Exercise sheet #10

Problem 1. Consider a dispersion of nanoparticles, i.e. particles with a radius $R < 1\mu m$.

a) Why do nanoparticles tend to aggregate?

b) What can you do to prevent aggregation?

c) You want to intravenously inject iron oxide nanoparticles into humans to enhance the contrast in magnetic resonance images that are used to determine if a patient has cancer. How would you ensure that these nanoparticles do not clog blood vessels?

Solution: a) Nanoparticles are subjected to attractive Van-der-Waals (VdW) interactions that are rather long ranged, thus they tend to aggregate.

b) Particles can be sterically stabilized by attaching polymers to their surfaces. They could also be electrostatically stabilized, if they are charged. 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.

□

Problem 2. A suspension of spherical polystyrene particles (density $\rho_p = 1050$ kg m^{-3}) is dispersed in water ($\rho_w = 1000$ kg m^{-3}, viscosity $\eta = 1.0 \times 10^{-3}$ Pa s) at room temperature $T = 298$ K. Each particle has radius $a = 500$ nm. Estimate the time to sediment a distance $h = 1$ cm by advection at velocity v. Comment on whether the particle suspension is well mixed.

Solution: The settling behavior of a colloidal particle can be estimated from its Stokes terminal velocity. For a spherical polystyrene particle of radius $a = 500$ nm suspended in water, the density difference between particle and solvent is small ($\Delta\rho = 50$ kg m^{-3}), and the viscosity of water gives rise to strong viscous drag at this scale. Using Stokes' law, the gravitational settling velocity is

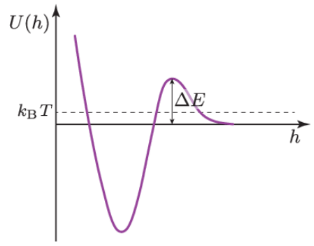
$$v = \frac{2}{9}\frac{\Delta\rho g a^2}{\eta},$$

which yields $v \approx 2.7 \times 10^{-8}$ m s^{-1}. At this speed, the time required to settle 1 cm is

$$t = \frac{h}{v} \approx \frac{0.01}{2.7 \times 10^{-8}} \approx 3.7 \times 10^5 \text{ s},$$

corresponding to roughly 4 days. Thus, even in a perfectly quiescent fluid the gravitational sedimentation of such submicron particles is exceedingly slow. Because the settling velocity is so small, thermal fluctuations easily overwhelm gravitational drift. A Stokes-Einstein estimate of the Brownian diffusion coefficient for 500 nm particle in water gives $D \approx 4 \times 10^{-13}$ m^2 s^{-1}. Comparing diffusive and advective transport through the sedimentation Péclet number, $\mathrm{Pe} = va/D$, one finds $\mathrm{Pe} \approx 0.03$, far below unity. This indicates that random Brownian motion is the dominant transport mechanism, and the particle explores its surroundings diffusively much faster than it sediments. Consequently, a suspension of particles of this size will remain well mixed on short timescales, and sedimentation becomes relevant only over distances of many millimeters and times of many hours or days. □

Problem 3. Suppose we have a dispersion of glass particles in water at room temperature. If they interact with the potential sketched in the figure below, the energy barrier may prevent particles from crossing into the attraction regime and consequently aggregating. In this problem, we are going to estimate the height of the barrier needed in order to keep the particles dispersed for the duration of a day. Let us consider a 10% dispersion by weight of glass particles with radius of $R = 100$ nm.



a) The relative density of glass is 2.5. Calculate the volume fraction of this suspension and show that the typical distance between colloids is of order 500 nm .

b) Calculate the Stokes-Einstein diffusion coefficient

c) Estimate the mean distance $\ell_1 \simeq \left(\left\langle V^2\tau^2\right\rangle\right)^{1/2}$ a bead moves during the time the velocity is correlated (This distance comes from considering $D \approx \frac{l_1^2}{\tau}$) and show that it is much smaller than the radius R of the beads. What do you conclude from this?

d) Show that the mean time t_{coll} it takes two colloids to 'collide' is of order 0.12 s. Hint: The conclusion you drew in c should convince you that the behavior of the colloids is diffusive also at the scale of microns, and hence that you can estimate the 'collision time' with the help of the results of band a.

e) Requiring the probability of two particles overcoming the energy barrier upon collision to be less than 1/ typical number of collisions, show that the height of the energy barrier should exceed about $13k_{\text{B}}T$.

Solution: a) The weight fraction of the glass particles is 10%, and the relative density is 2.5 , so the volume fraction is 10%/2.5 = 4%. This means that the volume of fluid associated with each spherical particle is 25 times the volume of the particle, or $25 \cdot \frac{4}{3}R^3$, where R is the particle's radius. Approximating the volume of fluid as a sphere with radius $(25)^{1/3}R \approx 3R$, we estimate that the particles are typically separated by a distance of $\approx 6R = 600$ nm.

b) $D = \frac{k_{\text{B}}T}{6\pi\eta R} = \frac{4.21\cdot 10^{-21}\ \text{J}}{2\cdot 10^{-2}\ \text{kg/ms} 100\cdot 10^{-9}\ \text{m}} \approx 2\cdot 10^{-12}\ \text{m}^2/\text{s}$

c) For a brownian particle $\tau = \Gamma^{-1} = \frac{2}{9}\frac{R^2\rho_P}{\nu\rho_{fl}}$, so the velocity correlation time is given by

$$\tau = \frac{2}{9}\frac{R^2}{\nu}\frac{\rho_{\text{p}}}{\rho_{\text{fl}}} \approx \frac{2}{9}\frac{10^{-14}\ \text{m}^2}{10^{-6}\ \text{m}^2/\text{s}} \cdot 2.5 \approx 5\cdot 10^{-9}\ \text{s}.$$

The mean velocity of the glass particles during this time can be estimated as

$$\left\langle v^2\right\rangle \approx \frac{D}{\tau} = \frac{2\cdot 10^{-12}\ \text{m}^2/\text{s}}{5\cdot 10^{-9}\ \text{s}} = 4\cdot 10^{-4}\ \text{m}^2/\text{s}^2.$$

Then, the length over which the bead moves during the time that the velocity is correlated

$$l \approx \sqrt{\langle v^2\rangle}\tau = \left(2\cdot 10^{-2}\ \text{m/s}\right)\left(5\cdot 10^{-9}\ \text{s}\right) = 10^{-10}\ \text{m} = 0.1\ \text{nm} \ll R$$

That is, at the scale that we are interested in, the glass particles move diffusively.

d) Using the distance between particles from step a and the diffusion constant from step b, we estimate the time between collisions to be

$$t_{\text{coll}} \approx \frac{(6R)^2}{D} = \frac{36 \cdot 10^{-14}\ \text{m}^2}{2 \cdot 10^{-12}\ \text{m}^2/\text{s}} = 0.18\ \text{s}$$

e) We would like to keep the particles dispersed for the duration of a day. In one day, the number of collisions is approximately

$$N \approx \frac{24 \cdot 60 \cdot 60\ \text{s}}{t_{\text{coll}}} = \frac{86400\ \text{s}}{0.18\ \text{s}} \approx 5 \cdot 10^5.$$

Equating the probability of the particles overcoming the energy barrier with $1/N$, we find

$$e^{-\Delta E/k_{\text{B}}T} \approx \frac{1}{5 \cdot 10^5} \Rightarrow \Delta E \approx 13 k_{\text{B}} T.$$

Hence, the height of the energy barrier should exceed about $13k_{\text{B}}T$.

□