MATRL 218/CHEM277: Assignment 4

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Due date: February 25th 2020 (in class, or under my door). Keep everything brief.

1. Why does the entropy of a liquid decrease when it is quenched to a glass, even though the effective structures of liquids and glasses (“snapshots”) are similar, suggesting similar configurational entropies?

2. The Lennard-Jones potential for a system of alike 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.

3. The 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.

4. The geometric Madelung constant for a pair or monovalent ions of opposite sign, separated by unit distance, is 1. Calculate the constants (on a 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 lattice, which is 1.74756. Bonus: Write a code to build increasingly larger cubes to do this calculation.

5. Sketch \( E \) vs. \( k \) diagrams for a 1D chain (unit cell parameter \( a \)) of \( s \) and \( p_x \) and \( p_z \) orbitals, with the corresponding sketches of the crystal orbitals.