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

Benasque, 15th August 2005
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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 $\varepsilon_r$)

- 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.
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 Å² per surfactant (experimental value observed by Bélorgey and Benattar, PRL 1991) at 298 K.

- Roughness OK! sims $\zeta(R \to \infty) \to 2.5$ Å experiments $\zeta = 2.7 \pm 0.1$ 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 $q_{OH}=-0.8476e$, $q_{HO}=+0.4238e$).
  - Correct density, $g(r)$ and diffusion coefficient of liquid water under ordinary conditions.
  - Dielectric constant $\varepsilon_r\approx70$ 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 CH₂ 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:

- No dielectric constant near charged interfaces
- In fact, it is not possible to define a local (constitutive) relation between applied field and response of the solvent.

\[ \tilde{P} = \tilde{\epsilon}_0 (\tilde{\epsilon}_r - 1) \tilde{E} \]

Polarization maximum at the interface \((P/\epsilon_0 \sim 10^9 \text{ V/m})\) and decays completely in 10 Å

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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 $\varepsilon_r$).


EXACT Poisson eq.

$-\varepsilon_r \frac{d\phi}{dz} = \rho_f(z) + \rho_w(z)$ charge distribution due to water computed in sims

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

Poisson eq. in a dielectric medium

$-\varepsilon_0 \frac{d\phi_{\text{tot}}}{dz} = \rho(z)$ water replaced by a dielectric medium

PB equation fails inside these films due to water response


Poisson eq.

$-\varepsilon_0 \frac{d\phi}{dz} = \rho_f(z) + \rho_w(z)$ charge distribution computed from sims

Poisson eq. in a dielectric medium

$-\varepsilon_0 \frac{d\phi_{\text{tot}}}{dz} = \rho(z)$ water replaced by a dielectric medium

Poisson -Boltzmann

$\left\{ -\varepsilon_0 \frac{d\phi_{\text{tot}}}{dz} = \sum_i q_i n_i(z) \right\}$ water replaced by a dielectric medium, ion distribution replaced by Mean-Field Boltzmann distribution

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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.

\[ F_{\text{field}}(H) = F^{(0)} + \frac{1}{2} \int \rho \phi dV \]

- 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 \( \Phi_{sd} \) derived assumed a dielectric medium (triangles).
- It is strongly attractive using Poisson-Boltzmann: charge density and electrostatic potential (solid line).

Water strongly increases the stabilizing electrostatic force

- Approximate calculation of the electrostatic Free Energy shows:

\[ F_{el} = F_{\text{field}} + F_{\text{mix}} \]

\[ F_{\text{field}}(H) = F^{(0)} + \frac{1}{2} \int \rho \phi dV \]

\[ F_{\text{mix}} = k_B T \sum \int n_i \ln X_i dV \]

- 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)).

\[ \Pi = \frac{1}{A} \frac{\partial F_{el}}{\partial H} \]

\[ \Pi = \Pi_0 e^{-\lambda H} \]

\[ \lambda = 2.35 \text{ Å} \]

\[ \Pi_0 = 4.09 \times 10^6 \text{ Pa} \]
... 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 Å² and aqueous core of thickness ≈ 25 Å.

- They do not 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, \( \vec{P} = \epsilon_0 (\epsilon_r - 1) \vec{E} \) with a water dielectric constant \( \epsilon_r = 2.5 \).

Dipalmitoylphosphatidylserine (DPPS-)

\[
\begin{align*}
1 & \text{CH}_3, \text{C}^- \quad 5 \\
2 & \text{CH} - \text{CH} - \\
6 & \text{CH}_3 \quad 3 \\
11 & \text{O} - \text{O} - 10 \\
12 & \text{CH} - \text{CH} - \\
14 & \text{CH}_3 \quad 33 \\
16 & \text{O} = 15 \quad \epsilon = 0 \quad 35 \\
17 & \text{CH}_2(\text{CH}_3)_2 \quad \text{CH}_2(\text{CH}_3)_2 \quad 36-49 \\
31 & \text{CH}_3, \text{CH}_2, \text{CH}_3 \quad 50
\end{align*}
\]

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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 \(\approx 12\) Å.

- 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.

\[ \text{(a) Electrostatic potential (Volts)} \]

\[ \text{l lipid} \]
\[ \text{water} \]
\[ \text{total} \]

Conclusion: explicit solvent effects are very important

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- 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 \((\varepsilon_r \approx 2.5)\).