Materiais Nanoestruturados e Nanotecnologias

Exercises on surfaces at the nanoscale, stabilization, fabrication and hybrid nanomaterials

---

Surfaces at the Nanoscale

1. Dispersions of very small droplets are used in the production of different nanomaterials.
a) Using the appropriate equation, explain why very small droplets have higher vapor pressure than the corresponding bulk liquid.
b) What are the implications to the stability of a polydisperse mixture of nanodroplets?
c) Name this process and briefly describe a strategy that could counteract this.

HINT: $r_m > 0 \Rightarrow P^c > P^\infty$, smaller r, larger vapor pressure (Kelvin eq.); smaller droplets tend to evaporate and contribute to the growth of larger droplets; Ostwald ripening, decrease surface tension with surfactants

2. Using the Young-Laplace equation for solid surfaces, explain why gold nanostars tend to lose their sharp edges if not appropriately stabilized. What is the effect of the increase in the number of arms of the stars?

HINT: sharp edges and corners (small positive curvature, i.e., $r > 0$ but small) are more soluble than flat and concave regions; decrease in plasmon energy (higher absorption wavelength)

3. The interaction of a liquid droplet of water with a surface in air is illustrated in the figure (the contact angle is shown on the top right corner of each panel). This interaction depends on the properties of the surface.
   a) Classify the surfaces shown in panels a - d based on their contact angles.
   b) Which models can we use to describe the contact angle for the interaction of the water droplet with superhydrophilic and superhydrophobic surfaces?
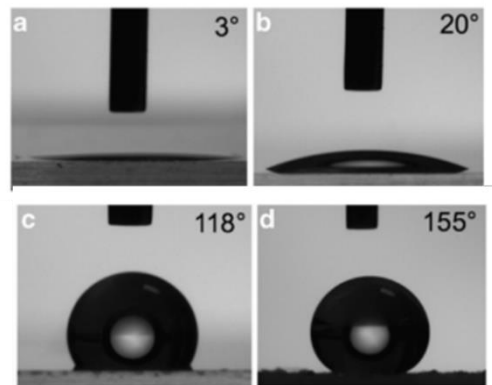
HINT: a-superhydrophilic, b-hydrophilic, c-hydrophobic, d-superhydrophobic

4. The figure shows the variation of the surface tension of a solution of an amphiphilic molecule in water with concentration.
 a) Explain the variation of the surface tension with concentration of the amphiphilic molecule shown in the figure.
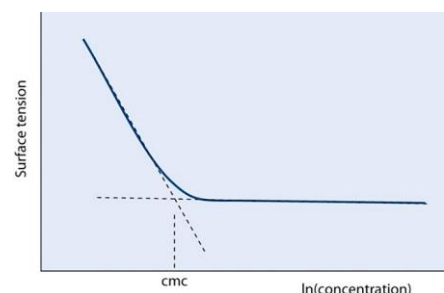
b) Which range of values should have the critical packing parameter (cpp) of a given surfactant to form spherical micelles?

5. Micro and nanoscale roughening of a solid surface can be used to dramatically change its wetting properties. For the case where the liquid follows the topography of the surface, show the relation between the effective contact angle of the roughened surface and the contact angle of a smooth surface of the same material.
What is the expected wetting behavior of the roughened surface if the corresponding smooth surface has a contact angle of 110°? And if it was 50°?
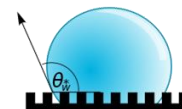
6. Explain why the lotus leaf is not wetted by water.

7. The interaction of liquids with nanostructured materials can differ considerably from their interaction with bulk materials. Consider a liquid water droplet resting on a nanostructured graphite surface (*figure on the right*), with a surface roughness that increases the contact area with the droplets by 3.5 times (compared to a flat surface of the same material).
a) What model would you use to estimate the effective contact angle of the droplet on this surface?
b) Calculate the water contact angle on the nanostructured graphite surface, and on the same surface after coating with dodecyltrichlorosilane (DDTS). The water contact angles with the corresponding flat surfaces are 75° (graphite) and 105° (DDTS coated graphite).
c) Comment on the wetting properties of the two nanostructured surfaces and their possible applications.
d) Discuss the effect of the solvent surface tension when drying mesoporous materials. What is the effect on the pressure difference when the pore diameter decreases from 30 nm to 3 nm?

Forces and Stability

1. The stability of nanoparticle dispersions depends on solvent-mediated interactions.
a) Draw the curves of the potential energy/kT of two nanoparticles as a function of their separation distance for the cases of: i) a stable dispersion; ii) a metastable dispersion; iii) an unstable dispersion; and iv) a dispersion showing flocculation.

b) According to the Hamaker theory, the attractive London (dispersion) interactions between two nanoparticles in a solvent can actually led to net repulsion between the particles. Explain how.

HINT:

$$A_{L12} = \left(\sqrt{A_{11}} - \sqrt{A_{LL}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{LL}}\right) \qquad A_{12} = \pi^2 \rho_1 \rho_2 \lambda_{12}$$

- If A_{LL} lies in between A_{11} and A_{22} then $A_{L12} < 0$

  ↳ Repulsion between **1** and **2** in medium **L**
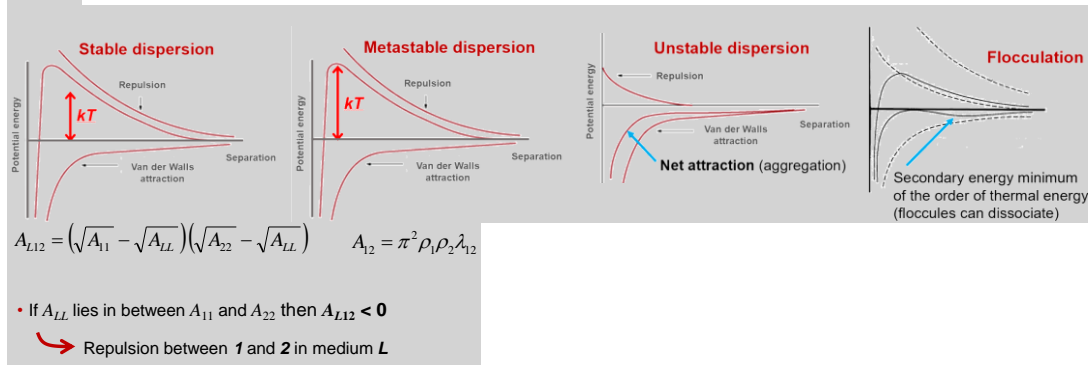
2. The DLVO theory combines the effects of attractive and repulsive interactions to describe the stability of nanoparticle dispersions.
a) What type of interactions are taken into account and how are they modeled in the DLVO theory?
b) How do these relate to curves A, B and C?
c) Explain what happens when the relative separation distance reaches the values D and E.
d) What is the effect of temperature on the stability of the nanoparticle dispersion described by the Figure?
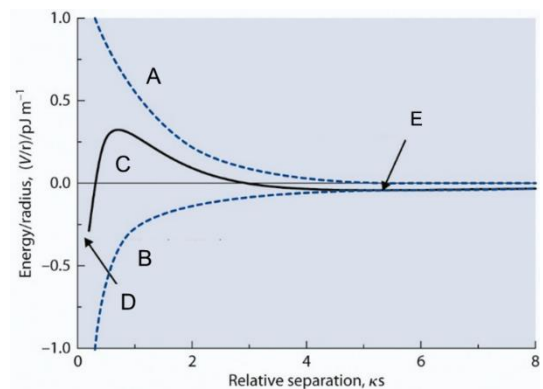
HINT: van der Waals attraction (Hamaker approximation) and electrostatic repulsion (electric double layer potential); A-electrostatic repulsion, B-Van der Waals attraction, C- resulting potential; D-aggregation, E-flocculation; kT < energy barrier in C, stable system (otherwise, unstable)

3. Explain the different distance range of van der Walls forces in nanoparticles and in molecules. What is the meaning of the Hamaker constant? Calculate the interaction energy of two gold spherical nanoparticles ($A_{Au} = 45.3 \times 10^{-20}$ J) of 5 nm radius in water ($A_w = 4.35 \times 10^{-20}$ J), whose centers are separated by an average distance of 20 nm. How does the stability of the system depend on temperature?

HINT: Hamaker - pairwise integration of all point dispersive interactions; ϕ = - 9×10^{-21} J; if no repulsion is present, would be stable if enough thermal energy is available to randomize the system, $|\phi| <$ kT, which corresponds to T > 378ºC (>> T_b of water!)

4. Explain the possible effects of adsorbing and non-adsorbing polymer chains in a nanoparticle dispersion. Suggest strategies to favor the stability of systems containing polymers and nanoparticles.

HINT: Adsorbing: steric repulsion, bridging flocculation; non-absorbing: depletion attraction; grafting polymer chains, adsorbing amphiphilic copolymers, etc.

5. The interaction energy between particles due to van der Waals forces depend on the medium.

a) Calculate the interaction energy between two polystyrene nanoparticles (diameter 100 nm) with separation between their surfaces of h=10 nm and h=1 nm, knowing the Hamakers constant of polystyrene (A=6,6x10^{-20} J) and water (3,7x10^{-20} J). Compare the values with the thermal energy at 25 ºC and comment the results.

b) Could the interaction be repulsive in a medium other than water? For which range of values of the Hamakers constant of the medium?

c) Indicate methods to prevent the flocculation/coagulation of the dispersion in water.

HINT: ϕ (10nm) = - 1.7x10^{-21} J, ϕ (1nm) = - 1.7x10^{-20} J; kT = 4.1x10^{-21} J, stable at 10 nm but not at 1 nm separation (if no repulsion present); for similar nanoparticles, the Hamaker constant is always positive (attractive interaction); electrostatic or steric repulsion necessary: discuss methods to have charge or polymer chains at the surface

6. The colloidal stability of dispersed nanoparticles can be achieved by solvent-mediated attraction/repulsion electrostatic interactions. What are these interactions and what are their roles? Describe the three possible stability states arising from their actuation and the corresponding outcome of the dispersion. Sketch the potential vs. distance curves for two particles in these states.

7. In the context of the DLVO theory, explain how the stability of a nanoparticle dispersion changes with: the Hamaker constant; the surface electrostatic potential; the particle size; the temperature; and the ionic strength.

8. How does Van der Waals attraction and electric double layer repulsion change with the distance between two nanoparticles grafted with polymer chains? Sketch the different types of interaction curves resulting for high and low polymer coverage at different temperatures.

9. Polymers that absorb to nanoparticles can have opposing effects on their stability: discuss these phenomena using the free energy of mixing for polymer-solvent interactions.

What are the methods that can be used to stabilize suspensions of nanoparticles?

Can one have electrostatic stabilization of nanoparticles in a solvent other than water? If yes, under which conditions? Describe other strategies for stabilization of nanoparticles in a dispersion.

Can one have steric stabilization in an aqueous medium? Explain how.

Discuss the effect of the ionic strength of the medium in the stability of colloidal dispersions.

Self-Assembling

1. Different interactions can be used for the self-assembling of nanostructured materials. Discuss the characteristic of the interactions that allow appropriate control over the process. Compare three such interactions discussing their advantages and disadvantages.
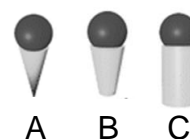
2. Amphiphilic molecules are used to obtain self-assembled monolayers (SAMs): discuss how to induce order in these structures.

3. Amphiphilic molecules can self-assemble to form structures that are often used as templates in nanofabrication methods.
a) What are the critical parameters that control the self-assembling of amphiphilic molecules? The molecules represented in the figure (*right, with hydrophilic part in dark*) originate different structures in water. Attribute three possible different structures to A, B and C (compatible with their relative shapes).
b) Describe a strategy to prepare mesoporous silica nanoparticles using a surfactant. What should be the characteristics of the surfactant molecules to obtain particles with aligned pores?

A   B   C

4. Layer by layer (LbL) assembly can be used to coat nanoparticles, modifying their surface properties.
a) Describe the type of materials and a process to obtain nanoparticles coated by the LbL method.
b) What kind of stabilization do you expect for these particles?
c) One way to organize these nanoparticles in a surface is to deposit them in a previously patterned surface produced by soft lithography. Describe one soft lithography technique that would allow the deposition of the nanoparticles in a pattern.

5. What are Metal Organic Frameworks (MOFs)? What are their main characteristics and how are they assembled?

6. Self-assembling is widely used to prepare multi-layer films for different applications. Describe one technique used to prepare such films and different film geometries that can be obtained. How would you include metal nanoparticles in this type of films.

7. In aqueous media, amphiphilic molecules self-assemble to form different structures. Explain how the shape of these aggregates can be predicted from the structure of the molecules.

8. Describe the *layer-by-layer* self-assembling technique specifying what type of materials can be used and how are they applied.

Microfabrication

1. What are the three most important unit operations used in microfabrication? Explain how can they be used to produce patterns on a substrate.

HINT: thin film deposition, pattern transfer by lithography, selective etching

2. Compare two different processes of pattern transfer by lithography used in microfabrication.

3. What are the main differences between the CVD and PVD techniques for thin film deposition?.

4. Explain 2 types of optical lithography processes. Discuss the advantages and disadvantages of optical and e-beam lithography.

5. Describe two different processes yielding isotropic and anisotropic etching.

Polymer Nanostructures and Metal Oxides

1. Polymer nanoparticles can be obtained by different techniques, namely emulsion and miniemulsion polymerization.
a) How can a miniemulsion be prepared?
b) What are the roles of monomer droplets in emulsion and in miniemulsion polymerization?
c) Briefly explain why it is easier to produce polymer nanoparticles with very low size dispersity using emulsion polymerization than using miniemulsion.
d) Miniemulsion polymerization is usually chosen over emulsion for encapsulation of hydrophobic cargo in polymer nanoparticles. Why?

HINT: Monomer is emulsified with surfactant and co-stabilizer using high shear stirring or ultrasound; in emulsion, droplets act as monomer reservoirs, in miniemulsion polymerization occurs in the droplets; in emulsion polymerization initiation starts in micelles (larger specific surface area), micelles with no radicals are depleted so there is no further nucleation (in miniemulsion droplet size distribution, depending on shear, etc., determines size dispersity); miniemulsion is preferred in the encapsulation of hydrophobic cargo because polymerization occurs inside the droplets containing the cargo.

2. Explain the common strategy used to control the size of polymer chains in controlled radical polymerization techniques. Give two examples of these techniques and one application for monodisperse polymer chains.

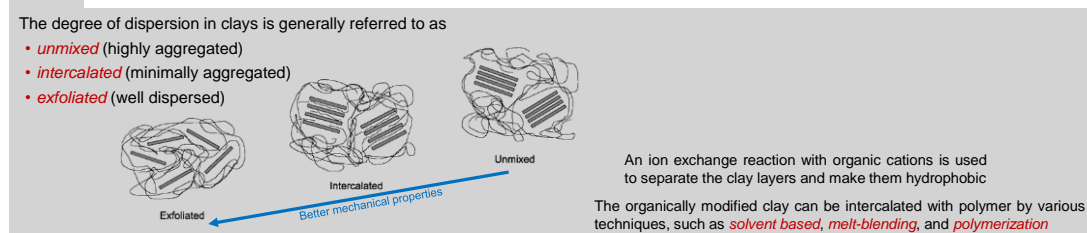**HINT**: they rely on slowing the polymerization kinetics to avoid radical deactivation

3. How would you produce mesoporous silica nanoparticles? Explain how can the nanoparticle size and the pore diameter be controlled independently. Explain the difference in nanoparticle diameter usually obtained by electron microscopy and light scattering techniques.

HINT: template of cylindrical micelles, sol-gel, silica precursor hydrolysis/condensation; cylindrical micelle (template) diameter controls pore diameter, stability of the micelles and formation of micelle bundles, reaction kinetics and shear, controls particle size; TEM/SEM gives dry diameter, DLS gives hydrodynamic diameter

Nanocomposites

1. Smectic clays, in particular montmorillonite (MMT), are use in clay-polymer nanocomposites. Use a diagram to explain the dependence of the performance of these nanocomposites on the dispersion of the clay in the polymer matrix. Describe a strategy to prepare the structure that yields the best nanocomposite properties.
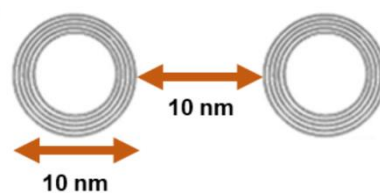
HINT:

The degree of dispersion in clays is generally referred to as
- *unmixed* (highly aggregated)
- *intercalated* (minimally aggregated)
- *exfoliated* (well dispersed)

Unmixed

Intercalated

Exfoliated

Better mechanical properties

An ion exchange reaction with organic cations is used to separate the clay layers and make them hydrophobic

The organically modified clay can be intercalated with polymer by various techniques, such as *solvent based*, *melt-blending*, and *polymerization*

2. Discuss the critical parameters for preparing polymer nanocomposites with carbon nanotubes (CNTs).
What is the approximate volume fraction of multi-wall carbon nanotubes (MWCNTs) with 10 nm in diameter that would be necessary to prepare a polymer nanocomposite in which the MWCNTs are 10 nm apart on average?
Compare the processability of this nanocomposite with that of an equivalent nanocomposite containing single-wall carbon nanotubes (SWCNTs) with the same average separation distance.

HINT: Critical factors to be addressed are the dispersion of CNTs in the polymer matrix, the alignment of CNTs and the CNT/matrix interfacial bonding; In the calculation use the section areas, assuming similar CNT lengths; MWCNT 40 vol% and SWCNT (ca. 1 nm diameter) 1 vol%; A composite with 40 vol% CNTs is much more difficult to process due to aggregation, etc.

3. Nanocomposites of graphene offer high mechanical strength at very low density, with huge potential for structural applications. Discuss the critical parameters of the preparation of graphene nanocomposites and suggest a process to implement their production.

$$P^\alpha - P^\beta = 2\gamma \; \frac{1}{r_m} \qquad P^c = P^\infty \; exp\left[\frac{\bar{V}}{RT}\left(\frac{2\gamma}{r_m}\right)\right] \qquad \frac{1}{r_m} = \frac{1}{2}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$\ln\left(\frac{C_c}{C_\infty}\right) = \frac{V_a}{KT}\left(\frac{2\gamma}{r_m}\right) \qquad \Delta\mu = \gamma V_a \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$A_{L12} = \left(\sqrt{A_{11}} - \sqrt{A_{LL}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{LL}}\right) \qquad \phi = -A\frac{R}{12\;d}$$

$$\cos\theta_W^* = f_1 \cos\theta_1 + f_2 \cos\theta_2 \qquad \cos\theta_{CB}^* = \alpha \cos\theta \qquad \gamma_{GS} = \gamma_{LS} + \gamma_{GL}\;\cos\theta$$

$$\Phi \propto \psi_0^2 \; exp(-\kappa\;d) - \frac{R\;A_{eff}}{12\;d}$$