Exam

Structure at Macro, Meso and Nano Scale

Advanced Materials Track

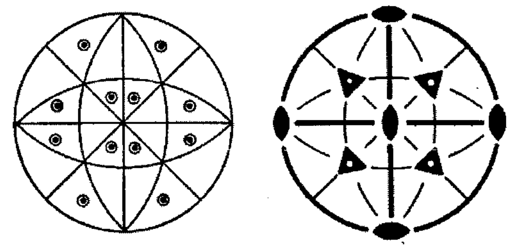
Jan. 26, 2016.

Write your name and student number clearly on every separate sheet of paper you hand in.
Write on the first sheet the total number of separate sheets of paper you hand in.
At least for exercises 3 and 5 start on a new sheet of paper.

Mark = 1 + 9 x (sum of the number of points scored)/(maximum number that can be scored)
(= 1 + (sum of the number of points scored)/10)

Exercise 1. (13 pts).

a. On the right a representation of the $m3$ (T_h) point group is given. To which types of Bravais lattices is this point group connected? Explain your answer. (2 pt)



b. Suppose we combine this point group with a lattice of F type to obtain the space group Fm3. When we put one atom on the general x,y,z coordinate, how many equivalent atomic positions will be occupied by the same type of atom within the unit cell of this space group? Explain your answer in about two sentences. (2 pts)

c. What do the different symbols in the space group $P6_3/mcm$ exactly mean? (4 pts)

d. When we distort a body-centered cubic lattice by changing the length of only one of the cube axes by a factor $(1+\delta)$, what (new) Bravais lattice will be formed? What are the lattice parameters of the new Bravais lattice in relation to the one of the initial lattice. (3 pts)

e. Describe shortly why decahedral or icosahedral nanoparticles can be related to quasi-crystals? Including a description of the vertex configuration(s) of the nanoparticles can be helpful for a short answer. (2 pts)

Exercise 2. (17 pts)

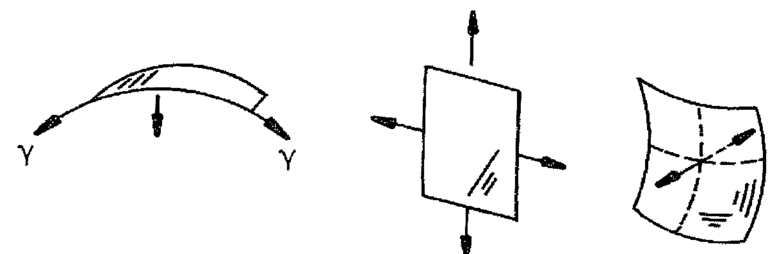
a. Si behaves as a strong (supercooled) liquid, whereas Se is a relatively fragile (supercooled) liquid. Draw in a plot the relation between viscosity and temperature for both (supercooled) liquids. Note: to do this clearly it is important to plot both axes in a specific way. Thus show clearly what you plot along the axes. (4 pts)

b. Metallic glasses have certain extraordinary mechanical properties. Explain which property makes metallic glasses attractive for applications. Which mechanical property on the other hand is not favourable and can prevent application of metallic glasses? (2 pts)

c. Phase-change materials have crystal structures that are prone to show (the so-called) Peierls distortion. Explain what a Peierls distortion is, when it can occur and why it can occur. (3 pt)

d. Phase transformations proceeding via nucleation and growth can generally be described by the following equation of the JMAK theory describing the fraction transformed x as a function of time t at a constant temperature: $x(t) = 1 - \exp(-kt^n)$. The factor n is called the Avrami exponent. Derive within the framework of the JMAK theory the kt^n term for a constant growth rate G of (2-dimensional) circular particles (in 2 dimensional space) when all nuclei are formed simultaneously with a total number of N per unit area after an incubation time t_0. (4 pts)

e. In the figure below three types of interfaces are shown where we assume that in all cases the interfacial energy is γ. In (a) a cylindrical boundary with a radius of curvature r is shown, (b) shows a planar interface and (c) a doubly curved boundary where the magnitude of the two curvatures are identical, but their directions opposite. Write for the three cases the magnitude of the force that acts within the plane of the boundary and the magnitude of the force that acts perpendicular to this plane. To answer correctly also the units have to be specified correctly. (4 pts)



(a) (b) (c)

Exercise 3. (14 pts)

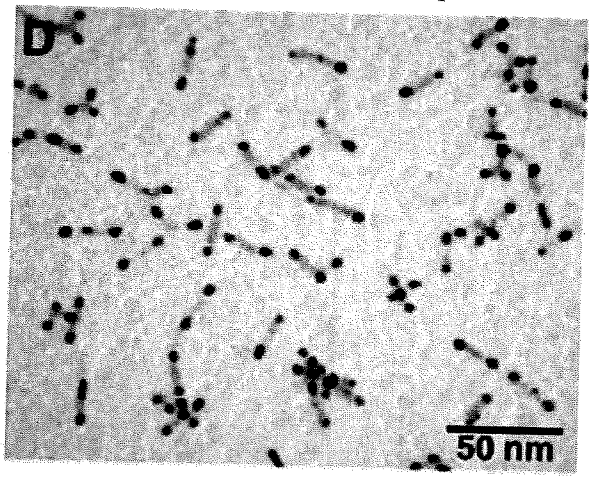
a. CdSe nanoparticles can be synthesised via the hot-injection method. Briefly describe the hot-injection method for synthesising CdSe nanoparticles. Note, you don't have to list the name of all the chemicals involved; just list the basic steps. (3 pts)

b. Why is there a critical size for nucleation in the type of synthesis described in part a? (3 pts)

c. Bulk CdSe has a band gap of 1.74 eV. Suppose the hot-injection method is used to synthesise CdSe nanoparticles. At the start of the reaction, the reaction mixture is colourless. How does the colour change during the subsequent growth of the particles? Explain your answer. (2 pts)

d. Bulk InP has the zincblende (Zb) structure. In vapour-liquid-solid (VLS) growth of InP nanowires, they can be grown in the Zb as well as the Wurtzite (Wz) structure, depending on the amount of zinc present. In either case the nanowires grow (with their long axis) in a direction parallel the normal of the close-packed planes in the structures, i.e. parallel to a <111> in case of Zb and parallel to [0001] in case of the Wz structure. So-called twinning superlattices were observed in the Zb structure above a certain Zn doping during the VLS growth process. Explain why it is possible that a twinning superlattice develops in the Zb structure, but that it can never develop in the Wz structure. (4 pts)

e. Barin *et al.* (Science **304**, 1787) succeeded in growing gold tips on CdSe nanorods, see picture to the right (the dark spots are the Au tips on the ends of CdSe nanorods). They did this by mixing a solution of $AuCl_3$ with a dispersion of CdSe nanorods (synthesised by the hot-injection method). Why does the gold preferentially grow at the tips and not the sides of the nanorods? (2 pts)



Exercise 4. (16 pts)

a. Does the band gap of a semiconducting single-wall carbon nanotube (SWCNT) depend on its chirality? Explain why the bandgap of the semiconducting CNTs will be directly proportional to the reciprocal diameter of the CNT. A full derivation is not needed, but describe the (three) essential requirements that are fulfilled in order to arrive at this conclusion. (4 pts)

b. Based on Euler's theorem for polyhedra, explain how many pentagons are needed to close a carbon nanotube, i.e. how many pentagons are needed to form the caps at the ends of carbon nanotubes. Assume that the carbon nanotube contains only hexagons and pentagons. (4 pts)
c. Sketch the density of states (DOS) of a metallic SWCNT and the DOS of a semiconducting SWCNT. (4 pts)
d. Compare the following three SWCNTs: (13,0), (11,2) and (12,1). Which one has the smallest bandgap? Which one has the largest bandgap? Explain both answers. (4 pts)

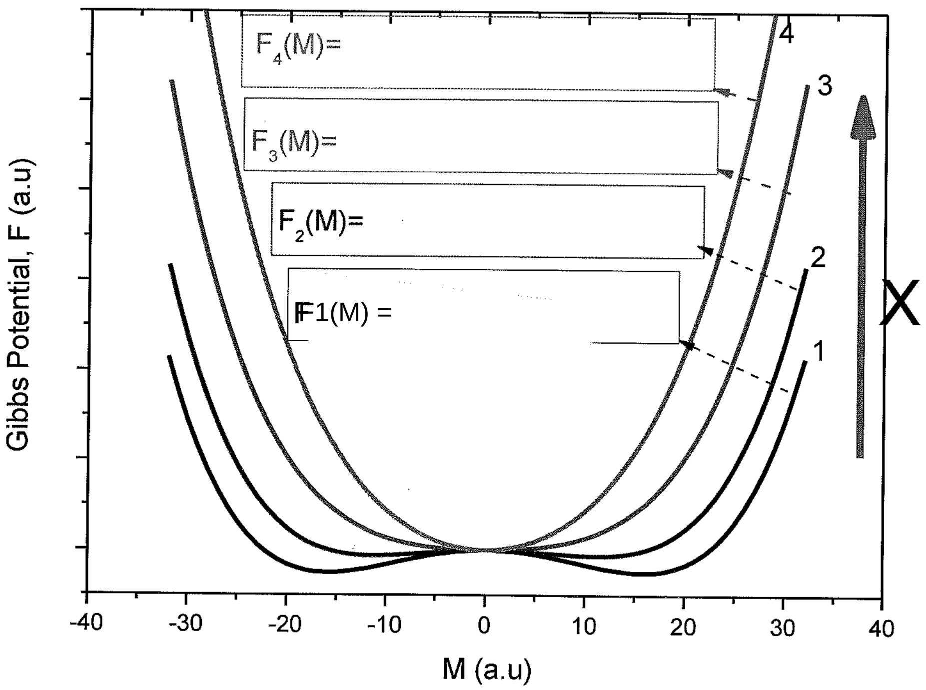
Exercise 5. (15 pts)

Knowing that the energy of a dipole with dipole moment, $\vec{p}$, in an electric field $\vec{E}$ is $E_p = -\vec{p}\cdot\vec{E}$

a. Calculate the free energy of a system of N paraelectric dipoles in a field $\vec{E}$, assuming that the dipoles can only align in two directions (parallel and antiparallel to $\vec{E}$). (7 pts)
b. Calculate the Polarization P(T,E) of this system. (5 pts)
   Note: *For this you need a) but the answer will be graded independently. If you could not get a), then explain how it should be done. (3 pts)*
c. What is the maximum Polarization that can be obtained? (3 pts)

Exercise 6. (15 pts)

The figure below shows four different curves representing the Landau free energy (Gibbs potential), F, of a system of N interacting spins at four different stages of the evolution upon changes of an external variable, X (as indicated by the large vertical arrow).



a. What does M represent? (3 pts)

b. Describe one plausible scenario that would give rise to such evolution of the free energy. (3pts)
c. Describe the evolution of the order parameter of the system in this scenario (with words or using a plot). (3pts)
d. Could the evolution of the free energy shown in the figure represent the coexistence of two magnetic phases around a phase transition? Explain your answer. (3 pts)
e. Write down (inside the rectangles in the figure) the general expression of the Landau functional for the different stages of the evolution. (3pts)

Note: By "general expression" it is meant that you do not need to write down the exact numerical expression. Instead, it is important that your answer shows: 1) which terms are present in the free energy, 2) their sign and 3) their evolution with X.

Bonus:

Suppose we consider a point group that combines a 6-fold rotation axis with a distinct 3-fold rotation axes and another distinct 2-fold rotation axes. To which types of Bravais lattices is this point group connected? Be careful here. First calculate which angles have to be present between these three different rotation axes? Note that this can be calculated using the so-called Euler equation:

$$\cos\left(\hat{AB}\right) = \frac{\cos\frac{\gamma}{2} + \cos\frac{\alpha}{2}\cos\frac{\beta}{2}}{\sin\frac{\alpha}{2}\sin\frac{\beta}{2}}. \qquad \text{(3 pts)}$$