MATRL 218/CHEM277: Assignment 4

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1. The Lennard-Jones potential for a system of identicals particles is:

\[ U(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \]

Where \( \epsilon \) is the well depth, and \( \sigma \) is the particle diameter. (i) Sketch the distance-dependence of this potential using scaled units, ie. set \( \sigma = 1 \) and \( \epsilon = 1 \). Approximately how many atomic diameters does one need to be separated by, before there is effectively no interaction. (ii) Determine by setting \( \partial U/\partial r = 0 \), the value of \( r/\sigma \) for which the potential is minimum.

2. The \textit{wrong} way to calculate the Madelung constant for the NaCl structure is to sit on one of the ions (say Na\(^+\)) and then calculate the attractive interactions to the next 6 Cl\(^-\), the repulsive interactions to the next 12 Na\(^+\) etc. Try and write a few terms of this series and state why this looks like a bad idea.

3. The geometric Madelung constant for a pair or monovalent ions of opposite sign, separated by unit distance, is 1. Calculate the constants (on a \textit{per-pair} basis) for a square of monovalent ions of alternating sign, and for a cube, where the square edge and cube edge are the same unit distance. How far are you from the Madelung constant of the NaCl structure, which is 1.74756.

4. Write a code to calculate the geometric Madelung potential for the NaCl lattice by building larger and larger cubes of ion pairs of Na\(^+\) and Cl\(^-\) assuming that all near-neighbor distances are 1. Make a plot of the Madelung potential against \( n \), where \( n \) is the number of ion pairs that form the edge of the cube. Submit this with the code. You can collaborate with one other person, and you have two weeks.