# Exam

# Structure at Macro, Meso and Nano Scale

**Advanced Materials Track**

**April 8, 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*)

**Exercise 1. (14 pts)**.

On the right a representation of the $\frac{4}{m}mm$ ($D_{4h}$) point group is given.
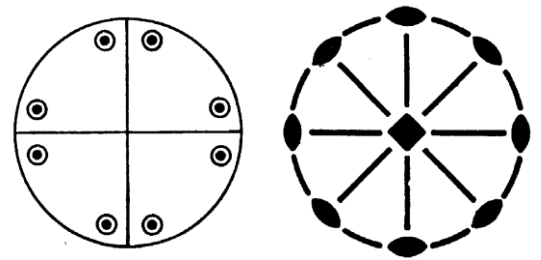
a. To which types of Bravais lattices is this point group connected? Explain your answer. (2 pts)

b. Suppose we combine this point group with a lattice of I type to obtain the space group I4/mcm. 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? When we put one atom on the 0,0,0 coordinate, how many equivalent atomic positions will be occupied by the same type of atom within the unit cell of this space group? Explain both answers in about two sentences. (3 pts)

c. What do the different symbols 4/mcm in the space group exactly mean? (3 pts)

d. When we distort a body centered cubic (bcc) lattice by changing the length of (only) one of the diagonals of the square faces 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 ones of the initial lattice. (4 pts) (Hint: Do not try to solve this in your head, but draw a schematic representation of the initial lattice projected along a viewing direction perpendicular to the square face and then notify what will be the highest symmetry solution after the distortion.)

e. Explain in a few sentences the close analogy between quasicrystals and Penrose tilings. (2 pts)

Answers:

a. A tetragonal lattice, because the 1st symmetry symbol is a 4, indicating the unique 4-fold rotation axis along the c-axis of the tetragonal unit cell. Next to this single 4-fold axis there are only perpendicular 2-fold axes. This structure cannot be cubic, because then the 2nd symmetry symbol has to be a 3. (In the cubic case these 3 fold rotation axes are parallel to <111> directions of the cubic structure and there are 4 distinct types of <111> directions).

b. I means body centered and this means that the number of atoms will be multiplied by a factor 2. The point group in the above figure on the left indicates that there are 16 atoms on the general $x,y,z$ coordinate. The answer for the general $x,y,z$ coordinate is thus 2 times 16 = 32. For the highest symmetry position 0,0,0 there are only 2 atoms per unit cell, with of course the 2nd position on the ½,½,½ coordinate.

c. The different symbols 4/mcm mean that there is a 4-fold rotation axis along the primary axis and since this is a tetragonal lattice, the primary axis is the [001]. The /m symbol means that perpendicular to the 4-fold axis there is a mirror plane. The c means that there is a glide plane perpendicular to the secondary axis, which for the tetragonal lattice is [100] and [010]. After mirroring in this plane there is a translation of ½c. The final m means that there is a mirror plane perpendicular to the tertiary axis which for the tetragonal lattice is [110] and [1-10].

d. The new Bravais lattice is a face-centered orthorhombic with lattice parameters: a√2, (a√2) (1+δ), a. This has been demonstrated graphically in the ppt slides answering question 4c of the first tutorial.

## Exercise 2. (16 pts)

a.  Explain based on Zachariasen's rules why $SiO_2$ can be (readily) produced as a glass whereas MgO (which in crystalline form has the rocksalt (NaCl) structure) cannot be made into a glass. (4 pts)

b.  Explain which (at least three) properties and which (at least one) application makes oxide glasses a widely abundant technical material in our society. (2 pts)

c.  A phase-change memory cell loses its memory after (exactly) 15 hours at 120 $^\circ$C and (exactly) 2 minutes at 150 $^\circ$C. Compute the activation energy for crystal growth. The Boltzmann constant is 8.617 $10^{-5}$ eV/K ($= 1.38$ $10^{-23}$ J/K). How long is this memory cell then stable at 80 $^\circ$C? (3 pts)

d.  Explain (qualitatively) why for first order phase transformations there is in general a nucleation barrier. (2 pts) (Equations can be useful for this question and the next one, but are not essential to formulate the proper answers.)

e.  Why is the nucleation barrier for heterogeneous nucleation lower than for homogeneous nucleation? What is the effect of the wetting angle in this respect? (2 pts)

f.  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 nucleation rate $I$ in 2-dimensional space and for a constant growth rate $G$ of parallel (i.e. in 1-dimension) growing needles with width $w$ (in 2-dimensional space). (3 pts)

length scales larger than the wavelength of the visible spectrum, i.e. no crystals with grain boundaries, (3) low price, e.g. single crystals could have the required properties similar as amorphous glass, but are much too expensive to produce or cannot be produced on the required length scale.

c.

d. First order phase transformation rely on producing a new phase with a distinct interface in a parent phase. Then, for small nuclei the surface/interface to volume ratio will always give rise to an energy barrier as shown below. Of course the actual critical size $r^*$ and the activation energy $\Delta G^*$ can vary largely, but an energy barrier is inevitable.



(a)          (b)
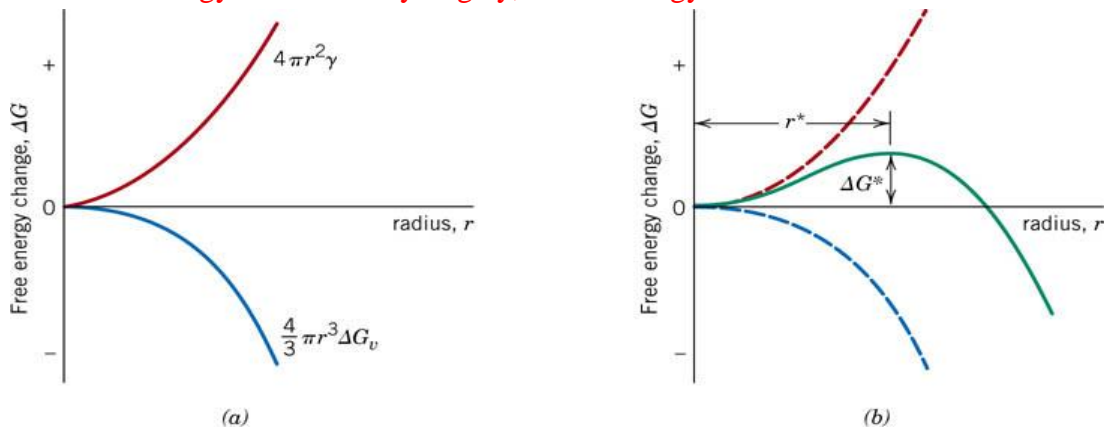
e. In heterogeneous nucleation on a (planar) surface the wetting angle θ determines that only a cap of a sphere has to nucleate and not the complete sphere as in homogeneous nucleation. This strongly reduces the energy barrier (by the factor S(θ)). The better the wetting, i.e. the smaller the angle θ, the smaller the cap and the lower the energy barrier.

$$r^* = \frac{2\gamma}{\Delta G_v}$$

$$\Delta G^*_{het} = \frac{16\,\pi\gamma^3}{3(\Delta G_v)^2} S(\theta)$$

$$S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4$$

f.

$$kt^n = x_{ext} = \int_0^t I(\tau)V(t-\tau)d\tau, \quad V(t-\tau) = wG(t-\tau)$$

$$x_{ext} = \int_0^t IwG(t-\tau)d\tau = \left[wIG\left(t\tau - \tfrac{1}{2}\tau^2\right)\right]_0^t = \tfrac{1}{2}wIGt^2$$

$$so, n = 2 \ and \ k = \tfrac{1}{2}wIG$$

### Exercise 3. (20 pts)

a.  What is the difference between nanorods and nanowires? (1 pt)

b.  Inorganic nanowires can be synthesized via the VLS method. What does VLS stand for? Describe how VLS works. (4 pts)

c.  VLS growth can yield nanowires with a uniform diameter, however in some cases tapered nanowires (i.e. the diameter changes along the length of the wire) are obtained. Why? Which end of the nanowire is thickest? (3 pts)

d.  Bulk InP has the zincblende (Zb) structure. In 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 to 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. Why does the twin lattice spacing depend on the diameter of the nanowires? Does the twin lattice spacing increase or decrease with increasing diameter? (3 pts)

e.  The TEM image below shows synergistic growth of nanowires (scale bar is 1 micron). The two outer nanowires have a larger diameter than the others. Explain why the thin nanowires closest to the thicker (outer) ones are longer than the nanowires in the middle. (4 pts).
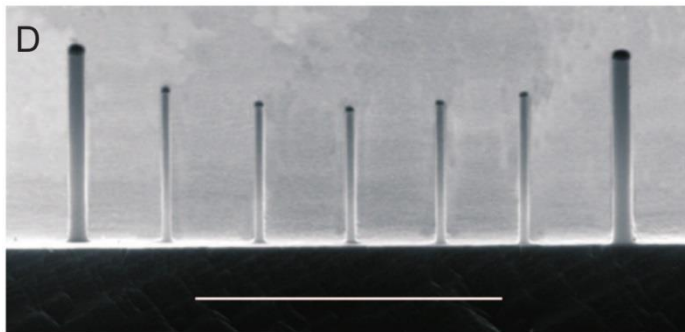


f.  The equilibrium shape of a crystal is related to the anisotropy of its surface energy. For a surface that makes an angle $\theta$ with one of the principle axes of the crystal, the surface energy shows a sharp minimum at $\theta=0$ (a cusp). Why? (3 pts)

g.  The equilibrium shape of nanoparticles can be obtained from the Wulff construction. Given the following equilibrium shapes, draw the simplest Wulff plots that would give rise to such equilibrium shapes. (2 pts)
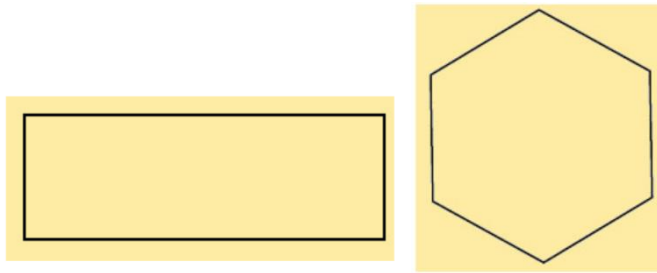
a. Nanowires have such a high aspect ratio that they become bendy.

b. VLS stands for vapour-liquid-solid growth. Metal (Au typically) nanoparticles deposited on a substrate. Precursors decompose at the surface of the metal particles and form an alloy upon heating (particle melts). High concentrations of precursors cause supersaturation of the nanoparticle and nucleation of the NW at the interface between substrate and particle. Growth continues in analogous way.

c. Tapered NWs are a result of the competition between VLS growth and lateral growth. The latter means that growth units are incorporated into the sides of the NWs. Therefore, the diameter is smallest near the top, i.e. near the catalyst particle.

d. Larger diameters yield longer segments, so the twin lattice spacing is longer (on average). The twins occur so as to keep the shape of the metal catalyst particle (droplet) close to spherical. Adding 1 monolayer to the wire will distort a small droplet more than it would a large droplet. So, larger diameters can grow in one mode for longer before twinning.

e. The decomposition of precursors scales with the droplet area, proving a higher supersaturation. For larger nanowire diameters effectively more catalyst material is available, compared to thinner wires. This locally results in an increase in the supersaturation, and therefore increased growth rates. The thin wires close to the larger diameter wires benefit from the locally increased supersaturation due to the diffusion through the gas phase. This results in an increased length for thin wires close to the larger diameters compared to thin wires that stand further away.

f. This can be understood by considering the broken bond model: this means that the surface energy is proportional to the number of broken bonds of a surface. At theta=0 the number of broken bonds is minimal. Any positive or negative theta yields additional broken bonds.

g. solution:
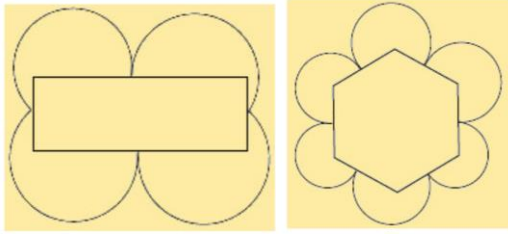
**Exercise 4. (10 pts)**

a. The Langmuir-Blodgett (LB) technique can be used to make very well defined organic thin films. Briefly describe the LB technique, and the role of the hydrophilic and hydrophobic parts of the molecules used in the film. (2 pts)

b. The molecules in LB films can be orientated in three ways (usually denoted as X, Y, and Z-type). Sketch these types of structures. (2 pts)

c. Single-wall carbon nanotubes are described on the basis of the vector in the graphene plane that exactly defines the circumference (i.e. perpendicular to the length) of the tube: the so-called chiral vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m)$, where the vectors $a_1$ and $a_2$ define the unit cell of graphene (see figure below). It can be derived that the reciprocal space vector $\vec{K}_1$ of this real space chiral vector remains parallel to $\vec{C}_h$ and can be described by:

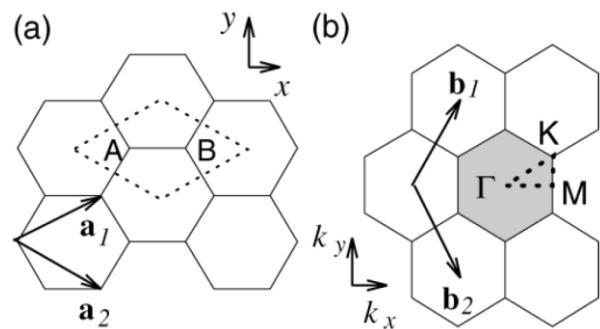$$\vec{K_1} = \frac{\pi}{a(n^2+nm+m^2)}\left(\sqrt{3}(n+m)\widehat{k_x} + (n-m)\widehat{k_y}\right).$$

In addition, the reciprocal space vectors $b_1$ and $b_2$ of the real-space vectors $a_1$ and $a_2$, which define the unit cell of graphene, are:

$$\vec{b_1} \perp \vec{a_2}, \text{ and } \vec{b_1} \cdot \vec{a_1} = 2\pi$$

$$\vec{b_1} = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}\widehat{k_x} + \widehat{k_y}\right)$$

$$\vec{b_2} \perp \vec{a_1}, \text{ and } \vec{b_2} \cdot \vec{a_2} = 2\pi$$

$$\vec{b_2} = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}\widehat{k_x} - \widehat{k_y}\right)$$



Now we have enough information in combination with the figure above to calculate whether an armchair or a zigzag nanotube is metallic or semiconducting. Do this calculation in a transparent manner so as to derive under what conditions (of *n* and *m*) an armchair or a zigzag nanotube is either metallic or semiconducting. (6 pts)

a. A Langmuir–Blodgett film contains one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing (or emersing) the solid substrate into (or from) the liquid. A monolayer is adsorbed homogeneously with each immersion or emersion step, thus films with very accurate thickness can be formed. The monolayers are assembled vertically and are usually composed of amphiphilic molecules with a hydrophilic head and a hydrophobic tail. This combination of hydrophilic and hydrophobic parts of the molecule make it go to the air/water interface, which is essential for the formation of a monolayer.

b. What we see here are the resulting LB films, the round part is the hydrophilic head that is orientated towards the water surface.
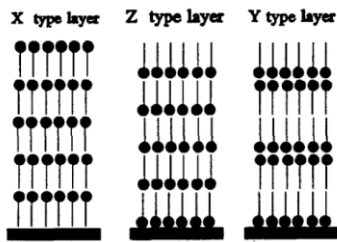


c. Armchair tube: n=m. Also, the tube will be metallic if r K1 =ΓM, where r is an integer. We know that ΓM = b1/2, so ΓM=2π/a√3. Also K1 and ΓM are both in the kx direction. The length of K1 (n=m) = 2π/an√3, so r K1 =ΓM can always be satisfied for n=r. Armchair tubes are therefore always metallic.

Zigzag: m=0, K1 = π/(na) (√3 kx + ky). ΓK = 2 π/a (kx/√3 + ky/3), so r K1 = ΓK if 2n=3r for some r. This only holds if n is a multiple of 3. So only zigzag tubes with n=multiple of 3 are metallic.

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**Please start with a new sheet of paper as Q5 and Q6 will be corrected by someone else. Clearly indicate your name and student number.**

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**Exercise 5. (12 pts).**

a) What is the order parameter of a phase transition? (3 points)

An order parameter of a phase transition is any property of the system that is different than zero in the low symmetry phase (below Tc) and zero above the phase transition (in the high symmetry phase).

b) What are the differences between a second order and a first order phase transition? Name six distinguishing facts or properties (6 points)

1) In a first-order phase transition, the change of phase takes place in such a way that **the first derivatives of the Gibbs free energy** (or potential) change **discontinuously** at the transition point. In a second-order phase transition, the first derivatives change **continuously** at the transition point, while the second derivative diverges at the transition point (1 points)
2) A first order transition involves **latent heat**, a second order transition doesn't (1 points)
3) A first order transition involves **phase coexistence**, a second order transition doesn't (1 points)

c) What do the critical exponents α, β and γ describe? (3 points)

## Exercise 6. (**18 pts**).

a) Write down a general expression for the Landau free energy (or Gibbs potential) that describes a ferroelectric crystal that undergoes a second order phase transition to a paraelectric phase at 320K. Do not forget to indicate the sign of the relevant parameters. (6 points)
Answer:

$$F = F_o + a_2 \frac{(T - 320K)}{320K} P^2 + A_4 P^4$$

with $a_2 > 0$ and $A_4 > 0$

b) Write down the general expression for the Landau free energy for a ferroelectric that undergoes a weakly first-order phase transition to a paraelectric phase at 320K (3 points) and use it to calculate an expression for the electrical polarization as a function of temperature (3 points). Do not forget to indicate the sign of the relevant parameters.

$$F = F_o + a_2 \frac{(T - 320K)}{320K} P^2 + A_4 P^4 + A_6 P^6$$

In equilibrium: $\frac{\partial F}{\partial P} = 0$; and this leads to $2a_2\frac{(T-320K)}{320K}P + 4A_4P^3 + 6A_6P^5 = 0$

An thus 2P= 0 (1) which is a maximum

and $a_2\frac{(T-320K)}{320K} + 2A_4P^2 + 3A_6P^4 = 0$ (2) which lead to the energy minima.

From (2): $P^2 = \dfrac{-2A_4 \pm \sqrt{(4A_4)^2 - 12A_6a_2\frac{(T-320K)}{320K}}}{6A_6}$ and thus $P(T) = \pm\sqrt{\dfrac{-2A_4 \pm \sqrt{(4A_4)^2 - 12A_6a_2\frac{(T-320K)}{320K}}}{6A_6}}$

 

c) Write down the general Landau free energy expression that describes a ferroelectric crystal at a tricritical point (3 points) and calculate the critical exponent β at such point. (3 points)

$F = F_o + a_2\frac{(T-Tc)}{Tc}P^2 + A_6P^6$ or $F = F_o + a_2tP^2 + A_6P^6$

where t= (T-Tc)/Tc

because the tricrititcal points signals the crossover between a first order A4<0 and second order (A4>0) phase transitions, and thus A4= 0.

β describes the dependence of P with T (or t) close to Tc (t→0)

In equilibrium: $\frac{\partial F}{\partial P} = 0 \rightarrow 2a_2tP + 6A_6P^5 = 0$

And thus P=0 (1) , a maximum of F and $2a_2t + 6A_6P^4 = 0$ (2) , which gives the equilibrium values (minima).

From (2): $P^4 = -\frac{2a_2}{6A_6}t$ and thus $P \propto t^{1/4}$ and β= 1/4