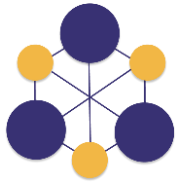


Monte Carlo of Molecular Systems

Chem 280

Berkeley
UNIVERSITY OF CALIFORNIA

College of Chemistry
College of Engineering

Statistical Mechanics

the description of physical phenomena in terms of a statistical treatment of the behavior of large numbers of atoms or molecules, especially with regard to the distribution of energy among them.

--Oxford Languages

Statistical Mechanics

In other words…

Statistical mechanics allows us to predict the properties of a large system by examining and analyzing the many possible configurations, or microstates, of its atoms or molecules.

Monte Carlo of Molecular Systems

According to **statistical mechanics**

We can use MC to evaluate this integral!

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

$\boldsymbol{Q}$ quantity which depends on atomic coordinates (r^N)

$\boldsymbol{\langle Q \rangle}$ average value of quantity Q (brackets denote average)

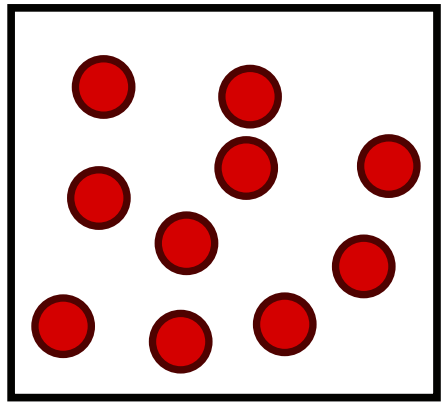
$\boldsymbol{r^N}$ atomic coordinates of N atoms.

$\boldsymbol{\rho(r^N)}$ probability density based on thermodynamic properties (beyond scope of this course)

Monte Carlo of Molecular Systems

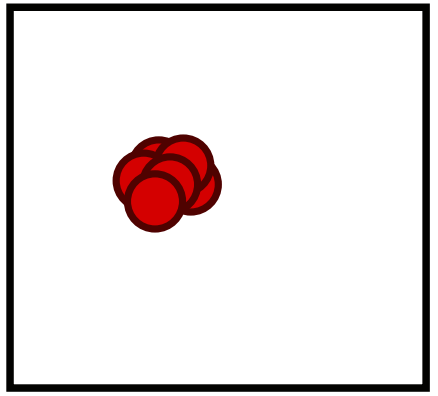
In order to evaluate this integral we have some special considerations

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



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. We want to sample configurations which are likely to occur.



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

Use the Metropolis Monte Carlo method

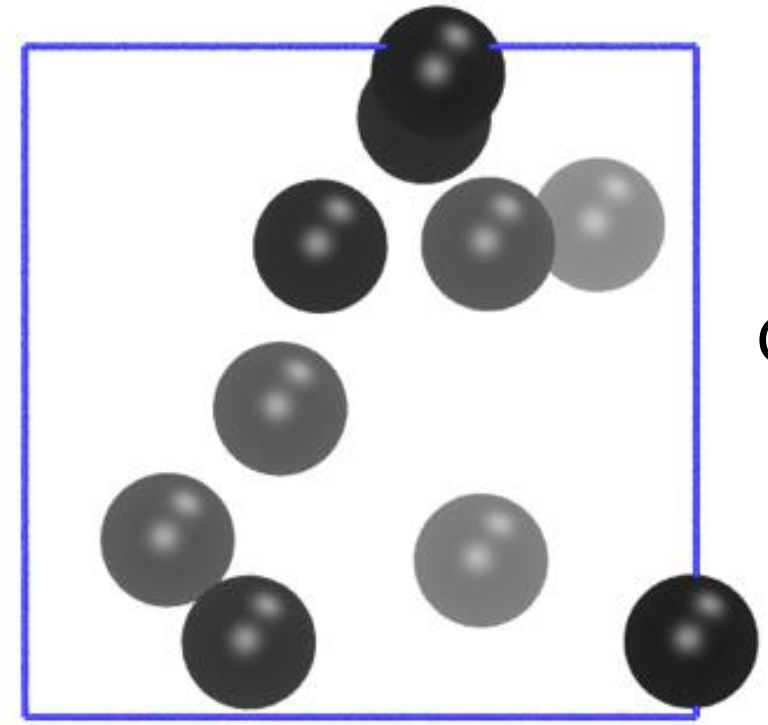
Importance Sampling

- No longer using a uniform distribution for coordinate generation.
- Instead, generate configurations with distribution - $\boldsymbol{\rho}(\boldsymbol{r}^{\boldsymbol{N}})$ - the probability density based on thermodynamic properties.

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

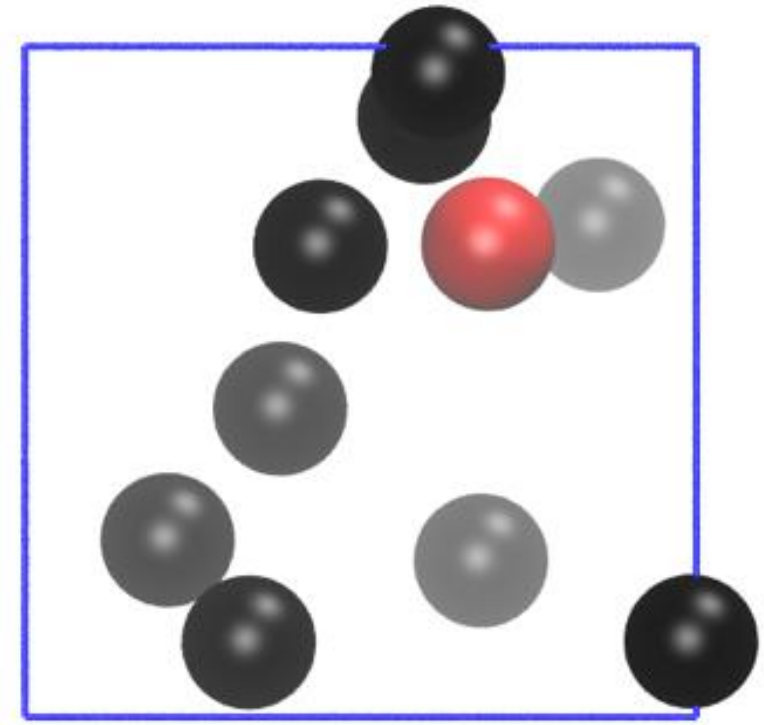
$$\langle Q \rangle = \frac{1}{N} \sum_{i=1}^{N} Q(r_i^N)$$

The Metropolis Monte Carlo Recipe



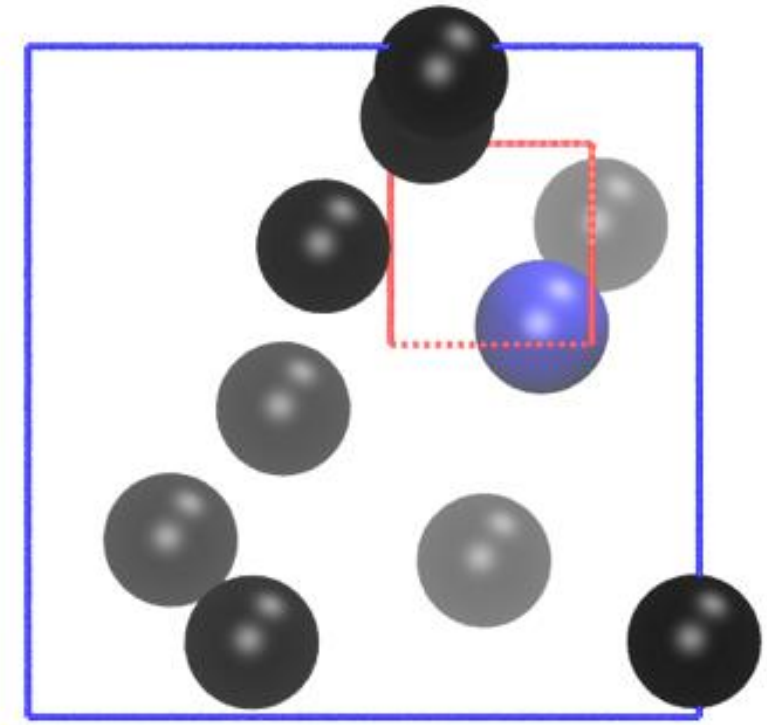
Generate an initial state *m* and calculate its energy.

The Metropolis Monte Carlo Recipe



Choose an atom with uniform probability

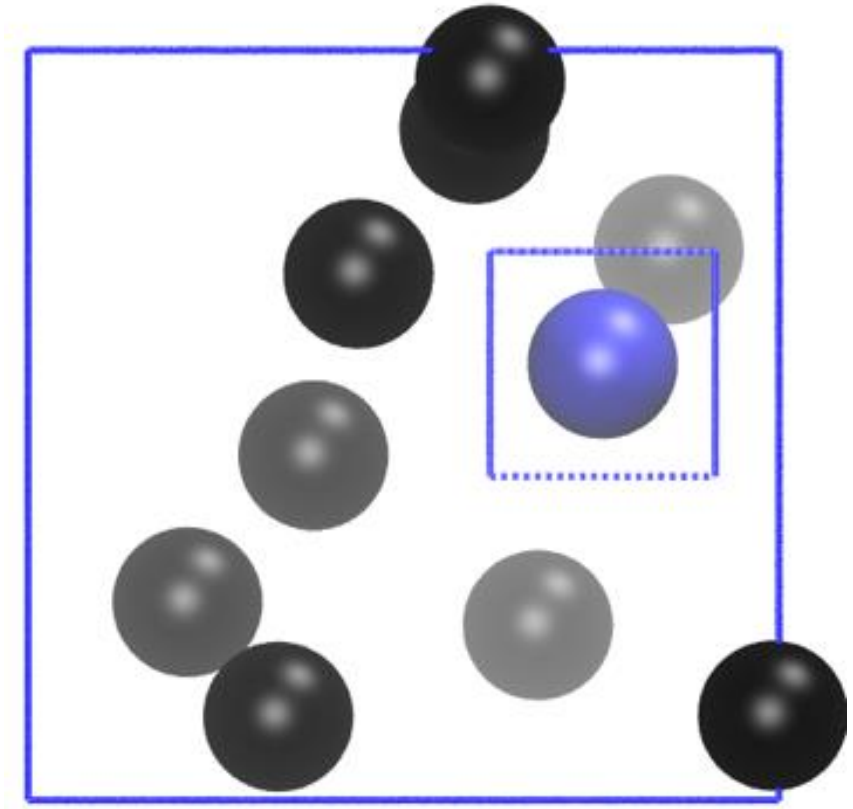
The Metropolis Monte Carlo Recipe



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.

Reduced Units

For Argon,

$$\varepsilon = 120\ K\ (k_B) = 1.68\ x\ 10^{-21}\ J \text{ and } \sigma = 3.4\ x\ 10^{-10}\ meters$$

These are really inconvenient numbers!

We will normalize our energy by ε and our distances by σ.

$$U^*(r) = \frac{U(r)}{\varepsilon}$$

$$r^* = \frac{r}{\sigma}$$

$$U^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$

This will make $U^*(r^*)$ be on the order of 1.