Nano Structured Materials

**Midterm Examination**

April 22nd, 2020

**PART 1**

1. **What are the main challenges that should be overcome in the fabrication of nanomaterials and nanostructure?**
2. Materials in the nanoscale exhibit a large surface area, and therefore huge surface energy. The challenge is to control the surface energy as it plays a significant role in thermal stability.
3. Achieve homogeneity in the fabrication processes. Challenge is to tailor the current fabrication techniques to ensure the product to have the desired properties with consistent size, uniform size distribution, morphology, crystallinity and chemical composition.
4. Due to the large surface energy, the system is prone to reduce the overall surface energy by agglomeration and Ostwald ripening. Challenge is to halt nanomaterials and nanostructures from coarsening.

* S. Weinberg, Introduction, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 1–17. https://doi.org/10.1142/9789814340571\_0001.
* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.

1. **What is the role of the chemical potential on the** **Ostwald ripening effect? Please justify your answer.**

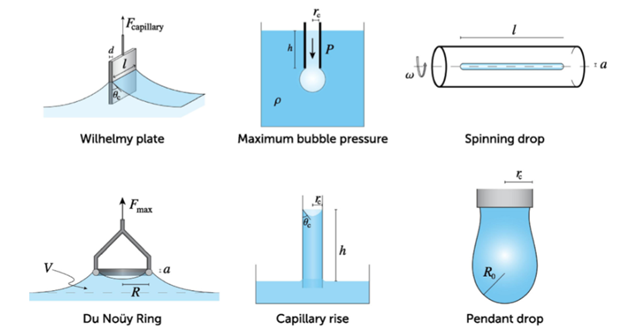
Spontaneous growth is a process driven by the reduction of Gibbs free energy or chemical potential. The Ostwald ripening effect can be understood as a self-assembly process where small particles are arranged/packed together by the reduction of overall chemical potential.

Thermodynamic-wise, the chemical potential decreases when mass is transferred from a flat surface to a concave surface. Meaning that a convex surface (small particle) possesses higher chemical potential, than a concave surface (large particle). In solution, the solubility of the small particle is larger than the solubility of the large particle, as the solute is deposited onto the large particle and the small particle continues to dissolve. Dissolution of the small particles will halt when the concentration of solid in the solvent equals to the equilibrium solubility of the large particles.

* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.
* G. Cao, Nanostructures and Nanomaterials, PUBLISHED BY IMPERIAL COLLEGE PRESS AND DISTRIBUTED BY WORLD SCIENTIFIC PUBLISHING CO., 2004. https://doi.org/10.1142/p305.

1. **You have a job interview and in the last round of interviews you are asked the following question: “tell me how would you measure surface tension of a solution with suspended nanoparticles”. Write down your answer(s)**

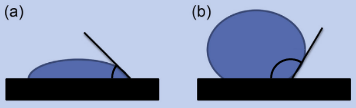
There are multiple techniques available for the measurement of surface tension (ST) of nanofluids, such as:



The surface tension measurement for nanoparticles solution with single specific method is hard to define as the surface tension for a solution varies with various parameters (temperature of the solution, surfactant addition, type and content of the nanoparticles, size distribution and loading concentration of nanoparticles in solution).

For simplicity and ease of use, the contact angle method can be implemented:

1. Ensure the nanoparticles are well dispersed
2. Measure the surface tension by contact angle. Lower contact angles (a), refer to increased wetting and therefore lower surface tension. A higher contact angle (b) indicate a higher surface tension.



1. Once the contact angle is obtained, the surface tension can be calculated with Young's equation.

Although contact angle measurement and capillary rise/fall measurements can be one of the most common techniques for surface tension measurements, such measurements in nanofluids is not straight forward and requires consideration of multiple parameters as mentioned above. A more complete measurement can be achieved with a rheometer, since the nanoparticles may change the fluid viscosity with applied stress, i.e. shear thinning or thickening behaviors.

* V.S. Kulkarni, C. Shaw, Surfactants, Lipids, and Surface Chemistry, in: Essent. Chem. Formul. Semisolid Liq. Dosages, Elsevier, 2016: pp. 5–19. https://doi.org/10.1016/B978-0-12-801024-2.00002-9.
* P. Estellé, D. Cabaleiro, G. Żyła, L. Lugo, S.M.S. Murshed, Current trends in surface tension and wetting behavior of nanofluids, Renew. Sustain. Energy Rev. 94 (2018) 931–944. https://doi.org/10.1016/j.rser.2018.07.006.

1. **You want to sell an oil solution loaded with paramagnetic nanoparticles (CoFeO4), but the particles do not form a stable suspension. How could you make them stable, so you can make a profitable business?**

Stability may be achieved by the introduction of a polymer stabilizer such as PVP or PVA. The polymer stabilizer can prevent nanoparticles to agglomerate, but it can also affect the growth process of nanoparticles depending on the solid chemistry, the solvent and temperature. On the other hand, stabilization can also be obtained without a stabilizing reagent by an electrostatic stabilization mechanism.

* M. Benelmekki, M. Benelmekki, Zero-Dimensional Nanostructures: Nanoparticles, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 61–141. https://doi.org/10.1142/9789814340571\_0003.

1. **Prove that droplets with small radius have a higher vapor pressure than the ones with higher radius.**

This is related to question 2. Concave surfaces in a material have lower surface energy than convex surfaces, this difference influences the equilibrium vapor pressure. The relationship between particle radius and vapor pressure can be described by the Kevin equation.

Where; is the equilibrium vapor pressure of the curved solid surface,

is the equilibrium vapor pressure of flat solid surface,

is the surface energy,

is the atomic volume,

is the Boltzmann constant,

is the radii of curvature, and

is the temperature.

As depicted if the equation, if the radius increases, the overall equilibrium vapor pressure decreases.

The Kevin equation is derived from the chemical potential as a function of surface curvature. For a spherical particle, its volume change is equal to the atomic volume Ω times , as follows: . On the other hand, the work per atom transferred is the change of chemical potential . Combining both equations, we have that: (known as Young–Laplace equation). For any curved surface, the Young–Laplace equation can be generalized by two main radii of curvatures and as follows: . Assuming the vapor of solid phase behaves as an ideal gas, the following describes the change in chemical potential for a flat surface: . Similarly for a curved surface the following is obtained: . By combining the previous two equations, we obtain: . The Kevin equation is obtained once the latest equation is simplified for a spherical particle.

Where; are the transferred atoms from a flat surface to a particle with radius ,

is the atomic volume,

is the change of chemical potential,

is the chemical potential of a vapor atom,

is the chemical potential of an atom on the curved surface,

is the chemical potential of an atom on the flat surface, and

is the equilibrium vapor pressure of the curved solid surface.

* Y. Tanwar, A. Sharma, Y. Tanwar, Physical Chemistry of Solid Surfaces, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 19–60. https://doi.org/10.1142/9789814340571\_0002.

1. **You are in charge of a nanoparticles production line and there is a problem with the size distribution that is too widespread and the client is asking you to narrow it down or She will look for another provider. Your boss asks you to make recommendations on how to make the distribution narrower. What would you recommend? (Justify your answer and list any assumptions you make).**

The problem can be tackled from two approaches: Ostwald ripening and diffusion-limited growth.

First, Ostwald ripening can be implemented to narrow the size distribution of nanoparticles by removing small particles as large particles grow at the expense of the smaller particles. With this approach, will narrow the size distribution, but will also increase the final size of the nanoparticles.

On the other hand, diffusion-limited growth would reduce the size distribution of the nanoparticles. Diffusion-limited growth can be achieved by:

1. Increasing the solution viscosity,
2. Introducing of a diffusion barrier (polymer layer) to limit the nanoparticles to further growth,
3. Keeping the concentration of growth species at low levels, and/or
4. Controlling the supply of growth species as the rate of reaction can be manipulated through the control of the concentration of the reactants.

However, some considerations are to be considered. Solutions a) and b) could introduce new reagents to the process which may increase the cost and/or composition of the final product, though the viscosity can me amended by temperature changes. Solutions c) and d) may not require additional reagents but may slow down the production.

The purpose of the processes listed above is to program all nuclei generation at the same and quick time interval. This requirement will ensure the nuclei size to be similar as they are generated under similar conditions along with their subsequent growth.

* S. Weinberg, Introduction, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 1–17. https://doi.org/10.1142/9789814340571\_0001.
* M. Benelmekki, M. Benelmekki, Zero-Dimensional Nanostructures: Nanoparticles, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 61–141. https://doi.org/10.1142/9789814340571\_0003.

1. **You want to produce a nanoporous silica glass, please explain how would you prepare such glass.**

The method involves the addition of an anionic silicate source such as tetraethylorthosilicate (TEOS) to an aqueous solution with a template/surfactant. Once the formation of the silica hydrogel is formed, the template is removed by calcination. Surfactants will be used in the synthesis of nanoporous silica glass (NSG) due to their tendency to form micelles. Silica sources tend to aggregate and form silica networks around these micelles.

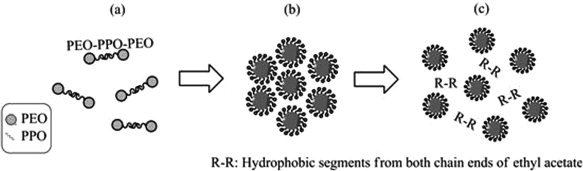
The synthesis of NSG will follow the process bellow:

1. Dissolve the surfactant/template in deionized water,
2. While stirring add TEOS slowly to the surfactant solution to create a gel,
3. Separate/filter the white precipitate,
4. Wash the product with deionized water, and
5. Remove the template by drying and heating the sample.

* M. Grün, K.K. Unger, A. Matsumoto, K. Tsutsumi, Novel pathways for the preparation of mesoporous MCM-41 materials: control of porosity and morphology, Microporous Mesoporous Mater. 27 (1999) 207–216. https://doi.org/10.1016/S1387-1811(98)00255-8.

1. **Explain how come Pluronics can act as a surfactant.**

Pluronics are triblock co-polymers (PEO-PPO-PEO). The hydrophilic PEO and the hydrophobic PPO segments within Pluronics, provide the “amphiphilic” properties of surfactants (as they contain both hydrophilic and hydrophobic portions on the same molecule). Pluronics with a longer PPO segment and shorter PEO segments will be hydrophobic and those with the reverse composition will be hydrophilic. Due to the “amphiphilic” properties, Pluronics are prone to the formation of micelles when used in bulk, as in the figure below.



Arrangement happens when PPO chains are placed outside on the surface and PEO chains inside the micellar structure towards the center.

* A. Sundblom, A.E.C. Palmqvist, K. Holmberg, Study of the Pluronic−Silica Interaction in Synthesis of Mesoporous Silica under Mild Acidic Conditions, Langmuir. 26 (2010) 1983–1990. https://doi.org/10.1021/la902144h.
* V.S. Kulkarni, C. Shaw, Surfactants, Lipids, and Surface Chemistry, in: Essent. Chem. Formul. Semisolid Liq. Dosages, Elsevier, 2016: pp. 5–19. https://doi.org/10.1016/B978-0-12-801024-2.00002-9.
* H.-R. Lin, P.-C. Chang, Novel pluronic-chitosan micelle as an ocular delivery system, J. Biomed. Mater. Res. Part B Appl. Biomater. 101B (2013) 689–699. https://doi.org/10.1002/jbm.b.32871.
* I.R. Schmolka, A review of block polymer surfactants, J. Am. Oil Chem. Soc. 54 (1977) 110–116. https://doi.org/10.1007/BF02894385.

**PART 2**

1. **Explain the differences and similarities between homogeneous nucleation and heterogeneous nucleation for the synthesis of nanoparticles.**

Nucleation is the process where a nuclei (or seed) act as a template for crystal growth and can describe several chemical syntheses. However, the formation of porous solids does not always follow the typical crystallization process in solution. Homogeneous nucleation occurs when nuclei form uniformly throughout the parent phase, whereas heterogeneous nucleation forms at structural deformities (container surfaces, impurities, grain, etc.) In a liquid phase, heterogeneous nucleation happens with ease, since a stable nucleating surface is already present.

The process of homogeneous nuclei formation can be described thermodynamically by studying the total free energy and the bulk free energy. The formation of nanoparticles by homogeneous nucleation requires a supersaturation of growth species. When the concentration of a solute in a solvent exceeds its equilibrium solubility or temperature decreases below the phase transformation point, homogeneous nucleation takes place with the development of a new phase. Since a supersaturated solution has a high Gibbs free energy, the energy of the system shall decrease by segregating the solute from the solution. The reduction of Gibbs free energy if the driving force for nucleation and particle growth.

Heterogeneous nucleation happens when a new phase develops on the surface of another material. Like homogeneous nucleation, the Gibbs free energy decreases with an increase in surface energy. The energy barrier for heterogeneous nucleation is always smaller than that of homogeneous nucleation, which explains the fact that heterogeneous nucleation is more likely to happen than homogeneous nucleation (in most cases).

* M. Benelmekki, M. Benelmekki, Zero-Dimensional Nanostructures: Nanoparticles, in: Nanostructures Nanomater., WORLD SCIENTIFIC, 2011: pp. 61–141. https://doi.org/10.1142/9789814340571\_0003.
* N.T.K. Thanh, N. Maclean, S. Mahiddine, Mechanisms of Nucleation and Growth of Nanoparticles in Solution, Chem. Rev. 114 (2014) 7610–7630. https://doi.org/10.1021/cr400544s.