020402 Quiz 1 Nanopowders

1) The properties of nano-particles are at least partly associated with the higher energetic state of surface monomers in a nano-cluster. When a cluster (solid phase) is in equilibrium with a solvated monomer, ML_m ,
   - -Give an expression for the surface energy of a monomer in a surface region, ψ^0.
   - -If you convert this surface energy to a per area basis, γ_0, does it depend on the cluster size, n, of a nano-cluster?
   - -Using this expression, how could the surface energy of a solid be reduced?

2) The Gibbs-Thompson equation, in the Ostwald-Freundlich form, relates the degree of supersaturation, $S = x/x_\infty$, to the surface energy per area, γ, and the nano-particle size, r.
   - -Write the Gibbs-Thompson equation giving the value for r for fixed values of S, T and γ.
   - -Use the known dependencies of these terms on n to write an expression for n.
   - -What does the Gibbs-Thompson equation suggest are the best conditions to grow nano-clusters?

3) Sketch $\Delta G/kT$ versus n for nanocluster formation and show n* and $\Delta G^*/kT$.
   - -Indicate the activation energy for nucleation in this plot.
   - -What is a critical nucleus for a nanocluster? (in words)
   - -How does the critical nucleus, n*, depend on nanocluster surface energy per surface monomer, ψ, and the supersaturation energy parameter, φ?

4) If Boltzmann statistics are used to describe the number concentration of nuclei larger than n*, what is the shape of the equilibrium number concentration of nuclei versus n?
   Does this present a problem for synthesis of nanoparticles?

Answers: 020402 Quiz 1 Nanopowders

1) The surface energy is related to the difference between the excess chemical potential of a monomer cluster in solution at concentration x=>1 and that at concentration x in equilibrium with the solid.

$\psi_0 = -kT\ln x$ where x is the concentration of the solvated clusters.

To convert to the surface energy per area you multiply by the number of surface monomers per cluster of size n, $\sim n^{2/3}$, and divided by the surface area per cluster which also scales with $n^{2/3}$ so there is no n dependence.

You can reduce the surface energy by lowering the concentration, x, of the monomers.

2) $r = 2v_1\gamma/(kT\ln(S))$

$n = \{2v_1\gamma/(kT\ln(S))\}^{1/3}$ Only r depends on n.

For nanoclusters you need low surface energy and a high degree of supersaturation.

3)

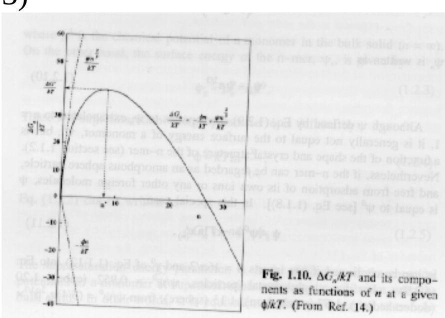

Fig. 1.10. $\Delta G_n/kT$ and its components as functions of n at a given ϕ/kT. (From Ref. 14.)

The y-value at the peak is the activation energy.

The critical nucleus is a cluster of size n* below which clusters dissipate and above which clusters grow.

$n^* = (2\psi/(3\varphi))^3$

4)

$$c_n^e = \frac{\exp\left(\frac{-\Delta G_n}{kT}\right)}{v_0} = \frac{\exp\left(\frac{n\varphi_n - n^{\frac{2}{3}}\psi}{kT}\right)}{v_0}$$

The equilibrium number concentration increases exponentially with n - kn$^{2/3}$. This means that it will be difficult to maintain a large population of small clusters unless kinetics are used to lock in early growth.