Problem sheet 1-PHYS6014

1. Assuming that the gold nanoparticles in a solution have spherical shape and uniform fcc crystalline structure. Show that the average number of atoms per gold nanoparticle can be calculated using the following formula:

$$N = \frac{\pi \rho D^3}{6 M_w} N_A$$

where:
N = number of atoms per nanoparticle
ρ = density of face centered cubic (fcc) gold
D = average diameter of nanoparticles
M_w = molecular weight of gold
N_A = number of atoms per mole

2. Assuming that the reduction of Au^{3+} to Au^0 is complete (i.e. all the Au^{3+} in solution is reduced to Au^0), show that the molar nanoparticle concentration, c, is given by:

$$c = \frac{N_T}{N V N_A}$$

c = molar concentration of nanoparticle solution
N_T = Total number of gold atoms added as HAuCl4
N = number of atoms per nanoparticle
V = volume of the reaction solution in L
N_A = number of nanoparticles per mole

3. The transmittance, T, of light through a liquid is given by Beer-Lambert's Law:

$$T = \frac{I}{I_0} = 10^{-\alpha l} = 10^{-\varepsilon l c}$$

with

α = absorption coefficient
l = distance the light travels through the material (i.e. the path length)
ε = molar absorptivity of the absorber
c = concentration of absorbing species in the material
I_0 = intensity (or power) of the incident light
I = intensity (or power) of the transmitted light

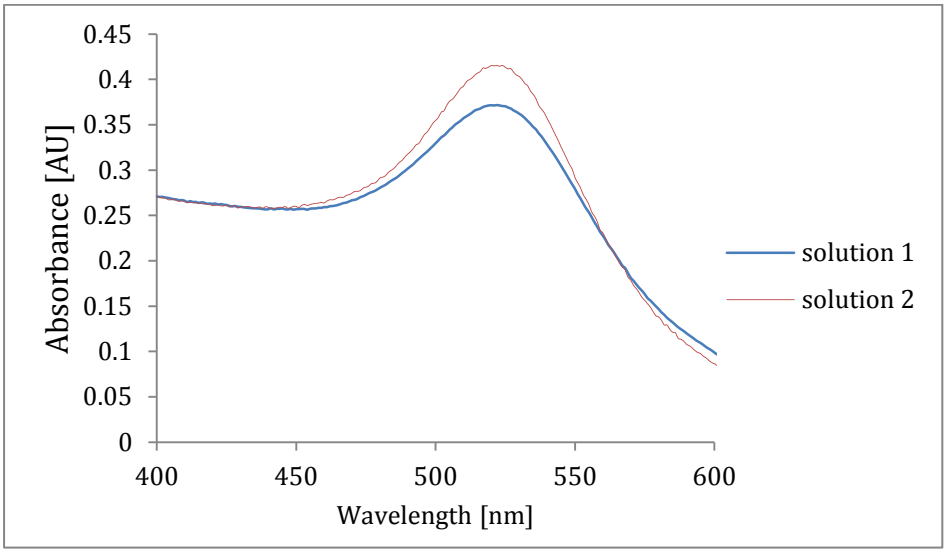
The absorbance, A, is defined as:

$$A = -log_{10}(T)$$

Using the given equations, show that the absorption at the plasmon peak maximum can be written as:

$A = \varepsilon l c$

3.1 The UV-visible spectrum of two colloidal gold solutions with same nanoparticle sizes is:



For solution **1** the maximum of absorbance is 0.37 at 522 nm and for solution **2** the maximum is 0.41 at 522 nm.

Estimate the concentration of nanoparticles in solution **2** when the concentration of nanoparticles in solution **1** is 5 *n*M.

4. Assume a spherical nucleus with a radius of *r*. The total change of the Gibbs energy, *ΔG*, for the formation of the nucleus, is given by:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

ΔG = change of Gibbs free energy
ΔG_v = change of volume free energy
γ = surface energy per unit area

A newly formed nucleus is stable only when its radius exceeds a critical size, *r**. At the critical size, the first derivative of ΔG vanishes:

$$r = r^* \Rightarrow \frac{d\Delta G}{dr} = 0$$

Show that critical size, *r**, and critical energy, *ΔG**, are defined by:

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

$$\Delta G^* = \frac{16\pi\gamma^3}{3\Delta G_v^2}$$

5. The size-dependent energy gap of a spherical semiconductor quantum dot is[1]:

$$E_g(d) = E_g(bulk) + \frac{h^2}{2m^* d^2} - 1.8\frac{e^2}{2\pi\varepsilon\varepsilon_0 d}$$

where:

Eg (d) = energy gap of a spherical semiconductor quantum dot (in eV)
Eg (bulk) = bulk band gap energy (in eV)
h = Planck constant (h ≈ 6.6261×10^{-34} Js)
e = elementary charge (*e* = 1.60217646×10^{-19} C)
d = diameter of the nanoparticle (in m)
ε = dielectric constant of the semiconductor
ε_0 = permittivity constant (ε_0 = 8,854×10^{-12} $\frac{C^2}{Nm^2}$)

*m** = the reduced mass of the exciton, given by:

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h}$$

m_e = is the effective mass of the electron (in kg)
m_h = is the effective mass of the hole (in kg)
eV = 1.602×10^{-19} J

For CdSe quantum dots, the bulk value for the energy gap is E_g *(bulk)* = 1.74 eV. The effective mass of electrons and holes are m_e = 0.13 m_0 and m_h = 0.40 m_0, respectively. m_0 is the mass of free electrons (m_0 = 9.1095 ×10^{-31} kg) and the dielectric constant is ε_{CdSe} = 5.8.

Determine the energy gap, *Eg (d)*, for colloidal CdSe quantum dots with diameter *d* = 3 nm and *d* = 5 nm and determine which color of the visible spectrum the emitted light has.

[1] Günter Schmid: *Nanoparticles: From Theory to Application*, p. 22

6. For an ideal surface, the interfacial free energy is given by:

$$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$$

where N_b is the number of broken bonds, ε is the bond strength, and ρ_a is the density of surface atoms.
For an fcc structure with a lattice constant a, the surface energies of the low-index crystallographic facets that typically encase nanocrystals can be estimated as:

$$\gamma_{\{1\,0\,0\}} = 4\left(\frac{\varepsilon}{a^2}\right)$$

$$\gamma_{\{1\,1\,0\}} = 3\sqrt{2}\left(\frac{\varepsilon}{a^2}\right)$$

$$\gamma_{\{1\,1\,1\}} = 2\sqrt{3}\left(\frac{\varepsilon}{a^2}\right)$$

Determine the energetic sequence for the surface energies of the low-index crystallographic facets.