PHYSICS 239.c : CONDENSED MATTER PHYSICS
HW ASSIGNMENT #2 SOLUTIONS

(1) For each of the following structures, indicate whether or not it is a Bravais lattice. If it is, give the three primitive vectors. If not, describe it as a Bravais lattice with the smallest possible basis.

(a) Base-centered cubic (simple cubic with additional points in the centers of the two horizontal faces).

This is a simple tetragonal lattice with elementary direct vectors
\[ a_1 = \frac{1}{2}a(\hat{x} - \hat{y}), \quad a_2 = \frac{1}{2}a(\hat{x} + \hat{y}), \quad a_3 = a\hat{z}. \]

(b) Side-centered cubic (simple cubic with additional points in the centers of the four vertical faces).

Not a Bravais lattice! To see why, note that the the side-centered sites at \( r_1 = \frac{1}{2}a(\hat{x} + \hat{z}) \) and \( r_2 = \frac{1}{2}a(\hat{y} + \hat{z}) \) differ by the vector \( \delta = r_2 - r_1 = \frac{1}{2}a(\hat{y} - \hat{x}) \). But while \( r_3 = 0 \) is a lattice site, \( r_3 + \delta \) is not a lattice site. Therefore the local environment of the side-centers is different from that of the simple cubic lattice sites.

(c) Edge-centered cubic (simple cubic with additional points at the midpoints of all nearest-neighbor links).

Not a Bravais lattice! The sites \( r_1 = 0 \) and \( r_2 = \frac{1}{2}a\hat{x} \) are separated by \( \delta = r_2 - r_1 = \frac{1}{2}a\hat{x} \). But while \( r_3 = \frac{1}{2}a\hat{y} \) is a lattice site, \( r_3 + \delta = \frac{1}{2}a(\hat{x} + \hat{y}) \) is a face center, and not an edge center, and hence is not in the lattice.

(2) Polycrystalline specimens of three different monatomic cubic crystals are analyzed with a Debye-Scherrer camera. It is known that one sample is fcc, one is bcc, and one has a diamond structure. The approximate angular position \( \phi \) of the first four diffraction rings are found to be

- A : 42.2°, 49.2°, 72.0°, 87.3°
- B : 28.8°, 41.0°, 50.8°, 59.6°
- C : 42.8°, 73.2°, 89.0°, 115°

(a) Identify the crystal structures A, B, and C.

Crystallographic extinctions occur when \( F(k) = 0 \), where \( F(k) = \sum_r e^{iG\cdot r} \) is a sum over all unique lattice points within the fundamental \( a\times a\times a \) cube and \( G = \frac{2\pi}{a}(h,k,l) \) is a reciprocal lattice vector. The locations \( r \) for the three structures are given by:

FCC : \( r_1 = (0,0,0) \), \( r_2 = \left(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a\right) \), \( r_3 = \left(\frac{1}{2}a, 0, \frac{1}{2}a\right) \), \( r_4 = (0, \frac{1}{2}a, \frac{1}{2}a) \)

BCC : \( r_1 = (0,0,0) \), \( r_2 = \left(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a\right) \)

DIA : \( r_1 = (0,0,0) \), \( r_2 = \left(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a\right) \), \( r_3 = \left(\frac{1}{2}a, 0, \frac{1}{2}a\right) \), \( r_4 = (0, \frac{1}{2}a, \frac{1}{2}a) \)
\( r_5 = \left(\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}a\right) \), \( r_6 = \left(\frac{1}{4}a, \frac{3}{4}a, \frac{3}{4}a\right) \), \( r_7 = \left(\frac{3}{4}a, \frac{1}{4}a, \frac{3}{4}a\right) \), \( r_8 = \left(\frac{3}{4}a, \frac{3}{4}a, \frac{1}{4}a\right) \).
Thus,

\[ F_{\text{FCC}}(h, k, l) = 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)} \]
\[ F_{\text{BCC}}(h, k, l) = 1 + e^{i\pi(h+k+l)} \]
\[ F_{\text{DIA}}(h, k, l) = (1 + e^{i\pi(h+k+l)/2}) (1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)}) \]

The allowed values of \((h, k, l)\) are thus given by

\[
\begin{align*}
\text{FCC} & : \{h, k\} \text{ all even or all odd} \\
\text{BCC} & : h + k + l \text{ even} \\
\text{DIA} & : \{h, k, l\} \text{ all even and } h + k + l = 4n, \text{ or } \{h, k, l\} \text{ all odd.}
\end{align*}
\]

We have \(\lambda = 2d_{hkl} \sin(\phi/2)\) with \(d_{hkl} = a/\sqrt{h^2 + k^2 + l^2}\), and so

\[
\sin^2\left(\frac{\phi}{2}\right) = \frac{\lambda^2}{4d_{hkl}^2} = \frac{\lambda^2}{4a^2}.
\]

For FCC we have the first four values of \(h^2 + k^2 + l^2\) are \((1, 1, 1), (2, 0, 0), (2, 2, 0),\) and \((3, 1, 1)\), corresponding to \(d_{hkl}^2 = 3, 4, 8,\) and \(11\), respectively. For BCC, we have \((1, 1, 0), (2, 0, 0), (2, 1, 1),\) and \((2, 2, 0)\), corresponding to \(d_{hkl}^2 = 2, 4, 6,\) and \(8\). Finally, for DIA, we have \((1, 1, 1), (2, 2, 0), (3, 1, 1),\) and \((4, 0, 0)\), corresponding to \(d_{hkl}^2 = 3, 8, 11,\) and \(16\). Comparing the ratios of these numbers, we find that crystal A is FCC, B is BCC, and C is DIA.

(b) If the wavelength of the incident X-ray is \(\lambda = 1.5\text{Å}\), what is the length of the side of the cubic cell in each case?

Plugging into the formula \(a = \frac{1}{2} \sqrt{h^2 + k^2 + l^2} \lambda\), we have \(a_A = 3.61\text{Å}, a_B = 4.26\text{Å},\) and \(a_C = 3.56\text{Å}.\)

(c) If the (monatomic) diamond structure were replaced by a (binary) zincblende structure, at what angles would the first four rings be observed?

Distinguishing the two FCC sublattices of diamond results in an FCC structure, so with \(\lambda/2a = 0.21\) we expect rings at \(\phi = 42.8°, 49.8°, 73.2°,\) and \(89.0°.\)

(3) A monolayer of atoms is deposited on a surface. The atoms form a regular hexagonal lattice. This problem deals with the vibrations of these atoms.

(a) Suppose the surface is perfectly smooth. The atoms interact by a potential

\[
\Phi = \frac{1}{2} \sum_{R,R'} v(|R + u_\perp(R) - R' - u_\perp(R')|) + \frac{1}{2} K z \sum_R u_z^2(R)
\]

where \(u_\perp = u_x \hat{x} + u_y \hat{y}\) is the displacement along the surface (perpendicular to the surface normal \(\hat{z}\)), \(R\) and \(R'\) denote sites of the hexagonal Bravais lattice, and the last
term describes the binding of the atoms to the surface \((u^z\) is the displacement along the surface normal). Show that the dynamical matrix for the lattice vibrations takes the form

\[
\hat{\Phi}(k) = \begin{pmatrix}
\hat{\Phi}^{xx}(k) & \hat{\Phi}^{x\gamma}(k) & 0 \\
\hat{\Phi}^{\gamma x}(k) & \hat{\Phi}^{\gamma\gamma}(k) & 0 \\
0 & 0 & \hat{\Phi}^{zz}(k)
\end{pmatrix}
\]

where the upper left \(2 \times 2\) block is given by

\[
\Phi^{\alpha\beta}(k) = 2 \sum_R \sin^2\left(\frac{1}{2} k \cdot R\right) \left\{ (\delta^{\alpha\beta} - \hat{R}^\alpha \hat{R}^\beta) R^{-1} v'(R) + \hat{R}^\alpha \hat{R}^\beta v''(R) \right\}
\]

with \(\alpha, \beta = 1, 2\), and \(\hat{\Phi}^{zz}(k) = K_z\) independent of \(k\).

The above result for \(\Phi^{\alpha\beta}(k)\) follows from Eqn. 3.54 of the Lecture Notes.

(b) Assuming that the above sum for \(\Phi^{\alpha\beta}(k)\) is dominated by the nearest neighbor terms, compute the phonon dispersions along the \((1,0)\) axis in reciprocal space. You should use \(M\) for the ionic mass, \(a\) for the lattice constant, and abbreviate \(A \equiv a^{-1} v'(a)\) and \(B \equiv v''(a)\).

We take \(a_1 = \frac{1}{2} a(x - \sqrt{3} y)\) and \(a_2 = \frac{1}{2} a(x + \sqrt{3} y)\). The elementary reciprocal lattice vectors are then \(b_1 = (2\pi/a\sqrt{3})(\sqrt{3} x - y)\) and \(b_2 = (2\pi/a\sqrt{3})(\sqrt{3} x + y)\). The nearest neighbor separations are then the six vectors \(\pm a_1, \pm a_2\), and \(\pm a_3\) where \(a_3 \equiv -a_1 - a_2 = -a \hat{x}\). With \(k = (\theta_1/2\pi) b_1 + (\theta_2/2\pi) b_2\) we have

\[
\Phi^{\alpha\beta}(k) = 4 \sin^2\left(\frac{1}{2} \theta_1\right) \left( (A \delta^{\alpha\beta} + (B - A) \hat{a}_1^\alpha \hat{a}_1^\beta) + 4 \sin^2\left(\frac{1}{2} \theta_2\right) (A \delta^{\alpha\beta} + (B - A) \hat{a}_2^\alpha \hat{a}_2^\beta) \\
+ 4 \sin^2\left(\frac{1}{2} \theta_3\right) (A \delta^{\alpha\beta} + (B - A) \hat{a}_3^\alpha \hat{a}_3^\beta) \right)
\]

where \(\theta_3 \equiv -(\theta_1 + \theta_2)\), and

\[
\hat{a}_1^\alpha \hat{a}_1^\beta = \frac{1}{4} \begin{pmatrix} 1 & 1 & -\sqrt{3} \\ -\sqrt{3} & -1 & 3 \end{pmatrix}, \quad \hat{a}_2^\alpha \hat{a}_2^\beta = \frac{1}{4} \begin{pmatrix} 1 & 1 & \sqrt{3} \\ \sqrt{3} & -1 & 3 \end{pmatrix}, \quad \hat{a}_3^\alpha \hat{a}_3^\beta = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}.
\]

Along \((1,0)\) we have \(\theta_2 = 0\) and thus \(\theta_3 = -\theta_1\). This yields

\[
\Phi^{\alpha\beta}(k) = \sin^2\left(\frac{1}{2} \theta_1\right) \begin{pmatrix} 3A + 5B & \sqrt{3}(A - B) \\ \sqrt{3}(A - B) & 5A + 3B \end{pmatrix}
\]

Thus the phonon dispersion is given by

\[
\omega_{\pm}(\theta_1, 0) = 2 \sin\left(\frac{1}{2} \theta_1\right) \sqrt{\frac{(A + B) \pm \frac{1}{2} |A - B|}{M}}
\]

Note there are two branches, because there are degrees of freedom per unit cell. At low frequency we have \(\omega_{\pm} = c_{\pm} k\). The general form of the dynamical matrix is

\[
\Phi^{11}(k) = (3A + B) \left[ \sin^2\left(\frac{1}{2} \theta_1\right) + \sin^2\left(\frac{1}{2} \theta_2\right) \right] + 4B \sin^2\left(\frac{1}{2} \theta_3\right)
\]

\[
\Phi^{22}(k) = (A + 3B) \left[ \sin^2\left(\frac{1}{2} \theta_1\right) + \sin^2\left(\frac{1}{2} \theta_2\right) \right] + 4A \sin^2\left(\frac{1}{2} \theta_3\right)
\]

\[
\Phi^{12}(k) = \sqrt{3}(A - B) \left[ \sin^2\left(\frac{1}{2} \theta_1\right) - \sin^2\left(\frac{1}{2} \theta_2\right) \right]
\]
and
\[ M\omega_c^2(\theta_1, \theta_2) = \frac{1}{2}(\phi^{11}(k) + \phi^{22}(k)) \pm \sqrt{\frac{1}{4}(\phi^{11}(k) - \phi^{22}(k))^2 + \phi^{12}(k)^2} \]
\[ = 2(A + B)(s_1^2 + s_2^2 + s_3^2) \pm 2|A - B| \cdot (s_1^4 + s_2^4 + 2s_1^2s_3^2 - 2s_2^4 - 2s_2^2s_3^2), \]
where \( s_j \equiv \sin^2(\frac{1}{2}\theta_j). \) Note that setting \( \theta_1 = \theta_2 = \pi \) yields \( M\omega_c^2 = 8\max(A, B) \) and \( M\omega_c^2 = 8\min(A, B) \) at an edge of the BZ, whereas \( \theta_1 = \theta_2 = \frac{\pi}{2} \) yields \( M\omega_c^2 = 3(A + B) \) at the zone corners. In the long wavelength limit, we have
\[ \phi^{11}(k) = \frac{1}{8}(3A + B)(k_x^2 + 3k_y^2)a^2 + Bk_x^2a^2 + \ldots \]
\[ \phi^{22}(k) = \frac{1}{8}(A + 3B)(k_x^2 + 3k_y^2)a^2 + Ak_x^2a^2 + \ldots \]
\[ \phi^{12}(k) = \frac{3}{8}(B - A)k_xk_ya^2 + \ldots \]
whence
\[ \frac{1}{2}(\phi^{11}(k) + \phi^{22}(k)) = \frac{3}{4}(A + B)k^2a^2 + \ldots \]
\[ \frac{1}{2}(\phi^{11}(k) - \phi^{22}(k)) = \frac{3}{8}(A - B)k^2a^2 + \ldots \]
and \( \omega_{\pm}(k) = c_{\pm}|k| \) with
\[ c_+ = \sqrt{\frac{3(3A + B)a^2}{8M}}, \quad c_- = \sqrt{\frac{3(A + 3B)a^2}{8M}}. \]

(c) Sketch the phonon density of states. Find the normalized density of states at low frequencies. Make clear any assumptions.

For each phonon branch in \( d = 2 \) dimensions, we have, in the long wavelength limit,
\[ g(\omega) \, d\omega = \frac{\Omega d^2k}{(2\pi)^2} = \Omega \frac{k \, dk}{2\pi} \quad \Rightarrow \quad g(\omega) = \Omega \frac{k \, dk}{2\pi \omega} = \frac{\Omega}{2\pi c^2} \, \omega, \]
where \( c \) is the phonon velocity. Thus, the phonon DOS for low frequencies is \( \frac{\omega}{2\pi c^2} \) where \( \frac{1}{2}c^{-1} = \frac{1}{2}(c_+^{-2} + c_-^{-2}) \). The DOS vanishes above the highest phonon frequency, which is \( 8\max(A, B) \).

(d) Find an expression for the low-temperature specific heat.

The general expression for the heat capacity per unit cell from phonons is
\[ c_v = k_B \int_0^\infty d\omega \, g(\omega) \left( \frac{h\omega}{2k_B T} \right)^2 \cosh^2 \left( \frac{h\omega}{2k_B T} \right) \]

With \( k_B T \ll h\omega_b \) we have
\[ c_v = A\Omega k_B \left( \frac{2k_B T}{h} \right)^2, \]
where \( A = \int_0^\infty ds \, s^3 \cosh^2(s). \)
(e) Find an expression for the amplitude $e^{-2W(G)}$ of the Bragg peaks in a neutron scattering experiment (the Debye-Waller factor). Show that $W(G)$ diverges for any nonzero value of $G$. Why does this happen? Suppose that the phonon dispersion is cut off at low frequencies at a scale $\omega_{\text{min}} \propto L^{-1}$, where $L$ is the characteristic linear dimension of the system. Show that the Debye-Waller factor is then finite and evaluate its leading dependence on $L$ in the limit $L \to \infty$.

We use Eqn. (3.170) from the Lecture Notes to approximate the DW factor as

$$2W(G) \approx \frac{G^2}{3M} \int_0^{\infty} d\omega \frac{g(\omega)}{2\omega} \frac{\hbar}{\omega} \coth \left( \frac{\hbar \omega}{2k_B T} \right).$$

This diverges logarithmically if $g(\omega) \propto \omega$. If we set a lower limit by $\omega_{\text{min}} = \hbar \bar{c}/L$, then we obtain

$$2W(G) \approx \frac{k_B T \Omega G^2}{2\pi M c^2} \ln \left( \frac{k_B T L}{2\pi \hbar \bar{c}} \right).$$

We now allow for the “corrugation” of the surface through an additional term in the potential energy

$$\Delta \Phi = \frac{1}{2} K_\perp \sum_R u_\perp^2 (R).$$

(f) Compute the new phonon frequencies for $k \approx 0$.

With the corrugation potential present, the phonons become Einstein phonons. Their density of states becomes $g(\omega) \approx 2 \delta(\omega - \omega_0)$ with $\omega_0 = \sqrt{K_\perp/M}$.

(g) What is the temperature dependence of the density of states?

I have no idea why I asked this question. The DOS for this problem shouldn’t be temperature-dependent.

(h) Show that the Debye-Waller factor is now finite even in the $L \to \infty$ limit.

There is no longer any infrared divergence in the DW integral, since the phonon frequencies are all finite. Note that the corrugation potential explicitly breaks translational symmetry in the plane, hence there are no longer any Goldstone modes, and consequently the HMW theorem does not apply.

(4) Find the longitudinal and transverse phonon speeds for a cubic crystal with mass density $\rho$ and nonzero elastic moduli $C_{11}, C_{12},$ and $C_{44}$ for the following cases: (a) $k \parallel (1, 0, 0)$, (b) $k \parallel (1, 1, 0)$, and (c) $k \parallel (1, 1, 1)$. 
This problem is solved in §3.2.10 of the Lecture Notes. In cubic crystals, there are three independent elastic moduli, $C_{11}$, $C_{12}$, and $C_{14}$. We then have

$$
p e^2(k) e^x = \left[ C_{11} \hat{k}_x^2 + C_{44} (\hat{k}_y^2 + \hat{k}_z^2) \right] \hat{e}^x + (C_{12} + C_{44}) (\hat{k}_x \hat{k}_y \hat{e}_y + \hat{k}_x \hat{k}_z \hat{e}_z)$$

$$p e^2(k) e^y = \left[ C_{11} \hat{k}_y^2 + C_{44} (\hat{k}_x^2 + \hat{k}_z^2) \right] \hat{e}^y + (C_{12} + C_{44}) (\hat{k}_x \hat{k}_y \hat{e}_x + \hat{k}_y \hat{k}_z \hat{e}_z)$$

$$p e^2(k) e^z = \left[ C_{11} \hat{k}_z^2 + C_{44} (\hat{k}_x^2 + \hat{k}_y^2) \right] \hat{e}^z + (C_{12} + C_{44}) (\hat{k}_x \hat{k}_z \hat{e}_x + \hat{k}_y \hat{k}_z \hat{e}_y) .$$

This yields a cubic equation for the propagation speed $c(k)$, but one that can be simplified by looking along a high symmetry direction in the Brillouin zone. Along the $(100)$ direction $k = k \hat{x}$, we have

$$\hat{e}_L = \hat{x} \quad \quad c_L = \sqrt{C_{11}/\rho}$$

$$\hat{e}_{T_1} = \hat{y} \quad \quad c_{T_1} = \sqrt{C_{44}/\rho}$$

$$\hat{e}_{T_2} = \hat{z} \quad \quad c_{T_2} = \sqrt{C_{44}/\rho} .$$

Along the $(110)$ direction, we have $k = \frac{1}{\sqrt{2}} k (\hat{x} + \hat{y})$. In this case

$$\hat{e}_L = \frac{1}{\sqrt{2}} (\hat{x} + \hat{y}) \quad \quad c_L = \sqrt{(C_{11} + 2C_{12} + 4C_{44})/3\rho}$$

$$\hat{e}_{T_1} = \frac{1}{\sqrt{2}} (\hat{x} - \hat{y}) \quad \quad c_{T_1} = \sqrt{(C_{11} - C_{12})/2\rho}$$

$$\hat{e}_{T_2} = \hat{z} \quad \quad c_{T_2} = \sqrt{C_{44}/\rho} .$$

Along the $(111)$ direction, we have $k = \frac{1}{\sqrt{3}} k (\hat{x} + \hat{y} + \hat{z})$. In this case

$$\hat{e}_L = \frac{1}{\sqrt{3}} (\hat{x} + \hat{y} + \hat{z}) \quad \quad c_L = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho}$$

$$\hat{e}_{T_1} = \frac{1}{\sqrt{6}} (2\hat{x} - \hat{y} - \hat{z}) \quad \quad c_{T_1} = \sqrt{(C_{11} - C_{12})/3\rho}$$

$$\hat{e}_{T_2} = \frac{1}{\sqrt{2}} (\hat{y} - \hat{z}) \quad \quad c_{T_2} = \sqrt{(C_{11} - C_{12})/3\rho} .$$