Explicit solvent effects in the electrostatics of Newton Black Films: evidence from computer simulations

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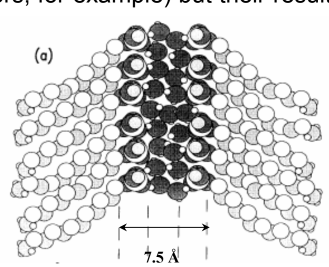
Motivation: to perform a test of basic hypothesis of theories on forces

- Electrostatics of aqueous systems usually described by **"primitive" theories** (solvent characterized by a constant ε_r)
- This hypothesis is **true at large length scales**, but it is not clear to be OK at colloidal scale. Several groups claim that the breakdown of this hypothesis can explain results related to **hydration forces** (see for example the classical review by Leikin, Parsegian and Rau (1993)).
- Some groups (Berkowitz 1995, Berendsen 1996) have tried to settle this issue by Molecular Dynamics simulations (of DPPC or DPPS bilayers, for example) but their results were not clear.
- We decided to perform simulations of SDS/water/SDS Newton Black films, taking advantage of the new UK national Supercomputing facility HPCx (Edinburgh).
- The model and potentials were relatively "easy" to construct for this system due to the availability of experimental data.



SDS [$Na^+CH_3(CH_2)_{11}OSO_3^-$]

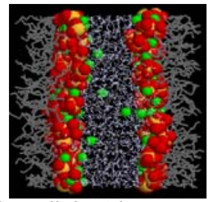
Conclusion: explicit solvent effects are very important

The analysis of our simulations and re-analysis of other authors simulations clearly show that explicit solvent effects strongly affect electrostatics in aqueous media

- Our Molecular Dynamics simulations of thin SDS/water/SDS films show that:

  ✓There is a strong polarization of water at the interfaces, which decays in 10 Å. This is **not in agreement** with the expected dielectric constant of water.

  ✓It is not possible to define a dielectric constant for the solvent (water) inside these films: there is no local (constitutive) relation between applied field and response of the solvent.

  ✓The solvent (water) has an important contribution to the **electrostatic potential profile** inside the film, which is **inconsistent with that expected from a dielectric medium.**

  ✓The **strong polarization of water** has an important **repulsive contribution to the electrostatic interaction** between surfactant layers (**hydration force**).

- Molecular Dynamics simulations of DPPC bilayers show a similar dielectric response of water.

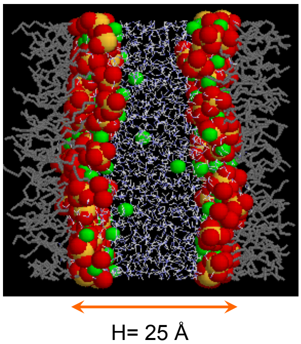
- Molecular Dynamics simulations of DPPS bilayers show a dielectric response of water consistent with a small dielectric constant ($\varepsilon_r \approx 2.5$)

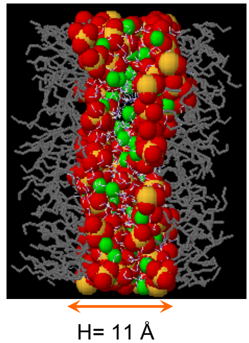
First, let us briefly describe our Molecular Dynamics Simulations

(this is a little boring part, but I need to do it)

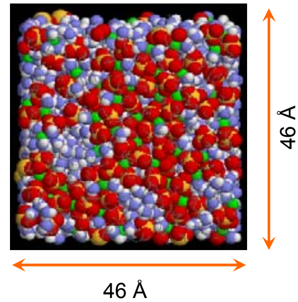
Simulations predict correct results for SDS/water/SDS films

- We have simulated films of different sizes (from H=32 Å to H=6 Å) with 33 Å^2 per surfactant (experimental value observed by Bélorgey and Benattar, PRL 1991) at 298 K.





Typical top view

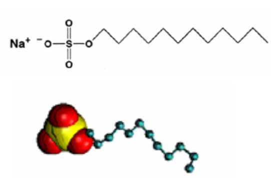


- Roughness **OK!** sims $\zeta(R \to \infty) \to 2.5\ \text{Å}$ experiments $\zeta = 2.7 \pm 0.1\ \text{Å}$
- Surface tension **OK!** sims $\gamma \approx 58$ mN/m experiments $\gamma \approx 63$ mN/m
- Other quantities (diffusion coefficients, tilt angle, electron density,…) **OK!**

The SDS and water models are standard and work very well

- The force field is based in AMBER 94 with some minor modifications, and reproduces thermodynamic data of SDS and water at ambient conditions. (FB & JF, Langmuir (2004))

- SPC/E model for water, standard in biomolecular simulations
  - -Low computational cost (tetrahedral water model with 0.1 nm OH distance and partial charges q_{ox}=-0.8476e, q_{Hyd}=+0.4238e).
  - -Correct density, g(r) and diffusion coefficient of liquid water under ordinary conditions.
  - -Dielectric constant $\varepsilon_r \approx 70$ at 1 atm and 300 K
- Surfactant and Na^+ model/effective potentials include description of:



- Bonds and bonds angles
- Bending and torsional potentials
- Nonbonding interactions (Lennard-Jones)
- Electrostatics (partial charges at S, O and CH_2 bonded to oxygen)

Now, let us see what happens inside the film

(this will be the funny part…)

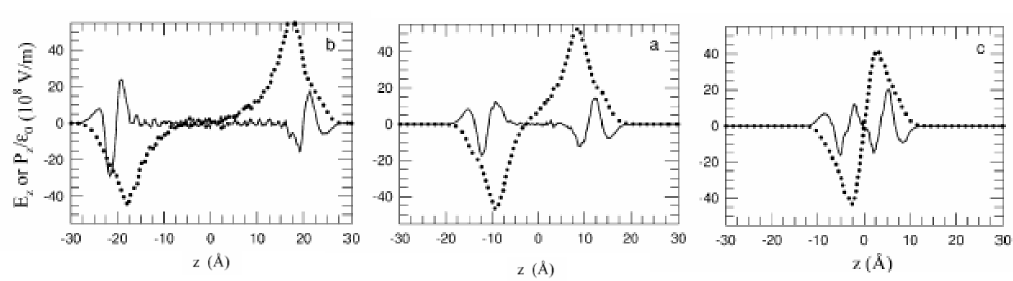
Dielectric constant is not well defined inside SDS/water/SDS films

- The comparison between the Electric field and the Electrostatic polarization shows:

$$\vec{P} \equiv \vec{D} - \varepsilon_0 \vec{E}$$

  - No dielectric constant near charged interfaces $\cancel{\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E}}$
  - In fact, it is not possible to define a local (constitutive) relation between applied field and response of the solvent.

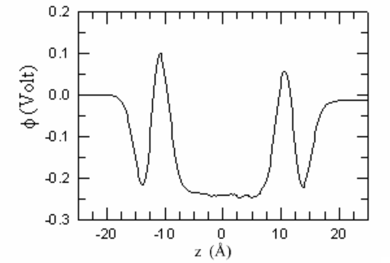
JF & FB, PRL **92**, 236102 (2004)



Polarization maximum at the interface (P/ε_0 ~10^9 V/m) and decays completely in 10 Å

Water strongly affects electrostatic potential inside films

- Electrostatic potential inside the aqueous core of the films is completely different (in value and shape) from that expected in a film containing a dielectric solvent (characterized with ε_r)



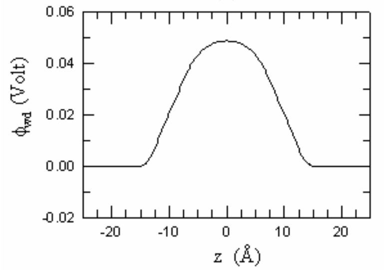
JF & FB, PRL **92**, 236102 (2004).

EXACT Poisson eq.

$$-\varepsilon_0 \frac{d\phi}{dz} = \rho_f(z) + \rho_w(z)$$

charge distribution due to **water** computed in sims

charge distribution due to **surfactant, Na+** (computed in sims)

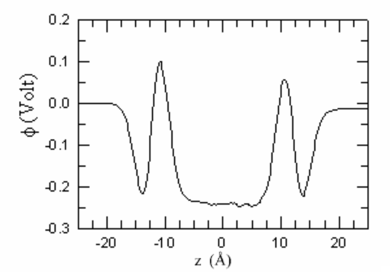


Poisson eq. in a dielectric medium

$$-\varepsilon_0 \frac{d\phi_{wd}}{dz} = \frac{\rho_f(z)}{\varepsilon_r}$$

water replaced by a dielectric medium

PB equation fails inside these films due to water response



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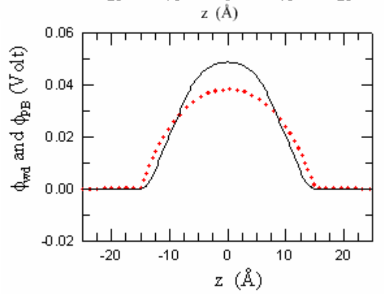
charge distribution computed from sims



Poisson eq. in a dielectric medium

$$-\varepsilon_0 \frac{d\phi_{wd}}{dz} = \frac{\rho_f(z)}{\varepsilon_r}$$

water replaced by a dielectric medium

Poisson -Boltzmann

$$\left\{ \begin{array}{l} -\varepsilon_0 \dfrac{d\phi_{PB}}{dz} = \sum_i q_i n_i(z) \\ n_i(z) = n_{0i} \exp\left[-\dfrac{q_i \phi(z)}{k_B T} \right] \end{array} \right.$$

water replaced by a dielectric medium, ion distribution replaced by Mean-Field Boltzmann distribution

Water strongly increases the stabilizing electrostatic force

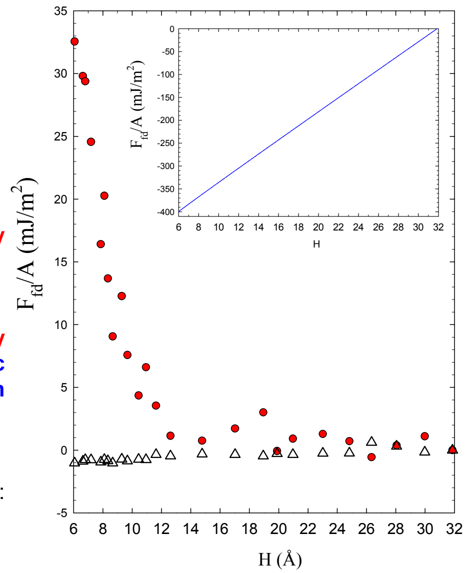
- Calculation of the field Free Energy shows an important repulsive contribution due to the polarization induced near the interfaces.

$$F_{field}(H) = F^{(0)} + \frac{1}{2}\int \rho_f \phi \, dV$$

➡ It is **strongly repulsive** using **SDS charge density and potential** computed from simulations (circles).

➡ It is **weakly attractive** using **SDS charge density computed from simulations** and the **electrostatic potential ϕ_{wd} derived assumed a dielectric medium** (triangles).

➡ It is **strongly attractive** using Poisson-Boltzmann: charge density and electrostatic potential (solid line).



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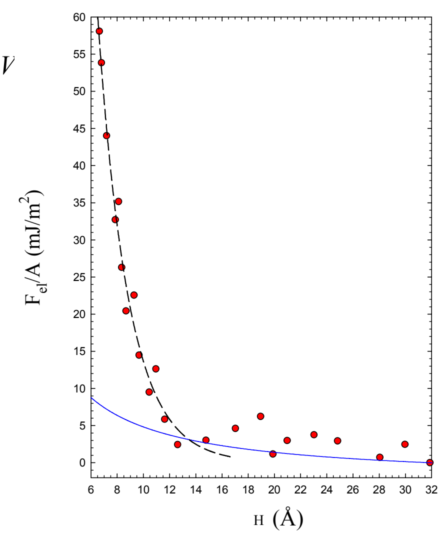
- Approximate calculation of the electrostatic Free Energy shows:

$$F_{el} = F_{field} + F_{mix} \quad \begin{cases} F_{field}(H) = F^{(0)} + \frac{1}{2}\int \rho_f \phi \, dV \\ F_{mix} = k_B T \sum_i \int n_i \ln X_i \, dV \end{cases}$$

➡ A **strong-short distance repulsion** due to **strong water polarization near interfaces.**

➡ The **repulsive pressure** has the typical exponential behaviour of the **so-called hydration force** (see review by Leikin, Parsegian & Rau (1993)).

$$\boxed{\Pi_{el} = -\frac{1}{A}\frac{\partial F_{el}}{\partial H}\bigg|_T \qquad \Pi = \Pi_0 e^{-H/\lambda} \qquad \begin{array}{l} \lambda = 2.35\ \mathrm{A} \\ \Pi_0 = 4.09\times 10^9\ \mathrm{Pa} \end{array}}$$

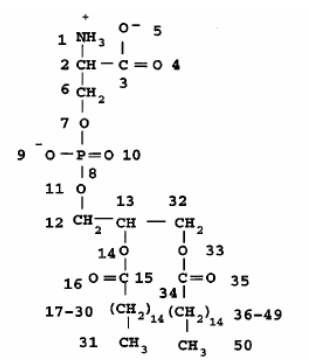


… and some more surprises appear by looking to other systems…

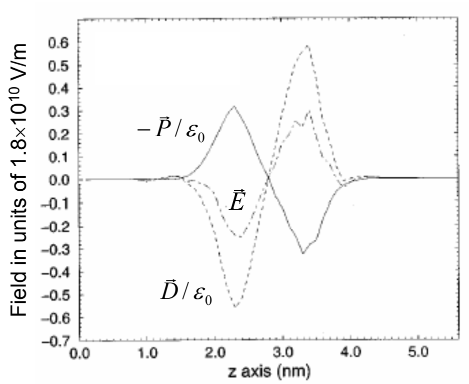
(this is the last part of the talk!!!)

Water inside DPPS films has a small dielectric constant

- Simulations of DPPS$^-$/water+Na$^+$/DPPS- by Berendsen group (1996) at 350 K and 1 atm, with an area per lipid 54 Å^2 and aqueous core of thickness ≈ 25 Å.
  - They do no analyze the electric field but it can be obtained from their published data.
  - The results are consistent with a relation between the electric field and water polarization, $\vec{P} = \varepsilon_0(\varepsilon_r - 1)\vec{E}$ with a **water dielectric constant ε_r≈2.5** !! .

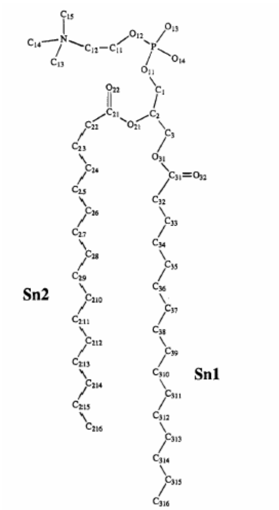


Dipalmitoylphosphatidylserine (DPPS$^-$)



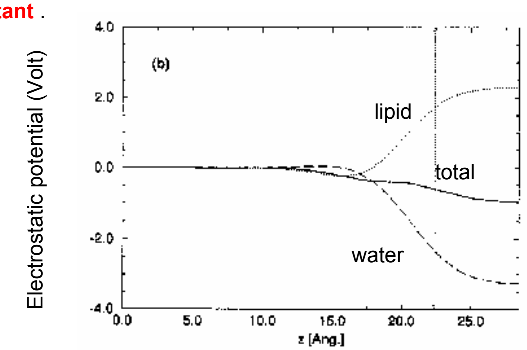
Re-examination of sims in other systems shows similar behaviour

- Simulations of DPPC bilayers in water by Berkowitz group (1995) at 333 K, with an area per lipid 65.8 Å^2 and aqueous core of thickness ≈ 12 Å.



4. Nomenclature of the atoms in the DPPC molecule.

- The electrostatic potential is monotonic (no oscillations!!).
- **Overcompensation**: The electrostatic potential created by water is larger (and opposite) than that created by the lipids.
- Using available data, it is not possible to introduce a well-defined **dielectric constant** .



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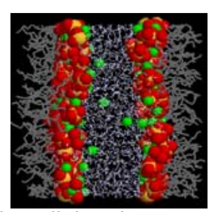

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