MASTER OF PHILOSOPHY Modelling of Materials

Wednesday 25 April 2007 9 to 12.00

MODELLING OF MATERIALS (1)

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) Draw the unit cells which define the six crystal systems in 3D, and indicate for each of those systems the different types of unit cell (primitive and non-primitive) which between them describe the 14 Bravais lattices.

   (b) Sketch the form of the electronic density of states for a typical elemental semiconductor, a simple metal and a transition metal. Identify where appropriate the following features: the valence and conduction bands, the presence of s, p or d-like states, the band gap, the Fermi level, critical points (van Hove singularities) and approximate functional forms.

   (c) Identify five general factors that need to be considered when deciding which type of computer model should be used to address a problem in material science.

   (d) Describe briefly the basis of a process you would recommend to form PET bottles for soft drinks. Estimate the thermal energy per kilogram required to produce molten PET using the data provided at the end of Section A. State clearly all assumptions, and compare this with the total energy required for the forming process.

   (e) A matrix **M** is said to be symmetric if it is equal to its own transpose; that is, for any values of *i* and *j*:

   $$M_{ij} = M_{ji} \qquad (*)$$

   Write a FORTRAN function `symm` which, when passed a two-dimensional integer array representing a 10×10 matrix, returns an integer result: one if the matrix is symmetric, or zero otherwise.

   (f) Explain the concept of a multiscale model in materials science. Illustrate your answer with an appropriate example and list some of the advantages and disadvantages of the approach.

(g) Explain what is meant by an *equation of state* for a molecular system, giving an example. How could Monte Carlo methods be used to calculate the equation of state for a monatomic non-ideal gas for which the interatomic potential energy function was known?

(h) How is the *Kuhn length* of a polymer chain, a_K, defined? Show that the characteristic ratio, defined by $C_\infty = \langle R^2 \rangle / Nl^2$, where N is the number of molecular repeat units of length l and $\langle R^2 \rangle$ is the mean-square end-to-end distance of the chain, is related to the Kuhn length by $C_\infty = a_K / l$.

(i) Describe the phenomenon of *Ostwald ripening* of precipitate particles in a matrix. What is the driving force for the ripening? Use a sketch to illustrate the diffusional fluxes involved. Explain why some particles shrink, even as the overall dispersion coarsens.

(j) A sample of aluminium alloy with a Young's modulus of 80 GPa and Poisson's ratio 0.35 is stressed along three principal axes x_1, x_2 and x_3 so that the elongations along x_1 and x_2 are equal and that along x_3 is zero. Determine the 'effective modulus', σ_1/ε_1, assuming that the alloy can be treated as an isotropic elastic material.

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Data required for Section A, question 1(d).

Polyethylene terephthalate (PET)

General properties				
Density	1290	-	1400	kg/m^3
Price	* 0.9204	-	1.012	GBP/kg
Mechanical properties				
Young's modulus	2.76e9	-	4.14e9	Pa
Yield strength (elastic limit)	5.65e7	-	6.23e7	Pa
Tensile strength	4.83e7	-	7.24e7	Pa
Elongation	30	-	300	%
Hardness - Vickers	1.667e8	-	1.834e8	Pa
Fatigue strength at 10^7 cycles	* 1.932e7	-	2.896e7	Pa
Fracture toughness	4.5e6	-	5.5e6	Pa.m^1/2
Thermal properties				
Thermal conductor or insulator?	Good insulator			
Thermal conductivity	0.138	-	0.151	W/m.K
Thermal expansion coefficient	114.7	-	119.3	µstrain/°C
Specific heat	* 1418	-	1474	J/kg.K
Melting point	485	-	538	K
Glass temperature	341	-	353	K
Maximum service temperature	340	-	360	K
Minimum service temperature	* 150	-	200	K
Electrical properties				
Electrical conductor or insulator?	Good insulator			
Electrical resistivity	3.3e12	-	3e13	ohm.m
Dielectric constant (relative permittivity)	3.5	-	3.7	
Dissipation factor (dielectric loss tangent)	* 3e-3	-	7e-3	
Dielectric strength (dielectric breakdown)	16.5	-	21.7	1000000 V/m
Optical properties				
Transparency	Transparent			
Refractive index	1.6	-	1.64	
Eco properties, material production				
Embodied energy	7.96e7	-	8.8e7	J/kg
CO2 footprint	2.21	-	2.45	kg/kg
Eco properties, processing				
Polymer molding energy	1.032e7	-	1.262e7	J/kg
Polymer extrusion energy	3.613e6	-	4.416e6	J/kg

[Source: Cambridge Engineering Selector – Version 4.6.1]

SECTION B

2. What is an *order parameter* as used in phase field theory?

[20%]

Kinetic theory based on phase fields relies on an expression for the free energy, g, of an atom in a non-uniform solution. The energy can be written as a function of the average concentration, c_0, the concentration gradient, $y = \mathrm{d}c/\mathrm{d}x$, and its curvature, $z = \mathrm{d}^2c/\mathrm{d}x^2$, using a multivariate Taylor expansion:

$$g\{y,z\} = g\{c_0\} + y\frac{\mathrm{d}g}{\mathrm{d}y} + z\frac{\mathrm{d}g}{\mathrm{d}z} + \ldots + \frac{1}{2}\left[y^2\frac{\mathrm{d}^2g}{\mathrm{d}y^2} + z^2\frac{\mathrm{d}^2g}{\mathrm{d}z^2} + 2yz\frac{\mathrm{d}^2g}{\mathrm{d}y\mathrm{d}z} + \ldots \right] + \ldots$$

Explain how this might be reduced to an expression of the form:

$$g = g\{c_0\} + \kappa_1\frac{\mathrm{d}c}{\mathrm{d}x} + \kappa_2\frac{\mathrm{d}^2c}{\mathrm{d}x^2} + \kappa_3\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)^2$$

where κ_i express the way in which the free energy depends on concentration gradient and its curvature, and x is a distance.

[60%]

How might this be further simplified?

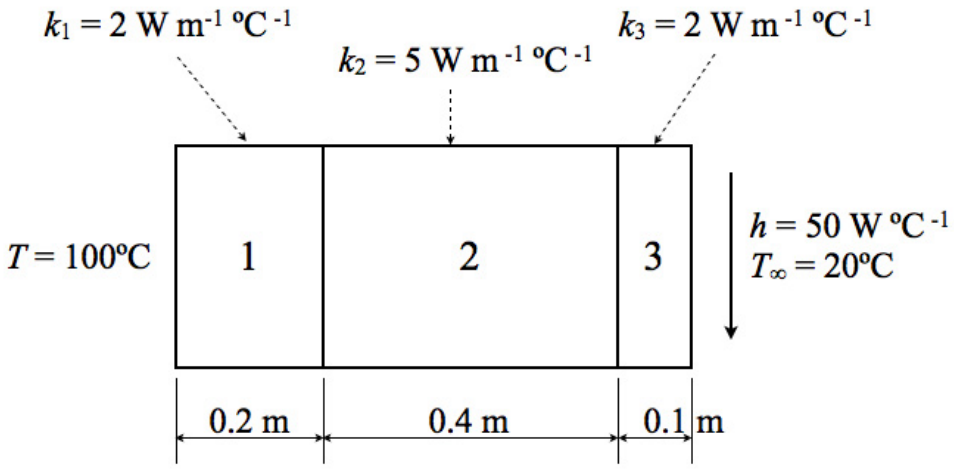
[20%]

3. Describe how convection, fixed temperatures and heat flux boundary conditions are accommodated in the construction of the equations used in one-dimensional finite element analysis.

[40%]

A wall consisting of three layers is shown below in which the thicknesses and thermal conductivities, k, of each layer are identified. The inner surface is maintained at 100ºC whilst the outer surface experiences convective heat transfer with a far-field temperature, $T_\infty = 20$ºC, and convective heat transfer coefficient, $h = 50$ W ºC^{-1}.

Using a model consisting of three, linear one-dimensional elements, calculate the temperature distribution in the wall.



[60%]

4. Describe the microstructural characteristics of normal grain growth and contrast with abnormal grain growth. Sketch the grain size distribution in each case.

[25%]

For a two-dimensional grain structure, explain how the stability of a grain is related to the number of its sides.

[25%]

What is the relevance of grain structure and grain growth for the electromigration-limited reliability of interconnects on integrated circuits?

[25%]

Computer simulations of grain growth can be based on a vertex model. In which way in this model unrealistic? Why, nevertheless, does the model lead to correct predictions of which grains will grow and which will shrink? Of the three common bases for simulations of grain growth (vertex model, Monte-Carlo model, front-tracking model), which is most likely to be most readily adaptable to analyse abnormal grain growth and why?

[25%]

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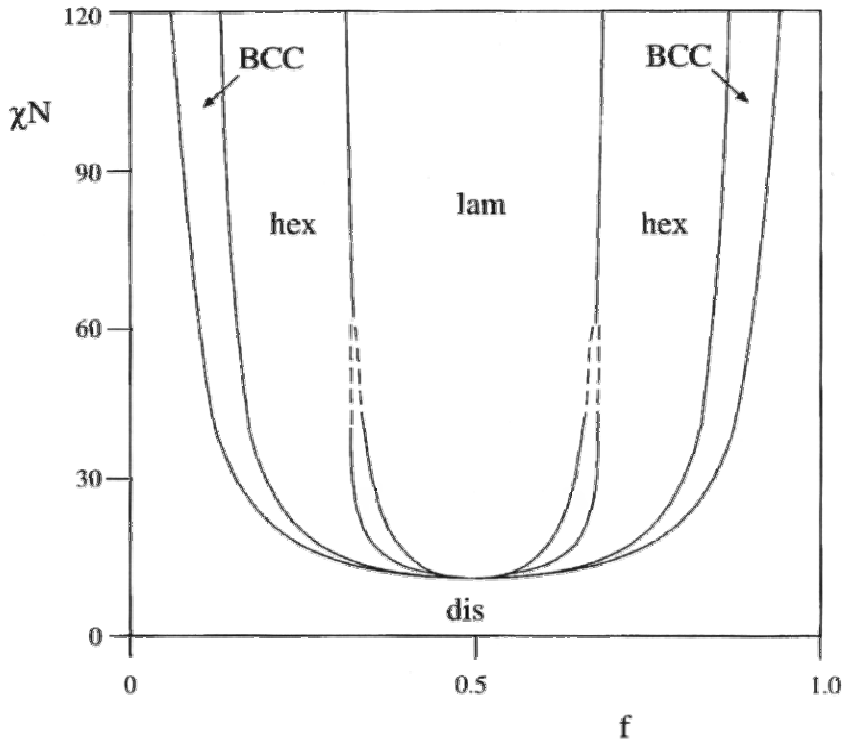
5. A schematic of the phase diagram for an AB diblock copolymer is shown below, where f is the fraction of each component, N is the total number of monomers and χ is the Flory-Huggins interaction parameter.



Describe the chemical structure of a diblock copolymer, and identify the various phases labelled on the diagram. Your answer should include a sketch of the morphologies in each region. Describe the morphology you might expect to find in the unlabelled region between the 'hex' and 'lam' regions at low χN.

[30%]

Outline a mesoscale simulation methodology suitable for investigating the phase transitions in a dense diblock copolymer melt as a function of composition f at $\chi N = 100$. Your answer should include a discussion of the methods required for parameterisation of the mesoscale model.

[70%]

SECTION C

6. If the energy of a one-dimensional simple harmonic oscillator, relative to the zero-point energy, is given by $E = hf\nu$, where h is Planck's constant, f is frequency and $\nu = 0, 1, 2 \ldots$ is the vibrational quantum number, show that the partition function is given by:

$$Z_1 = \frac{1}{1 - \exp(-\beta hf)}$$

where $\beta = 1/(k_B T)$. You may assume that the number of vibrational states is unlimited, and the sum to infinite terms of a geometric series is given by $a/(1-r)$, where a is the first term and r the constant ratio.

[20%]

Using the partition function given above, write down an expression for the internal energy of a system of N independent oscillators in thermal equilibrium. Hence, derive an expression for the heat capacity of the system.

[50%]

Given a system of oscillators 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 $E_N(v_1, v_2, \ldots, v_N)$, but are not required to carry out the calculation explicitly. State any other assumptions clearly.

[30%]

7. In the early development of atomistic modelling, semi-empirical pair potentials were often used to simulate metals. Describe the advantages and disadvantages of doing this. Give some examples of metallic properties that the pair potential approximation cannot predict correctly.

[30%]

Describe a current method used in atomistic models for describing the interatomic bonding in metals. Provide an expression for the total energy of the metal clearly defining all the terms involved and briefly justifying any functional forms that are used.

[30%]

One semi-empirical pair potential that has been used to simulate fcc copper is given by:

$$U(r) = D\left\{\exp\left[-2\alpha\left(r - r_0\right)\right] - 2\exp\left[-\alpha\left(r - r_0\right)\right]\right\}$$

where D, α and r_0 are parameters fitted to experimental data. Assuming only nearest neighbour atoms interact determine the parameters D, α and r_0 using the following data for copper:

Cohesive energy: 336 kJ mol^{-1}
Lattice parameter: 3.6 Å
Bulk modulus: 134 GPa

[40%]

You may assume that the bulk modulus $B = \nu\dfrac{\partial}{\partial\nu}\left(\dfrac{\partial E}{\partial\nu}\right)$ where ν and E are the volume and energy per atom respectively.

[Avogadro's constant is 6.022×10^{23} mol^{-1} and the electronic charge is 1.602×10^{-19} C.]

END OF PAPER