Interactions Between Metal Nanocrystals

Surface Phenomena

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Introduction

Metal nanocrystals are getting a great deal of attention recently due to the fact that they have optical and electronic properties that differ greatly from their bulk counterparts. Most nanocrystals are coated with some type of organic monolayer to control their solubility in solvents. The monolayer provides the steric repulsion necessary to keep the particles from flocculating. This allows for the particles to be redispersed into appropriate solvents, allowing for the formation of ordered lattices, wires, and other such assemblies. One of the most important applications of nanocrystals is in the form of a long range ordered superlattice. Formation of a superlattice requires robust particles with a very tight size distribution (within 10%). Since most nanocrystal synthesis techniques are unable to produce such tight particle distributions, it is important to be able to fractionate monodisperse particle samples.

The organic layer around the particle provides the necessary steric stabilization, necessary for particle stability. For sterically stabilized particles, it is important that the solvent is a good solvent for the organic layer. Other important issues are the size of the particle and the length of the layer. Monodisperse samples are collected by using a technique called size selective precipitation. This involves the addition of a miscible antisolvent into a particle solution. The antisolvent decreases the solvent quality (poor solvent regime). This leads to the flocculation of the particles. Since the solvent is not a very bad solvent, there is still some repulsion provided by the ligands. Since the larger particles have the most attraction, they flocculate, but the smaller particles are still stabilized by the organic layer. By controlling the amount of antisolvent added, it is possible to collect monodisperse size samples of the particles.

Analysis

The attractive (van der Waals) interaction from the metal cores can be estimated using the following equation.

$$\Phi_{vdW} = -\frac{A}{6} \left[\frac{2R^2}{d^2 + 4Rd} + \frac{2R^2}{d^2 + 4Rd + 4R^2} + \ln\left(\frac{d^2 + 4Rd}{d^2 + 4Rd + 4R^2}\right) \right]$$

Here, *R* is the particle radius and *d* is the surface-to-surface separation distance. Also, *A* is the hamaker constant for the pure silver particles interacting across the solvent. Using van der Waals interactions to explain nanocrystal behavior in solvents is commonly done in the literature, however, determining the hamaker constant accurately can be tricky. Values for the hamaker constant can be estimated from pure bulk silver properties, as have been done in the literature. It is important to realize that the hamaker constant is based primarily on the dielectric constant of the solvent and the particles; since the dielectric properties of nanocrystals is based on particles size, using bulk properties to determine an overall hamaker constant could potentially be a gross overestimation.

The stabilizing force is due to the organic monolayer. The stabilizing force considered is the osmotic force from the overlap of the monolayers. The analysis is the same as for electrostatic forces on two spheres. There is no electrical component; just a concentration based osmotic term. The relationship between the osmotic pressure and monomer concentration is shown below.

$$\Pi = \frac{RT\rho_2}{M_2}\phi_2 + \frac{RT}{V_1} \left(\frac{V_2\rho_2}{M_2}\right) \left(\frac{1}{2} - \chi\right) \phi_2^2$$

In this equation, *T* is the temperature, *R* is the gas constant and V_1 is the molar volume of the solvent. The rest of the variables relate to the polymer, ρ_2 is the density, V_2 is the molar volume and M_2 is the molecular weight. Also, ϕ_2 is the volume fraction polymer and χ is a measure of the interaction between the polymer molecules and the solvent molecules. This equation is derived from the Flory-Huggins Theory. Note, applying this equation to a CO₂ system (LCST) as proposed earlier may be problematic, because Sanchez-Lacombe predicts a different scaling for osmotic pressure with volume fraction. Based on this equation, the osmotic force can be determined for the polymer layer overlap.

It is also important to determine the shape of the organic layer. The shape for end-grafted polymer layers on a flat surface is shown below.

$$\phi(z) = \phi_o\left(1 - \left(\frac{z}{L}\right)^2\right)$$

For this equation, ϕ is the volume fraction of polymer, *L* is the length of the polymer brush and *z* is the direction outward from the wall that the polymer is grafted onto. This equation is based on numerical calculations, which indicate that the concentration profile of end-grafted polymers on a wall follows the shape of a parabola. The equation shown is a simplification of the actual numbers, allows us to remove solvent effects on the total size of the polymer layer. This shape assumes, that the polymer layer is not in the brush regime, and that the polymers are end-grafted, not homopolymers. This is reasonable, because the organic layers on the nanocrystals are also covalently bound through a thiol group.

Results

The analysis is done assuming theta conditions, $\chi = \frac{1}{2}$, and also including the χ parameter. The results show that indeed as the solvent conditions are worsened, the steric repulsion no longer is able to overcome the attractive force, and the particles will flocculate. Also included are the results for stability vs. particle size for a slightly bad solvent condition. Here, the size separation trend is seen, with larger particles becoming unstable, while smaller particles are still dispersible.

There are some important assumptions and limits that must be mentioned. The organic layer is not infinitely long. The layer has a finite thickness, which must be considered when doing the analysis. It is important to realize, that the concentration of polymer becomes 0 at the edge of the layer. It is not possible to solve the equation by using the boundary condition, $\phi(\infty) \rightarrow 0$. Also, the entropic effect of squeezing the organic layer, causing it to order, is not included, and could potentially be very important especially at small separations. Last, the organic layer concentration profile used was for a flat plane. In this geometry, it is going to fall of much faster, due to the extra curvature. This could lead to an overestimation of the stabilization force here.

References

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