06-640: Molecular Simulations
Mid-semester Project A: Monte Carlo Simulation of Polydisperse Systems

Many research groups around the world are interested in crystals formed by ordered arrays of spherical colloids. The square well potential you used in Phase I can be thought of as a very simple model for the interaction energy between two spherical colloids with short range attractive forces. Real colloids are always polydisperse, that is, the particle sizes are distributed about a mean value. In this part of the project you will examine what differences exist between ideal square well spheres and polydisperse square well spheres.

Please refer to the general handout regarding the mid-semester project for details on how your final report should be presented. You must have your NVT and NPT Monte Carlo codes from Phase 1 working to address the questions below.

We will consider polydisperse systems where the length scale for square well interactions, σ, is a normal distribution. That is, the probability of a particle having a length scale in the interval $(\sigma, \sigma + d\sigma)$ is

$$(2\pi K^2)^{-1/2} \exp\left(-\frac{(\sigma - \overline{\sigma})^2}{2K^2} \right) d\sigma.$$

Here, K has units of length and measures the polydispersity of the particle size distribution and $\overline{\sigma}$ is the average value. We will assume for simplicity that the energy scale associated with square well interactions is constant for all particles. That is, we will assume that the interaction between two particles with individual lengths σ_1 and σ_2 is (in dimensional units)

$$V_{12}(r) = \begin{cases} +\infty, r < \hat{\sigma} \\ -\varepsilon, \hat{\sigma} \le r \le 2\hat{\sigma}, \\ 0, r > 2\hat{\sigma}, \end{cases}$$

where we have defined $\hat{\sigma} = (\sigma_1 + \sigma_2)/2$.

Part I: Dilute Phases

1. Adapt the codes you developed in Phase I to perform NPT-MC of a system of polydisperse square well particles. Compute the average energy per particle as a function of density for several values of K and compare with the results you found for the monodisperse system. Be careful to choose values of K that don't give you particles with "negative size".

2. Use your code to determine the equation of state under the same conditions you used in Phase I. How strong does the polydispersity have to be in your system before you notice significant differences from the monodisperse results?

Part II: Solid Phases

1. Use your NPT-MC code from Phase I to compute the average energy per particle and g(r) for an FCC crystal of monodisperse square well particles at P = 0 and T = 0.1. As your colleagues who are working on Project B will show, this is the most stable solid phase of square well particles. What is the average lattice parameter at these conditions?

2. One of the objectives of making colloidal crystals is to make highly ordered arrays of colloids. It is important to have some idea how much polydispersity will affect the ordering of solid phases. Repeat the calculations you did above for polydisperse particles on an FCC lattice for several values of *K*. Describe how that lattice parameter of the FCC crystal and the radial distribution function are affected by polydispersity.