MASTER OF PHILOSOPHY Modelling of Materials

Examiners' Solutions to Paper 1

SECTION A

1(a)

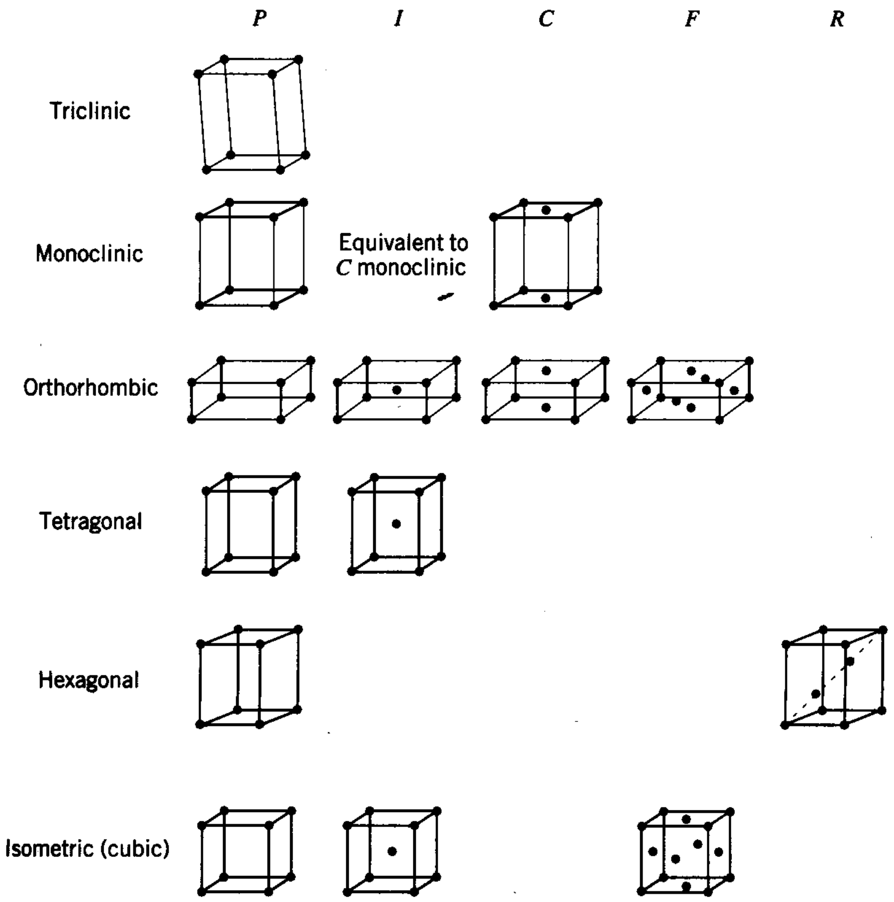
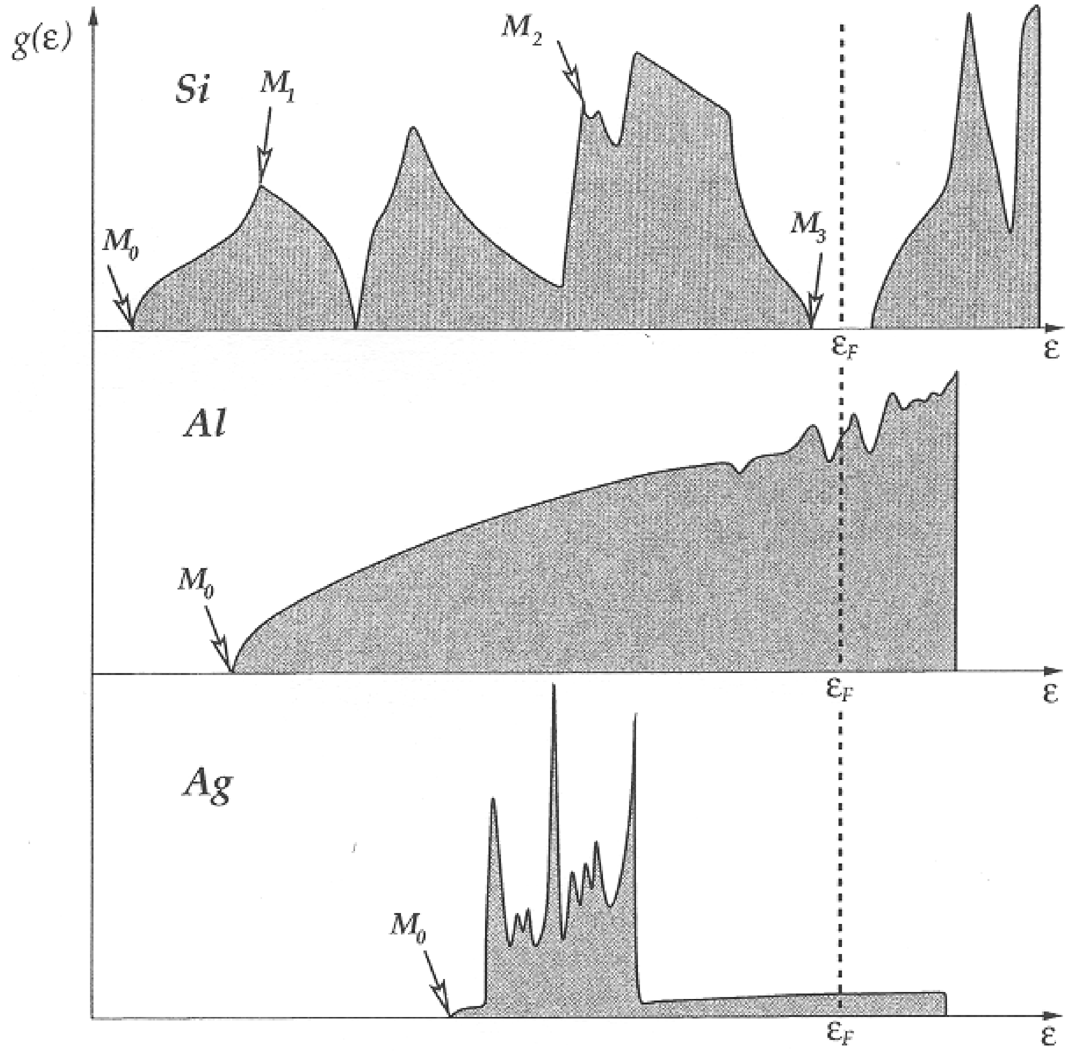


Figure 3.66 The fourteen Bravais lattices and the six crystal systems.

[source: Allen and Thomas p. 167.]

1(b)



Features:

Semiconductor (Si): Shows well defined valence and conduction bands separated by a band gap. Has a low energy s-band hump and a higher energy, broader, p-band. Critical points are labelled with Ms. Fermi level passes through the middle of band gap for undoped intrinsic material.

Simple metal (Al): Shows a broad s-p free-electron-like band with √ε functional form. Fermi level and critical points are labelled.

Transition metal (Ag): Shows a large multi-peaked band for the d-states with a much lower, broader band for the s-states that has a √ε functional form. For Ag, the Fermi level passes through the s-band but this may not be the case for other transition metals (e.g. Ti). There is s-d hybridization.

1(c)

Answer should include five of the following points.

---- Is an analytic solution possible?

---- What are the best time and length scales for the problem?

---- What are the dependent and independent variables?

---- How empirical should the model be? (i.e. degree of data fitting)

---- What are the appropriate boundary and initial value conditions?

---- What is the best simulation scale? (electronic, atomistic, microstructural, continuum)

---- What degree of precision is required?

---- Deterministic or stochastic? (i.e. evolves in time or based on statistical sampling)

---- Are experimental data available to test results?

---- Is a computer code already available? Are analysis tools available?

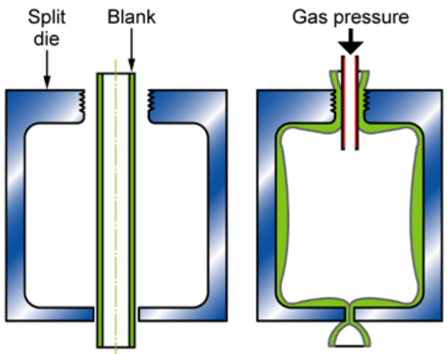
---- Which programming language, compiler or numerical solver ?

---- How fast is the chosen model? How much computer power is needed?

---- PCs, workstations, clusters or supercomputers?

1(d)

Recommended process: blow moulding or injection moulding.



In blow moulding, a tube or *parison* is extruded and clamped in a split mould with a hollow mandrel at one end. In injection blow moulding, a pre-form is injection moulded over a mandrel and transferred to the blowing die. Then in both cases, hot air is forced under pressure through the mandrel, blowing the polymer against the mould walls where it cools and freezes.

> [Extra credit can be given if an answer comments on *stretch blow moulding*, a variant in which the temperature is chosen such that the polymer is drawn as it expands, orienting the molecules in the plane of the surface to provide additional strength.]

Determination of energy: specific heat C_p = 1450 J/kg.K

melting temperature T_m = 238ºC

Energy to heat to melting point = $C_p \times T_m$ = 0.35 MJ/kg

Assumptions:

- for necessary fluidity, would need to heat to greater temperature than T_m but even if doubled (over estimate) would give total energy required of ~ 0.7 MJ/kg
- latent heat not included – could assume equivalent to heating to T_m so total energy now ~ 1 MJ/kg
- no heat losses included.

Comment: moulding energy from data sheet is 11.4 MJ/kg and this is much greater than ~ 1 MJ/kg. We conclude that energy to shape objects are determined by factors that do not relate directly to the material, but to the process itself, which clearly is not very energy efficient.

1(e)

```
      integer function symm (m)
      implicit none
      integer i, j, m(10,10)
*     note that we only need to scan the upper triangle of the matrix,
*     as the transposed element will be in the lower triangle;
*     there is of course no need to look at elements on the diagonal
      do 10, i = 1, 10
         do 10, j = i+1, 10
            if (m(i,j) .ne. m(j,i)) then
               symm = 0
               return
            end if
   10 continue
      symm = 1
      return
      end
```

1(f)

A multiscale model couples different models across the length scales. The hierarchy of models based on length scale (i.e. electronic, atomistic, microstructural and continuum) should be described. The main idea is to integrate two or more of them to create a hybrid model. Sketches of length scale against discipline or length scale against number of atoms would be appropriate. Additional credit could be given for pointing out that models on individual length scales are now well established and that multiscale modelling is the current challenge in modelling research (the intermediate scale problem).

Any example where it would be computationally advantageous to model different behaviour on different length scales simultaneously would suffice. Example given in lectures was fracture where the tip of the crack is modelled atomistically and the long-range strain field is modelled elastically. The scale of the models have to be chosen appropriately to target the main process that is occurring, e.g. bond breaking or bond stretching.

The main advantage is avoiding doing detailed microscopic or microstructural calculations in regions of the model where it is unnecessary and to account for long-range behaviour with macroscopic solutions.

The main disadvantage is the technical difficulty in making sure that the solutions are continuous across the boundaries between different models thus ensuring that no artefacts are introduced.

1(g)

An equation of state relates the pressure, volume and temperature of a system in thermal equilibrium. A simple example of an equation of state that is applicable to non-interacting particles in the gas phase is the *ideal gas* equation: $pV = nRT$, where p is the pressure, V is the volume, n is the number of moles of ideal gas, R is the molar gas constant (8.314 J K^{-1} mol^{-1} in conventional units) and T is the temperature. This equation is obeyed quite well for most gases at room temperature and pressure, and increasingly so as the pressure is decreased. However, at higher pressures and lower temperatures, interactions between the gas molecules become significant, and so a more complicated equation of state is required.

In the case of a non-ideal gas for which the interatomic potential energy function was known, an isothermal-isobaric Monte Carlo method could be used to compute the equation of state. A number simulations at constant pressure and temperature should be run at different (p,T) state points to determine the system volume. These data could then be used either to parameterise a semi-empirical equation of state of known analytical form, or determine the virial coefficients in a polynomial series expansion of the pressure in terms of the volume.

Computational details of MC simulations are not required in the answer.

1(h)

The Kuhn length of a polymer chain, a_K, is defined as the length over which orientational correlations between connected monomer segments in the chain can be ignored, i.e. the effective statistical segment length for which the chain can be treated as a random walk, and so $\langle R^2 \rangle = N_K l_K^2$, where N_K is the number of Kuhn segments and l_K is the Kuhn segment length.

$$C_\infty = \langle R^2 \rangle / Nl^2$$

From definition of Kuhn length above, $\langle R^2 \rangle = N_K l_K^2$, so:

$$C_\infty = N_K l_K^2 / Nl^2$$

However, since contour length of monomer chain and Kuhn chain must be equal, then $N_K l_K = Nl \Rightarrow \frac{N_K}{N} = \frac{l}{l_K}$. Substituting into expression above, yields:

$C_\infty = N_K l_K^2 / N l^2 = \frac{l}{l_K}\frac{l_K^2}{l^2} = \frac{l_K}{l}$ as required.

1(i)

A dispersion of precipitates in a matrix may undergo *Ostwald ripening* (also known as *coarsening*) on annealing. In this process the average particle diameter increases, while the total volume fraction of the precipitate phase stays constant, the driving force being the reduction in overall interfacial area (and therefore energy) between the two phases. If the average particle diameter is greater, there must then be fewer particles. This is achieved by the above-average-size particles growing at the expense of the below-average-size particles, the diffusion flux of solute being from small particles to large particles. Ultimately the small particles disappear. The solute concentration in the matrix around a precipitate is enhanced above the ideal value (i.e., the value for a planar interface) by an amount inversely proportional to the precipitate radius. Thus smaller particles have a larger solute concentration in the matrix around them, and the consequent diffusion of solute away from smaller particles forces them to shrink. The precipitate size distribution is typically log-normal and this distribution, and the overall microstructure, appear self-similar throughout the coarsening.

1(j)

$\varepsilon_1 = \varepsilon_2$ and $\varepsilon_3 = 0$. It follows that from Hooke's law in 3D that:

$$\varepsilon_1 = \frac{1}{E}\left(\sigma_1 - \nu(\sigma_2 + \sigma_3)\right)$$

$$\varepsilon_2 = \frac{1}{E}\left(\sigma_2 - \nu(\sigma_3 + \sigma_1)\right)$$

$$\varepsilon_3 = 0 = \frac{1}{E}\left(\sigma_3 - \nu(\sigma_1 + \sigma_2)\right)$$

Hence if we subtract the second of these equations from the first we find

$$0 = \frac{1}{E}(\sigma_1 - \sigma_2)(1-\nu)$$

Since neither $1/E$ nor $(1-\nu)$ are zero, we deduce that $\sigma_1 = \sigma_2$, as we would expect from symmetry.

Substituting this condition back into the equation for ε_3, we find:

$$\sigma_3 = 2\nu\sigma_1$$

and so in the ‘1’ direction we have

$$\varepsilon_1 = \frac{1}{E}\left(\sigma_1 - \nu(\sigma_2 + \sigma_3)\right) = \frac{\sigma_1}{E}\left(1 - \nu - 2\nu^2\right)$$

Therefore, the ‘effective modulus’, σ_1/ε_1, is simply

$$\frac{\sigma_1}{\varepsilon_1} = \frac{E}{1 - \nu - 2\nu^2}$$

It therefore follows that for the aluminium alloy, σ_1/ε_1 = 80/0.405 GPa = 198 GPa to 3 s.f.

SECTION B

2.

In the phase field method, the state of the entire microstructure is represented continuously by a single variable known as the *order parameter* ϕ. For example, $\phi = 1$, $\phi = 0$, and $0 < \phi < 1$, represent the precipitate, matrix and interface respectively. The latter is therefore located by the region over which ϕ changes from its precipitate value to its matrix value. The range over which it changes is the called the *width* of the interface. The set of values of the order parameter over the whole microstructure is the *phase field*.

[20%]

The second equation for g may be derived by simple substitution of $(\mathrm{d}c/\mathrm{d}x)$ for y and $(\mathrm{d}^2c/\mathrm{d}x^2)$ for z into the Taylor expansion. However, to obtain the form given in question, it is necessary to neglect third and higher order terms in concentration, *i.e.*

$$z^2\frac{\partial^2 g}{\partial z^2}+2yz\frac{\partial^2 g}{\partial y\partial z}$$

This is justified if the variations of composition are gentle.

[60%]

Further simplification comes from the fact that the free energy cannot depend on the sign of the concentration gradient, in which case the term $\kappa_1(\mathrm{d}c/\mathrm{d}x)$ must be zero, leaving

$$g = g\{c_0\}+\kappa_2\frac{\mathrm{d}^2c}{\mathrm{d}x^2}+\kappa_3\left(\frac{\mathrm{d}c}{\mathrm{d}x}\right)^2$$

[20%]

3.

(a) The system of equations in the finite element analysis of heat flow take the form $\mathbf{K}\,\mathbf{T} = \mathbf{R}$, where $\mathbf{K}$ is the global thermal conductivity matrix, $\mathbf{T}$ is the temperature vector and $\mathbf{R}$ is the heat rate vector.

Convective boundary conditions

To accommodate a convective boundary condition at, for example, $x = L$ we must add h to the (L, L)'th position of the global thermal stiffness matrix, $\mathbf{K}$ and hT_∞ to the (L)'th position of the global heat rate vector, $\mathbf{R}$.

e.g.

$$\frac{k}{l}\begin{bmatrix} 1 & -1 & \dots & 0 \\ -1 & 2 & \dots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \dots & (1 + hl/k) \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ \vdots \\ T_L \end{Bmatrix} = \mathbf{R} + \begin{Bmatrix} 0 \\ 0 \\ \vdots \\ hT_\infty \end{Bmatrix}$$

Fixed temperature boundary conditions

To accommodate a fixed temperature boundary condition, for example $T = T_0$ at $x = 0$, we want to avoid substituting numbers directly into the temperature vector, $\mathbf{T}$, as this complicates the solution step.

Instead we adopt one of two approaches:

1. The big spring or penalty approach in which we add a large value $C\frac{k}{l}T_0$ to both sides of the equation at the $x = 0$ node. This effectively fixes the value at this node in an analogous way to applying a very stiff spring to the displacement of node in a mechanical analysis.

   e.g.

$$\frac{k}{l}\begin{bmatrix} (1+C) & -1 & \dots & 0 \\ -1 & 2 & \dots & 0 \\ \vdots & \vdots & & \vdots \\ 0 & 0 & \dots & 1 \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ \vdots \\ T_L \end{Bmatrix} = \mathbf{R} + \begin{Bmatrix} CT_0 \\ 0 \\ \vdots \\ 0 \end{Bmatrix}$$

2. The elimination approach in which we delete the entries to $\mathbf{K}$, $\mathbf{T}$ and $\mathbf{R}$ associated with the fixed temperature and modify $\mathbf{R}$ accordingly

   e.g.

$$\frac{k}{l}\begin{bmatrix} k_{22} & k_{23} & \dots & k_{2L} \\ k_{32} & k_{33} & \dots & k_{3L} \\ \vdots & \vdots & & \vdots \\ k_{L2} & k_{L3} & \dots & k_{LL} \end{bmatrix} \begin{Bmatrix} T_2 \\ T_3 \\ \vdots \\ T_L \end{Bmatrix} = \mathbf{R} - \begin{Bmatrix} k_{21}T_0 \\ k_{31}T_0 \\ \vdots \\ k_{L1}T_0 \end{Bmatrix}$$

Heat flux boundary conditions To accommodate a heat flux boundary condition, for example $q = q_0$ at $x = 0$, we simply add the heat flux to the associated position in the heat rate vector, $\mathbf{R}$. e.g.

$$\mathbf{K}\,\mathbf{T} = \mathbf{R} + \begin{Bmatrix} -q_0 \\ 0 \\ 0 \\ 0 \end{Bmatrix}$$

Note: the sign convention for the input heat flux requires that heat flowing in has a negative sign and heat flowing out has a positive sign

[40%]

(b) The local thermal conductivity matrices are:

$$\mathbf{k_1} = \frac{2}{0.2}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

$$\mathbf{k_2} = \frac{5}{0.4}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

$$\mathbf{k_3} = \frac{2}{0.1}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

Assemble the global matrices taking in to account element connectivity.

$$\begin{bmatrix} 10 & -10 & 0 & 0 \\ -10 & 22.5 & -12.5 & 0 \\ 0 & -12.5 & 32.5 & -20 \\ 0 & 0 & -20 & 20 \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{Bmatrix}$$

Modify the matrices to accommodate the convective boundary condition.

$$\begin{bmatrix} 10 & -10 & 0 & 0 \\ -10 & 22.5 & -12.5 & 0 \\ 0 & -12.5 & 32.5 & -20 \\ 0 & 0 & -20 & 70 \end{bmatrix} \begin{Bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 1000 \end{Bmatrix}$$

Modify the matrices to accommodate the fixed temperature boundary condition at T_1. This can be accomplished by the penalty method (not shown) or the elimination approach (shown below).

$$\begin{bmatrix} 22.5 & -12.5 & 0 \\ -12.5 & 32.5 & -20 \\ 0 & -20 & 70 \end{bmatrix} \begin{Bmatrix} T_2 \\ T_3 \\ T_4 \end{Bmatrix} = \begin{Bmatrix} 1000 \\ 0 \\ 1000 \end{Bmatrix}$$

Solve the system of equations using Gaussian elimination (these steps are not shown). This gives:

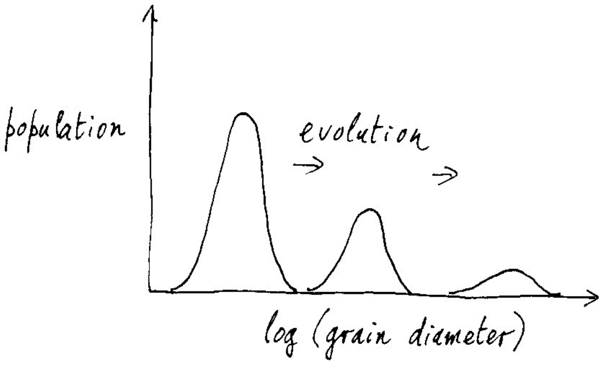
$$\begin{Bmatrix} T_1 \\ T_2 \\ T_3 \\ T_4 \end{Bmatrix} = \begin{Bmatrix} 100 \\ 68.0 \\ 42.4 \\ 26.4 \end{Bmatrix}$$

Note: The calculated values may differ in the 3rd or 4th significant figure if the penalty approach is used depending upon the constant used.

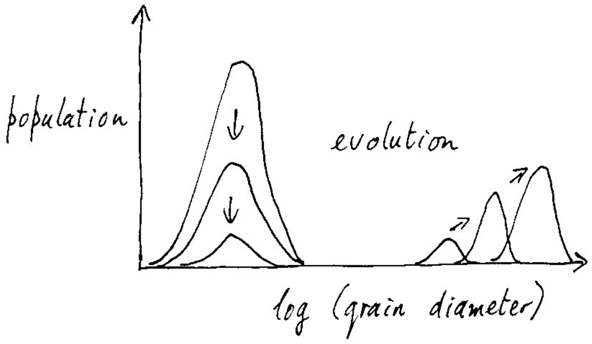
[60%]

4.

In normal grain growth, the average grain size increases with time, and the grain structure remains geometrically self-similar. The grain-diameter distribution is log-normal. Obviously, as the average diameter increases, the population of grains (no. per unit volume) must decrease:

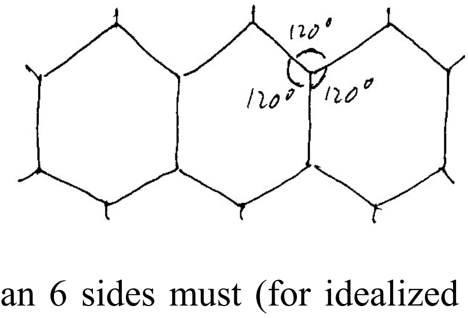


In abnormal grain growth, a few grains are favoured by low surface or strain energy and take over from the rest.

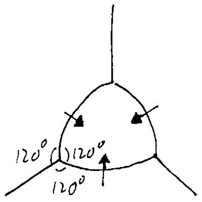


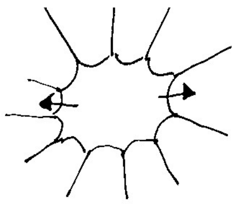
[25%]

Grain boundaries migrate if they are curved. Ideal grains with 6 sides can have straight boundaries and, on average, these have no tendency to grow or shrink.



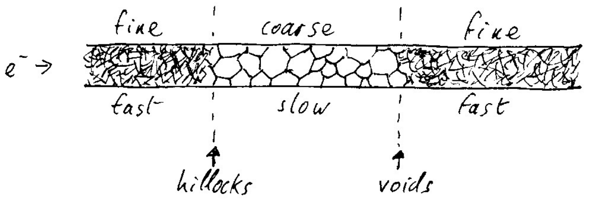
Grains with fewer than 6 sides must (for idealized junctions in which all the grain boundaries have equal energies and are in mechanical equilibrium meeting at 120°) have sides curved so that they will migrate inwards. These grains shrink and disappear. Grains with more than 6 sides have the opposite curvature of their sides and grow:



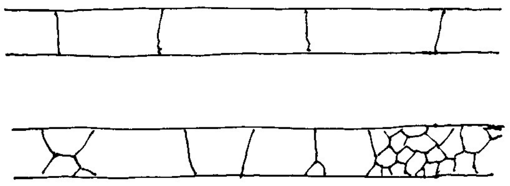


[25%]

When the metallization is based on aluminium, the main paths for atomic diffusion are grain boundaries and then the grain structure is directly relevant for electromigration. At a given temperature, variations in grain size along an interconnect lead to divergences of atomic flux and damage:



Ideally, the interconnects would have a bamboo grain structure. This can be approached on annealing, but stagnation may give a final structure which is a mixture of bamboo and polycrystalline segments. This is disastrous, as the bamboo segments block any atomic flux and the divergences are extreme.



[25%]

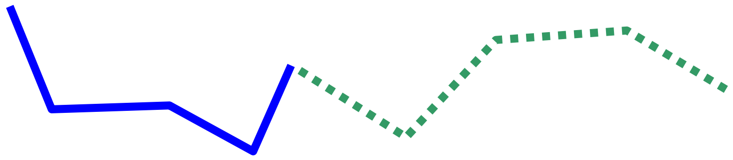
The vertex model has straight-sided grains. This is unrealistic in appearance and inconsistent with the link between grain-boundary curvature and migration. Nevertheless, by imposing straight sides, it is impossible for the forces at grain-boundary junctions to balance. In two dimensions, a grain with fewer than six sides will have an included angle of less than 120° at each vertex, which therefore moves inwards (i.e. the grain shrinks, just as would have been predicted from the boundary curvature if forces had been allowed to balance at the vertices).

The *Monte-Carlo model* can be most easily adapted, as the pixels in favoured grains can readily be assigned lower energies.

[25%]

5.

A simple coarse-grained representation of a diblock copolymer is shown as follows:

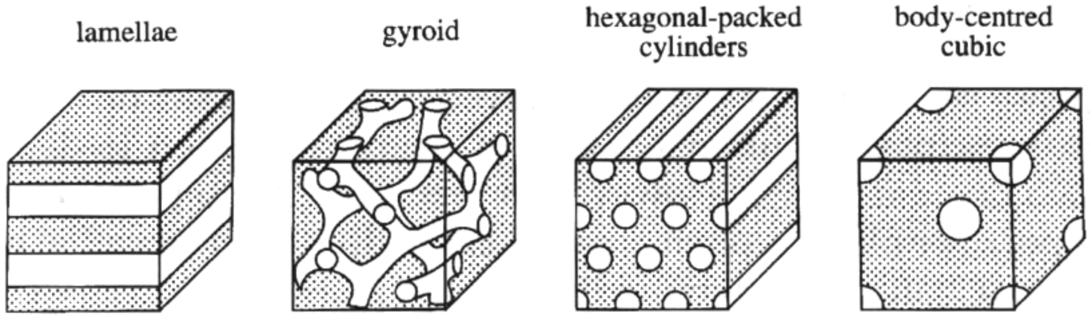


The two main parameters are:
(i) the length of A and B segments in terms of the number of monomers.
(ii) the interaction parameter χ (or the interaction energy ε_{AB} between the two types of segments).

For simplicity, we consider just a linear diblock copolymer (i.e. with sequence like …AAAABBBB…), where the fraction of A/B co-monomers is represented by the parameter f. It is then clear that the equilibrium phase for diblock copolymer is determined by the values of f and χN.

Below a certain value of χN (or above a certain temperature), the diblock polymer prefers to adopt a disordered (i.e. randomly mixed) phase for all compositions. At higher χN (lower temperatures), however, the system segregates into a number of spatially ordered phases (lamellar, gyroid, hexagonal, b.c.c.).

For symmetric diblocks ($f = 0.5$) there is no curvature of the interfaces, hence get a lamellar phase. With increasing asymmetry, the interfaces begin to curve, forming first cylinders of minority component (which pack in hexagonally in 2D) and then spheres (which pack in b.c.c. lattice).



Between lamellar and hexagonal phases, just below the limit of segregation, there is a peculiar bicontinuous cubic phase, known as the gyroid phase, which has some interesting properties (e.g. can form a 3D percolating network in both components, which leads to improved mechanical properties over random copolymer).

[30%]

Two appropriate models are: Dissipative Particle Dynamics (DPD), and Dynamic density functional theory (MesoDyn).

Key features;
DPD: particle based, soft non-bonded interaction potential, pairwise interactions-momentum conservation, energy dissipation, random noise (Brownian).

MesoDyn: concentration field based, free energy functional based, stochastic diffusion equation, mean field (Flory-Huggins) interactions.

To parameterise both types of models, require mean-field interaction parameters computed from molecular simulations, and descriptors of chain stiffness and/or DPD bead size, again obtained from molecular simulations.

[70%]

6.

In general, the partition function for a single oscillator is defined by the sum of Boltzmann factors over all microstates, with each state having degeneracy of one:

$$Z_1 = \sum_{\nu} \exp\left(-\beta E_{\nu}\right) = \sum_{\nu} \exp\left(-\beta hf\nu\right).$$

If we assume that there are an unlimited number of energy levels, then the sum over ν runs to infinity, which is simply the sum of a geometric series with first term unity and common ratio $\exp\left(-\beta hf\right)$ and gives result required:

$$Z_1 = \sum_{\nu=0}^{\infty} \exp\left(-\beta hf\nu\right) = \frac{1}{1-\exp\left(-\beta hf\right)}$$

[20%]

Hence, the partition function of a system of N indistinguishable, non-interacting oscillators can be written as:

$$Z_N = \frac{1}{N!}\left(Z_1\right)^N = \frac{1}{N!}\left(\frac{1}{1-\exp\left(-\beta hf\right)}\right)^N$$

The total internal energy of the system is defined in terms of the partition function as:

$$\begin{aligned}U &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \\ &= -N!\left(1-\exp\left(-\beta hf\right)\right)^N \cdot \frac{1}{N!} \cdot -Nhf\exp\left(-\beta hf\right) \cdot \left\{1-\exp\left(-\beta hf\right)\right\}^{-N-1} \\ &= \frac{Nhf\exp\left(-\beta hf\right)}{1-\exp\left(-\beta hf\right)}\end{aligned}$$

which is directly proportional to system size and has the correct units.

[20%]

Hence, the isovolumetric heat capacity can be calculated as:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial \beta}{\partial T}\right)_V \left(\frac{\partial U}{\partial \beta}\right)_V = -\frac{1}{k_{\mathrm{B}}T^2}\frac{\partial}{\partial \beta}\left(\frac{Nhf\exp(-\beta hf)}{1-\exp(-\beta hf)}\right)$$

$$= \frac{N(hf)^2}{k_{\mathrm{B}}T^2}\left(\frac{\exp(-2\beta hf)}{\{1-\exp(-\beta hf)\}^2} + \frac{\exp(-\beta hf)}{1-\exp(-\beta hf)}\right)$$

$$= Nk_{\mathrm{B}}(hf)^2\beta^2\left(\frac{\exp(-2\beta hf)}{\{1-\exp(-\beta hf)\}^2} + \frac{\exp(-\beta hf)}{1-\exp(-\beta hf)}\right)$$

which again is directly proportional to system size and has the correct units. The high temperature limit (not required) taken as $\beta \to 0$ gives $C_V = Nk_{\mathrm{B}}$, which is in agreement with classical equipartition, assuming that the temperature is high enough for all vibrational modes to be excited.

[30%]

If the system of oscillators is coupled by some long-ranged potential (pairwise acting, or otherwise) then the standard statistical mechanics approach of computing thermodynamic properties analytically via the partition function will become intractable. This is due to the difficulty of factorizing the total partition function Z_{N} in terms of the single oscillator partition function Z_1, which is only straightforward for non-interacting systems of indistinguishable oscillators where $Z_N = \frac{1}{N!}(Z_1)^N$.

An alternative approach can be used, which depends on statistical sampling of the thermodynamic states of the system weighted by their Boltzmann probabilities. A suitable computational method for a system at constant volume and temperature is the Metropolis Monte Carlo (MMC) algorithm. We will make the simplifying assumptions that the system of N oscillators is confined to a k-dimensional square lattice with periodic boundary conditions and one oscillator per site, and that the total energy can be calculated as a function of all the vibrational quantum numbers $E_N(v_1, v_2, \ldots, v_N)$. It may be that the energy is only a more local function of rotational states, or that a lattice sum (Ewald) method can be used to speed up the calculation, but this is not necessary.

The simulation then proceeds 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. total energy has converged to steady-state value when averaged over all sampled configurations).

A suitable initialization condition might be with all oscillators set to $\nu = 0$ ($T = 0$ K). A suitable ergodic perturbation in step 2 might be changing the vibrational quantum number of a randomly selected lattice site by ±1, provided $\nu \geq 0$. However, there are many other choices that would result in a more efficient simulation.

Once an equilibrated simulation has been generated, then the partition function can be computed by thermodynamically integrating along a pathway from $T = T_1$ to T_2.

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial(\ln Z)}{\partial \beta} \qquad \therefore Z = \exp\left(-\int_{T_1}^{T_2} E \cdot \mathrm{d}\beta\right)$$

[30%]

7.

The pair potential approximation: terminate the many-body expansion of the potential energy at the second term,

$$\text{i.e. } U = \sum_i V_1(r_i) + \sum_{ij} V_2(r_{ij})$$

In other words, ignore higher order terms such as the three-body potential. V_2 (the pair potential) is dependent only on the distance between two atoms and has no angular dependence.

Main advantages: computationally inexpensive to use and relatively easy to construct using very few fitting parameters.

Main disadvantage for metals: does not account for the cohesive energy of the electron gas. Electron density dependent potentials should be used such EAM and Finnis-Sinclair. Pair potentials incorrectly predict that the elastic constants $c_{12} = c_{44}$ (the Cauchy relation). They also give an energy/atom that is linear in atomic coordination. The energy/atom should decrease non-linearly with increasing coordination (concave negative).

Current methods for simulating metals are the embedded atom method (EAM) and Finnis-Sinclair potentials.

[30%]

Embedded Atom Method (EAM)

This is an empirical implementation of effective medium theory in which the total energy is written as the sum of 2 terms:

$$U_{tot} = U_A + U_R$$

where U_A = the attractive energy required to embed an atom into the density ρ of the neighbouring atoms where ρ is taken to be the superposition of atomic charge densities ρ^A

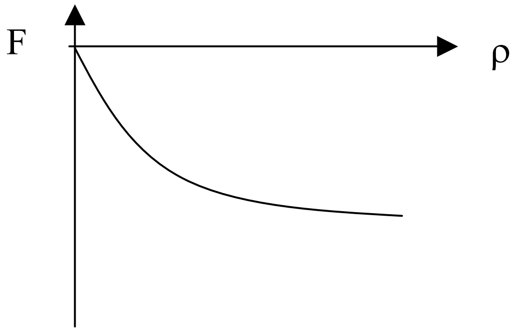
$$U_A = \sum_i F(\rho_i), \qquad \rho_i = \sum_{i_j} \rho^A(r_{ij})$$

and U_R = repulsive overlap energy between atom cores (a pair potential)

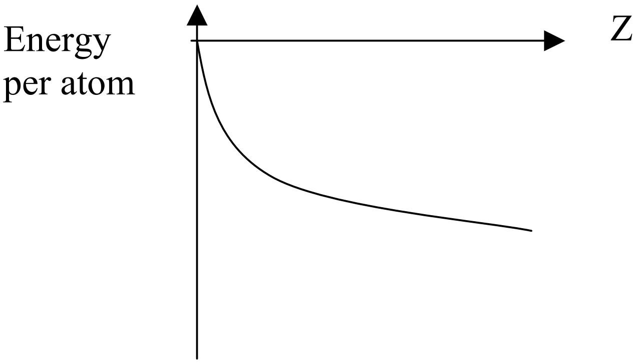
$$U_R = \frac{1}{2}\sum_{ij} \phi(r_{ij})$$

Various functions are used for $F(\rho_i)$ and $\phi(r_{ij})$ (e.g. power laws, exp.) and are fitted to match the bulk properties of metal (lattice parameters etc)

$F(\rho_i)$ should be a non-linear function of ρ (concave negative)



This reflects the fact that the energy/atom decreases non-linearly with increasing co-ordination Z

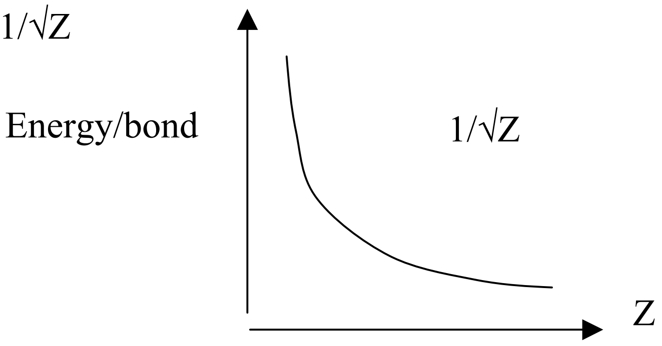


Finnis-Sinclair potential

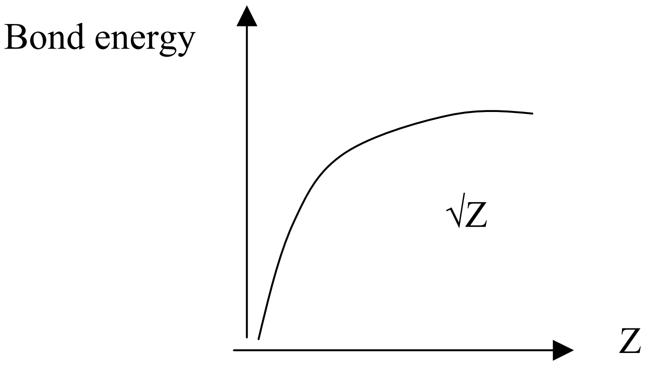
This is related to EAM but $F(\rho_i)$ takes a specific functional form.

Recall that the bond order (strength) $b \sim 1 \sqrt{Z}$ (from observation and tight-binding theory)

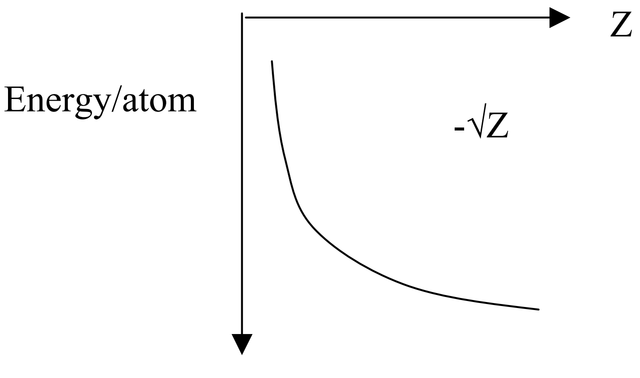
i.e. the energy/bond ~ $1/\sqrt{Z}$



Thus the bond energy/atom ~ $\sqrt{Z}$ (i.e. $(1/\sqrt{Z})Z$ or cohesive energy/atom)



or the energy /atom ~ $-\sqrt{Z}$ (negative of cohesive energy)



Thus in the Finnis-Sinclair model:

$$U_A = -\sum_i \sqrt{\rho_i}\,, \qquad \text{and} \quad \rho_i(r) = (r-d)^2 \quad \text{(a pair potential)}$$

$$U_R = \frac{1}{2}\sum_{ij}\phi(r_{ij}), \qquad \phi(r) \text{ is also a pair potential.}$$

[30%]

Calculation

$$U(r) = D\left\{\exp\left[-2\alpha\left(r-r_0\right)\right] - 2\exp\left[-\alpha\left(r-r_0\right)\right]\right\}$$

Hence $$\frac{dU}{dr} = D\left\{-2\alpha\exp\left[-2\alpha\left(r-r_0\right)\right] + 2\alpha\exp\left[-\alpha\left(r-r_0\right)\right]\right\}$$

Thus in equilibrium $\frac{dU}{dr} = 0$ when $r = r_0$. Since we assume nearest neighbour interactions only then r_0 is the 1st nearest neighbour distance in the fcc structure:

$$r_0 = \frac{a_0\sqrt{2}}{2} = 2.552 \text{ Å}$$

The cohesive energy $$E_{coh} = \frac{336 \times 10^3}{6.022 \times 10^{23} \times 1.602 \times 10^{-19}} = 3.483 \text{ eV/atom}$$

The total energy of N atoms at the equilibrium spacing is given by:

$$U_{tot}(N) = \frac{1}{2}N\sum_{nnb}U(r_0) = \frac{1}{2}N(-12D)$$

since there are 12 nearest neighbours. Thus the energy per atom is -6D.

Therefore $D = \frac{E_{coh}}{6} = 0.581$ eV/atom

$B = \nu \frac{\partial}{\partial \nu}\left(\frac{\partial E}{\partial \nu}\right)$. For the fcc lattice $\nu = \frac{a_0^3}{4}$. Therefore $\nu = \frac{r^3}{\sqrt{2}}$ where r is the nearest neighbour spacing.

Thus $\frac{\partial}{\partial \upsilon} = \frac{\sqrt{2}}{3r^2}\frac{\partial}{\partial r}$ and therefore $B = \frac{\sqrt{2}}{9} r \frac{\partial}{\partial r}\frac{1}{r^2}\frac{\partial}{\partial r}E$.

In equilibrium when $\frac{\partial E}{\partial r} = 0$ then $B = \frac{\sqrt{2}}{9r_0}\left.\frac{\partial^2 E}{\partial r^2}\right|_{r=r_0}$

$$\frac{\partial^2 E}{\partial r^2} = (6)D\left\{4\alpha^2 \exp\left[-2\alpha\left(r - r_0\right)\right] - 2\alpha^2 \exp\left[-\alpha\left(r - r_0\right)\right]\right\}$$

Therefore $B = \frac{12 D \alpha^2 \sqrt{2}}{9 r_0}$

Hence $\alpha = \left(\frac{9 B r_0}{12 D \sqrt{2}}\right)^{1/2} = \left(\frac{9 \times 134 \times 10^9 \times 2.552 \times 10^{-10}}{12 \times 0.581 \times 1.602 \times 10^{-19} \times \sqrt{2}}\right)^{1/2}$ $=1.396 \times 10^{10}$ m^{-1}

Thus, fitted parameters are $r_0 = 2.552$ Å, $D = 0.581$ eV and $\alpha = 1.396$ Å^{-1}

[40%]