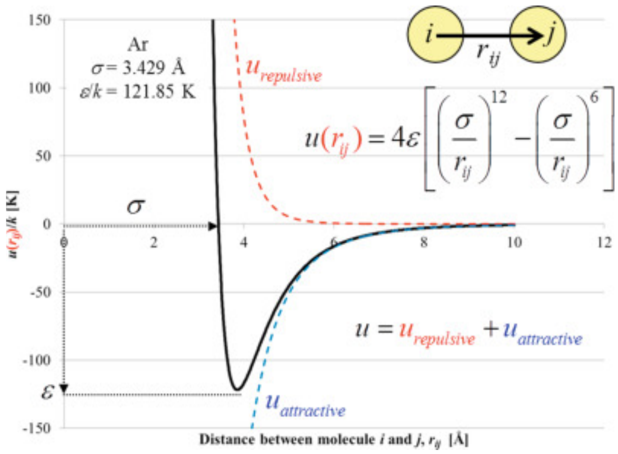


Energy $U(r_{ij})$ of two Argon atoms as a function of distance r_{ij} between them.

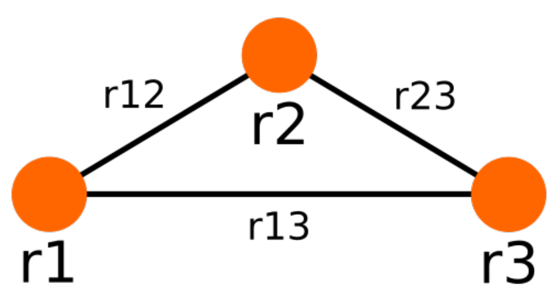
Problem 1.

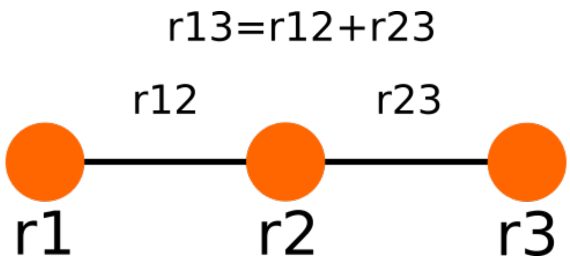
Energy of two Argon (Ar) atoms as a function of distance between them is shown in the figure. Assume that $\epsilon = 1/4, \sigma = 1$. The total energy of N atoms is the sum over all the pairs, e.g. for N=3, U = $U_{tot} = U_{12} + U_{13} + U_{23}$. As always, the correct (native) state of the system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

(a) (10 points).

A molecule (correct native state) of 2 Ar atoms has a certain r_{12}^m. 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?

(b) (15 points). What is the correct (native) state of a molecule made of 3 Ar atoms? Give the corresponding atom-atom distances, show a picture of how this molecule looks like. You can try to first solve the problem analytically; then try Mathematica's FindMinimum[] (simpler) or NMinimize[]. Hint: three points are always in a plane. U is now a function of 3 variables – pairwise distances between the atoms: $U = U(r_{12}) + U(r_{13}) + U(r_{23})$. Use Mathematica's minimization tools with all the default settings except the starting point – give a good argument for which one to take.





(c) (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 can assume that the middle atom is at r2=0. The 2nd atom is then distance r12 away from r2 to the left, the 3rd is distance r23 to the right. Thus, you need to minimize U = U(r12) + U(r23) + U(r12 + r23). Use NMinimize[] as described above.

(d) (EXTRA CREDIT, 25 points). Solve problem (b) with 4 Ar atoms. For the curious: this problem makes 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 18th 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?