Overview of Surface Forces

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Lecture: 1/7

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Important Forces

Energy is denoted W. Distance between objects id d. Force is then $F = -\partial W/\partial d$ (positive means repulsion).

• Van der Waal (always attractive).

• Electrostatic (charged surfaces) and counterion entropy.

• Osmotic pressure (solvent entropy).

• Solvent displacement (very close).

• Dipole-dipole (orientation-dependent on atomic level).

• Hydrophobic interactions (in water).

• Pauli exclusion (always repulsion eventually).

In addition, *surface tension* acts during wetting/drying.

$$F(d\rightarrow\infty) = 0$$

$$W(d\rightarrow\infty) = 0$$
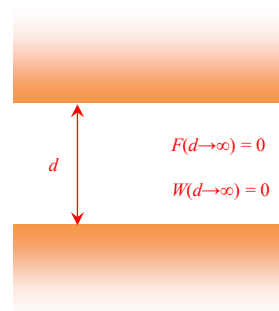
$$W(d) = \int\limits_{d}^{\infty} F(z)\,\mathrm{d}z$$

Generic Interaction Potential

The $W(d)$ curve looks different for different particles and molecules.

Objects normally attract each other, at least by van der Waal, but there must eventually be repulsion.

If the lowest energy is at a separation d_{min} this gives an interaction energy W_{int}.

Strongest W_{int} is for covalent bonds between molecules! (However, we will not talk about those in this course.)
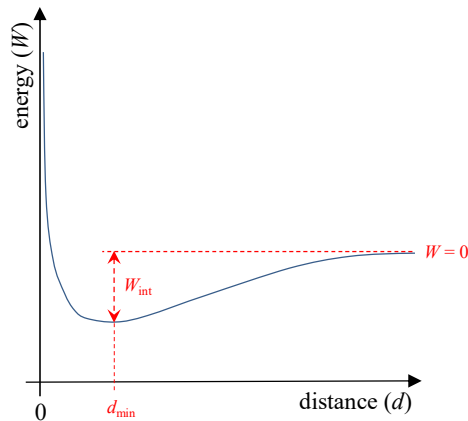
2024-01-18   Surface Engineering   3

Van der Waals Forces

Simplified physical explanation is charge fluctuations: Temporary interacting dipoles.

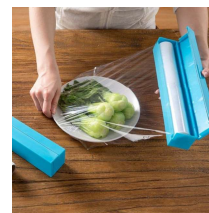From quantum mechanics: The interaction energy W of two uncharged atoms at separation distance r is:

$$W(r) = -\frac{\text{constant}}{r^6}$$

Three different forces, but same scaling law.

Always present!

Wikipedia: *van der Waals force*

AliExpress
http://www.aliexpress.com/

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Van der Waals Attraction

Imagine that we sum up the forces between all the atoms that interact with each other in two objects.

For the <u>planar</u> surfaces of two semi-infinite blocks separated by a distance d the interaction energy <u>per unit area</u> is:

$$\frac{W_{\text{flat}}(d)}{A} = -\frac{Z}{12\pi d^2}$$

Here Z is the *Hamaker constant*, which depends on the material but also the medium in between.

The Hamaker constant is closely related to refractive index and polarizability of matter.

Typical value: $Z \approx 10^{-19}$ J

Typical range where vdW interactions become important is ~1 nm.

Sphere Interactions

For other geometries, if d is smaller than the objects involved the geometric *Derjaguin approximation* can be used.
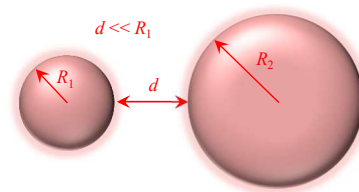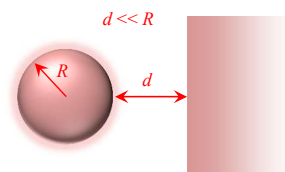
Sphere and planar surface:

$$F(d << R) = 2\pi R \frac{W_{\text{flat}}}{A} = -\frac{ZR}{6d^2}$$

$$W(d) = \int\limits_d^\infty F(z)\,\mathrm{d}z = -\frac{ZR}{6d}$$

Two spheres:

$$F(d << R_1 < R_2) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \frac{W_{\text{flat}}}{A} = -\frac{R_1 R_2}{R_1 + R_2} \frac{Z}{6d^2}$$

$$W(d) = \int\limits_d^\infty F(z)\,\mathrm{d}z = -\frac{R_1 R_2}{R_1 + R_2} \frac{Z}{6d}$$

$d << R$

R d
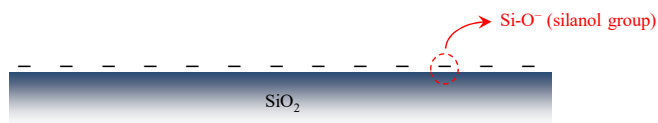
$d << R_1$

R_1 d R_2

Charged Interfaces

Most surfaces carry charges. Very important for stabilizing colloidal suspensions.

Unless we are doing electrochemistry, charges come from various chemical groups on the surface atoms or ions bound to the surface.
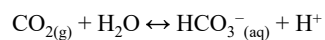
Example: Silica in water is negatively charged.

Si-O⁻ (silanol group)

SiO₂

The charge normally varies with pH, solvent and temperature!

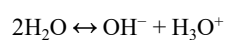## Ions

In a liquid environment there are always (at least some) <u>ions</u> present.

Example of carbon dioxide dissolving in water:

$CO_{2(g)} + H_2O \leftrightarrow HCO_3^-{}_{(aq)} + H^+$

Even in the absence of CO_2 there is self-protonation of water:

$2H_2O \leftrightarrow OH^- + H_3O^+$

Ions are <u>mobile</u> charges like the conduction band electrons in a metal. How do they respond to a charged interface?
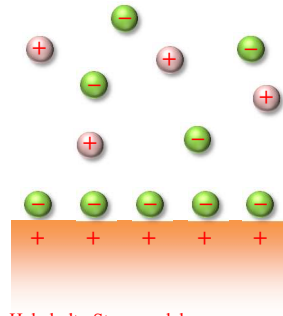
The <u>electric potential</u> close to a charged interface will be *screened* by ions.
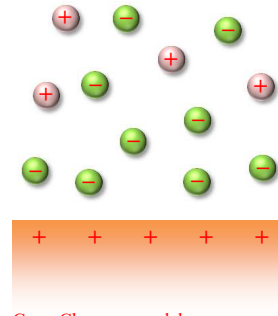
The Electric Double Layer

The standard theory for the charged interface is a *diffuse* Gouy-Chapman layer and/or a Helmholtz-Stern layer with physically *adsorbed* ions.

Adsorbed layer only is not realistic and diffuse layer does not work for higher potentials.

Helmholtz-Stern model, adsorbed ions.

Gouy-Chapman model, diffuse layer.

The Diffuse Layer

We reduce the problem to one dimension by assuming a <u>planar</u> surface.
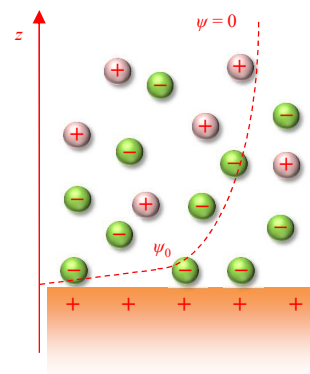
We want to know the potential ψ and the ion concentration C as a function of distance z.

The potential energy change when moving an ion a distance z from the location <u>where the diffusive layer starts</u> ($z = 0$) is:

$$\Delta W(z) = Q[\psi(z) - \psi_0]$$

Here ψ_0 is the potential at $z = 0$ and Q is the charge of the ion, which is determined by the valency v (…, -2, -1, 1, 2, …) by $Q = ve$.

(The elementary charge is $e = 1.602 \times 10^{-19}$ C.)

$\psi = 0$

z

ψ_0

Poisson-Boltzmann Equation

To get $\psi(z)$ at equilibrium, we use Poisson's equation from electrostatics:

$$e \sum_i v_i C_i(z) = -\varepsilon \varepsilon_0 \frac{\partial^2 \psi}{\partial z^2}$$

total charge density

Here $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1} is the permittivity of free space and ε is the relative permittivity of the medium in a static field ($\varepsilon = 80$ for water).

We use Boltzmann statistics for the ion concentration:

$$C(z) = C_0 \exp\left(-\frac{ve\psi(z)}{k_B T}\right)$$

for each ionic species

Note that C_0 is the concentration in the bulk (not at the surface). We can now combine these into the (complicated) Poisson-Boltzmann equation with boundary conditions:

still just one variable (z)

$$\frac{\partial^2 \psi}{\partial z^2} = -\frac{e}{\varepsilon \varepsilon_0} \sum_i v_i C_{0i} \exp\left(-\frac{v_i e \psi(z)}{k_B T}\right) \quad \psi(z \to \infty) = 0 \quad \psi(z = 0) = \psi_0 \quad \left\{\frac{\partial \psi}{\partial z}\right\}_{z \to \infty} = 0$$

Approximate Solution

For low ψ the equation can be linearized (Debye-Hückel) and approximately solved:

$$\psi(z) = \psi_0 \exp(-\kappa z)$$

Clearly, a very important parameter is κ which is given by:

$$\kappa = \left[\frac{e^2}{\varepsilon \varepsilon_0 k_B T} \sum_i v_i^2 C_{0i}\right]^{1/2}$$

bulk solution, bulk properties

One refers to κ^{-1} as the *Debye length*. It shows how far into solution surface charge effects extend.

changes in ion concentration and potential

κ^{-1}

For a solution containing only a monovalent salt $v_1 = v_2 = 1$ and:

$$\kappa = \left[\frac{2C_0 e^2}{\varepsilon \varepsilon_0 k_B T}\right]^{1/2}$$

charged interface

Note that surface properties do not influence κ^{-1}!
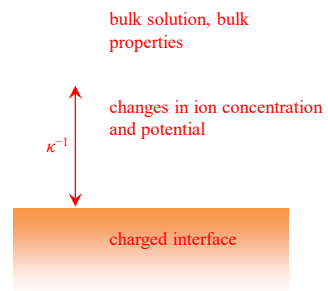
Model Limits

The exponential decay is only valid for low potentials (at least $|\psi| < 100$ mV).

The model is quite accurate in many practical situations, but this is just by luck…

It has many problems:

• Ions are treated as infinitely small.

• Continuous charge distributions rather than point charges.

• Hydration of ions neglected.

• Perfectly smooth surface.

Important: Even if the model gives good results there can still be <u>adsorbed</u> ions!

Dynamics

We have looked at the <u>equilibrium</u> picture. What about the <u>kinetics</u> of electric double layer formation?

This is extremely complicated to model, but we know the ions only need to move a distance κ^{-1}.
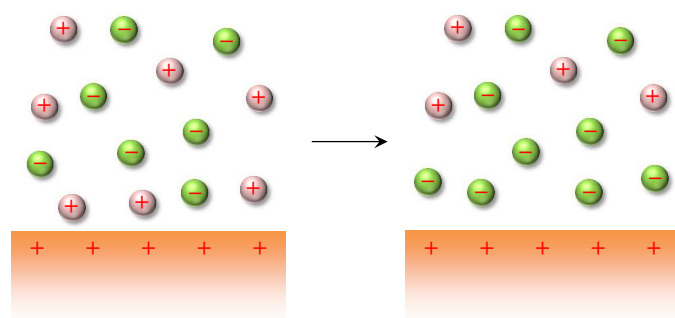
If the field is E, the force acting on each ion is veE.

The friction force can be estimated by Stokes:

$$F = fv = 6\pi\eta Rv$$

R is then the ion radius, η is the viscosity (10^{-3} Pas for water) and v is the drift velocity.

Acceleration is very fast in the "nanoworld" due to small masses. We can assume v is reached instantly!

01/15/2024

Grahame Equation

How can we relate ψ to charge density σ (C/m^2). A relation can be derived from the argument that the charges inducing the diffusive layer must compensate the net charge of the ions inside it. This gives the Grahame equation:
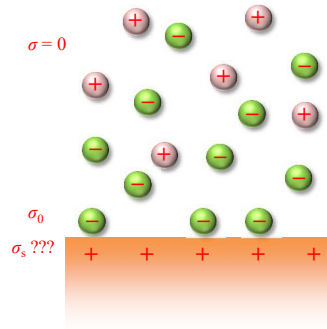
$$\sigma_0{}^2 = 2\varepsilon\varepsilon_0 k_{\rm B} T \left[\sum_i \{C_i\}_{z=0} - \sum_i C_{0\,i} \right]$$

Remember that we know C if we know ψ! For low potentials (<25 mV) an approximate relation is:

$$\sigma_0 \approx \varepsilon\varepsilon_0\psi_0\kappa$$

This formula can be interpreted as a capacitor with thickness equal to the Debye length.

Very important: We are still only considering the diffuse layer! The charge density will generally <u>not</u> be that at the solid surface.

Adsorbed Ions

The Helmholtz-Stern layer can be thought of as a plate capacitor. The field between two charged plates is $E = \sigma/[\varepsilon\varepsilon_0] = \Delta\psi/d$ and thus:

$$\psi_{\rm s} - \psi_0 = \frac{d\sigma}{\varepsilon\varepsilon_0}$$

Simple formula, but the values are very hard to know. The distance d can be approximated with the radius of the adsorbed ion. However, the permittivity is unknown.

Also, this does not take into account <u>chemical interactions</u> between ions and surface!

Again very important: Only a <u>part</u> of the surface charges are compensated by ions in the adsorbed layer!
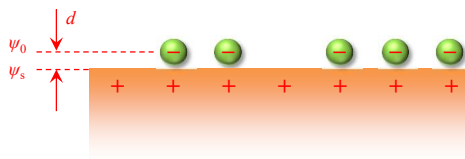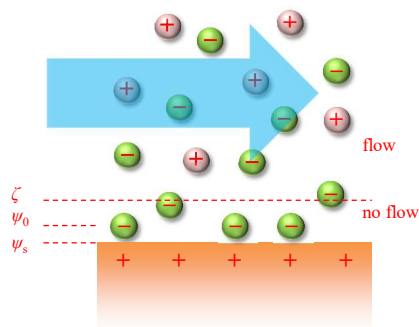
Zeta Potential

The *zeta potential* ζ is defined as the potential at the "no slip" position or the "shear plane" within the electric double layer. This is the distance at which ions and water molecules no longer are "stuck".

When the particle moves, water molecules and ions closer than the point of the zeta potential will move with the particle.

The zeta potential is sometimes assumed to be equal to the potential at which the diffuse layer starts ($\zeta = \psi_0$).

We can measure ζ but not ψ_0 or ψ_s!

Zeta Potential Measurements

Zeta potential (sometimes referred to as "streaming potential") can be measured on:

• Particles, based on the measured electrophoretic motion.

• Capillaries and porous materials.

• Planar surfaces, if mounted in pairs with a small gap!

$$\zeta = \frac{4\pi\eta v}{E\varepsilon\varepsilon_0} \qquad E = \frac{U}{d}$$

measured potential

Zeta potential will naturally depend on the surface charge density, but also the Debye length!

Commercial instruments exist!
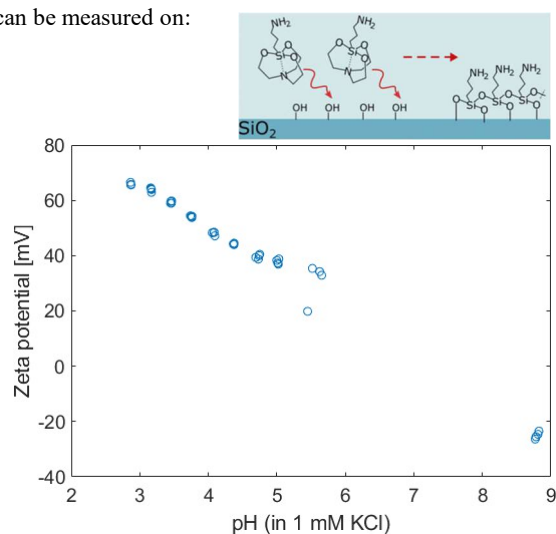
Repulsion Between Charged Interfaces

What is now the repulsive force between two charged surfaces in a solvent?

The repulsion is <u>not</u> simply electrostatic. It is mainly an <u>osmotic pressure</u> effect.
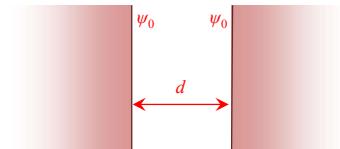
For two plates with d comparable to κ^{-1} the diffuse layer theory can be used to show that the pressure P (force per area) is:

$$P(d) = 64 k_\text{B} T C_0 \left[\frac{\exp\left(\frac{ve\psi_0}{k_\text{B}T}\right) - \exp\left(-\frac{ve\psi_0}{k_\text{B}T}\right)}{\exp\left(\frac{ve\psi_0}{k_\text{B}T}\right) + \exp\left(-\frac{ve\psi_0}{k_\text{B}T}\right)} \right]^2 \exp(-\kappa d)$$

Israelachvili
Intramolecular and Surface Forces **Academic Press 2011**

No derivation here, sorry…

Looking carefully, P is just proportional to $\exp(-\kappa d)$!

ψ_0 ψ_0

d

Interaction Energy for Spheres

The interaction energy <u>per area</u> for moving the plates together is then:

$$\frac{W_\text{flat}(d)}{A} = \int\limits_d^\infty P(z)\text{d}z = \kappa^{-1} P(d)$$

We can do the same approximation as for the van der Waals force. For sphere-surface:

$$F(d) \approx 2\pi R \frac{W_\text{flat}}{A} = 2\pi R \kappa^{-1} P(d)$$

$$W(d) = 2\pi R \kappa^{-1} \int\limits_d^\infty P(z)\text{d}z = 2\pi R \kappa^{-2} P(d)$$

For two spheres:

now representing repulsion

$$F(d) \approx -2\pi \frac{R_1 R_2}{R_1 + R_2} \frac{W_\text{flat}}{A} = -2\pi \frac{R_1 R_2}{R_1 + R_2} \kappa^{-1} P(d)$$

$$W(d) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \kappa^{-1} \int\limits_d^\infty P(z)\text{d}z = 2\pi \frac{R_1 R_2}{R_1 + R_2} \kappa^{-2} P(d)$$

Simplifications and Assumptions

Expression for $P(d)$ is strictly only valid for 1:1 electrolytes, but not so bad for other electrolytes as long as $|\psi_0| < 80$ mV. (But you must still calculate a new Debye length!)

If $|\psi_0| < 25$ mV the formula for osmotic pressure simplifies:

$$P(d) = 2\varepsilon_0 \varepsilon \kappa^2 {\psi_0}^2 \exp(-\kappa d)$$

The simplified Grahame equation can then be used:

$$P(d) = 2\frac{\sigma^2}{\varepsilon_0 \varepsilon} \exp(-\kappa d)$$

This simplifies the expressions for $W(d)$ and works for any electrolyte!

Remember: Grahame only relates ψ_0 to surface charge density σ.

Combining Van der Waals and Double Layer

The DLVO theory (Derjaguin and Landau, Verwey and Overbeek) combines van der Waals attraction and double layer repulsion:

$$W_{\text{tot}}(d) = W_{\text{vdW}}(d) + W_{\text{dl}}(d)$$

Van der Waals energy always gives d^{-1} dependence.

Double layer energy always approximately proportional to $\exp(-\kappa d)$.

Some limitations:

• No hydrophobic effect (solvent entropy)!

• The unavoidable repulsion at very small d is not included.

• Adsorbed ions! At what d do we have ψ_0?
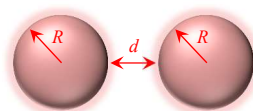
DLVO Curves

Curve type depends on ionic strength:

• High energy barrier.

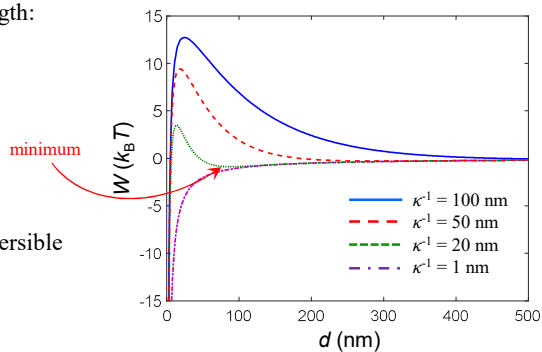• Secondary minimum.

• Monotonic decrease.

Secondary minimum indicates reversible semi-aggregation!

Example for:

$\psi_0 = 20$ mV
$T = 300$ K
$\varepsilon = 80$
$R = 50$ nm
$Z = 10^{-19}$ J

minimum

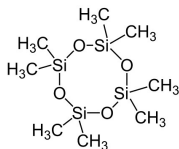just proof of principle, only accurate when $d \ll R$

Solvent Displacement

Oscillations can be detected in the $F(d)$ curve when d equals a few molecular layers.

Physical interpretation: Only a discrete number of molecules can fit.

But also many other complicated effects, in particular for water…

octamethylcyclotetrasiloxane

Horn, Israelachvili
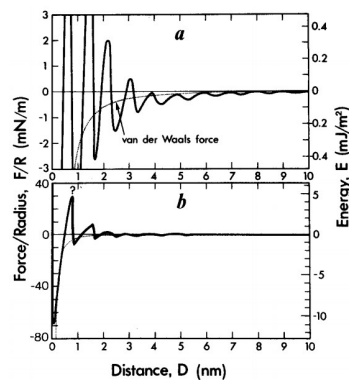*Journal of Chemical Physics* **1981**, 75 (3), 1400-1411.

FIG. 5. (a) and (b) Mean force law synthesized from a number of different experiments. For comparison the theoretically expected nonretarded continuum van der Waals force is also shown. (b) The net force plotted on a reduced scale. The right hand ordinate gives the corresponding interaction energy per unit area of two flat parallel surfaces, according to Eq. (1): $E = F/2\pi R$. The height of the first maximum is not known accurately for reasons discussed in the text.
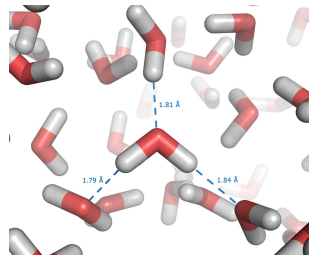
Hydrophobic Effect

Liquid water has peculiar properties because of the configurational entropy associated with the hydrogen bonding network.

Water molecules lose entropy close to hydrophobic surfaces. If two hydrophobic surfaces are brought into contact the water gains entropy because the contact area to water is reduced.

The solubility of hydrophobic compounds in water is very low overall, but it can also <u>decrease</u> with temperature!

Wikipedia: *Hydrophobic Effect*

Wikipedia: *Miscibility*

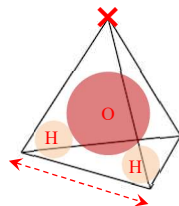# Quantifying Hydrophobic Interactions

Rough model: Each water molecule occupies a tetrahedron with 4 neighbors. There are 6 edges to orient along ($\Omega = 6$).

If one neighbor is replaced by something that water cannot hydrogen bond with, we get a triangle instead. Then there are 3 edges to orient towards ($\Omega = 3$).

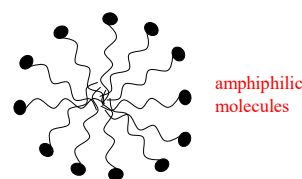Boltzmann gives entropy change: $k_B\log(\Omega_f/\Omega_i) = k_B\log(3/6) = -k_B\log(2)$

Adding a methyl group (about the same size as water) means contacting 4 water molecules, which thus costs $4k_B\log(2)$. (More than the entropy of mixing!)

Still does not explain attractive forces at longer distances…

amphiphilic molecules

Checklist 1

- Van der Waals interactions

- The Derjaguin approximation

- The electric double layer

- Debye length

- Grahame equation

- Zeta potential

- Hydrophobic interactions

Exercise 1.1

Assume we have a water solution with 150 mM NaCl (physiological) at room temperature. Calculate the concentration of Cl⁻ 0.5 nm from a surface with a potential of +200 mV using the Gouy-Chapman model (no adsorbed ions). Comment on the result!

Exercise 1.1

First calculate the Debye length. For monovalent salt:

$C_0 = 150$ mmolL^{-1} = 150 molm^{-3} = 150×6.022×10^{23} m^{-3}
$e = 1.602×10^{-19}$ C, $k_B = 1.381×10^{-23}$ JK^{-1}, $\varepsilon_0 = 8.854×10^{-12}$ Fm^{-1}
Water means $\varepsilon = 80$, room temperature is $T = 300$ K.

$$\kappa = \left[\frac{2C_0 e^2}{\varepsilon\varepsilon_0 k_B T}\right]^{1/2} = 1.257...×10^9 \text{ m}^{-1}$$

The potential at $z = 0.5$ nm is then:

$$\psi(z = 0.5 \text{ nm}) = 0.2 \times \exp(-\kappa \times 0.5 \times 10^{-9}) = 0.106... \text{ V}$$

The sought ion concentration is thus:

$$C = 0.15 \times \exp\left(-\frac{ve\psi(z = 0.5 \text{ nm})}{k_B T}\right) = 9.28... \text{ M}$$

So we get $C = 9.3$ M, but the maximum solubility of NaCl in water is 6.2 M at room temperature, so the model is not realistic for this surface potential.

Exercise 1.2

A polystyrene colloid has sulphate groups (-SO$_3^-$) on its surface. The zeta potential is −20 mV in 1 mM NaCl in water. Assume this is equal to the potential where the diffuse layer starts and that there are no adsorbed ions! Estimate how many sulphate groups there are on the colloid if it has a radius of 20 nm.

Exercise 1.2

If there are no adsorbed ions, for an estimate we can assume the zeta potential is equal to the surface potential ($\zeta = \psi_s$). We first calculate the Debye length assuming 300 K:

$$\kappa = \left[\frac{2C_0 e^2}{\varepsilon \varepsilon_0 k_B T}\right]^{1/2} = \left[\frac{2 \times 1 \times 6.02 \times 10^{23} \times [1.60 \times 10^{-19}]^2}{80 \times 8.85 \times 10^{-1} \times 1.38 \times 10^{-2} \times 300}\right]^{1/2} = 1.02...\times 10^8 \text{m}^{-1}$$

We can use the simplified Grahame equation to get σ:

$$\sigma = \varepsilon \varepsilon_0 \psi_0 \kappa = 80 \times 8.85 \times 10^{-12} \times 0.02 \times 1.02 \times 10^8 = 0.0015... \text{ Cm}^{-2}$$

Note the unit of C per m^2. The charge of each -SO$_3^-$ group is 1.602×10^{-19} C (negative, but this is cancelled by the sign of ψ_s). This gives 0.009 groups per nm^2.

The area of a colloid is ~5000 nm^2, which gives about 46 sulphate groups per colloid.

Exercise 1.3

Derive the "low potential" and "any electrolyte" version of DLVO theory for two spheres of radius R. (For the double layer repulsion, start with the simplified expression for $P(d)$ and use the Derjaguin approximation in the same manner.)

$\rightarrow$

$$W(d) = R\left[2\pi\varepsilon_0\varepsilon{\psi_0}^2 \exp(-\kappa d) - \frac{Z}{12d}\right]$$

Exercise 1.4

Make a rough estimate how fast the double layer will build up after an electrochemical potential is applied to an electrode in 1 M KCl solution. The field is 100 V/m. (Check slide 14.)

$\rightarrow$

Should be on the order of tens of microseconds.