MASTER OF PHILOSOPHY   Modelling of Materials

Friday 29 April 2005   9 to 12.00

MODELLING OF MATERIALS (2)

Answer **six** *parts from Section* **A** *(i.e. Question 1),* **two** *questions from Section* **B***, and* **one** *question from Section* **C***.*

Each **Section** *carries* **one-third** *of the total credit for this paper.*

Write on **one** *side of the paper only.*

The answer to **each question** *must be tied up* **separately***, with its own cover-sheet. All the parts of Question 1 should be tied together.*

Write the relevant **question number** *in the square labelled 'Section' on each cover-sheet. Also, on* **each** *cover-sheet, list the numbers of* **all** *questions attempted from this paper.*

For questions divided into parts, the **approximate** *fraction of credit allocated to each part is indicated by the percentages in square brackets.*

Special and/or stationary requirements for this paper: **graph paper**

You may not start to read the questions printed on the subsequent pages of this question paper until instructed that you may do so by the Invigilator.

SECTION A

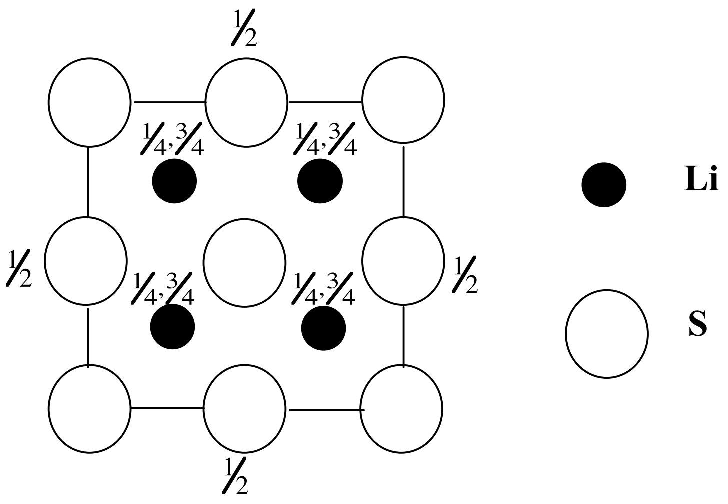
1. (a) FORTRAN 77 allows variables of several data types, including `integer`, `real` and `double precision`. Describe briefly the properties and possible uses of variables of each of these three types.

(b) In Density Functional Theory (DFT), what is meant by the term *exchange-correlation energy*? A researcher has used DFT simulations with the Local Density Approximation to calculate the lattice constants of graphite (hexagonal) and compare them with experimental observation as shown below.

DFT prediction	Experimental	Error
a = 2.44Å	a = 2.46Å	-0.8%
c = 7.11Å	c = 6.80Å	+4.6%

What is the Local Density Approximation? Suggest a reason why the error in the c-parameter is so much larger than that in the a-parameter.

(c) The diagram below shows a plan view of Li_2S which has a cubic structure. What is the lattice type and motif?



(d) In the theory of irreversible thermodynamics, the generalised flux J is found to be proportional to the generalised force X when their product can be written as:

$$JX = T\sigma$$

Describe the forces and fluxes in the theories of electrical current flow, heat flow and mass diffusion which are consistent with this equation.

(e) The distribution of solute when a thin layer of a fixed quantity of solute is plated onto a semi-infinite bar and allowed to diffuse, is given by an exponential function of distance and time. By contrast, when two semi-infinite bars of different composition are connected, diffusion leads to a concentration profile which is described by an error function of distance and time. Describe qualitatively the relationship between the exponential and error functions in this context.

(f) A database is to be constructed for selecting shaping processes. Summarise the technical and quality design requirements which can be addressed via a database of generic attributes for each process. In each case identify what type of data would be stored. Give examples of requirements for which generic attributes provide no useful discrimination between processes, and explain why this is the case. How might these more complex requirements be addressed?

(g) Distinguish between *intrinsic* and *extrinsic* properties of alloys, giving examples of each. Briefly discuss the implications for modelling to predict the properties.

(h) Distinguish between *homogeneous* and *heterogeneous* nucleation. How can homogeneous nucleation be detected? What are the key materials parameters needed to permit a prediction of the homogeneous nucleation rate? Why are such predictions likely to be imprecise? What are the additional problems in modelling heterogeneous nucleation?

(i) Derive the Hagen-Poiseuille law for the volume flow rate V of a Newtonian fluid with viscosity η passing through a cylindrical pipe of radius R and length L over a pressure drop Δp. You may assume that the velocity υ of a fluid element at radius r from the axis of the pipe is given by:

$$\upsilon = \frac{\Delta p}{4L\eta}\left(R^2 - r^2\right)$$

Qualitatively, how would you expect the flow rate to differ from this prediction for a typical industrial thermoplastic polymer?

(j) Explain carefully what is meant by *molecular chaos* in the context of atomistic molecular dynamics (MD) simulations. Given that all MD trajectories computed to finite numerical precision will eventually become chaotic, how is it possible to obtain useful information from such simulations?

SECTION B

2. Explain why a solid with one free electron per primitive unit cell *must* be a conductor whereas one with two such electrons is normally an insulator but could also be a semiconductor, semimetal or conductor. [25%]

Consider a two-dimensional divalent solid which is monatomic and has a square lattice with lattice constant *a*.

(i) Sketch the first and second Brillouin zones of this lattice in the extended zone scheme labelling the *k*-points in terms of *a*. [15%]

(ii) If the interactions between the electrons and atoms are ignored (free electron model) sketch the form of the electron energy dispersion curve *E(k)* along the [100] and [110] directions in *k*-space labelling the position of the 1st Brillouin zone. [15%]

(iii) Give expressions for the energy of the free electrons along each direction at the points where they meet the 1st Brillouin zone boundary. [15%]

(iv) If the interactions between electrons and atoms are not ignored how are the *E(k)* curves modified? Illustrate your answer with careful sketches. [15%]

(v) If the solid is to be a semiconductor, derive an expression for the minimum value of the energy gap at the 1st Brillouin zone boundary. [15%]

3. A two component system has complete miscibility in both the solid and liquid. Starting with the equations for the free energy of mixing of an ideal solution, describe how you would go about determining the phase diagram using the free energy of mixing curves.

[70%]

If in the solid state, the solid solution obeys a regular solution model with a positive heat of mixing, describe what is likely to happen on cooling.

[30%]

4. A panel to be loaded in 3-point bending is designed to have minimum weight, but must not fail under the given design load W. The length l and width b of the panel are fixed, but its depth d may be varied. The maximum stress in the panel is given by:

$$\sigma_{\max} = \frac{3Wl}{2bd^2}$$

Figure 1 shows a material property chart for strength against density. Note that the strengths indicated for ceramics and glasses are compressive strengths, and should not be used for failure in tension or bending (when the strength is much lower).

(a) Show that the performance index to be maximised for minimum weight is $M = \sigma_y^{1/2} / \rho$ where σ_y is the material strength, and ρ is the density.

[25%]

(b) A further limit on the design is that the panel thickness must not exceed a specified value. Show that this sets a limit on the material strength.

[25%]

(c) Show on a sketch of the material property chart in Figure 1 how the strength limit and the performance index for minimum weight are imposed graphically to guide the selection of suitable materials.

[25%]

(d) Use Figure 1 to identify a short-list of suitable materials, giving reasons why some of these are likely to be eliminated on other criteria.

[25%]

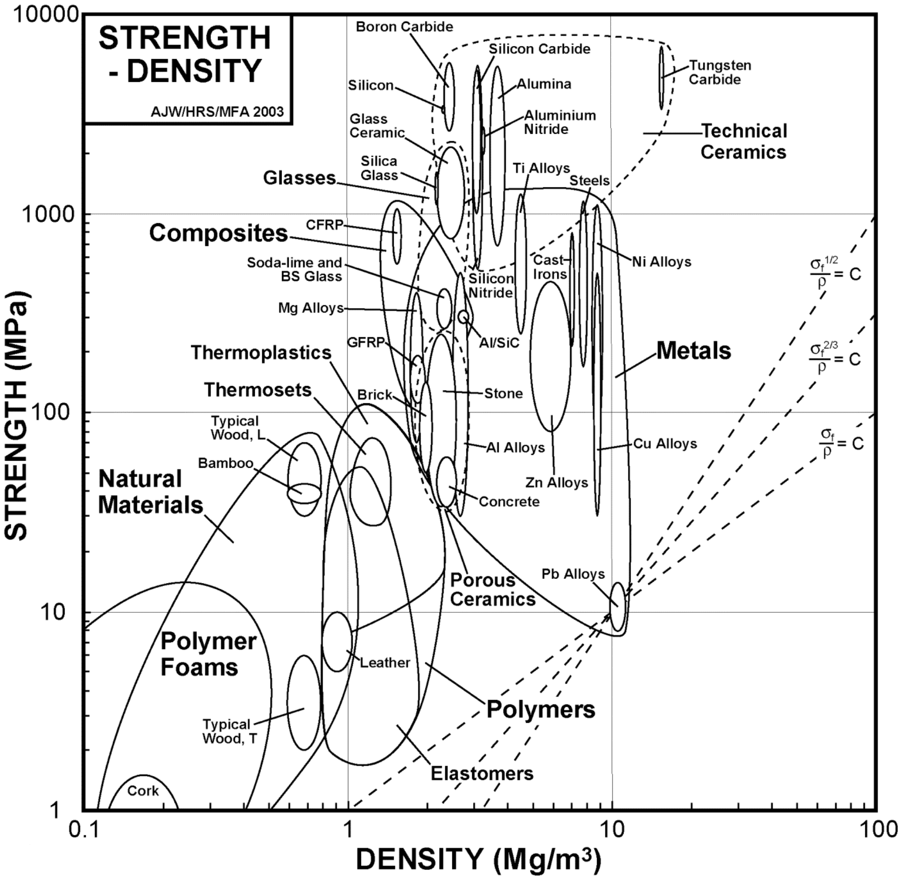


Figure 1

5. You work for a large materials company which has a modelling capability consisting of atomistic modelling using MD and MC (they have the Materials Studio^{TM} software package), and in another section, some limited finite element modelling associated with engineering design (ABAQUS^{TM} package).

The research director has just returned from a meeting where he has heard the phrase 'meso modelling'. Prepare a full briefing document for him which explains what meso modelling is, describes the different sub components of it and outlines the areas in which it might be useful. Remember that he already understands something of atomistic and finite element techniques.

[85%]

At the end of the piece, make suggestions of computer programs which may be useful in terms of providing the company with a meso-modelling capability.

[15%]

SECTION C

6. In two dimensions, a rigid diatomic molecule has rotational states with energy:

$$E(J) = \frac{\hbar^2 J^2}{2I}$$

where J is the rotational quantum number, $\hbar$ is Planck's constant divided by 2π, and I is the moment of inertia perpendicular to the bond axis.

Given that the degeneracy of each 2D state is unity, write down an expression for the partition function as an integral over microstates of a system of N indistinguishable, non-interacting rotors, assuming the temperature is high. You may use the identity:

$$\int_0^\infty \exp(-\alpha x^2)dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$ [20%]

Using your expression for the partition function, derive an expression for the Helmholz free energy and total internal energy of the system of rotors. Calculate the heat capacity of the system at constant volume. How does this compare with the classical result from equipartition?

[50%]

Given a system of rotors that interact via some arbitrary long-ranged pairwise potential, explain the difficulties with applying the above approach, and outline a suitable methodology for computing the partition function of the system at constant volume and temperature. You may assume that the total energy is a function of all the rotational states $E_N(J_1,J_2,\ldots,J_N)$, but are not required to carry out the calculation explicitly. State any other assumptions clearly.

[30%]

7. Describe the bonding characteristics of ionic solids. Illustrate schematically the electronic charge distribution around the ions in a typical I-VII compound. Consider the charge distributions around II-VI, III-V and IV-IV compounds and describe how they progressively change in relation to I-VII compounds. How does this affect their bonding?

[25%]

What is the Madelung constant and describe how it is used to calculate the electrostatic energy of a monovalent ionic AB compound? Why is an additional term needed to determine the total energy of the solid?

[25%]

Consider a one-dimensional crystal of $2N$ ions of alternating charge $\pm q$. Let the repulsive potential energy be A/R^n where A is a constant, R is the nearest neighbour separation and $n > 1$. Show that at the equilibrium separation R_O the total energy of the crystal is given by:

$$U(R_O) = -\frac{Nq^2 \ln 2}{2\pi\varepsilon_O R_O}\left(1 - \frac{1}{n}\right)$$

[50%]

$$\left[\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots\ldots\ldots\ldots \qquad (-1 < x \le 1)\right]$$

END OF PAPER