Physics 725: Assignment 3

(to be submitted by Thursday, February 28, 2019)

1. In class, we constructed the linear combinations of orbitals corresponding to the sp^2 hybridized form of carbon with trigonal bonds in the plane. Do the same for the tetrahedral sp^3 case.

2. Consider a single-crystal sample of solid argon. Suppose that each argon atom interacts pairwise with all the others according to a potential of Lennard-Jones form:

$$V(r) = \epsilon_0 \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^{6} \right],$$

with $\epsilon_0 = 0.041\,\text{eV}$ and $r_0 = 3.82\,\text{Å}$.

   (a) Show that the potential takes its minimum value at a separation distance r_0. Expand $V(r)$ as a power series around r_0. Identify the binding energy and spring constant for a pair of argon atoms.

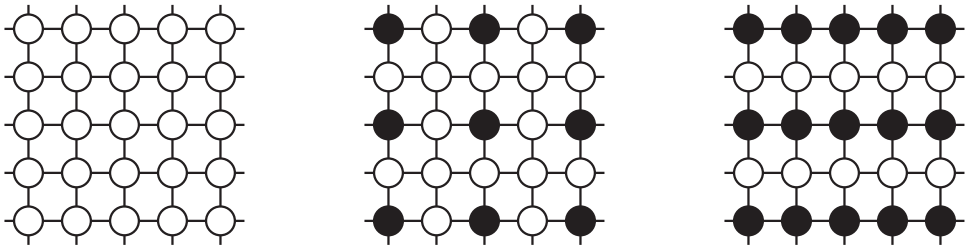
   (b) Comment on the anharmonic terms and what role they play in thermal expansion of material. Show that the relative linear expansion of the solid goes as $k_B T/\epsilon_0$.

   (c) The argon atoms pack like hard spheres, so the likely crystal structure is either fcc or hcp. In each case, estimate the total cohesive energy per atom. Which crystal structure is energetically favourable?

   (d) Argon melts at 83.8 K. Provide your own estimate of the melting temperature.

3. Elements A and B are alloyed to create a fictitious material $A_{1-x}B_x$. We'll imagine that the material is confined to two dimensions (perhaps as a monolayer arranged on a flat substrate). The pure A material ($x = 0$) forms a square crystal. Its lattice constant a is determined by the AA equilibrium bond length.

   When x is small, the B atoms act as substitutional impurities and are randomly distributed throughout the material. But as the fraction of B atoms becomes appreciable, the atoms develop a propensity to order. Two ordered configurations are stabilized.



   (a) These three diagrams correspond to which values of x?

   (b) Draw a plausible T–x phase diagram. Identity all the solid and liquid phases.

   (c) Explain what lattice symmetries are broken by the ordering of the B atoms.

   (d) In the $x = 0$ case, the dimensions of each square plaquet are $a \times a$. If the equilibrium bond lengths satisfy $\ell_{\text{AA}} > \ell_{\text{AB}} > \ell_{\text{BB}}$ but are otherwise close in magnitude, what can you say about the plaquet dimensions for the two other cases depicted?

   (e) For each of the three cases, find the lattice vectors and basis; also determine the reciprocal lattice and Brillouin Zone.

   (f) Compute the structure factor $S_{\boldsymbol{G}} = |\sum_j f_j e^{i\boldsymbol{G}\cdot\boldsymbol{\tau}_j}|^2$ in terms of atomic form factors $f_\circ$ and $f_\bullet$.

   (g) Comment on the possibility of "extinction": i.e., $S_{\boldsymbol{G}} = 0$ for otherwise valid Bragg scattering vectors.

4. Two species of ion are arranged to form a linear chain, uniformly spaced by a distance a. (We'll imagine that their motion is constrained to one dimension.) The ions have alternating charge $+e$ and $-e$ and interact over long range via the Coulomb potential

$$V_{i,j}^{\text{Coulomb}} = \frac{q_i q_j}{4\pi\epsilon r_{i,j}}.$$

It is convenient to use a site labelling scheme in which $r_{i,j} = a|i-j|$ is the separation between ions at sites i and j, and $q_i = e(-1)^i$ and $q_j = e(-1)^j$ are the corresponding charges. In addition, nearest-neighbours ions experience a short-range repulsion as a consequence of the Pauli exclusion of filled atomic orbitals:

$$V_{i,i+1}^{\text{Pauli}} = V_0\left(\frac{r_0}{r_{i,i+1}}\right)^{12}.$$

Here, V_0 and r_0 are constants with units of energy and length.

(a) Find an expression for the cohesive energy per atom as a function of the distance a.

(b) Determine the equilibrium value of a in terms of V_0, r_0, and e.

(c) Compute the dispersion relation for the vibrational normal modes. For simplicity, assume that the mass on the cation and anion are identical.