Solutions to Soft Matter Exercise - Chapter 9: Particles

1. Characterization of Nanoparticles

Dynamic light scattering is only accurate if particles do not sediment. Therefore, we assume that the particles are Brownian and test this assumption at the end of the exercise. We use the Brownian velocity to determine the particle size:

$$v_{\text{brown}} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2k_BT}{\rho\frac{4}{3}\pi r^3}}$$

From this, we determine:

$$r = \Big(\sqrt{\frac{2k_BT}{\rho\frac{4}{3}\pi}} \times \frac{1}{v_{\text{brown}}}\Big)^{\frac{2}{3}} = \Big(\sqrt{\frac{2\times 1.38\times 10^{-23}\ \frac{\text{J}}{\text{K}}\times 298\ \text{K}}{1040\ \frac{\text{kg}}{\text{m}^3}\times\frac{4}{3}\pi}} \times \frac{1}{2\times 10^{-3}\ \frac{\text{m}}{\text{s}}}\Big)^{\frac{2}{3}}$$

$$= 779\ \text{nm}$$

To test if the particle is Brownian, we calculate the sedimentation length:

$$I_{\text{sed}} = \frac{k_BT}{m^*g} = \frac{k_BT}{\frac{4}{3}\pi r^3\Delta\rho g} = \frac{1.38\times 10^{-23}\ \frac{\text{J}}{\text{K}}\times 298\ \text{K}}{\frac{4}{3}\pi\times(779\times 10^{-9}\ \text{m})^3\times(1040-1000)\frac{\text{kg}}{\text{m}^3}\times 9.8\ \frac{\text{N}}{\text{kg}}}$$

$$= 5.3\times 10^{-6}\ \text{m}$$

The sedimentation length is longer than the particle diameter. Therefore, our approximation that the particle is Brownian was correct.

2. Nanoparticle Stability

a. Nanoparticles are subjected to attractive Van-der-Waals (VdW) interactions that are rather long-ranged. The VdW interaction potential scales inversely with the inter-particle distance.

b. Particles can be sterically stabilized by attaching polymers to their surfaces. They could also be electrostatically stabilized if they are charged (the pH is shifted away from their isoelectric point). Finally, they could be electrostericaly stabilized, which is a combination of steric and electrostatic stabilization.

c. To prevent the agglomeration of nanoparticles, they should be sterically stabilized by adsorbing a biocompatible polymer brush onto the surface of the particles. The ion concentration in body fluids is high such that the electrostatic repulsion forces would be screened. Moreover, blood contains a lot of proteins, which would adsorb at the nanoparticle surfaces if they are not coated with polymers that prevent the adsorption of proteins. If proteins adsorb at the nanoparticle surfaces, nanoparticles will be recognized by the body as a foreign substance and will be rapidly excreted. Therefore, these particles must be sterically stabilized with a polymer brush that prevents both agglomeration and the adsorption of proteins.

3. Effective Volume Fraction

To calculate the effective volume, which is the combined volume of the particle and the stabilizing shell, we must determine the effective radius, which is the radius of the particle plus the thickness of the stabilizing layer that we can approximate as the Debye screening length.

$$r_{\text{eff}} = r_{\text{SiO}_2} + \frac{1}{\kappa}$$

We determine the Debye screening length using:

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \Sigma_i c_i z_i^2}}$$

a. NaCl is a monovalent salt. It's Debye screening length can be calculated as:

$$\frac{1}{\kappa} = \sqrt{\frac{8.85\times10^{-12}\ \frac{\text{F}}{\text{m}}\times80\times1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}\times293\ \text{K}}{(1.6\times10^{-19}\ \text{C})^2\times2\times0.005\ \frac{\text{mol}}{10^{-3}\ \text{m}^3}\times6.02\times10^{23}\ \text{mol}^{-1}\times1^2}} = 4.3\ \text{nm}$$

Therefore:

$$r_{\text{eff}} = r_{\text{SiO}_2} + \frac{1}{\kappa} = 50\ \text{nm} + 4.3\ \text{nm} = 54.3\ \text{nm}$$

and

$$\frac{V_{\text{eff}}}{V_{\text{SiO}_2}} = \frac{r_{\text{eff}}^3}{r_{\text{SiO}_2}^3} = \frac{(54.3\ \text{nm})^3}{(50\ \text{nm})^3} = 1.28$$

The effective volume would be 28% higher than the volume of the SiO_2 particle. Under these conditions, the volume of the stabilizing shell must be considered, leading to an total effective volume of SiO_2 within the suspension to be 12.8 vol%.

b. $$\frac{1}{\kappa} = \sqrt{\frac{8.85\times10^{-12}\ \frac{\text{F}}{\text{m}}\times80\times1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}\times293\ \text{K}}{(1.6\times10^{-19}\ \text{C})^2\times2\times0.1\ \frac{\text{mol}}{10^{-3}\ \text{m}^3}\times6.02\times10^{23}\ \text{mol}^{-1}\times1^2}} = 0.97\ \text{nm}$$

Therefore:

$$r_{\text{eff}} = r_{\text{SiO}_2} + \frac{1}{\kappa} = 50\ \text{nm} + 1\ \text{nm} = 51\ \text{nm}$$

and

$$\frac{V_{\text{eff}}}{V_{\text{SiO}_2}} = \frac{r_{\text{eff}}^3}{r_{\text{SiO}_2}^3} = \frac{(51\ \text{nm})^3}{(50\ \text{nm})^3} = 1.06$$

At this high salt concentration, which is in the range of physiological conditions, the effective volume is only 6% higher than the volume of the SiO_2 particles, leading to an total effective volume of SiO_2 within the suspension to be 10.5 vol%.

c. $$\frac{1}{\kappa} = \sqrt{\frac{8.85\times10^{-12}\ \frac{\text{F}}{\text{m}}\times80\times1.38\times10^{-23}\ \frac{\text{J}}{\text{K}}\times293\ \text{K}}{(1.6\times10^{-19}\ \text{C})^2\times2\times1\ \frac{\text{mol}}{10^{-3}\ \text{m}^3}\times6.02\times10^{23}\ \text{mol}^{-1}\times1^2}} = 0.3\ \text{nm}$$

Therefore:

$$r_{\text{eff}} = r_{\text{SiO}_2} + \frac{1}{\kappa} = 50 \text{ nm} + 0.3 \text{ nm} = 50.3 \text{ nm}$$

and

$$\frac{V_{\text{eff}}}{V_{\text{SiO}_2}} = \frac{r_{\text{eff}}^3}{r_{\text{SiO}_2}^3} = \frac{(50.3 \text{ nm})^3}{(50 \text{ nm})^3} = 1.02$$

At this very high salt concentration, the effective volume is very close to that of the SiO_2 nanoparticles so the contribution of the shell to the total volume can be neglected.

4. Steric Stabilization

a. The thickness of a polymer brush adsorbed onto a particle surface can be estimated using:

$$L_0 \approx N I^{5/3} \Gamma^{1/3}$$

To calculate L_0, we first determine the number of repeat units:

$$N = \frac{M_{W,\ PEG}}{M_{W,\ r.u.}} = \frac{2000 \ \frac{\text{g}}{\text{mol}}}{(2\times12+4\times1+16) \ \frac{\text{g}}{\text{mol}}} = \frac{2000 \ \frac{\text{g}}{\text{mol}}}{44 \ \frac{\text{g}}{\text{mol}}} \approx 45$$

From the text, we know $l = 0.36$ nm. Using this, we obtain:

$$\Gamma = \left(\frac{L_0}{N I^{5/3}}\right)^3 = \left(\frac{9\times10^{-9} \text{ m}}{45\times(0.36\times10^{-9} \text{ m})^{5/3}}\right) = 1.3 \times 10^{18} \ \frac{\text{molecules}}{\text{m}^2}$$

$$= 1.3 \ \frac{\text{molecules}}{\text{nm}^2}$$

b. PEG chains start to overlap if $\Gamma > 1/4R_g^2$. To determine if this is the case, we calculate the radius of gyration using:

$$\sqrt{\langle R_g^2 \rangle} = \sqrt{\frac{\langle r^2 \rangle}{6}}$$

Assuming that the PEG is dissolved in a theta solvent and the angle between two bonds is 109°, we obtain:

$$\langle r^2 \rangle = N l^2 \left(\frac{1+\cos\theta}{1-\cos\theta}\right) = 45 \times (0.36 \times 10^{-9})^2 \times \left(\frac{1+\cos 71^\circ}{1-\cos 71^\circ}\right) = 1.4 \text{ nm}$$

Therefore, $\Gamma > 1/4R_g^2 = 0.13 \text{ nm}^{-2}$ and the adjacent polymers come into contact with each other.

c. Thiol groups have a high affinity to gold surfaces. Therefore, the easiest method to stabilize gold nanoparticles with PEG chains is through the use of thiol-terminated PEG chains (PEG molecules with a thiol group located at a single end).

5. Colloidal Stability

The particles sediment because they agglomerate. Agglomeration is caused by the attractive depletion forces that result from the addition of smaller nanoparticles.

6. Colloidal Crystals

a. A colloidal crystal is an ordered array of particles displaying a narrow size distribution.

b. Colloidal crystals can be made through the self-assembly of particles with a narrow size distribution. To prevent the agglomeration of particles in solution, they must be repulsive. Particles can be assembled through direct assembly (e.g. sedimentation, electrophoretic, electrostatic deposition), by using liquid-liquid interfaces (e.g. Langmuir Blodgett or floating deposition), or by stamping to obtain patterns.

c. The packing density of a face centered cubic (fcc) structure is 0.74. Therefore, they occupy 74% of the volume.