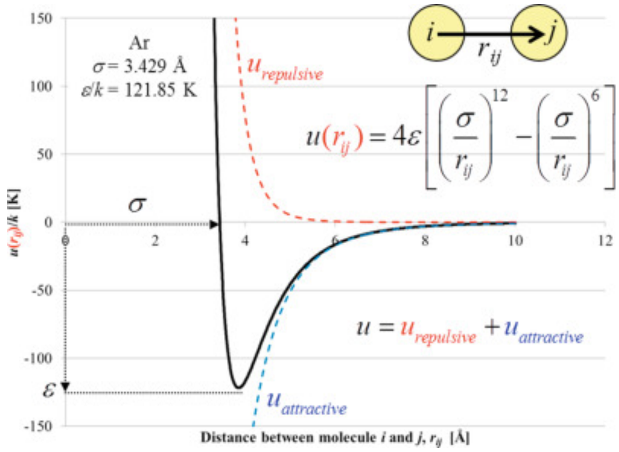
Problem 1.

The set-up: Energy of two Argon (Ar) atoms as a function of the distance between them is shown in the figure. Assume that $\epsilon = 1/4\,, \sigma = 1$. The total energy of N atoms is the sum over all the pairs, e.g. for N=3, $U = U_{tot} = U_{12} + U_{13} + U_{23}$. As always, the correct state of the system – the molecule -- is the configuration that minimizes its total energy.




Energy $U(r_{ij})$ of two Argon atoms as a function of the distance $r_{ij}$ between them.

(a) (5 points) Re-draw the $U(r_{ij})$ figure for $0.7 < r_{ij} < 1.5$, using the values of $\epsilon = 1/4\,, \sigma = 1$. From the graph, read off the approximate value of $r_{12}$ that minimizes U. Call it $r_{12}^*$.

(b) (10 points) Use the hard-coded Newton's method available in one of the scripts shown in class. Start the iterations at $r_{12}^*$. Show the convergence plot: values of U as a function of the iteration step, from k=1 to 4. Also show the sequence of residuals: $|\, r_{12}(k+1) - r_{12}(k)\, |$. Is the convergence closer to linear or quadratic?

(c) (5 points) A student who did not take the class, decides to pick the starting point in (b) as a random number in the interval [-1.5, 1.5]. Why is this a bad idea?

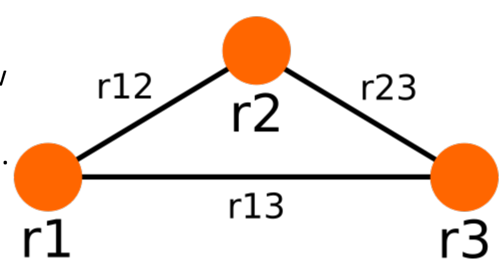
(d) (2 points) Find the exact $r_{12}^m$ analytically, via

$$\frac{\partial U}{\partial r} = 0$$

Use it to check the accuracy of your numerical solution in (b). How many correct significant digits does the numerical solution have?

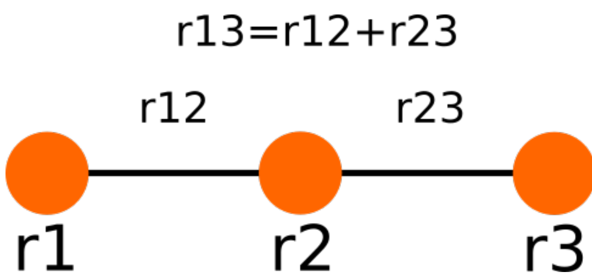
(e) (3 points). A molecule of 2 Ar atoms has a certain $r_{12}^m$, see above. Suppose you stretch the molecule so that the distance between the atoms is now $2r_{12}^m$, what is the corresponding increase in the total energy?

(f) (15 points). What is the correct state of a molecule made of 3 Ar atoms? Give the corresponding atom-atom distances, show a picture of how this molecule looks like.
Hint: three points are always in a plane. U is now a function of 3 variables – pairwise distances between the atoms: $U = U(r_{12}) + U(r_{13}) + U(r_{23})$.



You can try to solve the problem analytically, or use Mathematica's NMinimize[], with all the default settings except the starting point – give a good argument for which one to take.  See examples worked out in class.

(g) (10 points) Now suppose the 3 atoms are constrained to lie on a straight line. What is the minimum energy state now? Give picture and the total energy. What can you conclude about the effect of constraint on the objective function (total energy in this case)? In general, problems that involve constraints, in this case it is $r_{13} = r_{12} + r_{23}$, are harder than corresponding unconstrained problems. The general approach is to reduce the constrained problem to an equivalent unconstrained one.




Here, without loss of generality, we will assume that the middle atom is at r2=0. The $2^{nd}$ atom is then distance r12 away from r2 to the left, the $3^{rd}$ is distance r23 to the right. Thus, you need to minimize U = U(r12) + U(r23) + U(r12 + r23). Use NMinimize[] as described above.

(EXTRA CREDIT, 20 points). Now let's make a connection to a very hard problem that many smart people worked over many centuries – finding the closest packing of identical hard spheres. Look up Hilbert's $18^{th}$ problem, as well as what it is that C. Gauss proved for close packing of equal spheres. Another curiosity: what does this problem have to do with Sir W. Raleigh, after whom the capital of North Carolina is named?

Start with 3 identical marbles or 3 pennies (on a tabletop) -- which configuration gives you the closest packing? Take a picture, add it here.
Comparing the above result with your solution of (f) suggests that the general answer to the N-sphere packing problem is equivalent to finding the Ar molecule of N atoms. Solve it for N=4, show the resulting packing. Show the function you minimized, and the starting point you chose. You can confirm your intuition by playing with 4 identical marbles (in 3D space).