

## 06-640: Molecular Simulations

### Mid-semester Project B: Monte Carlo Simulation of Solid Alloys

In this project, you will use Monte Carlo simulations to study some properties of crystalline solids. For simplicity, we will look at model solids made up of square well spheres. It is important to note that the methods you develop here could also be applied to more general interatomic potentials.

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 in order to address the questions below.

#### Part I: Single Component Solids

In this part of the project you will determine the equilibrium crystal structure of a pure solid of square well particles.

1. Initialize your simulation cell so that it represents a bulk, periodic crystal with a simple cubic (SC) crystal structure. Note that you must choose the simulation cell width to be an integer multiple of the lattice spacing of your crystal. Compute the total potential energy per particle,  $U/N$ . Now repeat this calculation by holding the total number of particles fixed and varying the lattice spacing of your crystal (and hence the volume of your simulation cell). The results of this calculation give you the total energy,  $U/N$ , as a function of density for the simple cubic crystal. One useful way to interpret this result is that when  $T = 0$ , pressure is defined by  $P = -(\partial U / \partial V)_{N,T}$ . This means that the minimum in  $U/N$  as a function of density is the equilibrium density at  $T = 0$ .
2. To determine the true equilibrium crystal structure of the Lennard-Jones solid, it is important to test several plausible crystal structures. Repeat your calculations from 1. for the body-centered cubic (BCC) and face-centered cubic (FCC) crystal structures. As above, be careful in defining your simulation cell so that you generate a perfect bulk crystal with the desired crystal structure. What is the most stable structure of the Lennard-Jones solid at zero pressure and temperature?
3. To simulate binary alloys in phase II, you will use isobaric-isothermal Monte Carlo (NPT-MC) simulations. As a prelude to these simulations, perform two test calculations with your NPT-MC code. First, initialize the crystal in the equilibrium density of the most stable crystal structure and perform NPT-MC at  $P = 0$  and  $T = 0.2$  and  $0.1$ . Explain what you should expect to see and why it is not useful to perform the simulations at  $T = 0$ . Second, initialize the crystal at the equilibrium density of the most stable crystal, but with the structure of one of the other crystal structures you examined. Again, perform NPT-MC at  $P = 0$  and  $T = 0.2$  and  $0.1$  and explain what you find.

## Part II: Binary Alloys

In this section you will extend the methods you developed above to study binary alloys of the form  $A_xB_{1-x}$ , where A and B are different species that we will model using square well spheres. To fully specify the potentials for this system we need 6 parameters, the intra-species square well parameters,  $\sigma_{AA}$ ,  $\epsilon_{AA}$ ,  $\sigma_{BB}$ , and  $\epsilon_{BB}$ , and the cross-species square well parameters,  $\sigma_{AB}$  and  $\epsilon_{AB}$ . We will define the cross-species parameters using the common empirical mixing rules  $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB}) / 2$  and  $\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}$  and set  $\sigma_{BB} = 1.45\sigma_{AA}$  and  $\epsilon_{BB} = 1.2\epsilon_{AA}$ .

1. Extend the code you developed in Phase I to compute the total potential energy of a simulation cell containing particles from two species. Extend your NPT-MC code to allow zero pressure simulations of the two species mixture.
2. It is very difficult for atoms to rearrange in a conventional NPT-MC simulation of a crystalline phase. To perform accurate simulations, you must therefore add an additional type of MC move that interchanges the identities of two randomly chosen atoms. Apply the principle of detailed balance to derive an acceptance rule for this type of move, and implement the move in your code.
3. Once your augmented NPT-MC code is working, use it to simulate  $A_{1-x}B_x$  at zero pressure and low temperature for a randomly substituted FCC solid with  $x = 0.25$ . In particular, you should determine the equilibrium lattice parameter,  $a$ , of this alloy. Is this volume smaller or larger than the equilibrium volume of pure A? Repeat your calculations for  $x = 0.25, 0.5, 0.75,$  and  $1.0$ . Compare your measured lattice parameters with those predicted by Vegard's law, which states  $a(x) = a(0) + [a(1) - a(0)]x$ .
4. Use your NPT-MC code to compare the relative stability of several different crystal structures for a 50:50 alloy, that is,  $A_{1-x}B_x$  with  $x = 0.50$ . In particular, you should compare the potential energy per particle of an alloy with this composition in the randomly substituted FCC structure used in step 3 with an ordered BCC crystal and a crystal in an ordered NaCl structure. For these two ordered structures, you should not include the particle interchange moves described in part 2 above (why?).