MASTER OF PHILOSOPHY, Modelling of Materials

Thursday 24 April 2003 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.*

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) Define the terms *lattice*, *motif* and *crystal structure*. Draw a projection along the z–axis of the crystal structure of diamond, which has a cubic–F lattice with a motif of carbon atoms at 0,0,0 and at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$.

(b) What are the factors which contribute to the heat capacity of a metal? Explain in particular the role of the electrons. What additional factors contribute to the heat capacity of a polymer?

(c) What is meant by the terms "deterministic" and "stochastic" when referring to a computer model? Describe the distinguishing features of each class of model, and give an example of each.

(d) List and briefly describe some of the experimental methods that can be used to determine a binary phase diagram.

(e) Data can be passed between a FORTRAN subprogram and the program or subprogram which calls it. Two mechanisms are available: parameters, and common blocks. Discuss briefly the advantages and disadvantages of each mechanism.

(f) Describe an experiment which proves that diffusion in the solid state occurs by a vacancy mechanism.

(g) Briefly outline the Metropolis Monte Carlo algorithm, and give three examples of its use in materials modelling.

(h) What is the purpose of *coarse-graining* as applied to a model of an atomistic system?

(i) Give three advantages of liquid crystalline polymers (LCPs) over conventional polymers from the point of view of their processing. What disadvantages do LCPs have for the manufacture of goods?

(j) Explain what is meant by the terms *displacive* and *reconstructive* phase transformations, describing chemical compositions and strains associated with each mechanism.

SECTION B

2. Describe how to avoid overfitting when modelling a set of data using non-linear functions.

[30%]

Describe the use of the hyperbolic tangent function in neural network applications.

[30%]

The fitting uncertainty σ_y associated with a neural network with two input variables ($\mathbf{x} = (\, x_1 \quad x_2 \,)$) and one output ($y$) is described by the following variance-covariance matrix:

$$\mathbf{V} = \begin{pmatrix} 2.7 \times 10^{-5} & 0 \\ 0 & 1.8 \times 10^{-4} \end{pmatrix}$$

What is the significance of the fact that the off-diagonal terms in this matrix are zero?

[10%]

Calculate the value of σ_y for $\mathbf{x} = (\, 1 \quad 3 \,)$

[30%]

3. Describe briefly the microstructural characteristics of *normal grain growth*. What is the thermodynamic reason for grain growth? What is the driving force for local grain boundary migration?

[20%]

Show that for a grain structure evolving from a very small initial mean diameter, $\overline{D}_0$, the mean diameter $\overline{D}$ varies with time t according to the equation:

$$\overline{D} \propto t^{\frac{1}{2}}$$

[20%]

What are the disadvantages of this analytical approach?

[20%]

Computer simulations of grain growth are commonly based on a *vertex model*, a *Monte Carlo model* or a *front-tracking model.* Describe briefly the essential features of these models and compare their merits.

[40%]

4. Describe briefly how finite element analysis (FEA) may be used to model heat diffusion in solids.

[10%]

A finite element analysis of the Jominy end-quench test has been conducted using the following mesh, properties and boundary conditions:

(i) 20 linear elements of equal size;
(ii) bar of length 120 mm with constant thermal properties;
(iii) initial temperature $T_1 = 850°\text{C}$ throughout;
(iv) ambient temperature $T_0 = 20°\text{C}$;
(v) air convection on the sides and the end remote from the quench;
(vi) imperfect heat transfer for a water quench on the quenched end.

The table below provides selected output values from the analysis.

Distance from quenched end, x (mm)	Time from start of quench, t (s)	Temperature T (°C)
10	20	352
10	100	143
10	500	37
10	1000	22
65	100	595
65	500	115
65	1000	30

An analytical solution for the end-quenching of a semi-infinite steel bar, with perfect heat transfer, is given by:

$$\frac{T(x,t) - T_0}{T_1 - T_0} = \text{erf}(\frac{x}{2\sqrt{at}})$$

where a is the thermal diffusivity, and $\text{erf}(x)$ is the error function. It may be assumed that $\text{erf}(x) \cong x$ for $x < 0.75$.

Calculate the temperature predicted by the analytical solution for the positions and times given in the table, if the thermal diffusivity of the steel is 1.91×10^{-5} m^2 s^{-1}. Plot the cooling curves for $x = 10$ mm and $x = 65$ mm, in each case showing the numerical and analytical solution.

[50%]

What are the main reasons for the discrepancies between the two solutions?

[40%]

5. One method for computing the molecular dynamics (MD) of a system of atomic particles is the *Verlet algorithm* in which the atomic positions are evolved in time according to the equation:

$$\mathbf{r}(t+\Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) + \Delta t^2 \mathbf{a}(t)$$

where $\mathbf{r}(t)$ and $\mathbf{a}(t)$ are the positions and accelerations of the atoms as a function of time, and Δt is the time step.

By considering the Taylor series of $\mathbf{r}(t+\Delta t)$ and $\mathbf{r}(t-\Delta t)$, show that the largest error made by using the above expression to calculate the atomic positions is proportional to Δt^4.

[30%]

Given that there are many alternative algorithms whose numerical precision is higher than Δt^4, explain why the Verlet algorithm is often used in MD simulations.

[30%]

Discuss the factors which limit the time step length in molecular dynamics simulations of simple fluids and macromolecules. Describe how these limits can be exceeded for macromolecules such as polymers?

[40%]

SECTION C

6. Distinguish between the terms *mechanical mixture* and an *ideal solution*, explaining why the latter has a lower free energy than the former.

[20%]

Explain the process of *mechanical alloying*, which is used to produce a metallic solid solution beginning with a mechanical mixture of elemental powders.

[20%]

The configurational entropy of mixing in an ideal solution made of components A and B is given by:

$$\Delta S_M = -kN[(1-x)\ln\{1-x\} + x\ln\{x\}]$$

where k is the Boltzmann constant, x is the mole fraction of B and N is Avogadro's number.

Derive ΔG_M, the free energy of mixing for this ideal solution, and sketch its variation with the concentration x.

[20%]

Show that:

$$\frac{\partial \Delta G_M}{\partial x} = kTN\ln\left\{\frac{x}{1-x}\right\}$$

and that the slope $\partial \Delta G_M/\partial x$ tends to $-\infty$ or $+\infty$ at $x=0$ and $x=1$.

[20%]

Why might this result be a mathematical artifact, *i.e.* why are these slopes expected to be finite in practice?

[10%]

How might the ideal solution model be modified to take account of any enthalpy of mixing?

[10%]

7. In a perfect silicon crystal all of the atoms are covalently bonded, and tetrahedrally co-ordinated. Why is this is a stable configuration for silicon? Where would you expect the valence charge density to be concentrated? (You may find it useful to note that silicon has the electronic configuration [Ne]$3s^2 3p^2$, where [Ne] denotes the configuration of neon.)

[20%]

Why would you expect a simple pair potential expansion of the interaction energy to give a poor description of the material's properties?

[10%]

For bulk silicon, it is suggested that the interaction energy U, as a function of atomic separation $\mathbf{r}$, can be expanded as:

$$U(\mathbf{r}) = \sum_{ij} U_2(\mathbf{r}) + \sum_{ijk} U_3(\mathbf{r})$$

where i, j and k refer to atoms, with U_2 given by:

$$U_2(\mathbf{r}) = -\frac{A}{r_{ij}^6} + \frac{B}{r_{ij}^{12}}$$

and U_3 by:

$$U_3(\mathbf{r}) = \frac{C(\cos(\gamma_{jik}) + \frac{1}{3})^2}{(r_{ij} r_{ik})^3}$$

where A, B, C are positive constants, r_{ij} is the distance between atoms i and j, and γ_{jik} is the angle at atom i between its bonds with atoms j and k.

By considering one silicon atom and two of its nearest neighbours, decide whether U_3 is an attractive or repulsive contribution to the total energy. Calculate the minimum energy bond angle, keeping the bond lengths fixed. Sketch U_3 as a function of bond angle.

[20%]

Calculate the equilibrium bond length, in terms of A, B and C, for a fixed bond angle. Sketch the variation of the total energy as bond length changes for the optimal bond angle.

[25%]

Discuss the strengths and weaknesses of using the potential $U(\mathbf{r})$ in a simulation of bulk silicon, considering both its range of applications and the computational cost of the calculation. How could it be improved?

[25%]

END OF PAPER