Homework Weeks 10 and 11:
Exercises: 24-25

Material to study for next week:
Lecture notes
Ohshima Chapter 1, Chapter 1 (§1, §2, §3.1 and §3.1.1, §3.2 and §3.2.1)

List of constants:

The dielectric permittivity of free space: ε_0 = 8.85 x 10^{-12} C^2 J^{-1} m^{-1}
Dielectric constant of water/SiO_2 interface: ε = 43
Avogadro constant: N_A = 6.022 x 10^{23} mol^{-1}
Gas constant: R = 8.314 J K^{-1} mol^{-1}

Interfaces – The electrical double layer

During the lecture, we have seen various models to describe the microscopic structure of the electrical double layer. All of them require some assumptions on the ions, the solvent, and on the interactions between each component of the system.

24.

Consider a colloidal dispersion of SiO_2 particles in water. The point of zero charge, which indicates the average charge neutrality of the surface, is at pH = 2 for this material. As a consequence, the SiO_2 surface is negatively charged at pH = 7, due to deprotonation of a part of the silanol groups (Si-OH) at this pH. The deprotonation percentage at this pH is expected to be ~1 %, which corresponds to a surface charge density of -0.01 C/m^2. This surface charge density is considered low.

a. Which model describes the best this situation? Sketch the system, indicating the chemical structure at the surface, the ion distribution in the double layer and the potential decay.

We add an electrolyte to this system (0.1 M NaCl).

b. Two models are better suited to describe a surface exposed to a solution of higher ionic strength. Name them and explain their main differences.

We use the Gouy-Chapman-Stern model to treat our system. The Stern layer thickness is approximately 0.9 nm and the zeta potential is ζ = - 50 mV. 90% of the initial surface charge is compensated by a cation within the Stern layer.

c. Using an assumption on the position of the slipping plane, calculate the surface potential.

We now consider the Grahame model. The Gibbs free energy of interaction of the ion with its surroundings (in this case, water) for the sodium ion is: ΔG_{hyd} = - 365 kJ/mol for Na^+. For Ca^{2+}, it is notably higher: ΔG_{hyd} = - 1505 kJ/mol.

d. Based on ΔG_{hyd}, which ion is more susceptible to specifically adsorb at the SiO_2 surface? Explain why.

e. Can you make a prediction on the value of the surface potential of SiO_2 in the presence of a 0.1 M NaCl solution with respect to a 0.1 M $CaCl_2$ solution? In other words, is the surface potential in the presence of NaCl higher or lower than in the presence of $CaCl_2$?

25. Second Harmonic Imaging

We image a glass microcapillary in different aqueous solutions with second harmonic (SH) microscopy. glass is composed of SiO_2. The SH image of the microcapillary cross-section is shown in Fig. 4 for different bulk pH values of the aqueous solution (pH 2, pH 7 and pH 12). The pH is adjusted through HCl addition in the acidic case and through NaOH addition in the basic case. In the pH = 7 case, the aqueous solution contains 10 mM NaCl. The corresponding SH counts are shown on the right color axis. A conversion to surface potential (indicated as Φ_0 here) is provided on the right. Similar to question 24, the point of zero charge, which indicates the average charge neutrality of the surface, is at pH = 2 for SiO_2.

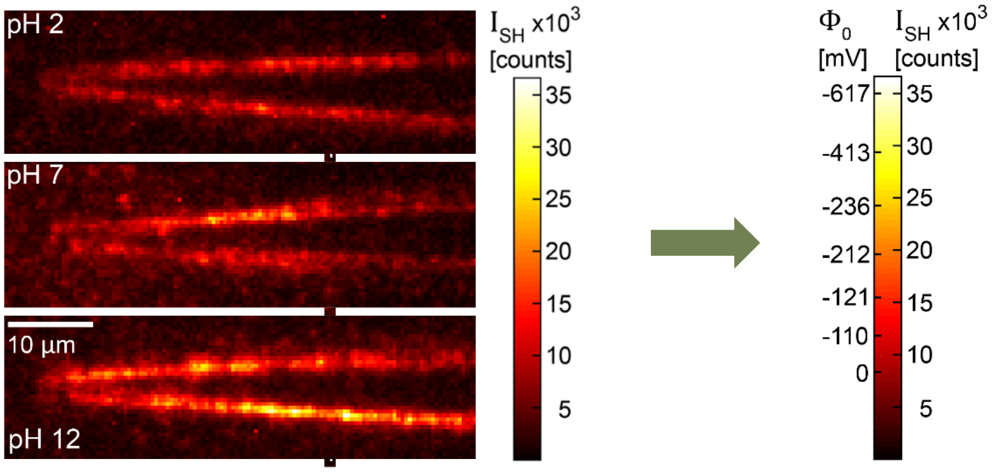

Figure 1: *Cross-sectional images of a glass microcapillary for different pH values of the electrolyte solution, recorded with an acquisition time of 5 s per image. The color bar indicate the SH intensity and the conversion to surface potential* Φ_0*.*

a. Show that the ionic strength for all three pH cases is the same. Why is it preferred to keep the ionic strength constant?

b. Knowing that the SH intensity is proportional to the square of the surface potential, explain why the surface potential increases with increasing pH.

c. The first image is collected at pH = 2 and shows appreciable intensity/surface potential values. How can this be?

Consider the case where the initial aqueous solution in the capillary is at pH = 2. We connect the system to a pump to make an aqueous solution at pH = 12 flow through the microcapillary at a constant flow rate (laminar flow). In laminar flow, the liquid at a certain point in space is refreshed on the microsecond timescale. The pH inside the microcapillary is changing with the flow. Fig. 5 shows the number of pixels that have a certain intensity value (in 10^3 counts/pixel) when the bulk solution in the microcapillary reaches pH = 7. The distribution is plotted for 1 s integration time and 5 s integration time. The standard deviation (σ on the graph) in the case of 1 s integration time is larger than in the case of 5 s integration time is larger.

d. Can you explain the difference between the two distributions?

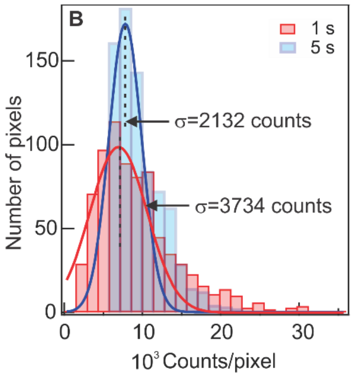

Figure 2: Spatial and temporal heterogeneities. *Histogram of SH counts/pixel for the pH neutral case.*