# Colloids and Surfaces: Exercises

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# Chapter 1

# Exercises

## 1.1 EDL near a flat plate (with python programs)

1. Plot the PB and DH solutions with a surface potential $\psi_s = 1$. Explain what you see and why.
2. Increase the surface potential progressively (e.g. 2, 3, 4, 5). Compare the PB and DH solutions. Explain what you see and why.
3. Focus on the PB solution. Keep increasing the potential (e.g. 6, 7, 8, 9, 10). What can you see ?
4. For a high value of the surface potential (say 10), replace the surface potential in the DH formula to try to match the PB result far from the surface. What is the value of this fictitious surface potential ? Find it theoretically from the PB solution.

## 1.2 Debye length calculation.

Let's recall the definition of the Debye length for an electrolyte in equilibrium with a salt reservoir (salt density $n_0$ or concentration $C_0 = n_0/(1000Na)$ in $mol/L$).

$$\lambda = \kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 kT}{e^2 \sum_i z_i^2 n_i}} \text{ and the ionic strength is } I = \frac{1}{2}\sum_i z_i^2 C_i$$

1. Compute $\lambda$ for $0.01\, mol/L$ solutions of 1:1, 2:1, and 3:1 electrolytes in the salt reservoir.
2. Suggest how these values can be adapted to other temperatures or media without complete recalculation.
3. In water at room temperature, a useful formula is $\lambda = 0.304/\sqrt{I}$, where $\lambda$ will be in $nm$ and $I$ must be given in $mol/L$. Prove this formula from the most general one above.

## 1.3 Link between the salt reservoir density and the average ion density (with python programs)

We prepare a colloidal suspension with silica particles. They are approximately spherical, with a radius $a = 9\, nm$, and a surface charge density $0.5\, e/nm^2$. The volume fraction is $\phi = 1\%$. Compute the Debye length in the following cases.

1. The suspension is equilibrated with a reservoir of $NaCl$ at a concentration of $10^{-3}\, M$.
2. The suspension is dialyzed, and then put in a beaker with $0.01\, M$ added $NaCl$ salt.
3. The suspension is dialyzed, and then put in a beaker with $10^{-4}\, M$ added $NaCl$ salt.
4. Why was the suspension dialyzed prior to the addition of salt ?

You will be able to use the cell model to compute ion densities. When calling the function solve(), the program computes $\psi(r)$ in the cell. From it, we know the ion densities $n^{\pm} = n_0 e^{\mp\psi}$ ($n_0$ is the ion density in the salt reservoir, and fixed by the ionic strength $I = n0/(1000Na)$ in the program). The function CountIons() will then integrate these density profiles to obtain the number of ions of each type in the cell. It returns the number of counter-ions (detached from the colloid surface), the number of positive additional ions, and then the number of negative additional ions. Finding the mean ion density is then just dividing by the cell volume.

## 1.4 Interaction between two flat, weakly charged, plates.

Two flat plates are separated by a distance $d$.

1. Compute the electrostatic potential $\psi(x)$ between the plates in the following cases.
   - Their surface potential is constant and equal to $\psi_s \ll 1$.
   - Their surface charge density $\sigma$ is constant and small enough to have a potential smaller than $kT/e$ everywhere.
2. The force per unit surface area exerted on the plates is given by $F = n_0 kT\psi_m^2$, where $\psi_m$ is the dimensionless potential at the mid-point between the plates.
   - Calculate this force if the plates have a surface potential $\Psi_s = 12.5\,mV$, are separated by $d = 10\,nm$, are in water ($\epsilon_r = 78$) at room temperature, and are in contact with a salt reservoir with ionic strength $0.01\,mol/L$.
   - Same question for a surface charge density of $0.05\,e/nm^2$ ($e = 1.6\,10^{-19}\,C$).
3. If plate material has a constant surface charge density, how does the force vary when $d \to 0$.
4. Same question for a constant potential.

## 1.5 Schulze-Hardy rule

You will assume the CCC is found when the DLVO potential has a maximum value of 0 (so it's derivative is also zero at this point). Prove the Schulze-Hardy rule with the potentials given in this course for thin EDL, and short distance approximations.

## 1.6 Schulze-Hardy rule, application

We want to use latex particles with a radius of 100 nm to diagnose the presence of a hormone in the urine (pregnancy test). The Hamaker constant for latex in water can be taken has $A = 10^{-19}\,J$. The Zeta potential of latex particles is –50 mV in the absence of hormone and -20 mV in the presence of hormone. The Hamaker constant applies to this system is $10^{-19}$ J.

1. Compute the maximum of the potential energy (potential barrier) between two latex particles in the presence and in the absence of hormone for 3 different electrolyte concentrations $10^{-4}$, $10^{-3}$, and $10^{-2}\,M$ in the case of a monovalent electrolyte.
2. Confirm the location of the potential barrier as a function of Debye Parameter
3. Give an order of magnitude of the ionic strength that has to be used for the suspension of latex being destabilized by the presence of hormone making the diagnosis possible.

All the calculations will be done at a temperature of 25°C, and the solvent is water.

## 1.7 Perikinetic aggregation

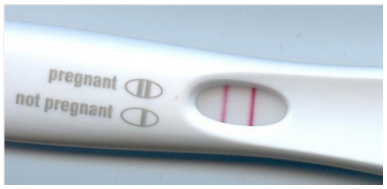
We want to aggregate a dispersion of nanometric particles prior to decantation. $T = 25^oC$, $\eta = 1\,mPa.s$, $a = 100\,nm$, initial particle density $n_0 = 33.5 \times 10^5\,m^{-3}$. We try to add KCl electrolyte to destabilize the suspension. We record the following aggregation times:

| $[KCl]\,(mM)$ | $n_0\,(m^{-3})$ | $\tau\,(s)$ |
|---|---|---|
| 20 | $33.5 \times 10^5$ | no aggregation |
| 30 | $33.5 \times 10^5$ | no aggregation |
| 65 | $33.5 \times 10^5$ | 360 |
| 80 | $33.5 \times 10^5$ | 19.5 |
| 100 | $33.5 \times 10^5$ | 20.3 |
| 200 | $33.5 \times 10^5$ | 20.7 |

1. Can you tell what is the CCC and why ?
2. If we increase the initial particle concentration by a factor 10 and keep the salt concentration at the CCC, do we expect a slower or faster decrease of particle concentration ? Why ?

## 1.8 Pregnancy test

Latex particles with a radius of 100 nm are used to diagnose the presence of a hormone (pregnancy test). The $\zeta$ potential of latex particles is –50 $mV$ in the absence of hormone and $-25\,mV$ in the presence of hormone. Band coloration is due to aggregation of latex particles, with a number density $4.45 \times 10^{15}\,m^{-3}$. Prior to the test, urine is mixed with a solution containing a given amount of electrolyte. We want to calculate an order of magnitude of the ionic strength that has to be used for the suspension of latex to be destabilized by the presence of hormone adsorbing on the latex particles making the diagnosis possible. We have calculated the maximum of the potential energy (potential barrier) between two latex particles in the presence and in the absence of hormone for 3 different 1-1 electrolyte concentrations.




| $I\,(M)$ | $V_{max}/kT$ for $\zeta = -50\,mV$ | $V_{max}/kT$ for $\zeta = -20\,mV$ |
|---|---|---|
| $1 \times 10^{-4}$ | 153.9 | 26 |
| $1 \times 10^{-3}$ | 100.12 | 2.1 |
| $1 \times 10^{-2}$ | 17.6 | / |

All the calculations will be done at a temperature of 25 degree C, and the solvent is water.

1. Calculate the stability ratio in the presence and absence of hormone for the 3 different electrolyte concentration.
2. Give a graphical representation of the variations of stability ratio as a function of electrolyte concentration in both cases.
3. Give an order of magnitude of the ionic strength that has to be used.
4. Calculate the CCC for the 50 and $20mV$ cases. Is it consistent with the variations of W ?
5. For a particle density of $4.45 \times 10^{15}\,m^{-3}$, compute the characteristic aggregation times. Is it consistent with the previous results ?

## 1.9 Capillary electrophoresis

An equipment of capillary electophoresis is used to measure the electrophoretic mobility of 2 proteins in mixture. The capillary tube used in this device is not closed at ends, its total length is L = 50 cm and

its internal radius 50 mm. Under the effect of an electric field of 10 kV applied between 2 electrodes located at the entrance and exit of the tube, the proteins move with a velocity: $u_{obs} = u_e + u_{eo}$ At a distance $L_d = 43\,cm$ from the entrance of the capillary is located a UV detector which allows to measure the elution time of each species present in the mixture. This elution time t is expressed by

$$t = \frac{L_d}{u_{obs}}$$

1. What condition must satisfy u eo so that analysis is feasible knowing that proteins are negatively charged. BSA radius: 3.61 nm. $\alpha$-lactalbumin radius : 2.06 nm. Electrolyte concentration (1:1) $C = 10^{-3}\,M$. T=25 degrees C. $\mu = .001\,Pa.s$

2. A neutral standard (glucose) is first injected. Its elution time at pH 6.2 being 8.53 min, calculate $u_e o$.

3. The mixture of BSA and $\alpha$-lactalbumin dissolved in a buffer at pH 6.2 is then analyzed. Knowing that the electrophoretic mobilities of these proteins are at this pH: BSA: $-19.7\,10^{-9}\,m^2/(Vs)$; $\alpha$-lactalbumin: $-10.2\,10^{-9}\,m^2/(Vs)$; Calculate the elution time expected for each protein. Deduce the value of their Zeta potential at this pH.

4. When the pH is changed, glucose and BSA elution times are:

| Elution time | pH 7.15 | pH 4.56 |
|---|---|---|
| t (glucose) | 8.74 min | 9.19 min |
| t (BSA) | 25.59 min | 9.12 min |

   Re-calculate for pH 7.15 and 4.56 the electrophoretic mobilities and the zeta potential of BSA.

5. Deduce the isoelectric point of this protein.