070123 Quiz 1 Nanopowders

1) Dr. Shanov discussed the formation of carbon nanotubes last week in a process that involved the use of an iron catalyst and diffusion of carbon precursor through a molten iron nano-droplet to the growing graphene tube. Compare this process to the formation and growth of carbon soot particles in a flame. Use the words *homogeneous* and *heterogeneous* nucleation and explain why soot formation in a flame leads to isotropic (structurally the same in different directions) nano-particles while the nanotube synthesis leads to highly anisotropic nano-particles. Which process would you expect to lead to smaller particles?

2) Sketch a plot of free energy versus composition for a solution above and below the critical temperature (or versus volume for a gas above and below the critical pressure) as well as a phase diagram, temperature versus composition for a solution (or pressure versus volume for a gas). Indicate how the free energy plot and phase diagram are related to each other.

3) Consider a nano-scale particle that has homogeneously formed in a vapor phase. Write an expression for the free energy difference for formation of such a particle as a function of the particle size "r" using the chemical potential and the surface energy. How would this expression differ for a particle formed at the surface of a heterogeneous seed? (You can assume a cube shape or disk shape with thickness the same as diameter or other shaped particles.)

4) Sketch a plot of free energy versus particle size "r" for the two expressions you wrote in question 3. Indicate two critical points in this plot. Show which of the two plots has the lower "barrier energy" for nucleation.

5) For homogeneous nucleation calculate two expressions for the critical sizes associated with the two critical points in question 4.

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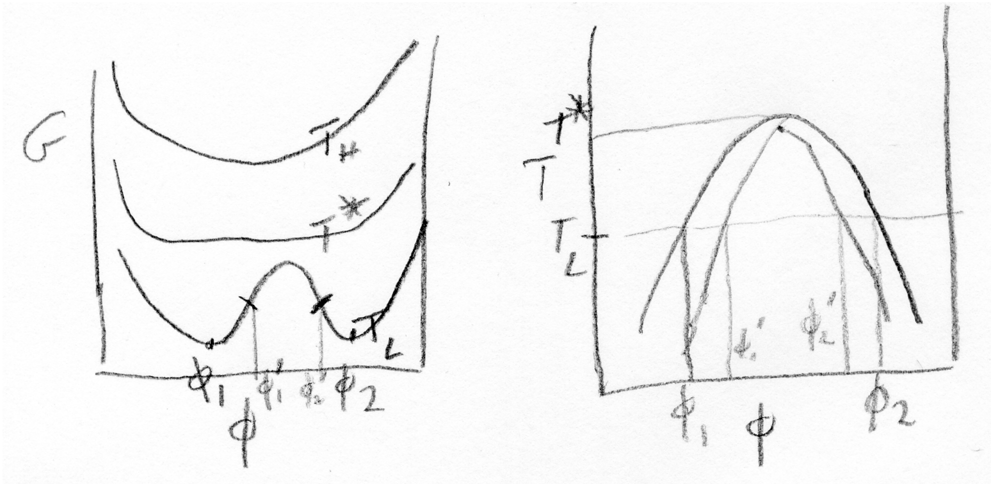
1) Carbon soot in a flame forms homogeneously while nanotubes grow by heterogeneous nucleation. Soot forms as an amorphous droplet and reduction in surface area leads to isotropic particles. For nano-tubes the heterogeneous growth is highly non-isotropic since growth is governed by the arrangement and size of the surface droplet of iron catalyst and transport of carbon to the catalyst surface. If you consider that graphene sheets are the most stable shape for carbon and that nucleation is more likely at the higher surface energy edges of the iron droplet, then it is reasonable to assume that the nanotube will grow from the circular edge of the catalyst droplet and that growth will produce a graphene cylinder.

The issue of which leads to a smaller particle is clouded by the asymmetry of the nano-tube and by the details of nano-tube synthesis. Generally surface nucleation leads to particles that are smaller by a factor of 2 compared with homogeneously nucleated particles as is shown in the answer to question 5. For nanotubes the tube diameter is largely governed by the diameter of the iron droplet from which they grow. The length is governed by the stability of the growth process and by the availability of the carbon source.

2)



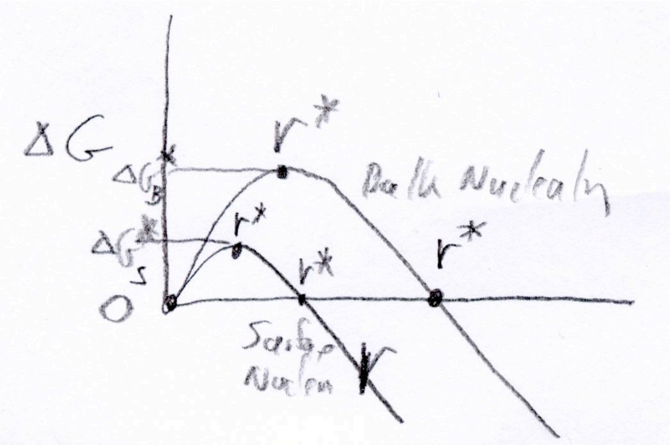
The phase diagram (right) is constructed from a series of free energy curves by considering points of constant $dG/d\phi$ such as the points ϕ_1 and ϕ_2 in the bottom free energy curve at T_L. These points for different temperatures yield the bimodal curve (outside curve in the phase diagram). The points of inflection (lines at ϕ_1' and ϕ_2' in the bottom free energy curve) yield the spinodal curve (inner curve in the phase diagram). Homogeneous nucleation occurs inside the spinodal curve, while only heterogeneous surface nucleation can occur between the bimodal and spinodal.

3) Assume a cubic particle such as a NaCl crystal. Each side has a free energy contribution $4 R^2\gamma$, so for the homogeneous cube the surface adds $24 R^2\gamma$, while for surface nucleated we add $16 R^2\gamma$. The bulk contribution is $8R^3\Delta\mu$.

$$\begin{aligned} \Delta G &= 24R^2\gamma + 8R^3\Delta\mu \quad \text{Homogeneous} \\ \Delta G &= 16R^2\gamma + 8R^3\Delta\mu \quad \text{Heterogeneous (Surface)} \end{aligned} \qquad (1),$$

where $\Delta\mu$ is negative and γ is positive.

4)



5) The critical energy is calculated by setting the first derivative of equation (1) to 0, obtaining r* at the peak and then using this r* in equation 1 to calculate ΔG*.

$$0 = 2\gamma + R^*_B\,\Delta\mu \quad \text{Homogeneous}$$

$$R^*_B = \frac{-2\gamma}{\Delta\mu}$$

$$0 = 4\gamma + 3\mathrm{R}^*_{\mathrm{S}}\,\Delta\mu \quad \text{Heterogeneous (Surface)}$$

$$\mathrm{R}^*_{\mathrm{S}} = \frac{-4\gamma}{3\Delta\mu}$$

$$\Delta G^*_B = \frac{32\gamma^3}{\Delta\mu^2} \quad \text{Homogeneous}$$

$$\Delta G^*_S = \frac{256\gamma^3}{27\Delta\mu^2} = \frac{9.48\gamma^3}{\Delta\mu^2} = 0.296\ \Delta G^*_B \quad \text{Heterogeneous (Surface)}$$

The critical size where growth is spontaneous (negative change in free energy) occurs when ΔG => 0 so:

$0 = 3\gamma + R^*_B \, \Delta\mu$ Homogeneous

$$R^*_B = \frac{-3\gamma}{\Delta\mu}$$

$0 = 2\gamma + R^*_S \, \Delta\mu$ Heterogeneous (Surface)

$$R^*_S = \frac{-2\gamma}{\Delta\mu}$$