Physics 601

HW 4 Solutions

1. For crystal diffraction we need $\lambda \sim 1\ \text{Å} \equiv \lambda_0$
since we need $\lambda \sim$ interatomic spacing.
Using the de Broglie relation

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \Rightarrow \text{Needed: } E = \frac{h^2}{2m\lambda_0^2}$$

$$m_{\text{neutron}} > m_{\text{electron}}$$

$$\Downarrow$$

$$E_{\text{neutron}} < E_{\text{electron}} \quad \left(E \sim \frac{1}{m}\right)$$

2. For crystal diffraction to occur we would like

$$\lambda \sim d$$

where we note that from Bragg's law

$$\lambda = 2d \sin\theta.$$

There is no diffraction for $\lambda > 2d$ (since $\sin\theta \leq 1$). Thus visible green (~ 5100 Å) light could provide diffraction spots when scattered from a crystal with lattice constant $d \sim 5000$ Å ; this is three orders of magnitude larger than that of crystals we see in Nature.

3. Powder Diffraction on CaF_2.

$\lambda = 0.1542$

We follow the protocol in Simon p. 154.

a)

Peak	θ	$d = \frac{\lambda}{2\sin\theta}$	$\frac{d_1^2}{d^2}$	$h^2+k^2+l^2$	$\{hkl\}$
1	14.16	.3151	1	3	111
2	16.41	.2729	1.334	4	200
3.	23.55	.1929	2.668	8	220
4	27.94	.1646.	3.668	11	311.

b)

Peak	$a = d\sqrt{h^2+k^2+l^2}$ (nm).
1	.54589
2	.54582
3	.54579
4	.5476

$\Downarrow$

$\bar{a} = 0.54582$ nm

Standard error of this estimate

$$\delta a = \left\{ \frac{1}{n(n-1)} \sum (a_i - \bar{a})^2 \right\}^{1/2}$$

$$\sim 2.821 \times 10^{-5} \text{ nm}$$

$$\Downarrow$$

Estimated lattice constant

$$\bar{a} = 0.5482 \pm .00003 \text{ nm}$$

c) $$\rho = \frac{m}{V} = \frac{1}{a^3} \left\{ 4 \underset{\downarrow \atop 40}{m_{Ca}} + 8 \underset{\downarrow \atop 19.}{m_F} \right\}$$

$$= 3,189 \text{ kg/m}^3$$

4.

Key points of the Donev et al. paper.

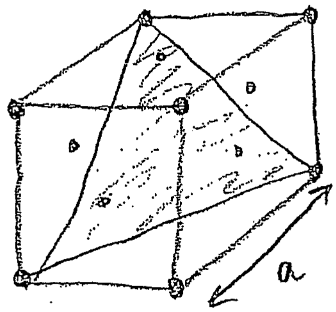
- Main result: Oblate spheroids (M&Ms) pack differently (more densely) than do spheres when poured randomly and shaken.
- Extensions of work w/ more experiments on spheroids w/ different aspect ratios and with computer simulations ⇒ random packing densities approach those of perfectly ordered arrangements of spheres
- Used MRI to check that there was no periodic

ordering in the center.

- Always assumed that periodic orderings are denser than are random ones ⇒ true for spheres but may not be the case for all spheroids.
- The change of shape sphere → spheroids leads to major change in random packing densities (such shape changes have minimal effects on non-random packing).

5. $\lambda = 1.54\ \mathring{A}$

a) $\theta = 19.2^\circ$ for (111) plane $\Rightarrow d_{111}$



(111)

Bragg's Law

$$n\lambda = 2d\sin\theta$$

We assume $n = 1$

$$d = \frac{\lambda}{2\sin\theta} = \frac{1.54}{2\sin 19.2}$$

$$\boxed{d_{111} = 2.34\ \mathring{A}}$$

For fcc lattice $d = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$

$\Downarrow$

$$a = d_{111}\sqrt{3} = 2.34\sqrt{3} = 4.05\ \mathring{A}$$

$$\boxed{a = 4.05\ \mathring{A}}$$

b) $$\rho = \frac{\text{\# Al atoms}}{\text{Volume of unit cell}} \times \frac{\text{molecular weight of Al (g-atom)}}{N \text{ (\# atoms in 1 g-atom)}}$$

$$\Downarrow$$

$$N = \frac{\text{\# Al atoms}}{\text{volume of unit cell}} \times \frac{M(\text{Al})}{\rho}$$

Al is fcc

- \# atoms / unit cell

$$= \frac{\text{8 corner atoms}}{\text{8 cells}} + \frac{\text{6 face atoms}}{\text{2 cells}}$$

$$= 1 + 3 = 4 \text{ atoms / cell}$$

$$\Downarrow$$

$$N = \frac{4 \text{ atoms}}{(4.05 \times 10^{-8})^3 \cancel{\text{cm}^3}} \times \frac{27 \cancel{\text{g}}}{2.7 \cancel{\text{g}}/1 \cancel{\text{cm}^3}}$$

$$= \frac{4}{(4.05)^3} \times 10^{25} \text{ atoms} = 6.02 \times 10^{23} \text{ atoms.}$$

$$\boxed{N = 6.02 \times 10^{23} \text{ atoms}}$$

6.

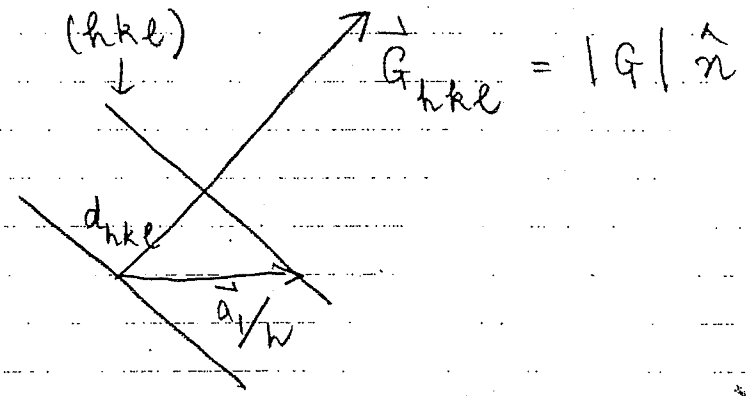
Interplanar Separation

The plane (hkl) is defined by the intercepts

$$\frac{\vec{a}_1}{h}, \quad \frac{\vec{a}_2}{k} \quad \text{and} \quad \frac{\vec{a}_3}{l}$$

a) We take two vectors in this plane

$$\vec{A} = \frac{\vec{a}_1}{h} - \frac{\vec{a}_2}{k}$$



$$\vec{B} = \frac{\vec{a}_1}{h} - \frac{\vec{a}_3}{l}$$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

$$\left.\begin{aligned} \vec{G}\cdot\vec{A} &= 0 \\ \vec{G}\cdot\vec{B} &= 0 \end{aligned}\right\} \Rightarrow$$ G must be perpendicular to (hkl)

b) Let $\hat{n}$ be the unit normal to the plane

$\Downarrow$

interplanar spacing is $\dfrac{\hat{n}\cdot\vec{a}}{h} = d(hkl)$

However

$$\hat{n} = \frac{\vec{G}}{|\vec{G}|}$$

$\Downarrow$

$$d(hkl) = \frac{\overbrace{\vec{G}\cdot\vec{a}_1}^{2\pi h}}{h\,|\vec{G}|} = \frac{2\pi}{|G|}.$$

c) For a simple cubic lattice

$$\vec{G} = \frac{2\pi}{a}\left(h\hat{x} + k\hat{y} + l\hat{z}\right)$$

$\Downarrow$

$$\frac{1}{d^2} = \frac{G^2}{4\pi^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

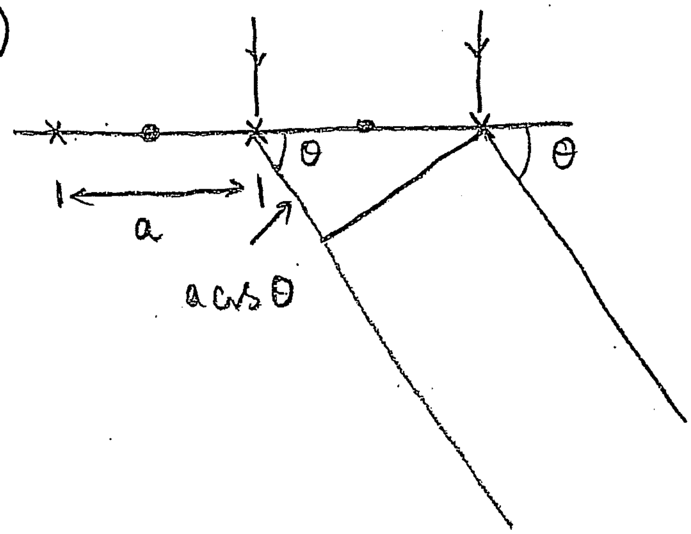
$\Downarrow$

$$\boxed{d^2 = \frac{a^2}{h^2 + k^2 + l^2}.}$$

7. Diatomic Line

Let $\times = A$, $\bullet = B$.

a)



Constructive interference iff

$$n\lambda = a\cos\theta$$

b) $$S_G = \sum_j f_j \, e^{-i2\pi v_1 x_j}$$

$x_A = 0$

$x_B = 1/2$

$$= f_A + f_B \, e^{-iv_1\pi}$$

v_1 even $\quad e^{-iv_1\pi} = +1$

v_1 odd $\quad e^{-iv_1\pi} = -1.$

Therefore

$$S_G = f_A - f_B \qquad v_1 \text{ odd}$$

$$S_G = f_A + f_B \qquad v_2 \text{ even}$$

$$\Downarrow$$

$$I \propto |S_G|^2 = \begin{cases} |f_A - f_B|^2 & v_1 \text{ odd} \\ |f_A + f_B|^2 & v_1 \text{ even} \end{cases}$$

c) $f_A = f_B$.

No reflection w/ v_1 odd

Same reflections as for monatomic lattice

w/ $a/2$ lattice spacing.

8. Hexagonal Space Lattice

Hexagonal lattice $\vec{a}_1 = \frac{\sqrt{3}}{2} a\hat{x} + \frac{a}{2}\hat{y}$

$$\vec{a}_2 = -\frac{\sqrt{3}}{2} a\hat{x} + \frac{a}{2}\hat{y}$$

$$\vec{a}_3 = c\hat{z}$$

(a) Cell volume $= \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)$

$$= \vec{a}_1 \cdot \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}}{2}a & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix}$$

$$= \left(\frac{\sqrt{3}}{2} a\hat{x}\right) \cdot \left(\frac{ac}{2}\hat{x}\right)$$

$$+ \left(\frac{a}{2}\hat{y}\right) \cdot \left(\frac{\sqrt{3}}{2} ac\,\hat{y}\right)$$

$$= \frac{2\sqrt{3}}{4} a^2 c = \frac{\sqrt{3}}{2} a^2 c.$$

(b) $$\vec{b}_1 = \frac{2\pi}{V_c}\left(\vec{a}_2 \times \vec{a}_3\right)$$

$$= \frac{2\pi}{\frac{\sqrt{3}}{2}a^2 c}\begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ -\frac{\sqrt{3}}{2}a & \frac{a}{2} & 0 \\ 0 & 0 & c \end{vmatrix}$$

$$\Downarrow$$

$$\boxed{\vec{b}_1 = \frac{2\pi}{\sqrt{3}\,a}\hat{x} + \frac{2\pi}{a}\hat{y}}$$

$$\vec{b}_2 = \frac{2\pi}{V_c}\left(\vec{a}_3 \times \vec{a}_1\right)$$

$$= \frac{4\pi}{\sqrt{3}a^2 c}\begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & c \\ \frac{\sqrt{3}}{2}a & \frac{a}{2} & 0 \end{vmatrix}$$

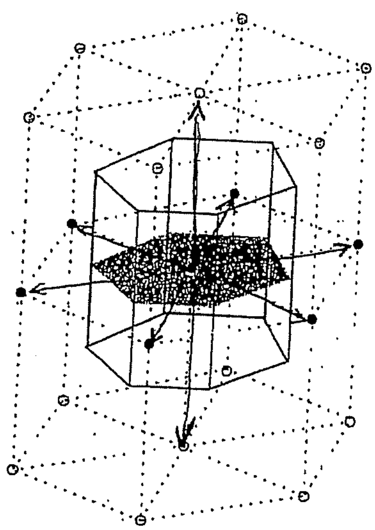
$$\boxed{\vec{b}_2 = +\frac{2\pi}{a}\left(-\frac{1}{\sqrt{3}}\hat{x} + \hat{y}\right)}$$

$$\vec{b}_3 = \frac{2\pi}{V_c} (\vec{a}_1 \times \vec{a}_2)$$

$$= \frac{4\pi}{\sqrt{3}\, a^2 c} \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\sqrt{3}}{2} a & \frac{a}{2} & 0 \\ -\frac{\sqrt{3}}{2} a & \frac{a}{2} & 0 \end{vmatrix}$$

$$\boxed{\vec{b}_3 = \frac{2\pi}{c} \hat{z}}$$

(c)



The reciprocal lattice is shown as dots and is shifted by an angle of 30° from the real-space lattice. The shaded BZ is also shown; it is oriented w/ the real space lattice (shifted from the reciprocal lattice by 30°).

9. Sample Mix-Up Problem

$$S_G(v_1\, v_2\, v_3) = \sum_j f_j \exp\left(-2\pi i \left\{ v_1 x_j + v_2 y_j + v_3 z_j \right\}\right)$$

bcc

(000) $\left(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}\right)$

$$S(v_1\, v_2\, v_3) = f\left(1 + \exp - i\pi\,(v_1 + v_2 + v_3)\right)$$

$$S = \begin{cases} 0 & \sum v_i = \text{odd integer} \\ 2f & \sum v_i = \text{even integer} \end{cases}$$

fcc (000) $\left(0\,\frac{1}{2}\,\frac{1}{2}\right)$ $\left(\frac{1}{2}\,0\,\frac{1}{2}\right)$ $\left(\frac{1}{2}\,\frac{1}{2}\,0\right)$

$$S(v_1\, v_2\, v_3) = f\left\{\begin{array}{l} 1 + \exp - i\pi\,(v_2 + v_3) \\ + \exp - i\pi\,(v_1 + v_3) \\ + \exp - i\pi\,(v_1 + v_2) \end{array}\right.$$

$$S = \begin{cases} 4f & \text{all } v\text{'s odd or even} \\ 0 & \text{otherwise} \end{cases}$$

(110) cannot occur for fcc but is OK for bcc

$\boxed{\text{Sample is bcc}}$

10. Error Analysis

Bragg's Law

$$d_{hkl} = \frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{\sqrt{N}}$$

$$\Downarrow$$

$$a = \frac{\sqrt{N}\,\lambda}{2\sin\theta}$$

$$|\delta a| = \left| \frac{\sqrt{N}\,\lambda}{2} \frac{\cos\theta}{\sin^2\theta} \right| \, |\delta\theta|$$

$$\Downarrow$$

$$\left|\frac{\delta a}{a}\right| = |\cot\theta| \, |\delta\theta|$$

note that even if $\delta\theta$ small and fixed, there will always be this uncertainty in $\delta a/a$

Reduction of error

- take many measurements at angles where $\cot\theta$ not large

Sources of error

- sample displacement (not centred)
- preferred orientation of crystallites
- beam width

Note that here we assume the $\Delta\lambda$ is negligible → my experimental colleagues tell me this is a reasonable assumption given other sources of error.

11. Marder 3.2 Hcp extinctions

a) From problem # 8.

$$\vec{a}_1 = \frac{a}{2}\begin{pmatrix}\sqrt{3} \\ 1\end{pmatrix}$$

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix}$$

$$\Downarrow \quad \theta = 30$$

$$\begin{bmatrix} 1 \\ \sqrt{3} \end{bmatrix} \Leftarrow \begin{bmatrix} \sqrt{3}/2 & -\frac{1}{2} \\ \frac{1}{2} & \frac{\sqrt{3}}{2} \end{bmatrix}\begin{bmatrix} \sqrt{3} \\ 1 \end{bmatrix}\frac{a}{2}.$$

$$\vec{b}_1 = \frac{2\pi}{a}\begin{bmatrix} 1 \\ \sqrt{3} \end{bmatrix}$$

from # 8

$$\Downarrow$$

real space and reciprocal lattices are rotated by $\theta = 30°$ from one another.

(b) Basis vectors

$$\underbrace{(0 \quad 0 \quad 0)}_{= \, v_1} \qquad \underbrace{\left(\frac{a}{\sqrt{3}} \quad 0 \quad \frac{c}{2}\right)}_{= \, v_2}.$$

Using $\vec{G}$ from Problem # 8

$\Downarrow$

$$\vec{v}_2 \cdot \vec{G} = \frac{\pi}{3}\left\{2(n_1+n_2) + 3n_3\right\}.$$

$\Downarrow$

$$F_q = \left| 1 + e^{\frac{i\pi}{3}\left\{2(n_1+n_2)+3n_3\right\}} \right|^2$$

c) $F_q = 0$ when $2(n_1+n_2) + 3n_3 = 3N$.

12. Marder 3.4 Laue Patterns

From Problem # 9

$$bcc \quad S = \begin{cases} 0 & \sum v_i = \text{odd} \\ 2f & \sum v_i = \text{even} \end{cases}$$

$$v_i \in \{h\ k\ l\}.$$

$$fcc \quad S = \begin{cases} 4f & \text{all } v\text{'s odd or even} \\ 0 & \text{otherwise} \end{cases}$$

All reflections are allowed for simple cubic lattice

a) Three Bragg angles $\theta_1 = 18.5$

$\theta_2 = 24$

$\theta_3 = 27$

Wavevector cutoff $= \dfrac{32}{a}$

$$\frac{2\pi}{\lambda_{min}} = \frac{32}{a} \Rightarrow \lambda_{min} = \frac{\pi a}{16}.$$

$$d = \frac{\lambda_{min}}{2 \sin \theta} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\frac{\pi a}{32 \sin (27)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$h^2 + k^2 + l^2 = \left(\frac{32 \sin 27}{\pi} \right)^2$$

$$= 21.4 \sim 21.$$

$$\Downarrow$$

$$h^2 + k^2 + l^2 << 21$$

$$h, k, l \doteq 0, 1, 2 \text{ or } 3.$$

$$\frac{\lambda}{2\sin\theta} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{a}{N_\theta^2}$$

$$\Downarrow$$

$$N_\theta^2 = \left(\frac{2a\sin\theta}{\lambda}\right)^2$$

$$N_\theta^2 = (h^2+k^2+l^2)_\theta$$

$$\frac{N_{\theta_2}^2}{N_{\theta_1}^2} = \left(\frac{\sin\theta_2}{\sin\theta_1}\right)^2$$

(assume due to roughly same λ)

$$\frac{N_{24}}{N_{18.5}} = 1.6 \qquad \frac{N_{26.5}}{N_{18.3}} = 1.9 \sim 2.$$

$$\frac{N_{26.5}}{N_{24}} = 1.2$$

Again - $h^2+k^2+l^2$

$\dfrac{N_{24}}{N_{18.5}} = 1.6 \quad \times 5$ 8 220.

$\dfrac{N_{26.5}}{N_{24}} = 1.2. \quad \times 5$ 6 211

$\dfrac{N_{26.5}}{N_{18.5}} = 1.9 \sim 2 \quad \times 5$ 10. 310

× fcc NOT all odd or all even

✓ bcc Σv_i = even

No other peaks (would be there for scc)

$\Downarrow$

Proposal <u>bcc</u>

13. Free electron lasers ⇔ noncrystalline samples.

- Diffraction due to constructive / destructive interference ⇒ crystallinity not necessary.
- Large flux of X-rays → single shot diffraction
- Problem: X-rays destroy samples!
- Idea: Pulsed X-rays / femtoseconds before destruction → diffraction pattern
- Alignment of biological molecules (e.g. electric dipole) to boost signal-to-noise
- Heating issues?