

Homework #2
Interstices and Lennard-Jones Phase Stability

Due 5pm Tuesday Oct. 15

Turn in outside of Durand 110 or email to duerloo@stanford.edu

1. Face-Centered Cubic interstices (e.g., Al, Cu, Ag, Au, Ni, Pd, Pt, γ -Fe)

(a) Identify and draw the positions of the FCC octahedral and tetrahedral interstices; write down their coordinates within the conventional unit cell using the basis atom coordinate notation introduced in class. Indicate the lattice vectors used to specify the cell and basis atoms using either crystallographic or solid state conventions. Determine how many of each interstitial type are found in the conventional unit cell.

(b) Calculate the size of these two interstices, relative to the diameter of the hard-sphere atoms. Assume the size of an interstice is the diameter of the largest hard-sphere that fits into the interstice without displacing any of the host atoms.

2. Hexagonal Close Packed interstices (e.g., Be, Mg, Zn, Cd, Co, Ti, Zr)

(a) Identify and draw the positions of the HCP octahedral and tetrahedral interstices; write down their coordinates within the conventional/primitive unit cell using the basis atom coordinate notation introduced in class. Indicate the lattice vectors used to specify the cell and basis atoms using either crystallographic or solid state conventions. Determine how many of each interstitial type are found in this unit cell.

(b) Calculate the size of these two interstices, relative to the diameter of the hard-sphere atoms.

3. Body Centered Cubic interstices (e.g., α -Fe, Li, Na, K, V, Nb, Ta, Cr, Mo, W)

(a) Identify and draw the positions of the BCC octahedral and tetrahedral interstices; write down their coordinates within the conventional unit cell using the basis atom coordinate notation introduced in class. Indicate the lattice vectors used to specify the cell and basis atoms using either crystallographic or solid state conventions. Determine how many of each interstitial type are found in this unit cell.

(b) Explain how these interstices are different from those found in the FCC and HCP structures. (e.g. are all the sides of equal length?)

(c) Calculate the sizes of the interstices with respect to the host atoms, and determine how many nearest neighbor atoms would be in contact with the largest hard sphere that fits in each interstice.

4. Iron.

(a) The alpha phase of iron exists in a BCC structure, and steel is created when carbon atoms are present in low concentration. The carbon atoms are observed to reside in octahedral interstices. Take the hard sphere radius ratio of carbon to iron to be $r_C/r_{Fe}=0.6$. Will carbon fit into an octahedral interstice?

(b) Suppose the conventional bcc unit cell is elongated uniaxially such that the c axis length is allowed to vary while the other axes remain fixed with length a . (Atom hard sphere sizes remain constant.) Note that uniaxial elongation eliminates the equivalency of the octahedral interstices – they are not all the same

geometry. What is the value of c/a (> 1) for which a C atom in at least one of the octahedral interstices is equidistant from 6 nearest neighbors? Microscopic uniaxial strain from sparse C interstitial atoms contributes to the hardness of steel.

4. Lennard-Jones crystal: Beyond the hard sphere model.

Consider the Lennard-Jones interatomic potential, which gives the potential energy of a pair of atoms as a function of the interatomic distance,

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

(a) Using the Lennard-Jones potential, calculate the lattice constants of the fcc, hcp, and bcc crystals at zero pressure and temperature.

The total energy for a perfect crystal with N atoms can be written,

$$E_{tot} = \frac{1}{2}N(4\epsilon) \left[\sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^6 \right] \quad (2)$$

where $p_{ij}R$ is the distance between an atom i and another atom j and R is the nearest neighbor distance. Note that the sum is only over atoms j rather than pairs. The summations can be evaluated for a given crystal structure. For the face-centered cubic structure,

$$\sum_j p_{ij}^{-12} = 12.13188 \quad (3)$$

$$\sum_j p_{ij}^{-6} = 14.45392 \quad (4)$$

and for the body-centered cubic structure,

$$\sum_j p_{ij}^{-12} = 9.11418 \quad (5)$$

$$\sum_j p_{ij}^{-6} = 12.2533 \quad (6)$$

and for the hexagonal close-packed structure,

$$\sum_j p_{ij}^{-12} = 12.13229 \quad (7)$$

$$\sum_j p_{ij}^{-6} = 14.45489 \quad (8)$$

Using these lattice sums, calculate the equilibrium nearest neighbor distances R_0/σ by setting $dE_{tot}/dR = 0$. How does the nearest neighbor distance compare with the minimum of the Lennard-Jones potential well? Explain this comparison.

(b) Calculate the cohesive energies (per atom, in units of ϵ) for these three crystals at their equilibrium lattice constants. Why is the bcc energy so different from hcp and fcc? Which structure would you expect to observe in the lab as the temperature approaches $T=0$?

- (c) Now assume that the interaction potential is non-zero only for nearest neighbor interactions, e.g. atoms in the crystal do not interact unless they are nearest neighbors. What is the energy difference between the fcc and hcp structures? What is the energy of an intrinsic stacking fault in an fcc crystal using this nearest-neighbor model?
- (d) In what crystal structure are Noble gas atoms (Ne, Ar, Kr, Xe) experimentally observed at low temperatures? Is this consistent with your calculations from (b)? If not, can you think of effects that might be omitted from this simple Lennard-Jones model?