# MASTER OF PHILOSOPHY Modelling of Materials (2005)

## Examiner's Solutions to Paper 2

## SECTION A

### 1(a)

**Integer** variables hold integer (whole number) quantities precisely, within a certain range. Thus an integer value will always be identical regardless of the calculation which produced it (ignoring overflow and truncation). Integers are used as subscripts for arrays, and as loop counters (the inaccuracies associated with real variables make these unsuitable for loops with many iterations).
**Real** variables hold values (which need not be integers) approximately. Once again, the values must lie within a certain range; but this range is much wider than the range for integers. The *machine epsilon* gives an indication of the accuracy to which such values are held: this is smallest quantity ε such that `1.0 + ε .ne. 1.0` when evaluated by the computer. Real variables do not have sufficient accuracy for all calculations (especially for ill-conditioned problems), but are often more than adequate for many (such as the plotting of graphs).
**Double precision** variables hold similar values to real variables, possibly with a larger range. However, the machine epsilon will be much smaller than for real variables; double precision values are typically held to twice as many digits of accuracy as real ones. Double precision variables require much more store than real ones (typically twice as much), and calculations on double precision values normally require longer than calculations on reals.

### 1(b)

The exchange energy is due to the Pauli exclusion principle, which automatically keeps electrons of parallel spin out of each others way, irrespective of their mutual repulsion. Because of the Coulomb repulsion between electrons, this effectively reduces the total energy of the system by what is called exchange energy. Correlation energy is the additional amount by which the energy is reduced due to the effect of the Coulomb repulsion further separating the electrons, in particular the ones with opposite spin.

The Local Density Approximation assumes that the exchange -correlation energy density at a particular point depends only upon the particle density at that point.

The c-planes are held to together by Van der Waals forces which are extremely weak, and are caused by instantaneous dipoles in the electron distributions of the planes. This is essentially electron correlation, which we have approximated crudely by the LDA, so the results are not very accurate (bonding is overestimated). In contrast the in-plane bonding is strong and dominated by the Hartree and kinetic energy terms, so that the errors due to the LDA are proportionally less.

1(c)

The lattice type is cubic-F, with a motif of S at (0,0,0) and Li at $\pm\left(\frac{1}{4},\frac{1}{4},\frac{1}{4}\right)$.

1(d)

In the case of electrical current, the flux is the current, and the force is the e.m.f. = $-\frac{\partial\phi}{\partial z}$ (potential gradient).

In heat flux, the force is $-\frac{1}{T}\frac{\partial T}{\partial z}$ and there is flux of heat.

In diffusion, the force is the chemical potential gradient $-\frac{\partial\mu_i}{\partial z}$ and the flux is that of matter. Note that it would be wrong to say that the force in this case is the concentration gradient.

1(e)

For a case where a thin layer of a fixed quantity of solute is plated onto a semi-infinite bar, a solution consistent with Fick's laws and the boundary conditions is

$$\text{boundary conditions:} \qquad \int_0^\infty C\{x,t\}dx = B \quad \text{and} \quad \mathrm{C}\{\mathrm{x},\mathrm{t}=0\}=0$$

$$C\{x,t\} = \frac{B}{\sqrt{\pi D t}} \exp\left\{\frac{-x^2}{4Dt}\right\}$$

This is a specific exponential function known as a Gaussian function. Now imagine that we create the diffusion couple, by stacking an infinite set of thin sources on one end of a semi-infinite bar of a different composition. Diffusion can then be treated by taking a whole set of exponential functions as above, each representing a thin layer but slightly displaced along the x-axis. This series of stacked exponential sources can then be summed (integrated) to find the net interdiffusion profile. The integral is in fact the error function, an integration of exponential sources

$$erf\{x\} = \frac{2}{\sqrt{x}} \int_0^x \exp\left\{-u^2\right\} du$$

1(f)

Design requirements for which generic attributes can usefully be stored in a selection database of shaping processes:

Technical:
material to be shaped – list of viable materials
product size or weight – numeric ranges
component shape and geometry – list of viable shapes/geometries
manufacturing constraints – searchable text

Quality:
Surface finish – numeric range
Dimensional precision – numeric range

Examples of quality requirements which do not fit this approach:
Avoidance of defects, and final product properties
Generic ranges would be very broad and non-discriminating – the extent of defects and the product properties depend in a complex, coupled way on the type of process variant (casting, forging etc), on the material being processed (Fe, Al, Cu etc) and on design details (such as component size, which affects things like cooling rates). A good way to approach this complexity, within a narrower domain of processing, is to build process models which capture the coupling between processing outcome and process, material and design.

## 1(g)

Intrinsic is used to describe those properties insensitive to microstructure. Examples are the elastic properties, dependent rather directly on interatomic potentials.

Extrinsic is used to describe those properties sensitive to microstructure. An example is the yield stress, which involves the motion of dislocations, and may depend on grain size, precipitate distribution or dislocation density.

Intrinsic properties are appropriately modelled at the atomic level. Extrinsic properties typically need modelling at greater length scales, sufficient to permit a description of the distribution of microstructural features.

## 1(h)

The sporadic appearance of a new phase within a uniform original phase as a result of thermal fluctuations constitutes homogeneous nucleation. When the original phase is non-uniform in some way (because of its surface, grain boundaries, dislocations or other phases within it), these heterogeneities are likely to be preferred sites for nucleation of the new phase; this is heterogeneous nucleation.

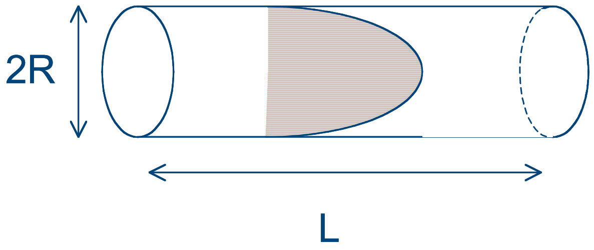
For the detection of homogeneous nucleation, the influence of heterogeneities must be limited. For solidification, for example, the liquid can be dispersed as an emulsion in another, inert liquid. It is possible to make the emulsion finer and finer, so that eventually the number of droplets of the liquid exceeds the number of heterogeneous particles originally present in the liquid. There must then be a population of droplets in which there are no particles, and in which the nucleation of solidification can be expected to be homogeneous. (This assumes that the liquid-liquid interface is not itself a potent substrate for heterogeneous nucleation.)

The rate depends on the atomic mobility, the thermodynamic driving force for transformation, and the energy per unit area $\gamma$ of the interface between the original and new phases. The first two can be estimated or measured to good accuracy, but $\gamma$ is rarely known well. Unfortunately, the nucleation rate is particularly sensitive to $\gamma$, as the critical work of nucleus formation is proportional to $\gamma^3$.

In modelling heterogeneous nucleation, the interactions with the nucleant substrates need to be taken into account, introducing further uncertainties. The potency of a substrate is commonly described in terms of the contact angle $\theta$ of the new phase on the substrate. Unfortunately, $\theta$ is mostly not known, and it may show some dispersion of values. The population, dispersion and size distribution of the nucleant substrates are also likely to be imperfectly known at best.

1(i)

Flow through volume element in pipe $dV = 2\pi r.\upsilon.dr$



and we are told that

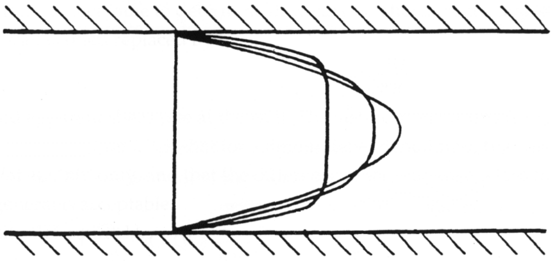
$$v = \frac{\Delta p}{4L\eta}\left(R^2 - r^2\right)$$

for a Newtonian fluid (laminar flow) and so substituting and integrating over the radius

$$dV = \frac{\pi}{2L\eta}\Delta p\left(R^2 r - r^3\right)dr$$

we get $$V = \frac{\pi R^4}{8L\eta}\Delta p$$

Since most thermoplastic polymers are shear thinning (due to chain alignment in shear field) then the viscosity would be a decreasing function of the shear rate at any point in the tube. The changes in flow profile are shown qualitatively below, but result in a net increase in volume flow rate if all other parameters remain fixed.



1(j)

The term molecular chaos refers to the fact that molecular dynamics trajectories calculated to finite numerical precision will diverge from the true continuous trajectories at an exponential rate, irrespective of the precision of the numerical algorithms used to perform the integration. This can be demonstrated by dropping a perfectly elastic sphere directly onto a fixed elastic sphere, and simulating the bouncing motion under gravity. Analytic solution of the equations of motion yields a solution that predicts an infinite number of bounces, however all numerical simulations will only produce a finite number due to the exponential accumulation of integration errors. However, molecular chaos is not a significant problem in most molecular dynamics simulations because the desired objective is not to predict the *exact* molecular conformation at some point in the future, but instead to compute thermodynamic properties of the system that depend on ensemble properties that are not sensitive to the exact future state of the system. In other words, the MD simulations are used to study ensemble average quantities at a particular thermodynamic state point, and therefore it is irrelevant which particular microstate the system is in provided it does not deviate systematically from the desired thermodynamic macrostate. The latter condition is guaranteed by ensuring that the Hamiltonian of the extended system is conserved by the equations of motion.

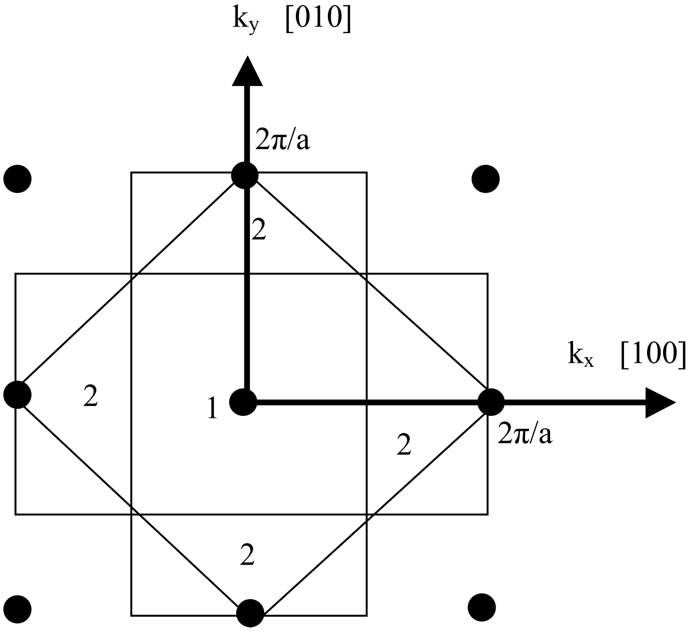
SECTION B

2.

Answer relies on the fact (which need not be proved) that the number of allowed electron states in a band is 2N where N is the number of primitive unit cells in the solid. This is an even number, therefore solids with one electron per primitive unit cell will have half filled bands and will be conductors. On the other hand, solids with two electrons per primitive unit cell will have full bands and will normally be insulators. However, if the band gap is small then at finite temperatures these solids could also be semiconductors. In addition if the band structure is anisotropic and there is band overlap then the solid would be semimetallic (small overlap) or conducting if the overlap is large.

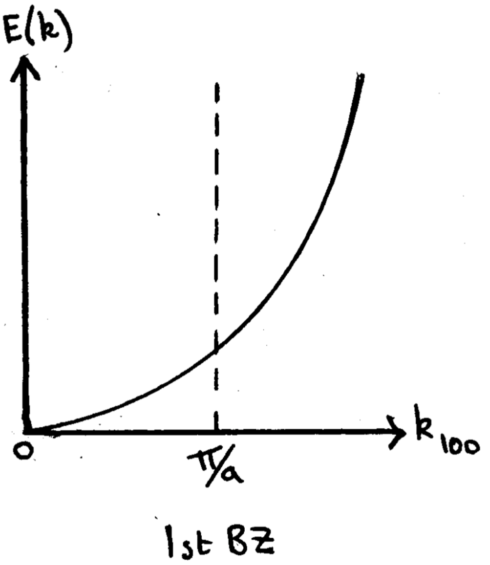
[25%]

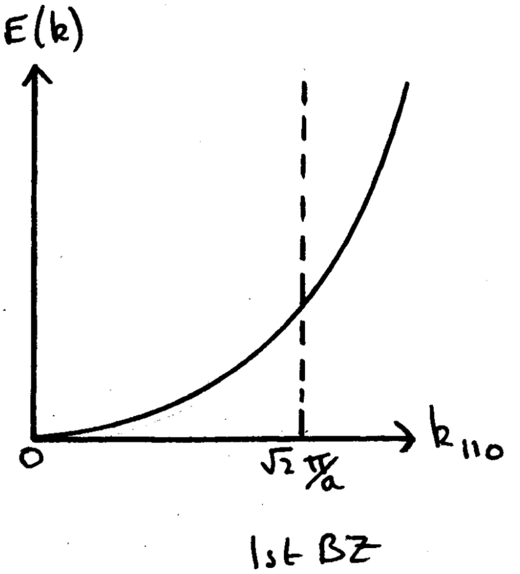
(i) Brillouin zones



[25%]

(ii) E(k) along [100] and [110] for free electrons (parabolic)





[15%]

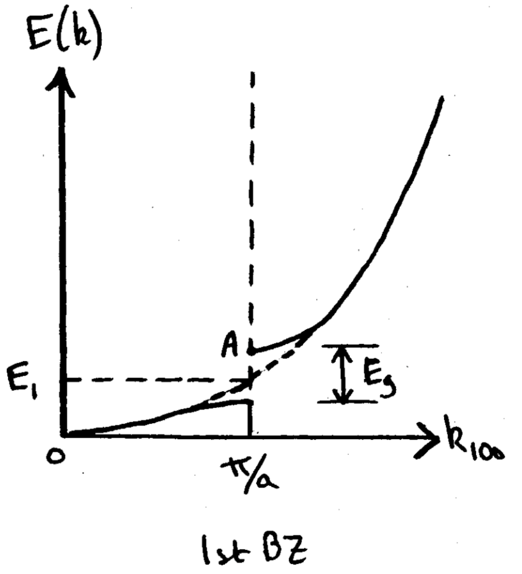
(iii) For free electrons $E(k) = \dfrac{\hbar^2 k^2}{2m}$

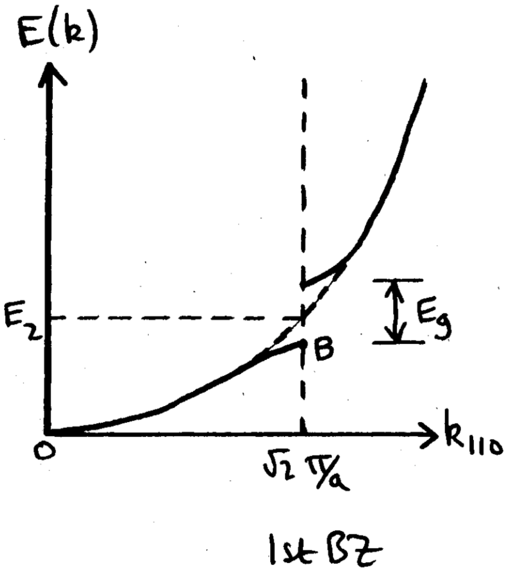
Along [100] at the 1st BZ boundary $E\left(\dfrac{\pi}{a}\right) = \dfrac{\hbar^2 \pi^2}{2ma^2}$ (=$E_1$ say)

Along [110] at the 1st BZ boundary $E\left(\dfrac{\sqrt{2}\pi}{a}\right) = \dfrac{\hbar^2 \pi^2}{ma^2}$ (=$E_2$ say)

[15%]

(iv) When there are electron-ion interactions energy gaps appear at the Brillouin zone boundaries. This is due to Bragg reflection at these planes. The electron travelling waves turn into standing waves at these special values of k and these standing waves have two different energies, one larger and one smaller than the free electron value. These energies split symmetrically about the free electron energy and together constitute an energy gap. If the energy gap at the 1st BZ boundary is $E_g$ then the E(k) curves may look like this:





[15%]

For the solid to be a semiconductor *E(B)* must be slightly lower than *E(A)* otherwise there would be no overall band gap.

$E(A) = E_1 + E_g/2$ and $E(B) = E_2 - E_g/2$

In the limit when $E(A) = E(B)$ $\quad E_1 + E_g/2 = E_2 - E_g/2$

i.e. $$Eg = E_2 - E_1 = \frac{\hbar^2\pi^2}{2ma^2}$$

This is the minimum energy gap at the 1st BZ boundary for the solid to be a semiconductor. Smaller energy gaps would result in a conductor.

[15%]

3.

Calculation of solidus and liquidus line for an ideal solution.

For an ideal solution $$\Delta G^M_{(l)} = RT\left(X_A \ln X_A + X_B \ln X_B\right)$$
$$\Delta G^M_{(s)} = RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

However, if these are plotted out the curves would be coincident due to the fact that the starting conditions are not the same. i.e

$$xA(s) + yB(s) = A_xB_y(s) \qquad (1)$$

and $$xA(l) + yB(l) = A_xB_y(l) \qquad (2)$$

Consider equation (1)

$$xA(s) + yB(s) = A_xB_y(s) \qquad \Delta G^M = RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

By adding the reaction $xA(l) = xA(s)$ $$\Delta G = -x\left(\Delta H_{f(A)} - \frac{T\Delta H_{f(A)}}{T_{f(A)}}\right)$$

gives $xA(l) + yB(s) = A_xB_y(s)$

$$\Delta G^M = RT\left(X_A \ln X_A + X_B \ln X_B\right) - x\left(\Delta H_{f(A)} - \frac{T\Delta H_{f(A)}}{T_{f(A)}}\right)$$

Similarly for equation (2)

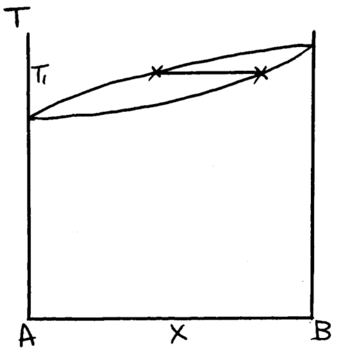
$$xA(l) + yB(l) = A_xB_y(l) \qquad \Delta G^M = RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

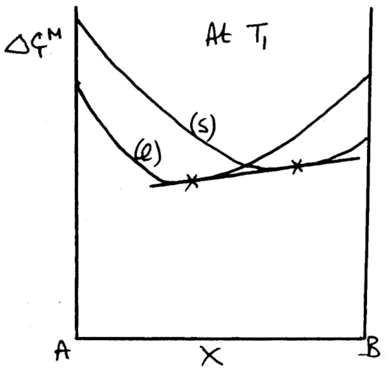
By adding the reaction $yB(s) = yB(l)$ $$\Delta G = y\left(\Delta H_{f(B)} - \frac{T\Delta H_{f(B)}}{T_{f(B)}}\right)$$

Gives $xA(l) + yB(s) = A_xB_y(l)$

$$\Delta G^M = RT\left(X_A \ln X_A + X_B \ln X_B\right) + y\left(\Delta H_{f(B)} - \frac{T\Delta H_{f(B)}}{T_{f(B)}}\right)$$

As both equations relate to the same starting conditions it is now possible to draw the curves and tangents to obtain the position of the liquidus and solidus.





[70%]

On cooling the enthalpy contribution to the free energy curve increases as it is almost independent of temperature whereas the entropy term contribution is very temperature dependent. When the enthalpy term predominates the free energy curve undergoes changes in curvature and the solid solution breaks down either by a nucleation and growth or spinodal mechanism. This can be drawn schematically.

[30%]

4.

(a) Mass of panel: $m = bld\rho$

Failure when max stress = material strength: $\sigma_y = \dfrac{3Wl}{2bd^2}$

Hence free variable, depth, given by: $d = \left(\dfrac{3Wl}{2b\sigma_y}\right)^{1/2}$

Substituting into equation for mass: $m = bl\rho\left(\dfrac{3Wl}{2b\sigma_y}\right)^{1/2}$ = constant $\dfrac{\rho}{\sqrt{\sigma_y}}$

Hence minimise mass by maximising performance index. $M = \dfrac{\sqrt{\sigma_y}}{\rho}$

[25%]

(b) Thickness and strength related by: $\sigma_y = \dfrac{3Wl}{2bd^2}$

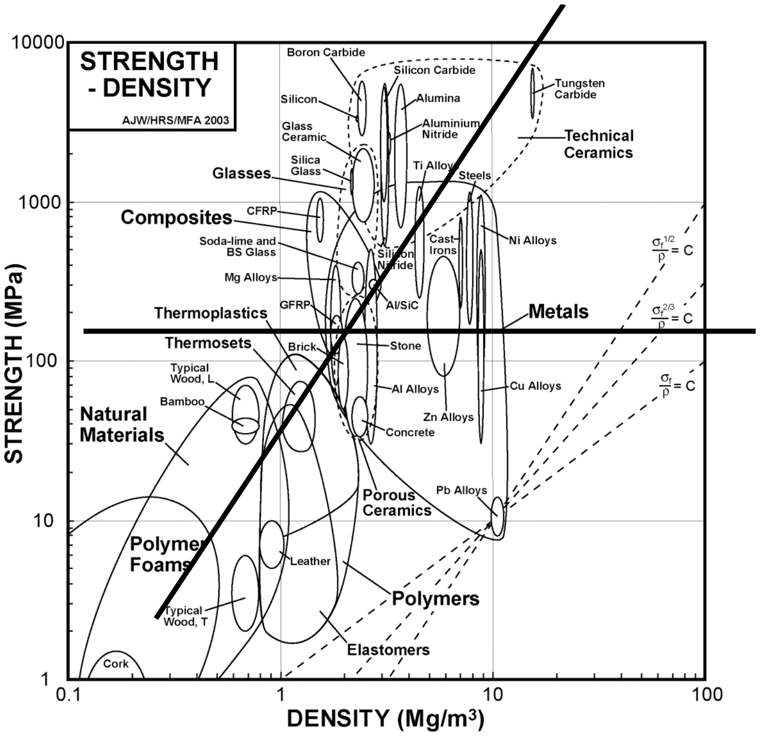
Hence maximum allowable thickness converts to a minimum allowable strength (depending on values for load, length, width and max. thickness)

[25%]

(c) On property chart, minimum allowable strength is a horizontal line (search above this line); and performance index is a line of slope 2 (guideline of correct slope indicated on the figure). Move performance line up to the left to leave short-list of remaining materials.

[25%]

Performance index, leaving possible materials above line



e.g. strength limit

(d) Selection results

| Material | Comments |
|---|---|
| Ceramics (alumina etc) | Disregard – data for compressive strength |
| CFRP | The best, but expensive |
| Mg alloys | The best of the metals |
| GFRP, Al alloys, Al-SiC | Lower cost alternatives |
| Ti alloys | More expensive alternative |
| Wood, higher strength polymers | May be below strength limit (i.e. need to be to thick), but would be low cost |

[25%]

5.

Answer should include the following:

A definition of “mesoscale” and mesoscale modelling. Although the term mesoscale is often used in a loose sense to refer to time and length scales intermediate between the microscopic and the macroscopic levels, it can be defined more precisely as any intermediate scale at which the phenomena at the next level down can be regarded as always having equilibrated, and at which new phenomena emerge with their own relaxation times. A classical example is Brownian motion and a good answer will briefly review this phenomenon in order to illustrate he general principle of mesoscale simulations: that any irrelevant degrees of freedom are integrated out, leaving the remainder to vary in the resulting equilibrated mean field. The definition of mesoscale modelling could also include a sketch of the spatio-temporal hierarchy of modelling techniques, showing the mesoscale bridging the gap between atomistic and continuum levels. [25%]

A description of the different sub components of mesoscale modelling: coarse-graining, parameterisation and construction of the model. Coarse-graining involves discarding as many degrees of freedom as possible from a system, whilst retaining universal features. Coarse-graining (either spatially or temporally) is a regressive process and is continued until a level of description is reached appropriate to the phenomena of interest. Reference to coarse-grained structural models for polymers would usefully illustrate the process. Parameterisation is a way of representing lost degrees of freedom. Construction of the model may be done by using either lattice mesoscale methods, particle based mesoscale methods or within a continuum framework. Each method could be illustrated with specific techniques, e.g lattice gas automata, lattice director models, lattice chain models, Brownian and Stokesian dynamics, and dissipative particle dynamics. [45%]

A list of areas of use: modelling hydrodynamic flow; long time scale phase segregation or transformation; processing of polymer melts; prediction of bulk mechanical properties to parameterise finite element simulations. [15%]

Mesoscale modelling packages: Mesodyn (dynamic mass DFT code), DPD (dissipative particle dynamics code), Lattice chain model (polymers). [15%]

## SECTION C

6.

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

$$Z_1 = \sum_J \exp(-\beta E_J) = \int_0^\infty \exp\left(-\frac{\beta\hbar^2 J^2}{2I}\right)dJ$$

Hence, the partition function of a system of $N$ indistinguishable, non-interacting rotors is:

$$Z_N = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}\left(\int_0^\infty \exp\left(-\frac{\beta\hbar^2 J^2}{2I}\right)dJ\right)^N$$

$$\therefore Z_N = \frac{1}{N!}\left(\frac{1}{2}\sqrt{\frac{2\pi I}{\beta\hbar^2}}\right)^N = \frac{1}{N!}\left(\frac{\pi I}{2\beta\hbar^2}\right)^{N/2}$$

[20%]

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

$$F = -k_B T \ln Z = -k_B T \ln\left\{\frac{1}{N!}\left(\frac{\pi I}{2\beta\hbar^2}\right)^{N/2}\right\}$$

Hence, using Stirling's approximation (justified as N is very large):

$$F = -k_B T\left\{\frac{N}{2}\ln\left(\frac{\pi I}{2\beta\hbar^2}\right) - \ln N!\right\} = -k_B T\left\{\frac{N}{2}\ln\left(\frac{\pi I}{2\beta\hbar^2}\right) - N\ln N + N\right\}$$

$$= -\frac{Nk_B T}{2}\left\{\ln\left(\frac{\pi I}{2\beta\hbar^2}\right) - \ln N^2 + \ln e^2\right\}$$

$$= \frac{Nk_BT}{2}\ln\left(\frac{2\beta\hbar^2e^2}{I\pi N^2}\right)$$

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

$$U = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -N!\left(\frac{\pi I}{2\beta\hbar^2}\right)^{-N/2}.\frac{1}{N!}.\frac{N}{2}.\frac{-\pi I}{2\beta^2\hbar^2}.\left(\frac{\pi I}{2\beta\hbar^2}\right)^{N/2-1}$$

$$U = \frac{N}{2}.\frac{\pi I}{2\beta^2\hbar^2}.\left(\frac{\pi I}{2\beta\hbar^2}\right)^{-1} = \frac{N}{2}.\frac{\pi I}{2\beta^2\hbar^2}.\frac{2\beta\hbar^2}{\pi I}$$

$$= \frac{N}{2\beta}$$

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

Hence, the isovolumetric heat capacity can be calculated as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{N}{2\beta}\right)_V = \frac{Nk_B}{2}$$

which corresponds exactly to the classical result expected from equipartition for a two dimensional rotor with one angular degree of freedom. We have assumed that the temperature is sufficiently high enough for all the rotational states to be excited.

[50%]

If the system of rotors 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 rotor partition function $Z_1$, which is only straightforward for non-interacting systems of indistinguishable particles 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* rotors is confined to a two-dimensional square lattice with periodic boundary conditions and one rotor per site, and that the total energy can be calculated as a function of all the rotational quantum numbers $E_N(J_1, J_2, \ldots J_N)$. 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 $E_\mu$
2. Generate a new state ν by a small ergodic perturbation to state μ and evaluate $E_\nu$
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 $\exp[-\beta(E_\nu - E_\mu)]$
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 rotors set to $J = 0$ ($T = 0$ K). A suitable ergodic perturbation in step 2 might be changing the rotational quantum number of a randomly selected lattice site by ±1, provided $J \geq 0$. 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 $T_2$.

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

[30%]

7.

Bonding characteristics of ionic solids:

Bonding results from electrostatic interactions between oppositely charged ions $\pm q^2/r$ (long range, pairwise, attraction and repulsion). Alkali halides or I-VII compounds are typical.

Valence electron distributions are spherical, highly localised and similar to that of free atoms. However, electron transfer occurs between atoms to form complete electron shells. This leaves the solid composed of positively and negatively charged ions. In the case of KCl, for example, one of the valence electrons on the K atom transfers to the Cl atom giving both atoms18 electrons but leaving K positively charged and Cl negatively charged. The spherical nature of the valence electron distribution means that to a good approximation the interatomic potentials will be spherically symmetric (i.e. radial and pairwise) and will be dominated by the 1/r Coulombic interaction. Illustration of a I-VII compound should show spherical distributions and charge transfer.

The transition from I-VII compounds to II-VI compounds and then to III-V and IV-IV compounds progressively leads to increasing covalency. Atoms become more and more difficult to ionize. Electron distributions become less spherical and electrons become more delocalised in the interstitial regions of the crystals. This is typically along near neighbour directions resulting in bond formation. So, for example, the electron concentration along near neighbour lines in a group IV compound may be 5 $e/\text{Å}^3$ compared to only 0.1 $e/\text{Å}^3$ in a I-VII compound. In II-VI and III-V compounds there may be some residual charge about the ion cores. Illustrations of charge distributions should reflect these changes in symmetry and distribution.

[25%]

The Madelung constant is the coefficient of the electrostatic energy of an ionic crystal. It is a lattice summation which depends on the structure of the crystal. Since the electrostatic energy falls off slowly with distance (1/r) the summation is not well defined for an infinite crystal. It is conditionally convergent and will depend on the order of the summation. However, there are ways to circumvent this (e.g. considering electrically neutral cells) and convergent sums can be obtained. In three dimensions this usually requires a computer. Defined with respect to the nearest neighbour distance $R$, the Madelung constant $\alpha$ is given by

$$\frac{\alpha}{R} = \sum_j \frac{(\pm)}{r_j}$$

where $r_j$ is the distance from the *jth* ion to a reference ion. If the reference ion is negatively charged then the + sign applies to positively charged ions in the summation and the – sign to negatively charged ions. The electrostatic energy is therefore given by:

$$U_e(R) = -\frac{\alpha q^2}{4\pi\varepsilon_o R} \qquad \text{(per ion pair)}$$

The electrostatic energy is the dominant contribution to the total energy but overestimates the binding since it ignores the positive potential due to short-range core-core repulsion. This is typically represented by an inverse power law or a Born-Mayer exponential function. So, for example, the total energy per ion pair could be written:

$$U(R) = -\frac{\alpha q^2}{4\pi\varepsilon_o R} + \lambda e^{-R/\rho}$$

[25%]

For the one-dimensional crystal consisting of *2N* ions (*N* molecules) with an inverse power repulsive term the total energy is given by:

$$U(R) = N\sum_j U_{ij} \qquad \text{(i≠j, where i is the reference ion)}$$

where $U_{ij} = -\frac{q^2}{4\pi\varepsilon_o R} + \frac{A}{R^n}$ (nearest neighbours)

or $U_{ij} = \pm\frac{q^2}{4\pi\varepsilon_o r_{ij}}$ (otherwise)

Therefore:

$$U(R) = N\left(-\frac{\alpha q^2}{4\pi\varepsilon_o R} + \frac{A}{R^n}\right)$$

[25%]

At the equilibrium separation $R_o$, $dU/dR = 0$

Thus:

$$\frac{dU}{dR} = N\left(\frac{\alpha q^2}{4\pi\varepsilon_o R^2} - \frac{nA}{R^{n-1}}\right) = 0$$

i.e $\frac{A}{R_o^n} = \frac{\alpha q^2}{4\pi\varepsilon_o n R_o}$

Thus the total energy at equilibrium is:

$$U(R_o) = N\left(-\frac{\alpha q^2}{4\pi\varepsilon_o R_o} + \frac{\alpha q^2}{4\pi\varepsilon_o n R_o}\right) = -\frac{\alpha N q^2}{4\pi\varepsilon_o R_o}\left(1 - \frac{1}{n}\right)$$

For the one-dimensional crystal choosing a negative ion to be the reference:

$\frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \ldots\ldots\ldots\ldots\right]$ (factor of 2 to account for the number of neighbours)

i.e. $\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \ldots\ldots\right] = 2\ln 2$ using the given expansion for ln(1+x)

Thus finally:

$$U(R_o) = -\frac{Nq^2 \ln 2}{2\pi\varepsilon_o R_o}\left(1 - \frac{1}{n}\right)$$

[25%]