte Carlo Recipe



Accept or reject new state according to the Metropolis criterion

The Metropolis Criterion

Accept move based on the energy change resulting from moving the particle and system temperature.

$$P_{acc}(m \rightarrow n) = \min[1, e^{-\Delta U/T}]$$

This means we will always accept moves which result in a decrease in energy ($-\Delta U$), and sometimes accept moves which are zero or positive.

In practice, we will generate a random number on the range zero to 1. If our calculated P_{acc} is greater than our generated number, we accept the configuration.