Excluded Volume Interactions (continued) + Electrostatic Force

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

Announcements

- Syllabus change
  - Invention disclosure assignment (15%) – removed
  - 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%

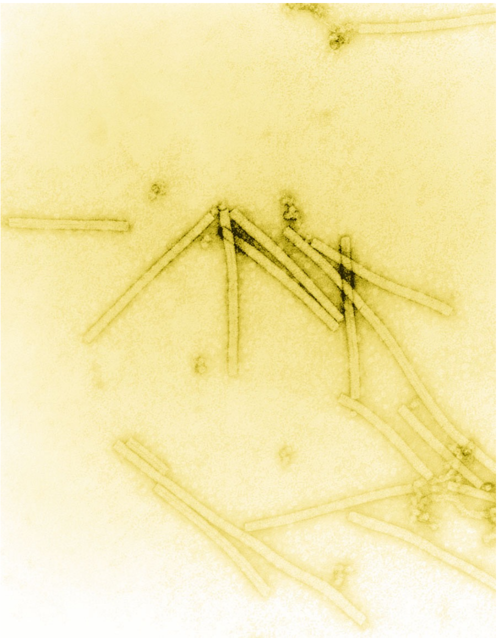
- Mid-term + final course reviews for the course (5%) bonus to final grade – please make sure to do it to not miss out – due Wednesday March 6 (tomorrow).

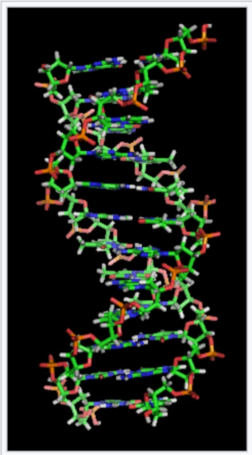
Announcements

- As a reminder, things that go into your participation grade (now 30%):
    - Attendance
    - Polls
    - Perusall
    - Peer presentation evaluations
    - Asking questions following presentations

Rigid Nonspherical Particles: The Nematic Phase

- For molecules that are not spherical, packing and ordering transitions can occur that are more complex than those for spherical molecules.
- the simplest nonspherical shape is a stiff, long cylinder





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

Transmission electron micrograph of TMV particles negative stained to enhance visibility at 160,000× magnification

Rod-Like Objects

tobacco mosaic virus

L= 300 nm long, d=18 nm wide

Diffusivity:

$$D = \frac{k_B T}{3\pi \mu_B L}\left(\ln\left(\frac{\mathrm{L}}{\mathrm{d}}\right) + 0.3\right)$$

https://www.google.com/search?q=tobacco+mosaic+virus+electron+micrograph&tbm=isch&source=iu&ictx=1&fir=VCHszPqFz02MJM%253A%252Cys5UEQPy3oxCoM%252C_&usg=__4QlVfGScIPhDHu33e-dV01X-65A%3D&sa=X&ved=0ahUKEwji5ZGC3KjYAhWr64MKHSdhCScQ9QEINjAE#imgrc=VCHszPqFz02MJM:

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

Lecture 5 Poll: Cylinder Packing

Consider only excluded volume effects, how should we expect the closest packing of cylindrical rods be compared to the HCP limit (~0.74) of hard spheres?

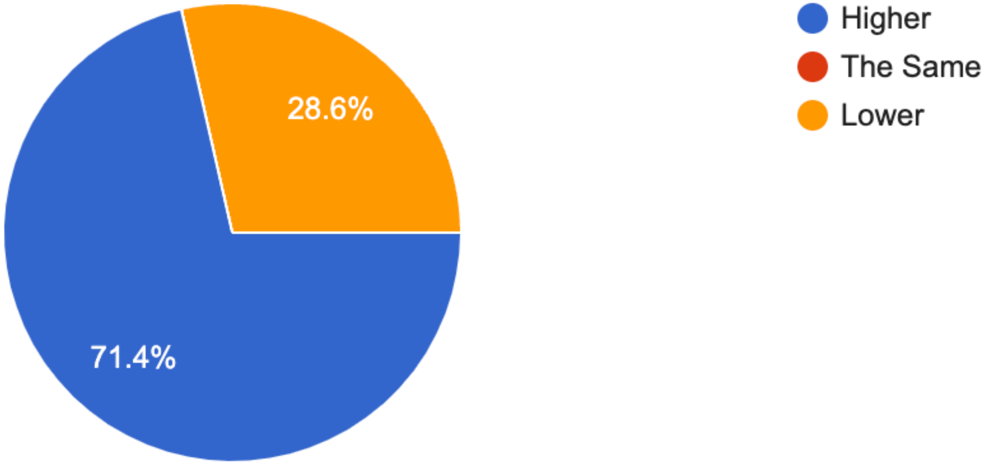
- A. higher
- B. the same
- C. lower

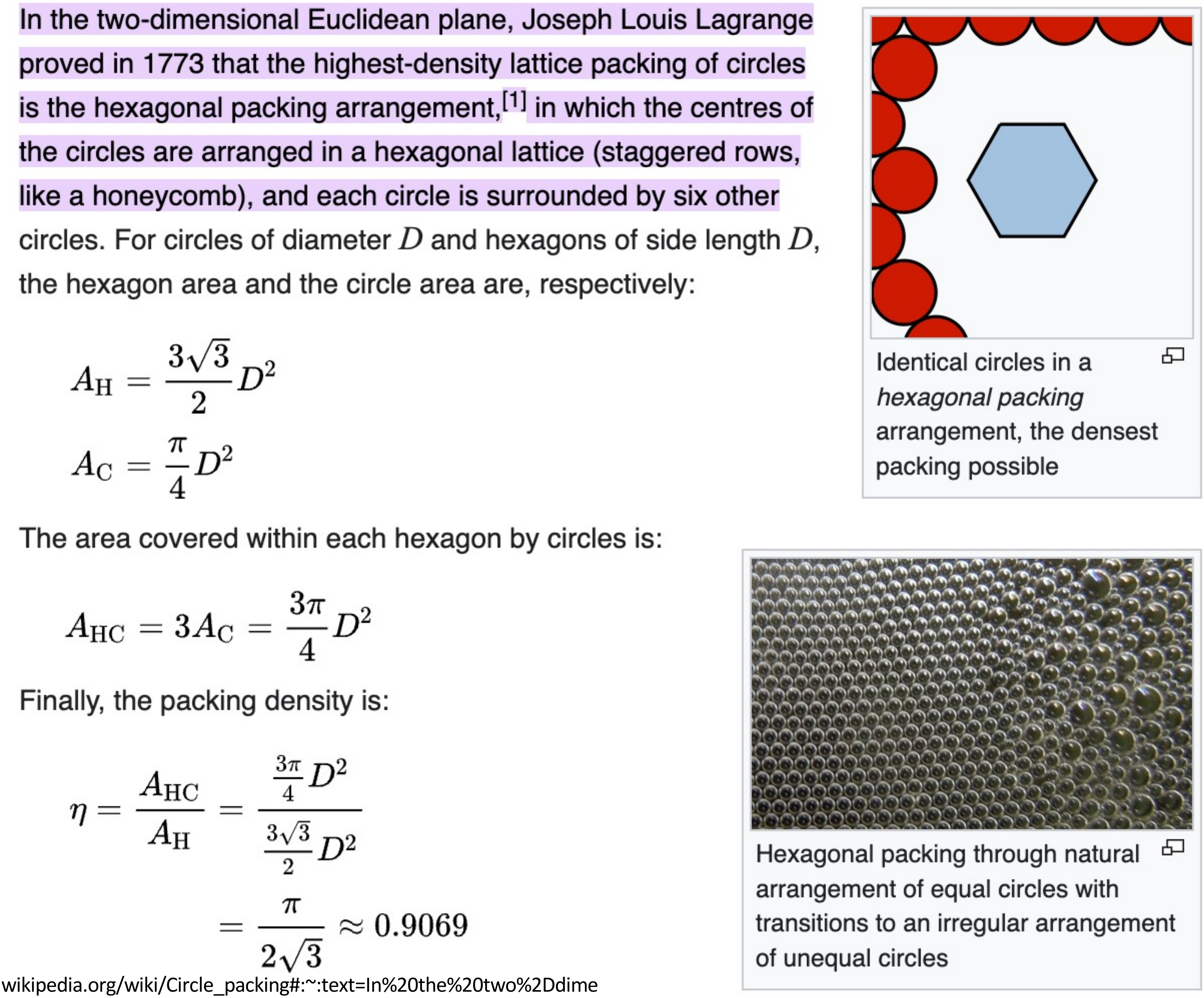
Long URL https://forms.gle/y4xy3HsbFV6npW956

Short URL https://shorturl.at/gkGR7

Consider only excluded volume effects, how should we expect the closest packing of cylindrical rods be compared to the HCP limit (~0.74) of hard spheres?

14 responses





In the two-dimensional Euclidean plane, Joseph Louis Lagrange proved in 1773 that the highest-density lattice packing of circles is the hexagonal packing arrangement,[1] in which the centres of the circles are arranged in a hexagonal lattice (staggered rows, like a honeycomb), and each circle is surrounded by six other circles. For circles of diameter D and hexagons of side length D, the hexagon area and the circle area are, respectively:

$$A_{\mathrm{H}} = \frac{3\sqrt{3}}{2} D^2$$

$$A_{\mathrm{C}} = \frac{\pi}{4} D^2$$

The area covered within each hexagon by circles is:

$$A_{\mathrm{HC}} = 3A_{\mathrm{C}} = \frac{3\pi}{4} D^2$$

Finally, the packing density is:

$$\eta = \frac{A_{\mathrm{HC}}}{A_{\mathrm{H}}} = \frac{\frac{3\pi}{4} D^2}{\frac{3\sqrt{3}}{2} D^2} = \frac{\pi}{2\sqrt{3}} \approx 0.9069$$

Identical circles in a *hexagonal packing* arrangement, the densest packing possible

Hexagonal packing through natural arrangement of equal circles with transitions to an irregular arrangement of unequal circles

https://en.wikipedia.org/wiki/Circle_packing#:~:text=In%20the%20two%2Ddimensional%20Euclidean,is%20surrounded%20by%20six%20other

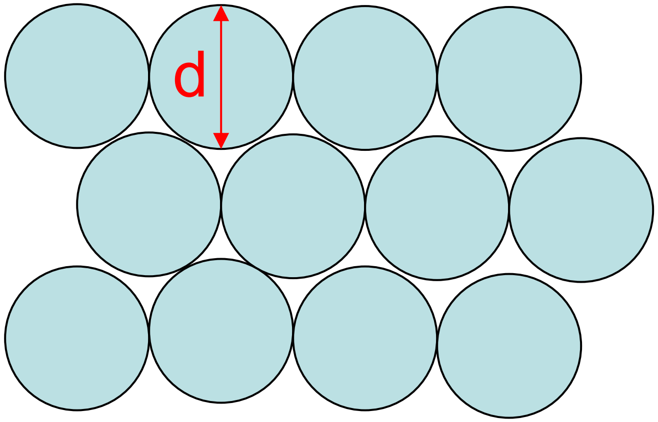
Packing of Cylinders

- The closest packing of **cylindrical rods** occurs when they are parallel to each other and **packed hexagonally in the plane orthogonal to their axes**; in this case, $\phi = 0.9069$.
- If the **density** of long ordered rods is **decreased**, a melting transition will occur in which the in-plane hexagonal order is lost, but the **orientational order** of the rod axes is **partially preserved**.
- This partially ordered state is called a **nematic**. States with partial order, including the nematic state, are common for stiff molecules of high aspect ratio.

Packing of Cylinders

L = cylinder length

end-on view of packed cylinders



hexagonal packing (2D)

$$\phi_{max} = 0.9069$$

ν = no. rods/vol.

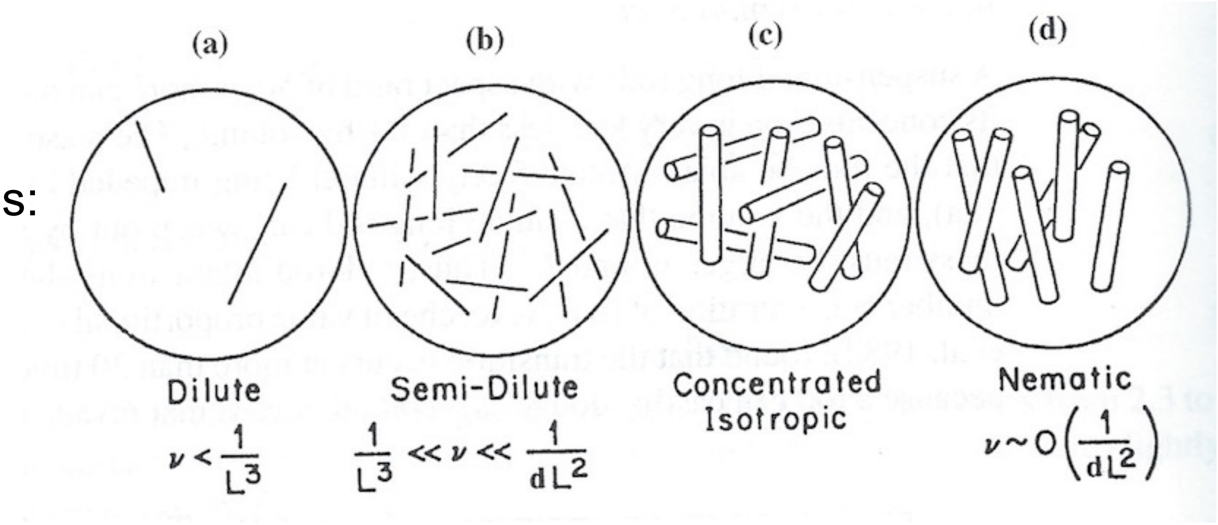
$$\phi = \nu \underset{\text{vol. of cylinder}}{\underline{\left(\frac{\pi}{4}\right) d^2 L}}$$

$if\,\phi \ll \phi_{max}$, i.e., $\nu < 1/d^2 L$ -> hexagonal packing disappears

but for long rods, *orientational order* can persist

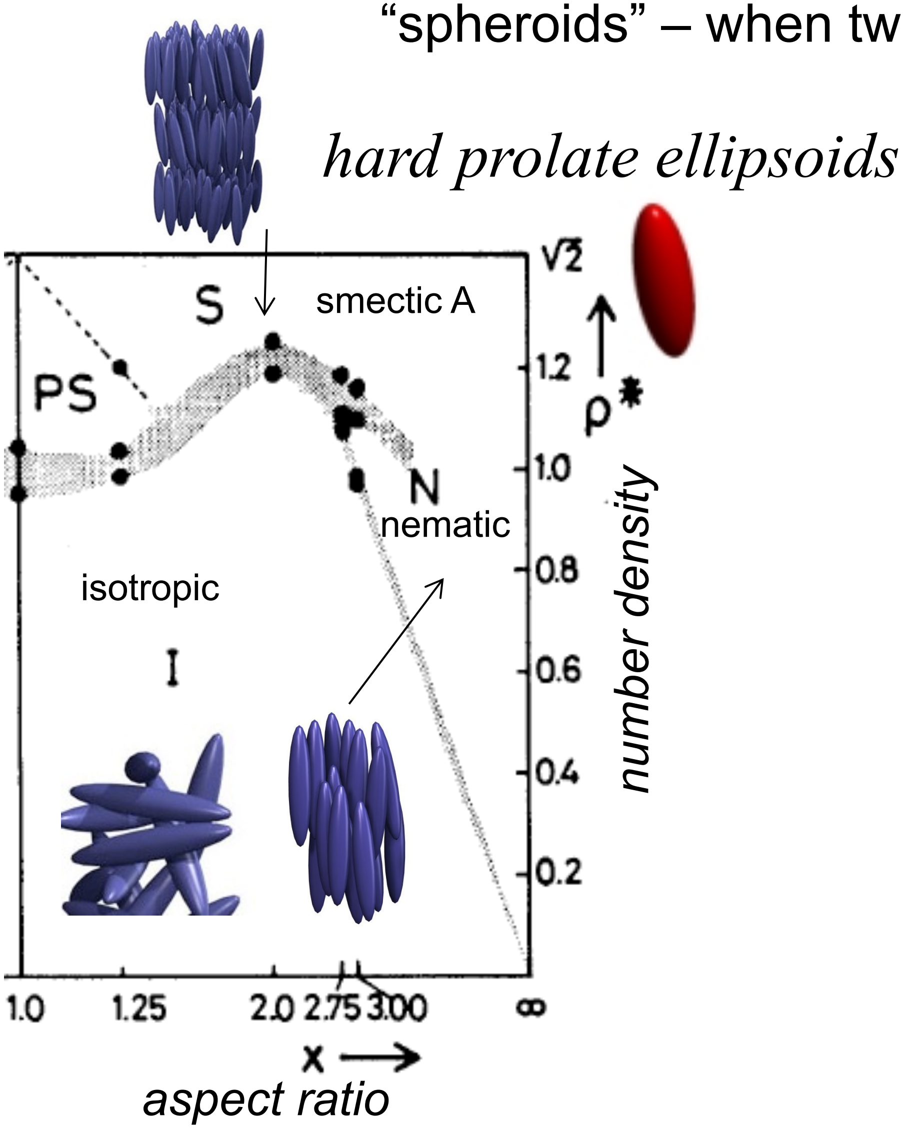
concentration regimes:

from Doi and Edwards, Oxford, 1986



Phase behaviour for non-attracting axisymmetric hard particles

“spheroids” – when two axes are same length



Frenkel and Mulder, Molecular Physics, 1985

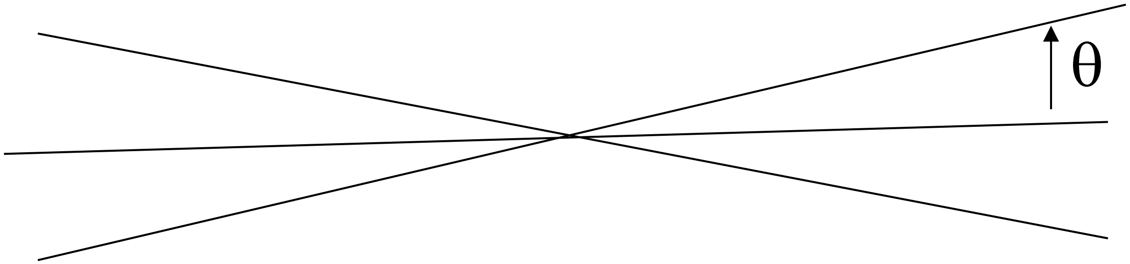
http://homepage.univie.ac.at/franz.vesely/

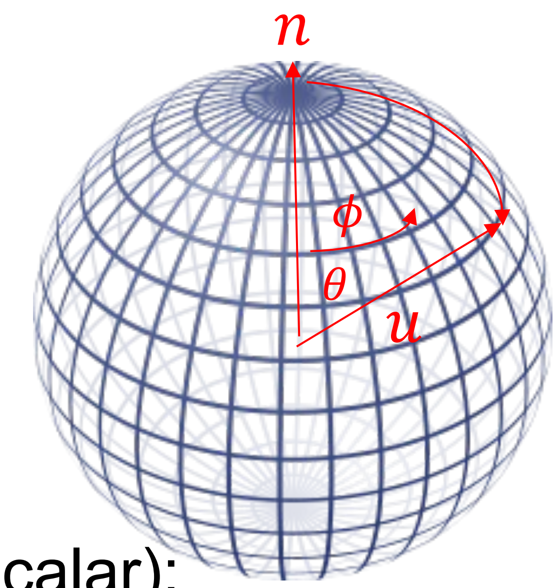
Packing of Cylinders

- The degree of **orientational order** in a nematic is described by an orientational **order parameter S**. **S** quantifies the degree to which molecular orientations are parallel to a common **nematic axis**. **S = 1 corresponds to a perfectly parallel orientation of all rod-like molecules or particles**, while S = 0 corresponds to a completely random, or isotropic, distribution of molecular orientations:

$$S \equiv \frac{3}{2} < cos^2 \theta > - \frac{1}{2}$$

Nematic Order





define nematic order parameter (scalar):

$$S \equiv \frac{3}{2} < cos^2\theta > -\frac{1}{2}$$

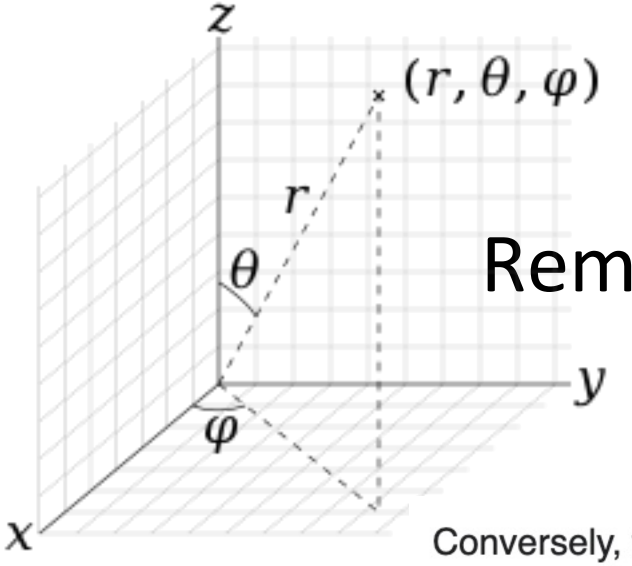
$0 < S < 1$

Note: S here is *not* entropy or structure factor

$$<\cdot> \equiv \int \cdot\, \psi(\boldsymbol{u})\, du^2 = \int_0^{2\pi}\int_0^{\pi} \cdot\, \psi(\theta,\phi) sin\,\theta d\theta d\phi$$

$\boldsymbol{u}$ is a unit vector, $\boldsymbol{u} = (sin\theta cos\phi, sin\theta sin\phi, cos\theta)$

$\psi(\boldsymbol{u})du^2$ = probability that a rod's orientation lies between $\boldsymbol{u}$ and $\boldsymbol{u}$ +d $\boldsymbol{u}$



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

Reminder: Spherical coordinate system

Conversely, the Cartesian coordinates may be retrieved from the spherical coordinates (*radius* r, *inclination* θ, *azimuth* φ), where $r \in [0, \infty)$, $\theta \in [0, \pi]$, $\varphi \in [0, 2\pi)$, by

$$\begin{aligned} x &= r \sin\theta \, \cos\varphi, \\ y &= r \sin\theta \, \sin\varphi, \\ z &= r \cos\theta. \end{aligned}$$

$$<\cdot> \equiv \int \cdot \, \psi(\boldsymbol{u}) \, du^2 = \int_0^{2\pi} \int_0^{\pi} \cdot \, \psi(\theta, \phi) sin \, \theta d\theta d\phi$$

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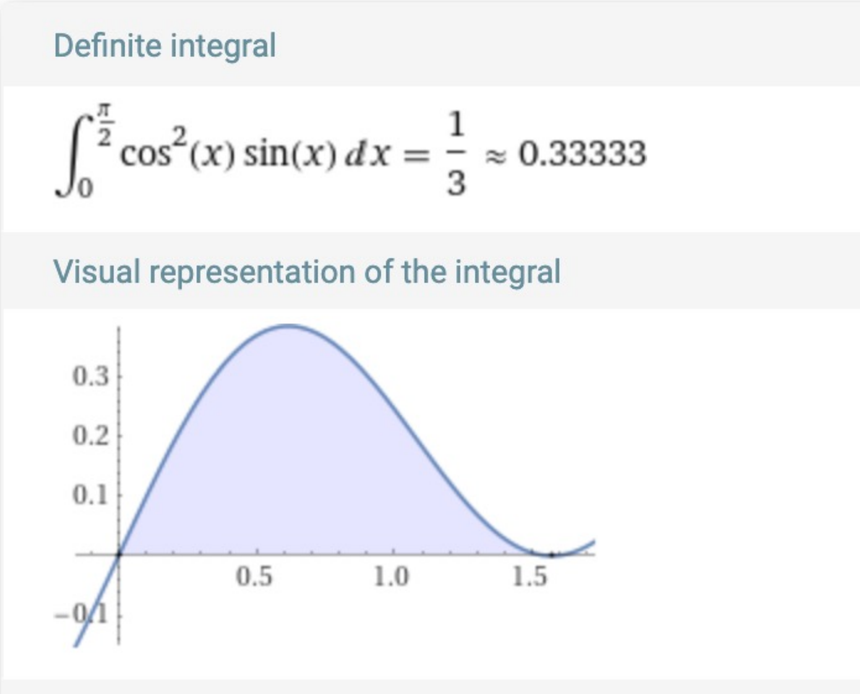
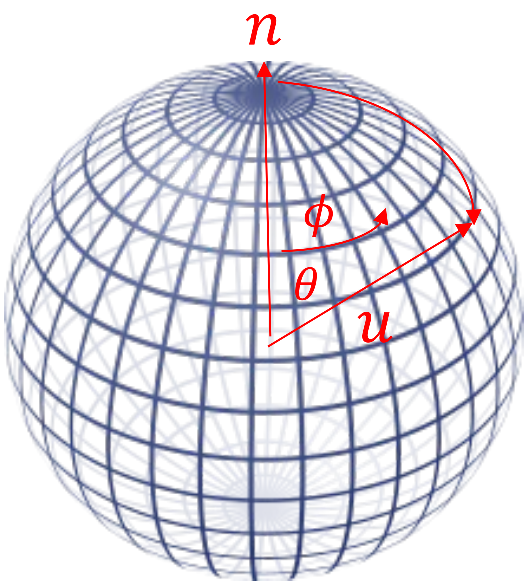


Definite integral

$$\int_0^{\frac{\pi}{2}} \cos^2(x)\sin(x)\,dx = \frac{1}{3} \approx 0.33333$$

Visual representation of the integral



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Onsager theory of nematic transition

Volume z excluded to center of a second rod (shaded area):

d = rod diameter; L = rod length

$$z(\boldsymbol{u},\boldsymbol{u}') \equiv \beta(\boldsymbol{u},\boldsymbol{u}') = 2dL^2|(\boldsymbol{u}\times\boldsymbol{u}')| = 2dL^2\sin(\mathbf{u}',\mathbf{u})$$

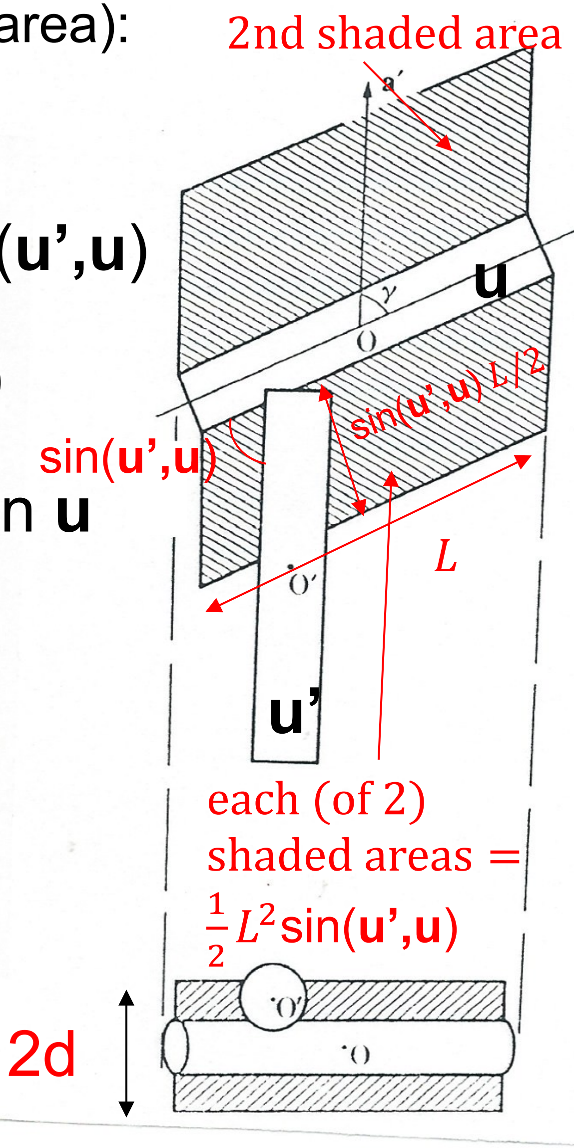
(induces rods to become more nearly parallel)

Average volume excluded to a rod of orientation **u**

$$\bar{z}(\mathbf{u}) = \int \psi(\boldsymbol{u}')\,\beta(\mathbf{u}',\mathbf{u})\,du'^2$$

change of entropy per unit volume:

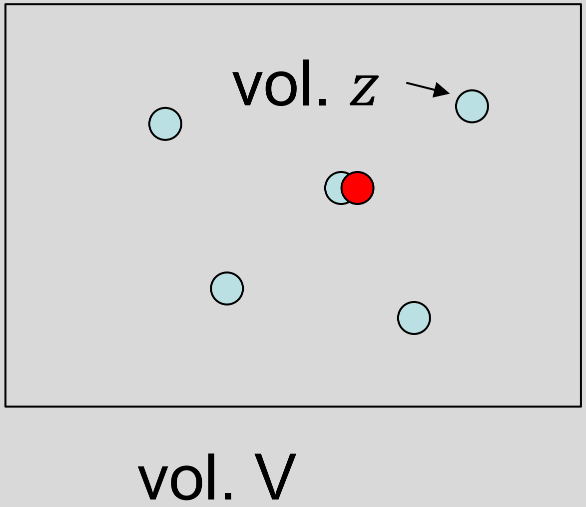
(due to excluded volume)



Excluded Volume Effects

z = excluded volume parameter

consider *dilute* particles



add a particle

probability that *a particular particle* overlaps another: vz = ϕ, volume fraction

for N particles, number of configurations:

$$\Omega \approx \frac{[V(1-vz/2)]^N}{N!\,\Lambda^{3N}}$$

factor of 2 avoids double counting

$$N = vV$$

$$S = k_B ln\Omega = -k_B N ln[v(1-vz/2)]$$ (ignore *const.)*

$$\approx \; -k_B\, V[v ln v + v ln\left(1-\frac{vz}{2}\right)]$$

change of entropy per unit volume: $k_B v ln\left(1-\frac{vz}{2}\right)] \approx -\frac{1}{2}k_B z v^2$

(due to excluded volume)

for small v

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$$\bar{z}(\mathbf{u}) = \ \int \psi(\boldsymbol{u}')\ \beta(\mathbf{u}',\mathbf{u})\ du'^2$$

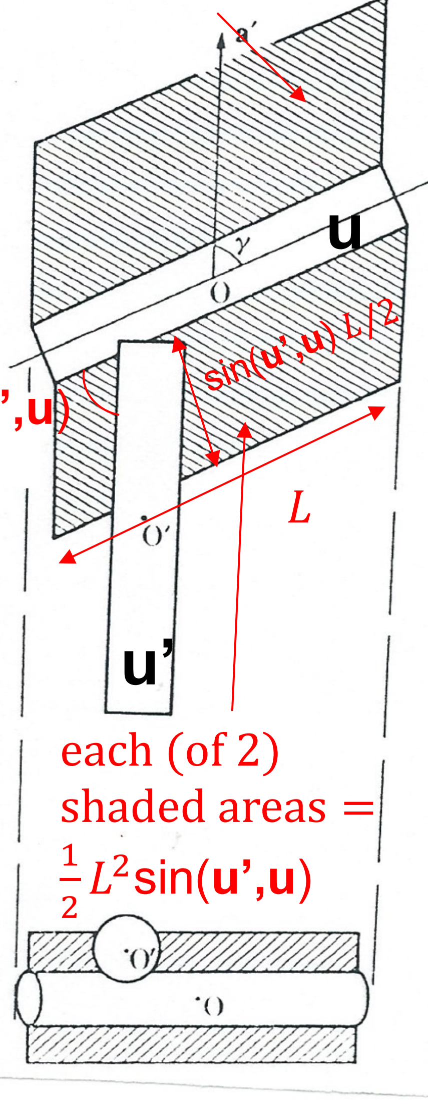
change of entropy per unit volume:

(due to excluded volume)

$$\Delta S \approx -\frac{1}{2}k_B z v^2 \text{ -> } -\frac{1}{2}k_B\bar{z}(\mathbf{u})\nu^2$$

spheres cylinders

ν= #rods/vol.



each (of 2) shaded areas = $\frac{1}{2}L^2$sin(**u’**,**u**)

Entropy S and free energy A are *per unit volume*

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Orientational Entropy

orientational free energy A and entropy S of a single rod (per unit volume V):

$$A_1[\psi] = -TS = \nu k_B T \int \psi(\boldsymbol{u}) ln[\psi(\boldsymbol{u})]\, du^2$$ (penalizes orientation)

$(equivalent\ to\text{: } S = -k_B N \sum_i P_i\, ln(P_i))$ like in Shannon entropy

ν = #rods/vol. = N/V

Recall Non-Interacting Particles

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

$A = -k_B T\, lnQ$ 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)

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

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

Pressure $P = vk_B T$

Recall Non-Interacting Particles (Generalization 3: non-uniform *probability* distribution)

$$A/k_BT = \boxed{-S/k_B} = \sum_i N_i\, ln(P_i)$$

$$\boxed{= N \sum_i P_i\, ln(P_i)}$$

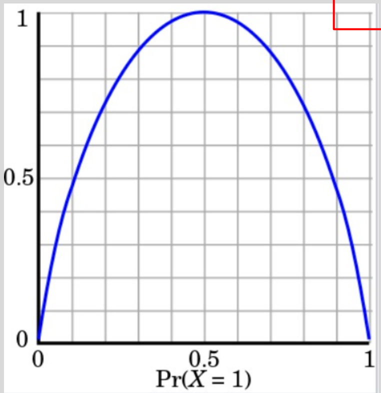
N_i =number of particles in state i

P_i =probability (or fraction of times) that particle is in state i = N_i/N

N = total number of particles

(equal *a priori* probability of each state)

Maximum entropy

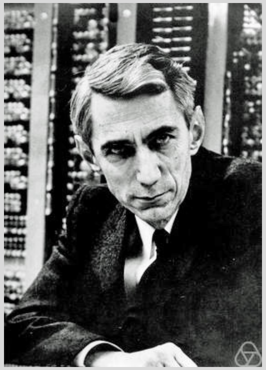


$$-\sum_i P_i\, ln(P_i)$$

= *Shannon entropy (per particle)* from information theory

high Shannon entropy means low information content, and vice versa

Claude Shannon,
Univ. of Mich. grad,
born in Petoskey, MI



"Information content of the known universe:" $10^{10^{123}}$

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(valid if concentration is not too high ~ 10% or so)

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$$A_2[\psi] = \frac{1}{2}\nu^2 k_B T [\underbrace{\int\int \psi(\boldsymbol{u})\psi(\boldsymbol{u}')\, \beta(\mathbf{u'},\mathbf{u}) du^2 du'^2}_{\bar{\bar{z}}}]$$ (favors orientation)

Excluded Volume Effects

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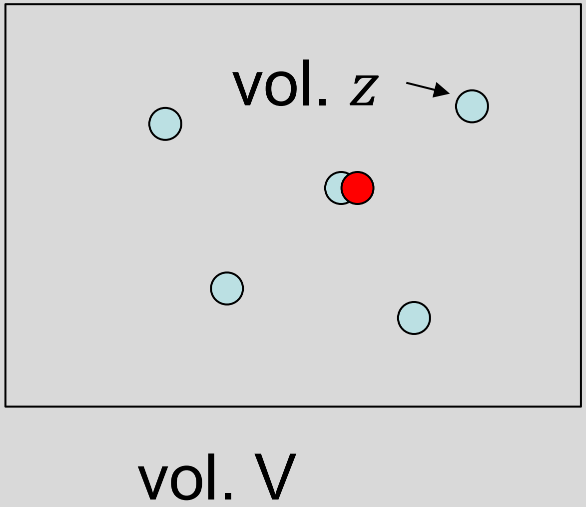

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$$\approx \; -k_B\, V\left[v \ln v + v \ln\left(1 - \frac{vz}{2}\right)\right]$$

change of entropy per unit volume: $k_B v \ln\left(1 - \frac{vz}{2}\right)] \approx -\frac{1}{2} k_B z v^2$

(due to excluded volume)

for small v

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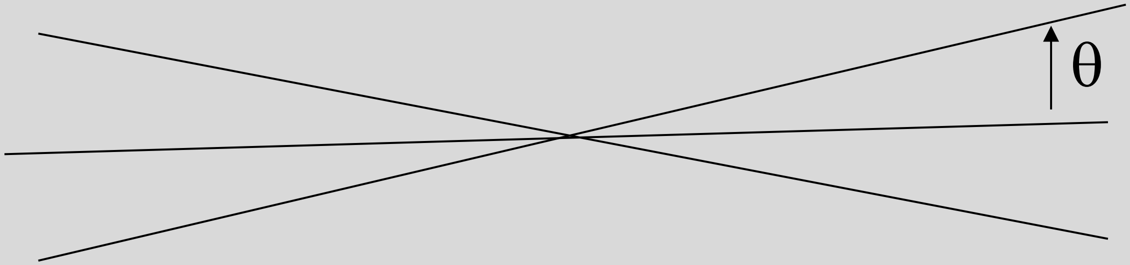
$$A_2[\psi] = \frac{1}{2}\nu^2 k_B T\left[\frac{\int\int \psi(\boldsymbol{u})\psi(\boldsymbol{u}')\, \beta(\mathbf{u}',\mathbf{u}) du^2 du'^2}{\bar{\bar{z}}}\right]$$ (favors orientation)

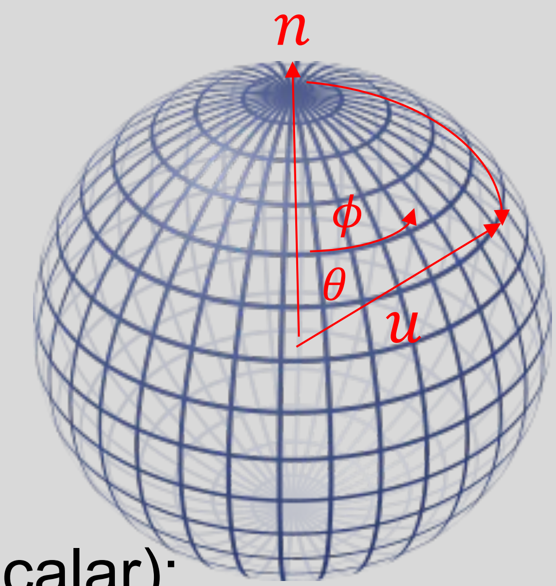
To find the distribution function $\psi(\boldsymbol{u})$ that minimizes the sum of these two free energy contributions, we must do calculus of variations using a Lagrange multiplier to maintain $\int \psi(\boldsymbol{u})\, du^2 = 1$

Onsager Nematic Potential $V_{nem}\ (\boldsymbol{u})$

- The distribution of orientations can, in principle, be computed theoretically from a **nematic potential** that expresses the influence of one rod's orientation on that of its neighbors.
- Onsager's theory was derived for an ideal solution of long, **perfectly stiff, hard rods** interacting only by **excluded-volume forces**, at concentrations dilute enough that **only pairwise interactions are significant**.
- From the potential $V_{nem}\ (\boldsymbol{u})$, one can obtain the rod **orientation distribution function $\boldsymbol{\psi}(\boldsymbol{u})$**, and hence the **order parameter S**, by a self-consistent calculation.

Nematic Order





define nematic order parameter (scalar):

$$\boxed{S \equiv \frac{3}{2} < cos^2 \theta > - \frac{1}{2}}$$

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$$\boxed{<\cdot> \equiv \int \cdot\, \psi(\boldsymbol{u})\, du^2 = \int_0^{2\pi} \int_0^{\pi} \cdot\, \psi(\theta, \phi) sin\ \theta d\theta d\phi}$$

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Entropy S and free energy A are *per unit volume*

Solution: Onsager Potential

$\boxed{\psi(\boldsymbol{u}) = const\ exp[-V_{nem}(\boldsymbol{u})\,/\,k_BT]}$ (Boltzmann principle)

$\int \psi(\boldsymbol{u})\,du^2 = 1 \quad (const)^{-1} = \int e^{-V_{nem}/k_BT}\,du^2$

(normalization const.)

average volume excluded per rod

$$V_{nem}(\boldsymbol{u}) = k_BT\nu\boxed{\bar{z}(\boldsymbol{u})} = k_BT\nu\int\psi(\boldsymbol{u}')\,\beta(\mathbf{u'},\mathbf{u})\,du'^2$$

$\beta(\mathbf{u'},\mathbf{u}) = 2dL^2\sin(\mathbf{u'},\mathbf{u})$ $\qquad$ ν = # rods/vol

$$\boxed{V_{nem}(\boldsymbol{u}) = 2\nu dL^2k_BT\int\psi(\boldsymbol{u}')\sin(\mathbf{u'},\mathbf{u})\,du'^2}$$

Solve for $V_{nem}(\boldsymbol{u})$ and $\psi(\boldsymbol{u})$ simultaneously

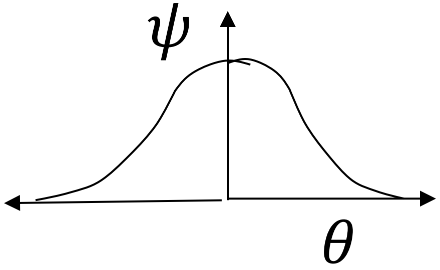
Note: $A_2[\psi] = \frac{1}{2}\nu^2k_BT[\int\int\psi(\boldsymbol{u})\psi(\boldsymbol{u}')\,\beta(\mathbf{u'},\mathbf{u})du^2du'^2]$

$= \frac{\nu}{2}[\int\psi(\boldsymbol{u})V_{nem}(\boldsymbol{u})\,du^2]$ $\quad$ $(i.e., A_2[\psi] = -T\Delta S = \frac{1}{2}k_BT\bar{\bar{z}}\nu^2)$

Solution to Onsager Theory

$\boldsymbol{u} \cdot \boldsymbol{n} = cos\theta$

To simplify the problem, Onsager suggested using an approximate form for the solution:



$$\psi(\boldsymbol{u}) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \boldsymbol{u} \cdot \boldsymbol{n})$$

where $\boldsymbol{n}$ is the *director*, a unit vector pointing in the direction of mean orientation

(the prefactor was chosen so that $\int \psi(\boldsymbol{u})\, du^2 = 1$)

Insert this into $A_1(\boldsymbol{u})$+ $A_2(\boldsymbol{u})$ and minimize wrt α

$$\cosh(x) \equiv \frac{e^x + e^{-x}}{2} \quad sinh(x) \equiv \frac{e^x - e^{-x}}{2}$$

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(valid if concentration is not too high ~ 10% or so)

$A_2 = \frac{1}{2} k_B T \bar{\bar{\bar{z}}} \nu^2$ $\bar{\bar{\bar{z}}}$ is average over both $\psi(\boldsymbol{u})$and $\psi(\boldsymbol{u}')$

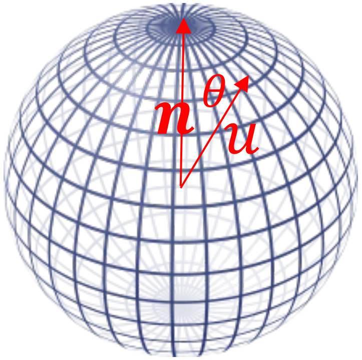
$$\boxed{A_2[\psi] = \frac{1}{2}\nu^2 k_B T \underset{\bar{\bar{\bar{z}}}}{\underline{[\int\int \psi(\boldsymbol{u})\psi(\boldsymbol{u}')\, \beta(\mathbf{u}',\mathbf{u}) du^2 du'^2]}}}$$ (favors orientation)

To find the distribution function $\psi(\boldsymbol{u})$ that minimizes the sum of these two free energy contributions, we must do calculus of variations using a Lagrange multiplier to maintain $\int \psi(\boldsymbol{u})\, du^2 = 1$

Order Parameter

$$S \equiv \frac{3}{2}\int \psi(\boldsymbol{u})\left[(\boldsymbol{u}\cdot\boldsymbol{n})^{2} - \frac{1}{3}\right] du^{2} = \frac{3}{2} < cos^{2}\theta > - \frac{1}{2}$$

using uniaxial symmetry:



$$S \equiv \pi \int \psi(\theta)[3cos^{2}(\theta) - 1]sin\theta\, d\theta$$

$$<\cdot> \equiv \int \cdot\, \psi(\boldsymbol{u})\, du^{2} = \int_{0}^{2\pi}\int_{0}^{\pi}\cdot\, \psi(\theta,\phi)sin\,\theta d\theta d\phi$$

$\psi(\boldsymbol{u})\mathrm{d}u^{2}$ = probability that a rod’s orientation lies between $\boldsymbol{u}$ and $\boldsymbol{u}$ +d $\boldsymbol{u}$

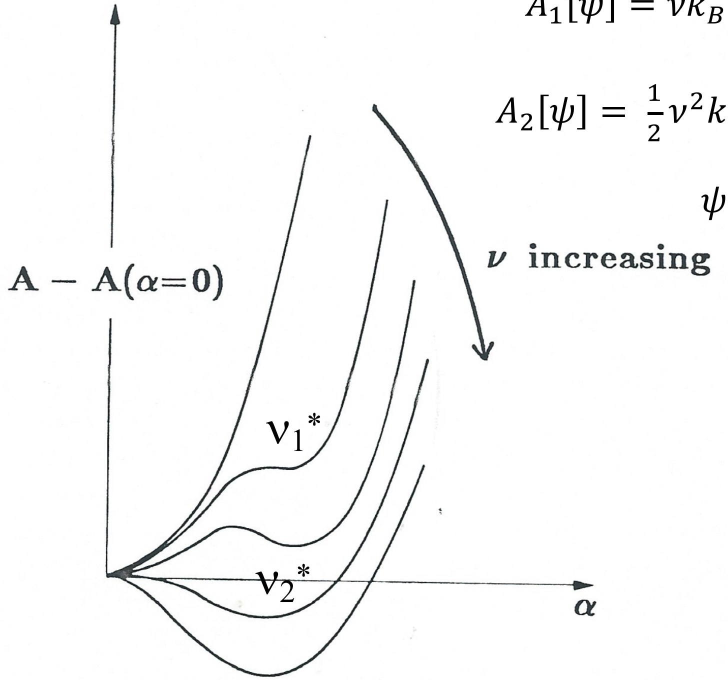
$\boldsymbol{n}$ is a unit vector point in direction of average nematic orientation

Free Energy Solution

$$A_1[\psi] = \nu k_B T \int \psi(\boldsymbol{u}) ln[\psi(\boldsymbol{u})]\, du^2$$

$$A_2[\psi] = \frac{1}{2}\nu^2 k_B T[\int\int \psi(\boldsymbol{u})\psi(\boldsymbol{u}')\, \beta(\mathbf{u'},\mathbf{u}) du^2 du'^2]$$

$$\psi(\boldsymbol{u}) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \boldsymbol{u}\cdot\boldsymbol{n})$$



for small ν, only one soln: S = 0 (α = 0; isotropic)

for larger ν (between ν_1^* and ν_2^*, S = 0 (α = 0) and S > 0 (α > 0) are solutions

As ν increases, the lowest free energy state switches from S = 0 to S ≠ 0 state.

Free Energy Solution

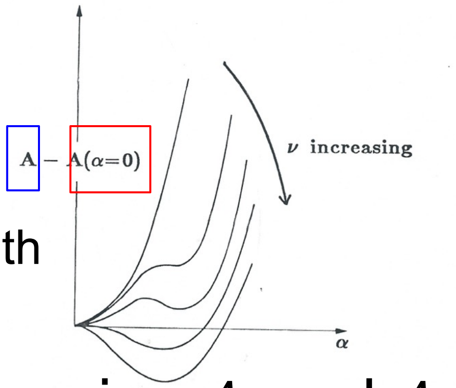
- For **low concentrations $\boldsymbol{\nu}$**, the only solution is the trivial one, ψ = const. = 1/4 , corresponding to the **isotropic state**.
- For a high enough value of ν, there is in addition to the isotropic solution **a stable nontrivial solution corresponding to a nematic state with S > 0**.
- As ν increases, the lowest free-energy state **changes from the isotropic to the nematic**.
- Onsager's potential is purely entropic; hence for a given rod diameter and length, the transition to the liquid crystalline state occurs at a concentration that is **independent of the temperature T**.
- And since the Onsager potential applies to a two-component system (rods + solvent), there is a **biphasic range** of concentrations over which the **isotropic and nematic phases coexist**.

Phase Separation

Add free energy from translational entropy

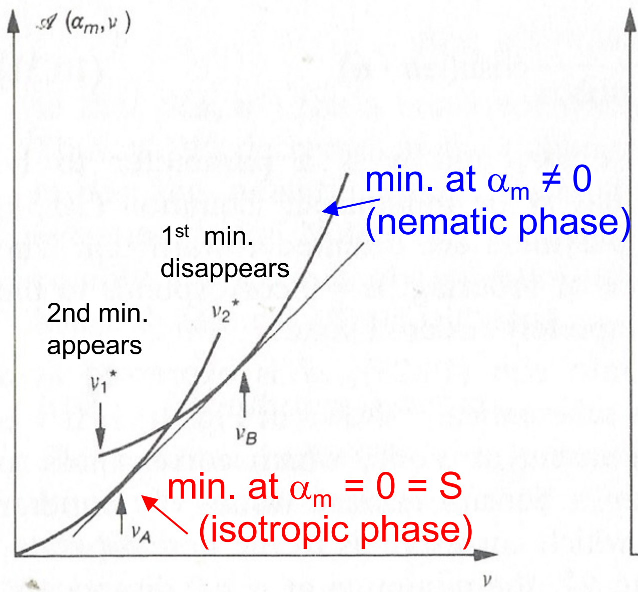
$$A_0(\nu) = \nu k_B T(\ln(\nu) - 1)$$

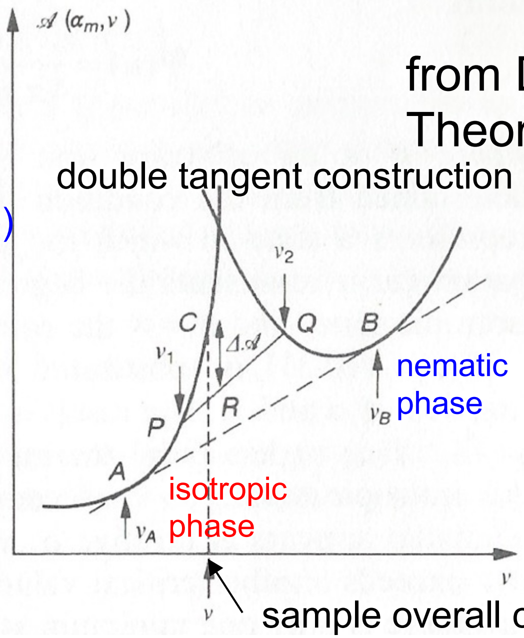
$$A[\psi,\nu] = A_0(\nu) + A_1[\psi,\nu] + A_2[\psi,\nu]$$ (sum over both phases)



Drive to reduce A_2 comes at the cost of increasing A_1 and A_0

Minimize free energy with respect to compositional variation



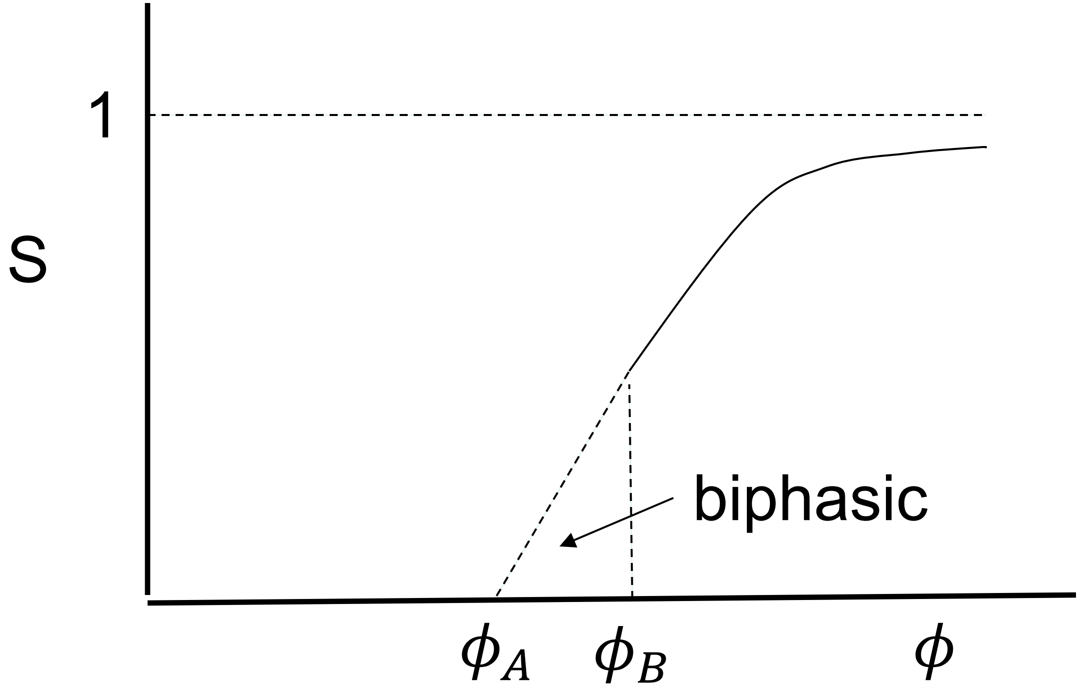


sample overall concentration

from Doi and Edwards, The Theory of Polymer Dynamics

Entropy can drive both orientation and phase separation

Nematic Order



to describe orientational interactions, we need a “nematic potential” $V_{nem}(\boldsymbol{u})$

Minimized Onsager Free Energy

Note that there are two minima for $\nu_1^* < \nu < \nu_2^*$

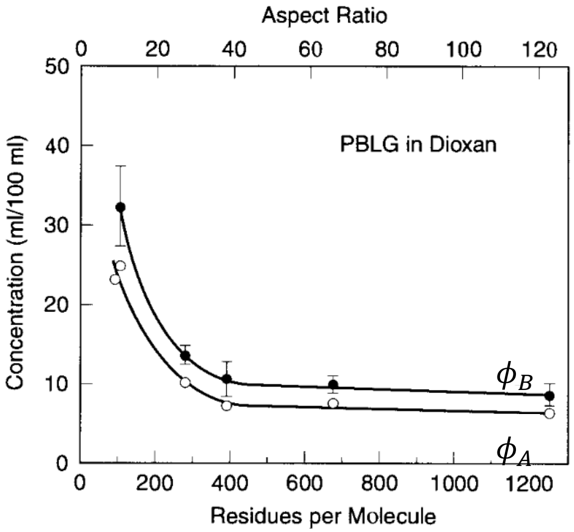
This means that there is two-phase equilibrium

Isotropic phase becomes unstable at $\nu = \nu^* = \nu_2^*$

$$\nu_A = \frac{4.25}{dL^2} \qquad \nu_B = \frac{5.27}{dL^2} \qquad \nu^* = \frac{5.1}{dL^2}$$

$$\boxed{\phi_A = \nu_A \frac{\pi d^2 L}{4} \approx 3.3\frac{d}{L} \qquad \phi_B = 4.1\frac{d}{L}} \quad \phi^* = \nu^* \frac{\pi d^2 L}{4} \approx 4\frac{d}{L}$$

these predictions of the Onsager theory for the dependence of S on ν seem to be in **qualitative agreement** with experimental measurements for **semirigid molecules** such as **poly(y-benzyl-1-glutamate) (PBLG).**



- shows the values of $\boldsymbol{\phi_A}$ and $\boldsymbol{\phi_B}$, the **volume fractions** of molecules corresponding to the **boundaries** of the biphasic region.
- for PBLG molecules, ϕ_A and ϕ_B **decrease roughly as 1/L with increasing molecular length**, in agreement with the Onager theory, up to a length of around 600 Å, corresponding to about 400 monomers.
- For longer molecules, ϕ_A and ϕ_B are roughly independent of molecular length, presumably because the **longer molecules no longer behave as rigid rods**

$$\phi_A = \nu_A \frac{\pi d^2 L}{4} \approx 3.3 \frac{d}{L} \qquad \phi_B = 4.1 \frac{d}{L}$$

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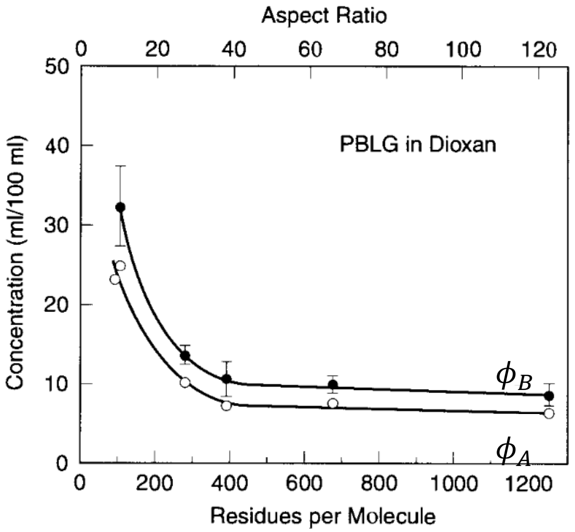

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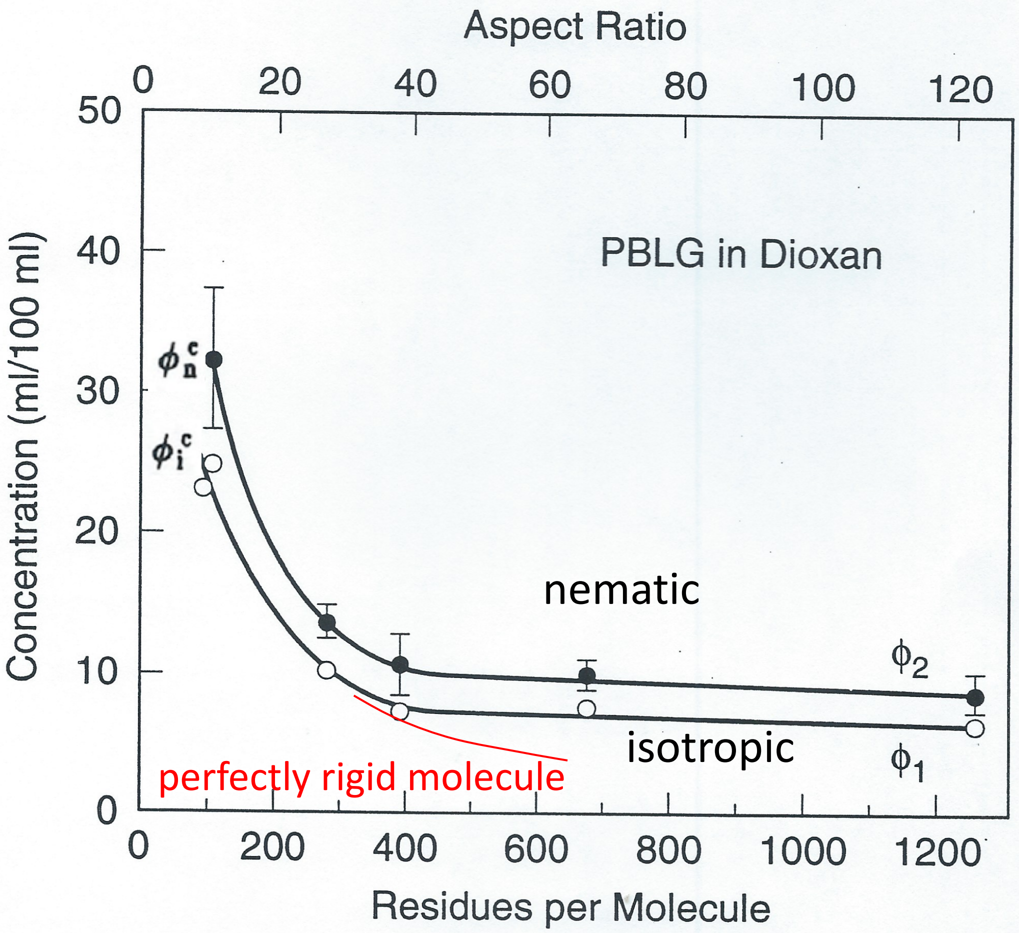
- For longer molecules, ϕ_A and ϕ_B are roughly independent of molecular length, presumably because the **longer molecules no longer behave as rigid rods**
- The Onsager theory and its extensions are valid only when the concentration is low enough that pairwise excluded-volume interactions are the dominant ones. Thus, these theories are not likely to apply to solvent-free bulk, or thermotropic, liquid crystalline phases, for which there are likely to be complex packing interactions and anisotropic energetic interactions, such as those produced by van der Waals forces.

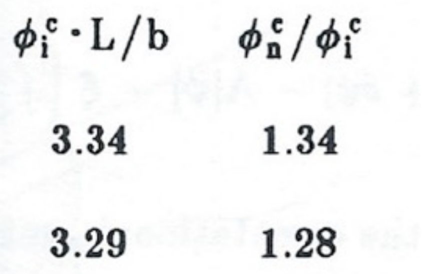
PBLG phase behavior

(poly-gamma-benzyl-L-glutamate)



(polymer length)

Onsager theory



$\phi_i^c \cdot L/b$	ϕ_n^c/ϕ_i^c
3.34	1.34
3.29	1.28

Why doesn't the volume fraction of nematic keep getting smaller?

the molecules are not completely rigid!

Glotzer Tedx talk on entropy 2012

https://www.youtube.com/watch?v=chS8dpGB0E0&ab_channel=TEDxTalks

Glotzer Kavli talk on entropy 2019

https://www.youtube.com/watch?v=JW1L_vZ6K1M

Electrostatic force

Reference text:

Colloidal Systems, Darrell Velegol

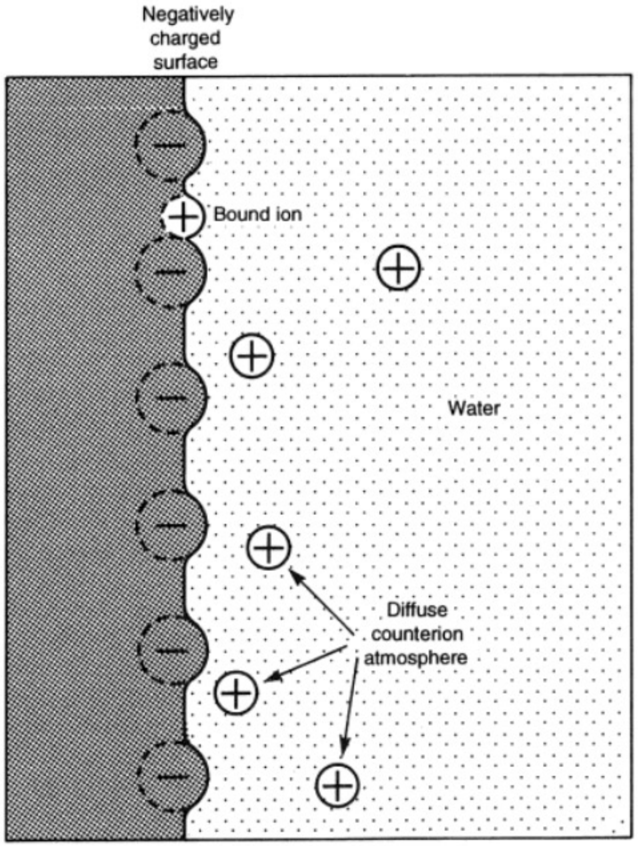
Colloidal Science and Nanoscale Engineering Slides, Orlin Velev

Intermolecular and surface forces, Jacob Israelachvili

- 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 ($\boldsymbol{\kappa}$)
- 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 ($\boldsymbol{\kappa}^{-1}$)
  - 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) = $\varepsilon\boldsymbol{\kappa}$($\Psi_0$)
  - 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) = $\varepsilon\boldsymbol{\kappa}$($\Psi_0$)
  - Surface charge density (ρ_s) using Debye-Huckel for **1 sphere**, for **2 plates**: for finite (ρ_s), (Ψ_0) → ∞ as gap → 0
- Electrostatic force per area ($\mathbf{f_{es}}$) between **2 plates**
  - Origin (contact value theorem): increased ionic concentration in gap → 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) ~ $\varepsilon\boldsymbol{\kappa}(\Psi(x))^2$
  - Plug in Debye-Huckel for **2 plates** for ($\Psi(x)$) to obtain exponential decay of electrostatic force per area ($\mathbf{f_{es}}$) with characteristic length ($\boldsymbol{\kappa}^{-1}$)
  - Integrate ($\mathbf{f_{es}}$) for electrostatic energy per unit area ($\mathbf{V_{es}}$) between **2 plates**
- Electrostatic energy ($\boldsymbol{\Phi}_{\mathbf{es}}$) between **2 spheres** and the Derjaguin approximation
  - Apply the Derjaguin approximation to obtain the electrostatic energy ($\boldsymbol{\Phi}_{\mathbf{es}}$) between **2 spheres**
  - Differentiate to calculate the electrostatic force ($\mathbf{F_{es}}$) between **2 spheres**

Without electrolyte

Origin of the electrostatic forces: Surface charge



With electrolyte

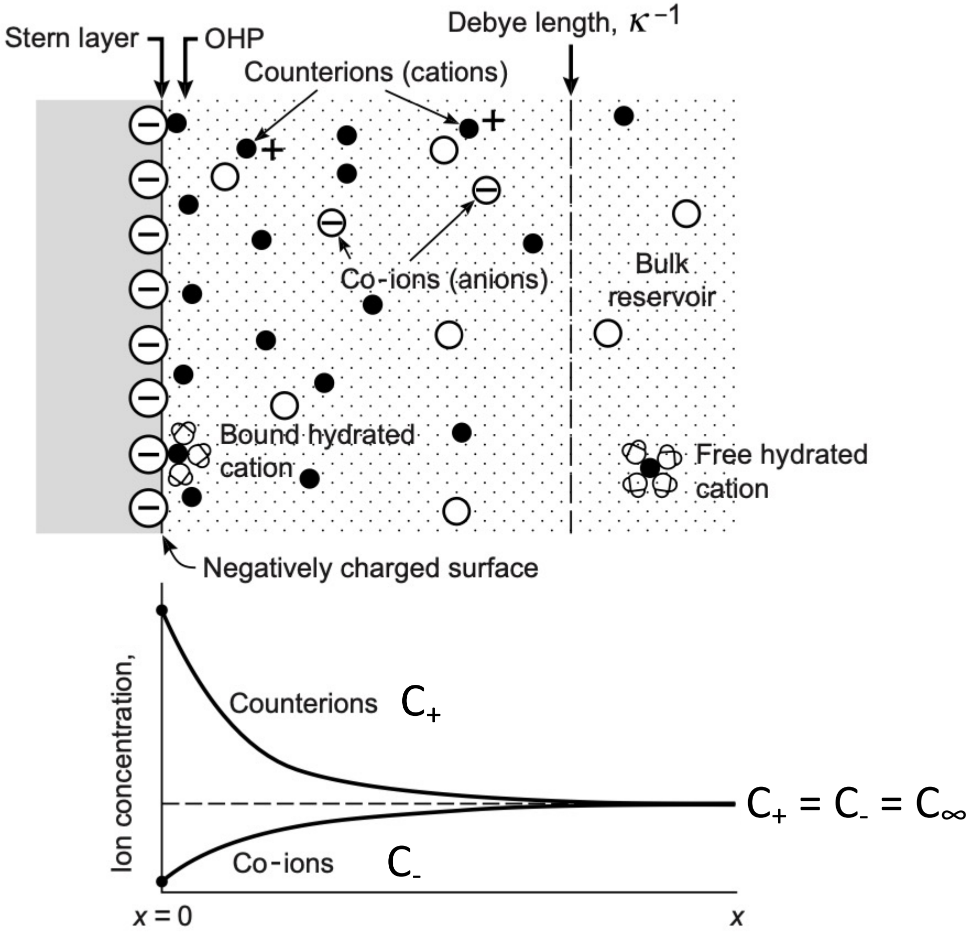


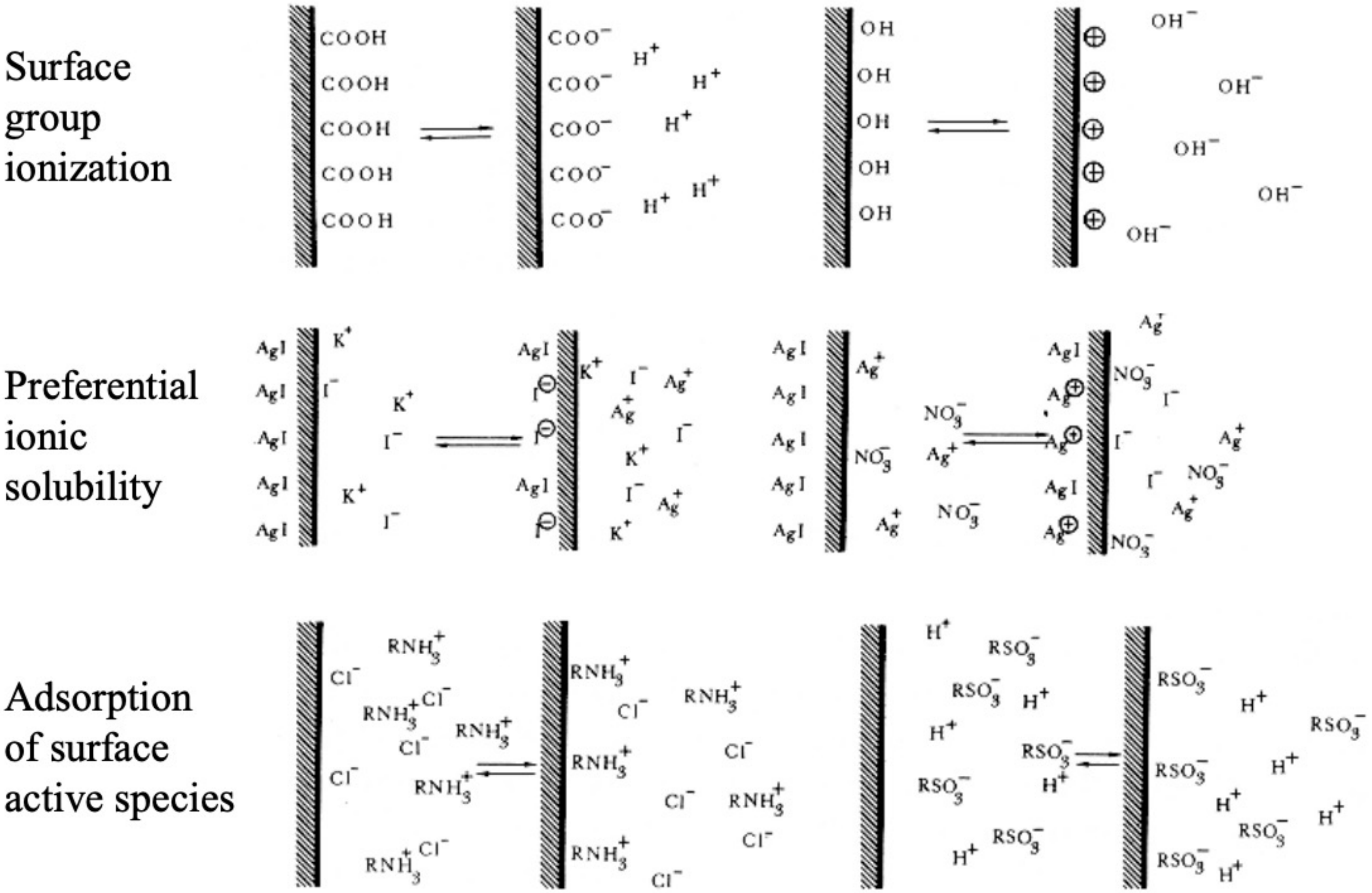
FIGURE 14.7 Near a negatively charged surface there is an accumulation of counterions (ions of opposite charge to the surface coions) and a depletion of coions, shown graphically below for a 1:1 electrolyte, where ρ_∞ is the electrolyte concentration in the bulk or "reservoir" at $x = \infty$. Counterions can adsorb to the surface in the dehydrated, partially hydrated, or fully hydrated state. The OHP is the plane beyond which the ions obey the Poisson-Boltzmann equation. This plane is usually farther out than the van der Waals plane.

Electrical double layer (EDL)

- What is “**double**” about the **electrical double layer** around a particle? There are two **charged layers**: 1) a **fixed layer of charges** on the particle surface, and 2) a **fluid layer** touching the particle surface, which contains **oppositely-charged “counter-ions”**. Together, the net sum of the charges on the particle plus the charges in the fluid layer add to zero, meaning they are together **electroneutral**.
- The primary quantities that we want to know about the EDL are the **electrical potential (Ψ)** on and around the particle, and sometimes the **spatial distribution of ions** in the fluid layer.

Electrical double layer (EDL)

Origin of the surface charge



Electrical double layer (EDL)

- In **aqueous solutions** the **particle surfaces** almost always become **charged**. If the charge group is a **carboxyl (-COOH)**, then when the pH of the fluid is greater than the pKa of the acid group – in this case, roughly 4 – the proton will dissociate, leaving a **negatively-charged COO- group bonded to the surface**.
- For **silica particles**, the surface groups first become **silanol groups (-Si-OH)** in water, and then the protons dissociates to give **negatively-charged Si-O- groups** at the surface.
- We often call this the "**fixed charged layer**"
- Colloid scientists frequently also refer to a **Stern layer**, which is an **additional layer** of species bound directly **near the fixed layer** of charges.

Electrical double layer (EDL)

- The charges on the particle arise due to the **solvating action** of the fluid on the particle. In turn the **ions in the solvent** re-distribute their positions in solution so that they form a layer – often only nanometers thick – that **counter-balances** the **fixed charges** on the particles.

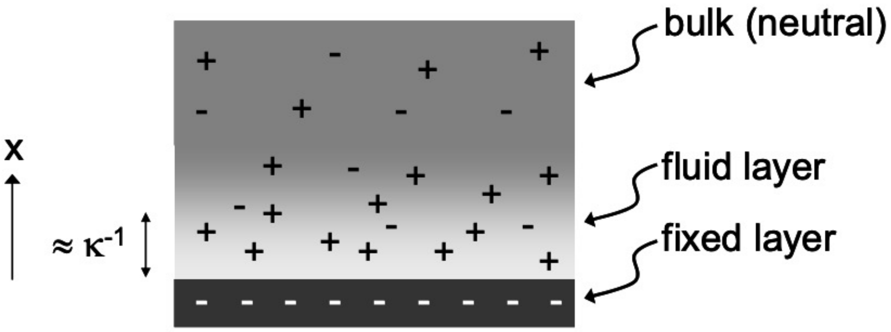


Figure 2-1. Electrical double layer (EDL). The "fixed charge layer" has charges bound on the surface, while the "fluid charge layer" – sometimes called the "diffuse layer" – has counter-ions, and a few co-ions, nearby in solution. This schematic does not show any Stern layer.

Electrical double layer (EDL)

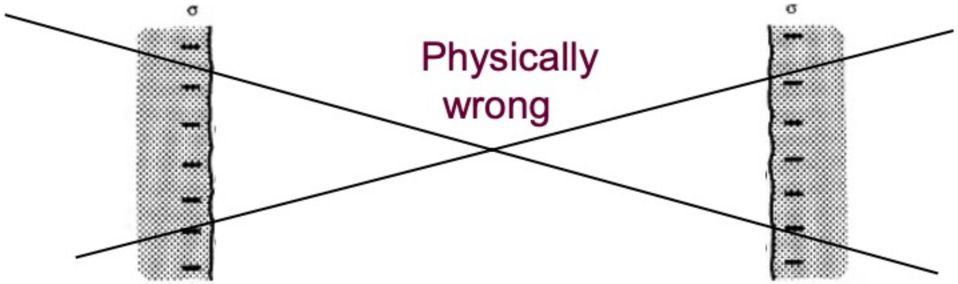
What is the origin of the repulsion force?

Electrostatic
repulsion between
charged surfaces?

Electrical double layer (EDL)

What is the origin of the repulsion force?

Electrostatic repulsion between charged surfaces?



Physically wrong

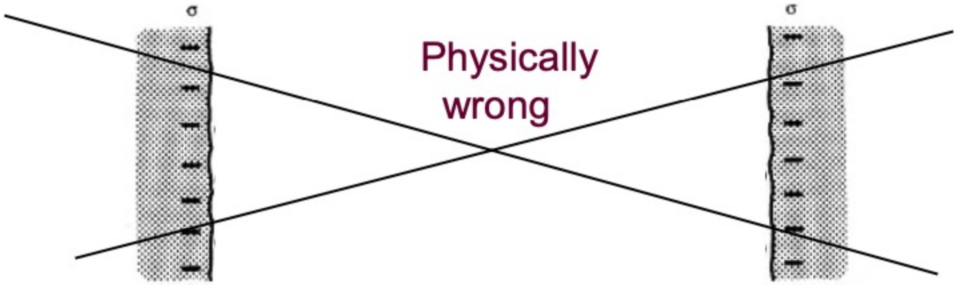
Electrostatic interaction between surfaces with counterions?

No interaction

Electrical double layer (EDL)

What is the origin of the repulsion force?

Electrostatic repulsion between charged surfaces?

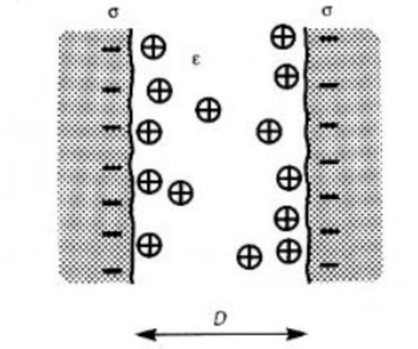


Physically wrong

Electrostatic interaction between surfaces with counterions?

No interaction

Overlap of ion layers equivalent to osmotic repulsion? ✓

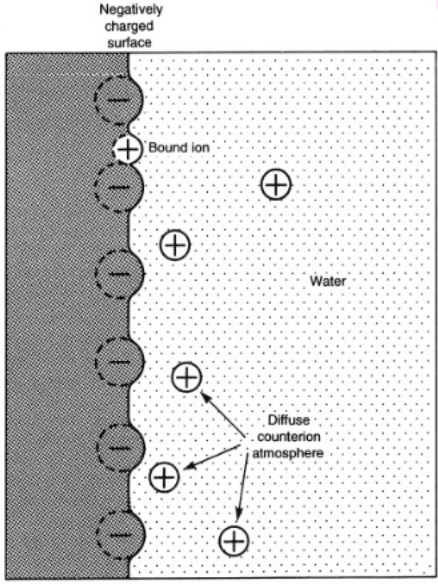


Electrical double layer (EDL)

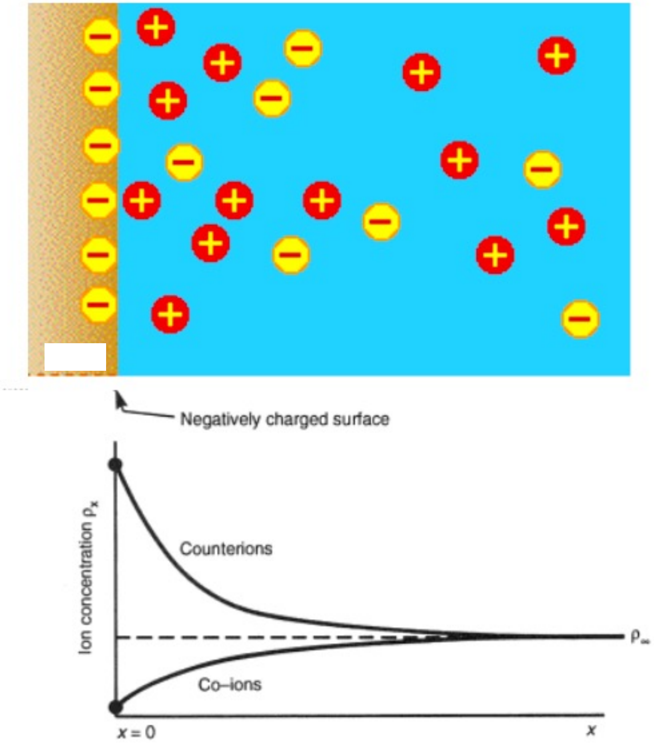
- Contrary to intuition, the **origin** of the **repulsive force** between **two similarly charged surfaces** in a **solvent containing counterions** and/or **added electrolyte ions** is **entropic** (**osmotic**), not **electrostatic**.
- What maintains the diffuse double-layer is the **repulsive osmotic pressure** between the counterions which forces them **away from the surface** and **from each other** so as to increase their **configurational entropy**.

Electrical double layer (EDL)

Electrostatics in the presence of electrolyte



Electrolyte added



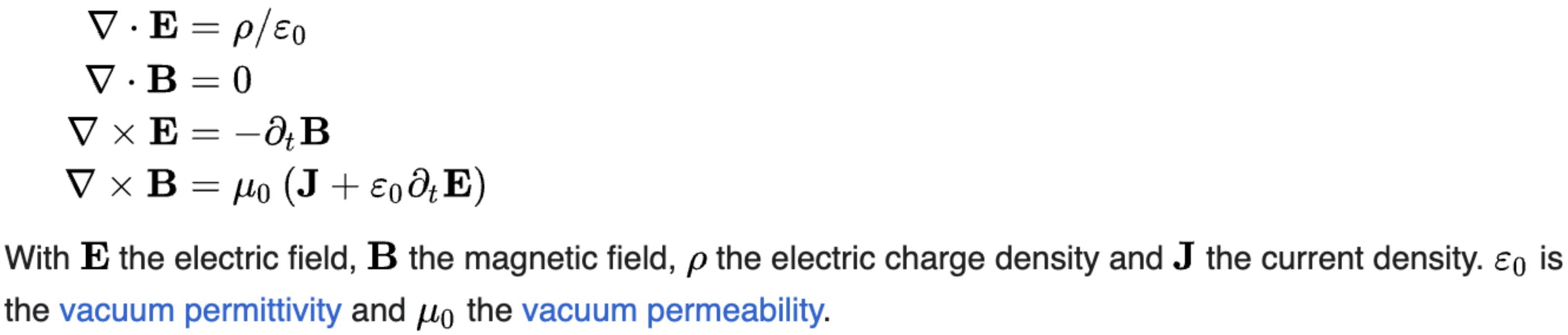
Parameters used:

Ψ = potential [Volt]

$E = (d\psi/dx) =$ field [Volt/m]

The Poisson-Boltzmann (PB) equation

- The **PB equation** is built on the Poisson equation of **electrostatics** and the Boltzmann equation of **statistical mechanics**.
- Poisson equation
- Maxwell equations



$$\begin{aligned} \nabla \cdot \mathbf{E} &= \rho/\varepsilon_0 \\ \nabla \cdot \mathbf{B} &= 0 \\ \nabla \times \mathbf{E} &= -\partial_t \mathbf{B} \\ \nabla \times \mathbf{B} &= \mu_0 \left(\mathbf{J} + \varepsilon_0 \partial_t \mathbf{E}\right) \end{aligned}$$

With $\mathbf{E}$ the electric field, $\mathbf{B}$ the magnetic field, ρ the electric charge density and $\mathbf{J}$ the current density. ε_0 is the vacuum permittivity and μ_0 the vacuum permeability.

- For the "**static** case" – which in colloid science effectively means when the **frequency is less than 10^9 s^{-1}** – we can **ignore the dynamic parts of the Maxwell equation**, the ∂/∂t parts, and simplify the full Maxwell equations.

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.

The Poisson equation

- The **permittivity** (**ε**) provides a measure of how **unwell** a material "**permits**" an **electric field** to **penetrate** through it. Vacuum has a value of $\varepsilon = \varepsilon_0 = 8.854\text{x}10^{-12}$ $C^2/N\text{-}m^2$, and readily permits an electric field through it; water has a value of about $80\ \varepsilon_0 = 7.1\text{x}10^{-10}$ $C^2/N\text{-}m^2$, which counteracts an applied field.

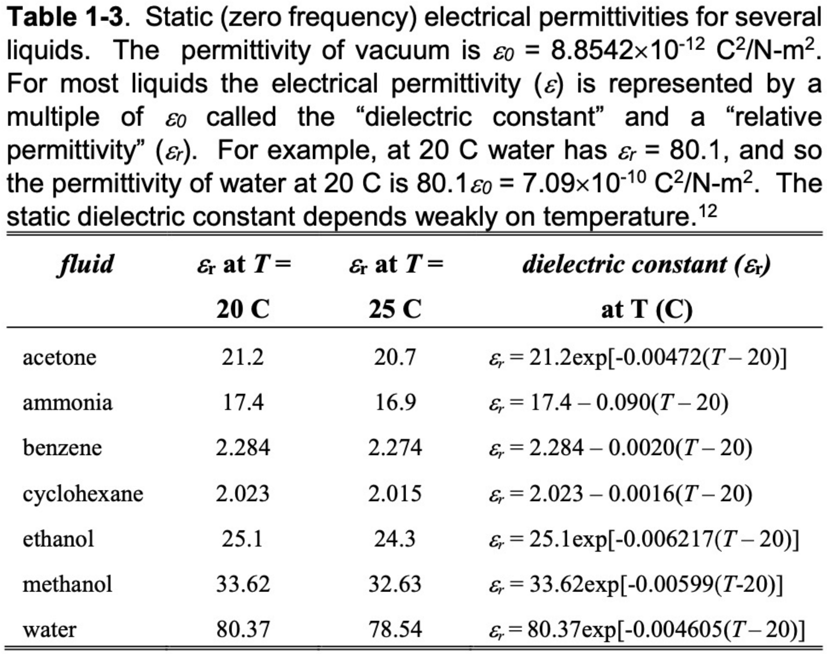


Table 1-3. Static (zero frequency) electrical permittivities for several liquids. The permittivity of vacuum is $\varepsilon_0 = 8.8542\times10^{-12}$ $C^2/N\text{-}m^2$. For most liquids the electrical permittivity (ε) is represented by a multiple of ε_0 called the "dielectric constant" and a "relative permittivity" (ε_r). For example, at 20 C water has $\varepsilon_r = 80.1$, and so the permittivity of water at 20 C is $80.1\varepsilon_0 = 7.09\times10^{-10}$ $C^2/N\text{-}m^2$. 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	$\varepsilon_r = 21.2\exp[-0.00472(T-20)]$
ammonia	17.4	16.9	$\varepsilon_r = 17.4 - 0.090(T-20)$
benzene	2.284	2.274	$\varepsilon_r = 2.284 - 0.0020(T-20)$
cyclohexane	2.023	2.015	$\varepsilon_r = 2.023 - 0.0016(T-20)$
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	$\varepsilon_r = 80.37\exp[-0.004605(T-20)]$

The Poisson equation

- How do we know the volumetric charge density ρ_e?
- By adding up the charge on each of the **N ion types** in the system, we know almost be definition that at any local position,

$$\rho_e = \sum_{i=1}^{N} z_i e c_i$$

Concentration of **ion type i**

Elementary charge

Volumetric charge density

Valence

- We expect that near to a **negative particle surface** we will have a higher concentration of **positive counter-ions** in solution, and fewer co-ions. But how do we quantify those concentrations, and thus evaluate the charge density?

The Boltzmann equation

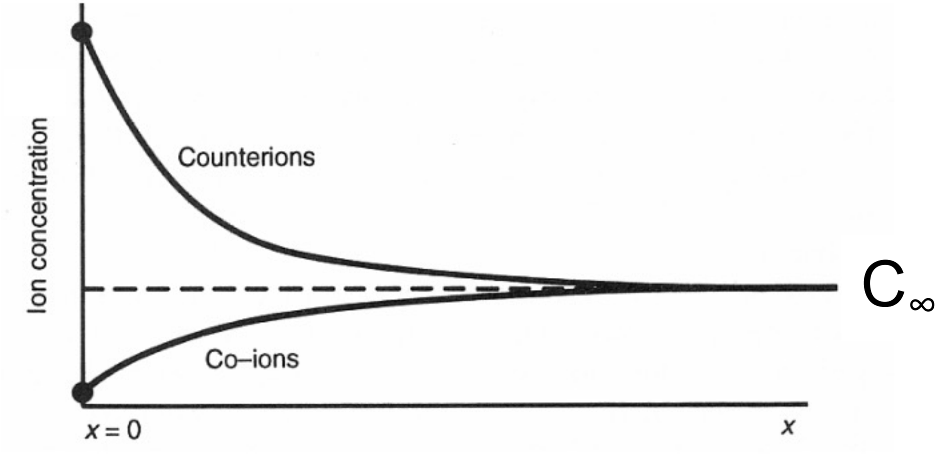
- The **Boltzmann distribution** predicts quantitatively what fraction of the time an entity – whether it is a stone, a gas molecule, or a colloidal particle – will spend in a local position of any given volume, given the energy at that local position.
- For example, we know that **gravitational potential 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 C_i**, the Boltzmann equation says for **ion type i**, that

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

The Boltzmann equation

- Example: NaCl solution

$$C_{Na+}(x) = C_{Na+}(\infty)\exp\left(-\frac{e\Psi(x)}{kT}\right); \qquad C_{Cl-}(x) = C_{Cl-}(\infty)\exp\left(+\frac{e\Psi(x)}{kT}\right)$$



The Poisson-Boltzmann (PB) equation

- The **energy for an ion** due to an **electric field** is **$E_i = z_i e \Psi$**, where in this case the potential is defined to be zero far from the particles, in the bulk solution (**$\Psi_\infty = 0$**).
- This expression for the ion's energy is an **approximation** because it **neglects**, for instance, **the VDW attraction between the ions**. But especially for univalent ions, the approximation works well, and importantly, it gives us an analytical result that we can use to think through EDL problems.
- inserting the Boltzmann expression for concentration into the expression for **charge density ρ_e**, and then the expression for charge density into the Poisson equation, we obtain the full Poisson-Boltzmann equation:

$$\nabla^2 \psi = -\frac{\sum_{i=1}^{N} z_i e c_{i\infty} \exp\left(-\frac{z_i e \psi}{kT}\right)}{\varepsilon}$$

The Poisson-Boltzmann (PB) equation

- Assuming a **symmetric** and **binary Z:Z electrolyte**, like NaCl (1:1) or Ca(SO$_4$) (2:2),

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

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

- The very famous parameter **κ^{-1}** is called "the Debye length". It plays a key role in determining the electrostatic potential near a surface.

the Debye length

Importance of the Debye length = 1/κ

$$\kappa = \left(\sum_i C_{\infty i} e^2 z_i^2 \Big/ \varepsilon \; kT \right)^{1/2} = \left[m^{-1} \right] \quad \rightarrow \quad 1/\kappa = [m]$$

- Relation between charge and potential

$$\rho_s \approx \frac{\varepsilon}{1/\kappa} \psi_0$$

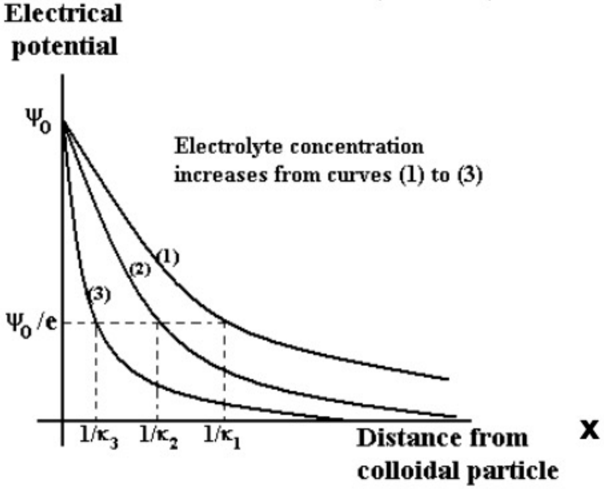
surface charge density (ρ_s [=] C/m^2)

- Similar to a formula for charging of capacitor with distance between the plates = 1/κ

Debye length* 1/κ *is the major estimator of the length of the electrostatic interactions

- Decay of surface potential due to electrolyte

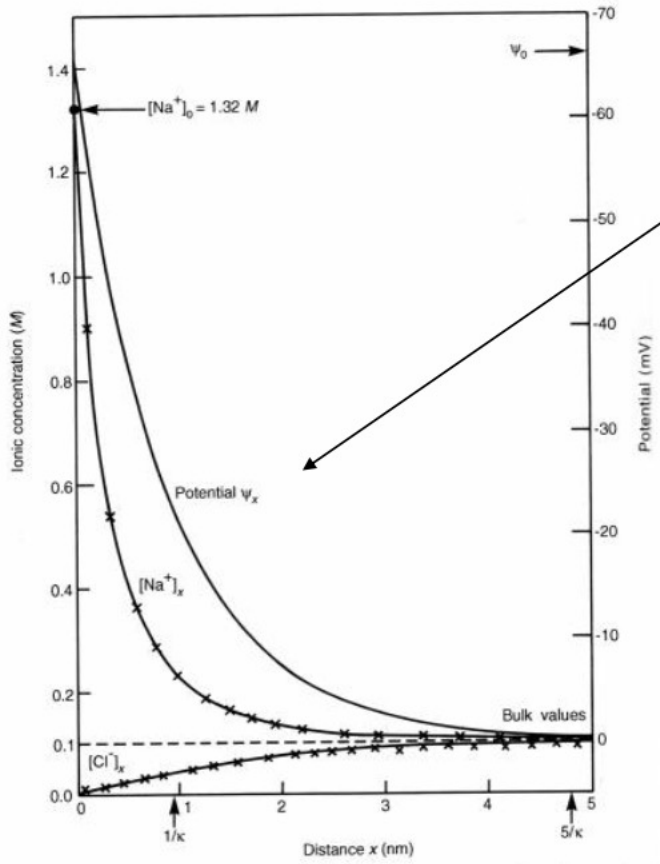
$$\psi(x) \approx \psi_0 \exp\left(-\frac{x}{1/\kappa} \right)$$



- The Debye length is equivalent to the decay length of the curve

the Debye length

Potential decay in the presence of electrolyte



Potential and ionic density profiles for a 0.1 M monovalent electrolyte such as NaCl near a surface of charge density $\sigma = -0.0621\ \text{C m}^{-2}$ (about one electronic charge per 2.6 nm^2), calculated from Eqs (12.39) and (12.25) with $\psi_0 = -66.2$ mV obtained from the Grahame equation. The crosses are the Monte Carlo results of Torrie and Valleau (1979).

- Planar surface at low potentials

$$\psi(x) \approx \psi_0 \exp\left(-\frac{x}{1/\kappa}\right)$$

- Debye length 1/κ is a major estimator for the **range** of the electrostatic interactions near the surface

$$\kappa = \left(\sum_i C_{\infty i} e^2 z_i^2 \Big/ \varepsilon \quad kT\right)^{1/2} = \left[m^{-1}\right]$$

More practical expressions

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

$$I = \frac{1}{2}\sum_i C_{\infty i} z_i^2 \quad [M] \quad \textit{Ionic strength}$$

the Debye length

Expressions and examples for Debye length = 1/κ

$$\kappa = 3.288\sqrt{I} \quad [nm^{-1}] \qquad I = \frac{1}{2}\sum_i C_{\infty i} z_i^2 \quad [M] \quad \textit{Ionic strength}$$

- Useful expressions

$$1/\kappa = \left\{ \begin{array}{ll} 0.304/\sqrt{[\mathrm{NaCl}]}\ \mathrm{nm} & \text{for 1:1 electrolytes (e.g., NaCl)} \\ 0.176/\sqrt{[\mathrm{CaCl_2}]}\ \mathrm{nm} & \text{for 2:1 and 1:2 electrolytes} \\ & \quad (\text{e.g., } \mathrm{CaCl_2} \text{ and } \mathrm{Na_2SO_4}) \\ 0.152/\sqrt{[\mathrm{MgSO_4}]}\ \mathrm{nm} & \text{for 2:2 electrolytes (e.g., } \mathrm{MgSO_4}) \end{array} \right\}$$

- Estimates of the Debye length for a 1:1 electrolyte (e.g. NaCl)

$$1/\kappa =$$

$$\approx 0.3 \text{ nm for } C_{el} = 1\,M \longleftarrow$$ *≈ molecular size – no long-range interactions*

$$\approx 1 \text{ nm for } C_{el} = 0.1\,M$$

$$\approx 10 \text{ nm for } C_{el} = 0.001\,M$$

$$\approx 960 \text{ nm for } C_{el} = 1\times 10^{-7}\,M \longleftarrow$$ *<u>not</u> achievable in normal experimental conditions*

the Debye length

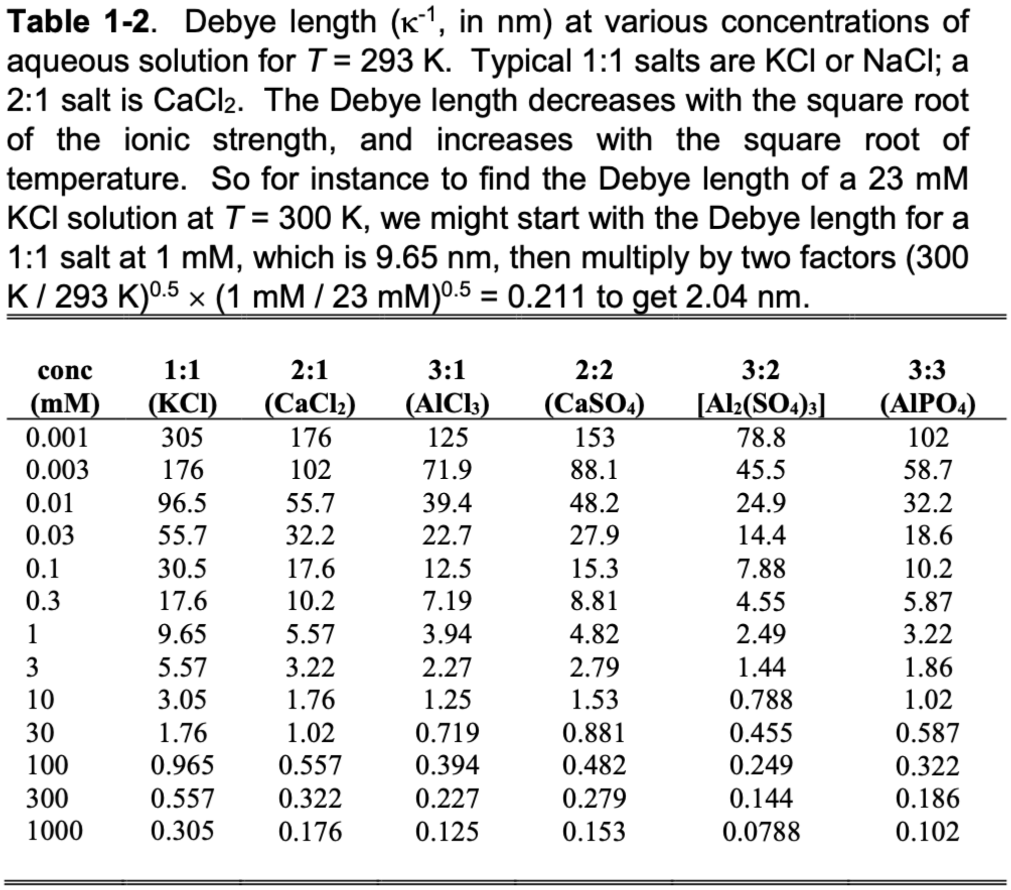


Table 1-2. Debye length (κ^{-1}, in nm) at various concentrations of aqueous solution for T = 293 K. Typical 1:1 salts are KCl or NaCl; a 2:1 salt is $CaCl_2$. The Debye length decreases with the square root of the ionic strength, and increases with the square root of temperature. So for instance to find the Debye length of a 23 mM KCl solution at T = 300 K, we might start with the Debye length for a 1:1 salt at 1 mM, which is 9.65 nm, then multiply by two factors $(300\ \text{K} / 293\ \text{K})^{0.5} \times (1\ \text{mM} / 23\ \text{mM})^{0.5} = 0.211$ to get 2.04 nm.

conc (mM)	**1:1 (KCl)**	**2:1 ($CaCl_2$)**	**3:1 ($AlCl_3$)**	**2:2 ($CaSO_4$)**	**3:2 [$Al_2(SO_4)_3$]**	**3:3 ($AlPO_4$)**
0.001	305	176	125	153	78.8	102
0.003	176	102	71.9	88.1	45.5	58.7
0.01	96.5	55.7	39.4	48.2	24.9	32.2
0.03	55.7	32.2	22.7	27.9	14.4	18.6
0.1	30.5	17.6	12.5	15.3	7.88	10.2
0.3	17.6	10.2	7.19	8.81	4.55	5.87
1	9.65	5.57	3.94	4.82	2.49	3.22
3	5.57	3.22	2.27	2.79	1.44	1.86
10	3.05	1.76	1.25	1.53	0.788	1.02
30	1.76	1.02	0.719	0.881	0.455	0.587
100	0.965	0.557	0.394	0.482	0.249	0.322
300	0.557	0.322	0.227	0.279	0.144	0.186
1000	0.305	0.176	0.125	0.153	0.0788	0.102

The Poisson-Boltzmann (PB) equation

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

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

- PB becomes $\boxed{\nabla^2\left(\frac{Ze\psi}{kT}\right) = \kappa^2\, sinh \frac{Ze\psi}{kT}}$ 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.

Debye-Huckel results for electric potential

- Let's look at the PB equation near to a charged plate, using only the x dimension, where **x = 0** at the **surface** of the plate and extends to infinity.
- Furthermore, we will make an approximation that Ψ is small, less than kT/e = 25.7 mV at room temperature.
- For small values of w, sinh (w) = w + $w^3/6$ + ... ≈ w, and so the PB equation can be approximated as

$$\boxed{\nabla^2\left(\frac{Ze\psi}{kT}\right)=\kappa^2\, sinh\frac{Ze\psi}{kT}} \Longrightarrow \boxed{\frac{d^2\psi}{dx^2}=\kappa^2\psi}$$

- In order to solve the PB equation we need two **boundary conditions**. Two common boundary conditions are

$$x=0:\psi=\psi_0$$
$$x\to\infty:\psi\to 0 \text{ or } d\psi/dx\to 0$$

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):

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

From Lecture 4:

Electrostatic forces

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

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

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:

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

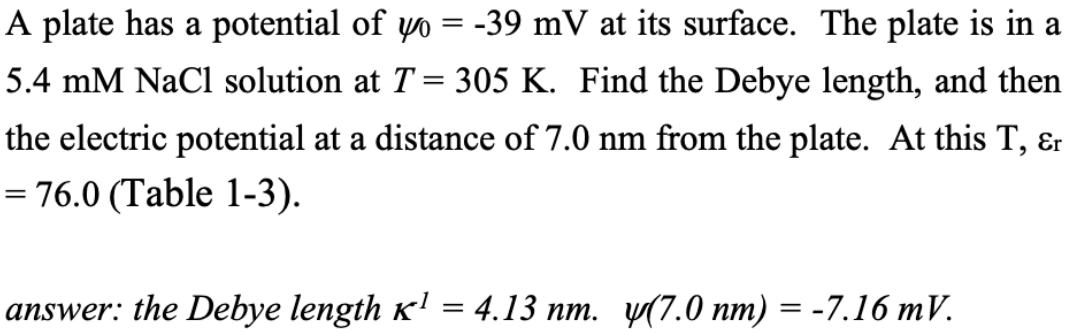
Electrical permittivity

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):

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

- 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 ψ_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, ε_r = 76.0 (Table 1-3).

answer: the Debye length κ^{-1} = *4.13 nm.* ψ*(7.0 nm) = -7.16 mV.*

Debye-Huckel results for electric potential

- **2nd case:** let's look now at the potential around a **spherical particle** of **radius** (**a**). For spherical coordinates

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)=\frac{d^2\psi}{dr^2}+\frac{2}{r}\frac{d\psi}{dr}=\kappa^2\psi$$

$$r=a:\psi=\psi_0$$

$$r\to\infty:\psi\to 0 \text{ or } d\psi/dr\to 0$$

- the **Debye-Huckel equation** for a **sphere** is

$$\boxed{\psi=\psi_0\frac{a}{r}exp[-\kappa(r-a)]}$$

- In fact, if we have a **large sphere**, so that if when we define **x ≡ r - a** we see **x/a ≪ 1**, this reduce to

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

"**flat earth** approximation"

Debye-Huckel results for electric potential

- **3rd 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:

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

Surface charge density

- Oftentimes we want to predict the surface charge density (ρ_s [=] C/m^2), 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

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

Surface charge density

- The condition of **electroneutrality** implies that

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

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

Surface charge density

- Recall the **electric field** at the surface is $E_0 = -\left(\frac{d\Psi}{dx}\right)_0$
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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 $\boxed{\mathbf{E} = -\nabla \psi}$
- 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.

Surface charge density

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- Turning attention to the **ionic concentration**, differentiating the Boltzmann distribution (summing over all species) yields:

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

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

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

Surface charge density

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$$\nabla^2\psi = -\frac{\sum_{i=1}^{N} z_i e c_{i\infty}\, exp\left(-\frac{z_i e\psi}{kT}\right)}{\varepsilon} \Longrightarrow \varepsilon\,\frac{d^2\Psi}{dx^2} = -\sum_i^N z_i e C_{i\infty} exp\left(-\frac{z_i e\Psi}{kT}\right)$$

The Poisson-Boltzmann (PB) equation

- The energy for an ion due to an electric field is $E_i = z_i e \Psi$, where in this case the potential is defined to be zero far from the particles, in the bulk solution.
- This expression for the ion's energy is an approximation because it neglects, for instance, the VDW attraction between the ions. But especially for univalent ions, the approximation works well, and importantly, it gives us an analytical result that we can use to think through EDL problems.
- inserting the Boltzmann expression for concentration into the expression for charge density, and then the expression for charge density into the Poisson equation, we obtain the full Poisson-Boltzmann equation:

$$\nabla^2 \psi = -\frac{\sum_{i=1}^{N} z_i e c_{i\infty} \exp\left(-\frac{z_i e \psi}{kT}\right)}{\varepsilon}$$

Surface charge density

- Recall the **electric field** at the surface is $E_0 = -\left(\frac{d\Psi}{dx}\right)_0$
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- Integrate from x→∞ to x =0:

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

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- Integrate from x→∞ to x =0:

$$\sum_i^N C_{i0} = \sum_i^N C_{i\infty} + \frac{\varepsilon}{2kT}\left(\frac{d\Psi}{dx}\right)_0^2$$

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- Integrate from x→∞ to x =0:

$$\sum_i^N C_{i0} = \sum_i^N C_{i\infty} + \frac{\varepsilon}{2kT}\left(\frac{d\Psi}{dx}\right)_0^2 = \sum_i^N C_{i\infty} + \frac{{\rho_s}^2}{2kT\varepsilon}$$

Surface charge density

- Recall the **electric field** at the surface is $E_0 = -\left(\frac{d\Psi}{dx}\right)_0$
- The condition of **electroneutrality** implies that

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

- 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 from x→∞ to x =0:

$$\boxed{\sum_i^N C_{i0} = \sum_i^N C_{i\infty} + \frac{{\rho_s}^2}{2kT\varepsilon}}$$

Total concentration of ions at an isolated surface of charge density ρ_s

Surface charge density

- To find the relation between the surface charge density ρ$_s$ and the surface potential Ψ$_0$, we invoke the Boltzmann distribution again:

$$\boxed{\sum_{i}^{N} C_{i0} = \sum_{i}^{N} C_{i\infty} + \frac{{\rho_s}^2}{2kT\varepsilon}}$$

Total concentration of ions at an isolated surface of charge density ρ$_s$

Surface charge density

Sometimes referred to as the **Grahame equation**

- To find the relation between the surface charge density ρ$_s$ and the surface potential Ψ$_0$, we invoke the Boltzmann distribution again:

$$\rho_s^2 = 2\varepsilon kT\left(\sum_i^N C_{i0} - \sum_i^N C_{i\infty}\right) = 2\varepsilon kT\left(\sum_i^N C_{i\infty} exp\left(-\frac{z_i e\Psi_0}{kT}\right) - \sum_i^N C_{i\infty}\right)$$

$$\sum_i^N C_{i0} = \sum_i^N C_{i\infty} + \frac{\rho_s^2}{2kT\varepsilon}$$

Total concentration of ions at an isolated surface of charge density ρ$_s$

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

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- To make the math simpler, let's consider a Z:Z salt, say NaCl if Z ≡ |z$_i$| = 1 and $C_{i\infty}$ = $[Na^+]_\infty$ = $[Cl^-]_\infty$ = $[NaCl]_\infty$ = C_∞

$$\rho_s{}^2 = 2\varepsilon kTC_\infty\left(exp\left(\frac{Ze\Psi_0}{kT}\right) + exp\left(\frac{-Ze\Psi_0}{kT}\right) - 2\right)$$

Surface charge density

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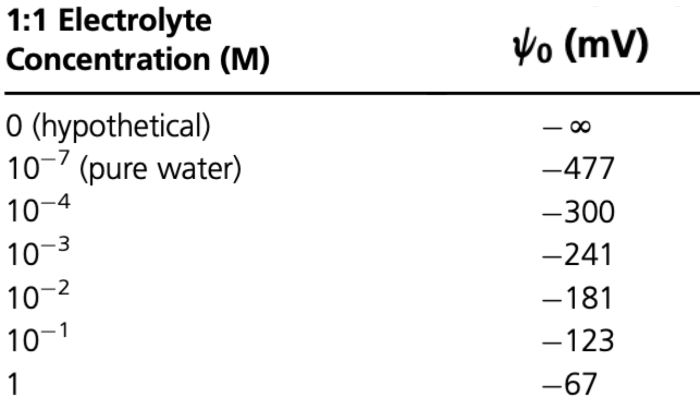
For an aqueous 1:1 electrolyte such as NaCl against a negatively charged surface of $\rho_s = -0.2\ \mathrm{C\ m^{-2}}$:



1:1 Electrolyte Concentration (M)	ψ_0 **(mV)**
0 (hypothetical)	$-\infty$
10^{-7} (pure water)	−477
10^{-4}	−300
10^{-3}	−241
10^{-2}	−181
10^{-1}	−123
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Surface charge density

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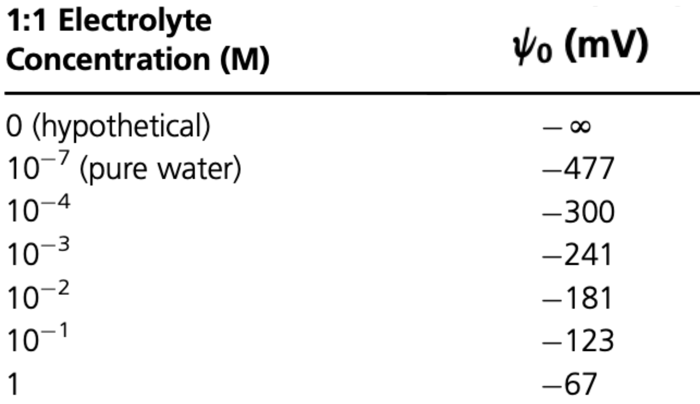

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- Note that for **no electrolyte** we obtain an **infinite potential**, which is unrealistic; a pure liquid such as water will always contain some dissociated ions.

If $C_\infty \rightarrow 0$, Ψ_0 needs to approach ∞ in order to maintain constant charge density ρ_s

Surface charge density

Sometimes referred to as the **Grahame equation**

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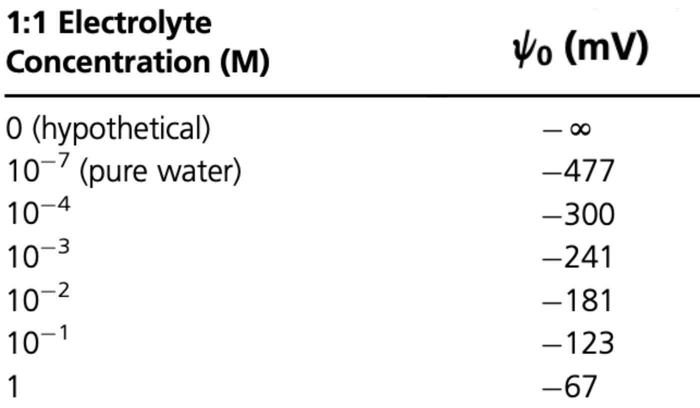

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- Note that for **no electrolyte** we obtain an **infinite** potential, which is unrealistic; a pure liquid such as water will always contain some dissociated ions.
- At **constant** surface charge density the surface potential **falls** progressively as the **electrolyte concentration rises**.

Surface charge density

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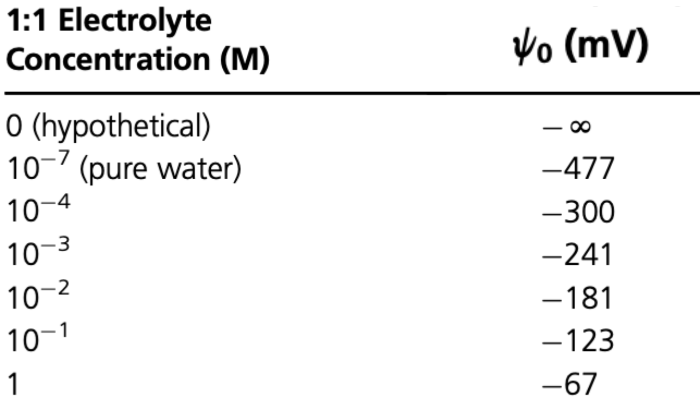
For an aqueous 1:1 electrolyte such as NaCl against a negatively charged surface of $\rho_s = -0.2$ C m^{-2}:

From the tabulated values of Ψ_0 we can determine the **ionic concentrations at the surface** using Boltzmann distribution:



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Surface charge density

Sometimes referred to as the **Grahame equation**

- To find the relation between the surface charge density ρ_s and the surface potential Ψ_0, we invoke the Boltzmann distribution again:

$$\boxed{\rho_s{}^2 = 2\varepsilon kT\left(\sum_i^N C_{i0} - \sum_i^N C_{i\infty}\right) = 2\varepsilon kT\left(\sum_i^N C_{i\infty} exp\left(-\frac{z_i e\Psi_0}{kT}\right) - \sum_i^N C_{i\infty}\right)}$$

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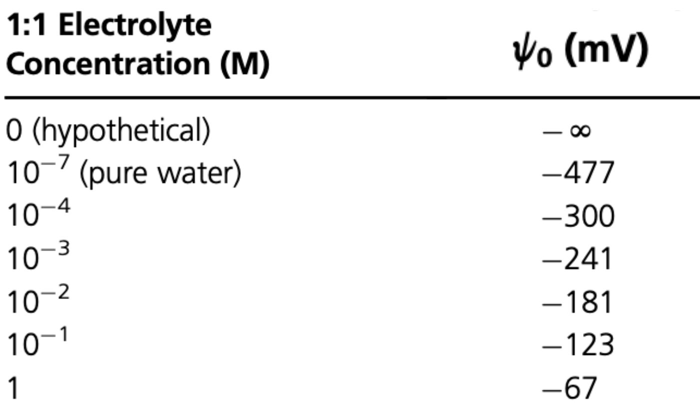

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From the tabulated values of Ψ_0 we can determine the **ionic concentrations at the surface** using Boltzmann distribution:

- in 10^{-7} M 1:1 electrolyte, where Ψ_0 = -477.1 mV, the counterion concentration at the surface is 11.64 M and 10^{-15} M for the co-ions. (total surface ion conc. ~11.64 M ≈ excess ion conc.)
- At 1 M, Ψ_0 = -67 mV, the surface conc. are 13.57 M and 0.07 M for counter- and co-ions. (total ~ 13.64 M, excess ~11.64M)

Surface charge density

Sometimes referred to as the **Grahame equation**

- To find the relation between the surface charge density ρ_s and the surface potential Ψ_0, we invoke the Boltzmann distribution again:

$$\boxed{\rho_s^{\,2} = 2\varepsilon kT\left(\sum_i^N C_{i0} - \sum_i^N C_{i\infty}\right) = 2\varepsilon kT\left(\sum_i^N C_{i\infty} exp\left(-\frac{z_i e\Psi_0}{kT}\right) - \sum_i^N C_{i\infty}\right)}$$

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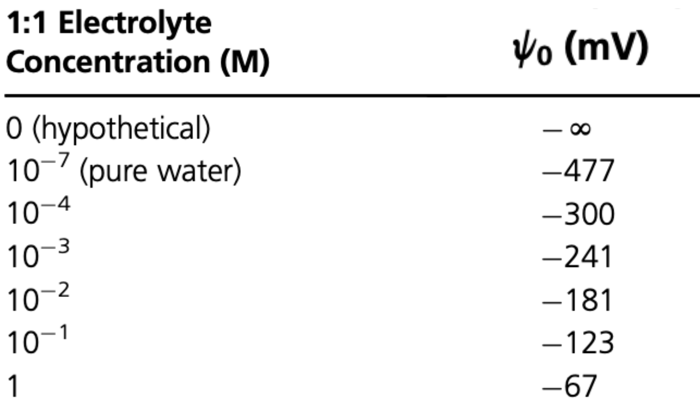

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the total ion concentration at the surface can be calculated as before, and the **excess** to **bulk** is set by ρ_s only.

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Surface charge density

- Recall the electric field at the surface is $E_0 = -\left(\frac{d\Psi}{dx}\right)_0$
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$$\rho_s = \varepsilon\left[\left(\frac{d\Psi}{dx}\right)_{x\to\infty} - \left(\frac{d\Psi}{dx}\right)_{x=0}\right] = \varepsilon\left[0 - \left(\frac{d\Psi}{dx}\right)_0\right] = -\varepsilon\left(\frac{d\Psi}{dx}\right)_0 = \varepsilon E_0$$

- 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:

$$\boxed{\sum_i^N C_{i0} = \sum_i^N C_{i\infty} + \frac{{\rho_s}^2}{2kT\varepsilon}}$$

Total concentration of ions at an isolated surface of charge density ρ$_s$

Surface charge density

Sometimes referred to as the **Grahame equation**

↑

- To find the relation between the surface charge density ρ_s and the surface potential Ψ_0, we invoke the Boltzmann distribution again:

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$${\rho_s}^2 = 2\varepsilon kTC_\infty\left(exp\left(\frac{Ze\Psi_0}{kT}\right) + exp\left(\frac{-Ze\Psi_0}{kT}\right) - 2\right)$$

- This can be factored into

$${\rho_s}^2 = 2\varepsilon kTC_\infty\left(exp\left(\frac{Ze\Psi_0}{2kT}\right) - exp\left(\frac{-Ze\Psi_0}{2kT}\right)\right)^2$$

In other words,

$$\rho_s = \sqrt{2\varepsilon kTC_\infty}\left(exp\left(\frac{Ze\Psi_0}{2kT}\right) - exp\left(\frac{-Ze\Psi_0}{2kT}\right)\right)$$

Surface charge density

- For **low** surface potentials (Ψ_0 < **25 mV**), use Taylor series $e^w = 1 + w + w^2/2 + \ldots$

$$\rho_s = \sqrt{2\varepsilon kTC_\infty}\left(\left(1 + \frac{Ze\Psi_0}{2kT} + \cdots\right) - \left(1 - \frac{Ze\Psi_0}{2kT} + \cdots\right)\right)$$

$$\rho_s \approx \sqrt{2\varepsilon kTC_\infty}\left(\frac{Ze\Psi_0}{kT}\right) = \sqrt{\frac{2\varepsilon C_\infty}{kT}}Ze\Psi_0$$

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- For the general case (where Z:Z is not a requirement, say $CaCl_2$ or mixtures of NaCl and $CaCl_2$) at **low** surface potentials ($\Psi_0 < \mathbf{25\ mV}$), the **Grahame equation** simplifies to

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

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Check for yourself that these two equations are indeed equivalent for Z:Z salts like NaCl

Surface charge density

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$$\rho_s = \sqrt{2\varepsilon kTC_\infty}\left(\left(1+\frac{Ze\Psi_0}{2kT}+\cdots\right)-\left(1-\frac{Ze\Psi_0}{2kT}+\cdots\right)\right)$$

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

And we recover the famous Debye length $\boldsymbol{\kappa}^{-1}$

- Which can be rewritten as: $\rho_s = \varepsilon\kappa\Psi_0$, where $\kappa \equiv \sqrt{\sum_i^N \frac{{z_i}^2 e^2 C_{i\infty}}{\varepsilon kT}}$

The Poisson-Boltzmann (PB) equation

- Assuming a symmetric and binary Z:Z electrolyte, like NaCl (1:1) or Ca(SO$_4$) (2:2),

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

- PB becomes $\boxed{\nabla^2\left(\frac{Ze\psi}{kT}\right) = \kappa^2 \sinh\frac{Ze\psi}{kT}}$ 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.

Check for yourself that these two Debye length $\boldsymbol{\kappa}^{-1}$ are indeed the same for Z:Z electrolytes

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

Surface charge density

- For **low** surface potentials (Ψ_0 < **25 mV**), use Taylor series $e^{w} = 1 + w + w^2/2 + \ldots$

$$\rho_s = \sqrt{2\varepsilon kTC_\infty}\left(\left(1+\frac{Ze\Psi_0}{2kT}+\cdots\right)-\left(1-\frac{Ze\Psi_0}{2kT}+\cdots\right)\right)$$

$$\rho_s \approx \sqrt{2\varepsilon kTC_\infty}\left(\frac{Ze\Psi_0}{kT}\right) = \sqrt{\frac{2\varepsilon C_\infty}{kT}}Ze\Psi_0$$

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- Which can be rewritten as:

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

From Lecture 4:

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

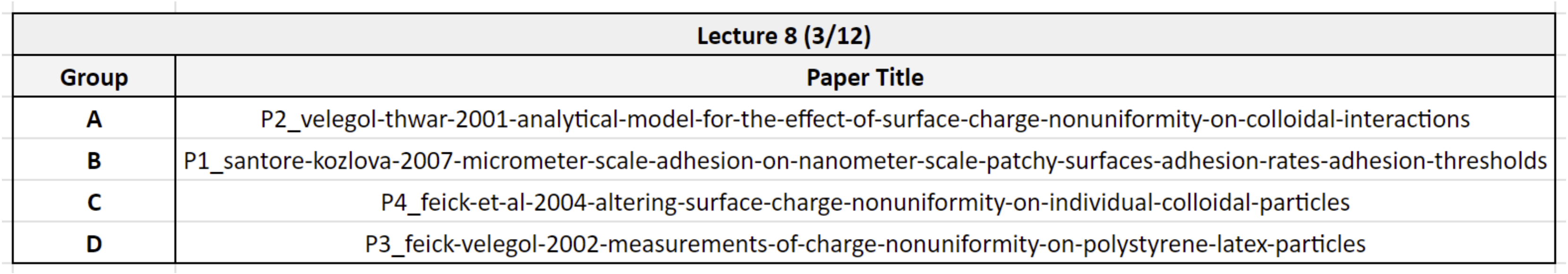
Distance from the surface

- 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:

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

Electrical permittivity

Journal club assignment for Lecture 8



Lecture 8 (3/12)	
Group	Paper Title
A	P2_velegol-thwar-2001-analytical-model-for-the-effect-of-surface-charge-nonuniformity-on-colloidal-interactions
B	P1_santore-kozlova-2007-micrometer-scale-adhesion-on-nanometer-scale-patchy-surfaces-adhesion-rates-adhesion-thresholds
C	P4_feick-et-al-2004-altering-surface-charge-nonuniformity-on-individual-colloidal-particles
D	P3_feick-velegol-2002-measurements-of-charge-nonuniformity-on-polystyrene-latex-particles