Electrostatic Force (2)

Reference text:

The Structure and Rheology of Complex Fluids, Ronald G. Larson

Statistical Mechanics, Donald A. McQuarrie

Soft Matter Physics, M. Doi

Slides from Complex Fluids and Soft Matter, Ronald G. Larson

Colloidal Systems, Darrell Velegol

Based on Midterm Teaching Eval

- Thank you for completing the eval and the positive feedback – it is very encouraging for the teaching team and we are motivated to do better.

- Thank you also for the suggestions on how to make this class better, we are working hard to adapt the second part of the semester to make this a better experience for you.

- Syllabus change
  - New grading scheme

ACTIVITY	Weight
Attendance and Participation*	20% + 10% = 30%
In-class Presentations	30%
NSF Fellowship Proposal	15% + 5% = 20%
~~Invention Disclosure (group)~~	~~15%~~
Final Project (group)	20%

- Paper 1 presentation grade will be released later this week.

- More VR, more particle related VR, more complex examples: we will have one more VR lab towards the end of the semester. We are actively developing materials right now.

Based on Midterm Teaching Eval

- Time management: move the student presentation to the front of the class. Please help me keep things on track: Youtube presentation: 10 mins total (including the 5 minutes video); Journal club presentation: 5 mins presentation + 5 minutes Q&A.

- Journal clubs:
    - "choose your own paper to read" --- we will do that for the final project, I also want to make sure you are exposed to the classics. As the semester moves along, we will transition into modern work.
    - "All of the papers are required to be read each week" --- we thought that would be too much work, you are always welcome to read them though and keep up that curiosity.

- Less lecturing, more group activities and at least a break: duly noted, we do want you to be exposed to some classic math and physics in condensed matter physics but I will try to put in more balance.

- Youtube presentations: many of you love them, some of you not as much. The purpose of this is to connect us better to practical things that you care about. We want to focus on technology to compliment the more theoretical stuff I talk about in lectures.

- Guest lectures: many of you want more and some of you want less, perhaps due to different lecture style. Today we will have an excellent speaker in MechE that I know you will enjoy.

Guest Lecture for today (MechE department seminar)

COLLEGE OF ENGINEERING
MECHANICAL ENGINEERING
UNIVERSITY OF MICHIGAN

Mechanical Engineering Seminar Series

Tanglemer: A Polymer Network in which Entanglements Greatly Outnumber Crosslinks

Zhigang Suo
Allen E. and Marilyn M. Puckett
Professor of Mechanics and Materials
Harvard University

3:00 PM
March 12, 2024
1200 EECS

Final project logistics

- This project is required for the graduate students in the course only.

- Working in self-selected pairs, your team will introduce a new frontier of research related to complex particles and present a selection of two or more papers to teach the class about this topic. This presentation will take the place of a final exam for the course.

- Presentations will be 15 minutes long with an additional 5 minutes for Q&A.

- Although the lower limit for the number of papers your team chooses to discuss is 2, there is no upper limit provided that all papers are discussed to a reasonable degree of depth and your presentation remains within the time limit.

Assignment	Submission Type	Date	Time
Topic Approval	Text Submission on Canvas	Friday, April 5	11:59 PM
Presentation Slides	PDF/PPTX on Canvas	Tuesday, April 23	1:30 PM
Final Presentation	Oral Presentation	Tuesday, April 23	In Class

Charge nonuniformity

Micrometer Scale Adhesion on Nanometer-Scale Patchy Surfaces: Adhesion Rates, Adhesion Thresholds, and Curvature-Based Selectivity

Maria M. Santore and Natalia Kozlova

View Author Information ∨

- The basic picture of a randomly "patchy particle" surface is

Analytical Model for the Effect of Surface Charge Nonuniformity on Colloidal Interactions

Darrell Velegol and Prasanna K. Thwar

View Author Information ∨

$$L \approx \sqrt{a\kappa^{-1}}$$

electrical double layer ($\sim\kappa^{-1}$)

2a
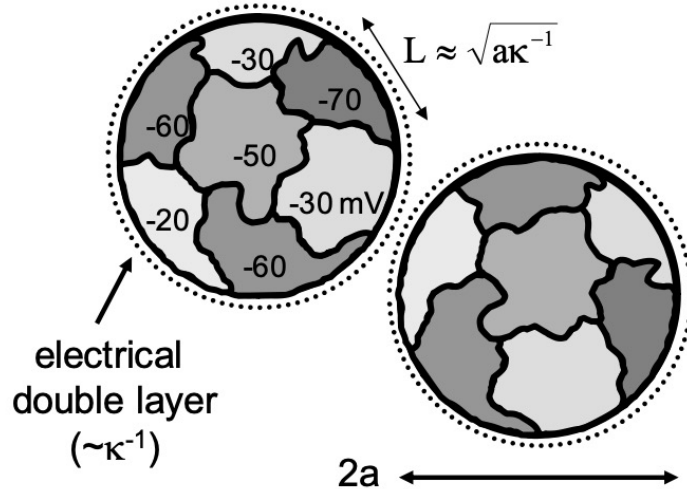
Figure 2-4. Charge nonuniformity on particles. The average surface potential is roughly -50 mV, which one would predict is sufficient to maintain stability in most cases. However, there might be regions on the particles where the surface potential is only -30 mV, as shown. In solution, particles undergo random Brownian rotation, and when two regions of -30 mV are adjacent, the electrostatic repulsion might not be sufficient to overcome the van der Waals attraction, and the particles could aggregate together.
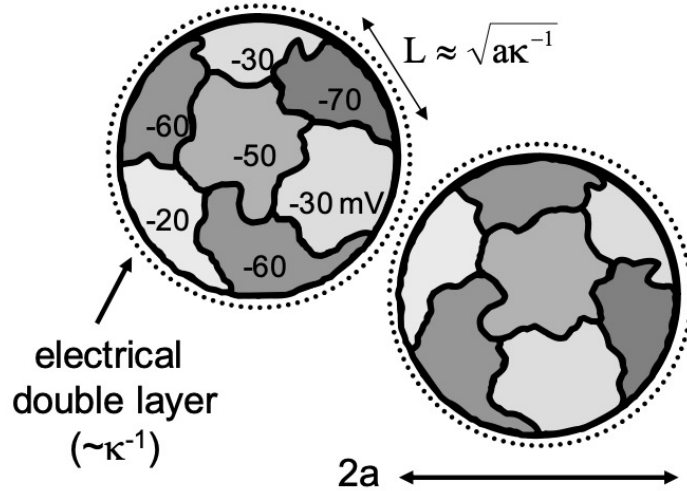
- When the patch size for the charge nonuniformity is very small, indeed going all the way to the level of the placement of individual ions, then the "discrete charge effect" is very small.

- However, if the patch size (L) becomes larger, say with a 10-50 nm length scale, the electrostatic forces can be significantly altered.

Charge nonuniformity

- The basic picture of a randomly "patchy particle" surface is

$$L \approx \sqrt{a\kappa^{-1}}$$

-30, -70, -60, -50, -30 mV, -20, -60

electrical double layer $(\sim\kappa^{-1})$

$2a$

- there is a significant variation of electrostatic forces, depending on the relative orientation of the two spheres:

  Standard deviation of repulsion

  $$\left| \frac{\sigma_\Phi}{\langle \Phi_{es} \rangle} \right| \approx \left| \frac{\sigma_\zeta}{\langle \zeta \rangle} \right|$$

  orientation average repulsive electrostatic energy between particles

- electrophoresis measures the average zeta potential over the particles surfaces:

  $$\langle \zeta \rangle \approx -50 \text{ mV}$$

- rotational electrophoresis measures the zeta potential standard deviation: $\sigma_\zeta \approx 20 \text{ mV}$

Charge nonuniformity

- The basic picture of a randomly "patchy particle" surface is

$L \approx \sqrt{a\kappa^{-1}}$

-30, -70, -60, -50, -30 mV, -20, -60

electrical double layer ($\sim \kappa^{-1}$)

2a

- Such variations in electrostatic repulsion can cause an unstable suspension – with the net interparticle energy being attractive at even larger separations – when measurements of the average zeta potential would have predicted a stable suspension.

- there is a significant variation of electrostatic forces, depending on the relative orientation of the two spheres:

Standard deviation of repulsion

$$\left| \frac{\sigma_\Phi}{\langle \Phi_{es} \rangle} \right| \approx \left| \frac{\sigma_\zeta}{\langle \zeta \rangle} \right|$$
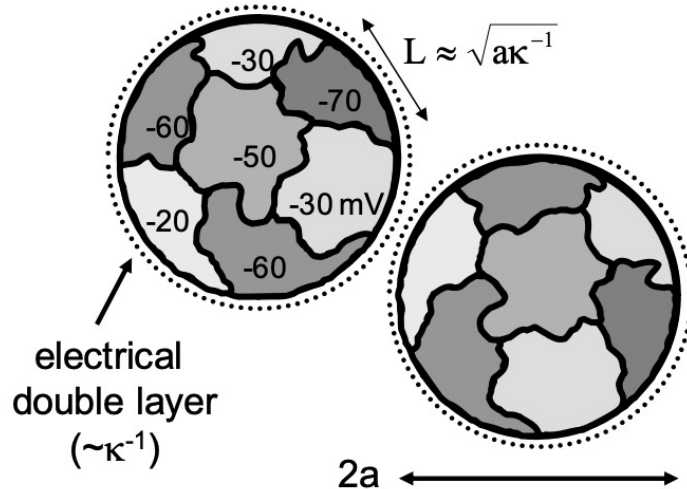
orientation average repulsive electrostatic energy between particles

- Electrical double layer

- Poisson-Boltzmann equation
  - Poisson equation, relate potential change to charge density
  - Boltzmann equation, relate ion distribution to potential energy
  - Poisson-Boltzmann: self-consistent description of electrostatic potential inside EDL, given bulk ion concentration (C_∞), introduce Debye length (κ)

- Debye-Huckel
  - For small surface potential and binary electrolyte, PB simplifies to Debye-Huckel, which give exponential decay of electrostatic potential ($\Psi(x)$) from surface potential (Ψ_0) inside EDL with characteristic length (κ^{-1})
  - Debye-Huckel ($\Psi(x)$) solutions for **1 plate**, **1 sphere**, between **2 plates**

- Surface charge density (ρ_s) for **1 plate**
  - Electroneutrality gives relation between (ρ_s) and (Ψ_0)
  - Differentiate Boltzmann and use PB equation to relate total ion concentration at surface of **1 pate** (C_0) to (C_∞) and (ρ_s)
  - Grahame equation, relate (ρ_s) to (Ψ_0) and (C_∞)
    - In binary electrolyte, example of Grahame used to calculate (C_0) from (Ψ_0) and (C_∞) with fixed (ρ_s)
    - For low (Ψ_0) and binary electrolyte, Grahame simplifies to (ρ_s) = $\varepsilon\kappa(\Psi_0)$
  - Differentiate Boltzmann and use PB equation also relates individual ion concentration ($C_i(x)$) to electrostatic potential ($\Psi(x)$)
  - For binary electrolyte, this simplifies to Gouy-Chapman's solution to ($\Psi(x)$), allow us to plot EDL: ($C_i(x)$), ($C_{i0}(x)$), ($\Psi(x)$), (Ψ_0), given (ρ_s) and (C_∞)
  - For low (Ψ_0) and binary electrolyte, Gouy-Chapman simplifies to Debye-Huckel, completing the full circle

- Surface charge density (ρ_s) using Debye-Huckel (low (Ψ_0) and binary electrolyte assumed)
  - Direct plugging Debye-Huckel into electroneutrality for **1 plate** will also give simplified Grahame: (ρ_s) = $\varepsilon\kappa(\Psi_0)$
  - Surface charge density (ρ_s) using Debye-Huckel for **1 sphere**, for **2 plates**: for finite (ρ_s), (Ψ_0) $\to \infty$ as gap $\to$ 0

- Electrostatic force per area (f_{es}) between **2 plates**
  - Origin (contact value theorem): increased ionic concentration in gap $\to$ increased **osmotic pressure** (π) exerted on plates
  - Navier-Stokes equation for static fluid reduces to balance of pressure and electrical forces on the fluid
  - Navier-Stokes + Poisson equations relates (π) to electric field ($d\Psi(x)/dx$)
  - Navier-Stokes + Poisson + Boltzmann equations solve (π) as a function of ($\Psi(x)$) and (C_∞)
  - For low (Ψ_0) and binary electrolyte, solution simplifies to (π) $\sim \varepsilon\kappa(\Psi(x))^2$
  - Plug in Debye-Huckel for **2 plates** for ($\Psi(x)$) to obtain exponential decay of electrostatic force per area (f_{es}) with characteristic length (κ^{-1})
  - Integrate (f_{es}) for electrostatic energy per unit area (V_{es}) between **2 plates**

- Electrostatic energy (Φ_{es}) between **2 spheres** and the Derjaguin approximation
  - Apply the Derjaguin approximation to obtain the electrostatic energy (Φ_{es}) between **2 spheres**
  - Differentiate to calculate the electrostatic force (F_{es}) between **2 spheres**

- **Electrical double layer**

- **Poisson-Boltzmann equation**
    - Poisson equation, relate potential change to charge density
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Electrostatic forces

- The electrical potential decays away from a flat surface at a rate given roughly by the **Debye-Huckel equation**:

$$\psi = \psi_0 e^{-\kappa x}$$

Surface potential

Distance from the surface

- Typical magnitudes of the **surface potential (Ψ)** are 10 to 150 mV, and can be negative or positive. Since these potentials arise due to the surface charges, the relationship between the surface charge density (units C/m^2) and the **surface potential** is:

$$\rho_s = \varepsilon \kappa \psi_0$$

Electrical permittivity

Surface charge density

- Note the potential becomes **proportional** to the surface charge density.

- The expression $\rho_s = \varepsilon \kappa \Psi_0$ is equivalent to a **capacitor** whose two plates are separated by a distance κ^{-1}, have charge densities $\pm\rho_s$, and potential difference Ψ_0.

- This analogy with a charged capacitor gave rise to the name **diffuse electric double-layer** for describing the ionic atmosphere near a charged surface, whose **characteristic length** or "**thickness**" is known as the **Debye length κ^{-1}**.

And we recover the famous Debye length κ^{-1}

$$\rho_s = \varepsilon \kappa \Psi_0, \text{ where } \kappa \equiv \sqrt{\sum_i^N \frac{z_i^2 e^2 C_{i\infty}}{\varepsilon k T}}$$

Surface charge density

- If we consider the change of **potential** $\Psi_x = \Psi(x)$ and **ionic concentrations** $C_x = C(x)$ away from the charge surface, we can use the previous result

$$\frac{d \sum_i^N C_i}{dx} = \frac{\varepsilon}{2kT} \frac{d}{dx} \left(\frac{d\Psi}{dx}\right)^2$$

And we recover the famous Debye length κ^{-1}

$$\rho_s = \varepsilon \kappa \Psi_0, \text{ where } \kappa \equiv \sqrt{\sum_i^N \frac{z_i^2 e^2 C_{i\infty}}{\varepsilon kT}}$$

Surface charge density

- Recall the electric field at the surface is $E_0 = -\left(\dfrac{d\Psi}{dx}\right)_0$

- The condition of electroneutrality implies that

$$\rho_s = \varepsilon\left[\left(\frac{d\Psi}{dx}\right)_{x\to\infty} - \left(\frac{d\Psi}{dx}\right)_{x=0}\right] = \varepsilon\left[0 - \left(\frac{d\Psi}{dx}\right)_0\right] = -\varepsilon\left(\frac{d\Psi}{dx}\right)_0 = \varepsilon E_0$$

- Turning attention to the ionic concentration, differentiating the Boltzmann distribution yields:

$$\frac{d\sum_i^N C_i}{dx} = -\sum_i^N \frac{z_i e C_{i\infty}}{kT} exp\left(-\frac{z_i e\Psi}{kT}\right)\left(\frac{d\Psi}{dx}\right) = \frac{\varepsilon}{kT}\frac{d^2\Psi}{dx^2}\left(\frac{d\Psi}{dx}\right) = \frac{\varepsilon}{2kT}\frac{d}{dx}\left(\frac{d\Psi}{dx}\right)^2$$

- Integrate:

$$\sum_i^N C_i(x=0) - \sum_i^N C_i(x\to\infty) = \frac{\varepsilon}{2kT}\int_{\left(\frac{d\Psi}{dx}\right)^2_{x\to\infty}}^{\left(\frac{d\Psi}{dx}\right)^2_{x=0}} d\left(\frac{d\Psi}{dx}\right)^2 = \frac{\varepsilon}{2kT}\left(\frac{d\Psi}{dx}\right)^2_0$$

Surface charge density

- If we consider the change of **potential** $\Psi_x = \Psi(x)$ and **ionic concentrations** $C_x = C(x)$ away from the charge surface, we can use the previous result

$$\frac{d\sum_i^N C_i}{dx} = \frac{\varepsilon}{2kT}\frac{d}{dx}\left(\frac{d\Psi}{dx}\right)^2$$

- Instead of integrating from $x \to \infty$ to 0 as we did previously, we can integrate to any x:

$$\sum_i^N C_i(x) = \sum_i^N C_i(x \to \infty) + \frac{\varepsilon}{2kT}\left(\frac{d\Psi}{dx}\right)_x^2 \implies \sum_i^N C_{ix} = \sum_i^N C_{i\infty} + \frac{\varepsilon}{2kT}\left(\frac{d\Psi}{dx}\right)_x^2$$

- For a 1:1 electrolyte (like NaCl), this reduces to:

$$\left(\frac{d\Psi}{dx}\right)_x = \sqrt{\frac{8kTC_\infty}{\varepsilon}}\, sinh\left(\frac{e\Psi_x}{2kT}\right)$$

Surface charge density

- This can be integrated to yield

$$\psi_x = \frac{2kT}{e} \log\left[\frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}}\right] \approx \frac{4kT}{e} \gamma e^{-\kappa x}$$ where $\gamma = \tanh(e\psi_0/4kT)$ and $\kappa^2 = \frac{2Z^2 e^2 c_\infty}{\varepsilon kT}$ with Z = 1

- This is known as the Gouy-Chapman theory.

$$\left(\frac{d\Psi}{dx}\right)_x = \sqrt{\frac{8kTC_\infty}{\varepsilon}} \, sinh\left(\frac{e\Psi_x}{2kT}\right)$$
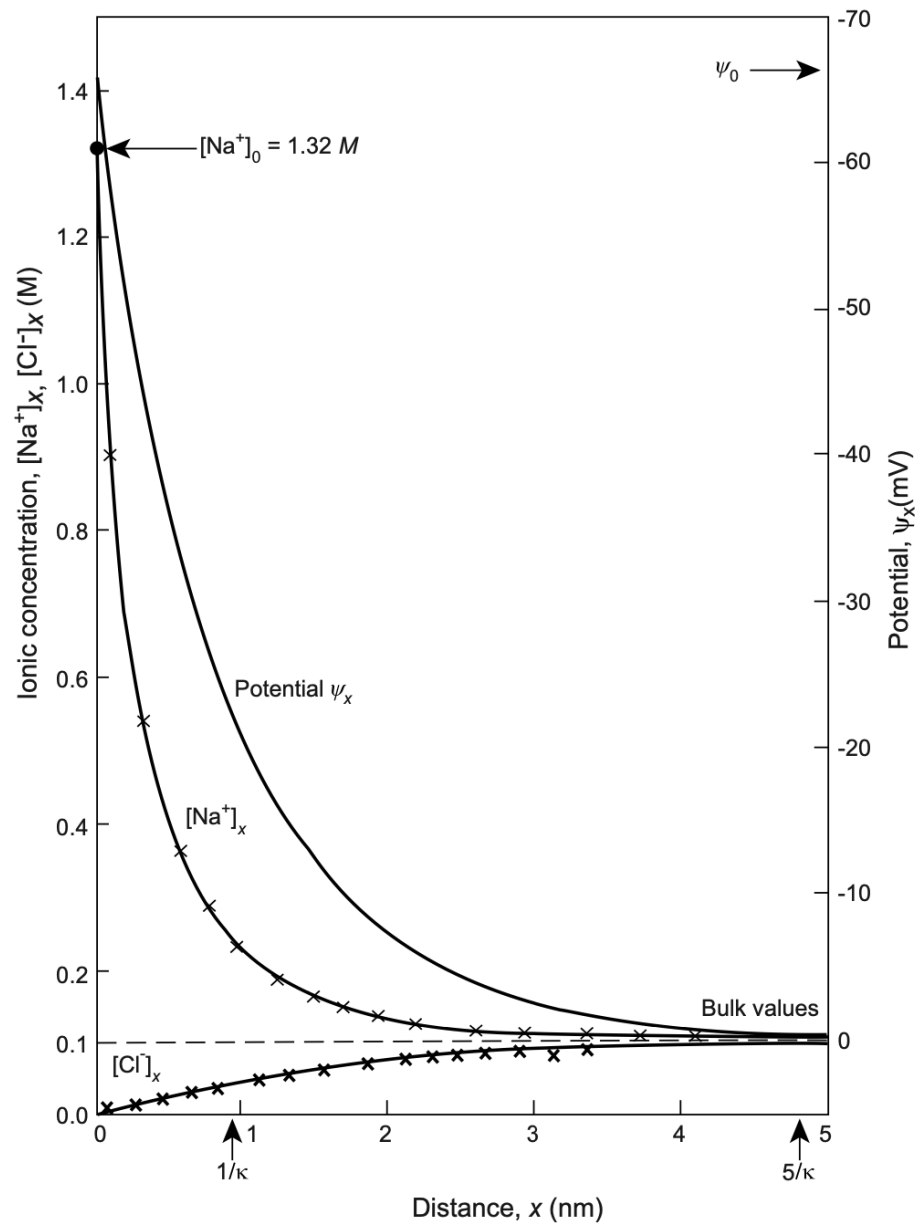
FIGURE 14.8 Potential and ionic density profiles for a 0.1 M monovalent electrolyte such as NaCl near a surface of charge density $\sigma = -0.0621$ C m^{-2} (about one electronic charge per 2.6 nm^2), calculated from Eqs. (14.39) and (14.25) with $\psi_0 = -66.2$ mV obtained from the Grahame equation. The crosses are the Monte Carlo results of Torrie and Valleau (1979, 1980). Note that the potential (and force between two surfaces) both decay asymptotically as $e^{-\kappa x}$, while the ionic concentrations decay much more sharply.

Surface charge density

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- This is known as the Gouy-Chapman theory.

- For **high** surface potentials γ → **1**, whereas for Ψ_0 < 25 mV, Gouy-Chapman reduces to the **Debye-Huckel** result derived previously:

$$\psi_x \approx \psi_0 e^{-\kappa x}$$

Debye-Huckel results for electric potential

- general solution: $\psi = B_1 e^{\kappa x} + B_2 e^{-\kappa x}$

- **Debye-Huckel equation** for electric potential near to a single flat plate (upon applying the boundary conditions):

$$\psi = \psi_0 e^{-\kappa x}$$

- At the plate surface the electric potential is Ψ_0, while just a few Debye lengths away, the electric potential decays to nearly zero.

- Example:

A plate has a potential of $\psi_0 = -39$ mV at its surface. The plate is in a 5.4 mM NaCl solution at $T = 305$ K. Find the Debye length, and then the electric potential at a distance of 7.0 nm from the plate. At this T, $\varepsilon_r = 76.0$ (Table 1-3).

answer: the Debye length $\kappa^{-1} = 4.13$ nm. $\psi(7.0$ nm$) = -7.16$ mV.

Surface charge density

- This can be integrated to yield

$$\psi_x = \frac{2kT}{e} \log\left[\frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}}\right] \approx \frac{4kT}{e} \gamma e^{-\kappa x}$$ where $\gamma = \tanh(e\psi_0/4kT)$ and $\kappa^2 = \frac{2Z^2 e^2 c_\infty}{\varepsilon kT}$ with Z = 1

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Surface charge density

- Oftentimes we want to predict the surface charge density (ρ_s [=] C/m²), knowing the surface potential, or vice versa.

- a **surface** plus its **EDL** form an **electroneutral** system. Thus, the charges at the surface and the charges in the bulk fluid **balance**. This can be written mathematically for a flat plate as

$$\iiint_V \rho_e dV + \iint_S \rho_s dS = 0 \Rightarrow \int_0^\infty \rho_e dx + \rho_s = 0$$

- This equation says that the surface charges must be balanced by the charges in the fluid from near the plate to infinity. A rearrangement of the Poisson equation tells us

$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon} \Rightarrow \rho_e = -\varepsilon \frac{d^2\psi}{dx^2}$$

integrate

$$\rho_s = \varepsilon \int_0^\infty \frac{d^2\psi}{dx^2} dx = \varepsilon \int_0^\infty d\left(\frac{d\psi}{dx}\right)$$

Surface charge density using Debye-Huckel

- Oftentimes we want to predict the surface charge density (ρ_s [=] C/m²), knowing the surface potential, or vice versa.

- a **surface** plus its **EDL** form an **electroneutral** system. Thus, the charges at the surface and the charges in the bulk fluid **balance**. This can be written mathematically for a flat plate as

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$$\frac{d^2\psi}{dx^2} = -\frac{\rho_e}{\varepsilon} \Rightarrow \rho_e = -\varepsilon \frac{d^2\psi}{dx^2} \quad \xrightarrow{\text{integrate}} \quad \rho_s = \varepsilon \int_0^\infty \frac{d^2\psi}{dx^2} dx = \varepsilon \int_0^\infty d\left(\frac{d\psi}{dx}\right)$$

- For small potentials near a plate, we have **Debye-Huckel**

$$\psi = \psi_0 e^{-\kappa x} \qquad \xrightarrow[\text{also yield}]{\text{Plug in } \rho_s} \qquad \rho_s = \varepsilon \psi_0 \kappa$$

Surface charge density using Debye-Huckel

- Example

A plate has a surface potential of -39 mV in 5.4 mM NaCl solution at T = 305 K. Find the surface charge density in C/m^2, and the average area per charge group, for monovalent charges. Use the result for the Debye length from Example 2-1.

$$\rho_s = \varepsilon \psi_0 \kappa$$

$$\kappa^2 = \frac{2Z^2 e^2 c_\infty}{\varepsilon k T}$$

answer: -0.00635 C/m^2 = -0.635 $\mu C/cm^2$. Since monovalent charges are 1.6×10^{-19} C, the spacing is one charge group per 25.2×10^{-18} m^2 = (5.0 nm)^2. About 1 $\mu C/cm^2$ is a typical magnitude of surface charge density.

Surface charge density using Debye-Huckel

- A similar analysis around a **sphere** gives

$$\rho_s = \varepsilon \kappa \psi_0 \left(\frac{1 + \kappa a}{\kappa a} \right)$$

- Between **parallel plates** having a surface potential (Ψ_0) and separated by a **distance** (**L**), the surface charge density is given by

$$\rho_s = \varepsilon \kappa \psi_0 \left(\frac{1 - e^{-\kappa L}}{1 + e^{-\kappa L}} \right)$$

- If L → ∞ this reduces to the flat plate limit:

$$\rho_s = \varepsilon \psi_0 \kappa$$

- Solving for Ψ_0:

$$\psi_0 = \frac{\rho_s}{\varepsilon \kappa} \left(\frac{1 + e^{-\kappa L}}{1 - e^{-\kappa L}} \right)$$

- As **L → 0** this equation becomes **singular**, meaning that a very **large potential** must arise from a **finite** ρ_s for **small gaps** between plates.

Electrostatic force between plates

- Once the electrostatic potential between two plates is known, we can evaluate the **force** or **potential energy** between the **two plates**.

- We will start with **two plates**, each with a surface potential (Ψ_0) and separated by a **distance** (**h**). The coordinate x runs perpendicular to the plates, with x = 0 halfway between the plates.
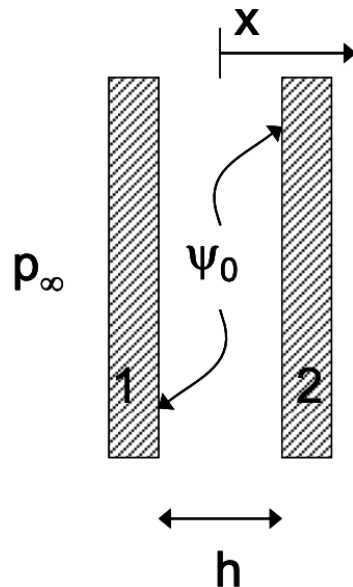

Figure 2-2. Two plates with electrostatic interactions. In the case shown, the electrostatic potential on the surface of both plates (1 and 2) is the same. As a result, the interaction energy is repulsive (positive). The pressure outside of the plates is p_∞, while the pressure inside the plates is higher due to both electrostatic forces on the fluid, as well as osmotic pressure.

Electrostatic force between plates

- Outside the plates the **bulk pressure** is **p_∞**, while **between the plates** the **pressure is higher** due to the **electrostatic force** on the fluid – charged, since it is in the EDL – and also due to a higher **osmotic pressure** between the plates since there are <u>more ions in the EDL than in the bulk fluid</u>.
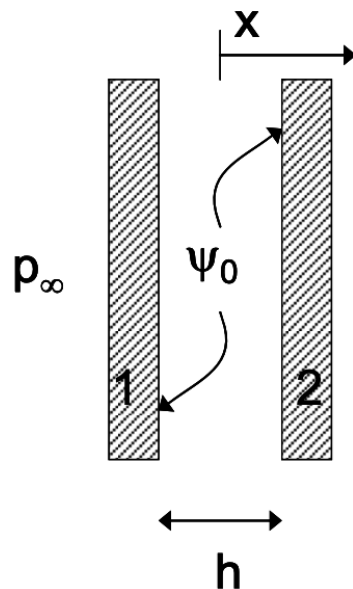

Figure 2-2. Two plates with electrostatic interactions. In the case shown, the electrostatic potential on the surface of both plates (1 and 2) is the same. As a result, the interaction energy is repulsive (positive). The pressure outside of the plates is p_∞, while the pressure inside the plates is higher due to both electrostatic forces on the fluid, as well as osmotic pressure.

Electrostatic force between plates

- If the plates have the **same** surface potential, they will repel with an **equal** but **opposite force**. Let's imagine that we hold the plates in place by applying a **force** (F_1) onto **plate 1** and a **force** ($F_2 = -F_1$) on **plate 2**. In this case the fluid between the plates will remain static, meaning that it will not accelerate, nor will it flow and dissipate energy. Our job at this point is to evaluate $F_1 = -F_2$.
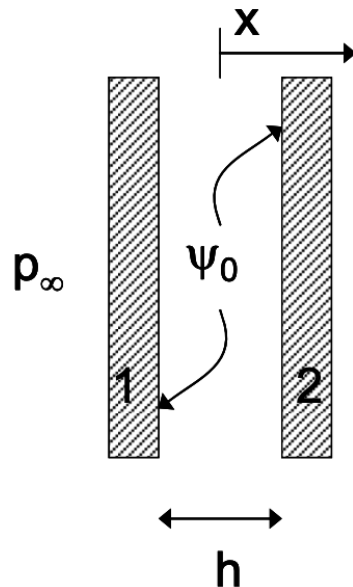

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Electrostatic force between plates

- evaluate the **electrostatic force per area** (**f$_{es}$**). For plates with an **area** (**A**), we have

$$f_{es} \equiv -\lim_{A \to \infty} F_1 / A = \lim_{A \to \infty} F_2 / A$$

- The **Navier-Stokes equation** is

isotropic pressure in the fluid   Local electric field

$$\rho_f \left(\frac{\partial \mathbf{v}}{\partial \mathbf{t}} + \nabla \cdot \mathbf{v}\mathbf{v} \right) = \eta \nabla^2 \mathbf{v} - \nabla p + \rho_e \mathbf{E} = 0$$

Fluid density   Fluid viscosity   Fluid velocity   Electrical charge density

- Charges move due to a finite electric field, whether the charges are **electrons** or **ions**. As the **local electric field** becomes stronger – meaning that the voltage change with distance becomes steeper – the ions in that region move faster.

Electrostatic force between plates

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- the x-direction **Navier-Stokes equation** with **v = 0** is

$$\frac{dp}{dx} = \rho_e E_x = -\rho_e \frac{d\psi}{dx}$$

- This gives the balance of **pressure** and **electrical forces** on the fluid. Where the fluid is static, these two forces balance at every position.

Electrostatic force between plates

- re-arranged version of the Poisson equation

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The Poisson equation

- define an "electrical potential" (Ψ, in V or mV), which is the voltage at any position in the system.

- the electric field (**E**) is defined as $\mathbf{E} = -\nabla \psi$

- The voltage arises due to charge groups on the particle, and changes through the EDL. For static systems the electric potential can be very accurately-described by a single scalar equation called "the Poisson equation":

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\rho_e}{\varepsilon}$$

- This partial differential equation predicts the electrical potential (Ψ, in V or mV) at any position (x,y,z), when the **volumetric charge density** (ρ_e, in C/m^3) is known everywhere.

Electrostatic force between plates

- re-arranged version of the Poisson equation

$$\rho_e = -\varepsilon \frac{d^2\psi}{dx^2}$$

- make a substitution for the volumetric charge density to give

$$\frac{dp}{dx} = \varepsilon \left(\frac{d^2\psi}{dx^2}\right)\left(\frac{d\psi}{dx}\right)$$

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- Recall from the chain rule

$$\frac{d}{dx}\left[\left(\frac{d\psi}{dx}\right)^2\right] = 2\left(\frac{d\psi}{dx}\right)\left(\frac{d^2\psi}{dx^2}\right) \quad\Longrightarrow\quad \frac{dp}{dx} = \frac{\varepsilon}{2}\frac{d}{dx}\left[\left(\frac{d\psi}{dx}\right)^2\right]$$

integrate

$$p = \frac{\varepsilon}{2}\left(\frac{d\psi}{dx}\right)^2 + B$$

Electrostatic force between plates

- The easiest place to evaluate **B** is at the midplane, where by **symmetry** we know that $d\Psi / dx = 0$. Therefore **B** is the **pressure at x = 0**.

- What contributes to this **pressure**? If the plates were uncharged, the pressure at the midplane would be simply the **ambient pressure** (p_∞).

- As charges are added to the plate, bringing **additional ions** into the **electrical double layer** region between the plates, there is also an **osmotic pressure** contribution.

$$p = \frac{\varepsilon}{2}\left(\frac{d\psi}{dx}\right)^2 + B$$
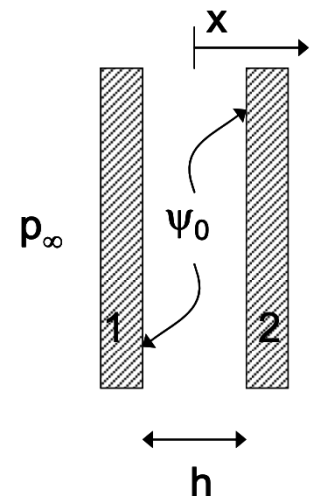
Electrostatic force between plates

- Because the **ions** are "**trapped**" in the **EDL** – there is an <u>analogy to being trapped behind a semi-permeable membrane</u> – the **osmotic pressure** at the midplane is higher in the **EDL** by an amount $\pi(x = 0)$.

$$p(x = 0) - p_\infty = \pi(x = 0) - \pi_\infty$$

- This simply says that the **pressure inside** the **EDL** between the plates is different from the **pressure outside** the plates by the difference in **osmotic pressure**.

- The π_∞ appears since the **bulk solution** will also have some **finite ionic strength**, even though it isn't as high as that between the plates.

- Since the fluid at $x = 0$ has a slightly higher **pressure**, it will push outward on the neighboring fluid, which in turn will push on the fluid all the way to the wall. The **electrical forces** on the fluid at $x = 0$ are **zero**, since by symmetry $d\Psi / dx = 0$ there, and thus **E = 0**.

- In the end the **pressure force** is the only force remaining:

$$f_{es} = p_\infty - p(x = 0)$$

Journal club assignments for L9

Lecture 9 (3/19)	
Group	**Paper Title**
A	P4_Kotov_kim-et-al-2024-direct-write-3d-printing-of-plasmonic-nanohelicoids-by-circularly-polarized-light
B	P2_Kotov_nmat4125
C	P1_Kotov_science.1177218
D	P3_Yao_s41586-019-1308-y