Light, Liquids & Interfaces
Micro-390

Lecture 4

Sylvie Roke

Organizational comments

Upcoming:

Nov. 7 - Week 8: Intermediate Test (ELG 116)

Key concepts Lecture 3

- The interaction energy is the average sum of all interactions for a given molecule; depends on position
- The pair potential (w): interaction energy between a pair
- Relationship between interaction energy and pair potential
- Importance of kT

- Properties of covalent bonds
- Force relevant for charge-charge interactions
- Properties of Coulombic interactions
- The Born energy and its use

Topic 2: Driving forces and interactions in liquids

Overview

Covalent interactions

- Interactions involving charges
- Interactions involving polar molecules

Interactions involving non-polar groups

Material to study for Topic 2: Chapters 3-6:
JN Israelachvili: Intermolecular and surface forces:
Notes & Chapter 3: paragraphs: 3.1 – 3.8
Notes & Chapter 4: paragraphs: 4.1 – 4.7; 4.9-4.11
Notes & Chapter 5: paragraphs: 5.1 - 5.4; 5.6;
Notes & Chapter 6: paragraph: 6.1;

Topic 2: Driving forces and interactions in liquids

Lecture 4:

Interactions involving charges:
Ion-ion interactions in crystals (exercise 9)
Ion-ion interactions in liquids: Debye-Hückel theory (ex. 10,11)

Material to study for Lecture 3:
JN Israelachvili: Intermolecular and surface forces:
Chapter 3.1 – 3.8

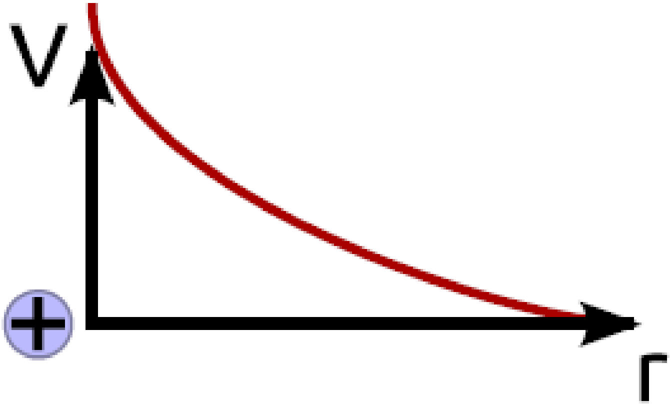
Ion – ion interactions in liquids: Debye-Hückel theory

Review from course MSE304 by M. Ceriotti

Screening in ionic solutions: Debye-Hückel theory

- Electric potential induced by an ion in a dielectric medium
  - Other ions interact with this potential
  - Mean-field model: ion distribution represented by a Boltzmann density
  - Can be solved analytically if **linearized**

$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$



Screening in ionic solutions: Debye-Hückel theory

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  - Mean-field model: ion distribution represented by a Boltzmann density
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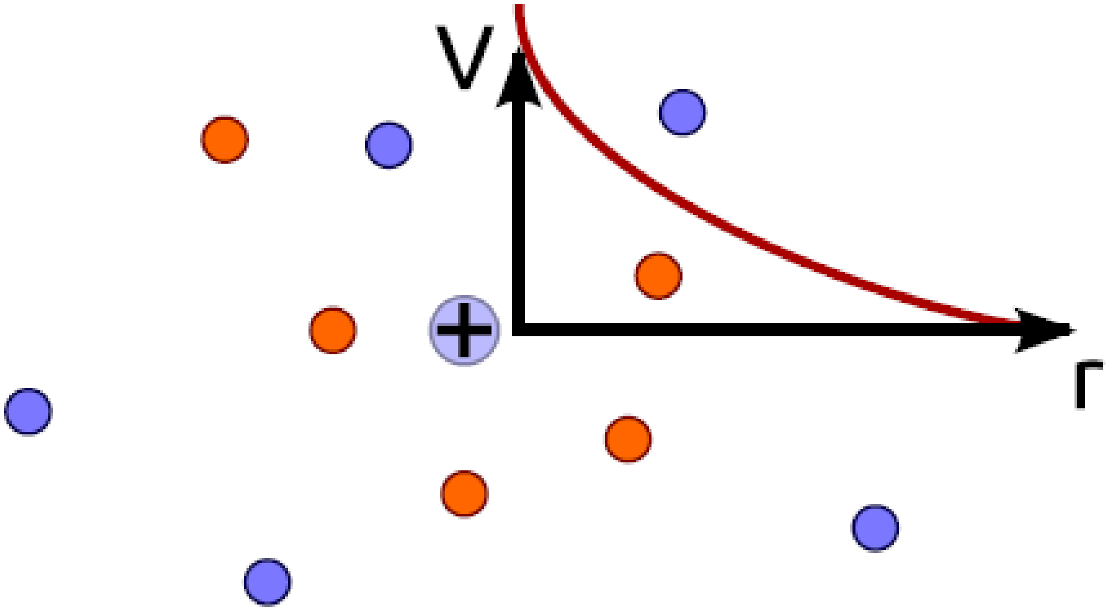
$$U^0_{\pm}(r) = e z_{\pm} \psi_0(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\frac{z_{\pm} z_{+}}{r}$$



Screening in ionic solutions: Debye-Hückel theory

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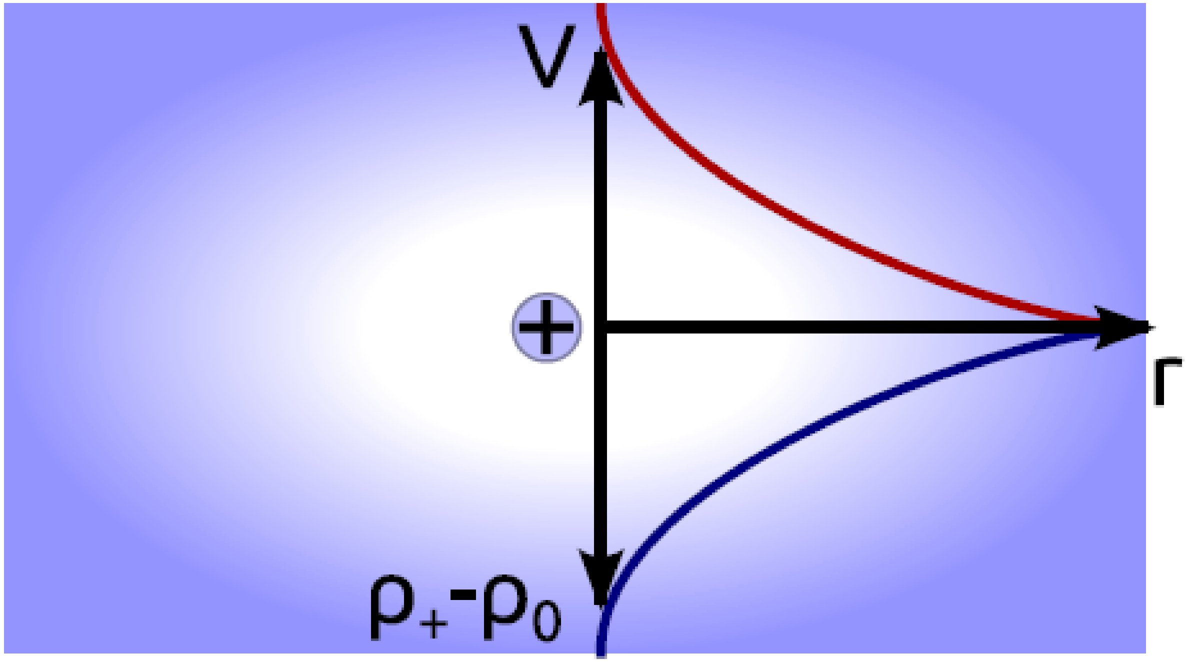
$$\rho_\pm = e n_0 e^{-z_\pm \psi(r)/kT}$$



$$\boldsymbol{E}(\boldsymbol{r}) = -\boldsymbol{\nabla}\psi(\boldsymbol{r})$$ Definition of electrostatic potential

$$\boldsymbol{\nabla} \cdot \boldsymbol{E}(\boldsymbol{r}) = \frac{\rho(\boldsymbol{r})}{\varepsilon_0 \varepsilon}$$ Gauss' Law

+

$$\nabla^2 \psi(\boldsymbol{r}) = -\frac{\rho(\boldsymbol{r})}{\varepsilon_0 \varepsilon}$$ Poisson equation

Screening in ionic solutions: Debye-Hückel theory

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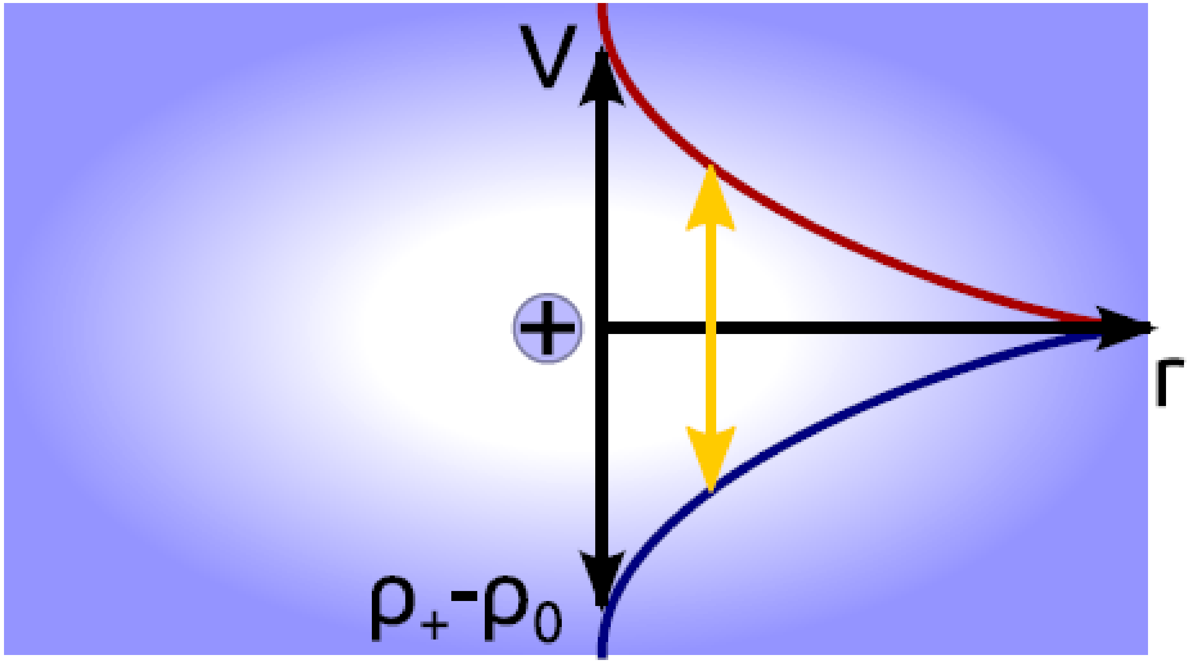
$$\nabla^2\psi = -\frac{\rho}{\epsilon_0\epsilon_r} = -\frac{e}{\epsilon_0\epsilon_r}\left[z_+\rho_+ + z_-\rho_-\right]$$



Screening in ionic solutions: Debye-Hückel theory

- Electric potential induced by an ion in a dielectric medium
  - Other ions interact with this potential
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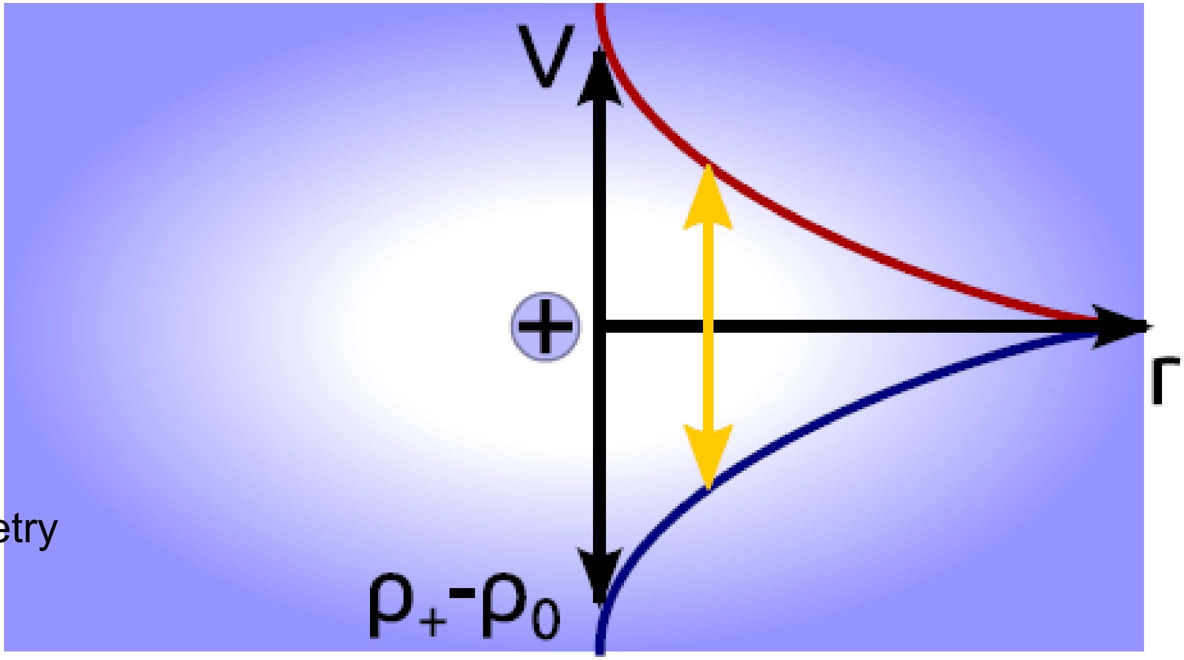
Question 10

$$\nabla^2\psi = -\frac{eC}{\epsilon_0\epsilon_r}\left[z_+n_+e^{-\frac{ez_+}{k_BT}\psi} + z_-n_-e^{-\frac{ez_-}{k_BT}\psi}\right] \overset{\downarrow}{\approx} \frac{e}{\epsilon_0\epsilon_r}\frac{eC}{k_BT}\left[n_+z_+^2 + n_-z_-^2\right]\psi = \kappa^2\psi$$



C = constant that is determined by the symmetry / asymmetry of electrolyte; 1:1 electrolyte, C=2

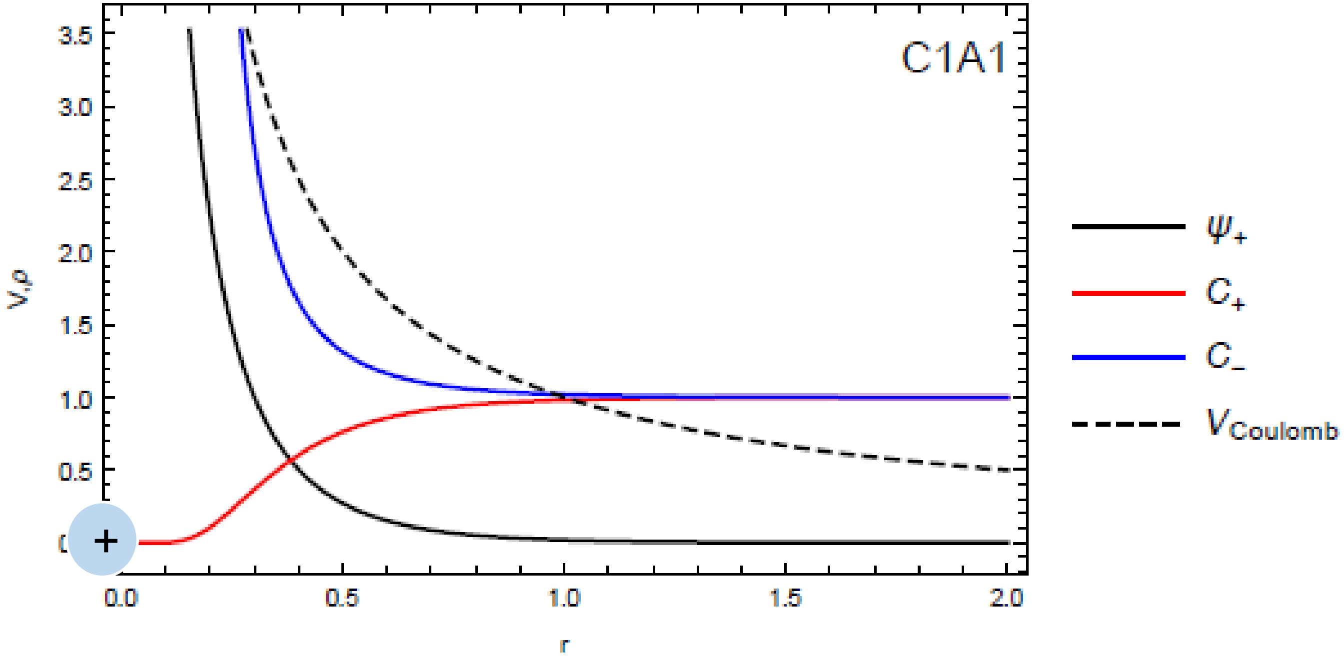
Solving the Poisson-Boltzmann equation for a ion

- The (radial) Laplacian in spherical coordinates:

$$\nabla^2 \equiv \frac{\partial^2 \cdot}{\partial r^2} + \frac{2}{r}\frac{\partial \cdot}{\partial r}$$

- Solving the Poisson-Boltzmann equation.

$$\psi(r) = \frac{e z_+}{4\pi\epsilon_0\epsilon_r}\frac{e^{-\kappa r}}{r}, \qquad \kappa^2 = \frac{e^2 C}{\epsilon_0\epsilon_r}\frac{n_+ z_+^2 + n_- z_-^2}{k_B T}$$



Ions in solution

Potential around a positive ion $\psi(r) = \dfrac{e\, e^{-\kappa r}}{4\pi\varepsilon_0 \varepsilon r} \longleftarrow$ κ = decay constant

$$\kappa = \sqrt{\frac{2e^2 \mathrm{n}_0}{(\varepsilon_0 \varepsilon k T)}} = \sqrt{\frac{2e^2 \mathrm{N}_{\mathrm{av}} 1000\ \mathrm{I}}{(\varepsilon_0 \varepsilon k T)}}$$

Debye screening parameter for a monovalent symmetric electrolyte

$1/\kappa$ Debye length [m]

n_0 Number density of ions in bulk solution [# / m^3]

I Ionic Strength [M]

$$I = \frac{1}{2} \sum_i c_i\, z_i^2$$

Takes into account both the number of ions (c [M]) as well as the charge per ion – better representation of the effect of an electrolyte than the concentration

Ions in solution

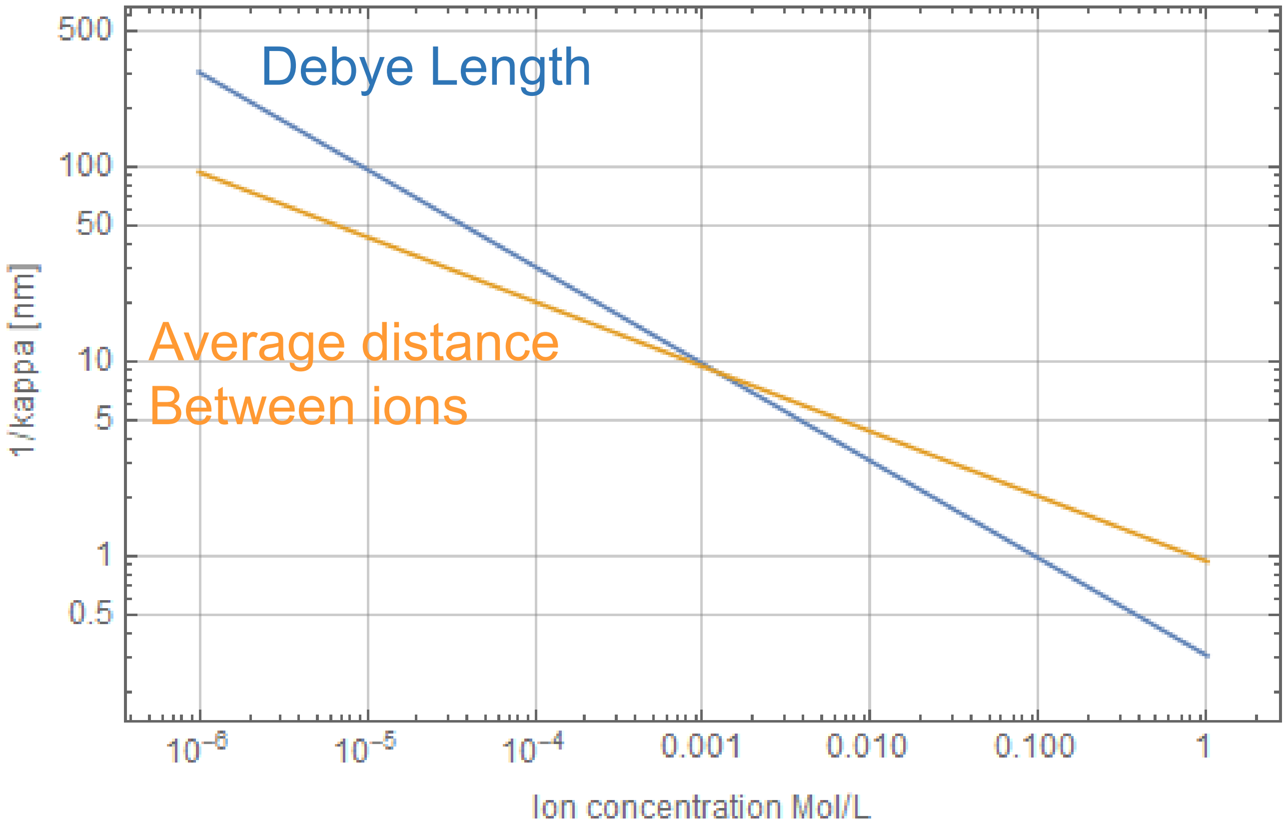
Potential around a positive ion $\psi(r) = \dfrac{e\, e^{-\kappa r}}{4\pi\varepsilon_0 \varepsilon r} \longleftarrow$ κ = decay constant

$$\kappa = \sqrt{\frac{2e^2 \mathrm{n}_0}{(\varepsilon_0 \varepsilon k T)}} = \sqrt{\frac{2e^2 \mathrm{N_{av}} 1000\ \mathrm{I}}{(\varepsilon_0 \varepsilon k T)}}$$

Debye screening parameter for a monovalent symmetric electrolyte

$1/\kappa$ Debye length [m]

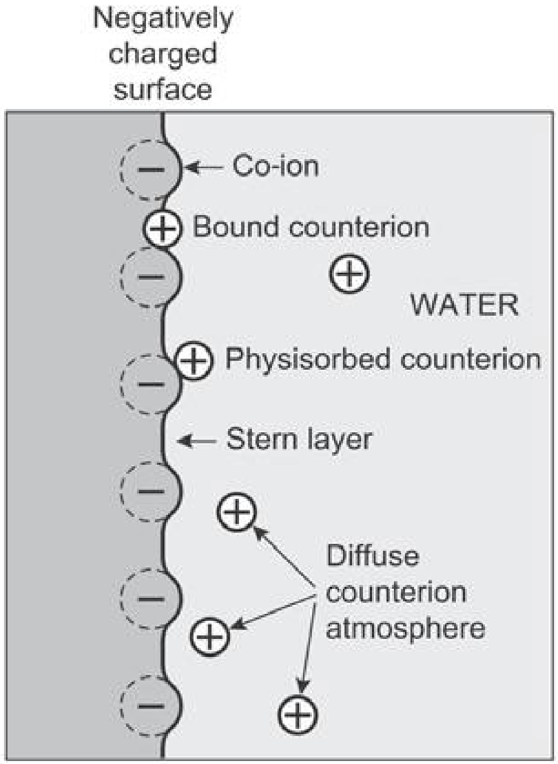
1:1 electrolyte

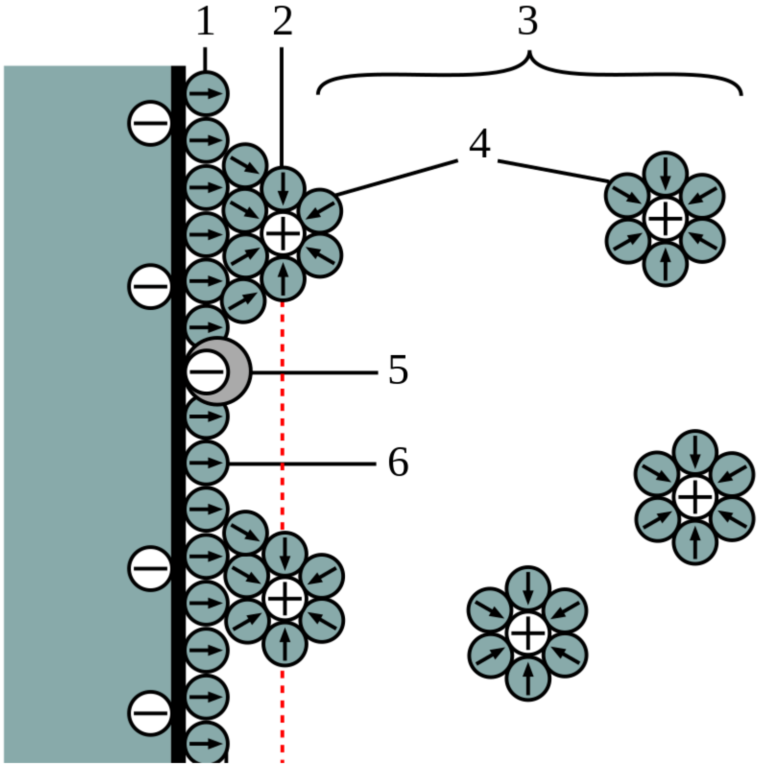


Examples:

Salting in and salting out
Self-assembly
Interfaces

Interfaces

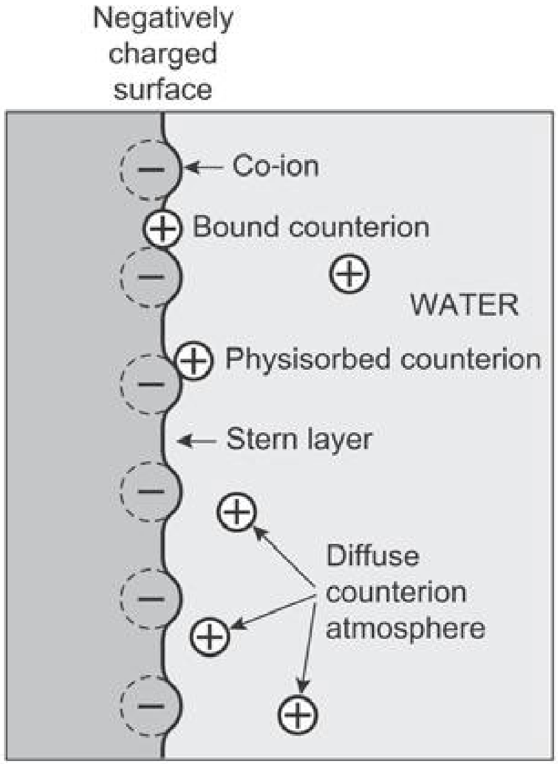


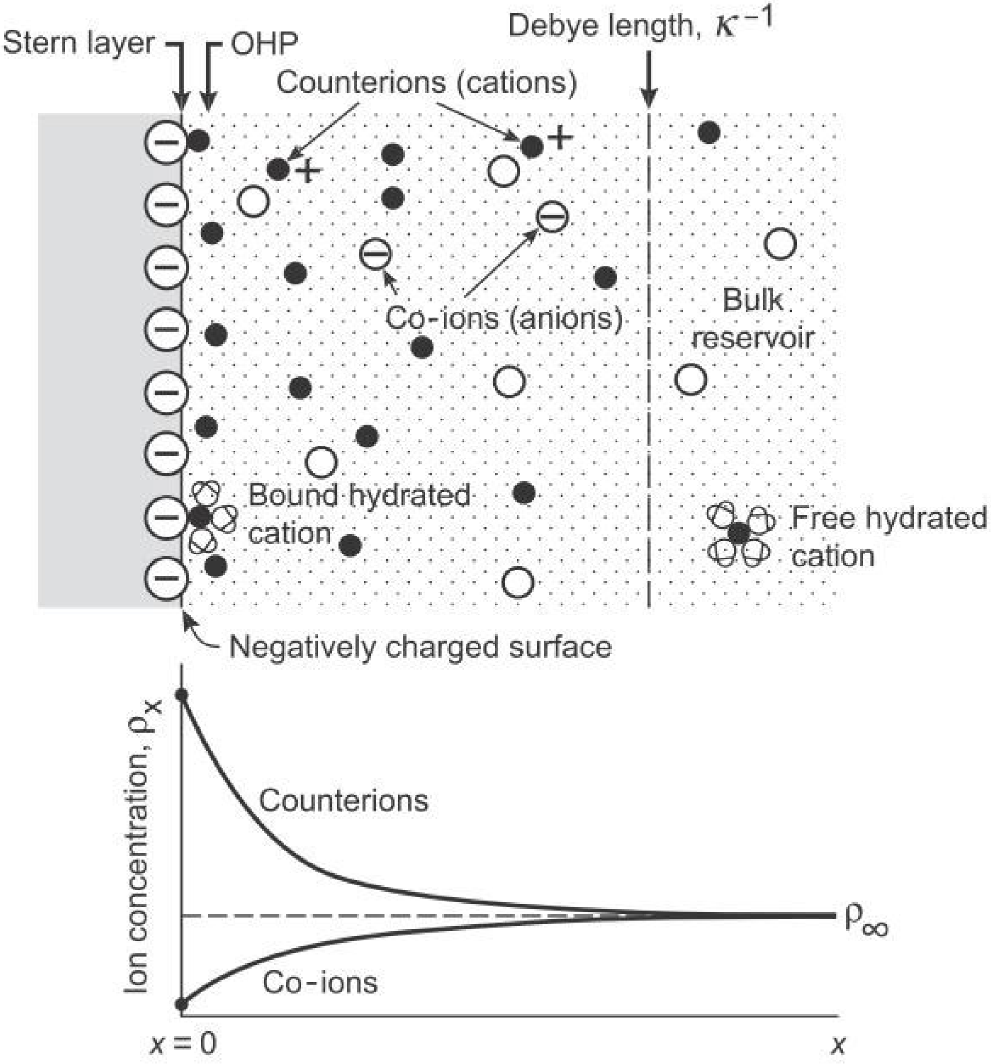


Typical representation of an electrode in a solution

1. Inner Helmholtz plane (IHP), center of solvent adsorbed to surface
2. Outer Helmholtz plane (OHP), centers of hydrated counter ions
3. Diffuse layer,
4. Solvated ions (cations)
5. Specifically adsorbed co-ions
6. Molecules of the solvent

Interfaces


Negatively charged surface
Co-ion
Bound counterion
WATER
Physisorbed counterion
Stern layer
Diffuse counterion atmosphere


Stern layer
OHP
Debye length, κ^{-1}
Counterions (cations)
Co-ions (anions)
Bulk reservoir
Bound hydrated cation
Free hydrated cation
Negatively charged surface
Ion concentration, ρ_x
Counterions
Co-ions
ρ_∞
$x = 0$
x

Topic 2: Driving forces and interactions in liquids

Overview
Covalent interactions
Interactions involving charges:
Ion-ion interactions in crystals
Ion-ion interactions in liquids – Debye-Hückel theory

Material to study, lecture 3:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 3.1 – 3.8

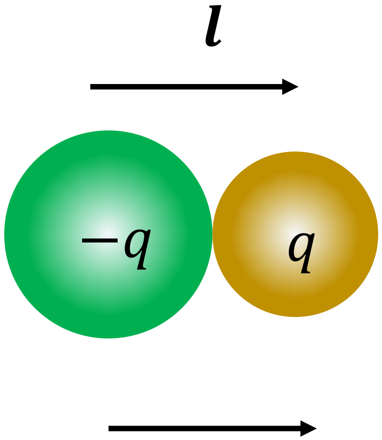
Topic 2: Driving forces and interactions in liquids

Interactions involving polar molecules
Charge-dipole interactions
Hydration shells
Angle averaged potentials

JN Israelachvilli: Intermolecular and surface forces:
Chapter 4: paragraphs: 4.1-4.7; 4.9-4.11.

Polar molecules

All heteronuclear groups are (di)polar:

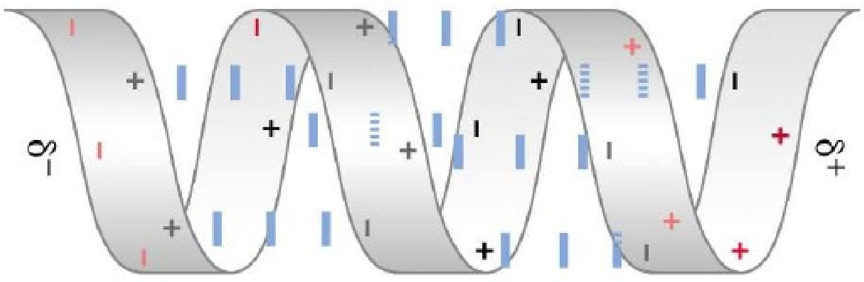


$$\boldsymbol{u} = \boldsymbol{l}q$$

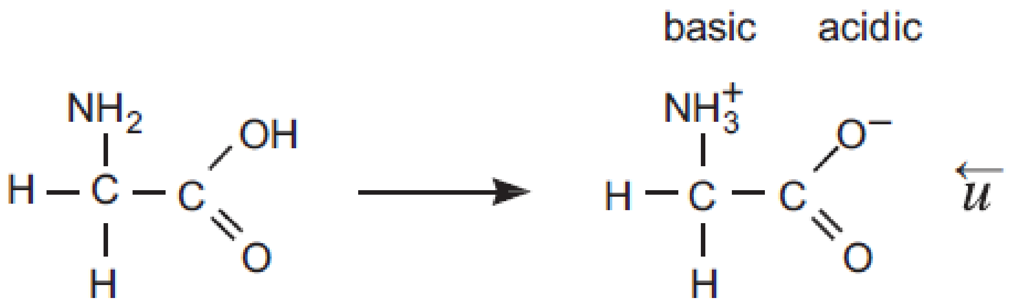
Unit: Debye [D]
1 D = 3.33 10^{-30} Cm

Dipole increase with increasing difference in electronegativity

Dipoles in molecules



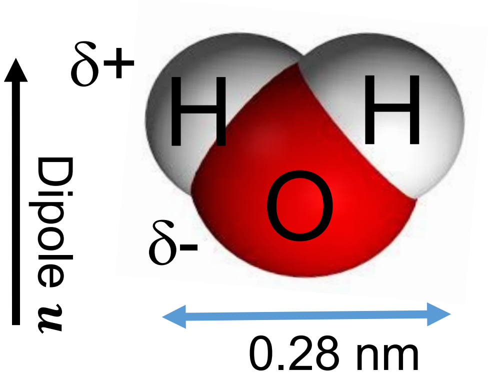
Macromolecular dipoles (proteins, DNA, RNA,..)



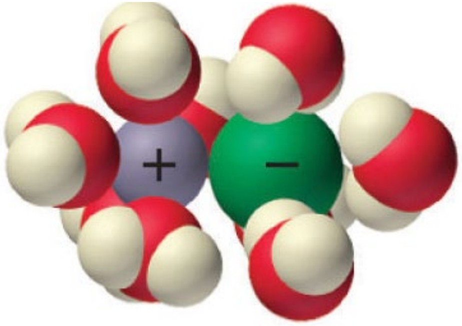
Glycine

Glycine in water

Dipole moment also in molecular ions



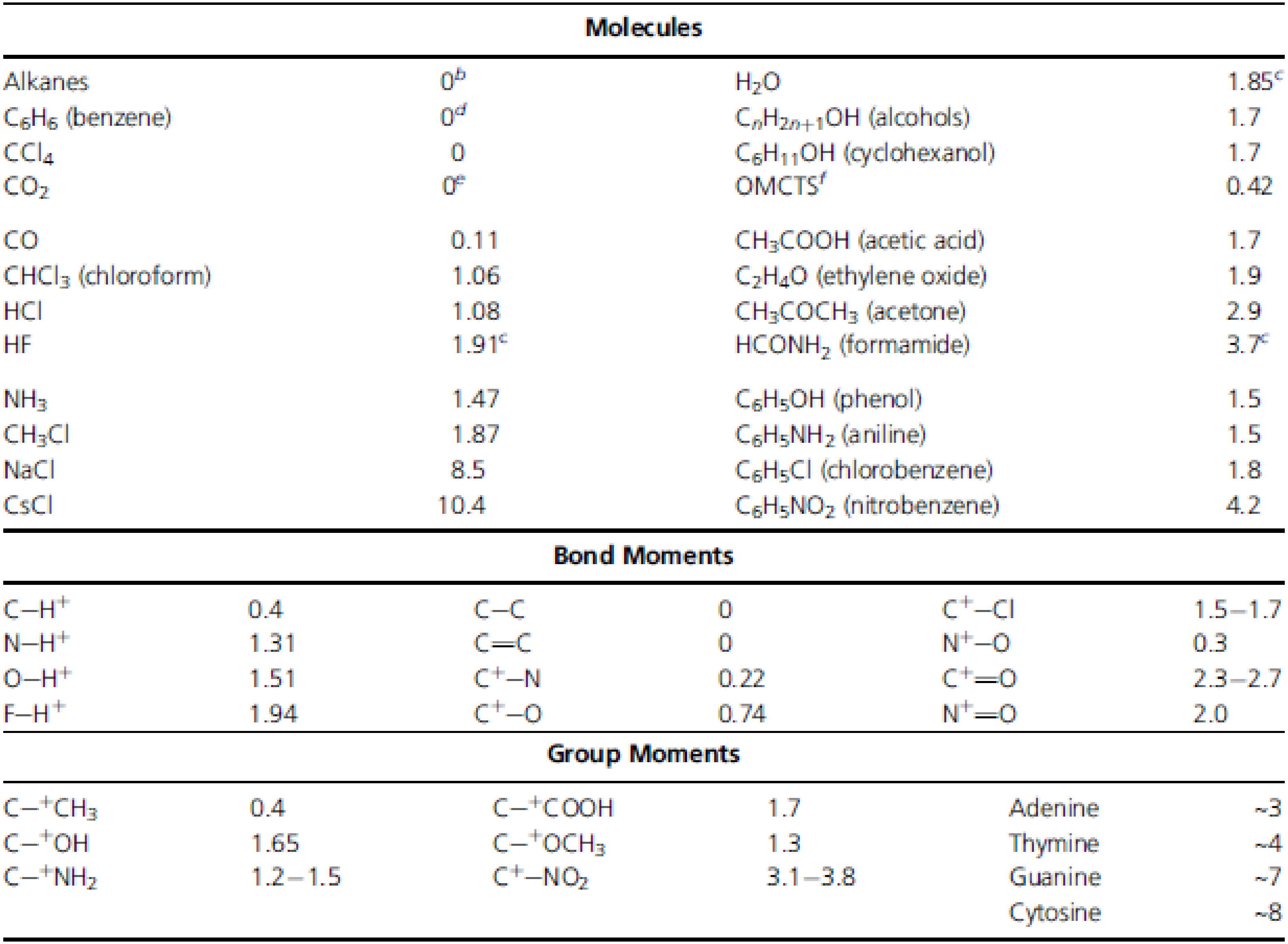
Water:
u=1.85 D
(gas phase)



ion pair

Ion pairs in solution

Dipole moments [D]



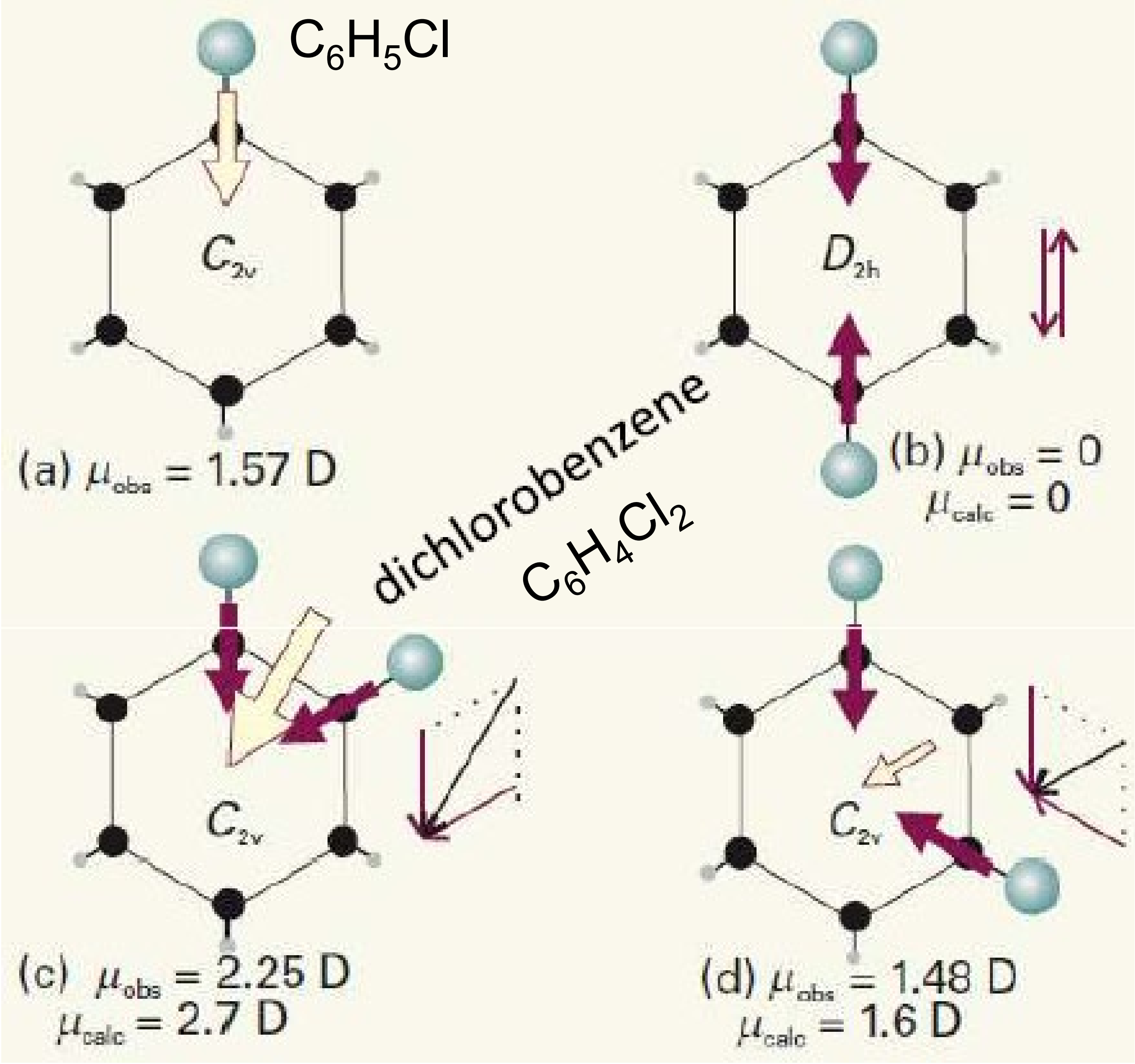
Molecules			
Alkanes	0[b]	H_2O	1.85[c]
C_6H_6 (benzene)	0[d]	$C_nH_{2n+1}OH$ (alcohols)	1.7
CCl_4	0	$C_6H_{11}OH$ (cyclohexanol)	1.7
CO_2	0[e]	OMCTS[f]	0.42
CO	0.11	CH_3COOH (acetic acid)	1.7
$CHCl_3$ (chloroform)	1.06	C_2H_4O (ethylene oxide)	1.9
HCl	1.08	CH_3COCH_3 (acetone)	2.9
HF	1.91[c]	$HCONH_2$ (formamide)	3.7[c]
NH_3	1.47	C_6H_5OH (phenol)	1.5
CH_3Cl	1.87	$C_6H_5NH_2$ (aniline)	1.5
NaCl	8.5	C_6H_5Cl (chlorobenzene)	1.8
CsCl	10.4	$C_6H_5NO_2$ (nitrobenzene)	4.2

Bond Moments					
$C{-}H^+$	0.4	$C{-}C$	0	$C^+{-}Cl$	1.5–1.7
$N{-}H^+$	1.31	$C{=}C$	0	$N^+{-}O$	0.3
$O{-}H^+$	1.51	$C^+{-}N$	0.22	$C^+{=}O$	2.3–2.7
$F{-}H^+$	1.94	$C^+{-}O$	0.74	$N^+{=}O$	2.0

Group Moments					
$C{-}^+CH_3$	0.4	$C{-}^+COOH$	1.7	Adenine	~3
$C{-}^+OH$	1.65	$C{-}^+OCH_3$	1.3	Thymine	~4
$C{-}^+NH_2$	1.2–1.5	$C^+{-}NO_2$	3.1–3.8	Guanine	~7
				Cytosine	~8

Dipole moments add up as vectors

Dipoles in molecules



Dipoles are additive by vector addition

Dipolar Self-Energy

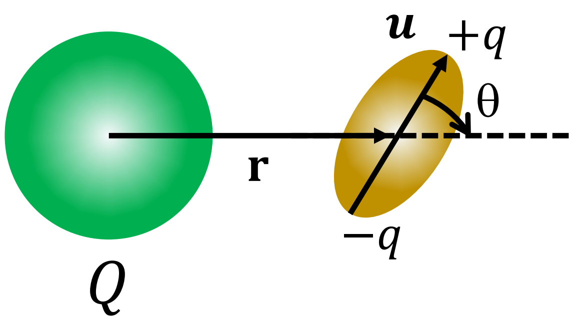
Just like the Born energy it requires energy to create a dipole

The procedure to compute the self energy of a dipole is identical to that of an ion; we compute the self energy of 2 displaced charged objects and add their contributions – because of the superposition principle of electrostatics.

$$\mu^i = \frac{u^2}{4\pi\varepsilon_0\varepsilon l^3}$$

Charge dipole interactions

Are important to understand dipolar liquid – ion interactions



$$\boldsymbol{u} = \boldsymbol{l}q$$

Interaction potentials can be summed:

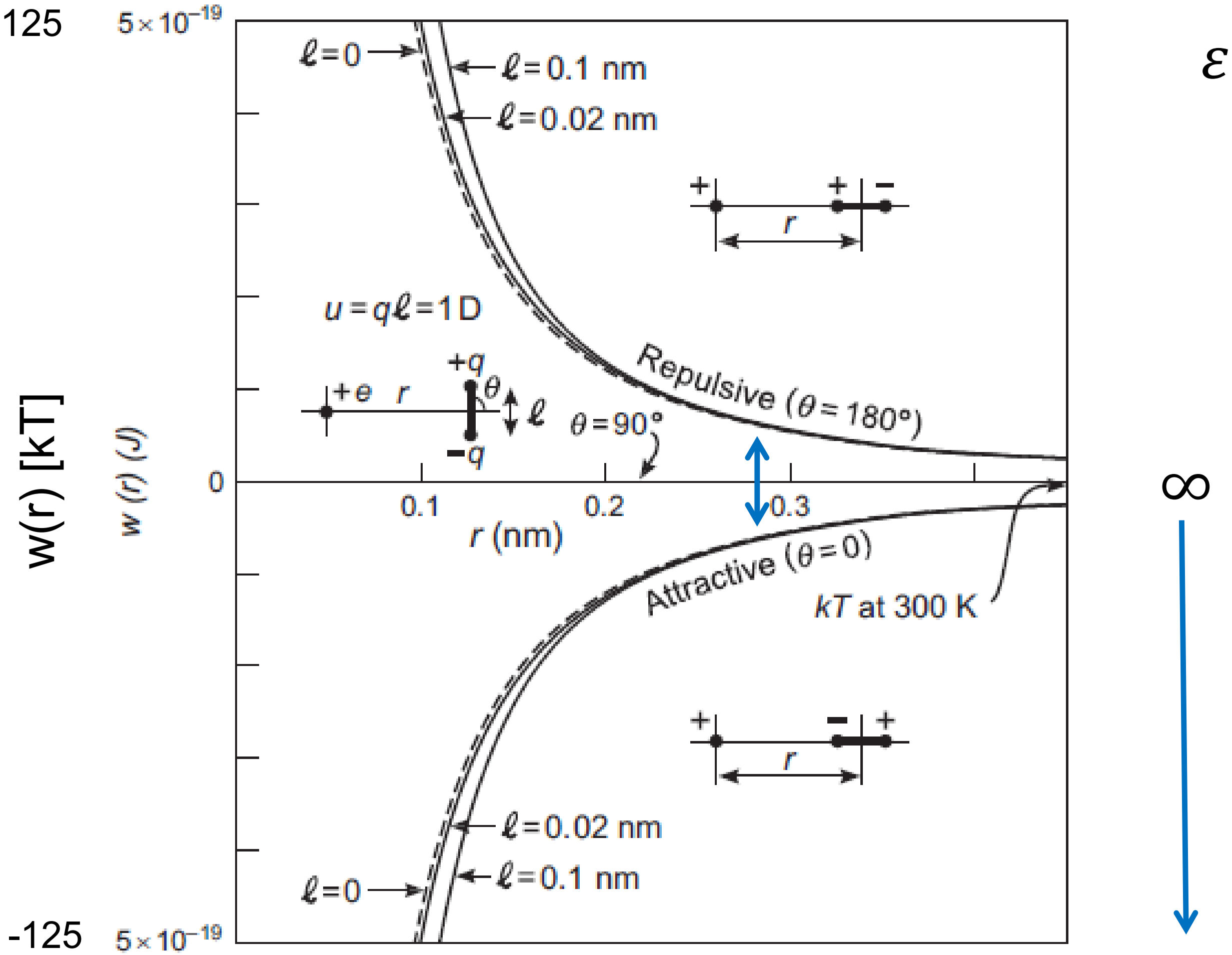
$$w(\boldsymbol{r}) = w(\boldsymbol{r})_{qQ} + w(\boldsymbol{r})_{-qQ}$$

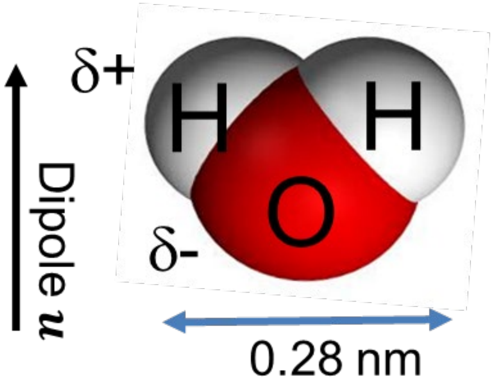
$$w(\boldsymbol{r}) = -\boldsymbol{u} \cdot \boldsymbol{E}(\boldsymbol{r})_Q$$

$$\mathrm{w}(r) = -\frac{uQ\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}$$

Charge dipole interactions

$\varepsilon = 1$ in air





Rotation determined
by interaction

Free
rotation

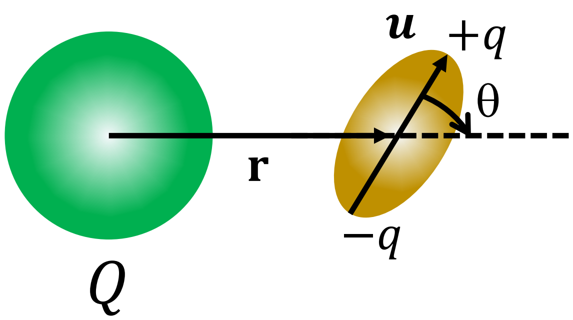
Example of interaction

Ion-dipole energy for Na^+ - H_2O pair: 39 kT

This interaction promotes the nucleation of rain drops in thunder clouds

Charge dipole interactions

Are important to understand dipolar liquid – ion interactions



$$\boldsymbol{u} = \boldsymbol{l}q$$

$$w(\boldsymbol{r}) = -\boldsymbol{u} \cdot \boldsymbol{E}(\boldsymbol{r})_Q$$

$$\mathrm{w}(r) = -\frac{uQ\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}$$

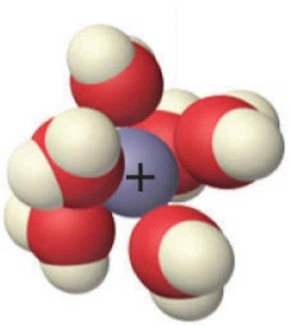
Properties:

- Depend on orientation of dipole
- Long range (w~1/r^2)
- ~40 kT or less; depends on medium

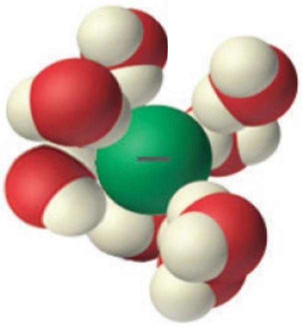
Charge dipole interactions & hydration shells

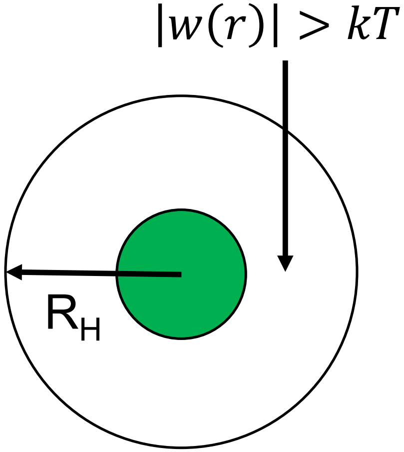
Hydration shells around ionic groups exist of water molecules that are restricted in their motion by the ion

Na^+



Cl^+





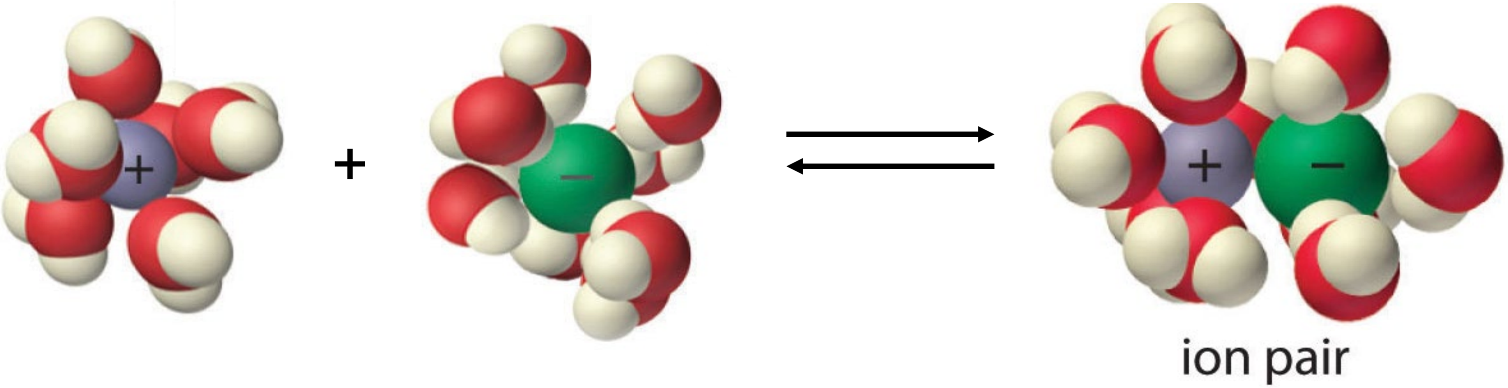
Hydration radius (R_H)

Hydration shell or **solvation shell**: the shell of water molecules that is restricted by the electrostatic field of the ion or ionic groups (or through other interactions). For charge-dipole interactions we can approximate this with the shell within $|w(r)| > kT$

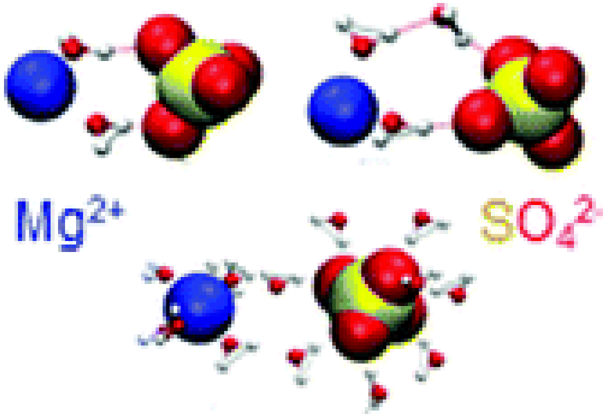
High salt concentration

At concentrations ~ > 1 M there is also the possibility of ion pairing

Na^+ Cl^+



$+ 5\ H_2O$



Ion pairs in $MgSO_4$ solution

Hydration shells

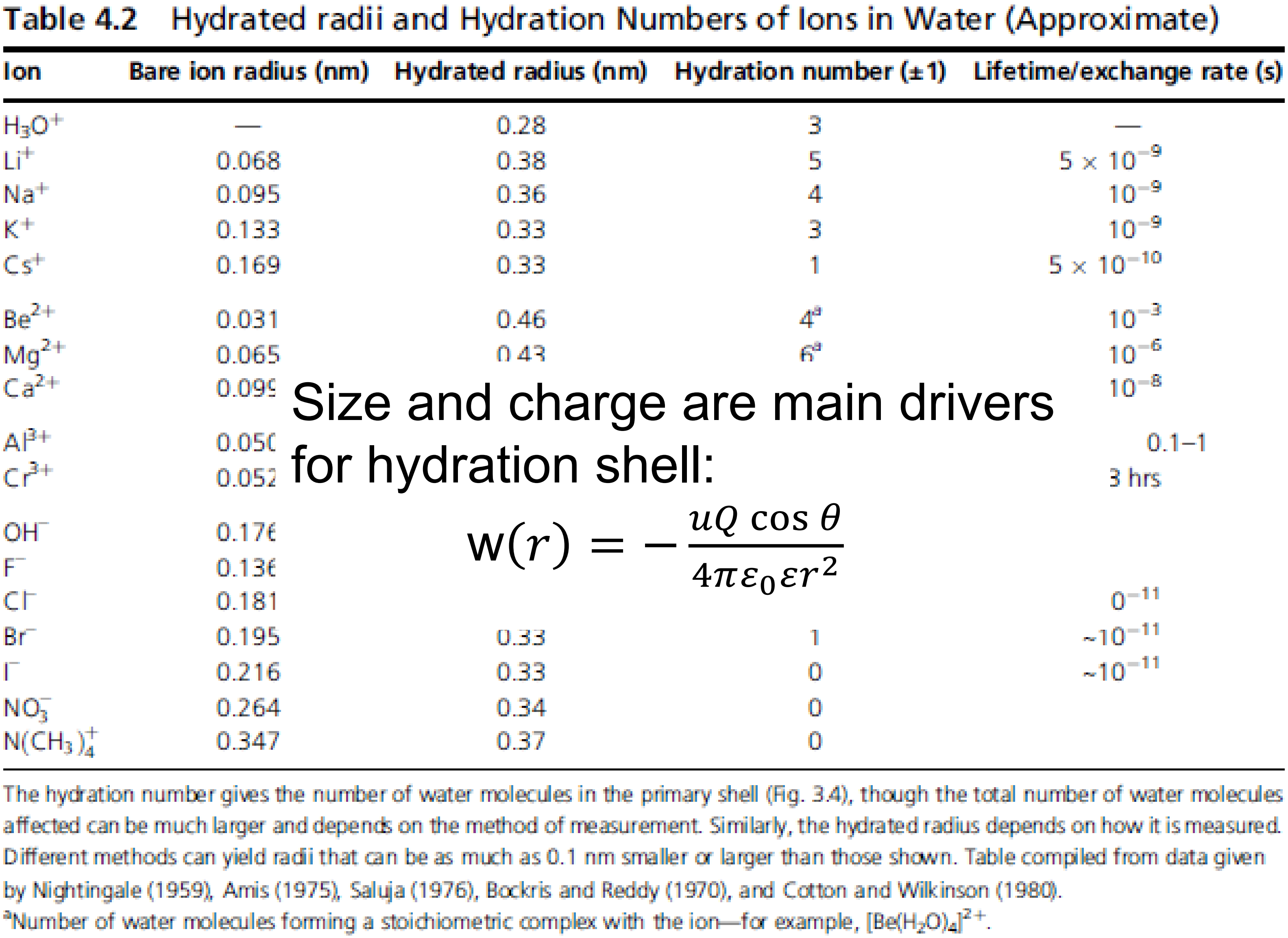


Table 4.2 Hydrated radii and Hydration Numbers of Ions in Water (Approximate)

Ion	Bare ion radius (nm)	Hydrated radius (nm)	Hydration number (±1)	Lifetime/exchange rate (s)
H_3O^+	—	0.28	3	—
Li^+	0.068	0.38	5	5×10^{-9}
Na^+	0.095	0.36	4	10^{-9}
K^+	0.133	0.33	3	10^{-9}
Cs^+	0.169	0.33	1	5×10^{-10}
Be^{2+}	0.031	0.46	4^a	10^{-3}
Mg^{2+}	0.065	0.43	6^a	10^{-6}
Ca^{2+}	0.09			10^{-8}
Al^{3+}	0.05			0.1–1
Cr^{3+}	0.05			3 hrs
OH^-	0.17			
F^-	0.13			
Cl^-	0.181			0^{-11}
Br^-	0.195	0.33	1	$\sim 10^{-11}$
I^-	0.216	0.33	0	$\sim 10^{-11}$
NO_3^-	0.264	0.34	0	
$N(CH_3)_4^+$	0.347	0.37	0	

The hydration number gives the number of water molecules in the primary shell (Fig. 3.4), though the total number of water molecules affected can be much larger and depends on the method of measurement. Similarly, the hydrated radius depends on how it is measured. Different methods can yield radii that can be as much as 0.1 nm smaller or larger than those shown. Table compiled from data given by Nightingale (1959), Amis (1975), Saluja (1976), Bockris and Reddy (1970), and Cotton and Wilkinson (1980).

[a] Number of water molecules forming a stoichiometric complex with the ion—for example, $[Be(H_2O)_4]^{2+}$.

Size and charge are main drivers for hydration shell:

$$w(r) = -\frac{uQ\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}$$

Key concepts Lecture 4

- Ions interact in liquids through screened potentials that arise from + and – charges interacting via Boltzmann weighted interactions
- Debye-Hueckel theory describes this interaction in the limit of a weak potential compared to thermal energy
- Impacts surface structure, protein folding, self-assembly

Dipole-charge interactions

- Dipolar self-energy
- Force relevant for charge-dipole interactions
- Properties of charge-dipole interactions
- Hydration shell definition