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 plane wave of X-rays is incident on a condensed matter system, for which the position vectors of each atom j are given by $\mathbf{r}_j$. The amplitude scattered by the system can be calculated from the equation

$$A(\mathbf{K}) = \sum_j f_j(\mathbf{K}) \exp^{i\mathbf{K}.\mathbf{r}_j} \tag{1}$$

(a) Identify the phase and amplitude terms on the right hand side of the above equation. **[1]**

(b) What do $\mathbf{K}$ and $f_j(\mathbf{K})$ represent? **[2]**

(c) Derive an expression for $\parallel \mathbf{K} \parallel$ in terms of the scattering angle 2θ and define any other quantities you introduce. **[2]**

(d) Sketch f as a function of θ for a typical atom such as Be and explain both (i) its form and (ii) its value at $\theta = 0$. Show how you would expect $f(\theta)$ to change when the two outer electrons are removed from the atom to produce the Be^{2+} ion, and explain the reasons for your answer. **[7]**

(e) If you used neutrons instead of X-rays, how would the form of $f(\theta)$ differ, and why? **[1]**

(f) For scattering from a macroscopic crystal, it can be shown that scattering is observed only for those $\mathbf{K}$ values that satisfy the Laue equations $\mathbf{K}.\mathbf{a} = 2\pi h$, $\mathbf{K}.\mathbf{b} = 2\pi k$, and $\mathbf{K}.\mathbf{c} = 2\pi l$ where h, k, l are Miller indices and $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ are lattice parameters of the crystal. Show, using equation (1) or otherwise, that the scattering amplitude from a macroscopic crystal is given by the structure factor $\mathbf{F}_{hkl}$ where

$$\mathbf{F}_{hkl} = \sum_j f_j(\mathbf{K}) \exp^{2\pi i[hx_j + ky_j + lz_j]}$$

and x_j, y_j, z_j are the fractional co-ordinates of the scattering centres in the unit cell of the crystal. **[3]**

(g) Hence derive the conditions for observed reflections for a body centred cubic lattice. Explain the physical reason for the absence of the other reflections. **[4]**

2. (a) Describe X-ray or neutron scattering experiments that could solve *four* of the following problems. For each case, specify which radiation you are using and why; describe the nature of the sample(s); show the general arrangement of the scattering experiment and describe the kind of information you expect to obtain. **[3 each]**

    i. The structure of a crystal of potassium chloride.
    ii. The ordering of hydrogens in a crystal of ice XI.
    iii. The structure of a surfactant at an air-water interface.
    iv. The detailed structure of a 10 mol % solution of methanol in water.
    v. The location of the nucleic acid in the foot and mouth disease virus.

   (b) Imagine you have been appointed the scientific director of a new pulsed neutron source that will have both hydrogen and ambient water moderators. Your brief is to provide a suite of instruments that will cater for the world's condensed matter community. List the functions of the five instruments you would build as your first priority, and justify your choice of these instruments. [**8**]

3. (a) Solid krypton crystallises in a face-centred cubic (fcc) lattice with an internuclear distance of 400 pm. Let's call it kryptonite. Sketch the fcc lattice and indicate interstitial sites surrounded by an octahedron of host atoms. These are the sites most likely to be occupied by a chemical impurity, such as hydrogen, in trace quantities. How many such sites are there per host atom, and why? **[4]**

   (b) Assuming a lattice of hard spheres in contact, calculate the largest size of interstitial or guest atom which can be accommodated at the octahedral sites. Show that both hydrogen and muonium atoms should fit comfortably. Sketch the 1s electron wavefunction for hydrogen and estimate the reduction in electron density at the nucleus on going from hydrogen to muonium. (The Bohr radius for hydrogen is 50 pm and for the hydrogen isotopes varies inversely with the reduced mass $\frac{mM}{m+M}$ of the electron.) **[6]**

   (c) Calculate the shortest distance between octahedral sites. This is the step length for interstitial diffusion of the impurity. What is the relation between the zero-point energies of interstitial hydrogen and muonium atoms and between the uncertainties in their positions? Sketch the corresponding probability densities or nuclear wavefunctions. (You could assume these light interstitial atoms move as simple harmonic oscillators about their equilibrium positions, for which the energy and rms displacement of a given vibrational level both vary as $\frac{1}{\sqrt{M}}$, or in some other potential of your choice.) How might these factors affect the way in which muonium moves or diffuses between adjacent interstitial sites? **[10]**

4. (a) Define a *colloid*. Give three examples from your own experience, stating the components of each. **[3]**

   (b) Justify the approximation of the van der Waals energy between two atoms separated by a distance r which is significantly greater than the atomic diameter as

$$U(r) = -C/r^6,$$

   where C is a constant. **[1]**

   (c) Using this approximation, show that the force per unit area between two parallel surfaces of identical semi-infinite solids, separated by a distance H, is attractive for all H and is given by

$$C\pi\rho^2/6H^3,$$

   where ρ is the number density of atoms in the solids. **[9]**

   (d) An extension of the above calculation to two colloidal spheres shows that they are also attracted to each other at all separations. However, experiment shows that colloidal systems can be stabilised by the addition of ions to the aqueous medium in which the colloidal particles are dispersed. By considering the nature of the interface between the particle and the fluid medium, explain how this addition of ions can stabilise the system. Why does the repulsion between the colloidal sphere *increase* as the electrolyte concentration is *decreased*? **[7]**

5. (a) Explain briefly how the structure of a glass differs from that of (i) a crystal and (ii) a liquid of the same material. **[4]**

(b) The figure on the next page shows the OO, OH, and HH partial radial distribution functions of both high density (HDA) and low density (LDA) amorphous ice derived from a recent series of neutron diffraction experiments. Note that the functions do not contain any intramolecular features. The table below shows the first shell co-ordination numbers obtained from these data.

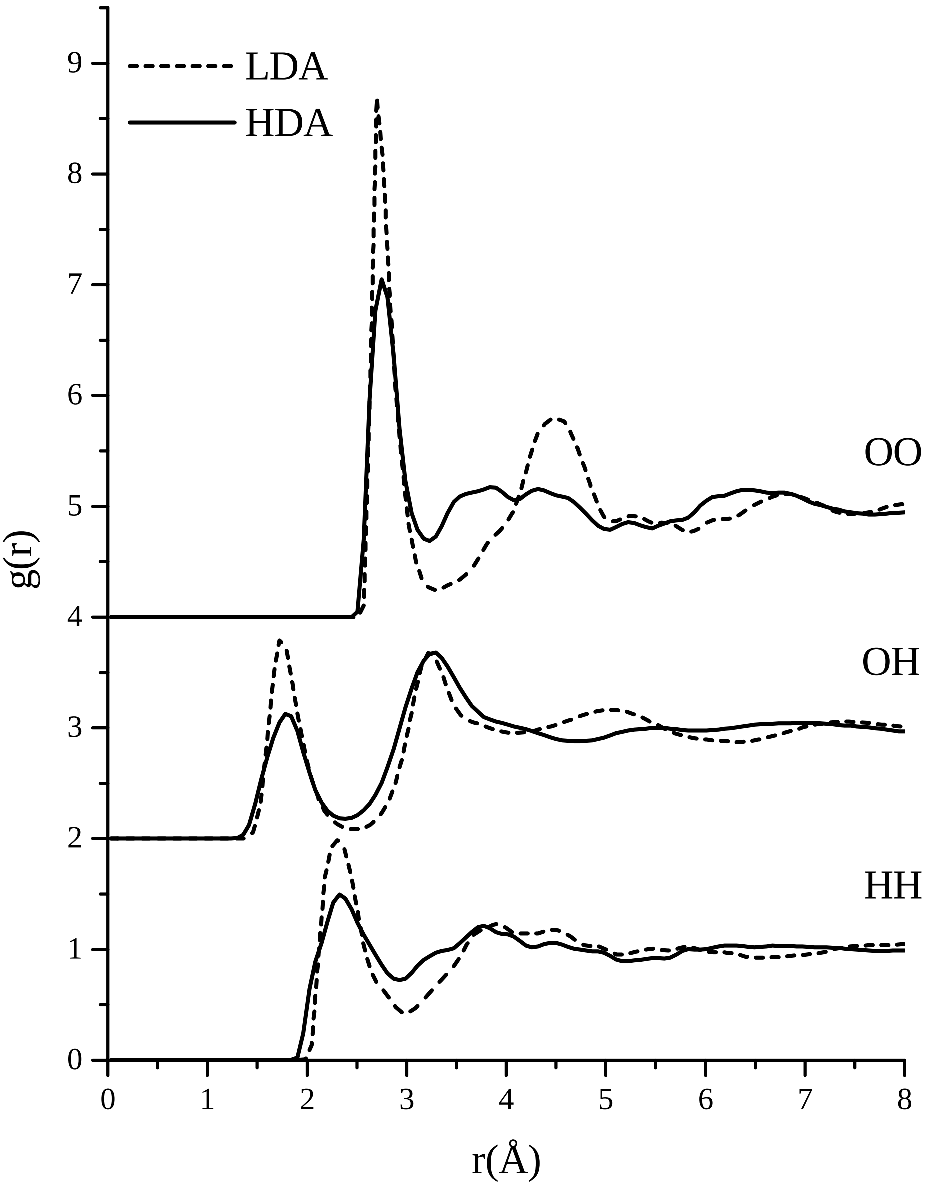
Atom pair	*HDA*	*LDA*
OO	5.0 ± 0.1	3.9 ± 0.1
OH	2.0 ± 0.1	1.9 ± 0.1
HH	6.6 ± 0.1	4.9 ± 0.1

i. Describe briefly how these co-ordination numbers would be obtained from these distribution functions. **[3]**

ii. From these co-ordination numbers, deduce the average number of hydrogen bonds in which each water molecule participates in each structure. Hence deduce the average hydrogen bonded water co-ordination in each case. *[Hint: look both ways before committing yourself!]* **[5]**

iii. By considering the partial radial distribution function for LDA, estimate the average O–O–O angle. Comment on this value with respect to the molecular geometry of the water molecule. **[4]**

iv. In the light of your answer to ii, comment on the OO first co-ordination number values given for LDA and HDA, and suggest what structural conclusions you might consequently draw concerning the first neighbour shells in these two amorphous structures. **[4]**



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