

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.*

<p>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</p>

SECTION A

1. (a) Show that $\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3$ represents the volume of a unit cell defined by the basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 , and that $\mathbf{a}_1 \cdot \mathbf{a}_1^* = 1$, where \mathbf{a}_1^* is a basis vector of the reciprocal lattice..
- (b) Describe what is meant by the term *Poisson's ratio* using the example of uniaxial tension. Show that during uniaxial tension at small strains, the volume of a material is conserved if the Poisson's ratio is 0.5.
- (c) Explain the basis of the post-iterative heat accumulation technique, used to account for latent heat evolution during melting or other phase changes, in the numerical simulation of heat transfer.
- (d) Describe how the bonding in solids may be classified in terms of the spatial distribution of the valence electrons.
- (e) FORTRAN is a contraction of "formula translation." What features of the language enable mathematical formulae to be converted to FORTRAN expressions straightforwardly? Give some simple examples.
- (f) Materials modelling is applied over a wide range of length scales, from an atom to large engineering components. List, in order of increasing length scale, four examples of materials modelling techniques. In each case, state the approximate length scale and the purpose of the modelling.
- (g) Explain why in a two-dimensional grain structure (such as in a thin film), grains with fewer than six sides tend to shrink, whereas those with more than six sides to grow. Why does this lead to an increase in the average grain size. What is the typical form of the grain-size distribution as grain growth proceeds?
- (h) Discuss the factors which influence the choice of time step length in a Molecular Dynamics (MD) simulation.
- (i) The heat flux across a unit area of a thin-walled tube is given by $q = \lambda \Delta T / t$, where λ is the thermal conductivity, ΔT the temperature difference across the wall which is of thickness t . The tube contains a liquid at a pressure P ; the resulting stress induced in the tube-wall is $\sigma = Pr/t$, where r is the tube radius. Assuming that the length and radius of the tube are fixed, show that the merit index required to maximise q is $M = \lambda \sigma_Y$, where σ_Y is the yield strength.
- (j) Describe how an interface is represented in a phase-field model.

SECTION B

2. Describe the properties of a pair-potential and discuss the types of materials to which it could be applied in an atomistic simulation. Sometimes pair potentials have been used to simulate metals. Give an example of a property of a metal that they will fail to reproduce.

The following pair potential has been used to perform atomistic simulations of α -iron (body-centred cubic, $a = 2.866\text{\AA}$).

$$V(r) = c_1(r + c_2)^3 + c_3r + c_4$$

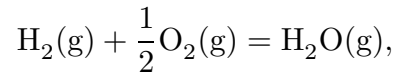
where the c parameters are given by:

Range (\AA)	c_1 (eV/ \AA^3)	c_2 (\AA)	c_3 (eV/ \AA)	c_4 (eV)
$1.9 < r \leq 2.40$	-2.196	-3.098	2.704	-7.436
$2.40 < r \leq 3.00$	-0.639	-3.116	0.478	-1.582
$3.00 < r \leq 3.44$	-1.115	-3.066	0.467	-1.548
$3.44 < r$	0	0	0	0

- (i) Estimate the vacancy formation energy in α -iron assuming that when an atom is removed from the metal, it resides on the surface where one half of the bonds that were broken are reconstituted.
- (ii) Consider the formation of a pair of vacancies in the nearest neighbour configuration, the second nearest neighbour configuration and the third nearest neighbour configuration. Which of these divacancy configurations will be the most stable? What computational factors have been ignored and will likely influence any comparison with experimental observations?

3. By considering the path-dependence of a property, explain what is meant by a *thermodynamic function of state*. Illustrate your answer with an example of a quantity which is a function of state and another which is not.

Show that for oxidation of hydrogen as given by:



the enthalpy change ΔH_T at a temperature T can be expressed in terms of the corresponding enthalpy change ΔH_{298}° at 298 K as follows:

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int \Delta c_P \, dT$$

where c_P is the specific heat capacity at constant pressure and

$$\Delta c_P = c_P(\text{H}_2\text{O}) - c_P(\text{H}_2) - \frac{1}{2}c_P(\text{O}_2)$$

4. Describe the mesoscale simulation technique of dissipative particle dynamics (DPD) and its relation to molecular dynamics (MD). What are the implications of the fluctuation-dissipation theorem for the mass transport of particles in a DPD simulation? How would this be affected by the presence of a gravitational field?

Consider the diffusion of a dissipative particle with frictional coefficient ξ moving in a gravitational field g . Given that the displacement Δx_0 of the particle in a direction parallel to the field is changed to $\Delta x_0 + (g/\xi)\Delta t$ when observed over some interval of time Δt , calculate the resulting change in diffusion coefficient.

5. Computer-based selection of manufacturing processes can be conducted by systematic screening on the basis of attributes of competing processes, followed by ranking on the basis of estimated cost.
- (i) Describe the criteria for screening and selecting primary shaping processes. Explain why it is easier to build a generic database of material properties than it is to build an equivalent database of attributes for processes.
 - (ii) In its simplest form, the cost of a component may be estimated from the equation

$$C = C_m + \frac{C_L}{\dot{n}} + \frac{C_C}{n}$$

where C_m is the cost of the material used per part, \dot{n} is the production rate and n is the total batch size. Define the meaning of the terms C_L and C_C in this equation. Sketch a typical curve for cost per part as a function of batch size, and explain which terms dominate the cost at very low and very large batch sizes.

- (iii) State two advantages of using modelling in the selection of a manufacturing process.

SECTION C

6. Distinguish between thermal and mechanical quantities in the context of molecular simulation, giving two examples of each. Explain why the determination of thermal quantities directly from ensemble-averaged simulation data is not straightforward. Outline the principles of thermodynamic integration, and describe how it can be used to locate phase coexistence curves.

The condensation of a dilute gas of weakly interacting particles is to be studied using atomistic simulation techniques. A quantity of gas is confined to a cell of fixed volume V_1 and compressed isothermally to a volume V_2 .

- (i) Explain how you would use thermodynamic integration to calculate the resulting Helmholtz free energy change, and describe a suitable simulation methodology that would produce the data you need. Justify your choice by comparison with at least one other technique that could be used in principle.
- (ii) A computer simulation of the compression process is carried out, giving the following results at 300 K, where the data are expressed in terms of the molar volume V_m .

Molar volume dm ³	Pressure Pa	Molar volume dm ³	Pressure Pa
2.104×10^4	0.540×10^5	0.606×10^4	2.067×10^5
1.796×10^4	0.632×10^5	0.484×10^4	2.656×10^5
1.362×10^4	0.852×10^5	0.221×10^4	6.848×10^5
1.155×10^4	0.954×10^5	0.105×10^4	20.30×10^5

Approximate the data to a virial equation of the form $P = \alpha(V_m/\phi)^\beta$, and hence produce a suitable plot to find the value of the exponent β , given that $\alpha = 7.29 \times 10^8$ Pa and $\phi = 1$ dm³.

- (iii) By integrating the virial equation obtained in (ii), calculate the free energy change on compression from $V_1 = 2.104 \times 10^4$ dm³ to $V_2 = 0.105 \times 10^4$ dm³.

- (iv) How would the above procedure have to be modified if the gas had condensed?

7. Why is it that a liquid does not freeze the moment it is cooled below the equilibrium freezing temperature, but instead requires an undercooling before solidification begins?

Show that the activation energy for nucleation during solidification varies as $\gamma^3/\Delta G_V^2$, where γ is the interfacial energy per unit area and ΔG_V is the magnitude of the free energy change per unit volume of the new phase.

Explain how the concept of extended space can be used to allow for the impingement of particles of growing from different locations in the parent phase, and hence derive the quantitative relationship between the real and extended volumes of the particles.

A phase begins to transform isothermally from N sites, with the transformed regions growing at 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

$$\xi = 1 - \exp\{-kG^3 Nt^3\}$$

where k is a constant.