# Problem set 2 – Soft Matter

## Problem 5

Two sapphire surfaces in a 1 mM NaCl solution ($\kappa^{-1} \approx 10$ nm, $\epsilon = 78$) are separated by $D = 20$ nm. The Hamaker constant for sapphire–water-sapphire is $A_{131} = 6.7 \cdot 10^{-20}$ J and surface charge $\sigma = 1.5$ mC m$^{-2}$.

a) Given that calculate the *attractive* pressure, $\Pi = -dU/dD$, due to the attractive van der Waals interaction, $U = -A/12\pi D^2$.

b) Calculate the *repulsive* pressure between the sapphire surfaces, $\Pi(D) = \frac{2\sigma^2}{\epsilon\epsilon_0} e^{-\kappa D}$, and compare the value you obtain to your answer in part a): is the repulsive pressure enough to prevent the sapphire surfaces from sticking to each other or not? ($\epsilon_0 = 8.85 \cdot 10^{-12}$ C$^2$ N$^{-1}$m$^{-2}$)

The interaction energy between spherical silica particles in a stable colloidal suspension at pH 7 in an aqueous NaCl solution is shown in the diagram below.

c) Explain the factors that determine the shape of the curve.

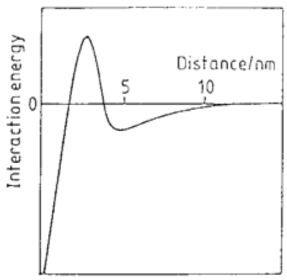
d) Explain why each of the following actions may lead to aggregation of the silica particles:

- increasing the NaCl concentration.

- adding a divalent electrolyte.

- adding methanol to the solution.

- reducing the pH (note: the isoelectric point of silica is around pH = 2).




## Problem 6

The one-dimensional (1D) motion of a colloidal particle with mass $m$ and radius $a$ in a fluid medium is described by the Langevin equation,

$$m\frac{dv(t)}{dt} = F - \xi v(t) + f(t),$$

where $v$ is the instantaneous velocity, $\xi$ the friction coefficient, $F$ the external force on the particle and $f(t)$ the fluctuating force.

a) Carefully explain the origin of Brownian motion and why $\langle f(t)\rangle = 0$.

Consider the steady-state diffusion of spherical particles down a concentration gradient, $dc/dx$. The force on a single particle is given by $F = -d\mu/dx$, in which the chemical potential has the form $\mu = \mu^{\ominus} + k_B T \ln c/c^{\ominus}$, where $\mu^{\ominus}$ and $c^{\ominus}$ are constants.

b) Find an expression for $F$ and hence show that

$$\langle v\rangle = -\frac{k_B T}{\xi c}\frac{dc}{dx}.$$

c) Write an expression for the flux $J$ (units mol m$^{-2}$ s$^{-1}$) in terms of $\langle v\rangle$, and by comparing it with Fick's First Law, $J = -D\ dc/dx$, show that the diffusion coefficient $D$ is given by (Stokes-Einstein)

$$D = \frac{k_B T}{\xi}.$$

Consider a suspension of $N$ colloidal particles of radius $R = 1$ $\mu$m in water ($\eta = 0.89 \cdot 10^{-3}$ Pa s) in a volume $V$ at $T = 298$ K. The volume fraction $\phi$ is defined as $\phi = \rho v_p$, where $\rho = N/V$ (number density) and $v_p$ the particle volume. The Stokes friction factor for a sphere of radius $R$ in a solvent of viscosity $\eta$ is $\xi = 6\pi\eta R$.

d) The mean squared displacement is given by $\langle r^2(t)\rangle = 6Dt$ (see also problem 8). Calculate the time it takes for a single colloidal particle (i.e. in the limit of $\phi \to 0$) to diffuse a distance equal to its own diameter (in 3D). How does this so-called 'Brownian time' vary with $R$?

e) Show that the typical time $\tau$ for a particle to travel the mean distance between the particles is proportional to $\phi^{-2/3}$ and calculate $\tau$ for a suspension with $\phi = 0.3$.

## Problem 7

In this problem, we will look at the entropy-driven transition from the isotropic to the nematic phase in suspension of hard colloidal rods, as first described by Lars Onsager (in the 1940s): "*The isotropic-nematic transition in a suspension of rods is driven by the loss of orientation entropy and the gain of free volume entropy.*"

a) Explain the differences between the isotropic and nematic phase in terms of ordering of the centres and orientations of the rods in both phases.

b) Now, we consider the *orientational* entropy of the isotropic and nematic phases. Using the Boltzmann equation for the entropy, $S = k_B \ln \Omega$, show that the change in orientational entropy for the isotropic-to-nematic transition can be estimated as

$$\Delta S_{or} = k_B \ln \frac{\Omega_N}{\Omega_I} \sim k_B \ln \frac{1}{4\pi} \sim -k_B.$$

Next, we consider the change in entropy due to the change in the excluded volume going from the isotropic to the nematic phase. To this end, we need the Gibbs-Duhem relation (from thermodynamics):

$$N d\mu = -S dT,$$

and the following expression for the chemical potential

$$\mu = \mu_0 - k_B T \ln \frac{V_i}{V},$$

where $\mu_0$ is a constant, $V$ the volume and $V_i$ the volume available to insert an extra particle. Note that $V_i = V - V_{excl}$, where $V_{excl}$ is the *excluded volume*, i.e. the volume where no extra particle can be inserted (due to the presence of another rod), and at low concentrations $V \gg V_{excl}$.

c) Show that at low concentrations the 'excluded volume entropy' (per particle) is given by

$$\frac{S_{excl}}{N} = k_B \ln \frac{V_i}{V} \approx -k_B \frac{V_{excl}}{V}.$$

**Hint**: $\ln(1 - x) \approx -x$.

d) Make a sketch to explain that the excluded volumes between two rods (length $L$ and diameter $D$) in the isotropic and nematic phases are (approximately) given by

Isotropic phase: $V_{ex}^I \sim L^2 D$ Nematic phase: $V_{ex}^N \sim D^2 L$.

e) Show that the change in $S_{excl}$ for the isotropic-to-nematic transition, $\Delta S_{excl} = S_{excl}^N - S_{excl}^I$, is

$$\Delta S_{excl} = k_B \rho L^2 D, \quad \text{where } \rho = N/V \text{ is the number density.}$$

f) Finally, the isotropic-nematic transition occurs at the number density ($\rho^*$) where the loss of orientational entropy is balanced by the gain of excluded volume entropy:

$$\Delta S_{or} + \Delta S_{excl} = 0.$$

Show that $\rho^* = 1/(L^2 D)$, which is equivalent to a volume fraction of $\phi^* = \rho^* v_p = D/L$, where $v_p$ is the volume of a rod, $D^2 L$. This explain that for rods with $L/D = 10$ (which is not even that long) this *entropy-driven* transition already happens at very low concentrations!

## Problem 8

Here, we follow Langevin's original paper (see the translation by D.S. Lemons and A. Gythiel, Am. J. Phys. 65, 1079 (1997)) to derive an expression for mean squared displacement of a Brownian particle of mass $m$. The Langevin equation in 1D is given by:

$$m\frac{d^2x}{dt^2} = F - \xi\frac{dx}{dt} + f(t),$$

where $F$ is an external (driving) force, $\xi$ is the Stokes friction factor and $f(t)$ is a fluctuating random force with $\langle f(t)\rangle = 0$.

a) Multiply both sides of the Langevin equation by $x$ and then use the hint below to show that

$$\frac{m}{2}\frac{d^2x^2}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = Fx - \frac{\xi}{2}\frac{dx^2}{dt} + xf(t).$$

**Hint:** Note that $\frac{d^2x^2}{dt^2} = \frac{d}{dt}\left(\frac{dx^2}{dt}\right) = 2\left[x\frac{d^2x}{dt^2} + (\frac{dx}{dt})^2\right]$ as is easily shown using $dx^2 = 2xdx$.

b) Next, by (i) assuming that there is no external force, (ii) taking the ensemble average and (iii) then applying the equipartition theorem $m\langle\left(\frac{dx}{dt}\right)^2\rangle = k_BT$, show that one obtains

$$\frac{m}{2}\left\langle\frac{d^2x^2}{dt^2}\right\rangle - k_BT = -\frac{\xi}{2}\left\langle\frac{dx^2}{dt}\right\rangle.$$

c) By taking $z = \langle dx^2/dt\rangle$, integrate the above equation to obtain

$$z = \frac{2k_BT}{\xi} + A\exp\left(-\frac{\xi t}{m}\right),$$

where $A$ is a constant that does not depend on $t$.

**Hint:** take the indefinite integral, i.e. no integration boundaries, just add an integration constant.

d) For long times, i.e. $t \gg m/\xi$, show this equation can be solved to obtain the mean squared displacement in one dimension:

$$\langle x^2\rangle = \frac{2k_BT}{\xi}t = 2Dt.$$