MASTER OF PHILOSOPHY Modelling of Materials

Friday 28 April 2006 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.*

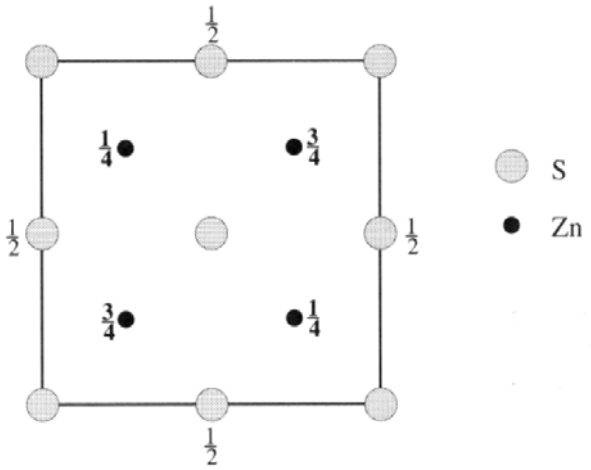
Special and/or stationery requirements for this paper: **graph paper**

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) Explain how the bonding characteristics between the atoms account for the following:
   (i) The hardness of diamond
   (ii) The malleability of gold
   (iii) The electrical conductivity of graphite

   (b) The figure below shows a plan view of the structure of zinc sulphide, ZnS (cubic, a = 0.541 nm).



   State the lattice type and motif. Calculate how many formula units there are in this unit cell. Determine the spacings of the (110) planes.

   (c) A unidirectional composite of carbon nanotubes in epoxy requires a stiffness of 80 GPa longitudinal to the direction of the fibres. Use the rule of mixtures for infinitely long fibres to calculate the loading of nanotubes required if the nanotubes have a stiffness of either (a) 1TPa, or (b) 100 GPa; and the stiffness of the epoxy matrix is 4 GPa.

(d) In an electronic structure calculation, describe briefly what is meant by *iterating to self-consistency in the density*. It may be useful to use a flow diagram.

(e) Describe some applications of loop constructions within FORTRAN, such as the `do` loop and the `do...while` loop. You need not give examples of FORTRAN code.

(f) Derive the expression for the mean-square end-to-end distance of a random walk polymer coil, and hence calculate an estimate for the size of a globular polypeptide containing 300 amino acids. Explain why 'real' polymers will swell to larger radii.

(g) Explain why thermodynamic temperature in an atomistic simulation is better defined by the parameter $\beta = \left(k_{\mathrm{B}}T\right)^{-1}$, where k_{B} is Boltzmann's constant.

(h) The melting temperature of fcc gold is significantly altered when it is in the form of a nanoparticle. By considering the critical nucleus size of fcc gold in the liquid, derive the melting temperature of a gold particle of diameter 5 nm.

[For gold: solid-liquid interfacial energy = 0.3 J m^{-2}, latent heat of melting = 1.25 GJ m^{-3}, bulk melting temperature = 1337 K]

(i) Explain the differences between conventional error minimising methods and the Bayesian approach. State Bayes' theorem and explain how it provides a means to calculate error bars associated with the uncertainty of fitting.

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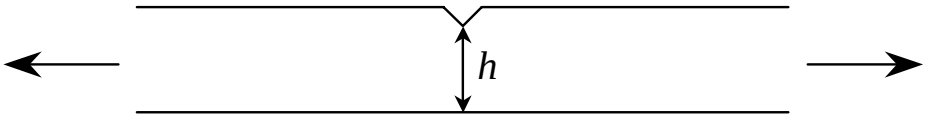
(j) A notched metallic bar of depth h and breadth b, so that $h << b$, where the depth of the notch is small in comparison with h, is deformed in plane strain uniaxial tension, as in the diagram below. Show how limit analysis can be used to predict a suitable lower bound and a suitable upper bound to the applied force required to cause the notched bar to deform plastically. Comment briefly on the values you obtain.



[You may assume without proof that the metal yields at a stress $2k$ in plane strain uniaxial tension where k is the shear yield stress.]

SECTION B

2. Define the density of *allowed* electron states in a system. Describe quantitatively how this relates to the density of *occupied* electron states.

[20%]

Consider a 1-D free electron metal at $T = 0$.

(i) Show that the density of allowed states is proportional to $1/\sqrt{E}$ where E is the electron energy. Sketch this quantity as a function of E and indicate the position of the Fermi energy.

[20%]

(ii) Determine the fraction of free electrons in the system that have energies above half of the Fermi energy.

[10%]

(iii) Is this fraction greater than or less than the corresponding value for a 2-D free electron metal where the density of allowed states is constant?

[10%]

(iv) Sketch the occupation density of states for the 1-D free electron metal at $T > 0$.

[20%]

(v) Sketch the allowed density of states for a 1-D *nearly free electron metal* explaining briefly the reason for any new features that are present.

[20%]

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3. Starting from the master equations, show that the Gibbs adsorption equation can written as:

$$\mathrm{d}\gamma = -RT\sum_i \Gamma_i.\mathrm{d}\ln C_i\,,$$

making clear any assumptions you make. Note that γ is the surface tension of the interface, R is the molar gas constant, T is the temperature, Γ_i is the surface excess and C_i is the bulk concentration of component i.

[40%]

The Szyszkowski relation:

$$\gamma = \gamma_{\mathrm{A}} - b\gamma_{\mathrm{A}}\ln\left(1 + C_{\mathrm{B}}/a\right)$$

gives the surface tension of a mixture in terms of the surface tension of the pure materials γ_{A}, and the concentration of the minor component, C_{B} where a and b are constants. Show that:

$$\Gamma_{\mathrm{B}} = \frac{C_{\mathrm{B}}}{RT}\left\{\frac{b\gamma_{\mathrm{A}}/a}{1 + C_{\mathrm{B}}/a}\right\}$$

and hence:

$$\Gamma_{\mathrm{B}} = \Gamma_{\mathrm{B}}^{\infty}\left\{\frac{\alpha C_{\mathrm{B}}}{1 + \alpha C_{\mathrm{B}}}\right\}$$

where $\Gamma_{\mathrm{B}}^{\infty} = b\gamma_{\mathrm{A}}/RT$ and $\alpha = 1/a$.

[60%]

[Note, you may assume that $\dfrac{\mathrm{d}}{\mathrm{d}x}\{\ln f(x)\} = \dfrac{1}{f(x)}\dfrac{\mathrm{d}}{\mathrm{d}x}\{f(x)\}$].

4. What is the rationale behind materials selection charts and how are they used? You may refer to the two selection charts provided at the **end of question paper** (Figure 1). [20%]

Suggest an expression for the maximum elastic energy per unit volume that can be stored in a spring loaded in a tensile or compressive manner in terms of the yield stress and modulus of the material used. Hence, derive an appropriate merit index to aid the selection of materials that can store the most energy per unit volume without failing. [25%]

What other material properties might influence your choice? Hence, suggest suitable materials for springs.

[10%]

If minimum weight was of importance, derive a merit index to aid selection of optimum materials and use this to re-examine possible materials for springs.

[15%]

For each of the following applications, justify the selection of a possible material:

(a) spring used as part of a car suspension system;
(b) a non-metallic torsional spring in the form of a long thread/fibre;
(c) the locking catch on a food container. [30%]

5. Describe the innovative features of the FHP lattice gas model that make it suitable as a mesoscopic model for complex fluids, and give three examples of possible applications in materials science.

[20%]

The microdynamics of the FHP lattice gas model are described by the following equation:

$$n_i(\mathbf{x}+\mathbf{c}_i, t+1) = n_i(\mathbf{x}, t) + \Delta_i\left[n(\mathbf{x}, t)\right]$$

Define each of the terms carefully, and show that if mass and momentum are conserved in each particle collision, then the total mass and momentum of the system are the same after each time step.

[50%]

In what ways is the FHP model deficient in comparison to continuum methods for modelling fluid flow?

[30%]

SECTION C

6. Define the term *equation of state* for a system in thermodynamic equilibrium, giving an example applicable to non-interacting particles in the gas phase. [10%]

A system of particles is simulated using a canonical molecular dynamics simulation in order to be fitted to the van der Waals equation of state:

$$p = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2} \qquad (*)$$

where p, V_m, T are the pressure, molar volume and temperature, respectively, a and b are the parameters to be determined, and R = 0.0821 dm^3 atm K^{-1} mol^{-1}.

List the conserved quantities of the canonical ensemble, and briefly describe a suitable molecular dynamics algorithm for generating configurations in this ensemble. Data for pressure as a function of volume at T = 150 K are given below. Use the fact that there exists a point of inflection at a particular critical pressure and volume to determine a and b by differentiation of the expression (*).

Volume [dm^3 mol^{-1}]	Pressure [atm]
0.0650	58.46
0.0736	50.22
0.0832	48.03
0.0919	47.76
0.1005	47.79
0.1091	47.72
0.1178	47.46
0.1264	47.02
0.1351	46.42

[60%]

Using thermodynamic integration, determine the change in Helmholtz free energy between initial and final states. [30%]

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7. By considering the surface and bulk energy, derive the Gibbs free energy for forming a cluster of n atoms from a saturated vapour, stating clearly any approximations required.

[20%]

(a) A laser is used to evaporate a sample from an Fe target. The initial temperature of the vapour is 3000 K, but this is reduced rapidly by a He carrier gas to 1400 K. The cooled Fe vapour has a partial pressure of 130 Pa. Calculate the number of atoms in the smallest cluster that is thermodynamically stable.

[The equilibrium vapour pressure of Fe at 1400 K is 1.3 Pa, the volume of an Fe atom is 1.4×10^{-29} m^3, the surface tension of Fe at 1400 K is 1.8 N m^{-1}, and the Boltzmann constant k_B is 1.38×10^{-23} J K^{-1}]

[30%]

(b) The Au-Si phase diagram is shown in Figure 2 **(see end of paper)**. Explain why there is not a significant region of the diagram in which a single solid phase containing both Au and Si is formed. List the phases present in the following mixtures:

(i) 80 at.% Au, 20 at.% Si, 900°C,

(ii) 90 at.% Au, 10 at.% Si, 500°C,

(iii) 50 at.% Au, 50 at.% Si, 200°C,

(iv) 20 at.% Au, 80 at.% Si, 700°C,

[15%]

(c) Describe the vapour-liquid-solid (VLS) process for Si nanowire growth, marking each stage onto a sketch of the Au-Si phase diagram.

[20%]

(d) Si nanowires can by produced by depositing Au islands on a substrate and then introducing $SiCl_4$ over them. Based on the phase diagram, estimate the lowest possible growth temperature for the nanowires and explain how the diameter and length of the wires can be controlled.

[15%]

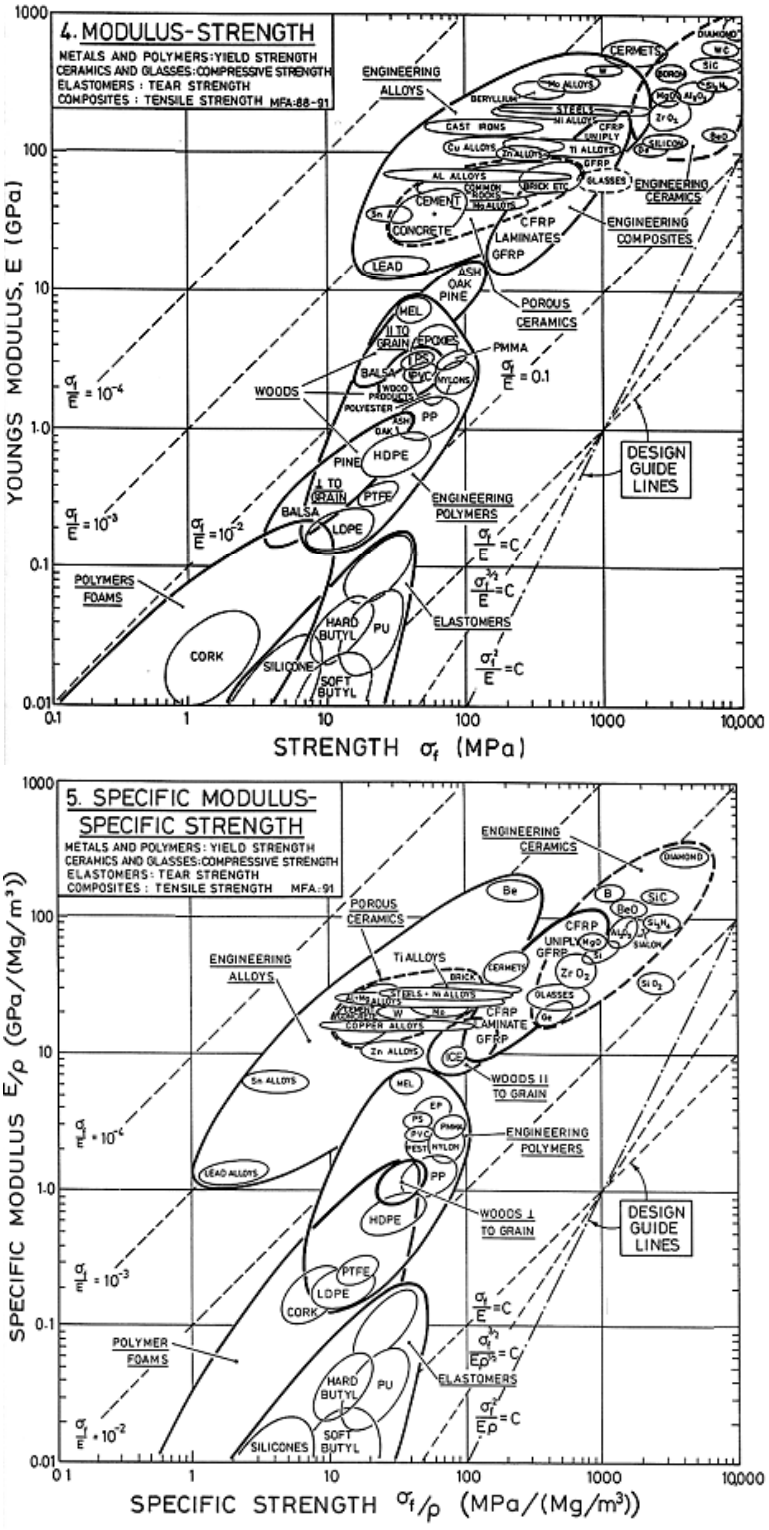

Figure 1 : Selection charts (required for Section B, question 4)

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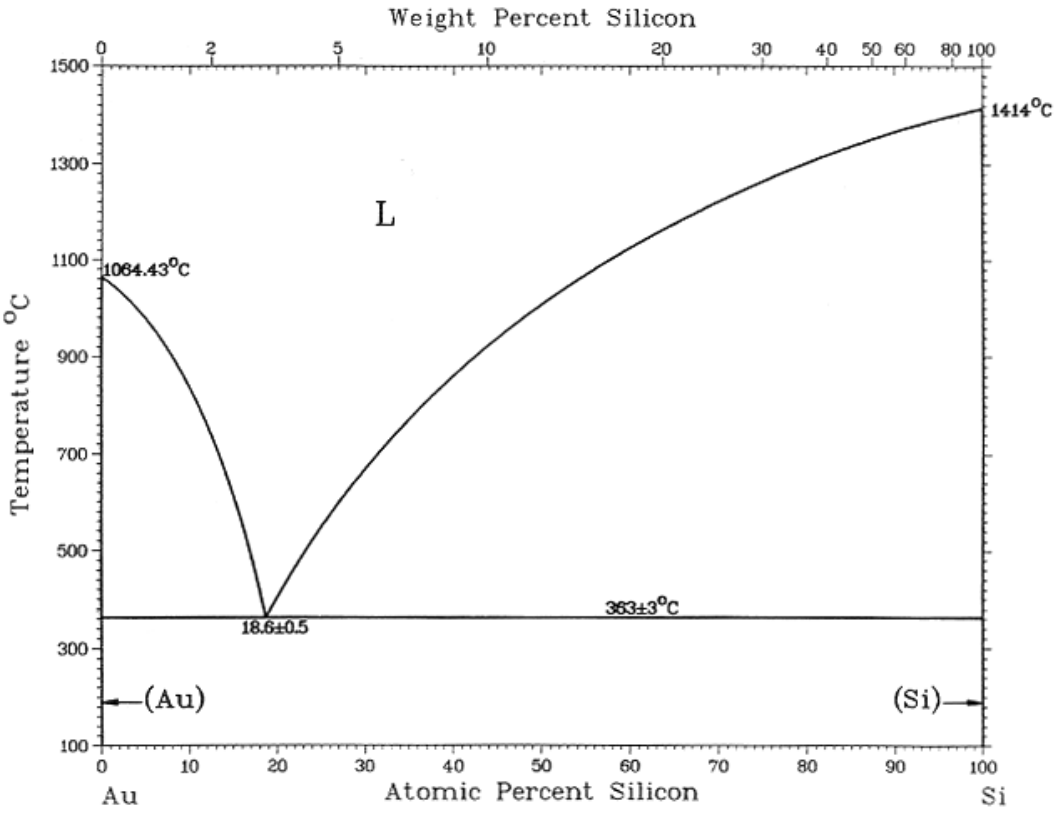

Figure 2 : Au-Si phase diagram (required for Section C, question 7)

END OF PAPER