**ChEn 513**

**Homework #6**

**Problem #1**

Do problem #12 from Section 8.8.1.

**Problem #2**

Do problem #13 from Section 8.8.1.

**Problem #3**

Extend the MC RDF code to molecules that can associate. The model that you should use consists of these parts:

1. The repulsion and dispersion interactions are modeled with the LJ potential.
2. Monomers freely rotate. Model this by doing a free rotation step with each accepted move if the monomer is not associated. By free rotation, we mean that all rotation trials are accepted – there is no energy barrier to the rotation – unless association has occurred.
3. Association is modeled with a square-well model. Assume that an association site is located at a specific point on the surface (*r* = σ) of each molecule. The square well potential then forms the attraction between these association sites (e.g., H-bond sites) whenever these sites are close enough to each other. The mathematical model for this is given by



where *n* is adjustable. This means that whenever the two association sites are within a distance σ, there will be an additional strong attraction as shown in the diagram at the right where association occurs between the two middle sites, but not with any of the others.

1. Rotations are restricted when association has occurred. Use the standard Metropolis acceptance criteria for the trial rotations when association has occurred. That is use the square-well energy in the acceptance criteria for rotations whenever two sites are within the association range so that some breaking of the association can occur, but the ability to do so is related to the thermal energy.

Use your simulation to generate *g*(*r*) for *n* = 0 and 10 and compare these on the same plot. Also calculate from your simulation the fraction of molecules associated. Identify differences in terms of the structure of the fluid and the degree of association.