MASTER OF PHILOSOPHY, Modelling of Materials

Thursday 25 April 2002 **9 – 12**

MODELLING OF MATERIALS (1)

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.*

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 a projection along the z–axis of the crystal structure of GaN which has a cubic–F lattice with a motif of Ga at 0,0,0 and N at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$.

   (b) Explain, using thermodynamic terms, why a material which is atomically ordered at low temperatures tends to disorder as the temperature is increased.

   (c) Describe why it is important to establish a synergy between theory, modelling and experiment in materials science. Explain the meaning of the terms *materials by design*, *ab initio materials–science* and *intelligent processing of materials*?

   (d) By appealing to the Ziman model (*i.e.* nearly free electron model), provide a qualitative explanation for the origin of band gaps in the electronic structure of materials.

   (e) The *trace* of a matrix is defined as the sum of the diagonal elements; that is

   $$\mathrm{Tr}A = \sum_i A_{ii}.$$

   Write a FORTRAN function which takes two arguments which are 3×3 `real` arrays representing matrices, and returns a `real` result which is the trace of their product.

   (f) State why, for an oxidation reaction such as the one given below, the standard free energy change increases as temperature is increased:

   $$\mathrm{M(s)} + \mathrm{O_2(g)} = \mathrm{MO_2(s)}$$

   (g) Given that the grand partition function gives us a complete thermodynamic description of a system, why is computer modelling at the atomistic level useful to a materials scientist?

   (h) Define *mesoscale*, and describe an example of a commonly occurring mesoscopic phenomenon.

   (i) During processing, a polymer melt with an average molecular weight of $10^4\,\mathrm{g\,mol^{-1}}$ is forced through a cylindrical die. Under these conditions, the Deborah number is around 0.1. Explain the consequences of tripling the molecular weight of the polymer.

   (j) Describe three experimental methods which may be used in the determination of equilibrium phase diagrams.

SECTION B

2. Derive the truncated Taylor series expansion giving the central difference approximation for the second spatial derivative of a dependent variable such as temperature. By using this expression, and a forward difference expression for the time derivative, show that the one-dimensional Fourier equation may be represented in finite difference formulation as the following explicit recurrence relation:

$$T_{i,j+1} = T_{i,j} + \frac{\alpha \Delta t}{\Delta x^2}(T_{i+1,j} - 2T_{i,j} + T_{i-1,j})$$

where $T_{i,j}$ is the temperature of element i after a time period $j\Delta t$, Δx is the element size and α is the thermal diffusivity.

Show that using such an explicit scheme leads to the requirement that

$$\Delta t \leq \frac{\Delta x^2}{2\alpha}$$

if numerical instability is to be avoided. Give a physical interpretation of how such instability arises if this condition is not satisfied.

3. What is the importance of the thermal history in the DC casting and extrusion of aluminium? In each case explain why numerical methods are useful in estimating the thermal history.

A finite element analysis of a Jominy end–quench test for steel used the following mesh, properties and boundary conditions:

(i) 10 linear elements of equal size;
(ii) constant thermal properties;
(iii) perfect insulation on the sides and the end remote from the quench;
(iv) perfect heat transfer on the quenched end.

Summarise the improvements which could be made to this model, in order to obtain greater accuracy in the prediction of the temperature history. Explain why it is more important to predict the cooling history accurately between 800 and 500 °C than from 350 °C to room temperature.

4. Give three examples of how nucleation behaviour can influence the microstructure or properties of materials.

   Explain the concept of critical nucleation size and show that for a spherical nucleus, the critical radius r^* is given by

   $$r* = 2\sigma/\Delta G_V$$

   where σ is the energy per unit area of the solid–liquid interface and ΔG_V is the free energy change driving the transformation. Distinguish between homogeneous and heterogeneous nucleation; explain qualitatively why heterogeneous nucleation has a smaller activation barrier than homogeneous nucleation and why it is mostly dominant in industrial situations. What are the problems in quantitative modelling of nucleation? Which modelling methods may be adopted?

5. Describe the different types of bonded (*i.e.* intramolecular) terms which are used in the generic force field DREIDING. Explain how Molecular Dynamics (MD) simulations of macromolecules can be accelerated by the use of multiple time step algorithms (MTA) for the bonded forces.

   The dynamics of a graphene sheet (*i.e.* a single layer of hexagonally bonded sp^2 hybridised carbon) consisting of N independent atoms with 2D periodic boundary conditions is to be studied. If the bonded forces are evaluated using DREIDING, write down the number of distinguishable terms of each type as a function of N. Assuming that the amount of processor time required for the force calculations is proportional to the total number of bonded terms, calculate the time saving obtained by using a MTA with $\Delta T_{torsion} = 5\Delta T_{bend} = 50\Delta T_{stretch}$.

SECTION C

6. Given a binary solution of N atoms of which xN are B atoms and the remainder A atoms, derive expressions giving the numbers of AA, BB, AB and BA nearest neighbours.

   Distinguish between an *ideal*, a *regular* and a *quasichemical* solution thermodynamic model.

   Explain, in the context of binary solutions, what is meant by the term 'chemical potential'. Hence justify the fact that the common tangent construction, on a free energy versus concentration plot, gives the equilibrium compositions of the phases.

   Show how the diffusion coefficient can be written in terms of the chemical potential gradient rather than the concentration gradient. In what circumstances might the diffusion flux oppose the concentration gradient?

7. State the basic assumptions underlying the free electron model.

   Using wave mechanics, show that free electrons contained in a three–dimensional box have quantised energies.

   Derive the following expression for the Fermi energy of the free electrons:

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n_c)^{\frac{2}{3}}$$

   where $\hbar$ is Plancks constant, m is the mass of an electron and n_c is the number of free electrons per unit volume.

   Estimate the Fermi energy of copper assuming that it is monovalent and can be adequately described by the free electron model. Calculate the wavelength and velocity of the electrons which have this energy.

   Explain why the free electron model works quite well for metals but fails for semiconductors and insulators. Give an example of a property of a semiconductor which cannot be predicted using the model.

   Describe how the free electron energies are affected by introducing a periodic crystal potential into the model. Sketch the form of the electron energy spectrum near a Brillouin zone boundary for free electrons and for Bloch electrons.

   $\hbar = 1.054 \times 10^{-34}$ J s; $m = 9.109 \times 10^{-31}$ kg;
   lattice constant of Cu (face–centred cubic lattice) is 0.362 nm