Chemical Engineering I5800 **Molecular Simulation** **Spring 2019**

Problem Set 5 – due Mar. 28

Do **either** of the following two problems.

1. Compute the Helmholtz free energy of the Lennard-Jones liquid at $T = 1$ and $\rho = 0.8$ (in LJ units) by computing the free energy difference between a known state and this one, using any method of your choice: thermodynamic integration, overlapping distributions or umbrella sampling

   One method would be to start with an ideal gas, whose free energy is known, and gradually turn on the potential by increasing the energy parameter ϵ in small steps from zero to one. Another possibility is to start at $T = 0$ where the free energy is just the internal energy, and increase T gradually. If you prefer, you can invent another protocol of this general type.

   Hand in the modified parts of the code, and a verbal description of what you're done to analyze the output, as well as the answer. Also explain how you chose the step size in ϵ or T or ...

2. This problem concerns the MC simulation of tunneling through a barrier. Generate an initial configuration of 100 LJ atoms at density 0.8 σ^{-3} in a cube, where there are NO atoms in the middle region: $\mathrm{box}/4 < x < 3 \cdot \mathrm{box}/4$. Add to the Lennard Jones interactions the external potential

   $$U_b(x) = \exp -(x - \mathrm{box}/4)^2/2 + \exp -(x - 3 \cdot \mathrm{box}/4)^2/2$$

   which has two barriers of height 1 (LJ units) enclosing the remaining atoms. In equilibrium, all of the box should be occupied, except for dips at the two barrier positions. One expects that if the typical kinetic energy is greater than the barrier height, atoms will easily pass over the barrier in an MC simulation and populate the middle region, but at low temperatures the energy cost of going through the barrier will suppress this process, and without an extremely long MC run an incorrect depleted distribution will result.

   Use both annealing (gradual lowering of the temperature) and tempering (exchange of MC runs with different temperatures) to find the density profile $\rho(x)$ at $T = 2.0$ and $T = 0.2$. Please submit the new parts of the code used, the results for $\rho(x)$, and a verbal description of what you've done.