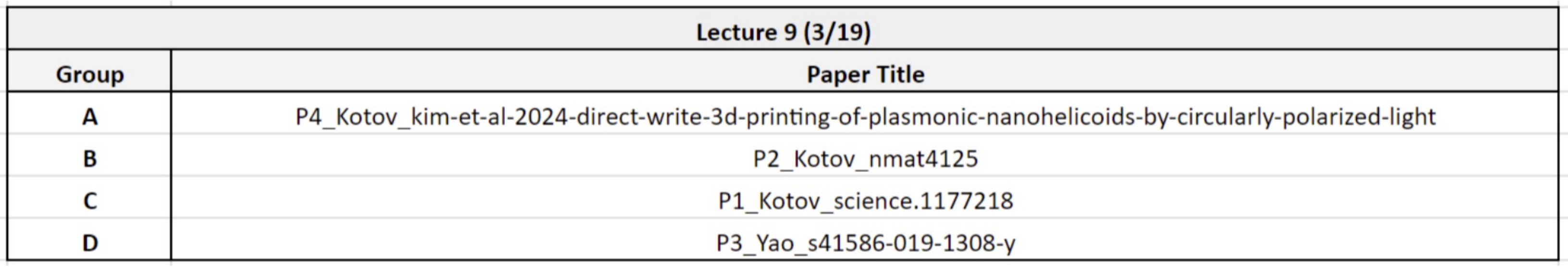
Electrostatic Force
(3)

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

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

- 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**
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    - Origin (contact value theorem): increased ionic concentration in gap → increased **osmotic pressure** (π) exerted on plates
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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

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

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

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

- 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

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

- make a substitution for the volumetric charge density to give

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

- Recall from the chain rule

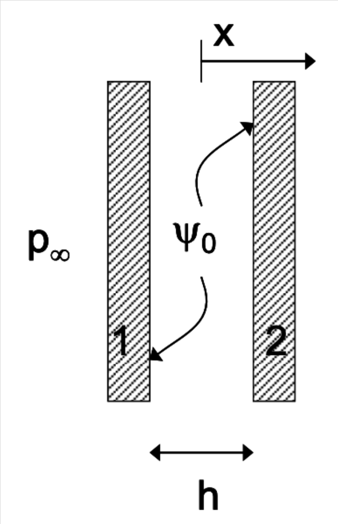
$$\frac{d}{dx}\left[\left(\frac{d\psi}{dx}\right)^2\right] = 2\left(\frac{d\psi}{dx}\right)\left(\frac{d^2\psi}{dx^2}\right) \Longrightarrow \boxed{\frac{dp}{dx} = \frac{\varepsilon}{2}\frac{d}{dx}\left[\left(\frac{d\psi}{dx}\right)^2\right]}$$

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

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.

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



Electrostatic force between plates

- Because the **ions** are "**trapped**" in the **EDL** – there is an analogy to being trapped behind a semi-permeable membrane – 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:

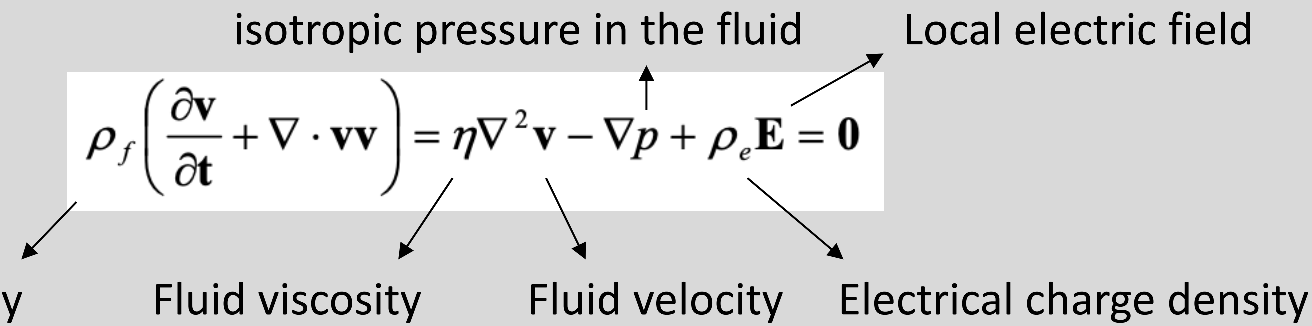
$$f_{es}=p_{\infty}-p(x=0)$$

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

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

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

- The job of finding the **electrostatic force** has thus been reduced to finding the **pressure difference** inside and outside the plate.
- **Osmotic pressure** is a well-established thermodynamic property. The osmotic pressure of a solution with a **dilute concentration** of **molecules** or **ions** (**n**) is given by the **van’t Hoff** result:

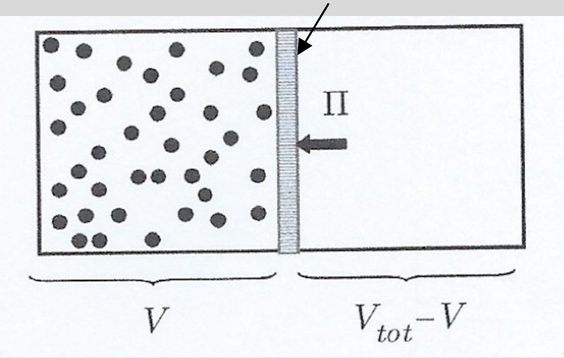
$$\pi = \underset{\downarrow}{n}kT$$

ion concentration (#/m^3)

Osmotic pressure is the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

Osmotic Pressure

Membrane allows water, but not particles, to pass through



Doi, Soft Matter Physics, 2013

Let A_{tot} be the total free energy, consisting of solution with volume V and pure solvent of volume $V_{tot} - V$

Remember: $dA = -SdT - \ pdV$

The work done by semi-permeable membrane is $-\Pi dV$

This must be equal to change in free energy dA_{tot}

Thus, $\boxed{\Pi = -\frac{\partial A_{tot}(V)}{\partial V}}$ $\quad \mathrm{f}(\phi) \equiv \frac{free\ energy}{vol}$ of uniform soln w/ vol. fraction ϕ

$$A_{tot} = V\mathrm{f}(\phi) + (V_{tot} - V)\mathrm{f}(0)$$

Note that $\phi = \frac{V_{solute}}{V} = \frac{Nz}{V}$

So that $\frac{\partial f(\frac{V_{solute}}{V})}{\partial V} = -f'\frac{V_{solute}}{V^2} \quad = -f'\frac{\phi}{V}$

So $\quad \Pi = -\mathrm{f}(\phi) + \phi f'(\phi) + f(0)$ Chain rule

Recall for Non-Interacting Particles

Helmholtz free energy of purely entropic system: $A = -TS$

$A = -k_B T\, lnQ$ $\quad Q$= partition function

overlapping (phantom) particles: E_j= 0, for every state j

$$Q = total\ number\ of\ unique\ states = \frac{V^N}{N!\Lambda^{3N}}$$

V = system volume, Λ = lattice spacing (or “deBroglie wavelength)”

V/Λ^3 = number of positions at which a particle can be placed

$A/k_B T = -lnQ \quad = -NlnV + \ln(N!) + const$ (const. involves Λ)

Stirling’s approx: $\ln(N!) \approx NlnN - N \quad \approx NlnN$ (*N* large)

$$\boxed{A/k_B T \ = -S/k_B \ = Nln\left(\frac{N}{V}\right)} = Nln(v) + const$$

$v = N/V$= number density

$A/(Vk_B T) \approx \ vln(v) + const$

Pressure $P = vk_B T$

Dilute Solution Expansion

lowest order term: $$\boxed{\Pi = \frac{N k_B T}{V} = \nu k_B T} = \frac{\phi k_B T}{z}$$

N = number of particles in V

(van't Hoff's law, analogous to ideal gas law)

z = vol. of solute

$$\phi = \frac{V_{solute}}{V} = \frac{Nz}{V}$$

higher order expansion: $$\Pi = \frac{\phi k_B T}{z} + A_2 \phi^2 + A_3 \phi^3 + \ldots.$$

A_2, A_3 = 2nd and 3rd *virial coefficients*

Derivation:

$$A/k_B T \approx N ln\left(\frac{N}{V}\right)$$

$$A \approx N k_B T ln\left(\frac{N}{V}\right)$$

$$\Pi = -\frac{\partial A_{tot}(V)}{\partial V} \approx -\frac{\partial A(V)}{\partial V} + f(0) \approx N k_B T \frac{1}{V} + 0 = \nu k_B T$$

Electrostatic force between plates

- The job of finding the **electrostatic force** has thus been reduced to finding the **pressure difference** inside and outside the plate.
- **Osmotic pressure** is a well-established thermodynamic property. The osmotic pressure of a solution with a **dilute concentration** of **molecules** or **ions** (**n**) is given by the **van’t Hoff** result:

$$\pi = \underset{\substack{\big\downarrow \\ \text{ion concentration (\#/m}^3\text{)}}}{n}kT$$

- <u>Alternative derivation:</u> the chemical potential of the water (solvent) decreases with the addition of solute, and increases with the addition of pressure (Δp), such that $RT\ln(x_w) + V_m\Delta p = 0$ at equilibrium, where V_m is the molar volume of the solvent. Recognizing the solute mole fraction $x = 1 - x_w = (\#/N_A)/V = n/N_A$ and defining $\pi = \Delta p$ as the additional pressure required for equilibrium give the **van’t Hoff** result.

Electrostatic force between plates

- Detailed alternative derivation:
- Chemical potential of solution: $\mu(\underset{\downarrow}{x_w}, p + \pi)$

Mole fraction of water

- Consider equilibrium between solution containing solute and solvent (water):

$$\mu(x_w, p + \pi) = \mu^0(p)$$

- For diluted (ideal) solution:

$$\mu(x_w, p + \pi) = \mu^0(p + \pi) + RTln(x_w)$$

- where

$$\mu^0(p + \pi) = \mu^0(p) + \boxed{\int_p^{p+\pi} \underset{\downarrow}{V_m}(p')dp'} \rightarrow \text{Energy of expansion}$$

Molar volume (m^3/mol)

$$\Longrightarrow \quad -RTln(x_w) = \int_p^{p+\pi} V_m(p')dp'$$

Electrostatic force between plates

- For incompressible liquid (water), molar volume is constant: $V_m(p') = V_m$

$$-RTln(x_w) = \int_{p}^{p+\pi} V_m(p')dp' \Longrightarrow -RTln(x_w) = \pi V_m$$

$$\Longrightarrow \pi = -\frac{RT}{V_m}ln(x_w)$$

- Mole fraction of solute: $x = 1 - x_w \Longrightarrow \pi = -\frac{RT}{V_m}ln(1-x)$

Ion concentration (#/m³)

- For small x, ln(1-x) ≈ -x: $\pi \approx \frac{RTx}{V_m} = \frac{RT}{V_m}\frac{n}{n+n_w} \approx \frac{RT}{V_m}\frac{n}{n_w}$ for small n

Water molecule concentration (#/m³)

- Recall molar volume of solvent (water): $V_m \equiv \frac{1}{molar\ conc.} = \frac{N_A}{n_w}$

$$\Longrightarrow \pi \approx nRT$$

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- Now we simplify our analysis to a Z:Z binary electrolyte.
- At x = 0, $\pi - \pi_\infty = \left(n_+ + n_- - 2n_\infty\right)kT$

Contact value theorem: the pressure is given by the **increase** in the **counterion concentration** at the surfaces as they approach each other.

Electrostatic force between plates

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- Now we simplify our analysis to a Z:Z binary electrolyte.
- At x = 0, $\pi - \pi_\infty = (n_+ + n_- - 2n_\infty)kT$
- The values of **n^+** and **n^-** are found from the Boltzmann factor for each ion or molecule, and the **extra "2n_∞"** in the equation results since for a Z:Z electrolyte there is both a positive and negative ion in the bulk.

$$\boxed{\pi - \pi_\infty = n_\infty\left[exp\left(\frac{Ze\psi}{kT}\right) + exp\left(\frac{-Ze\psi}{kT}\right) - 2\right]kT}$$

The Boltzmann equation

- The Boltzmann distribution predicts quantitatively what fraction of the time an entity – whether it is a stone, a gas molecule, or a colloidal particle – will spend in a local position of any given volume, given the energy at that local position.
- For example, we know that gravitational potential energy is given by mgh, and assuming gravitational constant (g) is constant and the mass of the oxygen molecule (m) is identically the same, the higher value of h increases the energy, meaning higher altitude will give you less oxygen.
- In terms of concentration of ions, the Boltzmann equation says for ion type i, that

$$\boxed{\begin{aligned} c_i(x,y,z) &= c_{i\infty}\, exp\left(\frac{-E_i(x,y,z)}{kT}\right) \\ &= c_{i\infty}\, exp\left(\frac{-z_i e\psi}{kT}\right) \end{aligned}}$$

Electrostatic force between plates

- Rearrange (factoring):

$$\pi - \pi_\infty = n_\infty kT\left[exp\left(\frac{Ze\psi}{2kT}\right) - exp\left(\frac{-Ze\psi}{2kT}\right)\right]^2$$

$$\boxed{\pi - \pi_\infty = n_\infty\left[exp\left(\frac{Ze\psi}{kT}\right) + exp\left(\frac{-Ze\psi}{kT}\right) - 2\right]kT}$$

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$$\pi - \pi_\infty = n_\infty kT\left[exp\left(\frac{Ze\psi}{2kT}\right) - exp\left(\frac{-Ze\psi}{2kT}\right)\right]^2$$

- For **low** surface potentials, Taylor expand $e^w = 1 + w + w^2/2 + \ldots$

$$\pi - \pi_\infty = n_\infty kT\left[\left(1 + \frac{Ze\psi}{2kT} + \ldots\right) - \left(1 - \frac{Ze\psi}{2kT} + \ldots\right)\right]^2$$

$$\approx \frac{Z^2 e^2 n_\infty}{kT}\psi^2$$

Electrostatic force between plates

- Rearrange (factoring):

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$$\approx \frac{Z^2 e^2 n_{\infty}}{kT} \psi^2$$

- Evaluate Ψ at the **midplane** (**x = 0**) for the potential between two plates:

Debye-Huckel results for electric potential

- **final case**: the electric potential between **two charged plates** with boundary conditions

$$x = -L/2 : \psi = \psi_1 \, , \quad x = L/2 : \psi = \psi_2$$

- This gives:

$$\boxed{\begin{aligned} \psi = {} & \left(\frac{\psi_2 e^{+\kappa L/2} - \psi_1 e^{-\kappa L/2}}{e^{+\kappa L} - e^{-\kappa L}} \right) e^{\kappa x} \\ & + \left(\frac{\psi_1 e^{+\kappa L/2} - \psi_2 e^{-\kappa L/2}}{e^{+\kappa L} - e^{-\kappa L}} \right) e^{-\kappa x} \end{aligned}}$$

Electrostatic force between plates

- Rearrange (factoring):

$$\pi - \pi_{\infty} = n_{\infty} kT \left[exp\left(\frac{Ze\psi}{2kT} \right) - exp\left(\frac{-Ze\psi}{2kT} \right) \right]^2$$

- For **low** surface potentials, Taylor expand $e^{w} = 1 + w + w^2/2 + \ldots$

$$\pi - \pi_{\infty} = n_{\infty} kT \left[\left(1 + \frac{Ze\psi}{2kT} + \ldots \right) - \left(1 - \frac{Ze\psi}{2kT} + \ldots \right) \right]^2$$

$$\approx \frac{Z^2 e^2 n_{\infty}}{kT} \psi^2$$

- Evaluate Ψ at the **midplane** (**x = 0**) for the potential between two plates:

$$\boxed{\psi(x=0) = \frac{2\psi_0 \left(e^{\kappa h/2} - e^{-\kappa h/2} \right)}{e^{\kappa h} - e^{-\kappa h}} \approx 2\psi_0 e^{-\kappa h/2}}$$

Electrostatic force between plates

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

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

- 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 $\mathbf{E} = \mathbf{0}$.
- In the end the **pressure force** is the only force remaining:

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

Electrostatic force between plates

- Putting all the pieces together now gives

$$f_{es} = \pi(x=0) - \pi_\infty = \frac{4Z^2e^2n_\infty}{kT}\psi_0^2 e^{-\kappa h}$$

- Putting this expression in terms of the Debye parameter,

$$\boxed{f_{es} = 2\varepsilon\kappa^2\psi_0^2 e^{-\kappa h}}$$

The Poisson-Boltzmann (PB) equation

- Assuming a symmetric and binary Z:Z electrolyte, like NaCl (1:1) or $Ca(SO_4)$ (2:2),

$z_+ = -z_i = Z$ $c_{+\infty} = c_{-\infty} = c_\infty$ $sinh\,x = \left(e^x - e^{-x}\right)/2$

- PB becomes $\nabla^2\left(\frac{Ze\psi}{kT}\right) = \kappa^2\, sinh\frac{Ze\psi}{kT}$ where $\boxed{\kappa^2 = \frac{2Z^2e^2c_\infty}{\varepsilon kT}}$

- The very famous parameter $\boldsymbol{\kappa}^{-1}$ is called “the Debye length”. It plays a key role in determining the electrostatic potential near a surface.

Electrostatic force between plates

- Putting all the pieces together now gives

$$f_{es} = \pi(x=0) - \pi_{\infty} = \frac{4Z^2e^2n_{\infty}}{kT}\psi_0^2 e^{-\kappa h}$$

- Putting this expression in terms of the Debye parameter,

$$\boxed{f_{es} = 2\varepsilon\kappa^2\psi_0^2 e^{-\kappa h}}$$

- If we want to know the **energy between two plates**, we can integrate. Just as we know for **gravity** that the **force F = -mg = dV/dh**, we can integrate to find the gravitational **potential energy V = mgh**, the **electrostatic potential energy per area** is:

$$\boxed{V_{es} = -\int_h^{\infty} \mathbf{f}_{es} \cdot d\mathbf{h}' = \int_{\infty}^{h} f_{es}\,dh' = 2\varepsilon\kappa^2\psi_0^2 \int_h^{\infty} e^{-\kappa h'}\,dh'}$$

- This integration leads to the final expression for the **electrostatic energy per unit area** between **two plates**:

$$\boxed{V_{es} = 2\varepsilon\kappa\psi_0^2 e^{-\kappa h} = \kappa^{-1} f_{es}}$$

You need to log in using your umich.edu account in order to access this poll

Lecture 9 Poll: electrostatic interaction between plates

Two plates have surface potentials of -24 mV in a solution with a Debye length of 4.2 nm. The **plates** are **separated** by **15.3 nm**. What is the **electrostatic potential energy per area** and the **electrostatic force per area** on the plates, for T = 293 K?

- A. $V_{es} = -5.1 \times 10^{-12}$ J/m^2, $f_{es} = 0.0122$ N/m^2
- B. $V_{es} = +5.1 \times 10^{-12}$ J/m^2, $f_{es} = 0.0122$ N/m^2
- C. $V_{es} = -5.1 \times 10^{-6}$ J/m^2, $f_{es} = 1220$ N/m^2
- D. $V_{es} = +5.1 \times 10^{-6}$ J/m^2, $f_{es} = 1220$ N/m^2

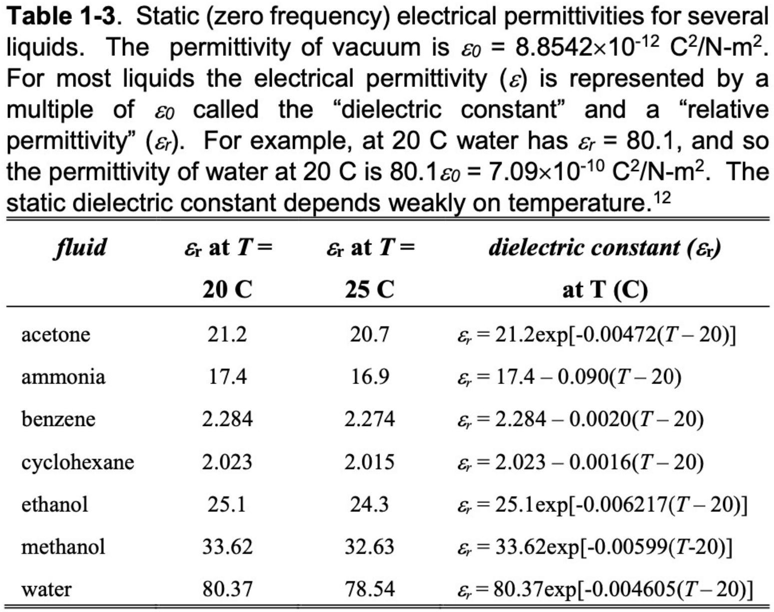

Table 1-3. Static (zero frequency) electrical permittivities for several liquids. The permittivity of vacuum is $\varepsilon_0 = 8.8542\times10^{-12}$ C^2/N-m^2. For most liquids the electrical permittivity (ε) is represented by a multiple of ε_0 called the "dielectric constant" and a "relative permittivity" (ε_r). For example, at 20 C water has $\varepsilon_r = 80.1$, and so the permittivity of water at 20 C is $80.1\varepsilon_0 = 7.09\times10^{-10}$ C^2/N-m^2. The static dielectric constant depends weakly on temperature.[12]

fluid	ε_r at $T =$ 20 C	ε_r at $T =$ 25 C	*dielectric constant* (ε_r) at T (C)
acetone	21.2	20.7	$\varepsilon_r = 21.2\exp[-0.00472(T-20)]$
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ethanol	25.1	24.3	$\varepsilon_r = 25.1\exp[-0.006217(T-20)]$
methanol	33.62	32.63	$\varepsilon_r = 33.62\exp[-0.00599(T\text{-}20)]$
water	80.37	78.54	$\varepsilon_r = 80.37\exp[-0.004605(T-20)]$

$$\boxed{f_{es} = 2\varepsilon\kappa^2\psi_0^2 e^{-\kappa h}}$$

$$\boxed{V_{es} = 2\varepsilon\kappa\psi_0^2 e^{-\kappa h} = \kappa^{-1} f_{es}}$$

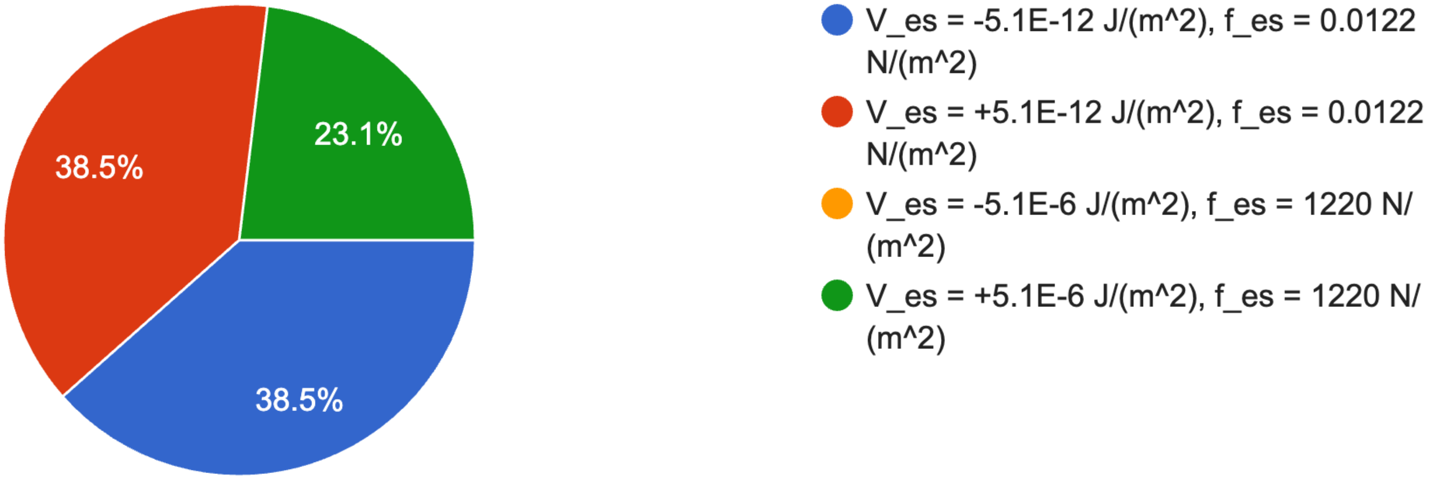
$$\boxed{\kappa^2 = \frac{2Z^2e^2c_\infty}{\varepsilon kT}}$$

Long URL https://forms.gle/uSKR2NJUaE8kY1h48

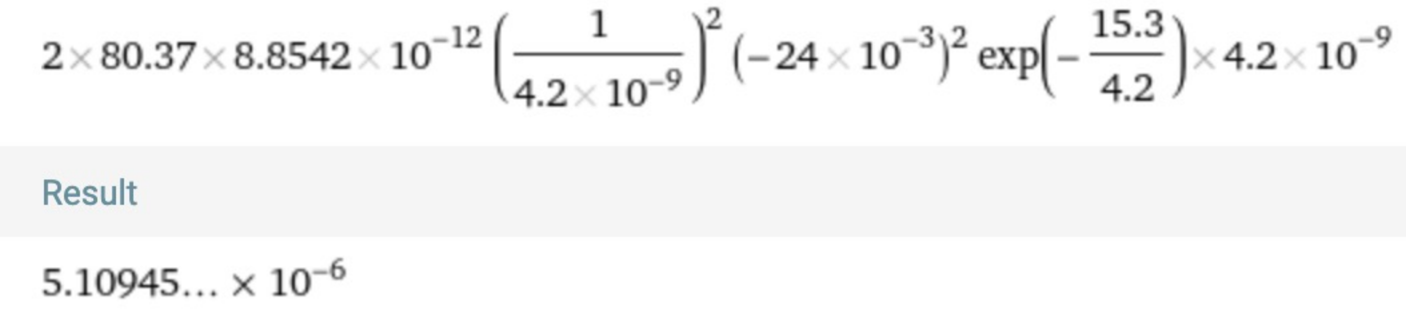
Short URL https://shorturl.at/aLQT8

Two plates have surface potentials of -24 mV in a solution with a Debye length of 4.2 nm. The plates are separated by 15.3 nm. What is the electrostatic ...static force per area on the plates, for T = 293 K?

13 responses



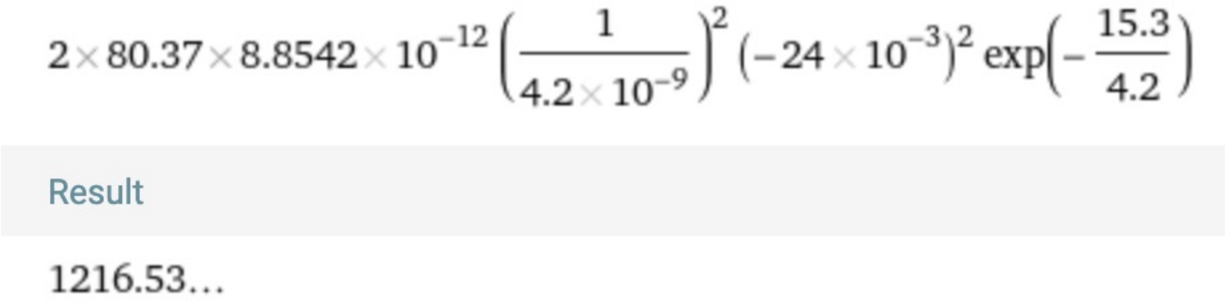
answer: $V_{es} = +5.1\times10^{-6}\ J/m^2$, $f_{es} = 1220\ N/m^2 = 0.177\ psi$.



$$2\times80.37\times8.8542\times10^{-12}\left(\frac{1}{4.2\times10^{-9}}\right)^2(-24\times10^{-3})^2\exp\left(-\frac{15.3}{4.2}\right)\times4.2\times10^{-9}$$

Result

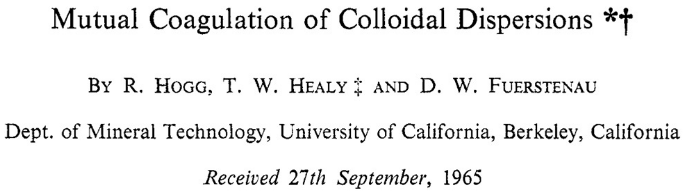
$5.10945\ldots\times10^{-6}$



$$2\times80.37\times8.8542\times10^{-12}\left(\frac{1}{4.2\times10^{-9}}\right)^2(-24\times10^{-3})^2\exp\left(-\frac{15.3}{4.2}\right)$$

Result

$1216.53\ldots$



Mutual Coagulation of Colloidal Dispersions *†

By R. Hogg, T. W. Healy ‡ and D. W. Fuerstenau

Dept. of Mineral Technology, University of California, Berkeley, California

Received 27th September, 1965

https://pubs.rsc.org/en/content/articlelanding/1966/tf/tf9666201638

Electrostatic force between plates

- Hogg, Healy, and Fuerstenau (HHF) developed a more exact result between **flat plates**, for arbitrary but small surface potentials, and for any gap between the plates. Their result is

$$\boxed{V_{es} = \tfrac{1}{2}\varepsilon\kappa\left[\frac{2\psi_1\psi_2}{\sinh\kappa h} + \left(\psi_1^2 + \psi_2^2\right)\left(1 - \frac{\cosh\kappa h}{\sinh\kappa h}\right)\right]}$$

- The **first term** in the brackets gives the interaction that is reducible to our results before. The **second term** includes additional physics resulting from an “**image charge**”, in which one charged surface actually induces a charge in the other material. For plates separated by a few Debye lengths, the **first term** decays roughly as exp(-**κ**h), while the **second term** decays more quickly as exp(-2**κ**h).

Spheres and the **Derjaguin approximation**

- Having the **electrostatic interaction energy** between **two flat plates** enables us to proceed to the interaction between **two spheres** (Φ_{es}, in Joules). "**Derjaguin approximation**" estimates

$$\Phi_{es} = V_{es}(h_0 = \delta)\pi r_0^2 + V_{es}(h_1)2\pi r_1 \Delta r + V_{es}(h_2)2\pi r_2 \Delta r + V_{es}(h_3)2\pi r_3 \Delta r + \dots$$

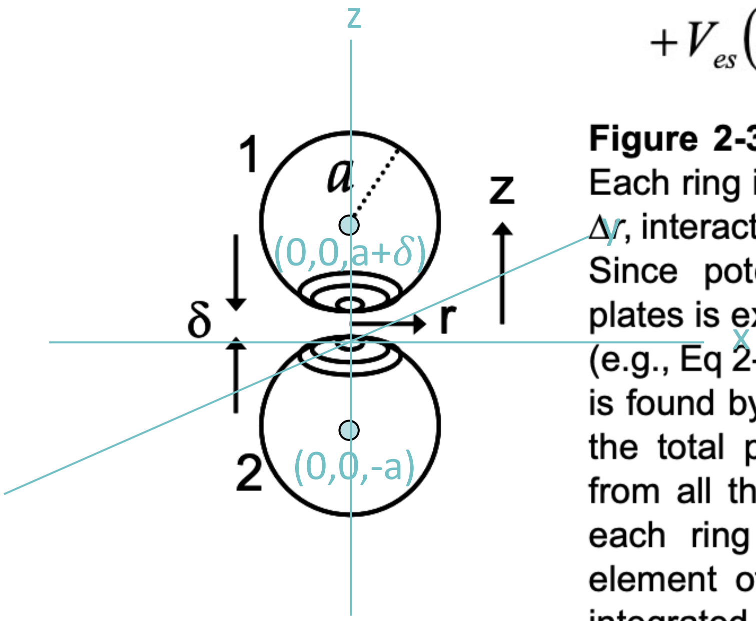
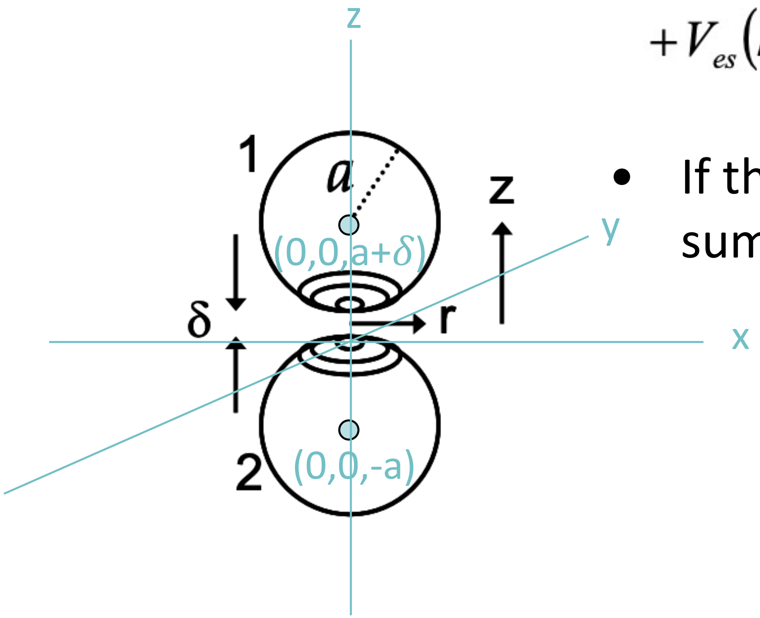


Figure 2-3. Derjaguin approximation. Each ring is treated as flat with a width Δr, interacting with "flat ring" opposite it. Since potential energy between flat plates is expressed as energy per area (e.g., Eq 2-41), the energy for each ring is found by multiplying by its area, and the total potential energy is summed from all the rings. In fact the size of each ring is taken as a differential element of area so that the result is integrated.

Spheres and the **Derjaguin approximation**

- Having the electrostatic interaction energy between **two flat plates** enables us to proceed to the interaction between **two spheres** (**Φ_{es}**, in Joules). "**Derjaguin approximation**" estimates

$$\Phi_{es} = V_{es}(h_0 = \delta)\pi r_0^2 + V_{es}(h_1)2\pi r_1 \Delta r$$
$$+ V_{es}(h_2)2\pi r_2 \Delta r + V_{es}(h_3)2\pi r_3 \Delta r + \ldots$$

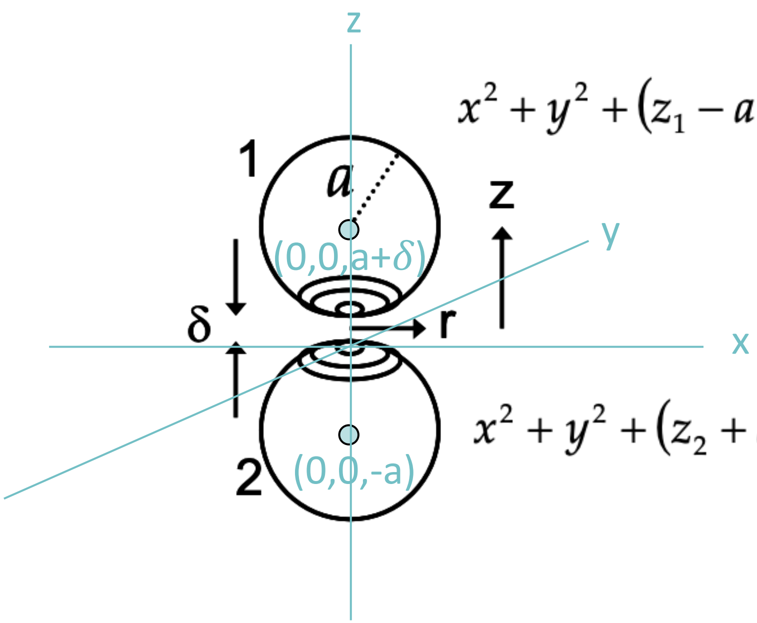


- If the rings are chosen as differential in size, the summation can be converted into an integral as

$$\boxed{\Phi_{es} \approx \int_0^A V_{es}[h(r)]2\pi r dr}$$

Spheres and the **Derjaguin approximation**

- Ordinarily this integral might be challenging analytically, but there is a helpful simplification that arises when the bottom of the **spheres** are approximated as **parabolas**.
- Normally the equations for the upper (1) and lower (2) spheres are



$$x^2 + y^2 + (z_1 - a - \delta)^2 = a^2$$

$$x^2 + y^2 + (z_2 + a)^2 = a^2$$

Spheres and the **Derjaguin approximation**

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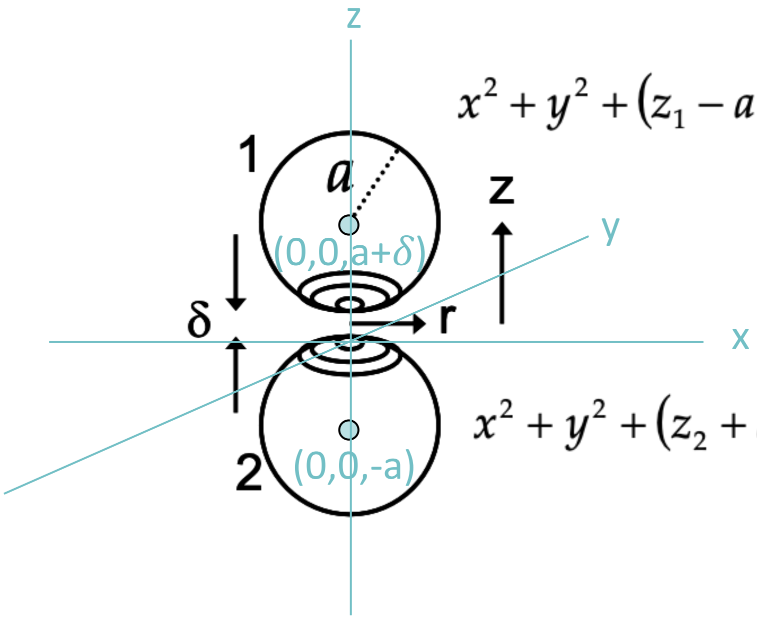


$$x^2 + y^2 + (z_1 - a - \delta)^2 = a^2$$

$$x^2 + y^2 + (z_2 + a)^2 = a^2$$

- Let $r^2 = x^2 + y^2$
- The gap is $h = z_1 - z_2$
- an expansion gives

$$\begin{aligned} z_1 &= a + \delta - \sqrt{a^2 - r^2} \\ &= a + \delta - a\sqrt{1 - r^2/a^2} \\ &\approx a + \delta - a\left(1 - r^2/2a^2\right) \end{aligned}$$

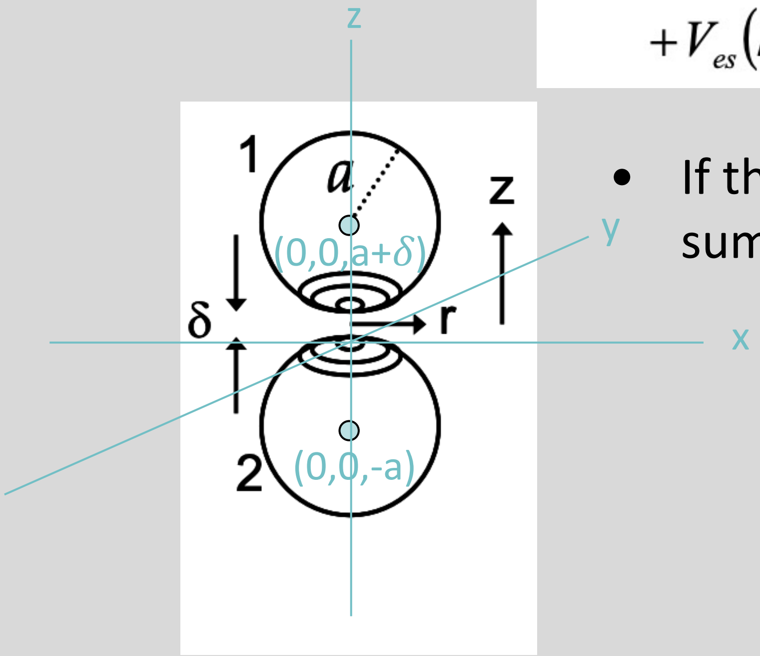
$$\Rightarrow \quad z_1 \approx \delta + r^2/2a \qquad z_2 \approx -r^2/2a$$

$$\Rightarrow \quad h = z_1 - z_2 \approx \delta + r^2/a$$

Spheres and the **Derjaguin approximation**

- Having the electrostatic interaction energy between **two flat plates** enables us to proceed to the interaction between **two spheres** (**Φ_{es}**, in Joules). "**Derjaguin approximation**" estimates

$$\begin{aligned}\Phi_{es} &= V_{es}(h_0=\delta)\pi r_0^2 + V_{es}(h_1)2\pi r_1\Delta r \\ &\quad + V_{es}(h_2)2\pi r_2\Delta r + V_{es}(h_3)2\pi r_3\Delta r + \ldots\end{aligned}$$



- If the rings are chosen as differential in size, the summation can be converted into an integral as

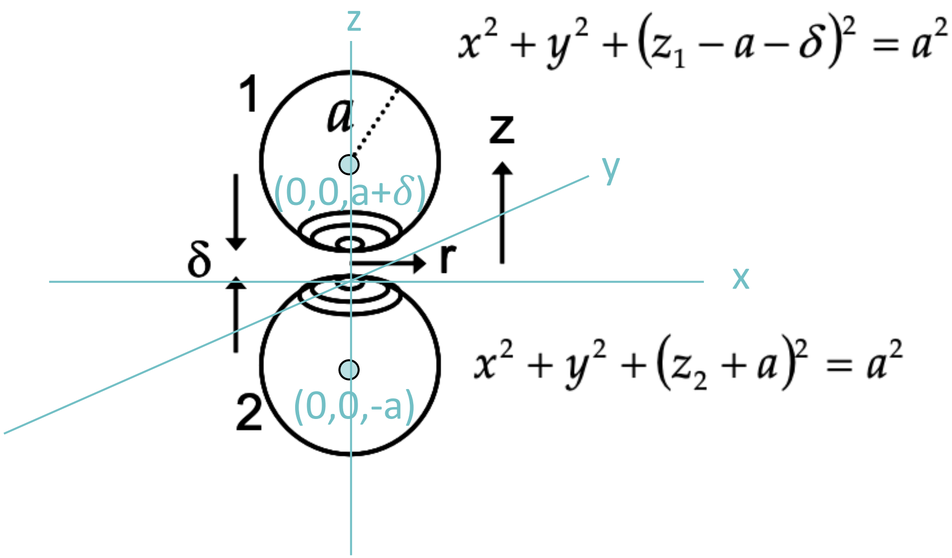
$$\boxed{\Phi_{es} \approx \int_0^A V_{es}[h(r)]2\pi r dr}$$

Spheres and the Derjaguin approximation

- Exchange the variable of integration from r to h: $dh = 2rdr / a$

$$\Phi_{es} \approx \int_0^A V_{es}[h(r)]2\pi r dr \Longrightarrow \boxed{\Phi_{es} \approx \pi a \int_\delta^\infty V_{es}(h)dh}$$

- The upper limit is written as h → ∞, because its exact value need not be specified, since the integrand decays rapidly with h.

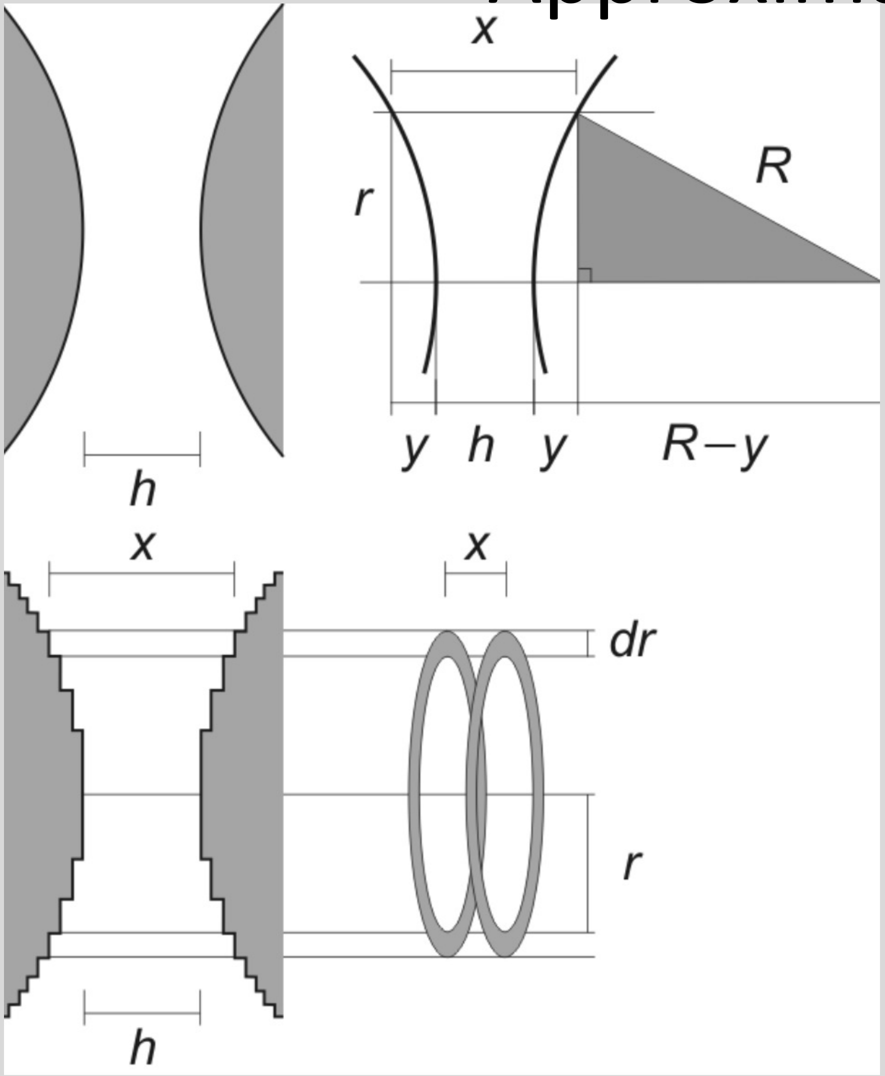


$$x^2 + y^2 + (z_1 - a - \delta)^2 = a^2$$

$$x^2 + y^2 + (z_2 + a)^2 = a^2$$

- We have not yet specified anything particular to **electrostatic forces**. We will use this expression for other energies such as **van der Waals energies**, since in fact the expression is quite general.

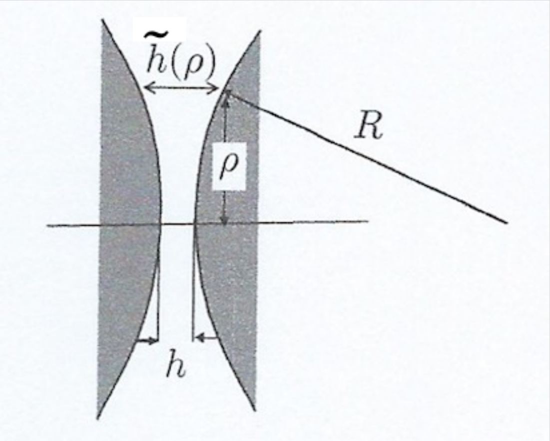
Curved surfaces & Thin Gaps: Derjaguin Approximation



Treat a thin region of variable gap as a series of small regions with parallel flat surfaces, with each region having a different gap

https://en.wikipedia.org/wiki/Derjaguin_approximation

Derjaguin Approximation for Two Spheres



$$\tilde{h}(\rho) = h + 2\left(R - \sqrt{R^2 - \rho^2}\right) \approx h + \frac{\rho^2}{R}$$

$$\sqrt{R^2 - \rho^2} = \mathrm{R}\sqrt{1 - \rho^2/R^2} \approx \mathrm{R}(1 + \rho^2/2R^2)$$

At position ρ, take a ring of width *dρ*, with area *2πρdρ*

If we have a potential *per unit area w(h)* between flat surfaces, then the potential *U(h)* between spheres is

$$U(h) = \int_0^R w(\tilde{h}) 2\pi\rho d\rho$$

new variable: $x \equiv h + \frac{\rho^2}{R} = \tilde{h}$

$$dx = 2\rho d\rho/R$$

$$U(h) \approx \pi R \int_h^\infty w(x) dx$$

$$F(h) = -\frac{\partial U(h)}{\partial h} = \pi R w(h)$$

Note: if spheres have unequal radii:

$$U(h) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \int_h^\infty w(x) dx$$

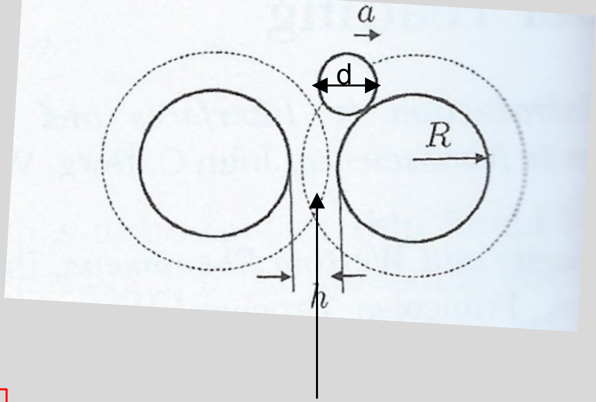
Depletion Potential for spheres

$v = concentration\ of\ depletant$

for flat plate: $w(h) = vk_BT(h-d), \text{for } h < d,$

$= 0, \ \ \text{for } h \ > d$

Doi, Soft Matter Physics, 2013



overlapping depletion region

for spheres, replace h with $\tilde{h}(x)$

$$w(h) = vk_BT\left(\tilde{h}(x) - d\right), \text{for } \tilde{h}(x) < d,$$

$$= 0, \ \ \text{for } \tilde{h}(x) \ > d$$

for two spheres: $\boxed{U(h) = \pi R\int_h^\infty w(\,x)dx}$

remember, $x \equiv h + \frac{\rho^2}{R} = \tilde{h}$

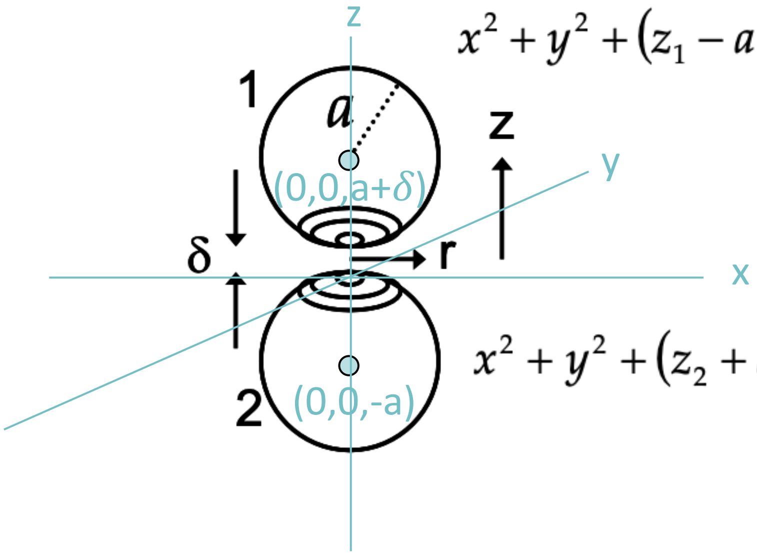
$$U(h) = vk_BT\underbrace{\pi R\int_h^d (x-d)\,dx}_{\text{volume of overlapping depletion regions}} \qquad = -\frac{1}{2}vk_BT\pi R(d-h)^2$$

Spheres and the **Derjaguin approximation**

- Exchange the variable of integration from r to h: $dh = 2rdr / a$

$$\Phi_{es} \approx \int_0^A V_{es}[h(r)]2\pi r dr \Longrightarrow \boxed{\Phi_{es} \approx \pi a \int_\delta^\infty V_{es}(h)dh}$$

- The upper limit is written as h → ∞, because its exact value need not be specified, since the integrand decays rapidly with h.



$$x^2 + y^2 + (z_1 - a - \delta)^2 = a^2$$

$$x^2 + y^2 + (z_2 + a)^2 = a^2$$

- Using the expression for **V_{es}**, integration gives the **electrostatic energy between two spheres**:

$$\boxed{\Phi_{es} = 2\pi\varepsilon a \psi_0^2 e^{-\kappa\delta}}$$

- This result is the one we have been after for the entire lecture.

From Lecture 4:

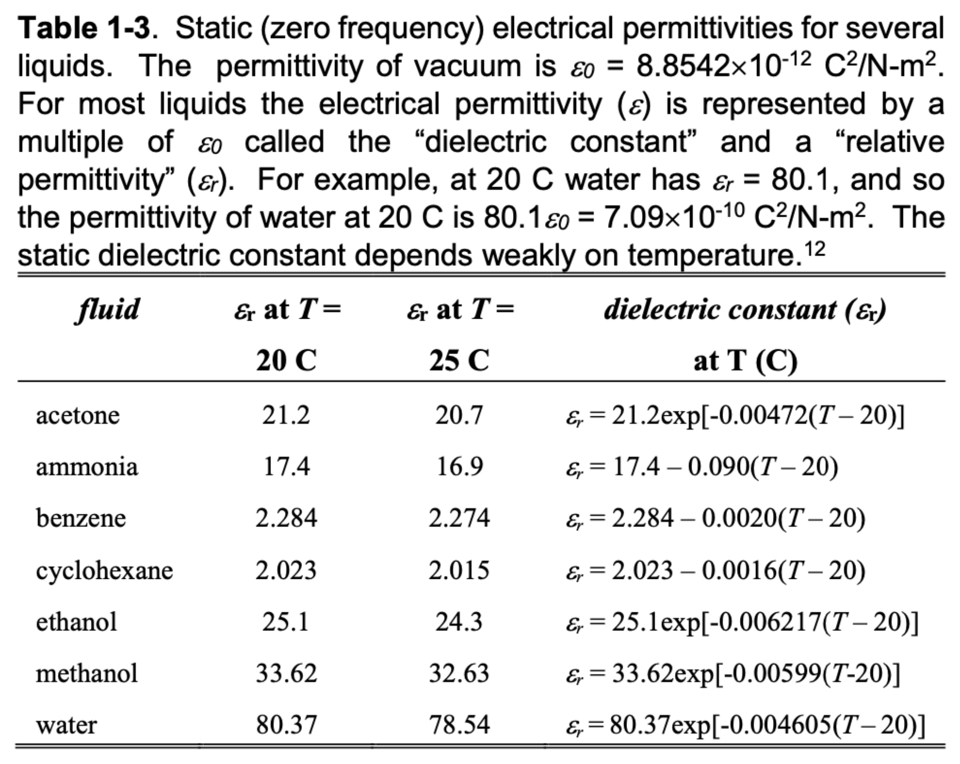
Electrostatic forces

- Between two particles of radius (*a*), the **electrostatic energy (Φ_{ES})** resulting from the electrical potentials on a particle separated by a distance of closest approach (δ) is approximated by

$$\boxed{\Phi_{ES} = 2\pi\varepsilon a\psi_0^2 e^{-\kappa\delta}}$$

Electrical permittivity

Fluids with higher dielectric constants give **larger electrostatic interactions energies**, not only since ε appears in equation above, but also since **particles tend to become more highly charged** – and therefore have a larger magnitude of surface potential – in these fluids.



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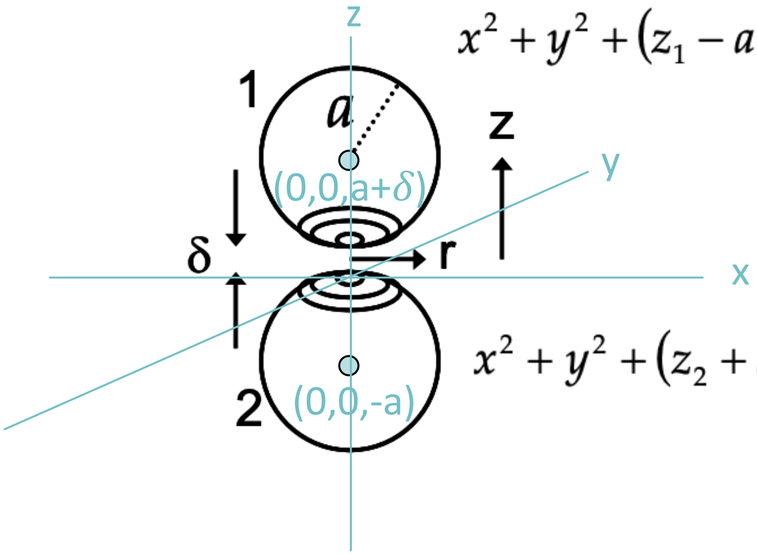


$$x^2 + y^2 + (z_1 - a - \delta)^2 = a^2$$

$$x^2 + y^2 + (z_2 + a)^2 = a^2$$

- Using the expression for **V_{es}**, integration gives the **electrostatic energy between two spheres**:

$$\boxed{\Phi_{es} = 2\pi\varepsilon a \psi_0^2 e^{-\kappa\delta}}$$

- The corresponding **electrostatic force** is:

$$\boxed{F_{es} = 2\pi\varepsilon a \kappa \psi_0^2 e^{-\kappa h} = \kappa \Phi_{es}}$$

Electrostatic force between plates

- Putting all the pieces together now gives

$$f_{es} = \pi(x=0) - \pi_{\infty} = \frac{4Z^2e^2n_{\infty}}{kT}\psi_0^2 e^{-\kappa h}$$

- Putting this expression in terms of the Debye parameter,

$$\boxed{f_{es} = 2\varepsilon\kappa^2\psi_0^2 e^{-\kappa h}}$$

- If we want to know the energy between two plates, we can integrate. Just as we know for gravity that the force F = -mg = dV/dh, we can integrate to find the gravitational potential energy V = mgh, the electrostatic potential energy per area is:

$$\boxed{V_{es} = -\int_h^{\infty} \mathbf{f}_{es} \cdot d\mathbf{h}' = \int_{\infty}^{h} f_{es}\,dh'} = 2\varepsilon\kappa^2\psi_0^2 \int_h^{\infty} e^{-\kappa h'}\,dh'$$

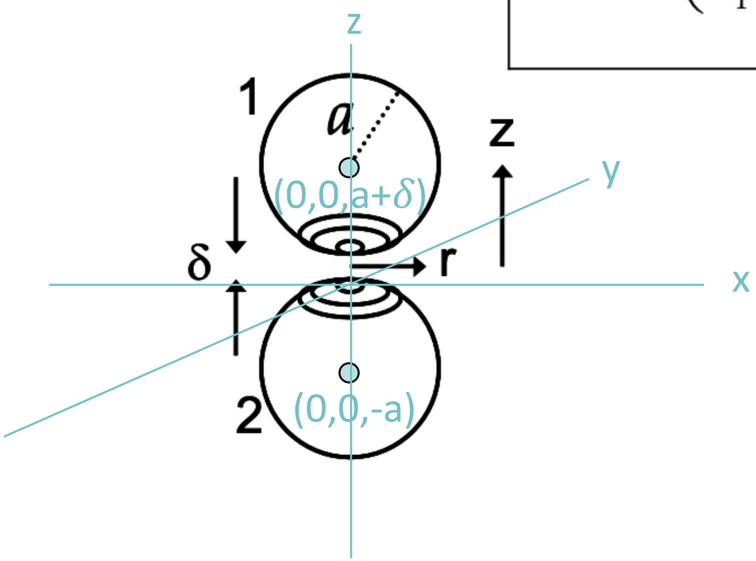
- This integration leads to the final expression for the electrostatic energy per unit area between two plates:

$$\boxed{V_{es} = 2\varepsilon\kappa\psi_0^2 e^{-\kappa h} = \kappa^{-1} f_{es}}$$

Spheres and the **Derjaguin approximation**

- If a more precise result is need, but still for **small** surface potentials with magnitude less than about 50 mV, we can use the HHF result for spheres:

$$\boxed{\Phi_{es} = \pi\varepsilon\left(\frac{a_1 a_2}{a_1 + a_2}\right)\left[2\psi_1\psi_2 \ln\left(\frac{1+e^{-\kappa\delta}}{1-e^{-\kappa\delta}}\right) + \left(\psi_1^2 + \psi_2^2\right)\ln\left(1-e^{-2\kappa\delta}\right)\right]}$$



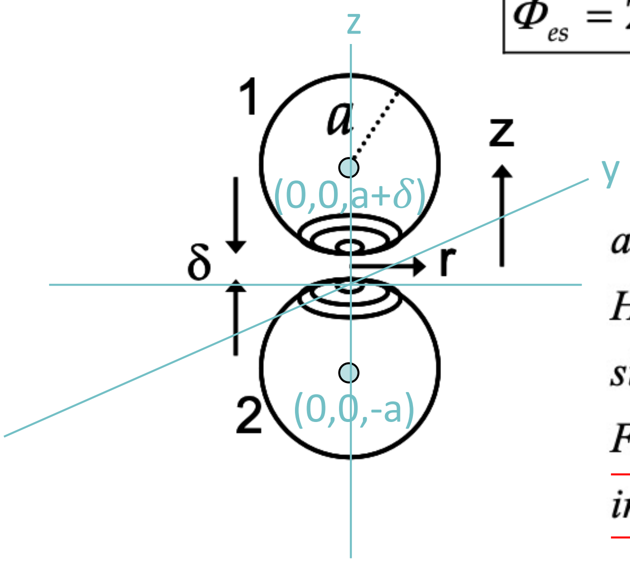
the **HHF force** can be found from differentiating Φ_{es}

Example: Electrostatic potential energy between **spheres**

Two 1.2 µm diameter spheres have surface potentials of -24 mV in a solution with a Debye length of 4.2 nm. The spheres are **separated** by **15.3 nm**. What is the **potential energy** between the spheres, for T = 293 K?

$$\boxed{\Phi_{es} = 2\pi\varepsilon a\psi_0^2 e^{-\kappa\delta}}$$

$$\boxed{\Phi_{es} = \pi\varepsilon\left(\frac{a_1 a_2}{a_1 + a_2}\right)\left[2\psi_1\psi_2 \ln\left(\frac{1+e^{-\kappa\delta}}{1-e^{-\kappa\delta}}\right) + \left(\psi_1^2 + \psi_2^2\right)\ln\left(1-e^{-2\kappa\delta}\right)\right]}$$

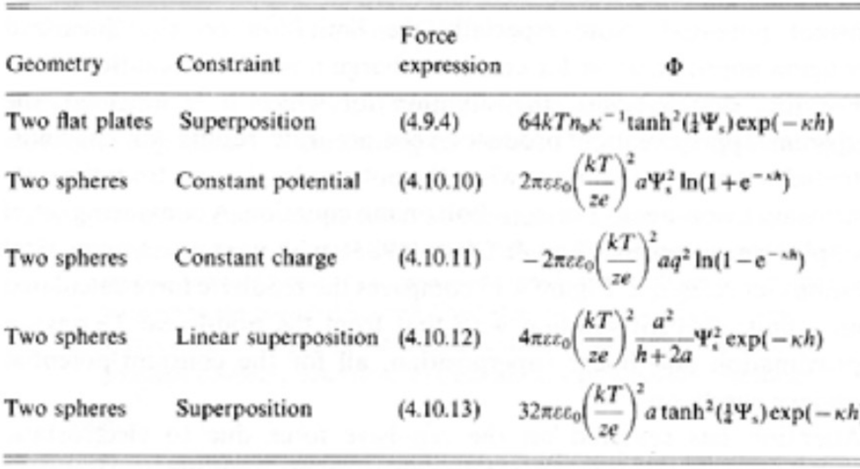


answer: $\Phi_{es} = 4.04\times10^{-20}$ J = 10.0 kT for the simple expression. The HHF gives $\Phi_{es} = 3.99\times10^{-20}$ J = 9.87 kT, quite close (1.3% difference), since the gap is large relative to κ^{-1} while still being small relative to a. For gaps with $\kappa\delta$ less than 2, the HHF result for spheres will give important differences, due to the image charge term.

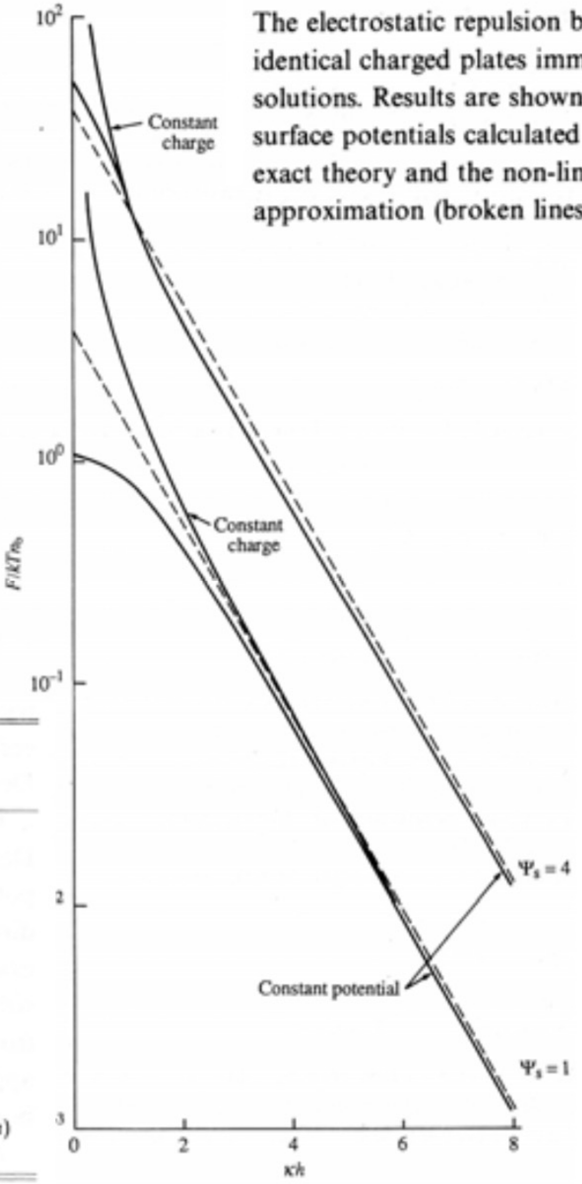
Real (hard) life: Surface charge may change during the approach

Constant charge > constant potential

A large variety of electrostatics interaction formulae are available – but pay attention to approximations and range of validity



Geometry	Constraint	Force expression	Φ
Two flat plates	Superposition	(4.9.4)	$64kTn_0\kappa^{-1}\tanh^2(\frac{1}{4}\Psi_s)\exp(-\kappa h)$
Two spheres	Constant potential	(4.10.10)	$2\pi\varepsilon\varepsilon_0\left(\frac{kT}{ze}\right)^2 a\Psi_s^2 \ln(1+e^{-\kappa h})$
Two spheres	Constant charge	(4.10.11)	$-2\pi\varepsilon\varepsilon_0\left(\frac{kT}{ze}\right)^2 aq^2 \ln(1-e^{-\kappa h})$
Two spheres	Linear superposition	(4.10.12)	$4\pi\varepsilon\varepsilon_0\left(\frac{kT}{ze}\right)^2 \frac{a^2}{h+2a}\Psi_s^2 \exp(-\kappa h)$
Two spheres	Superposition	(4.10.13)	$32\pi\varepsilon\varepsilon_0\left(\frac{kT}{ze}\right)^2 a\tanh^2(\frac{1}{4}\Psi_s)\exp(-\kappa h)$



The electrostatic repulsion between two identical charged plates immersed in ionic solutions. Results are shown for two differer surface potentials calculated according to th exact theory and the non-linear superpositic approximation (broken lines).

Constant charge vs. constant potential

- For **large distances** (several Debye lengths) between the interacting particles, there's no difference.
- For **small distances**, the first particle affects the electrostatic potential at the surface of the second, causing **change of the adsorption of all ionic species there**.
- Constant charge means that the adsorbed charge does not change. This corresponds to the highest possible interaction (**highest repulsion**, in case of two equivalent surfaces).
- In reality, when two positively charged particles are close to each other, the repulsion leads to the positive **ions being desorbed** (or similarly, negative ions being adsorbed). This leads to **smaller interaction**.
- The largest decrease one can get is the one between metal particles of fixed potential (two grounded spheres). Theory says you cannot get a larger drop of the surface charge then this fixed surface potential case.
- The **reality** is always **between** these **two limiting cases**.

Surface charge density using **Debye-Huckel**

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

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

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

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

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

$$\boxed{\rho_s = \varepsilon\psi_0\kappa}$$

- Solving for Ψ_0:

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

- 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.

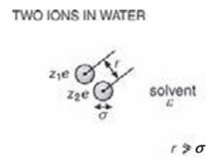
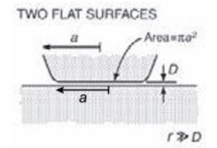
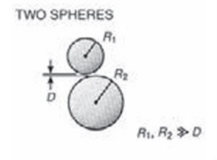
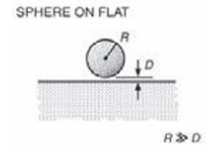
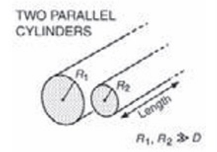
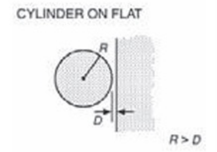
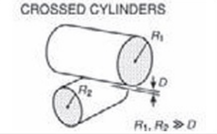
Geometry of bodies with surfaces *D* apart (*D*«*R*)		Electric 'Double-layer' Interaction	
		Energy, *W*	**Force, *F*= −*dW*/*dD***
Two ions or small charged molecules		$\dfrac{+z_1z_2e^2}{4\pi\varepsilon_0\varepsilon r}\dfrac{e^{-\kappa(r-\sigma)}}{(1+\kappa\sigma)}$	$\dfrac{+z_1z_2e^2}{4\pi\varepsilon_0\varepsilon r^2}\dfrac{(1+\kappa r)}{(1+\kappa\sigma)}e^{-\kappa(r-\sigma)}$
Two flat surfaces (per unit area)		$W_{\text{Flat}} = (\kappa / 2\pi)Ze^{-\kappa D}$	$(\kappa^2 / 2\pi)Ze^{-\kappa D}$
Two spheres or macromolecules of radii R_1 and R_2		$\left(\dfrac{R_1R_2}{R_1+R_2}\right)Ze^{-\kappa D}$	$\kappa\left(\dfrac{R_1R_2}{R_1+R_2}\right)Ze^{-\kappa D}$ Also $F = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)W_{\text{Flat}}$
Sphere or macro-molecule of radius *R* near a flat surface		$RZe^{-\kappa D}$	$\kappa RZe^{-\kappa D}$ Also $F = 2\pi RW_{\text{Flat}}$
Two parallel cylinders or rods of radii R_1 and R_2 (per unit length)		$\dfrac{\kappa^{1/2}}{\sqrt{2\pi}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}Ze^{-\kappa D}$	$\dfrac{\kappa^{3/2}}{\sqrt{2\pi}}\left(\dfrac{R_1R_2}{R_1+R_2}\right)^{1/2}Ze^{-\kappa D}$
Cylinder of radius *R* near a flat surface (per unit length)		$\kappa^{1/2}\sqrt{\dfrac{R}{2\pi}}\;Ze^{-\kappa D}$	$\kappa^{3/2}\sqrt{\dfrac{R}{2\pi}}\;Ze^{-\kappa D}$
Two cylinders or filaments of radii R_1 and R_2 crossed at 90°		$\sqrt{R_1R_2}Ze^{-\kappa D}$	$\kappa\sqrt{R_1R_2}\,Ze^{-\kappa D}$ Also $F = 2\pi\sqrt{R_1R_2}\,W_{\text{Flat}}$

FIGURE 14.10 Electrostatic double-layer interaction energies *W*(*D*) and forces ($F = -\mathrm{d}W/\mathrm{d}D$) between similar constant potential surfaces of different geometries in terms of the interaction constant *Z* defined by Eq. (14.52). For a monovalent 1:1 electrolyte such as NaCl ($z = 1$), $Z = 64\pi\varepsilon_0\varepsilon(kT/e)^2\tanh^2(e\psi_0/4kT) = (9.22\times10^{-11}\tanh^2(\psi_0/103)\ \mathrm{J\,m^{-1}}$ at 25°C and $(9.38\times10^{-11})\tanh^2(\psi_0/107)\ \mathrm{J\,m^{-1}}$ at 37°C (body temperature). The Debye length, κ^{-1}, is defined by Eq. (14.36).

Interaction constant

$$Z = 64\,\pi\,\varepsilon_0\,\varepsilon\left(\frac{kT}{e}\right)^2\gamma^2$$

$$\downarrow \ at\ 25^oC$$

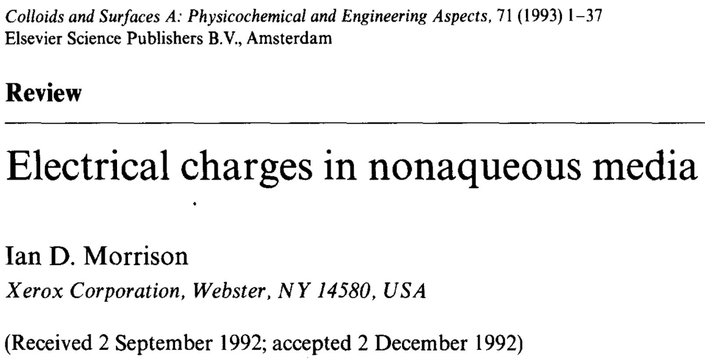
$$= 9.22\times10^{-11}\tanh^2\left(\frac{\psi_0}{103}\right)\quad [J\,m^{-1}]$$

where $\gamma = \tanh(z\,e\,\psi_0/4\,kT)$

also

$$\kappa = 3.288\sqrt{I}\quad [nm^{-1}]$$

https://www.sciencedirect.com/science/article/pii/092777579380026B



Colloids and Surfaces A: Physicochemical and Engineering Aspects, 71 (1993) 1–37
Elsevier Science Publishers B.V., Amsterdam

Review

Electrical charges in nonaqueous media

Ian D. Morrison
Xerox Corporation, Webster, NY 14580, USA

(Received 2 September 1992; accepted 2 December 1992)

Dielectric media (organic fluids)

- Electrostatic interactions in **dielectric media** like organic fluids can be much different from that in aqueous fluids. There are several reasons for this:
- **(1) Obtaining any charges in dielectric media is hard to do.** An important parameter arises from comparing the **electrostatic energy** (V_{es}) of two ions in solution (Coulomb's law, $V_{es} = (z_1 e)(z_2 e)/(4\pi\varepsilon r)$, for a separation (r) between the ions) with the thermal energy (kT) which tends to randomize ion positions throughout the solution.
- If we equate these energies, we find for a **symmetric Z:Z electrolyte** a distance (λ_B), known as the Bjerrum length, given by

$$\boxed{\lambda_B = \frac{Z^2 e^2}{4\pi\varepsilon kT}}$$

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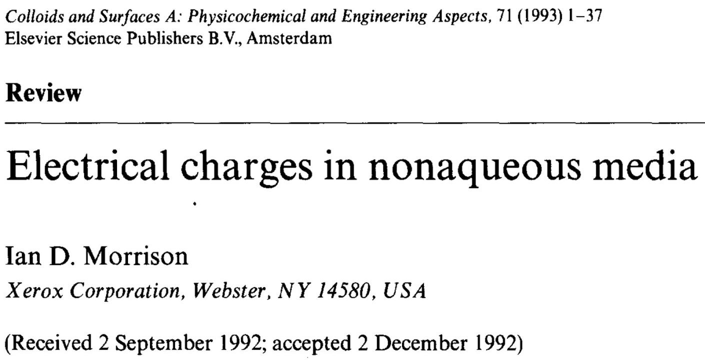
Dielectric media (organic fluids)



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- In water at room temperature, λ_B = **0.70 nm**. Thus, if I have NaCl dissociated into Na^+ and Cl^-, the **ions have to be really close** – in fact closer than water solvation allows – **in order for them to form NaCl** again (that’s why NaCl dissolves easily in water).
- In contrast, in hexane with a relative permittivity of 2.0, λ_B = **28 nm**. Thus, **the ions can be spaced far apart and still attract each other back into NaCl**.
- Interestingly, if we assume that we have one ion pair in a volume $1/\lambda_B^3$, then we can estimate a **saturation concentration**, which **scales as $1/Z^6$**. In water we find a saturation concentration for Z = 1 of 4.8 M. The actual saturation concentration of NaCl is 5.4 M, and for KCl it is 4.2 M. When λ_B = 28 nm, the saturation concentration for Z = 1 is 0.075 mM, and actual concentrations in dielectric media are usually much lower.

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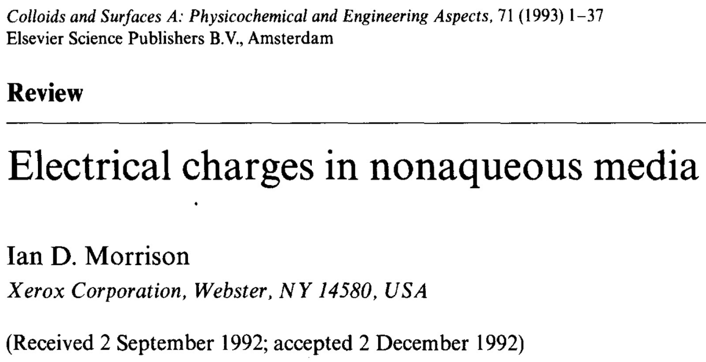
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Dielectric media (organic fluids)

- (2) The Debye length in the fluid can be micrometers, which is frequently **larger than the particles of interest**. Thus, <u>colloidal particles can look like point charges electrostatically</u>.
- (3) The **time required for electrostatic operations can be much longer than usual**. The free charge relaxation time (**t_{fcr}**) is given by

$$\boxed{t_{fcr} = \frac{\varepsilon}{\sigma}}$$

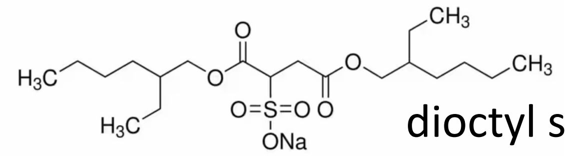
ε → permittivity
σ → conductivity

- In 10 mM aqueous KCl near room temperature, the permittivity

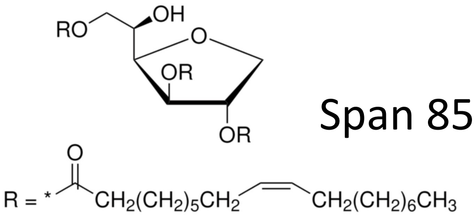
$$\varepsilon \approx 80\varepsilon_0 = 7.1\times10^{-10}\ \mathrm{C^2/N\text{-}m^2}$$

while the electrical conductivity is $\sigma \approx 1400\ \mu\mathrm{S/cm}$, giving **$t_{fcr}$** = 5 ns.

- In organic media, $\varepsilon \approx 2\varepsilon_0 = 0.177\times10^{-10}\ \mathrm{C^2/N\text{-}m^2}$ but $\sigma \sim 1\,\mathrm{pS/cm}$ or often much less giving **t_{fcr}** ~ 1 s or much more.
- Thus, dielectric media respond to electric fields **slowly**.



dioctyl sodium sulfosuccinate

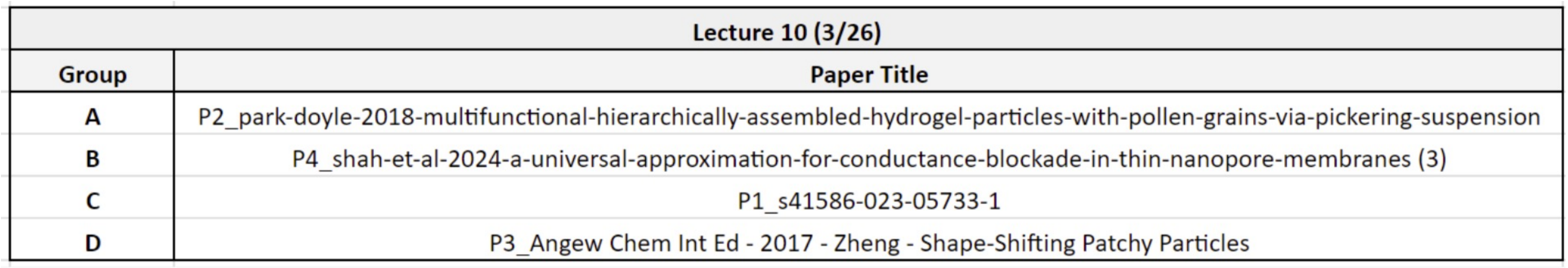


Span 85

Dielectric media (organic fluids)

- **(4)** Most fixed charges on particles in aqueous suspensions are **firmly bound**; in organic media, the charges can **detach more readily** from the particle surface, meaning that the **“fixed charge” is not always stable**.
- In fact, **to stabilize particles, one usually must add particular surfactants that produce charge in dielectric media**. Perhaps the best known of these is Aerosol OT (AOT, with a technical name dioctyl sodium sulfosuccinate, giving a conductivity ~20 nS/cm), although there are others such as OLOA by Chevron or the nonionic Span 85 from Sigma Aldrich that can give conductivities more than 10 times higher. These surfactants can provide enough charge to stabilize many suspensions of particles in dielectric media. Note that all of these conductivities are still low.

Journal club assignments for L10



Lecture 10 (3/26)	
Group	**Paper Title**
A	P2_park-doyle-2018-multifunctional-hierarchically-assembled-hydrogel-particles-with-pollen-grains-via-pickering-suspension
B	P4_shah-et-al-2024-a-universal-approximation-for-conductance-blockade-in-thin-nanopore-membranes (3)
C	P1_s41586-023-05733-1
D	P3_Angew Chem Int Ed - 2017 - Zheng - Shape-Shifting Patchy Particles