## PYU33P03: Condensed Matter I Assignment due 13/04/2022

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## Q1

We can rearrange the given relationships as follows to result in an expression for  $\sin \theta$  as follows:

$$\begin{split} n\lambda &= 2d\sin\theta\\ \implies \sin\theta &= \frac{n\lambda}{2d}\\ d &= \frac{2\pi}{||\vec{k}|||}\\ \implies \sin\theta &= \frac{n\lambda||\vec{k}||}{4\pi}\\ \vec{k} &= h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3\\ \implies \sin\theta &= \frac{n\lambda\sqrt{h^2b_1^2 + k^2b_2^2 + l^2b_3^2}}{4\pi} \end{split}$$

For a BCC lattice we have that  $||\vec{b}_1|| = ||\vec{b}_2|| = ||\vec{b}_3|| = a$ , and likewise for an FCC we have  $||\vec{b}_1|| = ||\vec{b}_2|| = ||\vec{b}_3|| = \frac{3a}{2}$ . Thus if we denote  $c^2 \equiv b_1^2 = b_2^2 = b_3^2$ , where c is either a or  $\frac{3a}{2}$ , then the above expression reduces to

$$\sin \theta = \frac{n\lambda c\sqrt{h^2 + k^2 + l^2}}{4\pi}.$$

As we do not know  $\lambda$  or c, we can take the ratio of the values of  $\sin \theta$  for successive peaks. Assuming monochromatic radiation and first-order diffraction, this leads to

$$\frac{\sin \theta_{i+1}}{\sin \theta_i} = \sqrt{\frac{h_{i+1}^2 + h_{i+1}^2 + l_{i+1}^2}{h_i^2 + k_i^2 + l_i^2}},$$

where  $\theta_i$  and  $(h_i, k_i, l_i)$  correspond to the diffraction angle and Miller indices of the  $i^{\text{th}}$  peak.

For a BCC structure, we have that peaks only occur whenever h + k + l is an even number. For an FCC structure, we have that peaks only occur whenver h, k and l are of the same parity. We can thus deduce the possible values of  $h^2 + k^2 + l^2$  for each structure as follows:

$$\begin{split} \text{BCC: } h^2 + k^2 + l^2 &= 1^2 + 1^2 + 0^2, 2^2 + 0^2 + 0^2, 2^2 + 1^2 + 1^2, 2^2 + 2^2 + 0^2, \\ 3^2 + 1^2 + 0^2, 2^2 + 2^2 + 2^2, 3^2 + 2^2 + 1^2, 4^2 + 0^2 + 0^2, \ldots \\ &= 2, 4, 6, 8, 10, 12, 14, 16, \ldots \\ &\implies \sqrt{\frac{h_{i+1}^2 + k_{i+1}^2 + l_{i+1}^2}{h_i^2 + k_i^2 + l_i^2}} = 1.414, 1.225, 1.155, 1.118, 1.095, 1.080, 1.069 \\ \\ \text{FCC: } h^2 + k^2 + l^2 &= 1^2 + 1^2 + 1^2, 2^2 + 0^2 + 0^2, 2^2 + 2^2 + 0^2, 3^2 + 1^2 + 1^2, \\ 2^2 + 2^2 + 2^2, 4^2 + 0^2 + 0^2, 3^3 + 3^2 + 1^2, 4^2 + 2^2 + 0^2, \ldots \\ &= 3, 4, 8, 11, 12, 16, 19, 20, \ldots \\ &\implies \sqrt{\frac{h_{i+1}^2 + k_{i+1}^2 + l_{i+1}^2}{h_i^2 + k_i^2 + l_i^2}} = 1.155, 1.414, 1.173, 1.044, 1.155, 1.090, 1.026 \end{split}$$

From the figure, the following values were found:

$$\begin{aligned} & 2\theta = 23^{\circ}, 27^{\circ}, 39^{\circ}, 46^{\circ}, 48^{\circ}, 56^{\circ}, 63^{\circ}, 70^{\circ} \\ \implies \frac{\sin \theta_{i+1}}{\sin \theta_i} = 1.171, 1.430, 1.171, 1.041, 1.154, 1.113, 1.098 \\ & \approx 1.155, 1.414, 1.173, 1.044, 1.155, 1.090, 1.026 \end{aligned}$$

The calculated values of  $\frac{\sin \theta_{i+1}}{\sin \theta_i}$  most closely resemble the allowed values of  $\sqrt{\frac{h_{i+1}^2 + k_{i+1}^2 + l_{i+1}^2}{h_i^2 + k_i^2 + l_i^2}}$  for the FCC structure, and so we can deduce that the data corresponds to an FCC structure.

## $\mathbf{Q2}$

From the attached diagram at the end, the distance between atomic steps is simply 4 times the diagonal of the base of a unit cell. Since tungsten has a BCC structure, each unit cell of tungsten has two atoms. Thus the volume of a unit cell is  $V = \frac{2m}{\rho}$ , where m is the mass of a tungsten atom. The length of each side of the unit cell is thus  $L = V^{\frac{1}{3}} = \left(\frac{2m}{\rho}\right)^{\frac{1}{3}}$ , and so the diagonal along the face of the unit cell is  $L\sqrt{2} = \sqrt{2}\left(\frac{2m}{\rho}\right)^{\frac{1}{3}}$ . We therefore have

$$d = 4 \cdot L\sqrt{2}$$
  
=  $4\sqrt{2} \left(\frac{2m}{\rho}\right)^{\frac{1}{3}}$   
=  $4\sqrt{2} \left(\frac{2 \cdot 3.0527348 \times 10^{-22} \text{ g}}{19.25 \text{ g cm}^{-3}}\right)^{\frac{1}{3}}$   
=  $1.7906 \times 10^{-7} \text{ cm}$   
 $d = 17.906 \text{ Å}$ 

 $\mathbf{Q3}$ 

a)

Classical: 
$$\Delta E = \int_{T_i}^{T_f} C_v \, dT \qquad \text{Quantum: } \Delta E = \int_{T_i}^{T_f} C_v \, dT \\ = \int_{0 \text{ K}}^{10 \text{ K}} 3R \, dT \qquad = \int_{0 \text{ K}}^{10 \text{ K}} dT \, 9N k_B \left(\frac{T}{\theta_D}\right)^3 \int_{0}^{x_D} dx \, \frac{x^4 e^x}{(e^x - 1)^2} \\ = 30 \text{ K} \cdot 8.3145 \text{ J} \text{ K}^{-1} \qquad \approx \frac{12\pi^4 R}{5\theta_D^3} \int_{0 \text{ K}}^{10 \text{ K}} T^3 \, dT \\ \text{(using the low-temperature limit as discussed in class)} \\ = 249.435 \text{ J} \qquad = \frac{12\pi^4}{5} \cdot \frac{8.3145 \text{ J} \text{ K}^{-1}}{(428 \text{ K})^3} \cdot \frac{(10 \text{ K})^4}{4} \\ = 0.0620 \text{ J}$$

As can be seen, the calculated required energies differ by several orders of magnitude depending on if the system is treated classically or quantum mechanically. The classical regime is only somewhat accurate for high temperatures, which is not the case for a temperature change from 0 K to 10 K, and so we can deduce that the answer obtained using quantum mechanical expressions is far more accurate.

Classical: 
$$\Delta E = \int_{T_i}^{T_f} C_v dT$$
  
=  $\int_{0 \text{ K}}^{300 \text{ K}} 3R dT$   
= 900 K · 8.3145 J K<sup>-1</sup>  
= 7483.05 J

Quantum: 
$$\Delta E = \int_{T_i}^{T_f} C_v \, dT$$
$$= \int_{0 \text{ K}}^{300 \text{ K}} dT \, 9N k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \, \frac{x^4 e^x}{(e^x - 1)^2}$$
$$= \frac{9R}{\theta_D^3} \int_{0 \text{ K}}^{300 \text{ K}} \int_0^{\frac{\theta_D}{T}} \frac{T^3 x^4 e^x}{(e^x - 1)^2} \, dx \, dT$$
$$= \frac{9R}{\theta_D^3} \left[ \int_{\frac{\theta_D}{300 \text{ K}}}^{\infty} \int_0^{\frac{\theta_D}{x}} \frac{T^3 x^4 e^x}{(e^x - 1)^2} \, dT \, dx + \int_0^{\frac{\theta_D}{300 \text{ K}}} \int_{0 \text{ K}}^{300 \text{ K}} \frac{T^3 x^4 e^x}{(e^x - 1)^2} \, dT \, dx \right]$$
switching the order of intervation by increasing of the graph of x against T (diagram at any

(switching the order of integration by inspection of the graph of x against T (diagram at end))

$$\begin{split} &= \frac{9R}{\theta_D^3} \left[ \int_{\frac{\theta_D}{300 \text{ K}}}^{\infty} \frac{\theta_D^4 e^x}{4 (e^x - 1)^2} \, dx + \int_0^{\frac{\theta_D}{300 \text{ K}}} \frac{(300 \text{ K})^4 x^4 e^x}{4 (e^x - 1)^2} \, dx \right] \\ &= \frac{9R}{4} \left[ \theta_D \int_{\exp\left(\frac{\theta_D}{300 \text{ K}}\right) - 1}^{\infty} \frac{du}{u^2} + \frac{(300 \text{ K})^4}{\theta_D^3} \int_0^{\frac{\theta_D}{300 \text{ K}}} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right] \\ &= \frac{9R}{4} \left[ -\frac{\theta_D}{u} \Big|_{\exp\left(\frac{\theta_D}{300 \text{ K}}\right) - 1}^{\infty} + \frac{(300 \text{ K})^4}{\theta_D^3} \int_0^{\frac{\theta_D}{300 \text{ K}}} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right] \\ &= \frac{9 \cdot 8.3145 \text{ J K}^{-1}}{4} \left[ \frac{428 \text{ K}}{e^{\frac{4288 \text{ K}}{300 \text{ K}} - 1}} + \frac{(300 \text{ K})^4}{(428 \text{ K})^3} \int_0^{\frac{428 \text{ K}}{300 \text{ K}}} \frac{x^4 e^x}{(e^x - 1)^2} \, dx \right] \\ &\approx 4223.38 \text{ J} \end{split}$$
 (using Mathematica)

Again, the classical and quantum answers differ by a significant amount, due to the fact that the steps used to calculate the classical energy assumes that the heat capacity is a constant 3R, which is not the case. These values are on the same order of magnitude however, unlike the 0 K to 10 K case, due to the fact that the classical approach is more applicable for higher temperatures. However, the temperature change is still not large enough to warrant a classical approach, and so yet again the quantum mechanical expressions are more accurate.

$$\frac{9 \times 8.3145}{4} \left( \frac{428}{e^{\frac{428}{300}} - 1} + \frac{300^4}{428^3} \operatorname{Integrate} \left[ \frac{x^4 e^x}{(e^x - 1)^2}, \left\{ x, 0, \frac{428}{300} \right\} \right] \right)$$

4223.38

**b**)

## $\mathbf{Q4}$

Denote by n the number of electrons in the Fermi sphere, and V the spatial volume of the system.

$$dn = \frac{V}{h^3} d^3 \vec{p}$$

$$n = \int (\text{degeneracy}) \frac{V}{h^3} d^3 \vec{p}$$

$$= \frac{2V}{h^3} \int p^2 \sin \theta \, dp \, d\theta \, d\phi$$

$$= \frac{2V}{h^3} \int_0^{2\pi} d\phi \int_0^{\pi} \sin \theta \, d\theta \int_0^{p_F} p^2 \, dp$$

$$= \frac{2V}{h^3} \cdot 2\pi \cdot 2 \cdot \frac{p_F^3}{3}$$

$$= \frac{\pi V}{3} \left(\frac{2h}{2\pi h}\right)^3 k_F^3 \qquad (p = \hbar k, \, \hbar \equiv \frac{h}{2\pi})$$

$$NZV = \frac{V}{3\pi^2} k_f^3 \qquad (n = NZV)$$

$$\implies k_F = \sqrt[3]{3\pi^2 NZ}$$

We can derive a similar expression for the 2-D case.

$$dn = \frac{A}{h^2} d^2 \vec{p}$$

$$n = \int (\text{degeneracy}) \frac{A}{h^2} d^2 \vec{p}$$

$$= \frac{2A}{h^2} \int p \, dp \, d\varphi$$

$$= \frac{2A}{h^2} \int_0^{2\pi} d\varphi \int_0^{p_F} p \, dp$$

$$= \frac{2A}{h^2} \cdot 2\pi \cdot \frac{p_F^2}{2}$$

$$= 2\pi A \left(\frac{h}{2\pi h}\right)^2 k_F^2$$

$$NZA = \frac{A}{2\pi} k_F^2$$

$$\implies k_F = \sqrt{2\pi NZ}$$

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Since N is simply  $\frac{1}{a^2}$  where a is the side length of a unit square in the square lattice, we have that  $k_F = \frac{\sqrt{2\pi Z}}{a}$ . For Z = 1, 2, 3, 4, we thus have

$$k_F = \frac{\sqrt{2\pi}}{a}, \frac{\sqrt{4\pi}}{a}, \frac{\sqrt{6\pi}}{a}, \frac{\sqrt{8\pi}}{a}$$
$$= \sqrt{\frac{2}{\pi}} \frac{\pi}{a}, \frac{2}{\sqrt{\pi}} \frac{\pi}{a}, \sqrt{\frac{6}{\pi}} \frac{\pi}{a}, 2\sqrt{\frac{2}{\pi}} \frac{\pi}{a}$$
$$\approx 0.798 \frac{\pi}{a}, 1.128 \frac{\pi}{a}, 1.382 \frac{\pi}{a}, 1.596 \frac{\pi}{a}$$

Writing the radii as factors of  $\frac{\pi}{a}$  simplifies the construction greatly, as the width of the first Brillouin zone is  $\frac{\pi}{a}$ . Attached is the diagram of the Fermi surfaces for a nearly free electron for Z = 1, 2, 3, 4, and the corresponding first four Brillouin zones.