Final Examination

This exam should be answered individually and no contact with other classmates is allowed for the purpose of answering this test. It should be turn in any time before 10:00 am on June13th, and it should be sent via e-mail with the *SUBJECT: Final NMS2020*

# How do you explain from a thermodynamic point of view the Ostwald ripening phenomenon?

The driving force in the Ostwald ripening process is the decrease of the total surface free energy, where large particles grow at the expense of smaller particles. Ostwald ripening occur by the nucleation and growth of particles from an oversaturated solution. The result are dispersed particles with varying sizes depending on the nucleation rate. The dispersed particles do not meet thermodynamic equilibrium as the particles’ configuration is not at the lowest energy due to the excess surface energy. Consequently, the Ostwald ripening process continues to the point where the surface energy is as low as much as possible. The total energy is reduced by the increase of particle size and thus, by the decrease of surface area [1,2].

A solution undergoing the Ostwald ripening process is typically near to the equilibrium of a 2-phase system, but it is not at the lowest energy state possible. The thermodynamic imbalance is due to the polydisperse essence of the mixture and the presence of high surface free energy. The total surface area of the system in time to reach thermodynamic equilibrium. The process by which the particles grow is through diffusion, where mass transfers from particles with high interfacial curvature to particles with low interfacial curvature. Particle growth is triggered by concentration gradients within the solution around the particles. The Gibbs-Thomson relation describes the particle growth by thermodynamic demand, as the concentration at the surface of particles in equilibrium with larger particles is lower than that with smaller particles [1,2].

A system of disperse particles will be thermodynamically unstable due to a large interface area. The system approaches equilibrium by particle coarsening, where the particle solubility depends on the particle radii which described by the Gibbs-Thomson equation [3–5].

A derivation of the Gibbs-Thomson equation is detailed in Lin et al.’s work [4].

where:

* is the solute concentration at a plane interface in the matrix in equilibrium with particle of infinite radius,
* is the solubility at the surface of a spherical particle with radius ,
* is the specific interfacial energy of the matrix-precipitate particle boundary,
* is the mean atomic (or molar) volume of the particle,
* is the universal gas constant,
* is the absolute temperature, and
* is the particle radius of curvature.

# A nanolayer of atoms are deposited through a chemical reaction on a flat surface and you are asked to develop a general deposition model considering that the reaction can be a first or second order. Assume that both cases are diffusion controlled, the reaction velocity constants (RVCs) are the same and the diffusion rate is X times that of the RVCs. Write the model and make a drawing (by hand) to depict the phenomenon.

[SKIPED QUESTION]

# It was found that a soap solution film with an unknown constant thickness reflects the day light and the resulting reflection is blue with a wavelength of 475 nm. The refractive index of the soap solution is 1.4. What is the thickness of the film?

The thickness of soap film solution can be calculated from the thin film interference effect, where light interferes with different surfaces of a thin film. Since interference effects are noticeable when light interacts with structures of similar size to the light wavelength, a thin film shall have a thickness smaller than a few times the wavelength. It is expected to observe different colors at different thicknesses of a film as color is associated with the light wavelength. Thin film interference happens when the light reflected from the top and bottom surfaces of a film interfere with each other as illustrated in Figure 1 [6–8].

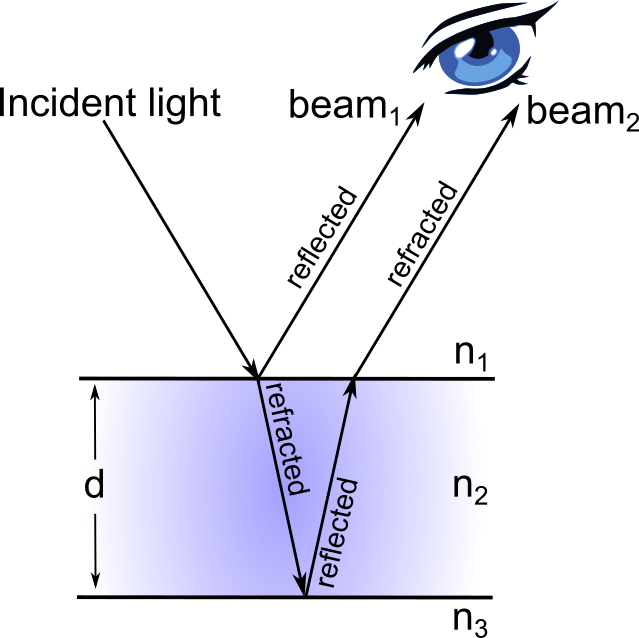


Figure 1 – The incident light is partially reflected at the top surface, and partially refracted to the bottom surface. The refracted beam is partially reflected at the bottom surface and is detected as beam2. The beam interference depends on the thickness of the film (d) and refraction index of the media (n1, n2, n3).

Then light is reflected from a material with higher refraction index than the material which the light is initially traveling, a shift takes place in the wavelength phase. If the film is a soap bubble, a shift exists for beam1 and none for beam2. Beam2 travels a longer distance that beam1, around farther. When the distance is a multiple od the wavelength in the medium, thin film interference happens depending on the phase change in either beam [9,10].

Looking back to Figure 1. If the soap thin film has a refraction index of and is surrounded between two media (air), then the light travels some distance inside the film which influences the optical path difference between beam1 and beam2. The optical path difference (OPD) is given by ; where is the refractive index of the soap film and is the distance traveled by the light, as is the thickness of the film. As a wavelength shift takes place, the film adds to the total path difference between the reflected beams of . Any constructive beam interference takes place when the path difference is a multiple of the wavelength such as . The total path difference is given by [6–8]:

The wavelength factor can be amended to by substituting as follows:

Where,

* is the thickness of the soap film for the two reflected beams to interfere constructively,
* is the phase of the interference,
* is the light wavelength, and
* is the refractive index of the soap film.

Substituting the given values in the previous equation, the soap thickness is given by:

is the minimum thickness of the film to reflect the blue color.

# You obtained a film of gold on a 1 cm2 silica wafer. The film is 10 nm thick and you are asked to produce gold nano dots:

The following assay is based on [11–15]. [16,17]

The gold nanodot fabrication technique will be based on the thermal dewetting method presented by Li et al. [17]. In their work, they proposed the fabrication od 2D gold nanodot array on a glass substrate. This process is comprised by the following steps:

1. deposition of a metal film on a substrate by sputter coating
2. patterning of a square nano-groove grid on the deposited metal film by the nanoplastic forming (NPF) technique
3. annealing of the patterned substrate in an electric furnace to cause dot aggregation.

The dot size and dot alignment can be controlled by adjusting the nanoplastic forming process parameters, by patterning a grid on the deposited gold film. The NPF is added before annealing into the fabrication process to achieve ordered nanodot arrays of uniform size, as shown in Figure 2.

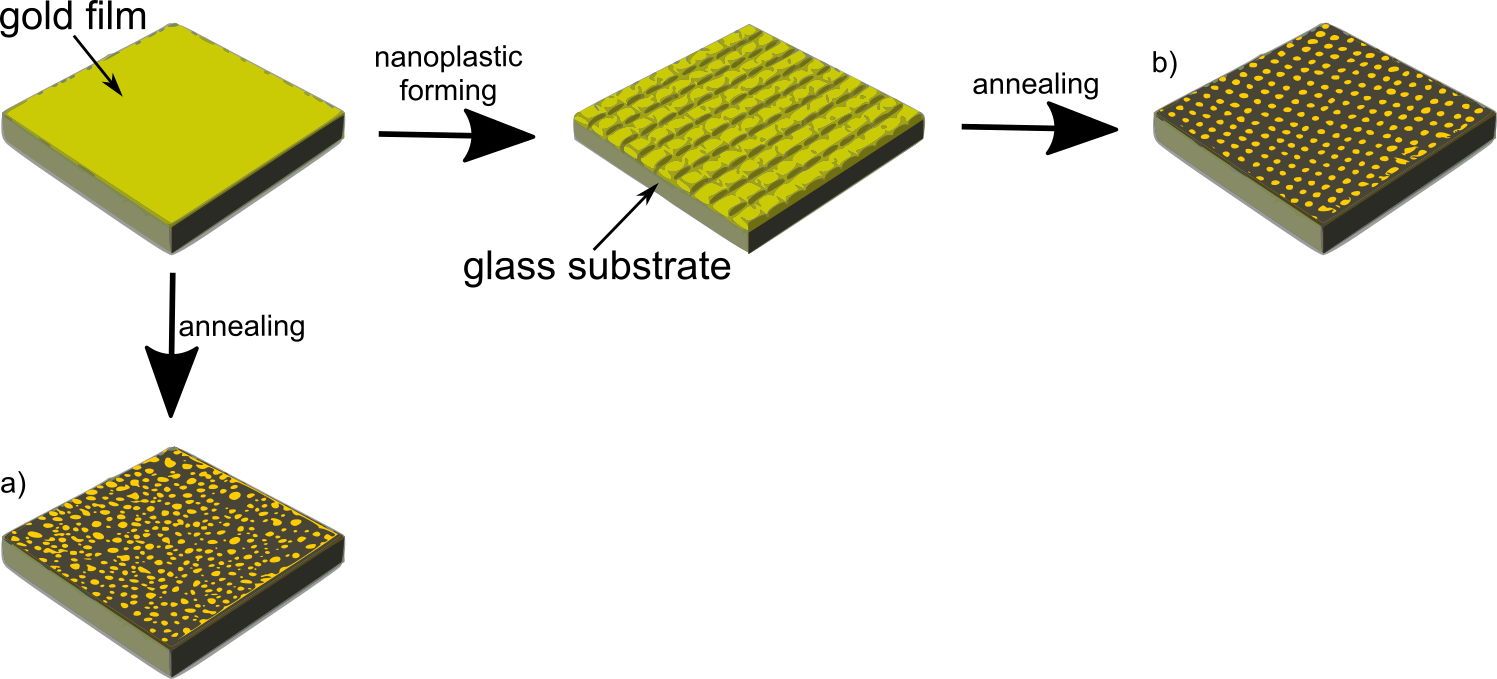


Figure 2 – Nanodot array fabrication process. a) disordered nanodot array annealed without nanoplastic forming. b) ordered nanodot array annealed with nanoplastic forming. Figure adapted from [17]

### Write an algorithm of the calculations you must do in order to determine the number of nanodots

* 1. First, assume a simplified model of the thermal dewetting process where a plane metal film agglomerates into a single spherical dot.
  2. Then, calculate the nanodot diameter from the diameter of a circular gold film that agglomerates into a single spherical nanodot.
  3. Finally, calculate the number of nanodots given the diameter of a circular gold film that agglomerates into a single spherical nanodot and the total gold film available on the glass substrate ().

The full calculation is presented in the following paragraphs.

### Write the equations, indicating what terms are temperature and surface tension dependent

### Show the calculations of how many nanodots you will get.

THEORY

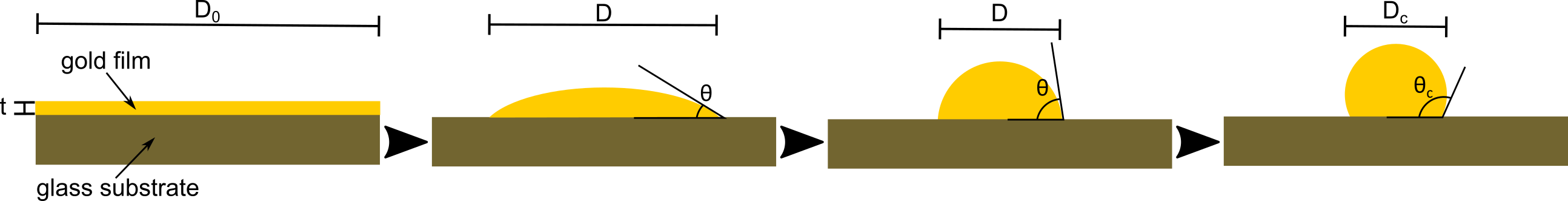


Figure 3 – Thermal dewetting process of a metal film deposited on a substrate [14]

As depicted in Figure 3, the thermal dewetting process takes place when a circular metal film of thickness and diameter agglomerates into a single spherical particle. is the transition particle diameter during agglomeration, and is the final dot diameter. The particle’s height increases throughout the process as the contact angle also increases [16]. The contact angle is related to the surface energy based on Young’s equation [18].

|  |  |  |
| --- | --- | --- |
|  |  | *(1)* |

Where:

* is the surface energy of gold,
* is the surface energy of the glass substrate in contact with the dot, and
* is the surface tension between the gold and the substrate.

Based on Young’s equation, the total free energy **before annealing** of the gold-glass system can be defined as:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  | (2) |

Where: *(3)* is the area of the substrate, such that

|  |  |  |
| --- | --- | --- |
|  |  | *(4)* |

As the total free energy of the system **during agglomeration** is comprised by , , and ; it can be calculated as follows:

|  |  |  |
| --- | --- | --- |
|  |  | (5) |

Where:

* is the surface area of the gold dot, and
* is the area in contact between the gold and the substrate.

When the angle in transition  **is** **below 90°**,

|  |  |  |
| --- | --- | --- |
|  |  | (6) |
|  |  | (7) |

Therefore, substituting *(1)*, *(6)* and *(7)* in *(5)*, is:

|  |  |  |
| --- | --- | --- |
|  |  | (8) |

The by agglomeration is given by [16]:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  | (9) |

When the angle in transition  **is** **above 90°**,

|  |  |  |
| --- | --- | --- |
|  |  | (10) |
|  |  | (11) |

Substituting *(1)*, *(10)*, *(11)* in *(5)* gives:

|  |  |  |
| --- | --- | --- |
|  |  | (12) |

The change/decrease in surface free energy by agglomeration is given by [16]:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  | (13) |

On the other hand, the volume of the gold hemisphere can be computes as [16,19,20]:

|  |  |  |
| --- | --- | --- |
|  |  | (14) |

Assuming that the metal volume is conserved throughout the dewetting process as the annealing temperature is above the melting point but below the boiling temperature of the deposited gold, the volume of the hemisphere is equal to the initial gold film volume:

|  |  |  |
| --- | --- | --- |
|  |  |  |
|  |  | (15) |

Hence, the dot diameter is:

|  |  |  |
| --- | --- | --- |
|  |  | (16) |

CALCULATION

Assuming the following values:

* [21],
* [22],
* [23], and
* [12].

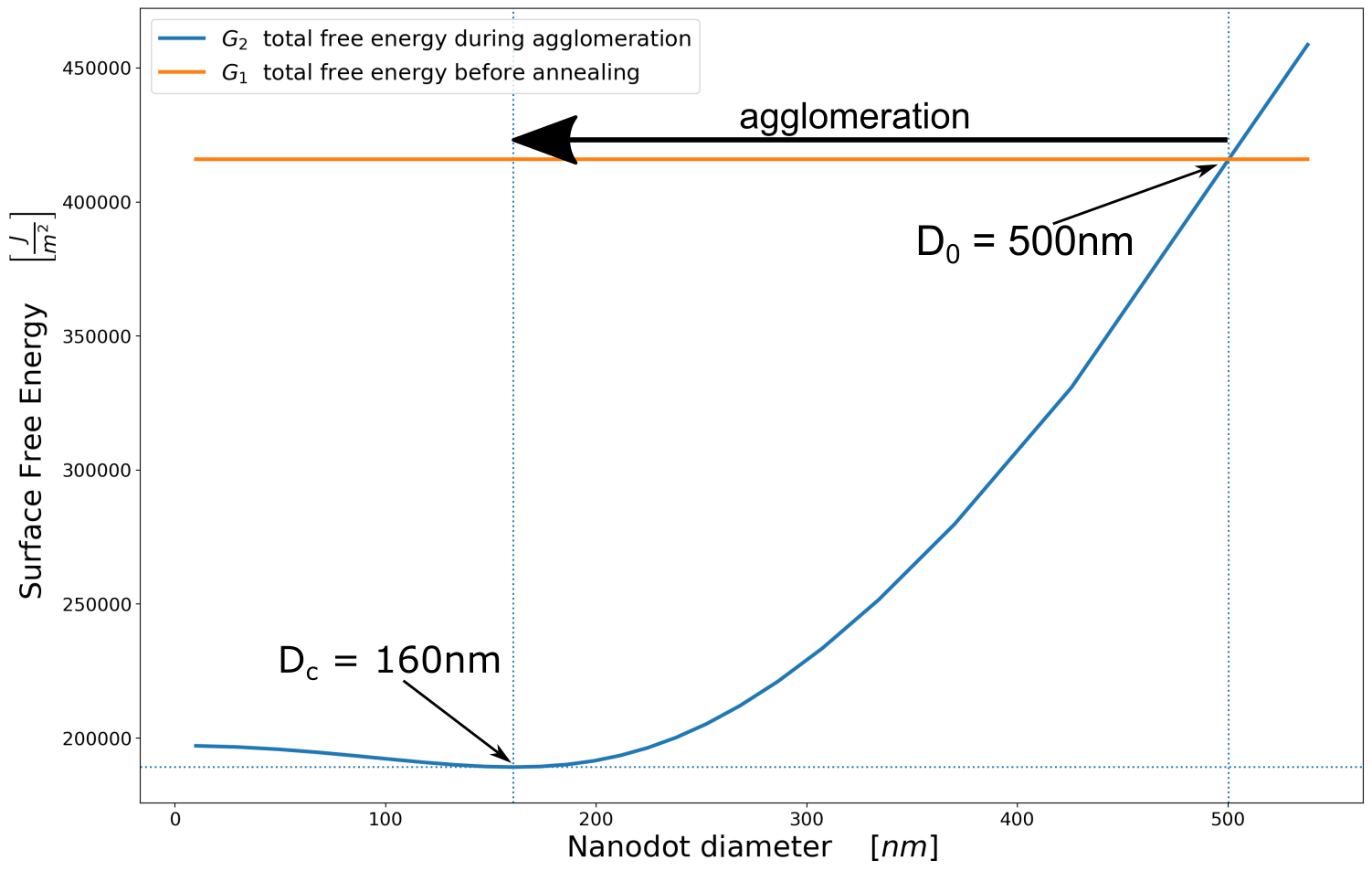


Figure 4 – Surface free energy in function of the gold nanodot diameter

As depicted in Figure 4, the gold nanodot agglomeration starts with a diameter of and ends at when the surface free energy during agglomeration reaches its minimum value with a contact angle of 134°.

As stated by Yoshino et al. and Iwamatsu [16,19], The diameter of the substrate is too small, the gold film is not able to agglomerate into a hemispherical structure. As depicted in Figure 5; if the initial conditions are the same as in Figure 4 but with a , then agglomeration cannot happen as the surface free energy does not decrease below the energy of the system before annealing.

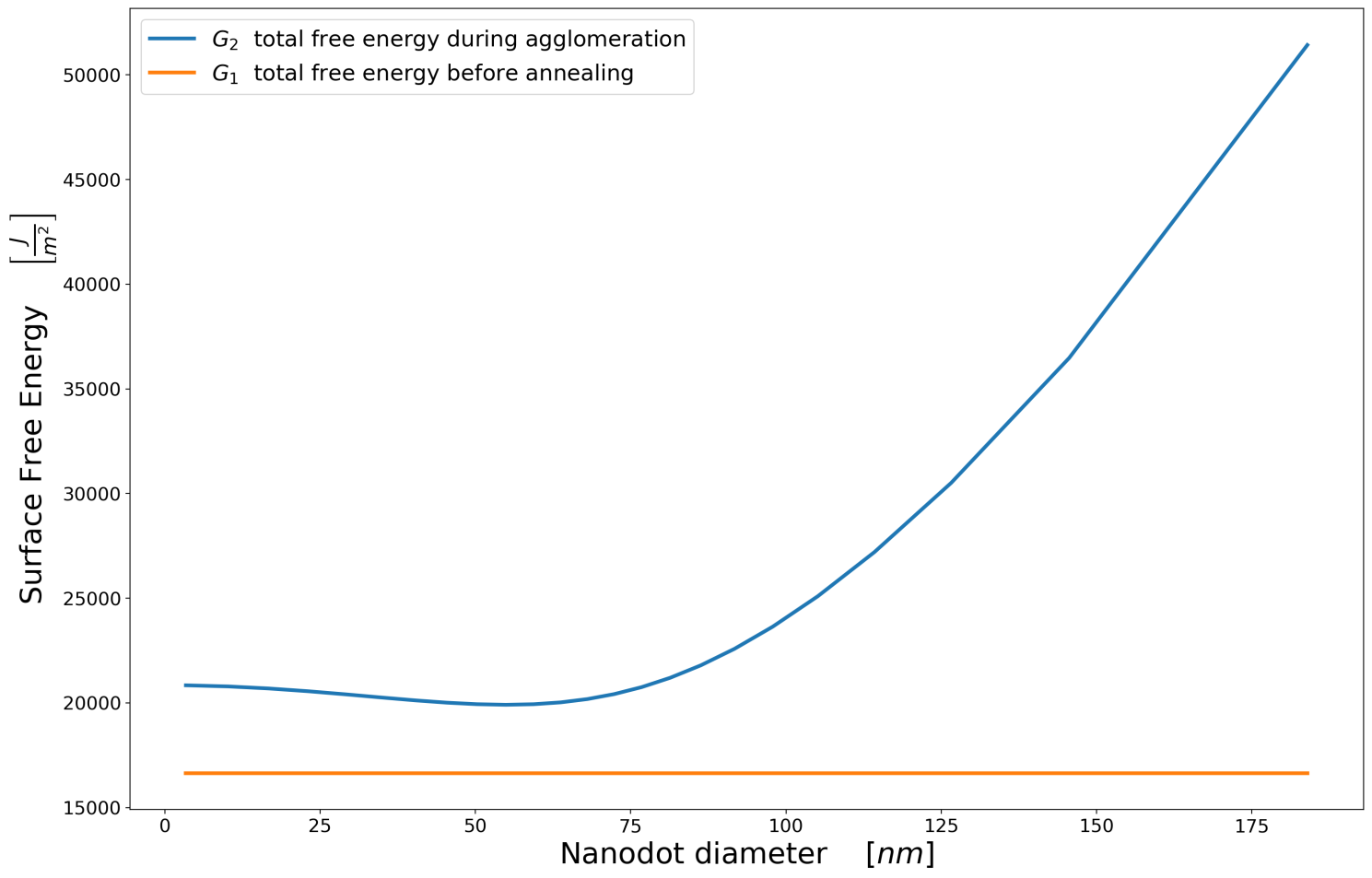


Figure 5 - Surface free energy in function of the gold nanodot diameter. Agglomeration is inhibited as the lowest surface free energy exists before annealing.

Following the simulation of Figure 4, 1 nanodot requires a circular substrate of diameter . Therefore, a single gold nanodot needs an area . If a film of gold is obtained on a 1 cm2 silica wafer, then the number of nanodots is given by:

A gold film of thickness will yield about 509295817 gold nanodots in a silicon substrate.

### Determine de % of area the nanodots will have on the 1 cm2 silica wafer.

Following the simulation of Figure 4, each gold nanodot will cover an area of . 509295817 gold nanodots will cover , the percentage of area covered by the nanodots in a is given by:

The nanodot yield will cover about 10% of the area of the silica wafer.

**Note:** Do not use the size of nanodots published in the literature to answer this question. However, you can use reported data for surface tension, density, etc.

# You are being interviewed by the CEO of the company Non-Gray Metals, and they asked you make a 3 slide power point presentation based on the paper: **“Laser coloration of metals in visual art and design”**. You should be very careful and need to be very professional on explaining the phenomenon that makes a metal to have different colors.

# Observe the surface of the gold nanoporous film given in the paper **“Localized surface plasmon resonance of nanoporous gold”**. How would you measure the surface tension and the morphology of the film?

# You want to start your own company on the fabrication of nano-porous membranes. You found the article: **“Nanoporous aluminum oxide membranes for biomedical micro hydraulic devices”** to get started but you want to create a membrane with less pore size dispersion. What factor would you alter to make the distribution narrower?

# References

[1] P.W. Voorhees, The theory of Ostwald ripening, J. Stat. Phys. 38 (1985) 231–252. https://doi.org/10.1007/BF01017860.

[2] P.W. Voorhees, Coarsening, Modeling Grain Growth, in: Encycl. Mater. Sci. Technol., Elsevier, 2001: pp. 1255–1258. https://doi.org/10.1016/B0-08-043152-6/00236-9.

[3] A. Baldan, Progress in Ostwald ripening theories and their applications in nickel-base super alloys, J. Mater. Sci. 37 (2002) 2379–2405. https://doi.org/10.1023/A:1015408116016.

[4] M. Lin, G. Gottstein, L.S. Shvindlerman, Generalized Gibbs-Thomson equation for nanoparticles at grain boundaries, Acta Mater. 129 (2017) 361–365. https://doi.org/10.1016/j.actamat.2017.03.007.

[5] J.W. Gibbs, On the equilibrium of heterogeneous substances, Am. J. Sci. s3-16 (1878) 441–458. https://doi.org/10.2475/ajs.s3-16.96.441.

[6] C.C. Lee, C.C. Kuo, Optical coatings for displays and lighting, in: Opt. Thin Film. Coatings From Mater. to Appl., Elsevier Ltd, 2013: pp. 564–595. https://doi.org/10.1533/9780857097316.4.564.

[7] R. Grunwald, Thin Film Micro-Optics, Elsevier, 2007. https://doi.org/10.1016/B978-0-444-51746-3.X5000-7.

[8] P.P. Urone, R. Hinrichs, K. Dirks, M. Sharma, College Physics, OpenStax, 2012. https://openstax.org/books/college-physics/pages/preface.

[9] M. Brindza, R.A. Flynn, J.S. Shirk, G. Beadie, Thin sample refractive index by transmission spectroscopy, Opt. Express. 22 (2014) 28537. https://doi.org/10.1364/OE.22.028537.

[10] T.K. Sarma, A. Chattopadhyay, Simultaneous Measurement of Flowing Fluid Layer and Film Thickness of a Soap Bubble Using a UV−Visible Spectrophotometer, Langmuir. 17 (2001) 6399–6403. https://doi.org/10.1021/la010594z.

[11] S.J. Henley, J.D. Carey, S.R.P. Silva, Pulsed-laser-induced nanoscale island formation in thin metal-on-oxide films, Phys. Rev. B. 72 (2005) 195408. https://doi.org/10.1103/PhysRevB.72.195408.

[12] Y. Nakata, K. Murakawa, N. Miyanaga, A. Narazaki, T. Shoji, Y. Tsuboi, Local Melting of Gold Thin Films by Femtosecond Laser-Interference Processing to Generate Nanoparticles on a Source Target, Nanomaterials. 8 (2018) 477. https://doi.org/10.3390/nano8070477.

[13] T. Höche∗, R. Böhme, J.W. Gerlach, B. Rauschenbach, F. Syrowatka, Nanoscale laser patterning of thin gold films, Philos. Mag. Lett. 86 (2006) 661–667. https://doi.org/10.1080/09500830600957357.

[14] Q. Xia, S.Y. Chou, The fabrication of periodic metal nanodot arrays through pulsed laser melting induced fragmentation of metal nanogratings, Nanotechnology. 20 (2009) 285310. https://doi.org/10.1088/0957-4484/20/28/285310.

[15] J. Lee, M. Nakamoto, T. Tanaka, Thermodynamic study on the melting of nanometer-sized gold particles on graphite substrate, J. Mater. Sci. 40 (2005) 2167–2171. https://doi.org/10.1007/s10853-005-1927-6.

[16] M. Yoshino, M. Terano, Fabrication of Metallic Nanodot Arrays, in: 2018: pp. 1–35. https://doi.org/10.1007/978-981-10-6588-0\_23-1.

[17] Z. Li, M. Yoshino, A. Yamanaka, Fabrication of three-dimensional ordered nanodot array structures by a thermal dewetting method, Nanotechnology. 23 (2012) 485303. https://doi.org/10.1088/0957-4484/23/48/485303.

[18] T. Young, An essay on the cohesion of fluids, Philos. Trans. R. Soc. London. 95 (1805) 65–87. https://doi.org/10.1098/rstl.1805.0005.

[19] M. Iwamatsu, Size-dependent contact angle and the wetting and drying transition of a droplet adsorbed onto a spherical substrate: Line-tension effect, Phys. Rev. E. 94 (2016) 042803. https://doi.org/10.1103/PhysRevE.94.042803.

[20] A. Sommers, A.M. Jacobi, Calculating the Volume of Water Droplets on Aluminum Surfaces, Int. Refrig. Air Cond. Conf. (2008) 1–8.

[21] S. Dukarov, A. Kryshtal, V. Sukhov, Surface Energy and Wetting in Island Films, Wetting and Wettability. (2015). https://doi.org/10.5772/60900.

[22] N. Martinez, Wettability of silicon, silicon dioxide, and organosilicate glass, 2009. http://digital.library.unt.edu/ark:/67531/metadc12161/m1/1/high\_res\_d/thesis.pdf.

[23] B.P. Azeredo, S.R. Yeratapally, J. Kacher, P.M. Ferreira, M.D. Sangid, An experimental and computational study of size-dependent contact-angle of dewetted metal nanodroplets below its melting temperature, Appl. Phys. Lett. 109 (2016) 213101. https://doi.org/10.1063/1.4968005.