

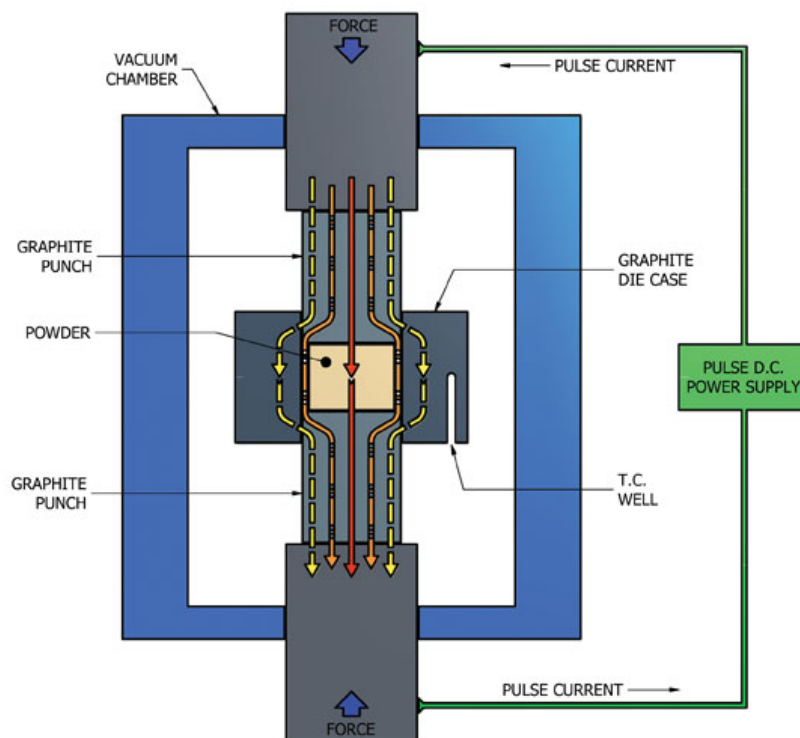


TMT4320 Nanomaterials, fall 2015

EXERCISE 10 - SOLUTION

PROBLEM 1

- a) Spark plasma sintering (SPS) is a process where the work piece (compacted powder) is placed in a matrix and subjected to a uniaxial pressure coupled with internal 'heating' of the sample by means of a large pulsed current (see figure below). The idea behind this process for densifying powdery materials is to combine uniaxial compaction with an intense electric discharge of between 2 000 and 20 000 A in a few ms. Although they can easily exceed 2 000 °C locally, average SPS sintering temperatures across the sample would nevertheless be 200 to 500 °C lower than sintering temperatures used in conventional procedures. Moreover, vaporization, melting and sintering steps can all be carried out in the space of a few minutes (5–20 min), from start to finish, including ramping up the temperature at the beginning and cooling at the end.



Taken from R. Aalund, Ceramic Industry,
http://www.ceramicindustry.com/Articles/Feature_Article/BNP_GUID_9-5-2006_A_1000000000000321084#

- b) The main difference of spark plasma sintering compared to natural or conventional sintering techniques is that the sample is heated from within rather than from the outside. As a consequence, the significantly reduced sintering times and sintering temperatures mean that dense bulk materials can be produced within which coarsening due to growth remains almost totally inhibited.
- c) Nano-sized grains can modify several properties related to for example mechanical behavior or electronic and ionic conductivity. In some materials (for example certain ceramic materials) ionic and/or electronic conductivity is greatly enhanced along grain boundaries. For such materials an increase in the amount of grain boundaries, by decreasing the average grain size, will improve the total conductivity for the material. Although small grains can give enhanced properties, this is not always the case. In the case of photovoltaic materials, grain boundaries will work as recombination centers for electron and electron hole pairs. This will have the effect of decreasing the life time of the excited electrons and thereby decreasing the efficiency of the solar cell. In good electronic conductors small grains may also be problematic since grain boundaries tend to enhance scattering of electrons and thereby reduce the conductivity of the material.

PROBLEM 2

- a) The possible range of the equilibrium center-to-centre distance (C) is between $2R$ and $2R + 2(d_{\text{SAM}})$; $68 \text{ \AA} < C < 104 \text{ \AA}$.

The equilibrium center-to-centre distance (C) is the distance at which the interaction potential has its minimum value. The interaction potential (E_{total}) is the sum of the van der Waals potential E_{vdW} given in equation 1 and the steric repulsion potential between carbon chains E_{steric} given in equation 2.

$$E_{\text{total}} = E_{\text{vdW}} + E_{\text{steric}}$$

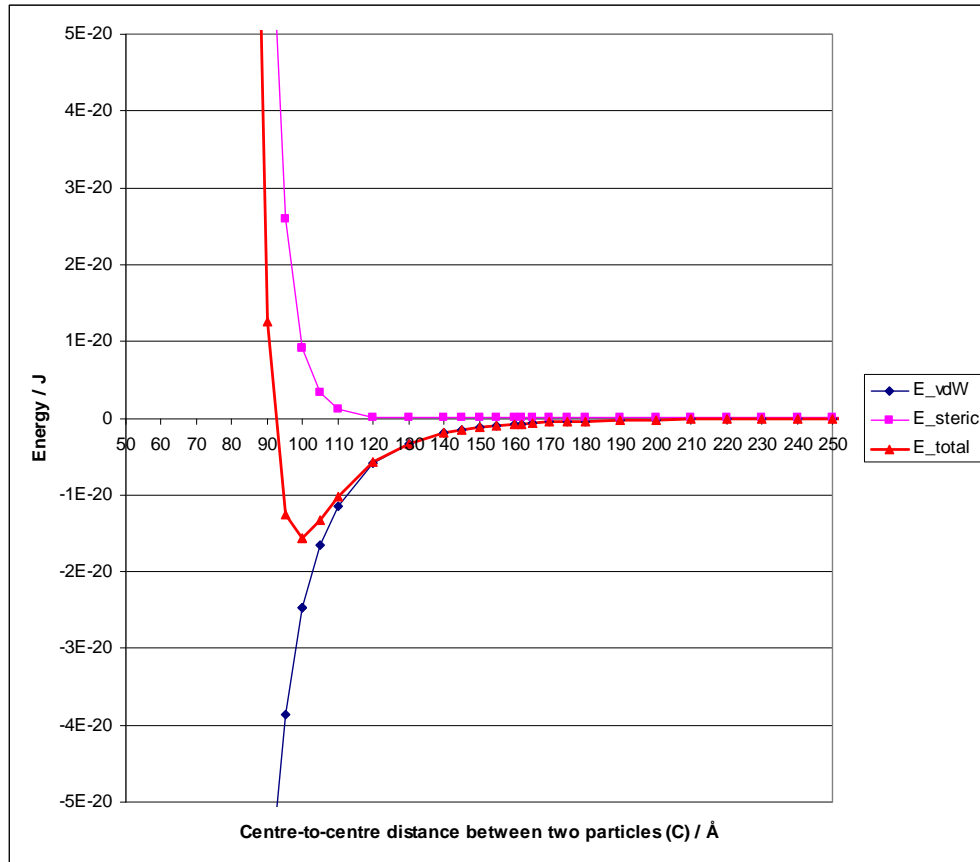
$$E_{\text{total}} = -\frac{A}{12} \left(\frac{4R^2}{C^2 - 4R^2} + \frac{4R^2}{C^2} + 2 \ln \frac{C^2 - 4R^2}{C^2} \right) + \frac{100R\delta_{\text{SAM}}^2}{(C - 2R)\pi\sigma_{\text{thiol}}^2} kT \exp \left(-\frac{\pi(C - 2R)}{\delta_{\text{SAM}}} \right)$$

C can be found from $dE_{\text{total}}/dC = 0$, but it is not easy. By plotting E_{total} as a function of C for $C > 68 \text{ \AA}$, one can find the minimum value of the interaction potential. The E_{total} in J with \AA as the length parameter is:

$$E_{\text{total}} = -\frac{1.9 \text{ eV}}{6.242 \times 10^{18} \text{ eV/J}} \left(\frac{4(68 \text{ \AA})^2}{C^2 - 4(68 \text{ \AA})^2} + \frac{4(68 \text{ \AA})^2}{C^2} + 2 \ln \frac{C^2 - 4(68 \text{ \AA})^2}{C^2} \right) +$$

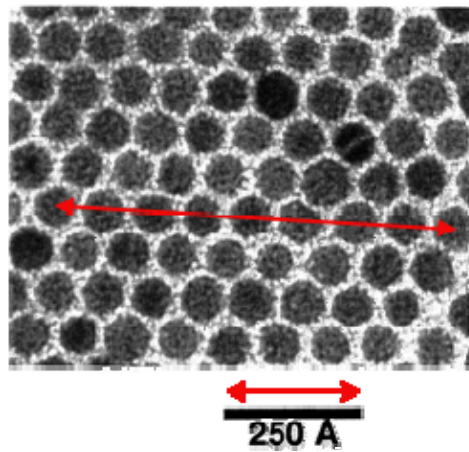
$$\frac{100 \cdot 68 \text{ \AA} \cdot (18 \text{ \AA})^2}{(C - 2 \cdot 68 \text{ \AA})\pi(4.3 \text{ \AA})^2} 1.380658 \times 10^{-23} \text{ J/K} \cdot 298 \text{ K} \cdot \exp \left(-\frac{\pi(C - 2 \cdot 68 \text{ \AA})}{4.3 \text{ \AA}} \right)$$

A plot of E_{total} against C is shown below:



The minimum of E_{total} is located at $C = 99 \text{ \AA}$, where $E_{\text{total}} = -1.567 \times 10^{-20} \text{ J}$.

- b) An average value for C for the 2D structure in the image can be found by measuring the centre-to-centre distance over several nanoparticles and dividing by the number of distances measured. A value in \AA is found by comparing the length measured with the scale bar. The distances measured here is shown in red in the image below.



$$C' = 5.6 \text{ cm} / 8 = 0.7 \text{ cm}$$

$$\frac{C}{C'} = \frac{250 \text{ \AA}}{l'}$$

$$C = \frac{250 \text{ \AA}}{l'} C = \frac{250 \text{ \AA}}{1.9 \text{ cm}} 0.7 \text{ cm} = 97 \text{ \AA}$$

The value of C from a) (99 Å) compares well with the value from the image (97 Å), given the uncertainties in measuring the distances in the image.

- c) The parameter $\chi = 2L/D_{\text{core}} = \delta_{\text{SAM}}/R$ is a determining parameter for the crystal structure of an assembly of nanoparticles covered by carbon chains.

$$\chi = \frac{\delta_{\text{SAM}}}{R} = \frac{18 \text{ \AA}}{34 \text{ \AA}} = 0.529$$

As $\chi < 0.73$, a close-packed structure such as face-centered cubic (fcc) or hexagonal close-packed (hcp) is favored. The 2D structure in the image has a close-packed hexagonal packing of the nanoparticles and is therefore consistent with the χ value.

[The image in the problem was taken from B.A. Korgel *et al.*, *J. Phys. Chem. B*, 1998, 102, 8379. Equation 2 is modified from “Nanomaterials and Nanochemistry” (equation 22.4) and Korgel *et al.*, with $(\sigma_{\text{thiol}})^2$ instead of $(\sigma_{\text{thiol}})^1$ as in NaN and $(\sigma_{\text{thiol}})^3$ in Korgel. This gives similar values as in Korgel and correct unit symbols.]

PROBLEM 3

- a) The functions of the chemical compounds used to synthesize the Au, Ag, Pd and Fe₂O₃ nanoparticles are listed below:

Toluene – solvent

Dodecyltrimethylammonium bromide (DDAB) – surfactant forming reverse micelles

AuCl₃ – cation precursor

AgNO₃ – cation precursor

PdCl₂ – cation precursor

NaBH₄ – reducing agent

1-dodecanethiol – surfactant adsorbing on the metal surfaces

Ethanol – precipitating agent (the nanoparticles agglomerate and can be removed from the dispersion)

Iron pentacarbonyl – cation precursor

Triethylamine – solvent (and passivating agent and stabilizer)

Oleic acid – surfactant adsorbing on the surface

Trimethylamine N-oxide – oxidizing agent (oxidizes Fe to γ -Fe₂O₃)

- b) The maximum size distribution for obtaining self-assembled superlattices is in general 13%. If the size distribution is broader, 2D/3D lattices will not form over large distances but can form lattices over small distances.

- c) The governing factors behind the assembly of binary nanoparticle superlattices are much the same as the factors governing ‘standard’ nanoparticle superlattice assembly:

- Size distribution < 13%
- Length of carbon chains (‘hard’ versus ‘soft’ spheres)
- Substrate (roughness, substrate-nanoparticle interactions)
- Nanoparticle charge

In addition, a few governing factors are more specific for binary nanoparticle superlattices:

- The packing symmetry depends on the size ratio of the small and large spheres ($R_{\text{small}}/R_{\text{large}}$)
- Nanoparticle charge becomes more important because of Coulombic interactions between the two types of nanoparticles

- d) The superlattice structure can change when a carboxylic acid or tri-*n*-octylphosphine oxide (TOPO) is added to the binary nanoparticle mixture because the nanoparticle charge is changed. When the charge changes the electrostatic interactions between the nanoparticles change and a new structure may be more energetically favorable.

PROBLEM 4

- a) Carbon black can be separated from fullerenes and carbon nanotubes simply by heat treatment in air at a few hundred degrees. Carbon black, being amorphous, vaporizes at a substantially lower temperature than fullerenes and carbon nanotubes. Carbon nanotubes and fullerenes can then be separated based on their solubility since they will be soluble in different solvents. Fullerenes can be dispersed in non-polar organic solvents, such as toluene, while carbon nanotubes do not tend to form stable dispersions with toluene. In addition, due to their high aspect ratios carbon nanotubes tend to bundle up. In toluene this effect will be further enhanced due to the unfavorable interactions with toluene and the nanotubes. If a mixture of fullerenes and carbon nanotubes are mixed with toluene the fullerenes will form a stable dispersion while the nanotubes will bundle up and form large agglomerates. The nanotubes can then easily be separated out for example by centrifugation.

*Note: Not all the fullerenes are stable in toluene and similar solvents. For example C_{72} will not form a stable dispersion with toluene. However, the most stable and therefore most abundant fullerenes like C_{60} and C_{70} are stable in toluene and similar solvents. **On a final exam you would not be expected to know this.***

- b) For gold nanoclusters to form a stable dispersion they need to be capped with some surfactant or other capping ligand. As an example take gold nanoclusters that are capped with alkane thiolate. These clusters will form a stable dispersion with toluene. If a small amount of a non-solvent such as acetone is added to the solution of capped nanoclusters, the largest clusters will start to precipitate while the smaller ones will remain in solution. These clusters can then be separated out. When the largest clusters are removed more acetone can be added to precipitate out the next size group. As more and more acetone is added smaller and smaller crystals will precipitate out. This mechanism can be explained as follows: When a non-solvent is added, nanocrystal-nanocrystal contacts start to become more favorable than nanocrystal-solvent interactions. The larger diameter capped gold nanoclusters interact via the chains of the alkanethiolate capping ligands more strongly than the smaller ones due to the smaller curvature of their surface and the resulting greater interaction area. As a result the largest crystals are caused to aggregate and crystallize first. Depending on the amount of non-solvent added each time, it is possible to obtain many solutions with quite monodispersed gold nanoclusters.