Problem Set 9 – due may 2

The problem is to compute the surface tension of the liquid/vapor interface of the Lennard-Jones liquid using the result derived in class:

$$\gamma = \frac{1}{2A}\left\langle \sum_{a<b} \frac{r_{ab}^2 - 3z_{ab}^2}{r_{ab}} V'(r_{ab}) \right\rangle$$

where the average is over equilibrium states. The expression for γ can easily be evaluated in subroutine eval, but the tricky part is to set up a slab of liquid oriented parallel to the x-y plane and surrounded by vapor.

Start from the standard program lj.f, reset the number of particles to 1372 (nc=7) and the temperature to tr = 0.8, and make the simulation box into a rectangular region of dimensions X*Y*Z = cube*cube*(3*cube) with the atoms initially in a slab in the middle of the box with empty space at the top and bottom. This requires a simple modification of subroutine fcc, but the periodicity in z must be adjusted. Either introduce a new length cubez=3*curve, and modify the statements in eval and corr which involve the minimum image convention and shifting the particles to stay the box, or else add a repulsive force field at the top and bottom to confine the atoms in the z-direction.

Secondly, if the temperature is set to 0.8 at the start the atoms will immediately evaporate to fill the whole box and only condense after some (long) time. One remedy is to start at a low temperature (0.1 say) and gradually ramp it up to the desired value 0.8 and equilibrate before "taking measurements." In this case parameters such as aheat and vscale must be adjusted to correspond to the running ramp temperature. Alternatively, the atoms could be confined by force fields centered above and below the central region while equilibrating, and then the force centers gradually moved away to the boundaries.

If you would like an analytic exercise, you can derive the formula for surface tension by starting with the expression for the free energy in the canonical ensemble $F = -k_B T \log Z$ for a box of atoms with an interface in equilibrium, and differentiating with respect to the area. To do this, inside Z rescale the coordinates

$$(x, y, z) \rightarrow (Ls_x, Ls_y, \frac{V}{L^2}s_z)$$

where L is the side of a cube, differentiate with respect to L, and convert this to $\partial F/\partial A$.