Electrostatic dipole interactions in phospholipid bilayers

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I. Introduction

In Molecular Dynamics (MD) simulations of lipid bilayers, there is the question of how to handle the long range electrostatic interactions. Explicit treatment of the interactions at a certain cutoff distance, $r_c$, typically 1.8 nm, or inclusion of all interactions out to infinity in a periodic system by Ewald summation or Particle Mesh Ewald (PME). Since Ewald techniques are computationally more expensive, alternative, the question of whether or not long range forces are necessary to accurately describe the lipid membrane becomes important. Simulations show little or no difference in area per lipid between PME and cutoff, as long as the system is made large enough. By employing detailed MD simulations in a simplified model for the electrostatics, the aim is to find an explanation for this.

The model system

A system containing 1024 lipids (DPFC) and a water content corresponding to 28 water per lipid was simulated using the Gromacs MD software at a temperature of 303 K and atmospheric pressure. The simulation reached 5 ns in length. PME was used for the long range electrostatic interactions. Both the area and volume per lipid produced in this setup (0.654 nm$^2$, 1.228 nm$^3$) fall close to their experimental values (0.64 nm$^2$, 1.272 nm$^3$).

II. Electrostatics in a simplified model

The dipole component $\vec{r}$ and $\varphi$ are readily extracted from the simulation. The relative permittivities, $\varepsilon_r$ and $\varepsilon_r$, have to be calculated in some fashion.

Calculating relative permittivities

A numerical value for $\varepsilon_r$ is obtained from a fit of the electrostatic potentials across the monolayer which is obtained by solving Poisson’s equation for water and lipids separately:

$$\varepsilon_r = \frac{1}{\varepsilon_0 + \varepsilon_L}$$

where $\varepsilon_0$ is the permittivity of the lipid only and $\varepsilon_L$ from lipids plus water. The potential is set to zero at the center of the monolayer, and the relative permittivity is calculated at $r = 10$.

III. Results

Using values for the dipole components, membrane surface area, and calculated relative permittivities obtained from the simulation, the contributions to the surface tension from long range (more than 1.8 nm) electrostatic interactions are calculated:

$$\gamma_{\text{intr}} = 0.8$$

$\gamma_{\text{dip}} = 0.02 \text{ mN/m}$

Long range contributions from parallel components are attractive, but negligible. The perpendicular component gives rise to a repulsion which, together with an experimental area compressibility:

$$K_A = \frac{1}{2} \frac{\delta A}{\delta N}$$

corresponds to an increase in area of approximately 9%.

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IV. Conclusions

The long range electrostatic interaction in lipid bilayers may accurately be described using a dipole approximation. The head group dipole can be decomposed into two components which are treated separately.

Component parallel to the membrane plane:

- Large
- Interaction is attractive
- Interaction scales with distance $1/r^6$
- Scaled by a relative permittivity $\varepsilon_r$ with $\varepsilon_r = 9$

The last two features make long range contributions from the dipole interactions negligible.

Component perpendicular to membrane plane:

- Small
- Interaction is repulsive
- Interaction scales with distance $1/r^2$
- Scaled by a relative permittivity $\varepsilon_r$ with $\varepsilon_r = 20$

Although smaller in magnitude than the parallel component, these components dominate the interactions at large distances.

References

The range and shielding of dipole/dipole interactions in phospholipid bilayers