Monte Carlo of Molecular Systems

Chem 280

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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

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

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We can use MC to evaluate this integral!

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

This integral gets complicated very quickly. Consider a system of 10 atoms in 3 dimensions.

3 dimensions x 10 atoms = 30 dimensional integral!

This integral would be very difficult to evaluate analytically, but we can use Monte Carlo Integration to estimate the value.

Today we will build a model for the energy of a molecular system (U). This energy is a function of molecular coordinates, and can represent Q.

The Lennard Jones Potential

The Lennard Jones Potential is an equation that is often used to model the interaction energy of nonbonded atoms:

$$Q(r^N) = U(r) = 4\varepsilon[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}]$$

This interaction is pairwise, meaning it occurs between two particles.

r – distance between two particles
ε – strength of particle interaction
σ – particle size

ε and σ – are parameters which are dependent on particle identity

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First proposed in 1924. You can read the paper: https://royalsocietypublishing.org/doi/10.1098/rspa.1924.0081

The Lennard Jones Potential

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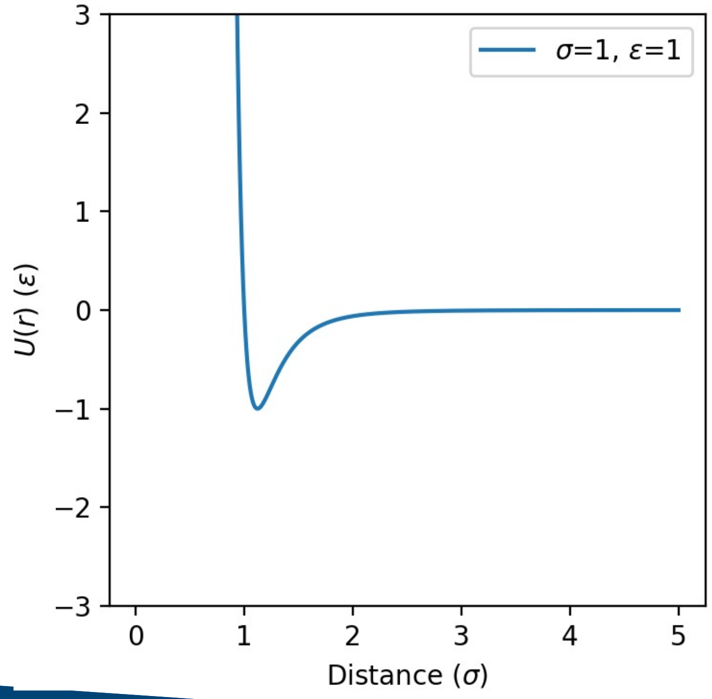

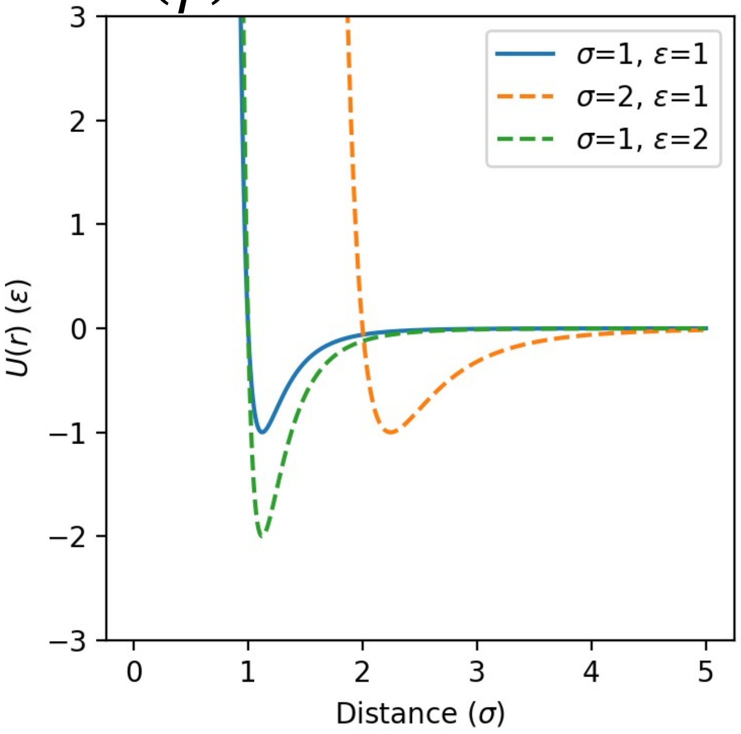

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Reduced Units

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 $\boldsymbol{U^*(r^*)}$ be on the order of 1.

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