Answer THREE questions

The numbers in square brackets in the right-hand margin indicate the provisional allocation of maximum marks per sub-section of a question.

1. (a) A plane wave of X-rays is incident on an element of charge at a position $\mathbf{r}$ from an origin. Show that the phase difference of the scattered beam with respect to scattering of the X-ray from the origin is given by

$$e^{i\mathbf{K}.\mathbf{r}}.$$

In the above expression, the scattering vector $\mathbf{K} = \mathbf{k}' - \mathbf{k_0}$, where $\mathbf{k}'$ and $\mathbf{k_0}$ are vectors representing the direction and wavelength of the scattered and incident waves respectively, with moduli $2\pi/\lambda$ where λ is the X-ray wavelength. **[4]**

(b) The scattering $f_a(\mathbf{K})$ of X-rays by an *atom* can be derived from considering the scattering from an electronic charge distribution that is related to the wave functions of the electrons in the atom, and normalising to the scattering from a single point charge. Sketch the form of $f_a(\mathbf{K})$ for an atom of your choice, and explain the physical reasons for both (i) the value at $\mid \mathbf{K} \mid = 0$ and (ii) the variation with $\mid \mathbf{K} \mid$. Explain with reasons how your sketch would change if you used neutrons rather than X-rays. **[4]**

(c) By considering the scattering of X-rays from identical atoms arranged in a crystal lattice of lattice parameters **a**, **b**, **c**, show that for an infinite crystal at very low temperature, sharp peaks are observed for scattering vectors $\mathbf{K}$ that satisfy the three Laue equations

$$\mathbf{K}.\mathbf{a} = 2\pi h, \quad \mathbf{K}.\mathbf{b} = 2\pi k, \quad \mathbf{K}.\mathbf{c} = 2\pi l$$

where h,k,l are integers. **[10]**

Describe the changes you would see in these peaks if you raised the temperature of the crystal to room temperature **[2]**

2. Cubic ice has water molecules placed with their oxygen atoms on the carbon sites of the diamond structure. The distance between neighbouring hydrogen-bonded oxygens is 2.76Å.

   (a) Draw a unit cell plan showing the positions of the oxygen atoms. **[2]**

   (b) Calculate the unit cell side **a**. **[2]**

   (c) How many water molecules are there in each unit cell? **[1]**

   (d) On three further unit cell plans of the oxygen atoms, respectively:

      i. draw lines linking hydrogen-bonded neighbours;

      ii. for an orientationally *ordered* structure, place hydrogens in appropriate locations;

      iii. place possible hydrogens for an orientationally *disordered* structure. **[2,4,4]**

   (e) Assuming the water molecule has an effective radius of 1.35Å, calculate the packing density of cubic ice. **[2]**

   (f) Pressure is applied to cubic ice such that it passes through a change of phase to another higher density phase, ice VII, which retains cubic symmetry yet has a density almost double that of cubic ice. Suggest the likely arrangement of water molecules in this new structure. **[3]**

3. $Ti_{0.68}Zr_{0.32}$ is a chemically disordered crystalline alloy. This means that the probability of finding either a titanium or zirconium atom on any crystallographic site in the structure is directly proportional to the material's chemical composition. For the quoted alloy this means that there is a 68% chance of a site being occupied by a titanium atom and a 32% chance of it being occupied by a zirconium atom.

(a) Write down the relationship between the total structure factor $F(Q)$ that is accessible by a neutron diffraction experiment, and the partial structure factors $S_{\alpha\beta}(Q)$ derived from specific atomic correlations between atomic species α and β. Define any other terms you introduce. **[3]**

(b) From the information supplied in the table below and your knowledge of the total structure factor of this alloy, show why $Ti_{0.68}Zr_{0.32}$ is an excellent material for the construction of sample containers used in neutron scattering experiments. **[6]**

(c) Vanadium is also a common material used for the construction of sample containers used for neutron scattering experiments on structure. Why is it appropriate? **[1]**

(d) What is novel about the structural signal that would be measured from a sample consisting of a mixture of 64% H_2O and 36% D_2O? **[4]**

(e) In what is termed the 'Small Angle Scattering' regime, neutron diffraction techniques only see structural correlations that occur over length scales upwards of approximately 20Å. As this technique is focussed on these large length scales, the probe cannot resolve individual atom correlations and it is then possible to treat the scattering length of water as simply the average scattering length of its atomic constituents.

i. Assuming that H_2O and D_2O are structurally identical, what mixture of H_2O and D_2O can create an 'invisible' solvent for neutron scattering studies performed on these length scales? **[3]**

ii. Illustrate why this composition does not work as an invisible solvent if one can resolve the interatomic correlations. **[3]**

Element	Coherent scattering length b (fm)	Coherent scattering cross-section σ_c(barn)	Incoherent scattering cross-section σ_I(barn)	Total scattering cross-section σ_s(barn)	Absorption cross-section σ_a(barn)
Ti	3.438	1.485	2.87	4.35	6.09
Zr	7.16	6.44	0.02	6.46	0.185
V	-0.3824	0.018	5.08	5.1	5.08
H	-3.74	1.757	80.26	82.02	0.3326
D	6.671	5.592	2.05	7.64	0.0005
O	5.803	4.232	0.0008	4.232	0.0002

4. (a) Explain what is meant by a *colloid*. Give one example of each of (i) a solid in liquid colloid, (ii) a liquid in liquid colloid and (iii) a liquid in gas colloid. **[5]**

(b) Consider a dilute solution of isotropic colloidal particles each of volume V, radius of gyration R_G, neutron scattering density ρ, immersed in a medium of neutron scattering density ρ_0. With reasonable assumptions, we can calculate the scattering density $I(K)$ as a function of scattering vector K to be

$$I(K) = (\rho - \rho_0)V^2 \exp(-K^2 R_G^2/3).$$

Show that for small scattering angles ε, this can be written as

$$\ln I(K) = \ln\left[(\rho - \rho_0)V^2\right] - 4\pi^2 R_G^2 \varepsilon^2/3\lambda^2.$$

[3]

(c) Scattering data using monochromatic neutrons of wavelength 5Å were taken on a dilute solution of a spherical virus in (i) D_2O and (ii) a mixture of H_2O and D_2O whose neutron scattering density matched that of the protein coat. The following scattering intensities were observed in these two experiments:

Scattering angle ε	0.3°	0.7°	1.0°	1.3°
Scattering intensity I in D_2O	2080	400	48	2.9
Scattering intensity I in H_2O/D_2O mixture	43	14.4	3.6	0.7

Assuming that the protein coat is well approximated as an external spherical shell, and that the RNA occupies a spherical volume within the protein coat, use these data to estimate (i) the radius of gyration of the RNA core and (ii) the thickness of the protein coat. You can assume that for a spherical body the radius of gyration is related to the geometrical radius r through $R_G = 0.77r$. **[12]**

5. (a) Consider an isolated linear polymer molecule with N elements, each separated from its two linked neighbours by a distance a. A simple restricted random walk calculation shows that its radius of gyration R_G is given by

$$R_G^2 \simeq Na^2/9.$$

Taking R_G as the effective radius of the molecule, and v as the average volume occupied by each element of the chain, show that the packing fraction of the polymer can be approximated by **[3]**

$$\frac{6v}{a^3\sqrt{N}}.$$

(b) Crystallographic measurements on hydrocarbon chain systems show that the average volume v for a polyethylene chain can be well approximated by

$$v = (1.5)\frac{4}{3}\pi a^3.$$

Using the results from part (a), obtain a numerical estimate for the packing fraction of a polyethylene chain consisting of 10^5 monomers, and comment on the value you obtain with respect to typical packing fractions such as those observed in simple liquids and crystals. **[2,3]**

(c) This polymer molecule is now dissolved in a solvent. Discuss the driving forces which may affect the way in which the polymer structure responds to solution conditions. What is meant by a 'theta solvent'? **[4,1]**

(d) A large number of identical polymer molecules are formed into a melt. Outline a scattering experiment that could be undertaken to measure the radius of gyration of an average polymer molecule in the melt. **[3]**

(e) The result of such an experiment shows that the average radius of gyration is essentially the same as that of the isolated polymer. A density measurement on the same polymer melt showed that the packing density in the melt was about 0.5. Using this information and your knowledge of the packing fraction of the isolated polymer estimated above, suggest the way in which the polymer molecules may be arranged with respect to one other in the melt. **[4]**

END OF PAPER