Molecular dynamics in a density dependent inhomogeneous dielectric

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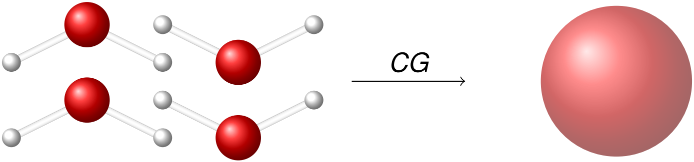
Electrostatic screening: Atomistic vs coarse-grained

Atomistic molecular dynamics:

- *Charges are resolved*
- *Screening is modeled directly*

Coarse-grained molecular dynamics:

- *Charge resolution is lost*
- *Screening modeled modelled indirectly*



$$\text{Idea}: \quad \nabla \cdot (\epsilon(\mathbf{r}) \nabla \psi(\mathbf{r})) = -\rho(\mathbf{r}).$$ (Generalized Poisson equation)

External potential in a density dependent dielectric

Electrostatic interaction energy:

$$W_{\mathrm{elec}}[\{\phi(\mathbf{r})\}] = \frac{1}{2}\int \mathrm{d}\mathbf{r}\,\frac{\mathbf{D}(\mathbf{r})\cdot\mathbf{D}(\mathbf{r})}{\epsilon(\mathbf{r})},$$

$\{\phi\}$*: number densities.* $\mathbf{D}$*: displacement field.* ϵ*: permitivity.*

Potential felt by particles of type K:

$$V_{\mathrm{ext},K}(\mathbf{r}) = \frac{\delta W_{\mathrm{elec}}}{\delta\phi_K(\mathbf{r})} = \underbrace{\int \mathrm{d}\mathbf{r}'\,\frac{\delta W_{\mathrm{elec}}}{\delta\mathbf{D}(\mathbf{r}')}\frac{\delta\mathbf{D}(\mathbf{r}')}{\delta\phi_K(\mathbf{r})}}_{q_K\psi(\mathbf{r})} + \underbrace{\frac{\delta W_{\mathrm{elec}}}{\delta\epsilon(\mathbf{r})}\frac{\partial\epsilon(\mathbf{r})}{\partial\phi_K(\mathbf{r})}}_{-\frac{1}{2}\frac{\partial\epsilon(\mathbf{r})}{\partial\phi_K(\mathbf{r})}|\mathbf{E}(\mathbf{r})|^2}$$

ψ*: electrostatic potential.* $\mathbf{E}$*: electrostatic field* ($\mathbf{E} = -\boldsymbol{\nabla}\psi = \epsilon\mathbf{D}$).

Modelling of density dependence of the dielectric

Density weighted average:

$$\epsilon(\{\phi(\mathbf{r})\}) = \frac{\sum_K^M \epsilon_K \phi_K(\mathbf{r})}{\phi_0(\mathbf{r})},$$

ϵ_K: dielectric of particle type K. ϕ_0: local total particle density.

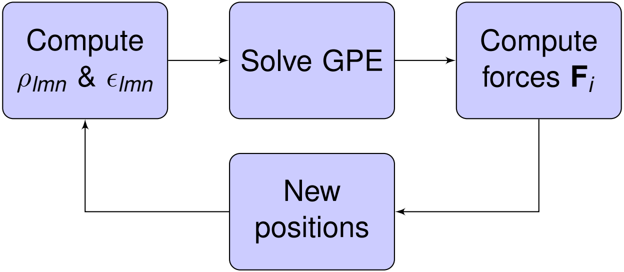
Potential felt by particle of type K:

$$V_{\mathrm{ext},K}(\mathbf{r}) = q_K \psi(\mathbf{r}) - \frac{1}{2} \frac{\epsilon_K - \epsilon(\mathbf{r})}{\phi_0(\mathbf{r})} \left|\mathbf{E}(\mathbf{r})\right|^2,$$

Forces on particle of type K:

$$\mathbf{F}_K = -\nabla V_{\mathrm{ext},K}(\mathbf{r}) = q_K \mathbf{E}(\mathbf{r}) + \frac{1}{2} \nabla \left(\frac{\epsilon_K - \epsilon(\mathbf{r})}{\phi_0(\mathbf{r})} \left|\mathbf{E}(\mathbf{r})\right|^2 \right)$$

Force computation and molecular dynamics

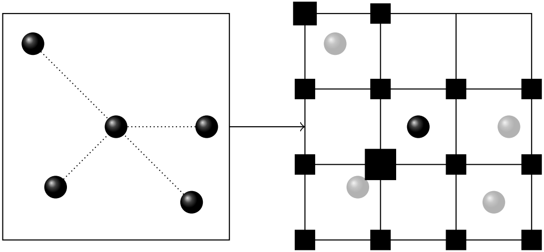


Hybrid particle field method

Mesoscale potentials in molecular dynamics:

$$V_{\mathrm{ext},i} = \frac{1}{\tilde{\phi}_0}\left(k_\mathrm{b}T\sum_j \chi_{ij}\phi_j(\mathbf{r}) + \frac{1}{\kappa}\left(\sum_j \phi_j(\mathbf{r}) - \tilde{\phi}_0\right)\right)$$

χ_{ij}: Flory-Huggins parameter. κ: compressibility. $\tilde{\phi}_0$: system density.



$\{\phi\}$ & $\{\nabla\phi\}$ Computed on a grid

Interpolated forces from $F = -\nabla V_\mathrm{ext}$

$\sum_{i<j} V_{ij}$ $\qquad$ $\sum_i V(\{\phi(\mathbf{r}_i)\})$

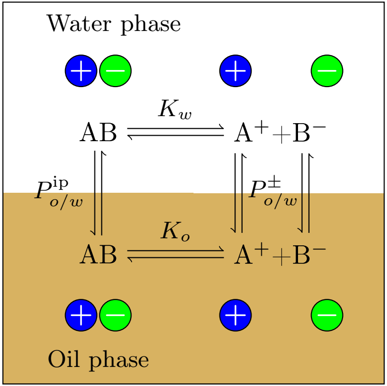
Partitioning of ions (1)

Ions in a phase separated oil/water mixture of ϵ_o and ϵ_w. ($RT \times \chi_{ow}$ =30 kJ mol^{-1})

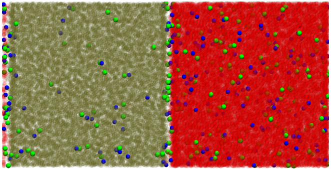
Distribution coefficient:

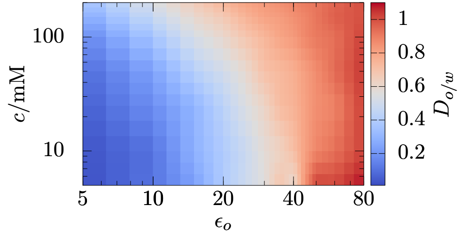
$$D_{o/w} = \frac{c_o}{c_w}$$

c_0 and c_w: concentration of ions within each phase.



Partitioning of ions (2)



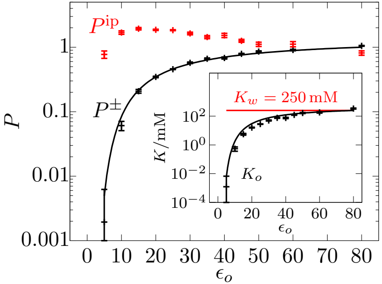


$$D_{o/w} = f(c, P^{\pm}_{o,w}, P^{\mathrm{ip}}_{o,w}, K_w)$$

c: concentration of ions.

Born theory of ions:

$$\log P^{\pm}_{o/w} = \gamma \left(\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right)$$



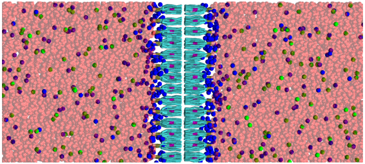
Ion permeability for a charged membrane

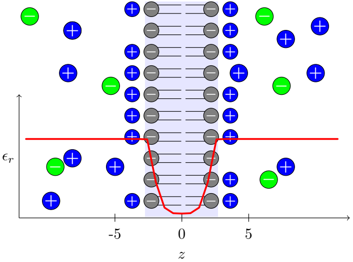
Homogeneous dielectric:

$$\epsilon_{15} = 15$$

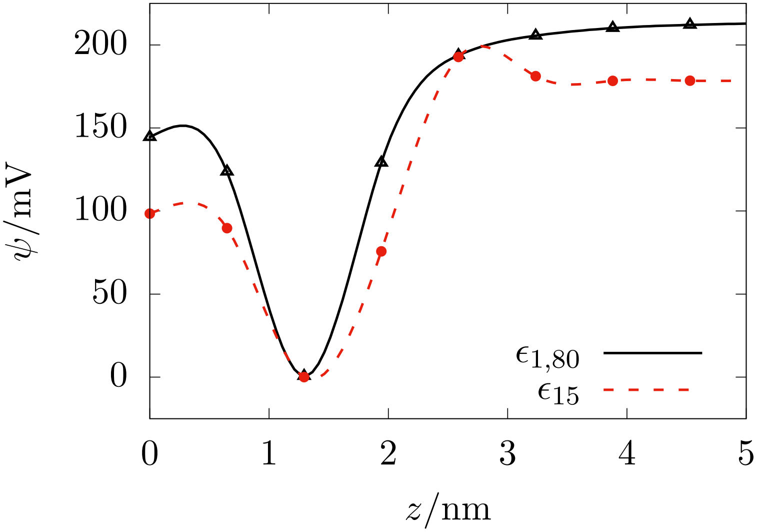
Inhomogeneous dielectric:

$$\epsilon_{1,80} = \begin{cases} 1, & \text{lipids} \\ 80, & \text{solvent} \end{cases}$$

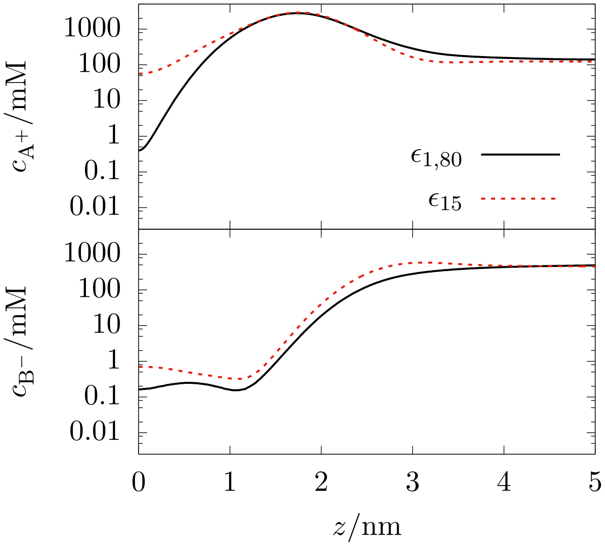




Electrostatic potential



Concentrations of ions



Conclusions and outlook

- New method for computing electrostatic forces in MD.
- Qualitative correct description of partitioning phenomena.
- Potentially a valuable method for multiphase simulation
- Manuscript in preparation
- Parallelize the numerical solver for the GPE.

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OCCAM Molecular Dynamics

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