Chemical Engineering I5800 **Molecular Simulation** **Sprint 2019**

Problem Set 7 – due Apr.11

The problem is to add a “better” thermostat to the Lennard-Jones MD program lj.f, and test it. The constant-kinetic-energy theromstat provided with the program is useful during the initial stages of a run, to provide a system near an equilibrium configuration, but does not produce a canonical ensemble. Add to the program either a Nosé-Hoover or a Langevin thermostat (your choice) which would be called at each time step once the system has settled down. Compute the resulting velocity distribution for 500 atoms at density $0.8\sigma^{-3}$ and temperature $1.2\epsilon/k_B$, and verify that it is in fact the Boltzmann distribution at this temperature. You should run the simulation long enough to obtain a reasonably smooth result for the velocity histogram.

If you’d like to do some analytic work for a change: show that in the canonical (NVT) ensemble, the probability distribution function of the kinetic energy K is

$$\rho(K) = \frac{\beta}{(3N/2-1)!} e^{-\beta K} (\beta K)^{3N/2-1}$$

where $\beta = 1/k_B T$. Show that for $N \gg 1$, this formula reduces to a Gaussian distribution; to do this, expand about the mean value of K, assuming K is close to the mean value, and use Stirling’s formula. Lastly, show that the resulting Gaussian distribution is consistent with the Boltzmann distribution of velocities, so if the previous part of the question works out, you have verified this result as well.