Solutions for Homework Set 1

1. *The face-centered cubic is the most dense and the simple cubic is the least dense of the three cubic Bravais lattices. The diamond structure is less dense than any of these. One measure of this is the packing fraction for the respective Bravais lattice in a close-packing arrangement using solid spheres.*

   Suppose identical solid spheres are distributed through space in such a way that their centers lie on the points of each these four structures, and spheres on neighboring points just touch without overlapping. Assuming that the spheres have unit density, determine the density of a set of close-packed spheres on each of following structures:

   (a) simple cubic

   (b) body-centered cubic

   (c) face-centered cubic

   (d) hexagonal closed packed Hint: See problem 4.6 in Ashcroft and Mermin. Also look at A. Donev et al, Science vol. 303, p. 990 (2004) for a way to improve packing using random packing.

   (e) Bonus: Determine the packing fraction for a diamond structure.

Solution

(a) **Simple Cubic**: The close packing requirement implies that the diameter of each sphere is identically the distance to the nearest neighbour at each lattice point. For simple cubic lattice the nearest neighbour distance is given by the lattice constant a. Hence the radius of each sphere is $a/2$. If we consider a cube of side a with spheres at each point then each lattice point has $1/8V_{\mathrm{sph}}$ of each sphere inside the cube. Hence, the packing fraction f is given by

$$\begin{aligned} f &= \frac{8 \times V_{\mathrm{sph}}/8}{a^3}, \\ &= \frac{\pi}{6}, \end{aligned} \tag{1}$$

where $V_{\mathrm{sph}} = (4/3)\pi a^3/a^3$.

(b) **BCC**: This is similar to SC except there is now a sphere at the centre of the cube. The nearest neighbour distance is now $a\sqrt{3}/2$. Hence,

$$V_{\mathrm{sph}} = \frac{\sqrt{3}\pi a^3}{16},$$

and

$$f = \frac{\sqrt{3}\pi}{8}. \tag{2}$$

(c) **FCC**: For our cube of side a there are now 8 corner points as for (a), but there are also lattice points, centred of each of the 6 faces. Each of the 6 face-centred points have half of the sphere inside the cube. The nearest neighbour distance is given by $a/\sqrt{2}$. Hence, the volume of the sphere V_{sph} is

$$V_{\mathrm{sph}} = \frac{\pi a^3}{\sqrt{2}},$$

and

$$f = \sqrt{2}\pi/6. \tag{3}$$

(d) **HCP**: The HCP lattice is a bit trickier, but we can simplify the problem by considering the lattice as two interpentrating simple hexagonal Bravais lattices. The packing fraction for the HCP lattice is then twice the packing fraction for one of the simple hexagonal Bravais lattice structures. Consider the simple hexagonal lattice spanned by the lattice vectors

$$\begin{aligned} \mathbf{a_1} &= a\mathbf{i}, \\ \mathbf{a_2} &= a\sqrt{3}/2\mathbf{i} + a/2\mathbf{j}, \\ \mathbf{a_3} &= c\mathbf{k}. \end{aligned} \tag{4}$$

Then, the unit cell spanned by these lattice vectors is a triangular prisim which has a volume $V = \sqrt{3}a^2c/4$. It has 3 corner lattice points on each of the triangle faces, in which each of the spheres have $(1/12)V_{\mathrm{sph}}$

inside the prisim (this is a simple exercise in counting). The nearest neighbour distance is given by a as the prisim is close packed. Hence, the packing fraction for HCP is:

$$\begin{aligned} f &= 2 \times \frac{6 \times 1/12 \times V_{\text{sph}}}{\sqrt{3}a^2c/4}, \\ &= \frac{a^3\pi/6}{\sqrt{3}a^2c/4}, \\ &= \frac{\pi}{\sqrt{18}}, \end{aligned} \tag{5}$$

where we've used the ratio $c = \sqrt{8/3}a$ for a HCP lattice.

(e) (Bonus) **Diamond Lattice**: The diamond lattice consists of a FCC lattice with a two point basis. The basis atoms are the lattice point itself and a single atom displaced from the lattice point by a vector $\mathbf{d} = (a/4)(\mathbf{i}+\mathbf{j}+\mathbf{k})$. Hence, the nearest neighbour distance is $a\sqrt{3}/4$. Only four of the basis atoms sit inside the unit cube, as well as 1/8 of the 8 corner spheres and 1/2 of the 6 face centred spheres (the same as FCC). The packing fraction is therefore

$$\begin{aligned} f &= \frac{4 \times V_{\text{sph}} + 1/8 \times 8 \times V_{\text{sph}} + 1/6 \times 6 \times V_{\text{sph}}}{a^3}, \\ &= \frac{8(4/3)\pi(\sqrt{3}/8)^3a^3}{a^3}, \\ &= \frac{\pi\sqrt{3}}{16}. \end{aligned} \tag{6}$$

2. *Kittel Problem 2.2*

Solution

(a) From Kittel, the primitive translation vectors of the hexagonal space lattice are given by

$$\mathbf{a_1} = \sqrt{3}a/2\mathbf{i} + a/2\mathbf{j}, \tag{7}$$

$$\mathbf{a_2} = -\sqrt{3}a/2\mathbf{i} + a/2\mathbf{j}, \tag{8}$$

$$\mathbf{a_3} = c\mathbf{k}. \tag{9}$$

The volume of the primitive cell is given by $V = \mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})$, which is the volume of the parallelepiped spanned by the lattice vectors $\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3}$ above. This volume is the same for all choices of primitive unit cell (including the Wigner-Seitz cell discussed on Wednesday). Simply evaluating the scalar triple productive then gives

$$V = (\sqrt{3}/2)a^2c. \tag{10}$$

(b) The reciprocal lattice vectors are given by

$$\mathbf{b_1} = 2\pi\frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \tag{11}$$

$$\mathbf{b_2} = 2\pi\frac{\mathbf{a_3} \times \mathbf{a_1}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \tag{12}$$

$$\mathbf{b_3} = 2\pi\frac{\mathbf{a_1} \times \mathbf{a_2}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \tag{13}$$

We now simply evaluate the cross products and divide by the volume calculated in (a) giving:

$$\mathbf{b_1} = \frac{2\pi}{a\sqrt{3}}\mathbf{i} + \frac{2\pi}{a}\mathbf{j}, \tag{14}$$

$$\mathbf{b_2} = -\frac{2\pi}{a\sqrt{3}}\mathbf{i} + \frac{2\pi}{a}\mathbf{j}, \tag{15}$$

$$\mathbf{b_3} = \frac{2\pi}{c}\mathbf{k}. \tag{16}$$

Thus the reciprocal lattice is a hexagonal lattice given by rotating the direct lattice by $\pi/6$ in the x-y plane and scaled by sending $a \to 4\pi/(3a)$ and $c \to 2\pi/c$.

(c) The 1st Brillouin zone of hexagonal space lattice is the Wigner-Seitz cell of the reciprocal lattice. In the x-y plane the Wigner-Seitz cell is given by regular hexagon. Therefore including the z direction we see that the 1st Brillouin Zone is a hexagonal prism.

3. *Kittel Problem 2.3*

As the hint suggests the volume of the 1st Brillouin Zone is equal to the volume of the parallelepiped form by the basis vectors $\mathbf{b_1}$, $\mathbf{b_2}$ and $\mathbf{b_3}$ of reciprocal space. Thus, $V_{\mathrm{BZ}} = \mathbf{b_1} \cdot (\mathbf{b_2} \times \mathbf{b_3})$.

We claim that

$$\mathbf{b_1} \cdot (\mathbf{b_2} \times \mathbf{b_3}) = \frac{(2\pi)^3}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}. \tag{17}$$

To see this note that

$$\mathbf{b_1} \quad = \quad 2\pi \frac{\mathbf{a_2} \times \mathbf{a_3}}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}, \tag{18}$$

and so

$$\mathbf{b_1} \cdot (\mathbf{b_2} \times \mathbf{b_3}) = 2\pi \frac{(\mathbf{a_2} \times \mathbf{a_3}) \cdot (\mathbf{b_2} \times \mathbf{b_3})}{\mathbf{a_1} \cdot (\mathbf{a_2} \times \mathbf{a_3})}. \tag{19}$$

Then, using the vector identity

$$(\mathbf{A} \times \mathbf{B}) \cdot (\mathbf{C} \times \mathbf{D}) = (\mathbf{A} \cdot \mathbf{C})(\mathbf{B} \cdot \mathbf{D}) - (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}), \tag{20}$$

we have

$$\begin{aligned} (\mathbf{a_2} \times \mathbf{a_3}) \cdot (\mathbf{b_2} \times \mathbf{b_3}) &= (\mathbf{a_2} \cdot \mathbf{b_2})(\mathbf{a_3} \cdot \mathbf{b_3}) - (\mathbf{a_2} \cdot \mathbf{b_3})(\mathbf{a_3} \cdot \mathbf{b_2}), \\ &= (2\pi)^2, \end{aligned} \tag{21}$$

using the orthonormality of the lattice vectors viz. $\mathbf{a_i} \cdot \mathbf{b_j} = (2\pi)\delta_{ij}$. Hence,

$$V_{\mathrm{BZ}} = \frac{(2\pi)^3}{V_{\mathrm{c}}}. \tag{22}$$