MASTER OF PHILOSOPHY, Modelling of Materials

Friday 25th April 2003 **9 – 12**

MODELLING OF MATERIALS (2)

Answer **six** *parts from Section* **A** *(i.e. Question 1), which carries* **one–third** *of the credit for this paper.*

Two *questions should be answered from Section* **B***; these two questions carry* **one–third** *of the credit for this paper.*

One *question should be answered from Section* **C***; this carries* **one–third** *of the 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*

SECTION A

1. (a) Show that the scalar product of the vector representing the direction $\mathbf{b} = u\mathbf{a}_1 + v\mathbf{a}_2 + w\mathbf{a}_3$ and a reciprocal lattice vector representing the plane normal $\mathbf{c}^* = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^*$ is given by $\phi = uh + vk + wl$, where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the basis vectors of a unit cell, and $\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are the corresponding reciprocal lattice vectors. What is the value of ϕ when $\mathbf{b}$ lies in the plane whose normal is $\mathbf{c}^*$?

(b) What is meant by the *hydrostatic* and *deviatoric* components of the stress tensor? Express the two dimensional uniaxial stress tensor

$$\begin{pmatrix} \sigma_1 & 0 \\ 0 & 0 \end{pmatrix}$$

in terms of its hydrostatic and deviatoric components.

(c) Write down the Lennard-Jones expression for the energy of a van der Waals bonded pair of atoms. Explain the physics behind each of the terms, and sketch the form of the potential.

(d) Many computer simulations involving density functional theory make use of the Born-Oppenheimer approximation. What is this approximation, and how is it usually justified? Give two examples of specific cases in which you would expect it *not* to work, and explain why.

(e) The Levi-Civita symbol, ϵ_{ijk}, has three subscripts, each of which range from 1 to 3 inclusive. ϵ_{123}, ϵ_{231} and ϵ_{312} have the value 1; ϵ_{132}, ϵ_{213} and ϵ_{321} have the value -1; and ϵ_{ijk} is zero for all other values of i, j and k. Write the portion of a FORTRAN program required to declare and initialise the real array `eps`, such that `eps(i,j,k)` contains the value ϵ_{ijk}.

(f) Distinguish between *homogeneous* and *heterogeneous* nucleation. Why is homogeneous nucleation difficult to study? Describe briefly one method by which it can be studied.

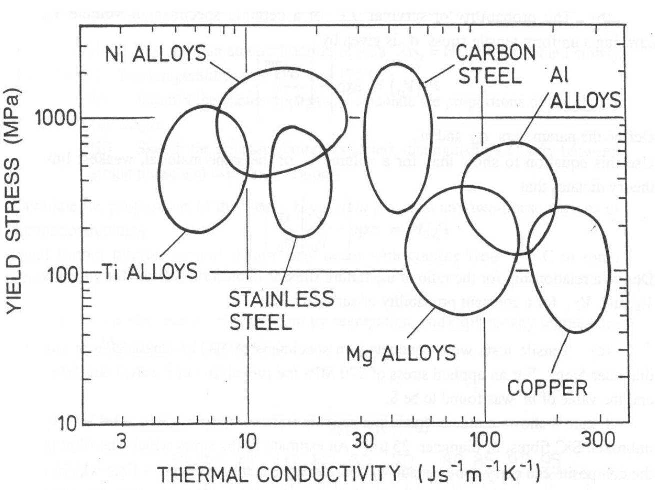
(g) How would you test the accuracy of a standard macromolecular valence force field such as DREIDING?

(h) In the context of finite element modelling, briefly explain what is meant by the following terms: axisymmetric mesh, graded mesh, linear and quadratic elements, and automatic remeshing.

[Section A continued on Page 3

(i) Describe conditions under which dendrites form during the solidification of a *pure* liquid.

(j) A simple heat exchanger between two liquids at different temperatures is constructed from a thin-walled tube containing liquid A passing through liquid B. The merit index for the construction of the tube is $M = \lambda\sigma_y$, where λ is the thermal conductivity of the tube material and σ_y is its yield stress. Use the selection chart below to identify the best two classes of material for the tube, illustrating your answer using a sketch of the chart.



SECTION B

2. A quantum particle in 1-dimension obeys the time-independent Schrödinger equation, which can be expressed in natural units by

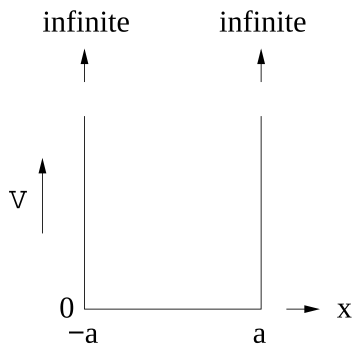
$$-\frac{1}{2}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

where $\psi = \psi(x)$ is the wavefunction of the particle, $V = V(x)$ is the external potential, E is its energy, and x is the position.

What are the solutions to this Schrödinger equation for a free particle (*i.e.* where $V(x) = 0$ everywhere)?

[40%]

If the particle is confined to the infinite potential well in the figure below, calculate the ground state (*i.e.* lowest energy) wavefunction, ψ_0, and the first excited state (*i.e.* next-lowest energy) wavefunction, ψ_1.



[40%]

Sketch the modulus-squared of each of these wavefunctions as a function of position, and determine the most probable position of the particle. How does this differ from the probability distribution of a classical particle?

[20%]

3. Sketch and label the binary phase diagrams (temperature versus composition) for (a) two components which show complete solid solubility, and (b) a eutectic system showing negligible solid solubility.

[30%]

In each case, sketch the free energy curves for the different phases present at four or five appropriate temperatures, in order to explain the form of the diagram.

[50%]

How does the phase diagram of (b) change as solid solubility increases? Again, use free energy curves to explain what happens.

[20%]

4. A family of triblock copolymers known as “Pluronics” consist of linear sequences of polyethylene oxide (PEO) and polypropylene oxide (PPO) with the chemical formula PEO_n-PPO_m-PEO_n, where n and m are the number of monomer units in each block.

Describe how you would construct a discrete element coarse-grained model for Pluronics, including a discussion of the parameters which could be used to map the model onto the atomistic level.

[30%]

Given that the characteristic ratios of PEO and PPO in solution are 4.25 and 5.05, respectively, suggest an appropriate parameterisation for the Pluronic PEO_{13}-PPO_{30}-PEO_{13}.

[20%]

Compare and contrast an example of a lattice mesoscale simulation technique with an equivalent off-lattice method that could be used to carry out computer simulations of the phase-separation of Pluronics in dilute solution with water and a hydrophobic substance. Which aspects of the atomistic copolymer behaviour would you expect to be well reproduced by these simulations, and which not? Suggest how such simulations might be used in conjunction with molecular dynamics to investigate the detergency properties of Pluronics.

[50%]

5. A customised selection system is to be built for metal cutting processes. Summarise the key parameters specific to this manufacturing task, which could be used for an initial screening stage in the selection.

[30%]

Explain why selection based purely on single attributes becomes inadequate when the selection problem is refined to the level of the specific task of metal cutting. Give two examples of design requirements in metal cutting which require a more complex approach and, for a specific cutting process, identify the information required to evaluate that process in the selection procedure.

[30%]

Give an example from one other manufacturing task where single attribute screening is insufficient, and more complex analysis is required to address a design requirement. Outline an example of the application of process modelling to the problem of discriminating between competing manufacturing processes.

[40%]

[TURN OVER

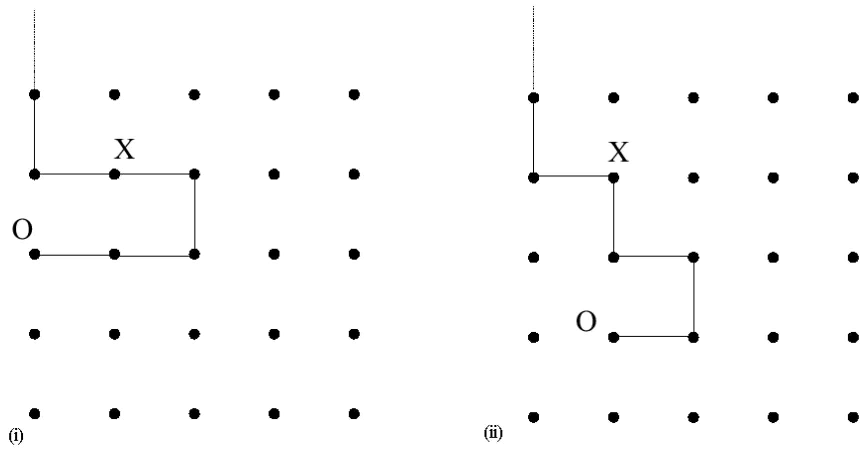
SECTION C

6. Explain the principles of the Metropolis Monte Carlo (MMC) method, giving an outline of the computational algorithm, and describe an application to a primitive 2D square lattice model for a polymer chain in which connected sites are restricted to single occupancy (*i.e.* the chain segments have excluded volume) and where there is an interaction energy ϵ associated with each pair of nearest-neighbour, non-bonded sites.

[30%]

The figure below shows two different configurations of the free end (marked O) of an isolated polymer chain during an MMC simulation described above. Given that the chain configurations are identical up to the point marked X, calculate the probability of the system ending up in final state (ii) starting from initial state (i).

[20%]



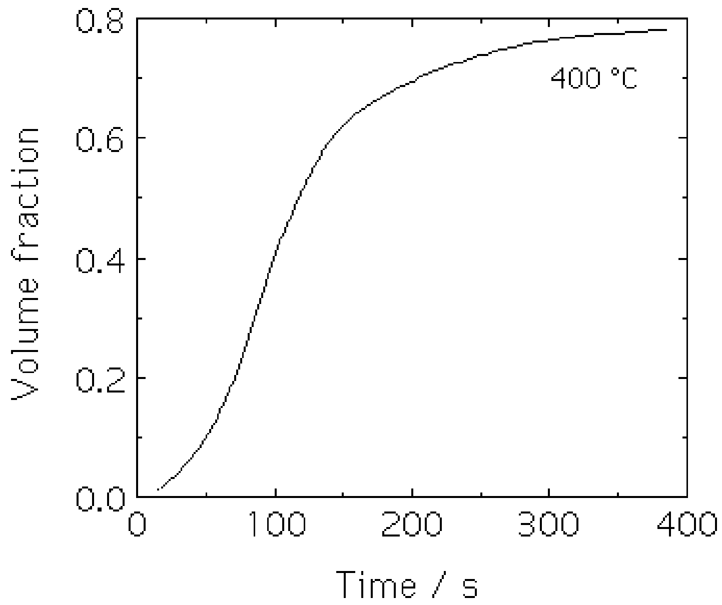
Explain how the MMC method can be modified to use the Rosenbluth configurational bias scheme. Compute the Rosenbluth factors of the two chain ends shown above, generated from the point X, noting that diagonal moves are forbidden on the square lattice. Thus, calculate the acceptance probability of state (ii) given that it was generated from initial state (i).

[30%]

Given that $\epsilon = -10$ kJ mol^{-1} and $k_{\mathrm{B}}T = 5$ kJ mol^{-1}, compare the probabilities obtained using the standard MMC algorithm and the Rosenbluth scheme and comment on the result. What advantages and disadvantages would each method have for studying the flow of an entangled melt of three dimensional polymer chains?

[20%]

7. The figure below shows how the volume fraction of a phase evolves during isothermal transformation in the solid-state. Explain qualitatively why the reaction begins slowly, then accelerates and slows down again.



[10%]

Describe how you could use isothermal transformation data for a variety of temperatures to construct a time-temperature-transformation diagram. Why do the curves on such diagrams have a characteristic 'C'-shape?

[20%]

Explain how the concept of extended space can be used to allow for the impingement of particles growing from different locations in the parent phase, and hence derive the quantitative relationship between the real and extended volumes of the particles. How can this concept be adapted when there are two transformations occurring simultaneously?

[30%]

A phase begins to transform isothermally with a constant nucleation rate I per second per unit volume. Each of the nucleated particles grows at a constant rate G. Derive an expression for the extended volume of the transformed phase. Hence show that the real volume fraction ξ of the transformed phase is given by:

$$\xi = 1 - \exp\{-k_a G^3 I t^4\}$$

where k_a is a constant.

[40%]

END OF PAPER