Physics 525, Condensed Matter

Homework 2

Due Tuesday, 3rd October 2006

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Problem 1

Consider a trigonal Bravais lattice generated by the primitive vectors $\vec{a}_i$ for $i = 1, 2, 3$ such that $\vec{a}_i \cdot \vec{a}_j = a^2 \cos\theta$ for $i \neq j$.

a) We are to determine for what angles θ this lattice is three-dimensional.

There are many ways by which this answer can be visualized, but to be a bit more mathematically explicit (and ergo avoiding the necessity of diagrams), we will proceed differently. If the vectors $\vec{a}_i$ are to be taken as a basis in three-dimensions, then the volume element is given by the square-root of the determinant of the corresponding metric—the metric's elements are $g_{ij} = \vec{a}_i \cdot \vec{a}_j$. That is,

$$(\text{Volume form})^2 = a^2 \begin{vmatrix} 1 & \cos\theta & \cos\theta \\ \cos\theta & 1 & \cos\theta \\ \cos\theta & \cos\theta & 1 \end{vmatrix} \propto (\cos\theta - 1)^2(\cos\theta + \tfrac{1}{2}). \quad \text{(a.1)}$$

From the above, it is clear that the space is three-dimensional iff the volume-form is real and non-vanishing. We therefore see that when $\cos\theta = 1, -\frac{1}{2}$ the volume vanishes—corresponding to a two-dimensional lattice. Furthermore, we see that because equation (a.1) has a positive coefficient for $\cos^3\theta$ and it's lowest root at $\cos\theta = -\frac{1}{2}$, the expression is negative for $\cos\theta < -\frac{1}{2}$ which amounts to an imaginary volume element[1].

Therefore, a three-dimensional Bravais lattice is obtained only for $\theta \in (0, 2\pi/3)$.

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b) Let us show that as θ varies, the trigonal lattice becomes each of the higher-symmetry cubic lattices.

There are three values of θ which give rise to enhanced symmetry. The first, and most obvious to see, is for $\theta = \pi/2$ which clearly gives rise to a simple cubic lattice. The other two cases are a bit more subtle.

Consider the plane spanned by $\vec{a}_1$ and $\vec{a}_2$. When $\theta = \pi/3$, we see that a two-dimensional lattice of equilateral triangles is spanned. Now, because $\vec{a}_3$ lies out of the plane at an equal angle, the four points $\vec{0}, \vec{a}_1, \vec{a}_2, \vec{a}_3$ form the corners of a regular tetrahedron, which obviously gives rise to enhanced symmetry. We know that this structure—an equilateral triangle of points with a point on the next layer directly in the center—gives rise to the close-packing of spheres in three-dimensions, so our lattice must either be face-centred-cubic (fcc) or hexagonal-close-packed (hcp). It is not hard to see that our Bravais lattice gives only fcc: if a corner of the 'canonical' fcc cube is taken as the origin, then the vectors $\vec{a}_i$ correspond to the points at the centres of the three faces which are coincident at the corner in question.

The last case of enhanced symmetry arises when $\{\vec{a}_1, \vec{a}_2, \vec{a}_3, -(\vec{a}_1 + \vec{a}_2 + \vec{a}_3)\}$ form a regular tetrahedron. For those of us who loved high-school chemistry, we know that the internal angle of a regular tetrahedron—which is the angle between two hydrogen atoms in CH_4—is $\arccos(-1/3) \approx 109.5^o$. And so our answer is: when $\theta = \arccos(-1/3)$ the trigonal Bravais lattice is the body-centred-cubic (bcc) lattice.

Just to motivate the answer for bcc a little better, recall from the textbook that the bcc Bravais lattice can given as follows: let a corner of the 'canonical' bcc cube be placed at the origin with the three edges meeting at the corner coincident with the x, y and z-axes. Then the bcc Bravais lattice can be spanned by $\vec{a}_i$ which point toward the

[1] There are really clear ways of visualizing the unacceptability of $\cos\theta < -1/2$. For example, consider the case where $\cos\theta$ is very near -1: here, we see that this means that $\vec{a}_2$ and $\vec{a}_3$ are both to be nearly anti-coincident with $\vec{a}_1$, which means that they cannot be mutually so.

centres of the cubes in, e.g., the $(+++)$, $(--+)$, and $(-+-)$ quadrants. And the centre of the cube in the $(+--)$ quadrant is given by $-\sum_i \vec{a}_i$. Now, there are a lot of fancy tricks to determine the internal angle of a tetrahedron; but we shall be brief, dry and boring and simply compute it directly. In our coordinates, in units of the lattice spacing a, the vectors $\vec{a}_1 = \frac{1}{\sqrt{3}}(1,1,1)$ and $\vec{a}_2 = \frac{1}{\sqrt{3}}(-1,-1,1)$. Being unit vectors, $\vec{a}_1 \cdot \vec{a}_2 = \frac{1}{3}(1-2) = -1/3 = \cos\theta$. Therefore, the angle θ is given by $\arccos(-1/3)$.

c) We are to find the reciprocal lattice of the trigonal lattice and verify the special cases found above.

We can use the canonical expressions for the reciprocal lattice vectors:

$$\vec{b}_i \equiv \pi \frac{\epsilon^{ijk}(\vec{a}_j \times \vec{a}_k)}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \tag{c.1}$$

where Einstein summation convention is employed[2]. At any rate, we find easily that $\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = a^3 \sin^2\theta$ and that this implies $|\vec{b}_i| = \frac{2\pi}{a \sin\theta}$. Using the usual identities about the inner product of two pairs of cross-products, we see that

$$\vec{b}_i \cdot \vec{b}_j = \frac{4\pi^2}{a^6 \sin^4\theta}\left(a^4 \cos^2\theta - a^4 \cos\theta\right) \qquad \text{for } i \neq j. \tag{c.2}$$

Therefore, the angles between the reciprocal basis vector $\vec{b}_i$ are all equal, and given by φ where

$$\begin{aligned} \cos\varphi &= \frac{\vec{b}_1 \cdot \vec{b}_2}{|\vec{b}_1|^2}, \\ &= \left(\frac{a^2 \sin^2\theta}{4\pi^2}\right)\left(\frac{4\pi^2}{a^2 \sin^4\theta}\right)\left(\cos^2\theta - \cos\theta\right), \\ &= \frac{\cos^2\theta - \cos\theta}{1 - \cos^2\theta}, \end{aligned}$$

$$\boxed{\therefore \cos\varphi = \frac{-\cos\theta}{1+\cos\theta}.} \tag{c.3}$$

For the special values of θ which correspond to the three cubic lattices, we see

- fcc: $\theta = \pi/3 \implies \cos\varphi = \frac{-1/2}{1+1/2} = -\frac{1}{3}$. This is the angle which was found to generate the bcc lattice.
- simple cubic: $\theta = \pi/2 \implies \cos\varphi = 0$ which corresponds to another simple cubic lattice.
- bcc: $\cos\theta = -1/3 \implies \cos\varphi = \frac{1/3}{1-1/3} = 1/2$; so $\varphi = \pi/3$, which corresponds to a fcc lattice.

These results match our understanding of reciprocal these reciprocal lattices.

[2]The factor of π in the expression is correct: it accounts for the fact that when summing over jk there will be two contributions.

Problem 2

Consider an ideal, two-dimensional honeycomb lattice of atoms—this could be, for example, graphene. For specificity, take the honeycomb lattice to be aligned in the xy-plane with the y-axis parallel to one of the nearest-neighbour atomic spacings. Call the distance between nearest-neighbours d.

a) We are to specify and sketch the reciprocal lattice and state the magnitude of the smallest reciprocal lattice vector for graphene, where $d \cong 1.4$ Å.

The honeycomb lattice can be considered a (2-dimensional) trigonal Bravais lattice with a basis containing two atoms. For specificity, a little trigonometry tells us that if d is the spacing between two atoms, then in our chosen orientation of the plane, our Bravais lattice is generated by

$$\vec{a}_1 \equiv d\sqrt{3}(1,0) \quad \text{and} \quad \vec{a}_2 \equiv d\sqrt{3}\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right). \tag{a.1}$$

The Bravais lattice with basis generated by these vectors is illustrated in Figure 1.

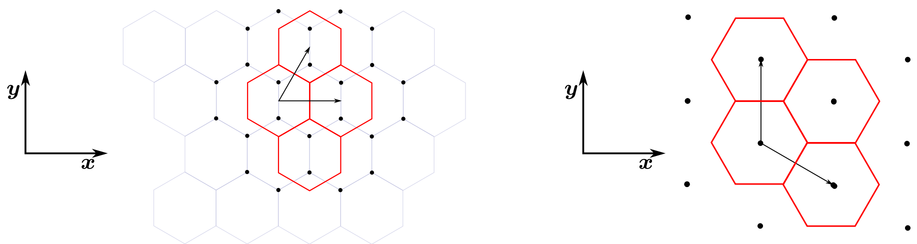

FIGURE 1. This figure shows the original honeycomb lattice, as viewed as a Bravais lattice of hexagonal cells each containing two atoms, and also the reciprocal lattice of the Bravais lattice (not to scale, but aligned properly).

To find the corresponding reciprocal lattice, we must satisfy the defining equations $\vec{b}_1 \cdot \vec{a}_1 = 2\pi$ and $\vec{b}_1 \cdot \vec{a}_2 = 0$, and a similar system for $\vec{b}_2$. These are easily found by hand, and it is seen at once that the required reciprocal lattice is generated by

$$\vec{b}_1 \equiv \frac{4\pi}{3d}\left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right) \quad \text{and} \quad \vec{b}_2 \equiv \frac{4\pi}{3d}(0,1). \tag{a.2}$$

This clearly generates the same lattice as $\vec{a}_1$ and $\vec{a}_2$, but rotated by $\pi/2$. This is illustrated also in Figure 1.

Using our expression in equation (a.2) above, we see that if $d \cong 14$ nm, then the smallest reciprocal lattice vector has magnitude $\frac{4\pi}{3d} \cong 2.46$ Å^{-1}.

b) Treating the atoms as identical scatterers, we are to determine the intensity of all the Bragg peaks, normalized so that the strongest peak has unit intensity.

If we let $\vec{r}_0 = (0, d/2)$, then the density function $\rho(\vec{r})$ over one cell is given by

$$\rho(\vec{r}) = \delta(\vec{r} - \vec{r}_0) + \delta(\vec{r} + \vec{r}_0), \tag{b.1}$$

which gives a form factor of

$$\left\{e^{i\vec{q}\cdot\vec{r}_0} + e^{-i\vec{q}\cdot\vec{r}_0}\right\} \propto \cos(\vec{q} \cdot \vec{r}_0). \tag{b.2}$$

We know that the wave function in $\vec{q}$ space can be expressed as this form factor times a piece from the Bravais lattice; the Bravais lattice piece gives a multiplicative factor of N (the number of lattice cells) and enforces that $\vec{q}$ is in the reciprocal lattice—that is, the wave function identically vanishes for $\vec{q}$ not in the reciprocal lattice.

Now, an arbitrary $\vec{q}$ in the reciprocal lattice is given by $\vec{q} = n_1\vec{b}_1 + n_2\vec{b}_2$, where $n_1, n_2 \in \mathbb{Z}$ and $\vec{b}_1, \vec{b}_2$ are given in equation (a.2). This shows us immediately that for $\vec{q}$ in the reciprocal lattice,

$$\vec{q}\cdot\vec{r}_0 = \frac{\pi}{3}\left(2n_2 - n_1\right). \tag{b.3}$$

Combining this with our work above, we see that

$$I \propto |\psi_s|^2 \propto \cos^2\left(\frac{\pi}{3}\left(2n_2 - n_1\right)\right), \tag{b.4}$$

and furthermore, the expression has the desired feature of intensity—that the strongest peak has unit intensity—so that we find the normalized intensity to be given by

$$I(n_1, n_2) = \cos^2\left(\frac{\pi}{3}\left(2n_2 - n_1\right)\right). \tag{b.5}$$

This is shown in Figure 2.

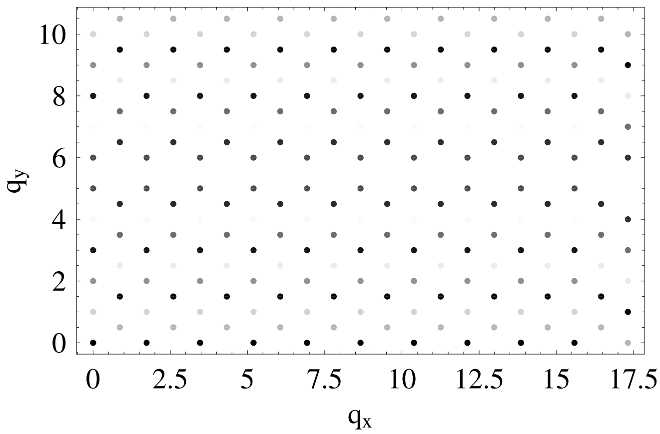

FIGURE 2. This is a plot of the intensity as a function of $\vec{q}$ (in units where the smallest reciprocal vector is of unit length). Only at discrete values of $\vec{q}$ is there any scattering, and the intensity is given by the expression (b.5).

c) Consider the cases where the two atoms in the unit cell are distinct, call them A and B, each with different scattering amplitudes f_A and f_B. We may assume that they are both real. What condition on the relative scattering amplitudes will cause the intensities of some of the Bragg peaks to vanish?

Because both f_A and f_B are real, we may without loss of generality suppose that $f_B = \beta f_A$. Just to be exceedingly explicit, we will say that the A atoms are located at $\vec{R} + \vec{r}_0$ and the B atoms are located at $\vec{R} - \vec{r}_0$ where $\vec{R}$ is the Bravais lattice and $\vec{r}_0 = (0, d/2)$ as above. With separate scattering sites, we see that the wave function for scattering goes like[3]

$$\begin{aligned}\psi_s &\sim f_A \sum_{\vec{R}} e^{i\vec{q}\cdot(\vec{R}+\vec{r}_0)} + f_B \sum_{\vec{R}} e^{i\vec{q}\cdot(\vec{R}-\vec{r}_0)},\\ &\propto f_A\left(e^{i\vec{q}\cdot\vec{r}_0} + \beta e^{-i\vec{q}\vec{r}_0}\right).\end{aligned}$$

Therefore, we find that the intensity evolves like

$$\begin{aligned}I \propto |\psi_s|^2 &\propto \left(1 + \beta e^{2i\vec{q}\cdot\vec{r}_0} + \beta e^{-2i\vec{q}\cdot\vec{r}_0} + \beta^2\right),\\ &= 1 + 2\beta\cos\left(2\vec{q}\cdot\vec{r}_0\right) + \beta^2,\\ &= 4\beta\cos^2\left(\vec{q}\cdot\vec{r}_0\right) + \left(1-\beta\right)^2.\end{aligned}$$

[3] In the second line we make use of the fact that the amplitude is non-vanishing only for $\vec{q}$ in the reciprocal lattice.

Now, to see if there is any β which will cause some of the Bragg peaks to vanish, we merely need to see if there are any roots to the equation above. It is a simple quadratic and it is easily reduced to $I = 0$ iff

$$\beta = 1 - 2\cos^2(\vec{q}\cdot\vec{r}_0) \pm 2\cos(\vec{q}\cdot\vec{r}_0)\sqrt{\cos^2(\vec{q}\cdot\vec{r}_0) - 1}. \tag{c.1}$$

Because we have assumed that both amplitudes are real, $\beta \in \mathbb{R}$; and because $\cos^2(\theta) \leq 1$, we see that there is a solution iff $\cos^2(\vec{q}\cdot\vec{r}_0) = 1$, for which we see that $\beta = -1$.

Therefore, if $\beta = -1$ there is interference causing all the Bragg peaks for which $\cos^2(\vec{a}\cdot\vec{r}_0) = 0$; this is satisfied if $2n_2 - n_1 = 3m$ for some $m \in \mathbb{Z}$, which correspond to the momentum transfers $\vec{q} = \frac{4\pi}{3d}\left(n_2\sqrt{3} + 3m\frac{\sqrt{3}}{2}, 3m\right)$.

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d) Now let us assume that the atoms A and B are placed randomly on the honeycomb lattice with an even probability distribution. For this random crystal, we are to determine what fraction of the total scattering intensity is in the Bragg peaks (i.e. not diffuse scattering).

Let us define a map $\sigma : \vec{R} \to \{-1, 1\}$, a function whose value is either $+1$ or -1 for each point of the Bravais lattice $\vec{R}$. It must have the property that $|\sigma^{-1}(-1)| = |\sigma^{-1}(1)|$, which means that its average value over the lattice is zero. We will take $\sigma(\vec{R})$ to signify the direction of the A atom relative to the center of the cell at the Bravais lattice point $\vec{R}$. With this in mind, the atom density functions for A and B are given by

$$\rho_A(\vec{r}) = \sum_{\vec{R}} \delta\left(\vec{r} - \vec{R} - \sigma(\vec{R})\vec{r}_0\right) \quad \text{and} \quad \rho_B(\vec{r}) = \sum_{\vec{R}} \delta\left(\vec{r} - \vec{R} + \sigma(\vec{R})\vec{r}_0\right), \tag{d.1}$$

where we again use the definition $\vec{r}_0 = (0, d/2)$.

Let us again say that $f_B = \beta f_A$. We now find that the scattering amplitude goes like[4]—*This is where the equation goes wrong: because of the assumption stated in the footnote, we are effectively only calculating the Bragg contribution.*

$$\psi_s \sim f_A\left\{\sum_{\vec{R}} e^{i\vec{q}\cdot\left(\vec{R}+\sigma(\vec{R})\vec{r}_0\right)} + \beta\sum_{\vec{R}} e^{i\vec{q}\cdot\left(\vec{R}-\sigma(\vec{R})\vec{r}_0\right)}\right\},$$
$$\propto \left\{\sum_{\vec{R}} e^{i\sigma(\vec{R})\vec{q}\cdot\vec{r}_0} + \beta\sum_{\vec{R}} e^{-i\sigma(\vec{R})\vec{q}\cdot\vec{r}_0}\right\}.$$

Now, when we expand out the two sums we find that because $\sigma(\vec{R}) = +1$ for half of the sites and $\sigma(\vec{R}) = -1$ for the other half, each sum has an equal number of terms with positive exponents and negative exponents. Recall that $\exp\{+i\theta\} + \exp\{-i\theta\} = 2\cos(\theta)$. Therefore, up to a constant of proportionality, we have

$$\psi_s \propto \{\cos(\vec{q}\cdot\vec{r}_0) + \beta\cos(\vec{q}\cdot\vec{r}_0)\}. \tag{d.2}$$

This is not right.

[4]In the second line we again make use of the fact that the amplitude will in general vanish unless $\vec{q}$ is in the reciprocal lattice, i.e. $\vec{q}\cdot\vec{R} = 2\pi$ for all $\vec{R}$ in the Bravais lattice.

e) Let us consider fully three-dimensional graphite which has a simple hexagonal Bravais lattice. We are to show that the reciprocal lattice of a simple hexagonal Bravais lattice is also a simple hexagonal lattice. For graphite, we are to show that the internal symmetries of the basis gives rise to to the vanishing of certain Bragg scattering directions and list which reciprocal lattice vectors show this complete interference.

First, let us state the vectors which generate the Bravais lattice of graphite. It is not hard to extend our two-dimensional analysis to three-dimensions:

$$\vec{a}_1 \equiv (d\sqrt{3}, 0, 0) \qquad \vec{a}_2 \equiv \left(d\frac{\sqrt{3}}{2}, d\frac{3}{2}, 0\right) \qquad \vec{a}_3 \equiv (0, 0, \lambda), \tag{e.1}$$

where λ is the height between the graphite layers.

Using our general expression for the reciprocal lattice vectors, equation (1.c.2), we can quite directly compute

$$\vec{b}_1 \equiv \frac{2\pi}{3d}\left(\sqrt{3}, -1, 0\right) \qquad \vec{b}_2 \equiv \frac{4\pi}{3d}(0, 1, 0) \qquad \vec{b}_3 \equiv \frac{2\pi}{\lambda}(0, 0, 1). \tag{e.2}$$

To see that these generate a simple hexagonal lattice, notice that the angle between $\vec{b}_1$ and $\vec{b}_2$, called θ_{12} is given by

$$\cos\theta_{12} = -\frac{1}{2}, \tag{e.3}$$

which obviously generates a hexagonal lattice in the xy-plane; and because $\vec{b}_3$ is in the z-direction, we see that the set $\vec{b}_i$ generate a simple hexagonal lattice.

If we consider scattering off a perfect graphite lattice, we know that there will be a Bragg condition forcing the momentum transfers $\vec{q}$ to be elements of the reciprocal lattice:

$$\vec{q} = n_1\vec{b}_1 + n_2\vec{b}_2 + n_3\vec{b}_3. \tag{e.4}$$

Recall that, for a perfect crystal

$$\psi_s(\vec{q} \in \vec{G}) \propto \int_{\text{one cell}} d\vec{r} \quad \rho(\vec{r})e^{i\vec{q}\cdot\vec{r}}, \tag{e.5}$$

and ψ_s vanishes for $\vec{q} \notin \vec{G}$, where $\vec{G}$ denotes the reciprocal lattice. Now, in the basis cell, there are four atoms located at

$$\vec{r}_1 = (0,0,0) \quad \vec{r}_2 = (0,d,0) \quad \vec{r}_3 = (0,d,\lambda/2) \quad \vec{r}_4 = (\sqrt{3}d/2, d/2, \lambda/2). \tag{e.6}$$

These give delta-functions in the density, which turn the integral into a discrete sum:

$$\psi_s \propto \left\{\sum_{i=1}^{4} e^{i\vec{q}\cdot\vec{r}_i}\right\}. \tag{e.7}$$

Notice that $\vec{r}_3 = \vec{r}_2 + \vec{r}_4 - \vec{a}_2$. Therefore, we see that

$$\psi_2 \propto \left(1 + e^{i\vec{q}\cdot\vec{r}_2}\right)\left(1 + e^{i\vec{q}\cdot\vec{r}_4}\right) = \left(1 + e^{i\frac{2\pi}{3}(2n_1-n_2)}\right)\left(1 + e^{i\pi n_3}e^{-i\frac{\pi}{3}(n_1+n_2)}\right). \tag{e.8}$$

Now, the exponential in the first parenthesis cannot be -1 because there are no integer solutions to the equation $2n_2 - n_1 = \frac{3}{2}$. Therefore, the only way for the intensity to vanish is if the second term in parenthesis vanishes, which requires that simultaneously,

$$(n_1 + n_2) = 0 \mod 3 \qquad \text{and} \qquad n_3 \in (2\mathbb{Z} + 1). \tag{e.9}$$

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