Monte Carlo of Molecular Systems

MSSE Bootcamp

August 12, 2020

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College of Chemistry
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Monte Carlo Connection to Molecular Systems

According to **statistical mechanics**

We can use MC to evaluate this integral!

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

$\boldsymbol{Q}$	quantity which depends on atomic coordinates (r^N)
$\boldsymbol{\langle Q \rangle}$	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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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 our model for the thermodynamic quantity, Q.

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The Lennard Jones Potential

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

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

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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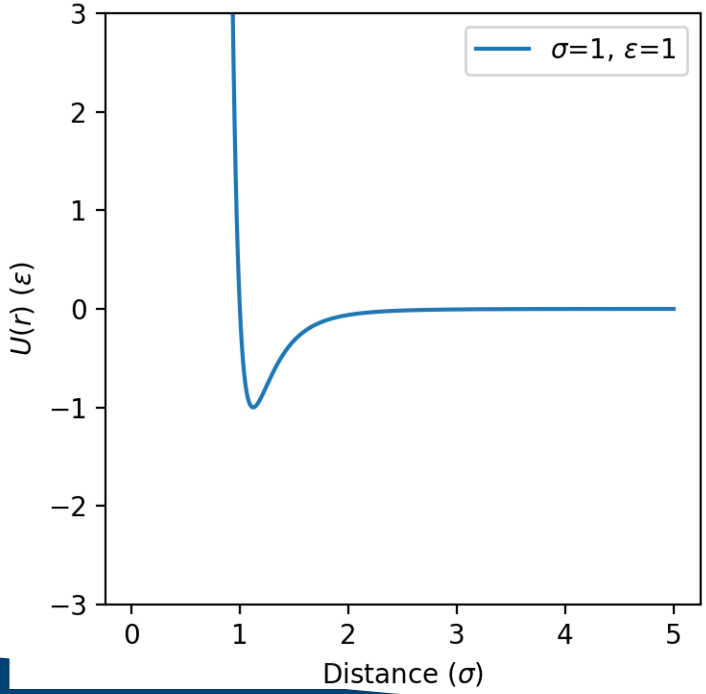

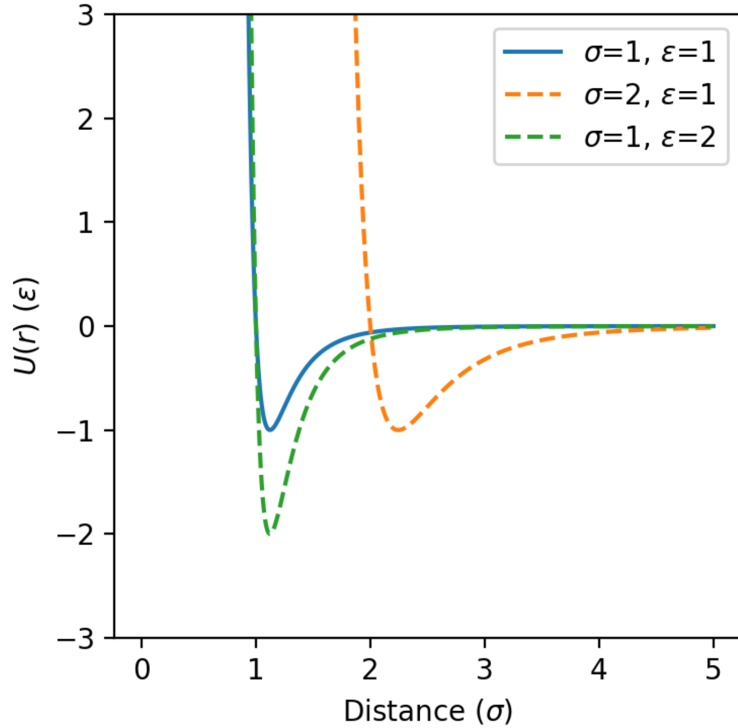

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Reduced Units

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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