

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.

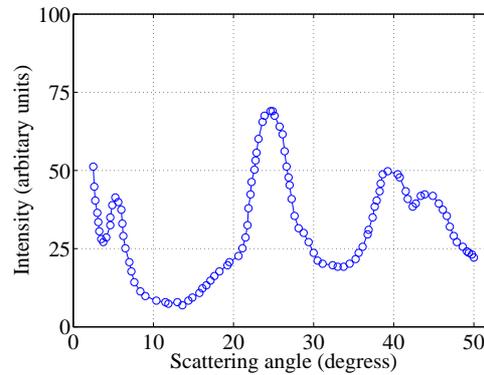
1. The zinc blende structure, adopted by semiconductors such as CdTe, is related to that of the diamond structure. Diamond may be thought of as two interpenetrating face centred cubic (fcc) structures displaced along the body diagonal (i.e. [111] direction) by a quarter of a unit cell. In the zinc blende structure one of the fcc lattices is populated with Cd ($Z=48$) and the other with Te ($Z=52$).

(a) The unit cell structure factor $F(\mathbf{Q})$ for the scattering of X-rays from a single crystal may be written in the form

$$F(\mathbf{Q}) = \sum_j f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_j}.$$

Starting from the scattering amplitude for a distribution of electrons, outline the derivation of this expression, and explain the terms on the right hand side of the equation. [3]

(b) Using the conventional cubic cell draw cross-sections perpendicular to the [001] direction through the structure of CdTe for $z=0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ and 1, where z is the fractional coordinate. Hence write down the (x, y, z) coordinates of the 4 Cd and 4 Te atoms in the basis of the unit cell, and derive a general expression for the unit cell structure factor. (Assume that Cd is in the $z=0$ layer.) [6]



(c) The X-ray powder diffraction pattern from CdTe nanocrystals (cubic unit cell parameter $a=6.3 \text{ \AA}$) is shown above for an X-ray wavelength of 1.54 \AA . Determine the Miller indices of the Bragg peaks found at scattering angles of $2\theta=24.6$ and 40.0 degrees, and calculate their structure factors. Where should the (200) Bragg peak appear, and why is it absent? [7]

(d) The relative width in Q of a Bragg peak is inversely proportional to the size of the crystal. In one dimension it can be shown that the full width at half maximum is to a good approximation proportional to $1/N$, where N is the number of unit cells. Estimate the size of the nanoparticles from the data shown above. Explain the origin of the peak near the scattering angle of 5° , and use this to obtain an independent estimate of the diameter of the nanoparticles. [4]

2. A simple model of a polymer regards it as a freely jointed chain made up of N links each of length a .

(a) If \mathbf{r} is the vector connecting the ends of the polymer, show that the root mean squared (r.m.s) end-to-end distance is given by [3]

$$\langle r^2 \rangle^{\frac{1}{2}} = aN^{\frac{1}{2}}.$$

(b) In the limit of large N , the probability distribution function $P(\mathbf{r}, N)$ describing the distribution of possible end-to-end distances is Gaussian and may be written as

$$P(\mathbf{r}, N) = \left(\frac{3}{2\pi Na^2} \right)^{\frac{3}{2}} \exp \left(-\frac{3\mathbf{r}^2}{2Na^2} \right).$$

Write down the configurational entropy $S(r)$, and hence find an effective elastic contribution to the free energy as a function of r and temperature. [3]

(c) In a real polymer chain the links are self avoiding which alters how $\langle r^2 \rangle^{\frac{1}{2}}$ scales with N . By considering the polymer to be a gas of N molecules occupying a volume of r^3 , show that the reduction in entropy due to excluded volume effects leads to a repulsive contribution to the free energy of the form

$$F = k_B T v \frac{N^2}{r^3}.$$

(You may use the fact that for a gas of volume V where each molecule occupies a volume v the entropy per atom is reduced relative to the ideal gas result by $k_B v N/V$.) Hence show that in equilibrium the r.m.s end-to-end distance of the self-avoiding chain scales as [6]

$$r \sim aN^{\frac{3}{5}}.$$

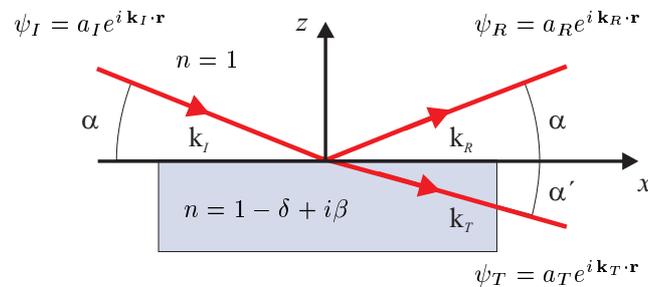
(d) By comparing the results in (a) and (c) discuss how excluded volume effects alter the size of the chain, including a sketch of the dependence of the excluded volume effects on N . [3]

(e) Up to this point we have assumed that the chain is freely jointed, and have ignored polymer/solvent interactions. Describe how these may be included in the theory, including a description of the physical consequences of the Theta Condition. [5]

3. The refractive index n for x-rays is less than unity and may be written as

$$n = 1 - \delta$$

with $\delta = (\rho r_0 \lambda^2 / 2\pi) \ll 1$. Here ρ is the electron density, r_0 is the Thomson scattering length, λ is the X-ray wavelength, and we have neglected absorption. The fact that n is less than unity gives rise to the phenomenon of total external reflection, which may be used to derive detailed information on the nature of surfaces and interfaces. The geometry of a reflectivity experiment is shown in the figure below, where ψ_I , ψ_R , ψ_T represent the incident, reflected and transmitted waves respectively.



(a) By imposing the boundary conditions that the wave and its derivative at the interface $z=0$ must be continuous derive the following two equations relating to the amplitudes [2]

$$\begin{aligned} a_I + a_R &= a_T \\ a_I \mathbf{k}_I + a_R \mathbf{k}_R &= a_T \mathbf{k}_T. \end{aligned}$$

(Note: The wavenumber in vacuum is denoted $k = |\mathbf{k}_I| = |\mathbf{k}_R|$ and in the material is $nk = |\mathbf{k}_T|$.)

(b) By considering the components of \mathbf{k} parallel to the surface, solve the equations derived in (a) to derive Snell's law and show that in the small-angle (reflectivity) limit it reduces to

$$\alpha'^2 = \alpha^2 - \alpha_c^2 \quad (1)$$

where $\alpha_c = (2\delta)^{1/2}$ is the critical angle defined by the condition that $\alpha' = 0$. [4]

(c) Derive expressions for the amplitude reflectivity $r = a_R/a_I$ and transmittivity $t = a_T/a_I$, in terms of α and α' . These are the Fresnel equations. [5]

(d) By considering solutions to equation (1) determine the behaviour of the reflectivity for $\alpha \ll \alpha_c$, $\alpha \gg \alpha_c$ and for $\alpha = \alpha_c$. Hence make a sketch of the intensity reflectivity $R = |r|^2$ as a function of incident angle α . [5]

(e) One important application of X-ray mirrors is as the first optical component in the “white” beam produced by synchrotrons. The mirror is normally placed before the monochromator crystal which is typically a Si(111) crystal. Explain why the mirror is necessary and how it works. [4]

4. (a) Discuss how the arrangement of atoms in the glass, liquid and crystalline forms of matter differ. Particular attention should be given to describing both the structure and dynamics of the three phases, and the consequences that they have for the measured physical properties. [7]

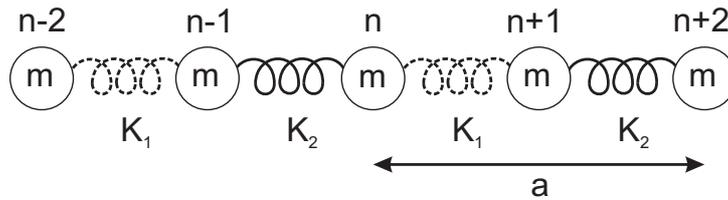
(b) Explain how you would measure the diffraction patterns from these three phases using X-rays or neutrons, and describe the expected results by drawing sketches of the scattered intensity versus the scattering vector. What are the relative merits of neutron and X-ray scattering for the experiments you propose. [7]

(c) Lindemann proposed in 1910 that a solid melts at a temperature when the amplitude of atomic vibration exceeds a critical fraction α of the atomic spacing. Assuming Lindemann's theory to be correct, show that for a simple cubic structure of lattice constant a , and where the atoms execute simple harmonic motion, α is given by

$$\alpha = \left(\frac{2k_B T_m}{E a^3} \right)^{\frac{1}{2}}.$$

Here E is Young's modulus, defined as the ratio of stress to strain, and k_B is Boltzmann's constant. You may make use of the fact that the mean total energy of a simple harmonic oscillator is equal to $kx^2/2$, where k is the spring constant and x is the displacement. Estimate the value of α for Lead for which $T_m \approx 600$ K (Key data for Lead: $E=1.60 \times 10^{10}$ N m⁻², density $\rho = 11.3 \times 10^3$ kg m⁻³, the molar mass is $M=0.207$ kg, and the gas constant is $R=8.3$ J mol⁻¹ K⁻¹). [6]

5. The stretching vibrations of a polymer chain may be modelled as a linear chain of identical masses m connected by springs of alternating spring constants K_1 and K_2 , as shown schematically for a length of chain in the figure below.



(a) By considering the forces show that the masses at positions n and $n - 1$ on the chain obey the respective equations of motion:

$$\begin{aligned} m\ddot{u}_n &= K_1 u_{n+1} - (K_1 + K_2)u_n + K_2 u_{n-1} \\ m\ddot{u}_{n-1} &= K_2 u_n - (K_1 + K_2)u_{n-1} + K_1 u_{n-2} \end{aligned}$$

where u_n is the displacement of the n th mass. [2]

(b) Show that

$$\begin{aligned} u_n &= A \exp(i[kna/2 - \omega t]) \\ u_{n-1} &= \alpha A \exp(i[k(n-1)a/2 - \omega t]) \end{aligned}$$

represent solutions to the equations of motion, where α is a phase factor. Derive two alternative expressions for α as a function of frequency ω and wavenumber k . [5]

(c) Hence show that the characteristic frequencies of the chain are given by

$$\omega^2 = \frac{K_1 + K_2}{m} \left[1 \pm \left(1 - \frac{4K_1 K_2 \sin^2(ka/2)}{(K_1 + K_2)^2} \right)^{\frac{1}{2}} \right]. \quad [4]$$

(d) By considering solutions to the above equation in the limits that $k \rightarrow 0$ and $k \rightarrow \pm\pi/a$ sketch the dispersion curves for the optic and acoustic branches of the vibration spectrum. You may assume that $K_1 > K_2$. [6]

(e) Describe the form of the phonon dispersion curves displayed by three-dimensional crystals, and explain how they may be determined experimentally. [3]