MASTER OF PHILOSOPHY Modelling of Materials

Examiner's Solutions to Paper 2

SECTION A

1(a)

A dislocation is a line of discontinuity in a crystalline material with translational symmetry. The character of the dislocation is described by the angle between the line of dislocation and a vector, known as the Burgers vector, which gives the magnitude and direction of the lattice displacement generated by the presence of the dislocation. Dislocations where the Burgers vector is normal to the dislocation line are known as edge dislocations, and those where the Burgers vector is parallel to the dislocation line are known as screw dislocations. Dislocations where the angle is intermediate between zero and ninety degrees are known as mixed character dislocations.

A dislocation enables the crystal planes to glide in a piecewise manner rather than the rigid displacement of the entire plane. This greatly reduces the stress required to cause slip, and leads to yield stresses that are well below the theoretically calculated maximum based on a perfect crystal.

1(b)

Stress and strain tensors are both symmetric. This is a requirement to prevent them from describing rotation as well as deformation. This means that they each have 6 independent elements rather than 9, reducing the number of constants to $6 \times 6 = 36$. Further symmetry considerations reduce the most general case to 21 for deformation of the least symmetric solid.

(i) 21, as described above
(ii) An isotropic system requires only 2 constants to describe the behaviour, *e.g.* Young's modulus and Poisson's ratio.

1(c)

In large-scale materials production and processing, the commercial success of the product is very sensitive to cost; great efforts are therefore made to minimize costs by optimising the processing. The development of effective process changes could be by ‘trial and error’, but large-scale experimental trials are extremely costly, both in terms of material used and in terms of the temporary loss of production time. Therefore modelling is an attractive alternative. Even if an entire process is not modelled in its full complexity, idealised modelling can be useful in identifying key parameters for experimental investigation. (A superior answer should include one or two examples.)

1(d)

The Bragg condition in *k*-space is that the difference between the incident and scattered wave vectors must equal a reciprocal lattice vector **g**.

i.e. $\mathbf{k} - \mathbf{k}' = \mathbf{g}$ ($\mathbf{k}'$ is scattered wave vector)

In electron diffraction, the scattering process is elastic and energy is conserved so that the magnitudes of k and k′ are equal. Thus

$(\mathbf{k} + \mathbf{g})^2 = k^2$ *i.e.* $2\mathbf{k}.\mathbf{g} = g^2$

or $k \cos\theta = g/2$ (θ is angle between **k** and **g**)

This means that the component of the incident wave vector **k** along the reciprocal lattice vector **g** must be half the length of **g**. Thus an incident wave vector **k** will satisfy the Bragg condition if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of *k*-space to a reciprocal lattice point **g**. Such planes in *k*-space are called Bragg planes or Brillouin zone boundaries.

Thus Brillouin zones are defined by sets of planes that are the perpendicular bisectors of reciprocal lattice points. The 1st BZ is the set of *k*-points that can be reached from the origin without crossing any Bragg plane. The *n*th BZ is the set of *k*-points that can be reached from the origin by crossing $n-1$ Bragg planes but no fewer.

1(e)

FORTRAN has two very similar classes of subprogram: functions, which return value to the calling code, and subroutines, which do not. Uses of these subprograms in the FORTRAN language include:

- Using functions provided by the language to return common mathematical results which would be laborious to calculate otherwise (such as SQRT).

- Using subprograms to invoke other code that the user has not written, and may not understand in detail; for example, a graphics library.
- Using subprograms to hold code that is used in several parts of the program; for example, a program might need to evaluate the determinant of several matrices. A function to calculate this would make the calling code clearer, and reduce the possibility of error.
- Subprograms can be used simply to clarify the structure of a program; for example, one subprogram could read parameters, another perform calculations with them, third print out the results.
- Subprograms can be used to keep together code that might require modification for another installation (which is format- or implementation-dependent, for example).

1(f)

Grain boundaries are defects and have an excess free energy. With a larger average grain diameter, there is a reduced area of grain boundary per unit volume of material and therefore a favourable reduction of free energy.

To have an increased average grain size in a given volume of material, there must be fewer grains. Therefore there must be a mechanism of grain death. Grain growth relies on having a distribution of grain size, smaller grains shrinking and disappearing, larger grains growing.

The motion of a grain boundary is governed by its curvature and it will move towards its centre of curvature. Smaller grains tend to have fewer sides with a curvature such as to cause the grain to shrink. Larger grains have scalloped surfaces with centres of curvature outside the grain; they therefore tend to grow. The curvature of the grain boundaries arises from the force balance at their junctions tending to give 120° angles between the boundaries. While 120° junctions in a 2-D grain structure of equal-sized hexagons gives straight (non-migrating) boundaries, other less ideal grain structures always have curved boundaries. (This part of the answer may be illustrated with sketches of grains in 2-D, showing that those with less than 6 sides shrink, while those with more than 6 sides grow.)

1(g)

Thermal importance sampling means that each state of a system is sampled from a thermodynamic ensemble according to its Boltzmann probability. For systems in equilibrium, the expectation values of the thermodynamic state functions can be found by arithmetically averaging over states sampled according to their thermal importance. Hence, states that are thermodynamically unimportant do not contribute to the averages.

The Metropolis Monte Carlo method achieves thermal importance sampling using a stochastic algorithm, which can be summarised as follows:

1. Start with system in arbitrarily chosen state μ and evaluate the internal energy E_μ
2. Generate a new state ν by a small ergodic perturbation to state μ and evaluate E_ν
3. If $E_\nu - E_\mu < 0$, then accept the new state. If $E_\nu - E_\mu > 0$, then accept the new state with probability $\exp\left[-\beta(E_\nu - E_\mu)\right]$
4. Return to step 2 and repeat until equilibrium is achieved (i.e. thermodynamic state function of interest has converged to steady-state value when averaged over all configurations)

1(h)

The three distinct processing stages are: pre-processing, analysis, and post-processing.

Pre-processing requires specification of the dimensionality of the problem, definition of the shape or outline of the body under consideration, generation of the mesh and definition of the boundary conditions.

Analysis involves solving the field variables at the nodes of the various elements. This is accomplished by solving the governing differential equations subject to the constraints of the boundary conditions. Typically, this involves solving large linear systems of equations using Gaussian elimination.

Post-processing involves visualisation of the solution and interpolation. Since the analysis only determines the values of the field variables at the nodes, interpolation is required to obtain numerical values at all other points.

Of all the three stages, pre-processing is the most influential stages in FE analysis.

1(i)

For solid state systems, Gibbs' phase rule can be expressed as: $F = c - p + 1$, where F is the number of degrees of freedom, c is the number of components in the system, and p is the number of phases in the system.

The phase rule specifies the number of degrees of freedom for a given system at equilibrium. In thermodynamics, the number of degrees of freedom is the smallest number of intensive variables (*i.e.* pressure, temperature, and concentrations of components in each phase) that must be specified to completely describe the state of the system. For a solid state system, under normal circumstances, constant pressure (1 atm) is assumed and therefore one degree of freedom is already defined.

For three phases to be in equilibrium in a two-component system, the system temperature, pressure and concentration of all the components must be fixed, as the number of degrees of freedom is zero.

1(j)

Common process attributes to consider for selection of shaping process are: compatibility with material, size, minimum section thickness, surface roughness, dimensional tolerance, and process economics.

CES contains separate databases for joining and surface treatment, since selection in these process classes poses different questions to the designer, specific to these process classes – for example:

- Joining processes: compatibility of component shape and process with joint geometry.
- Surface treatment processes: the function of the surface treatment (corrosion, wear, aesthetics etc).

Processing rate is not a simple characteristic of a given process, since the rate in a given situation usually depends on complex interactions between process parameters, aspects of the design, and the material being processed. For example, in cutting processes, the rate depends on the type of process mechanism (mechanical, thermal etc), the component thickness, and the properties of the material being cut (thermal or mechanical).

SECTION B

2.

Assumptions of the free electron model:

- The solid is composed of a gas of negatively charged electrons that is neutralised by a positive background charge.
- Explicit electron-ion interactions are ignored (the free electron approximation).
- Explicit electron-electron interactions are ignored (the independent electron approximation).

The *E(k)* curve for free electrons in one dimension is parabolic ($\sim k^2$). At zero Kelvin, the Fermi energy E_F is defined as the energy of the highest occupied energy level. The Fermi wave-vector k_F is the wave-vector corresponding to the Fermi energy. At finite temperatures, the Fermi energy is defined as the energy for which the probability of occupation is 1/2. The Fermi surface for free-electrons in 3-D (at zero Kelvin) is a sphere in *k*-space. Deviations from the spherical shape are expected in reality because of the presence of an electron-ion interaction which causes Bragg scattering and discontinuities in *E(k)*.

[30%]

The density of states is defined as the number of electron states *N(E)* per unit energy range and given mathematically by $D(E) = \frac{dN(E)}{dE}$. Note that a state is defined by both a level and a spin. The number of states = twice the number of levels due to the Pauli exclusion principle.

Consider free electrons in a 3-D box of volume $V = L^3$

In k-space, the volume per k-point is $\left(\frac{2\pi}{L}\right)^3 = \frac{(2\pi)^3}{V}$

If the box contains *N* electrons, then the volume of the Fermi sphere is

$$\frac{1}{2}N\frac{(2\pi)^3}{V}$$

The factor of 1/2 comes from the Pauli exclusion principle since 2 electrons can occupy each k-state.

Note that the number of electrons *N* equals the number of states.

Hence $$\frac{1}{2}N\frac{(2\pi)^3}{V}=\frac{4}{3}\pi k_F^3$$

therefore $k_F=\left(3\pi^2 n_c\right)^{1/3}$ where n_c (electron density) = N/V

and $$E_F=\frac{\hbar^2 k_F^2}{2m}=\frac{\hbar^2}{2m}\left(3\pi^2 n_c\right)^{2/3}$$

Re-arranging this equation gives the number of states *N(E)* with energies up to a given energy *E*:

$$N(E)=\frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

hence $$D(E)=\frac{dN(E)}{dE}=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}$$

[50%]

To calculate the average electronic energy at zero Kelvin:

$$\langle E\rangle=\frac{\text{total electron energy}}{\text{total no. of electrons}}=\frac{\int^{E_F} E\,D(E)\,dE}{\int^{E_F} D(E)\,dE}=\frac{\int^{E_F} E^{3/2}\,dE}{\int^{E_F} E^{1/2}\,dE}=\frac{3}{5}E_F$$

[20%]

3.

Thermodynamic models can be used to predict the free energies of each phase of a system as a function of temperature and the concentrations and interaction parameters of the components. The total free energy is then minimised by taking the phase with the lowest free energy, or by using the double tangent construction, as appropriate. The excess Gibbs free energy for binary and ternary systems is defined as the free energy in excess of an ideal solution, *i.e.* one in which the enthalpy of mixing is zero. The excess free energy is thus related to the interactions between the components, and the degree to which they are mixed. The regular solution model assumes random mixing, and gives an enthalpy of mixing which is proportional to the product of the concentrations of each component in a binary system.

[40%]

The advantages of using thermodynamic models are that they allow analytical computation of the phase boundaries and require only a few crucial experiments to be carried out in order to parameterise the model (as opposed to many experiments needed to follow the phase boundaries in the absence of a good model). The main disadvantage is that the models do not always work for the systems being described, *e.g.* the regular solution model breaks down for systems where there is non-random mixing (in which case the quasi-chemical model can be used).

[20%]

$$\Delta G_{mix} = \omega x_{\mathrm{A}} x_{\mathrm{B}} + RT\left(x_{\mathrm{A}} \ln x_{\mathrm{A}} + x_{\mathrm{B}} \ln x_{\mathrm{B}}\right)$$

Assuming binary mixture, and writing $x_{\mathrm{A}} = 1 - x_{\mathrm{B}}$

$$\frac{\mathrm{d}\left(\Delta G_{\mathrm{mix}}\right)}{\mathrm{d}x_{\mathrm{B}}} = \omega\left(1 - 2x_{\mathrm{B}}\right) + RT\ln\left(\frac{x_{\mathrm{B}}}{1 - x_{\mathrm{B}}}\right)$$

$$\frac{\mathrm{d}^2\left(\Delta G_{\mathrm{mix}}\right)}{\mathrm{d}x_{\mathrm{B}}^2} = RT\left(\frac{1}{x_{\mathrm{A}}} + \frac{1}{x_{\mathrm{B}}}\right) - 2\omega = 0 \text{ when } x_{\mathrm{A}} x_{\mathrm{B}} = \frac{RT}{2\omega}$$

Hence $T_C = \dfrac{\omega}{2R} = \dfrac{20\times 10^3}{2\times 8.314} = 1203\ \mathrm{K}$

[40%]

4.

Mass of strut: $m = \rho A L$ and of panel: $m = \rho B D L$

Dimensional variable for strut is area A; from stiffness equation: $A = \dfrac{L}{S E}$

Hence mass of strut: $m = \rho\, L^2 / SE$, so for minimum mass, minimise (ρ / E)

Dimensional variable for panel is thickness D; from stiffness equation:

$$D = \left(\frac{C_1 L^3}{E B S} \right)^{1/3}$$

Hence mass of panel: $m = \rho L B \left(\dfrac{C_1 L^3}{E B S} \right)^{1/3}$, so for minimum mass,

minimise $(\rho / E^{1/3})$

[30%]

Values of performance indices:

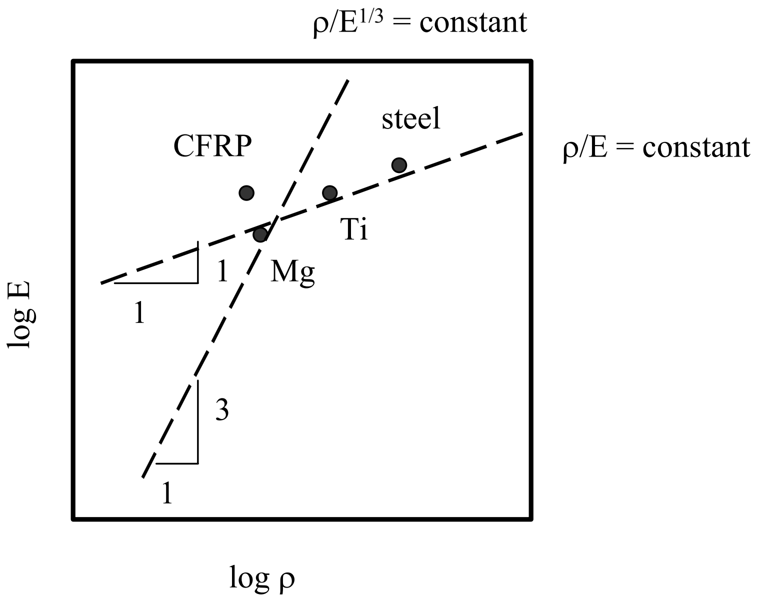
	E (GPa)	ρ (Mg/m^3)	(ρ / E) (× 100)	$(\rho / E^{1/3})$ (× 100)
Low alloy steel	209	7.85	3.76	1.32
Ti alloy	105	4.6	4.38	0.98
Mg alloy	44.5	1.85	4.16	0.52
CFRP	110	1.55	1.41	0.32

For the strut, CFRP has a clear advantage, and the metals compete quite closely. For the panel, CFRP is still the best, but the metals now show a definite ranking, with Mg closest to CFRP. However, CFRP is the most expensive material per unit mass.

[40%]

Graphical approach on a material property chart of log(E) – log (ρ):

Constant values of the performance indices plot as straight lines of slope 1 and 3 respectively. Materials lying on a line are equally good; materials above the line are better.



[30%]

5.

The Frisch Hasslaucher Pomeau (FHP) lattice gas model is constructed of discrete, identical particles that move from site to site on a triangular lattice, colliding when they meet, always conserving particle number and momentum. FHP showed that it is possible to derive the Navier-Stokes equations from the micro dynamics of this system. The innovative feature of FHP model is the simultaneous discretisation of space, time, velocity and density. No more than one particle may reside at a given site and move with a given velocity. Unlike purely diffusive lattice gases, momentum is conserved in each collision and so the system is Galilean invariant and therefore displays hydrodynamic behaviour. Unlike the hydrodynamic lattice gas models that preceded it, the FHP model has an isotropic hydrodynamic limit because of the underlying symmetry of the triangular lattice.

The lattice director model can be used to study degree of orientation and defect structure in nematic liquid crystalline systems. In the lattice director model, the average molecular director field is spatially coarse-grained onto a multi-dimensional grid. Adjacent sites on the lattice interact through a simple Hamiltonian, and the model is relaxed to a state of minimum energy. The aims are to reveal the microstructure in a bulk sample, understand how this evolves during processing and how the microstructure affects the properties.

[30%]

A suitable Hamiltonian for an elastically isotropic system is:

$$f = k\sum_{i=1}^{n}\sin^2(\theta_i - \theta)$$

where $\theta_i - \theta$ is the angle between the average molecular director θ_i in cell *i* and the nematic director θ, and *k* is an average elastic constant. The sum runs over all adjacent cells (4 in 2D, 6 in 3D for a cubic lattice). This is sometimes called the Lebwohl-Lasher potential.

A standard Metropolis Monte Carlo simulation can be used to relax the lattice director model to the lowest free energy, and an outline of the algorithm should be given.

[40%]

The Lebwohl-Lasher potential could also be implemented on a finite element grid, where the strain field between adjacent nodes is minimised by a deterministic finite difference algorithm. The differences between this method and the probabilistic Monte Carlo algorithm are that dynamical information about the coarsening process could easily be extracted, and that there is no thermal noise in the system. The absence of thermal noise could lead to the system becoming trapped in metastable states, and so a stochastic element may be introduced to avoid this.

[40%]

6.

The molecular mechanics approach to modelling atomistic systems is based on the construction of a classical potential energy surface, called a force field, which contains terms representing the interactions between the atoms.

The commonly-used DREIDING force field is represented by the following potential energy function:

$$V = \frac{k_\mathrm{b}}{2}\left(r_{ij} - r_0\right)^2 + \frac{k_\theta}{2}\left(\theta_{ijk} - \theta_0\right)^2 + \frac{k_\varphi}{2}\left(1 + \cos 3\varphi_{ijkl}\right) + D_0\left\{\left(\frac{R_0}{r_{ij}}\right)^{12} - 2\left(\frac{R_0}{r_{ij}}\right)^{6}\right\} + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

where the *k* are force constants, r_{ij} the interatomic separations, θ_{ijk} the angles between adjacent triplets of bonded atoms, φ_{ijkl} the dihedral angles between adjacent quartets of bonded atoms, D_0 is the well-depth and R_0

the equilibrium separation for the van der Waals interactions and q the electrostatic charges on the atoms. The first three terms are called bonded terms, and represent the internal degrees of freedom of the molecule, and the last two terms are the non-bonded terms, and represent the interactions between molecules.

[20%]

The technique of using energy minimisation can be used to find the lowest potential energy structure of an atomistic system, and is often very useful in situations where the interactions are very strong or the thermal energy is very low. It can also be useful to prepare molecular models for molecular dynamics simulations, which require a stable initial configuration from which to initialise the force arrays from the gradient of the potential energy.

An example of a numerical method that would be suitable for energy minimisation of a large atomistic system would be a first derivative method such as conjugate gradients or steepest descents. In practice, a combination of methods can be used to achieve optimum speed of convergence both far from and closer to the local energy minimum.

Strictly speaking, energy minimisation should only be used for systems at zero Kelvin, and is therefore incapable of describing entropic effects. Also, there is no known algorithm that is guaranteed to find the global minimum energy state in a finite period of time, and for large systems it can be impossible to judge whether the global minimum has been found or is even close by. Since simple energy minimisation strategies usually follow a monotonically decreasing energy pathway, the system is very easily caught in local minima.

[40%]

Since the electrostatic potential energy is given by $qE\left(r-r_0\right)$, then the total potential energy of the system is:

$$V(r)=\tfrac{1}{2}k\left(r-r_0\right)^2-qE\left(r-r_0\right)$$

Hence, minimising with respect to r:

$$\frac{\mathrm{d}V}{\mathrm{d}r}=k\left(r-r_0\right)-qE=0$$

gives $r = r_0 + \frac{qE}{k} \Rightarrow \frac{r}{r_0} = 1 + \frac{qE}{r_0 k}$

Using the numerical values provided, $\frac{r}{r_0} = 1 + 9.6532 \times 10^{-3} \simeq 1.0096532$.

[40%]

7.

According to effective medium theory, the total energy of the solid can be written:

$$U_{tot} = \sum_i U_i(\overline{\rho}_i) + U_R$$

where the first term is the energy to embed the *i*th atom in the jellium of density $\overline{\rho}_i$ (attractive) and the second term is the repulsive electrostatic overlap interaction.

The method can be used to construct semi-empirical potentials by formulating physically reasonable forms for the attractive embedding function U_i and the repulsive overlap energy U_R. The former is a non-linear function of ρ (usually concave negative to reflect the fact that the energy/atom decreases like this with increasing coordination) while the latter can be simple pair potential (exponentials, polynomials *etc.*)

In the embedded atom method U_i has been implemented in several functional forms (powers, exponentials) and is taken as the energy to embed an atom in an electron gas ρ where ρ is calculated as linear superposition of atomic electron densities.

In the Finnis-Sinclair approach U_i takes a square root functional form. This is justified by tight-binding theory and experimental observation.

One approach is to start with the concept of bond order (bond strength). Observation suggests that bond order is a decreasing function of local coordination Z. Tight-binding says that bond order goes as $1/\sqrt{Z}$. Thus the energy/bond goes as $1/\sqrt{Z}$ and the bond energy/atom goes as $\sqrt{Z}$. In other words the energy/atom goes as $-\sqrt{Z}$ (the negative of cohesive energy and a concave negative function).

[30%]

The expression for the energy/atom in the second part of this question is a Finnis-Sinclair potential where the electron density has been taken as a pair potential.

First nearest neighbour distance $r_1 = a_o\sqrt{3}/2$
Second nearest neighbour distance $r_2 = a_0$

Hence using the given data we obtain

$V_1 = 0.4063$ eV, $\phi_1 = 2.7526$ eV
$V_2 = 0.0210$ eV, $\phi_2 = 1.5252$ eV

[20%]

A reference atom in the bcc structure has 8 first nearest neighbours and 6 second nearest neighbours. The total energy of these 14 atoms with the reference atom present is given by

$$U_{perfect}^{total} = \sum_{j=1}^{14} \left\{ \frac{1}{2} \sum_{i \neq 0} V(r_i) - A\left(\sum_{i \neq 0} \phi(r_i) \right)^{1/2} \right\} = 14\left(\frac{1}{2}(8V_1 + 6V_2) \right) - 14A\left(8\phi_1 + 6\phi_2\right)^{1/2}$$

The total energy of these 14 atoms with the reference atom absent given by

$$U_{vacancy}^{total} = 8\left(\frac{1}{2}(7V_1 + 6V_2) \right) + 6\left(\frac{1}{2}(8V_1 + 5V_2) \right) - 8A\left(7\phi_1 + 6\phi_2\right)^{1/2} - 6A\left(8\phi_1 + 5\phi_2\right)^{1/2}$$

Thus the vacancy formation energy is given by

$$E_V = U_{vacancy}^{total} - U_{perfect}^{total}$$

$$= -\left(4V_1 + 3V_2\right) - A\left[8\left(7\phi_1 + 6\phi_2\right)^{1/2} + 6\left(8\phi_1 + 5\phi_2\right)^{1/2} - 14\left(8\phi_1 + 6\phi_2\right)^{1/2} \right]$$

[40%]

Substituting in values for V_1 , ϕ_1 , V_2 , and ϕ_2 gives $E_V = 3.7116$ eV. This value will be higher than the experimental value since it ignores atomic relaxation around the vacancy.

[10%]