Solutions to Soft Matter exercise, Chapter 10: Particles

1. **Nanoparticles in solution**

a. To determine if these particles sediment over time, we calculate their sedimentation length

$$l_{sed} = \frac{k_B T}{m^* g} = \frac{k_B T}{\frac{4}{3}\pi r^3 \Delta\rho g} = \frac{1.38\times10^{-23}\frac{J}{K}\times 298K}{\frac{4}{3}\pi\times\left(100\times10^{-9}m\right)^3\times\left(2650-1000\right)\frac{kg}{m^3}\times 9.8\frac{N}{kg}} = 6.1\times10^{-5}m$$

This sedimentation length is longer than the particle diameter such that sedimentation can be neglected.

To estimate the time needed for particles to reach the end of the pipe, we determine the mean end-to-end distance a particle diffuses during a time *t* that can be described in 3D as

$$\left\langle r^2\right\rangle = 6Dt$$

Using this equation, one can calculate the time needed to diffuse a distance *r.*

$$t = \frac{\left\langle r^2\right\rangle}{6D}$$

To calculate the diffusion coefficient, we use the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta r} = \frac{1.38\times10^{-23}\frac{J}{K}\times 298K}{6\pi\times 0.001Pas\times 100\times10^{-9}m} = 2.2\times10^{-12}\frac{m^2}{s}$$

and obtain

$$t = \frac{\left\langle r^2\right\rangle}{6D} = \frac{0.3^2 m^2}{6\times 2.2\times10^{-12}\frac{m^2}{s}} = 6.9\times10^9 s \approx 1.91\times10^9 h \approx 8\times10^4 d \approx 218 years,$$

In the absence of any forced flow, these particles will, within the lifetime of a pipe, never reach the end of the pipe.

b. To determine if the particles are Brownian, we calculate the sedimentation length

$$l_{sed} = \frac{k_B T}{m^* g} = \frac{k_B T}{\frac{4}{3}\pi r^3 \Delta\rho g} = \frac{1.38\times10^{-23}\frac{J}{K}\times 298K}{\frac{4}{3}\pi\times\left(1\times10^{-9}m\right)^3\times\left(2650-1000\right)\frac{kg}{m^3}\times 9.8\frac{N}{kg}} = 60.7m$$

The sedimentation length is much longer than the particle size such that sedimentation can be neglegted.

We calculate the diffusion coefficient using the Stokes-Einstein equation

$$D = \frac{k_B T}{6\pi\eta r} = \frac{1.38\times10^{-23}\frac{J}{K}\times 298K}{6\pi\times 0.001Pas\times 1\times10^{-9}m} = 2.2\times10^{-10}\frac{m^2}{s}$$

and obtain

$$t = \frac{\left\langle r^2\right\rangle}{6D} = \frac{0.3^2 m^2}{6\times 2.2\times10^{-10}\frac{m^2}{s}} = 6.88\times10^7 s \approx 1.91\times10^4 h \approx 800d \approx 2.2 years$$

Even in this case, sedimentation can be neglected.

c. The sedimentation velocity can be determined by equating the graviational force and the drag force, resulting in

$$v_{sed} = \frac{2r^2 \Delta\rho g}{9\eta} = \frac{2\left(100\times10^{-9}m\right)^2 \times \left(2650-1000\right)\frac{kg}{m^3}\times 9.8\frac{N}{kg}}{9\times 0.001 Pas} = 3.6\times10^{-8}\frac{m}{s}$$

Using this sedimentation velocity, we can calculate the time needed to sediment 0.3 m as

$$t = \frac{l}{v_{sed}} = \frac{0.3m}{3.6\times10^{-8}\frac{m}{s}} = 8.4\times10^{6}s \approx 2.3\times10^{3}h \approx 97d$$

d. Using the same equations we obtain

$$v_{sed} = \frac{2r^2 \Delta\rho g}{9\eta} = \frac{2\left(1\times10^{-9}m\right)^2 \times \left(2650-1000\right)\frac{kg}{m^3}\times 9.8\frac{N}{kg}}{9\times 0.001 Pas} = 3.6\times10^{-12}\frac{m}{s}$$

and

$$t = \frac{l}{v_{sed}} = \frac{0.3m}{4.2\times10^{-12}\frac{m}{s}} = 8.4\times10^{10}s \approx 2.3\times10^{7}h \approx 9.7\times10^{5}d \approx 2.7\times10^{3}years$$

This time is much longer than that determined in (b) for Brownian motion. This means, these small particles will not sediment within a reasonnable observation time. The time it takes for these particles to reach the bottom of the tube will be equal to 2.2 years, as determined in (b).

2. Characterization of nanoparticles

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

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

Hence

$$r = \left(\sqrt{\frac{2k_B T}{\rho\frac{4}{3}\pi}}\frac{1}{v_{brown}}\right)^{\frac{2}{3}} = \left(\sqrt{\frac{2\times1.38\times10^{-23}\frac{J}{K}298K}{1040\frac{kg}{m^3}\frac{4}{3}\pi}}\frac{1}{2\times10^{-3}\frac{m}{s}}\right)^{\frac{2}{3}} = 779nm$$

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

$$l_{sed} = \frac{k_B T}{m^* g} = \frac{k_B T}{\frac{4}{3}\pi r^3 \Delta\rho g} = \frac{1.38\times10^{-23}\frac{J}{K}\times 298K}{\frac{4}{3}\pi\times\left(779\times10^{-9}m\right)^3\times\left(1040-1000\right)\frac{kg}{m^3}\times 9.8\frac{N}{kg}} = 5.3\times10^{-6}m$$

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

3. Surface area

The volume of a cube with 1 cm long edges is

$$V_1 = \left(1\times 10^{-2} m\right)^3 = 10^{-6} m^3$$

A cube has an area of

$$A_1 = 6\times\left(1\times 10^{-2} m\right)^2 = 6\times 10^{-4} m^2$$

The total surface energy of this cube is

$$E = \gamma A = 0.07\frac{J}{m^2}\times 6\times 10^{-4} m^2 = 4.2\times 10^{-5} J = 1\times 10^{16} k_B T$$

a. Volume of a 1 μm sized cube = 10^{-18} m^3

Hence, the initial cube can be cut into 10^{12} smaller cubes with areas $A_2 = 6\times\left(1\times 10^{-6} m\right)^2 = 6\times 10^{-12} m^2$

The total surface area of 10^{12} cubes is 6 m^2 and we find

$$E = \gamma A = 0.07\frac{J}{m^2}\times 6 m^2 = 0.42 J = 1\times 10^{20} k_B T$$

Notice that cutting a cube with an edge size of 1 cm into cubes with edge sizes of 1 μm increases the surface energy by four orders of magnitude.

b. Volume of a 100 nm sized cube = 10^{-21} m^3

Hence, the initial cube can be cut into 10^{15} smaller cubes with areas $A_2 = 6\times\left(1\times 10^{-7} m\right)^2 = 6\times 10^{-14} m^2$

Total surface area of 10^{15} cubes: 60 m^2 and we find

$$E = \gamma A = 0.07\frac{J}{m^2}\times 60 m^2 = 4.2 J = 1\times 10^{21} k_B T$$

c. Volume of a 1 nm sized cube = 10^{-27} m^3

Hence, the initial cube can be cut into 10^{21} smaller cubes with areas $A_2 = 6\times\left(1\times 10^{-9} m\right)^2 = 6\times 10^{-18} m^2$

Total surface area of 10^{21} cubes: 6000 m^2 and we find

$$E = \gamma A = 0.07\frac{J}{m^2}\times 6000 m^2 = 420 J = 1\times 10^{23} k_B T$$

Cutting a larger volume into smaller pieces strongly increases the surface energy of the system. One means for the smaller particles to reduce the surface energy is to form aggregates. In all cases, the surface energies are much higher than the thermal energy such that, once particles or cubes are in contact, they will, under realistic experimental conditions, never come apart any more.

4. Nanoparticle stability

a. Nanoparticles are subjected to attractive Van-der-Waals (VdW) interactions that are rather long ranged; the VdW interaction potential scales with the inverse 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 electrosterically stabilized, which is a combination of steric and electrostatic stabilization.

c. To prevent agglomeration of nanoparticles, they should be sterically stabilized by adsorbing a biocompatible polymer brush onto the particle surface.

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 protein adsorption. If protein 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 agglomeration as well as adsorption of proteins.

5. Electrostatic stabilization

a. The Debye screening length is defined as

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}}$$

KCl is a monovalent salt such that we can calculate the Debye screening length as

i. $$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85\times10^{-12}\frac{F}{m}\times 80\times 1.38\times10^{-23}\frac{J}{K}\times 293K}{\left(1.6\times10^{-19}C\right)^2\times 2\times 1\frac{mol\times 6.02\times10^{23}}{10^{-3}m^3\times mol}\times 1^2}} = 0.3nm$$

ii. $$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85\times10^{-12}\frac{F}{m}\times 80\times 1.38\times10^{-23}\frac{J}{K}\times 293K}{\left(1.6\times10^{-19}C\right)^2\times 2\times 0.01\frac{mol\times 6.02\times10^{23}}{10^{-3}m^3\times mol}\times 1^2}} = 3nm$$

iii. $$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85\times10^{-12}\frac{F}{m}\times 80\times 1.38\times10^{-23}\frac{J}{K}\times 293K}{\left(1.6\times10^{-19}C\right)^2\times 2\times 10^{-4}\frac{mol\times 6.02\times10^{23}}{10^{-3}m^3\times mol}\times 1^2}} = 30nm$$

iv.

For $CaCl_2$, we must consider that the concentration of Cl^- is twice as high as that of Ca^{2+}, hence, z_{Cl} = 1 whereas z_{Ca} = 2. Hence, we obtain

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85 \times 10^{-12} \frac{F}{m} \times 80 \times 1.38 \times 10^{-23} \frac{J}{K} \times 293K}{(1.6 \times 10^{-19} C)^2 \times (1 \times 2^2 + 2 \times 1^2) \times \frac{mol \times 6.02 \times 10^{23}}{10^{-3} m^3 \times mol}}}$$

$$= 0.18nm$$

b. NaCl is a monovalent salt and KCl is also a monovalent salt. Hence, we obtain

$$\frac{1}{\kappa} = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85 \times 10^{-12} \frac{F}{m} \times 55 \times 1.38 \times 10^{-23} \frac{J}{K} \times 328K}{(1.6 \times 10^{-19} C)^2 \times 2 \times 1^2 \times \frac{mol \times 6.02 \times 10^{23}}{10^{-3} m^3 \times mol}}}$$

$$= 0.27nm$$

6. Effective volume fraction

To calculate the effective volume, which is the volume of the particle and that of 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 approximate as the Debye screening length

$$r_{eff} = r_{SiO_2} + \frac{1}{\kappa}$$

We determine the Debye screening length using

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}}$$

a. NaCl is a monovalent salt such that we can calculate the Debye screening length using

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{e^2 \sum_i c_i z_i^2}} = \sqrt{\frac{8.85 \times 10^{-12} \frac{F}{m} \times 80 \times 1.38 \times 10^{-23} \frac{J}{K} \times 293K}{\left(1.6 \times 10^{-19} C\right)^2 \times 2 \times 0.005 \times \frac{mol \times 6.02 \times 10^{23}}{10^{-3} m^3 \times mol} \times 1^2}} = 4.3nm$$

Hence,

$$r_{eff} = r_{SiO_2} + \frac{1}{\kappa} = 50nm + 4.3nm = 54.3nm$$

and

$$\frac{V_{eff}}{V_{SiO_2}} = \frac{r_{eff}^3}{r_{SiO_2}^3} = \left(\frac{54.3nm}{50nm}\right)^3 = 1.28$$

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.

b. $$\frac{1}{\kappa}=\sqrt{\frac{\varepsilon_0\varepsilon_r k_B T}{e^2\sum_i c_i z_i^2}}=\sqrt{\frac{8.85\times10^{-12}\frac{F}{m}\times80\times1.38\times10^{-23}\frac{J}{K}\times293K}{\left(1.6\times10^{-19}C\right)^2\times2\times0.1\times\frac{mol\times6.02\times10^{23}}{10^{-3}m^3\times mol}\times1^2}}=0.97nm$$

Hence,

$$r_{eff}=r_{SiO_2}+\frac{1}{\kappa}=50nm+1nm=51nm$$

and

$$\frac{V_{eff}}{V_{SiO_2}}=\frac{r_{eff}^3}{r_{SiO_2}^3}=\left(\frac{51nm}{50nm}\right)^3=1.06$$

At this high salt concentration, that is in the range of physiologic conditions, the effective volume is only 6% higher than the volume of the SiO_2 particles.

c. $$\frac{1}{\kappa}=\sqrt{\frac{\varepsilon_0\varepsilon_r k_B T}{e^2\sum_i c_i z_i^2}}=\sqrt{\frac{8.85\times10^{-12}\frac{F}{m}\times80\times1.38\times10^{-23}\frac{J}{K}\times293K}{\left(1.6\times10^{-19}C\right)^2\times2\times1\times\frac{mol\times6.02\times10^{23}}{10^{-3}m^3\times mol}\times1^2}}=0.3nm$$

Hence,

$$r_{eff}=r_{SiO_2}+\frac{1}{\kappa}=50nm+0.3nm=50.3nm$$

and

$$\frac{V_{eff}}{V_{SiO_2}}=\frac{r_{eff}^3}{r_{SiO_2}^3}=\left(\frac{50.3nm}{50nm}\right)^3=1.02$$

At these very high salt concentrations, the effective volume is very close to that of the SiO_2 nanoparticles such that the contribution of the shell to the total volume can be neglected.

7. Steric stabilization

a. The thickness of a polymer brush adsorbed on a particle surface can be estimated using $L_0\approx Nl^{\frac{5}{3}}\Gamma^{\frac{1}{3}}$

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

$$N=\frac{M_{w,PEG}}{M_{w,r.u.}}=\frac{2000\frac{g}{mol}}{\left(2\times12+4\times1+16\right)\frac{g}{mol}}=\frac{2000\frac{g}{mol}}{44\frac{g}{mol}}\approx45$$

From the text, we know l = 0.36 nm. Hence, we obtain

$$\Gamma=\left(\frac{L_0}{Nl^{\frac{5}{3}}}\right)^3=\left(\frac{9\times10^{-9}m}{45\times\left(0.36\times10^{-9}m\right)^{\frac{5}{3}}}\right)^3=1.3\times10^{18}\frac{molecules}{m^2}=1.3\frac{molecules}{nm^2}$$

b. PEG chains start to overlap if $\Gamma > \frac{1}{4R_g^2}$

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

$$\langle r^2 \rangle = Nl^2 \left(\frac{1 + cos\theta}{1 - cos\theta}\right) = 45 \times (0.36 \times 10^{-9})^2 \times \left(\frac{1 + cos71°}{1 - cos71°}\right)$$
$$= 1.15 \times 10^{-17} m^2$$

and thus

$$\sqrt{\langle R_g^2 \rangle} = \sqrt{\frac{\langle r^2 \rangle}{6}} = \sqrt{\frac{1.15 \times 10^{-17} m^2}{6}} = 1.4nm$$

Hence $\Gamma > \frac{1}{4R_g^2} = 0.13 \frac{1}{nm^2}$ and the adjacent polymers come in contact with each other ➔ the chains form brushes.

c. Thiol groups have a high affinity to gold surfaces. Hence, the easiest method to stabilize gold nanoparticles with PEG chains is to take PEG-thiol chains, which are PEG chains containing a thiol group attached to one of their ends.

8. Colloidal stability

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

9. Colloidal crystals

a. A colloidal crystal is an ordered array of particles displaying a narrow size distribution.
b. Colloidal crystals can be made through self-assembly of particles with a narrow size distribution. To prevent 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. Hence, they occupy 74% of the volume.