Ion Distributions at Liquid-Liquid Interfaces

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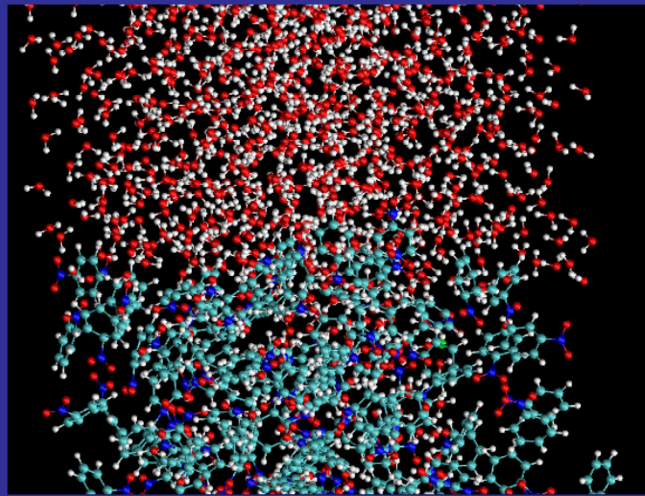
**Liquid Interfacial Macroscience:
Oil spill test facility**

www.mms.gov/tarprojectcategories/ohmsett.htm

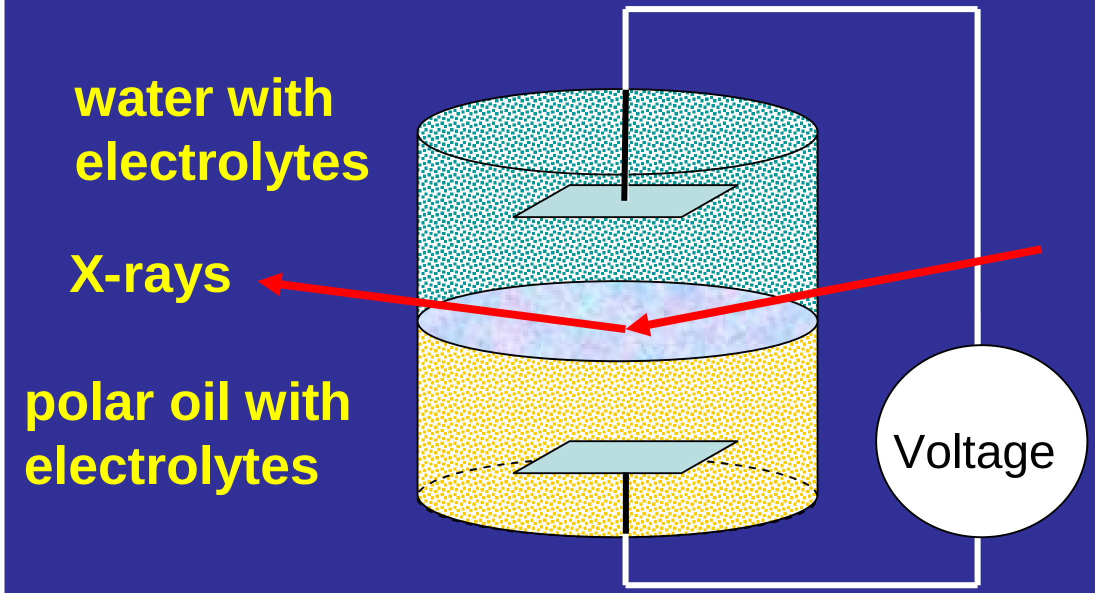
**Liquid Interfacial Nanoscience:
"Oil spill test facility"**



Ilan Benjamin, MD simulation
water/nitrobenzene interface

***Gratefully acknowledged support*: NSF-CHE, For Sector 15: NSF (CHE & DMR),**

Control of Electrical Potential Across the Interface



Some Applications:

Photoinduced electron transfer (photosynthesis and photocatalysis)

Separation membranes

Drug transport

Sensor design (microfluidics)

Phase transfer catalysis

Extraction processes

Requires an interface between two polar liquids - small potential (~0.1 V) yields large electric field across interface ~10^8 V/m

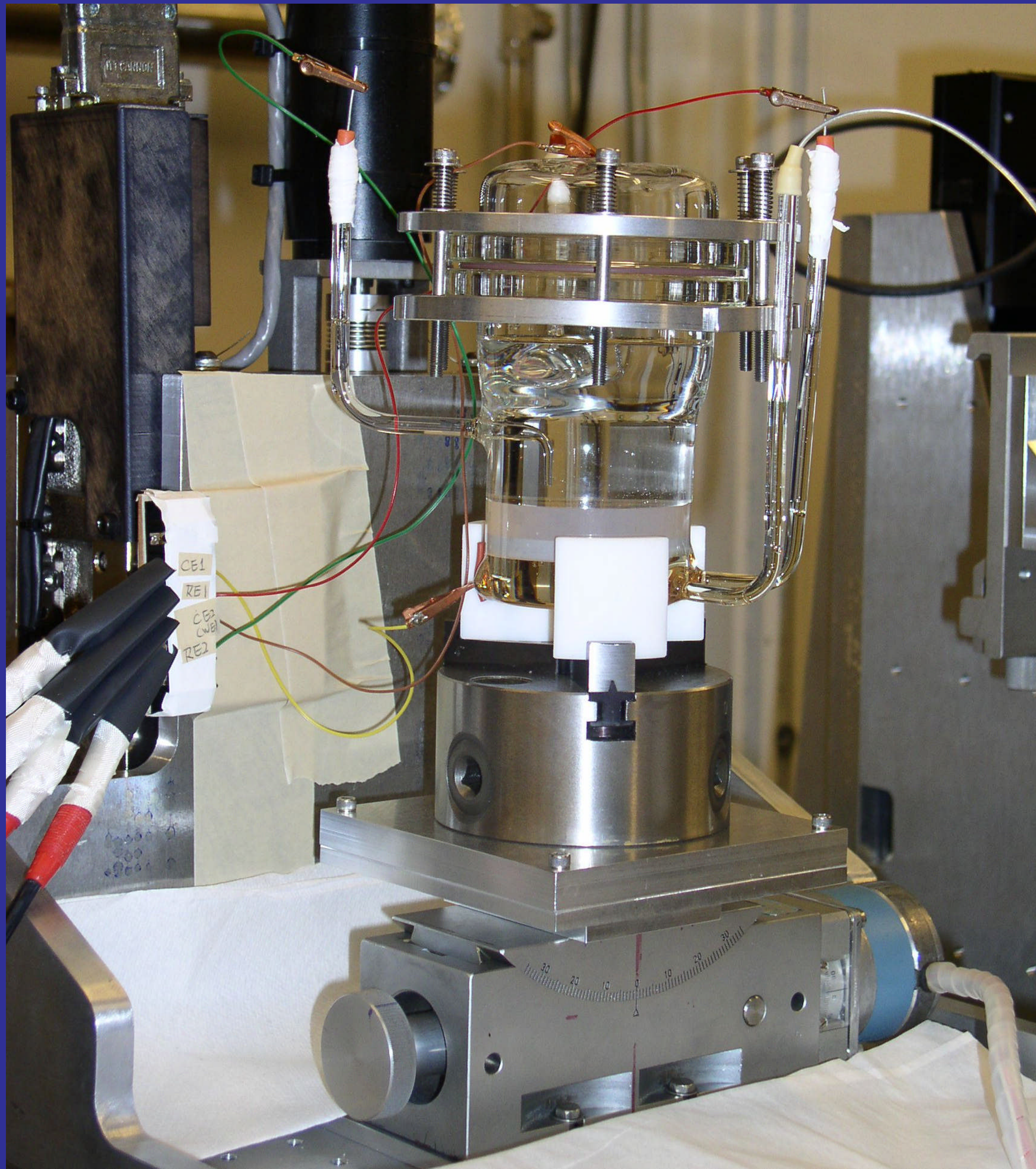
Interfacial Electrical Potential can be used to

Alter concentration and species of ions at interface

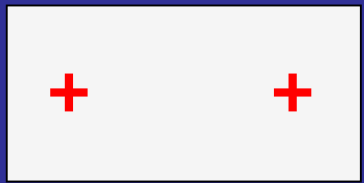
Change physical properties of interface

Control molecular transport through interface

Sample Cell

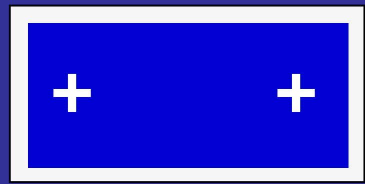


Ion Interactions



Two isolated point charges: Coulomb's Law

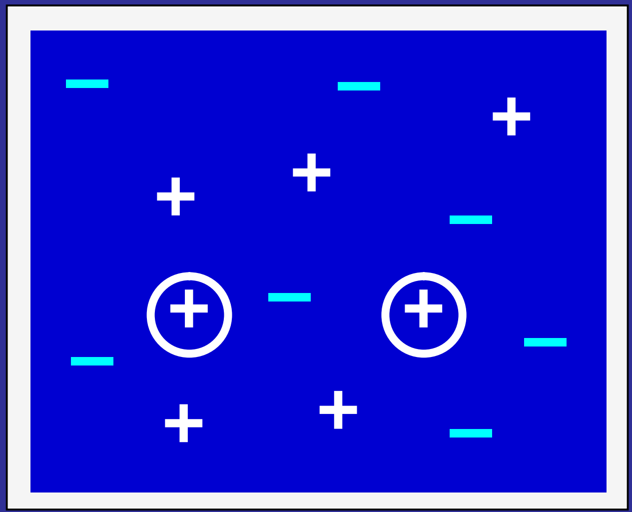
Electric potential: $\phi = \dfrac{1}{4\pi\varepsilon_o}\dfrac{q}{r}$



Two point charges in continuum dielectric: Coulomb's Law

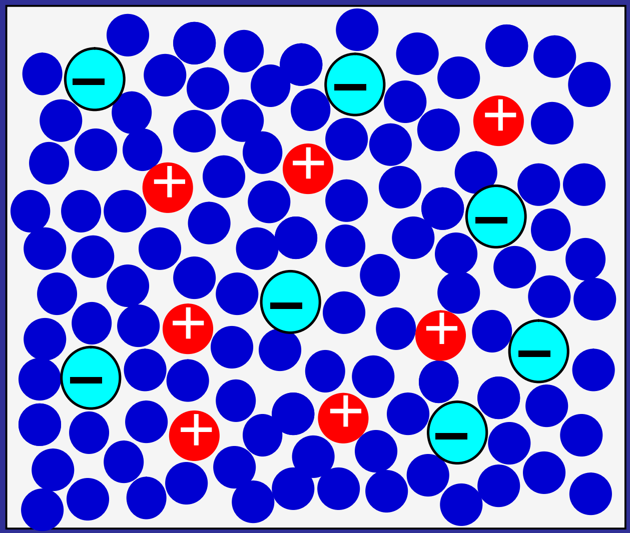
Electric potential: $\phi = \dfrac{1}{4\pi\varepsilon_o\varepsilon_r}\dfrac{q}{r}$

Ion Interactions



Two charges
interacting in continuum dielectric
with other point charges
Debye-Huckel Screening

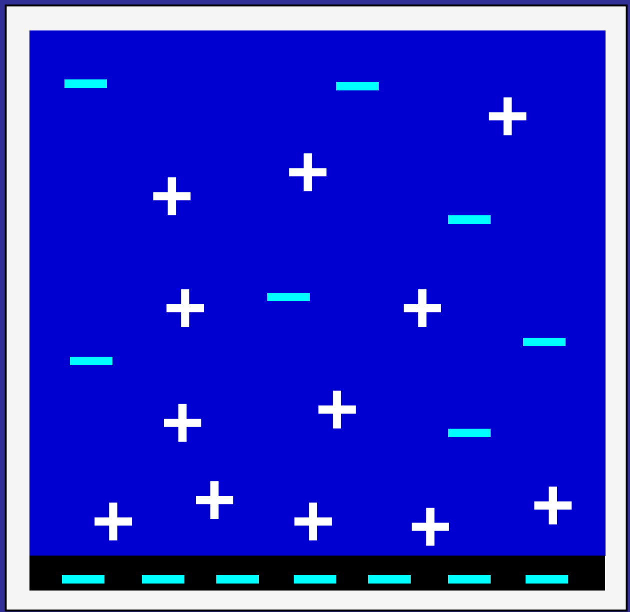
$$\phi = \frac{1}{4\pi\varepsilon_o\varepsilon_r}\frac{q}{r}e^{-\kappa r}$$



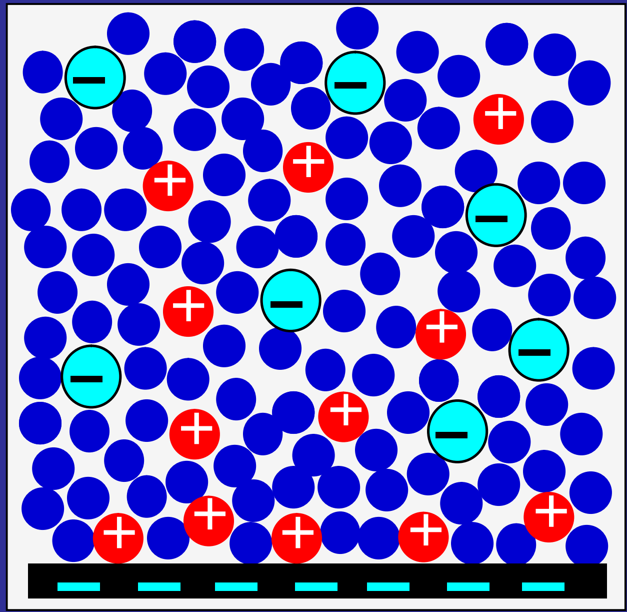
Include Liquid Structure:

Correlations important -
solvent-solvent
solvent-ion
ion-ion

Ion Distributions at Interfaces



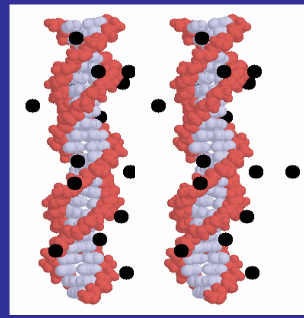
Point charges in continuum solvent
near charged surface:
Gouy-Chapman theory
Electrostatic interactions treated as a mean field
lead to screening of the charged surface.



Spatial correlations are important
solvent-solvent
solvent-ion
ion-ion

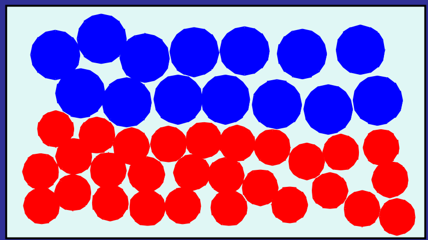
Why is knowing the effect of liquid structure on ion distributions important?

Screening determines forces between charged macromolecules such as polyelectrolytes

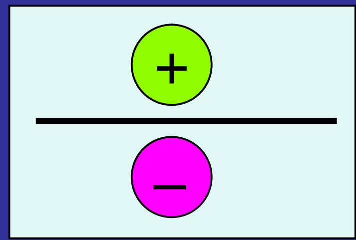


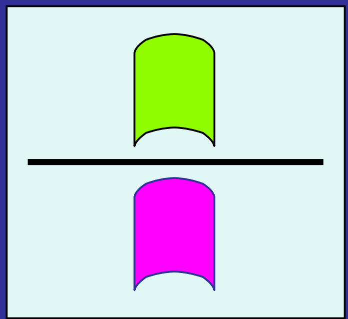
L. Pollack's web site

Liquid-liquid interface

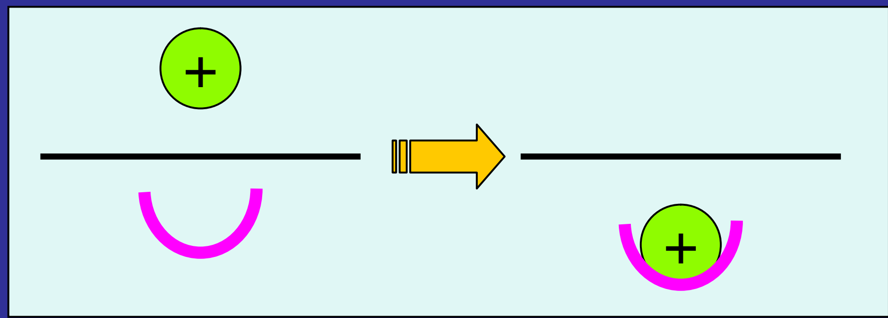


Effect of ion pairing on chemical reactions and electron transfer



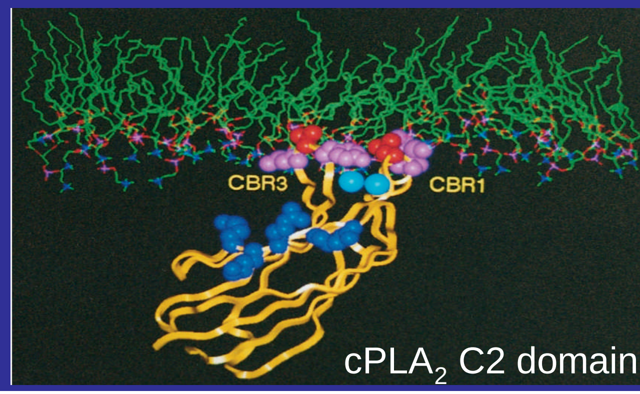


Ion or electron transfer across the interface



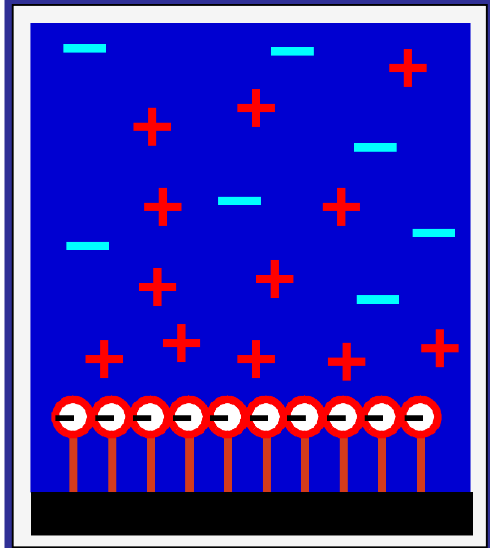
Assisted ion transfer

Protein-lipid interactions mediated by multivalent ions

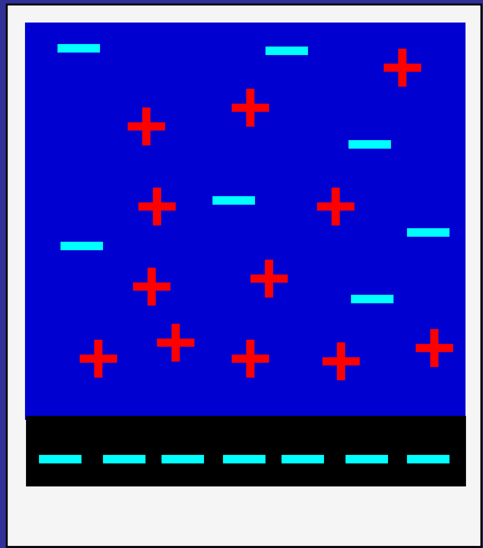


cPLA$_2$ C2 domain

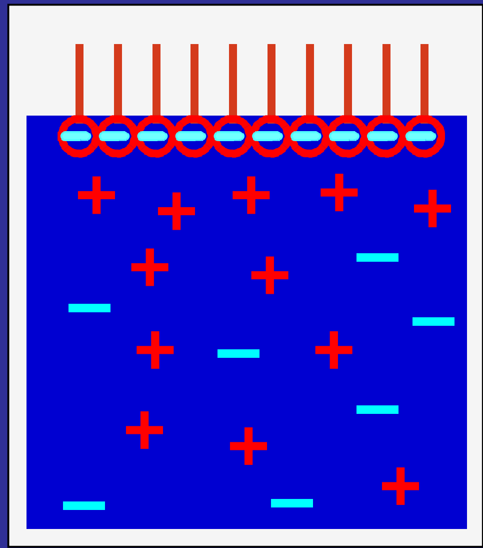
Ion Distributions Near Charged Objects in Electrolyte Solutions



self-assembled monolayer on solid/solution
Bedzyk et al. Science
248, 52 (1990)

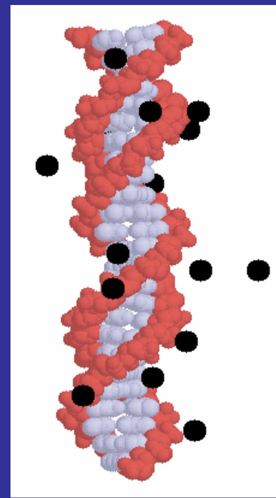


mineral/water
Fenter et al.
J. Coll. Int. Sci.
225, 154 (2000)



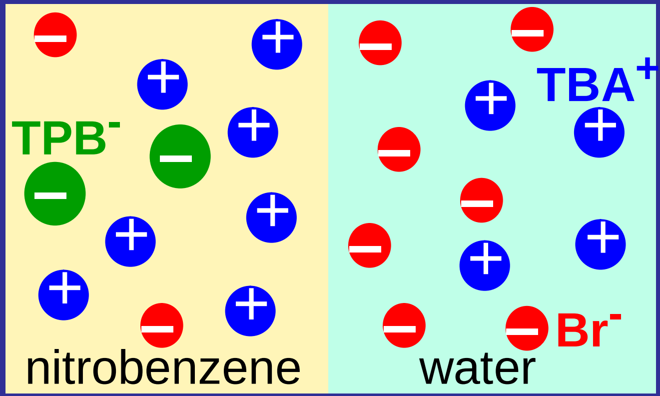
Langmuir layers
Vaknin et al.
PRL 90, 178102 (2003)

L. Pollack's web site



Cations & DNA
Das et al. PRL 90, 188103 (2003)
Andresen et al. PRL 93, 248103 (2004)

Electrified Nitrobenzene/Water Interface



TBA^+ Br^- in water

TBA^+ TPB^- in nitrobenzene

Common ion in both phases - ion partitioning produces electric potential across interface

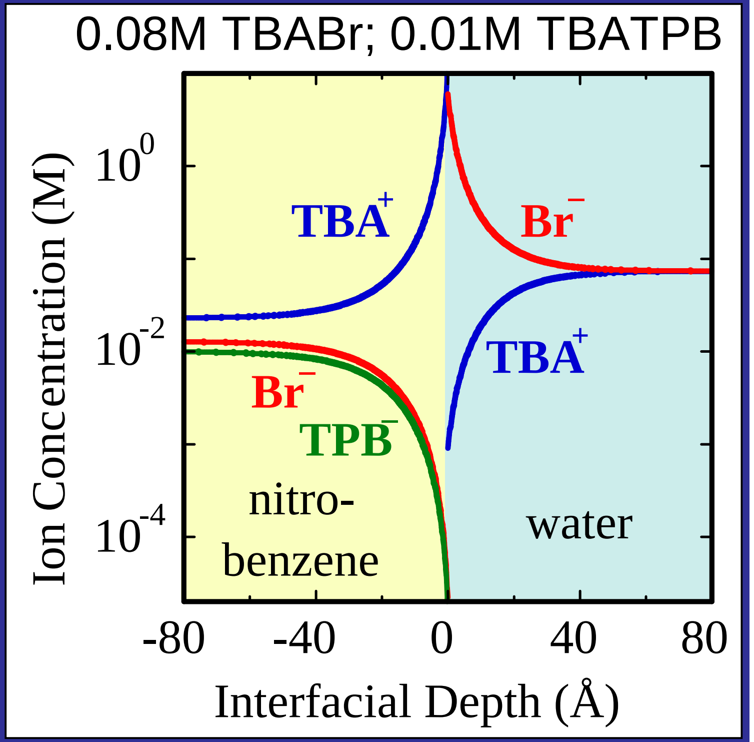
Fix initial solution concentration of TBATPB at 0.01 M in nitrobenzene, vary TBABr concentration to vary electric potential.

Predict electrolyte distributions from Gouy-Chapman theory (point charges in continuum solvent)

Poisson equation: $$\frac{d^2\phi}{dz^2} = -\frac{\rho(z)}{\varepsilon}$$

Boltzmann statistics for ion distribution:

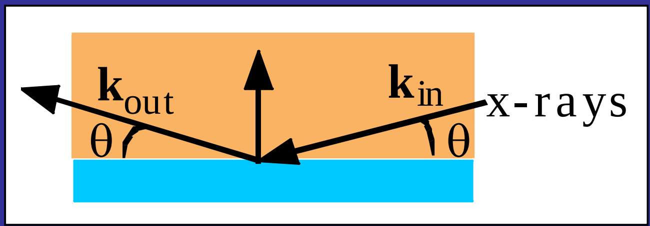
$$\frac{d^2\phi}{dz^2} = -\frac{1}{\varepsilon}\sum_{ions} c_i^o \exp(-e_i\,\phi(z)/kT)$$



X-ray Liquid Surface/Interface Instrument

X-ray reflectivity probes the electron density as a function of depth through the interface (and averaged over the x-ray footprint)

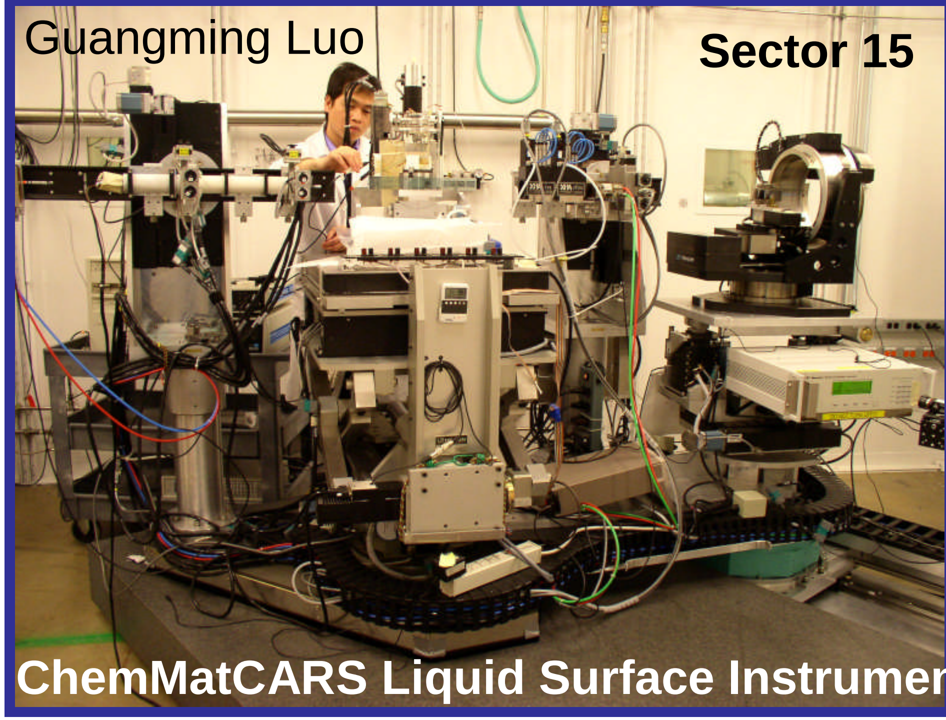
$Q_z = k_{out} - k_{in} = (4\pi/\lambda)\sin\theta$



$\lambda = 0.4$ Å

$$\frac{R(\theta)}{R_F(\theta)} \approx \left| \frac{1}{\rho_\infty} \int dz \frac{\partial \langle \rho(z) \rangle_{xy}}{\partial z} e^{iQ_z z} \right|^2$$

$\rho(z)$ electron density profile
$R(\theta)$ reflected intensity



ChemMatCARS Liquid Surface Instrument

ChemMatCARS Liquid Surface Instrument
Advanced Photon Source
Argonne National Lab
Binhua Lin, Mati Meron
Jeff Sundwall,
Jeff Gebhardt, Tim Graber
Harold Brewer, Frank Westferro
P. James Viccaro

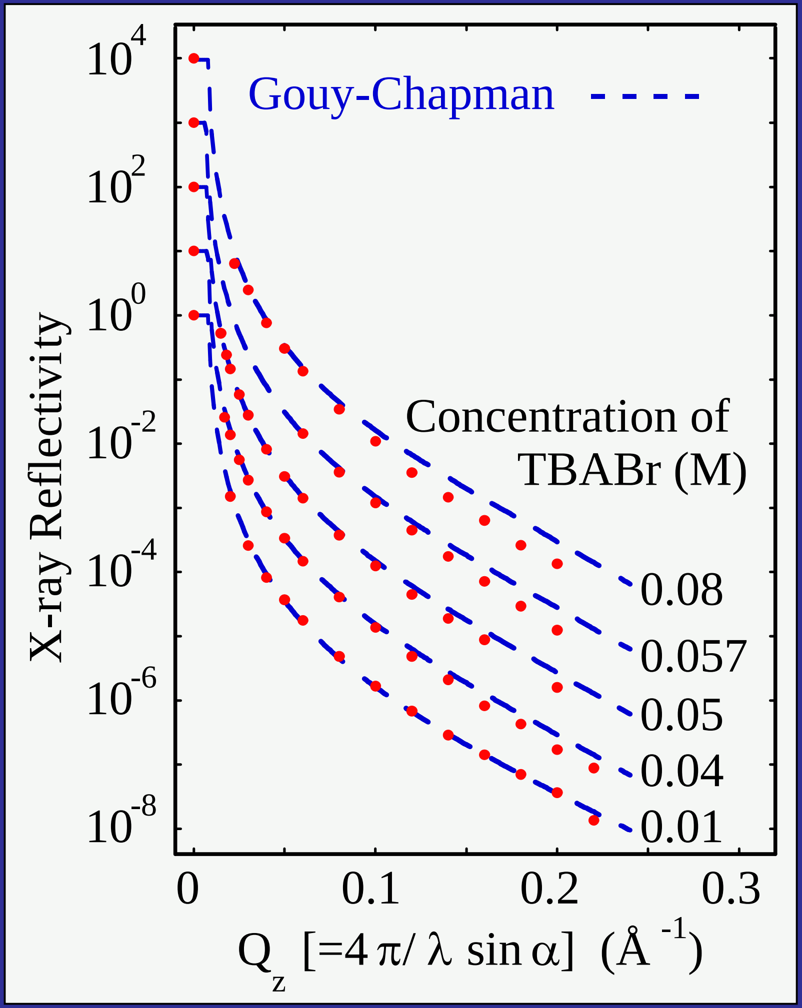
Rev. Sci. Instrum. **68**, 4372-4384 (1997)
Physica B, **336**, 75 (2003)

X-ray Reflectivity Data & Gouy-Chapman Prediction

X-rays probe electron density

Convert ion distributions to electron density using ion sizes from radial distribution functions from MD simulations and other measurements.

Add thermal fluctuations of interface by using capillary wave theory. The capillary wave interfacial width is determined by our interfacial tension measurements.



Science 311, 216 (2006)

Potential of Mean Force and Poisson-Boltzmann Equation
The Effect of Liquid Structure on the Ion Distributions

$$\frac{d^2}{dz^2}\phi(z) = -\frac{1}{\varepsilon}\sum_i e_i c_i^{o} \exp[-E_i(z)/k_B T]$$

$E_i(z)$ **is the ion energy**

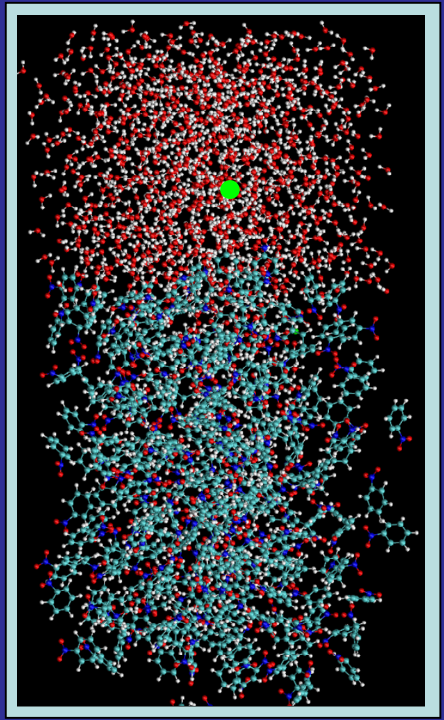
Gouy-Chapman: $E_i(z) = e_i\phi(z)$ **Electrostatic energy only**

mean field electrostatic interaction between point ions located in a structureless solvent medium

Potential of Mean Force $f_i(z)$ $E_i(z) = e_i\phi(z) + f_i(z)$

Integrate average force on a single ion at different interfacial depths.

$$f_i(z) - f_{i,o} = -\int_{z_o}^{z} \left\langle F_{i,z}(z')\right\rangle dz'$$

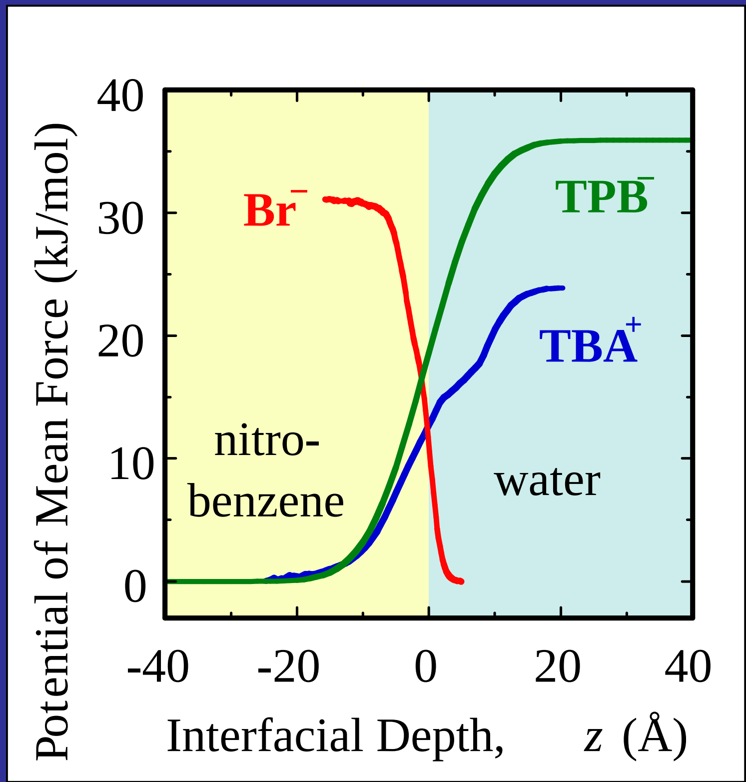


Calculate with Molecular Dynamics simulations

Accounts for solvent-solvent, ion-solvent interactions and correlations, ion and solvent sizes

Potential of Mean Force from MD Simulations

(Ilan Benjamin, UC Santa Cruz)

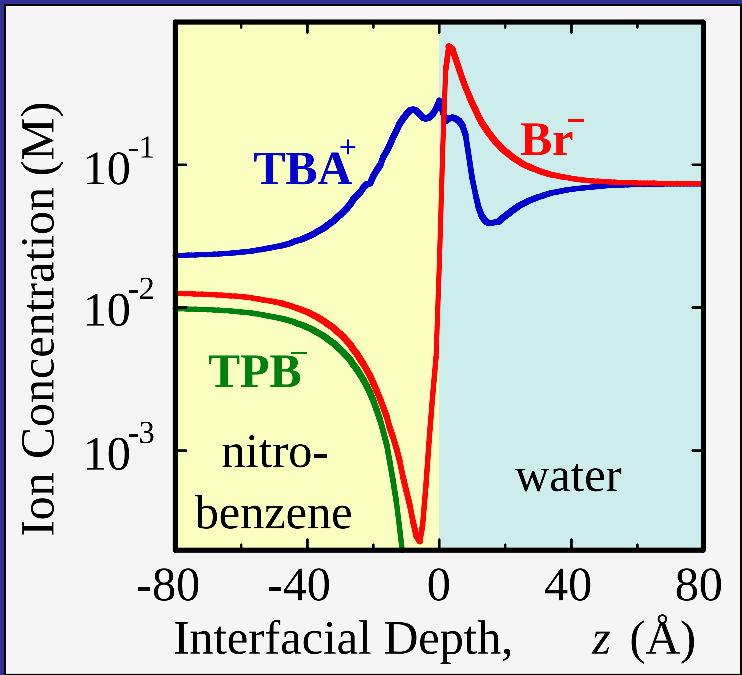


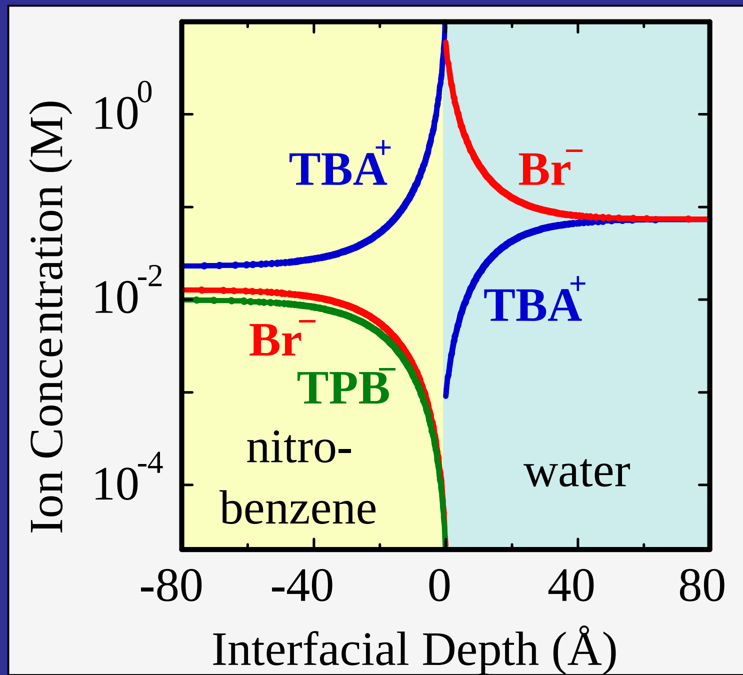
Br^- and TBA^+ from MD simulations

TPB^- from analytic expression

Ion Distributions

0.08M TBABr in water; 0.01M TBATPB in nitrobenzene



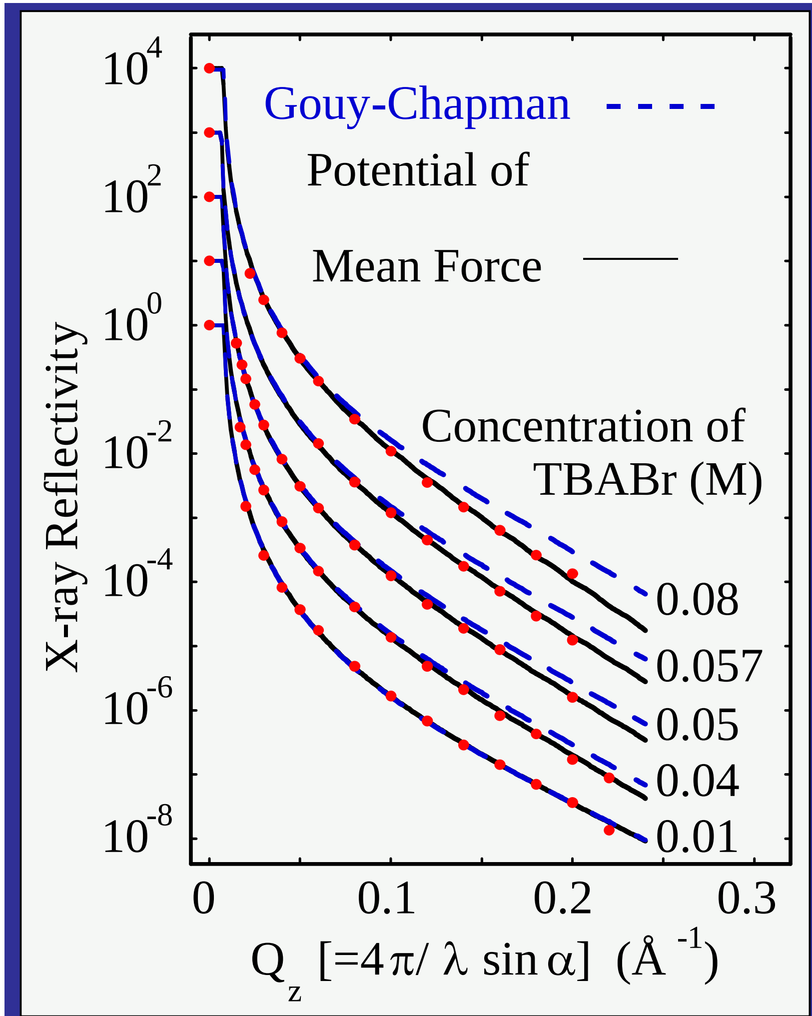


From Potential of Mean Force

Includes liquid structure:
finite size ions
realistic interactions
ions can penetrate interface

From Gouy-Chapman Theory

No liquid structure:
point ions in structureless solvent



Prediction from Potential of Mean Force matches the x-ray data.

No adjustable parameters and no fitting in this analysis.

X-ray Reflectivity Data Gouy-Chapman and Potential of Mean Force Predictions

Conclusions on Ion Distributions

Importance of liquid structure on ion distributions in electrolyte solutions is demonstrated.

Straightforward method to include effect of liquid structure on ion distributions given by use of MD potential of mean force in Poisson-Boltzmann equation -- requires negligible ion-ion correlations.

Method to test potential of mean force produced by either analytical theory or simulation.

Apply to multivalent ion distributions and biomolecular interactions

Collaborators

Research Group at UIC who work on these projects

Dr. Guangming Luo (post-doctoral)

Sarka Malkova (graduate student, now a postdoc at IPNS, Argonne National Lab)

Jaesung Yoon (graduate student)

Binyang Hou (graduate student)

At NIU **Professor Petr Vanysek**

At UC Santa Cruz **Professor Ilan Benjamin**

Experiments were performed at:

ChemMatCARS Sector 15 **(Advanced Photon Source, Argonne National Lab) Dr. Jim Viccaro, Dr. Binhua Lin, Dr. Mati Meron, Dr. David Schultz (UIC), Dr. Tim Graber, Jeff Gebhardt**