SAND2013-9613P

Polarization as a field variable from molecular dynamics simulations

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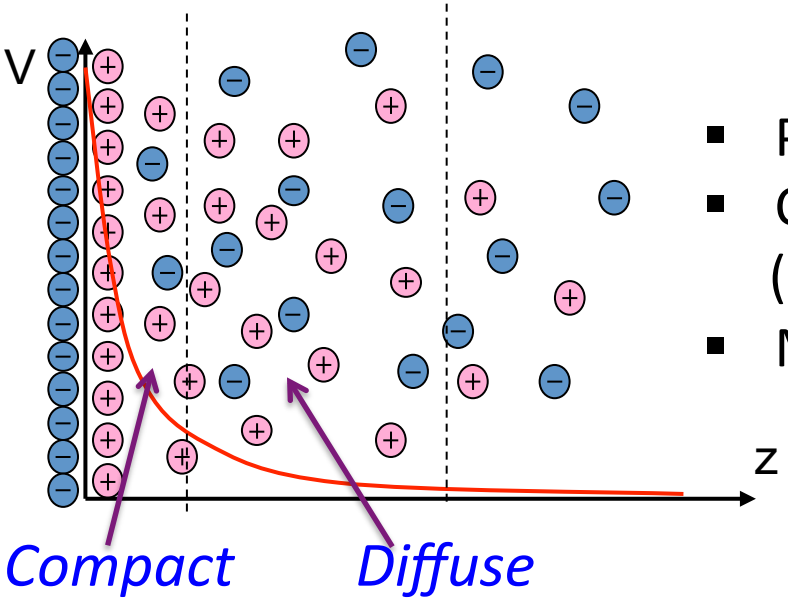
Electrical Double Layers

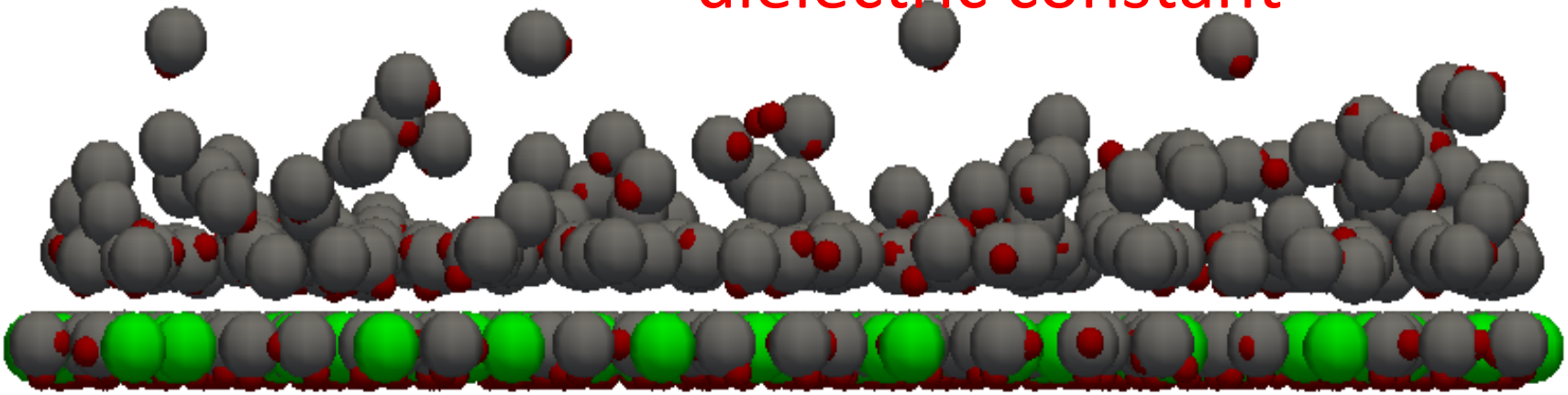


Models:

- Poisson-Boltzmann Theory
- Compact-Diffuse Layer Models (Kilic et. al. 2007)
- Mean-Field Models (Borukhov et. al. 2000)

$$D = \varepsilon E = \varepsilon_0 E + P$$

All layers modeled by bulk dielectric constant



We need better polarization models to depict reality.

Objective

Macroscopic Electrostatics:

$$\nabla \bullet D = \rho_f^M$$

$$D = \varepsilon_0 E + P = \varepsilon E$$

ρ_f^M → macroscopic free-charge density

D → macroscopic electric displacement

E → macroscopic electric field

ε → dielectric constant

P → macroscopic polarization

How do we calculate "P" using Molecular Information using Molecular Dynamics?

Today…

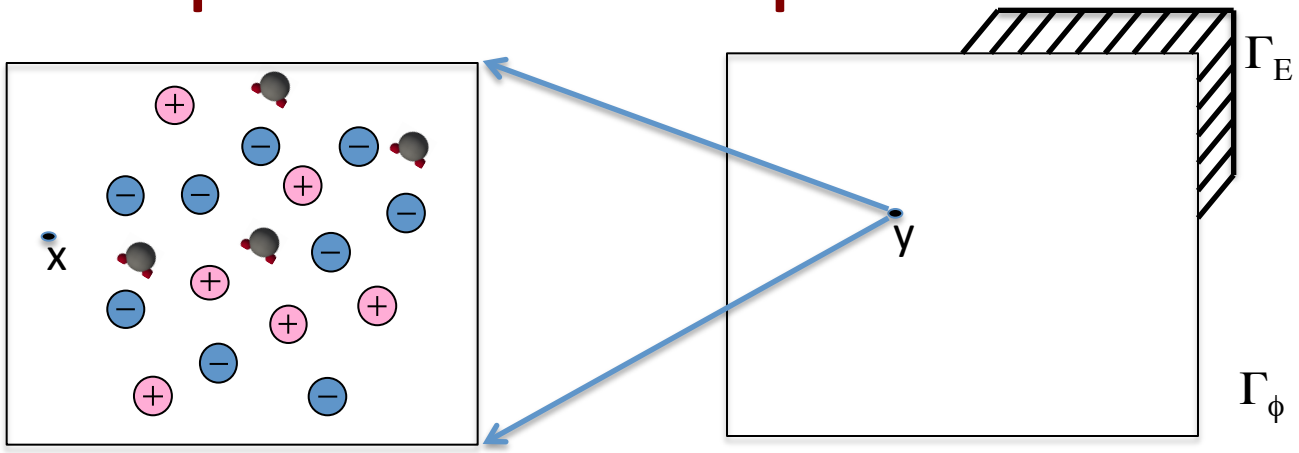
- Polarization in terms of molecular positions and charges.

- Dielectric constant of bulk water

- Application to electrical double layers

- At the interface
  - Water at the interface: Dipole and Quadrupole Moments

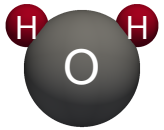
Microscopic-Macroscopic Connection



Microscale *Macroscale*

$$\nabla \cdot \mathbf{e}(\mathbf{x},t) = \frac{1}{\epsilon_0}\rho^m(\mathbf{x},t) \xrightarrow{\text{Coarse Grain}} \nabla \cdot \mathbf{D}(\mathbf{y},t) = \rho_f^M(\mathbf{y},t)$$

$$\rho^m(\mathbf{x},t) = \sum_{j=1}^{N_f} q_j \delta(\mathbf{x}-\mathbf{x}_j) + \sum_{n=1}^{N_m}\left(\sum_{j=1}^{N_n} q_j^n \delta(\mathbf{x}-\mathbf{x}_j^n)\right)$$



Can we derive macroscopic electrostatics equation from the microscopic electrostatics equation?

Mandadapu et. al. J. Chem. Phys. (2013);
Jackson, Classical Electrodynamics (1999)

Microscopic-Macroscopic Connection

Coarse-graining Charge:

$$\rho^M(\mathbf{y},t) = \int_{\mathcal{R}}\int_{\mathbf{\Gamma}} \rho^m(\mathbf{x},t)\Delta(\mathbf{y}-\mathbf{x})f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\,\mathrm{d}\mathbf{x}$$

Phase-space distribution

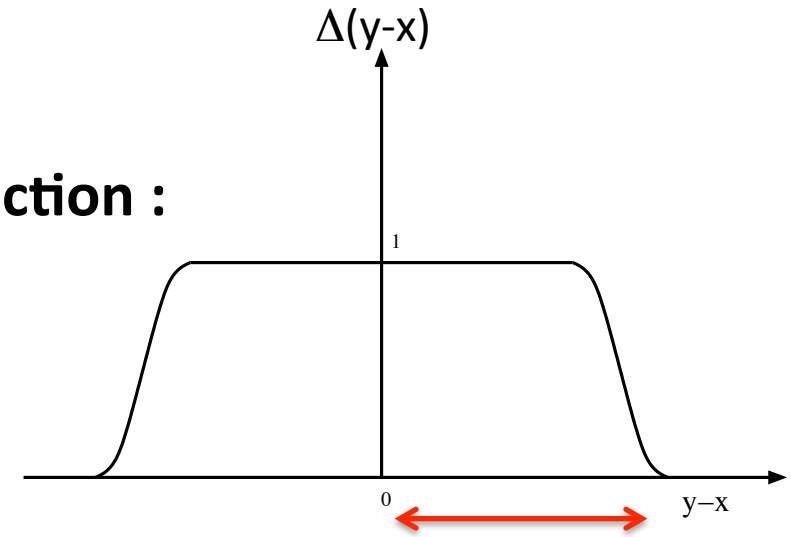
Coarse-graining function

Properties of coarse-graining function :

$$\int_R \Delta(y-x)dx = 1$$

$$\Delta(y-x) = 0, \ \ when\ x \in \partial R$$

$$supp\ \Delta << R$$



Intermediate asymptotic length scale
Or
Coarse-graining length scale

Mandadapu et. al. J. Chem. Phys. (2013)

Coarse-graining the microscopic electrostatic equation:

$$\int_{\mathcal{R}}\int_{\Gamma}\frac{\partial}{\partial \mathbf{x}'}\cdot\epsilon_0\mathbf{e}(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\mathrm{d}\,\mathbf{x}' \;=\; \int_{\mathcal{R}}\int_{\Gamma}\rho^m(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\,\mathrm{d}\mathbf{x}'$$

Macroscopic electric field

$$\frac{\partial}{\partial \mathbf{x}}\cdot\epsilon_0\mathbf{E}(\mathbf{x},t) \;=\; \int_{\mathcal{R}}\int_{\Gamma}\rho^m(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\,\mathrm{d}\mathbf{x}'$$

$$\rho^m(\mathbf{x},t) \;=\; \sum_{j=1}^{N_f} q_j\delta(\mathbf{x}-\mathbf{x}_j) + \sum_{n=1}^{N_m}\Big(\sum_{j=1}^{N_n} q_j^n\delta(\mathbf{x}-\mathbf{x}_j^n)\Big)$$

Macroscopic free charge

$$\sum_{n=1}^{N_m}\Big(\sum_{j=1}^{N_n} q_j^n\Delta(\mathbf{x}-\mathbf{x}_n-\mathbf{x}_{jn})\Big)$$

Gives rise to dipole and quadrouple moments when expanded around the center of mass of the solvent molecule.

$$\frac{\partial}{\partial \mathbf{x}} \cdot \epsilon_0 \mathbf{E}(\mathbf{x},t) = \int_\Gamma \left[\sum_{j=1}^{N_f} q_j \Delta(\mathbf{x}-\mathbf{x}_j) + \sum_{n=1}^{N_m} \left(\sum_{j=1}^{N_n} q_j^n \Delta(\mathbf{x}-\mathbf{x}_n) \right) \right] f(\mathbf{\Gamma},t) \mathrm{d}\mathbf{\Gamma} +$$

$$\frac{\partial}{\partial \mathbf{x}} \cdot \left[\int_\Gamma \sum_{n=1}^{N_m} \sum_{j=1}^{N_n} q_j^n \mathbf{x}_{jn} \Delta(\mathbf{x}-\mathbf{x}_n) \, f(\mathbf{\Gamma},t) \mathrm{d}\mathbf{\Gamma} - \int_\Gamma \sum_{n=1}^{N_m} \sum_{j=1}^{N_n} q_j^n \frac{\mathbf{x}_{jn} \otimes \mathbf{x}_{jn}}{2!} \cdot \frac{\partial}{\partial \mathbf{x}} \Delta(\mathbf{x}-\mathbf{x}_n) \, f(\mathbf{\Gamma},t) \mathrm{d}\mathbf{\Gamma} + \ldots \right]$$

Macroscopic Dipole Moment

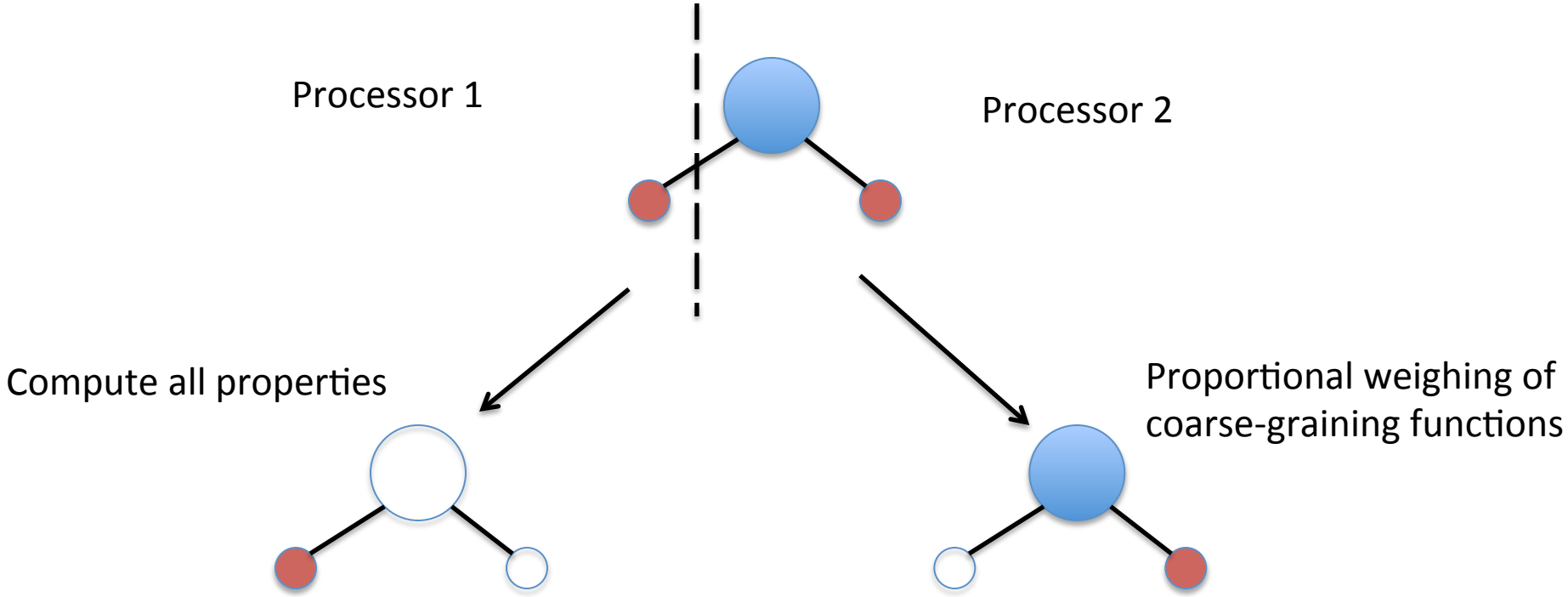
Macroscopic Quadrupole Moment

Order of Coarse Graining function Δ:

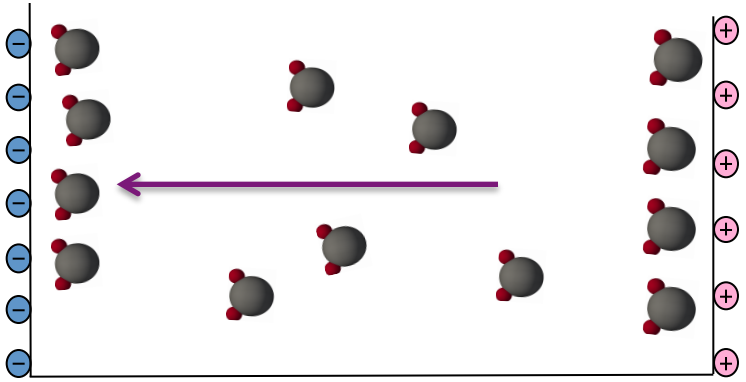
- Constant: gives only dipole moment
- Linear: gives up to quadrupole moment

Mandadapu et. al., J. Chem. Phys (2013)

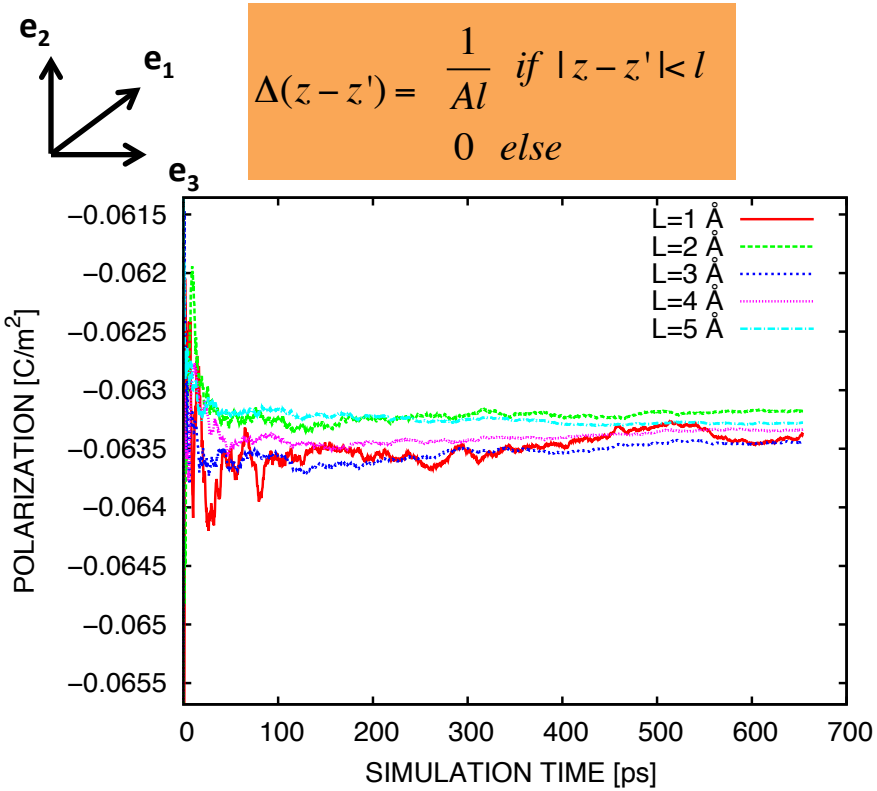
Scalable Implementation



Bulk Water-TIP3P(Validation)

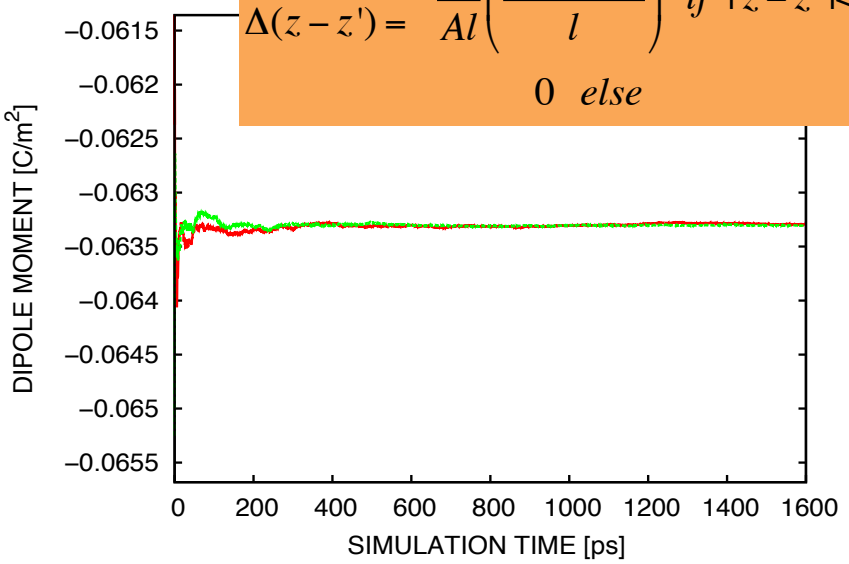


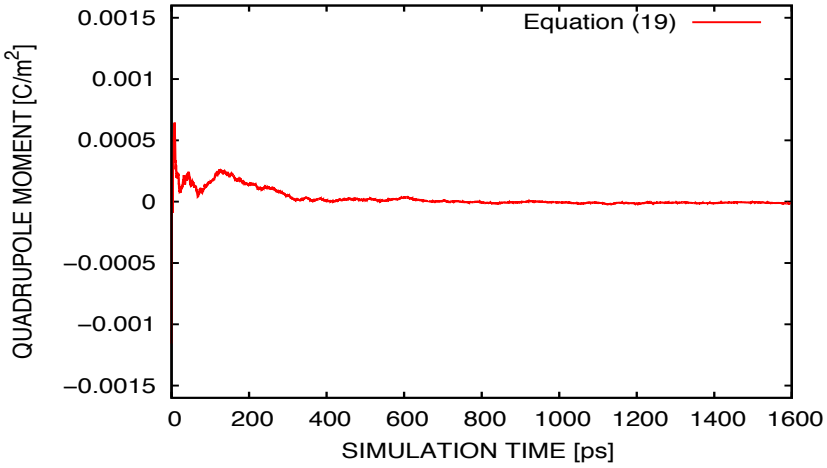
$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'| < l \\ 0 & else \end{cases}$$



Polarization as a time average at the center of the simulation box for varying averaging length

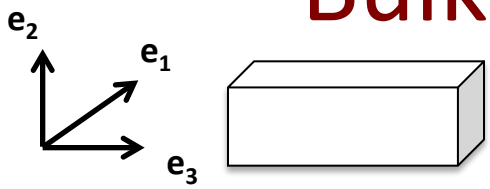
$$\Delta(z-z') = \begin{cases} \frac{1}{Al}\left(\frac{l-|z-z'|}{l}\right) & if\ |z-z'| < l \\ 0 & else \end{cases}$$





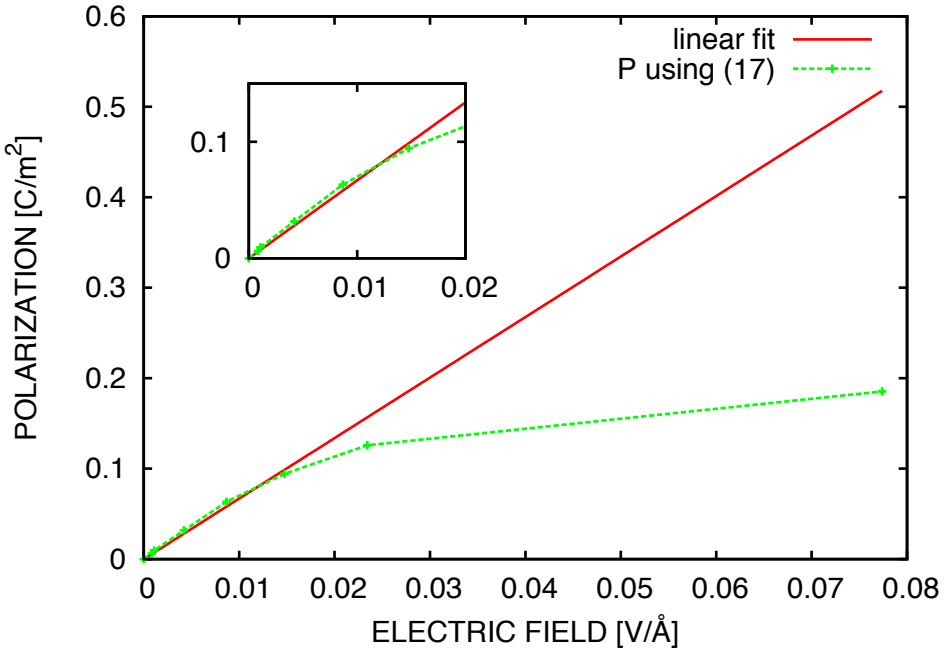
Quadrupole moments are negligible in the bulk. No surprises !

Bulk Water-TIP3P(Validation)



Applied field

$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'| < l \\ 0 & else \end{cases}$$

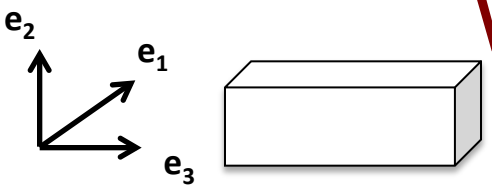


Polarization vs. Resultant electric field

$$\frac{\varepsilon}{\varepsilon_0} = 73$$

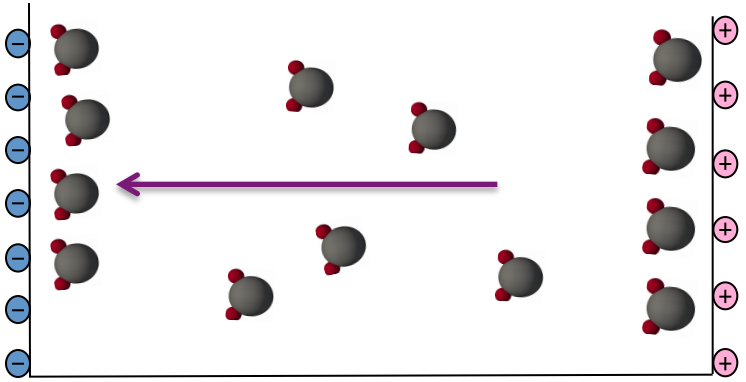
Note that the resultant electric fields are supposed to be averaged with the same averaging volume.

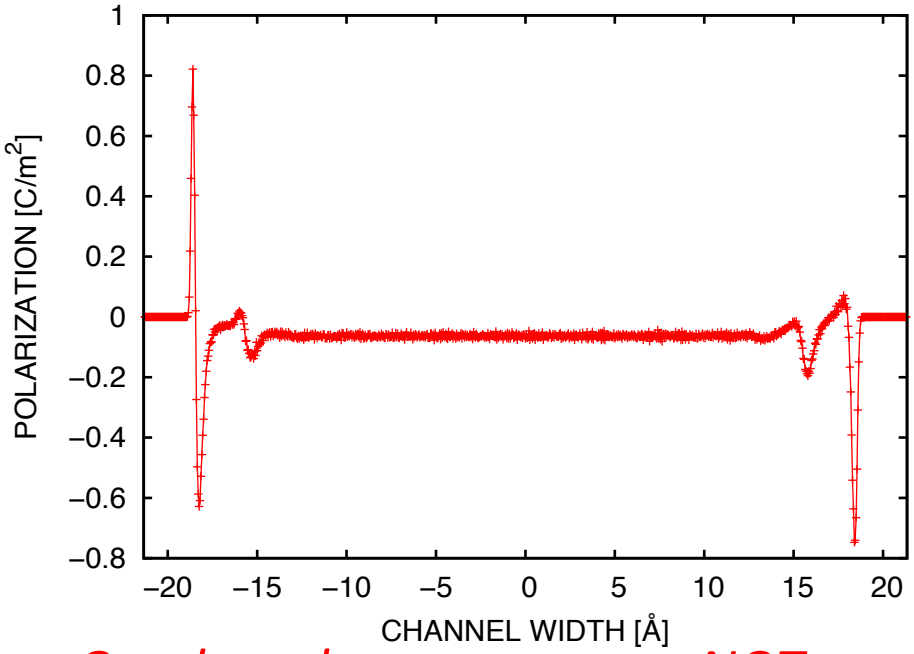
Water at the Interfaces

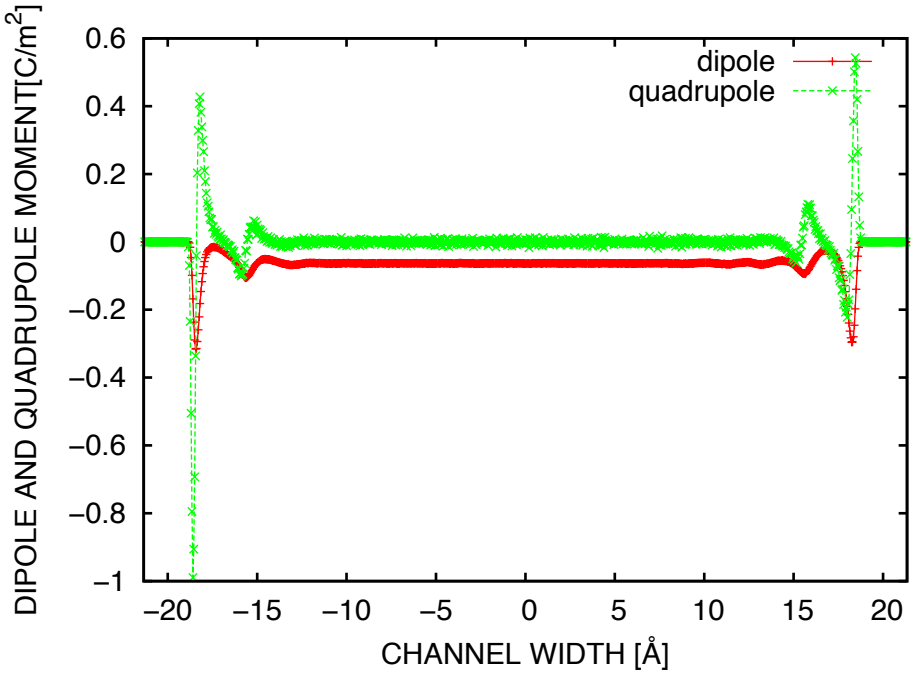


Applied field

$$\Delta(z-z') = \frac{1}{Al}\left(\frac{l-|z-z'|}{l}\right) \quad if \ |z-z'|<l$$
$$0 \quad else$$



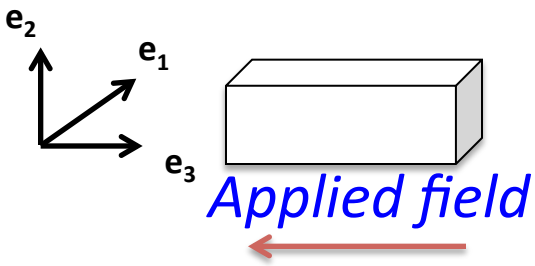


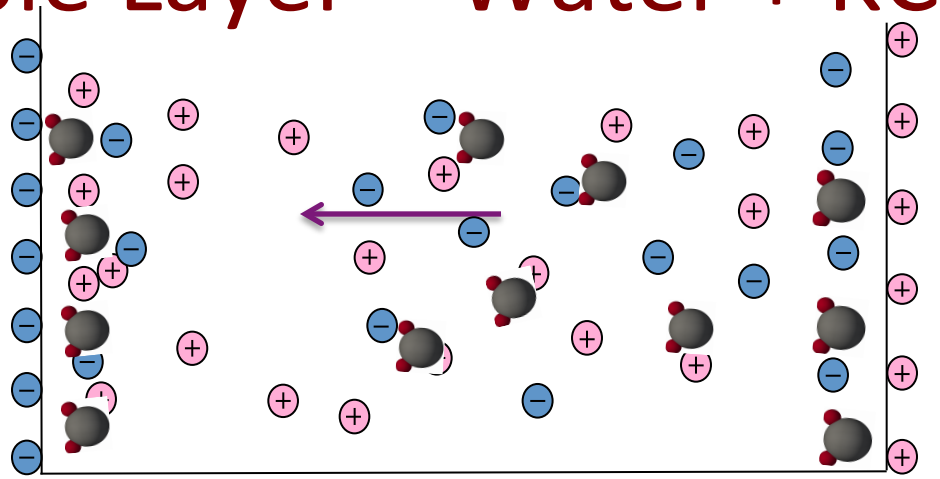


Quadrupole moments are NOT negligible at the interface !!!

Dipole and Quadrupole Moments across the channel width for averaging length of 0.05 Angstroms.

Electrical Double Layer – Water + KCl

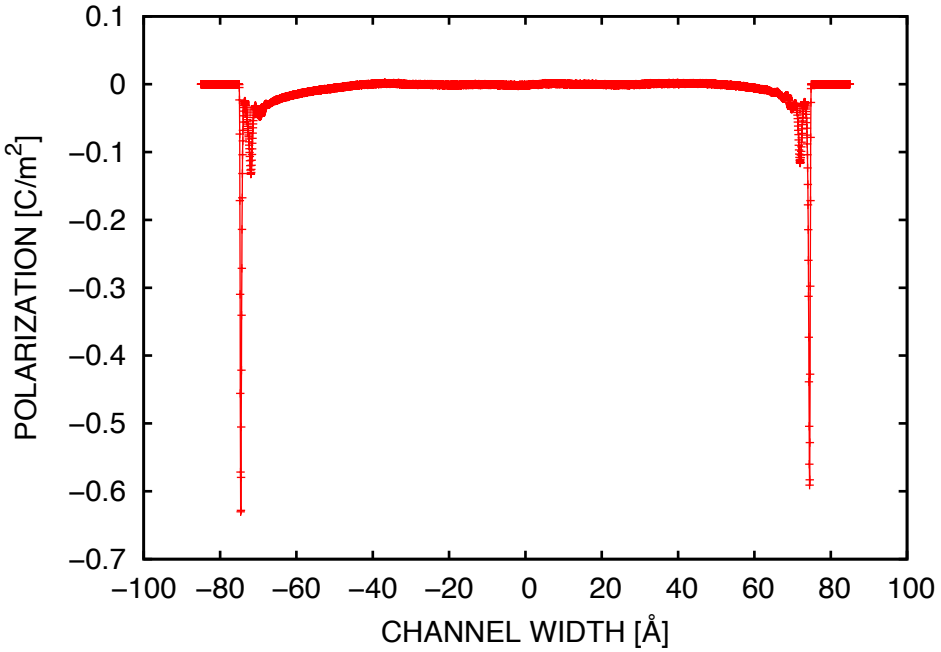




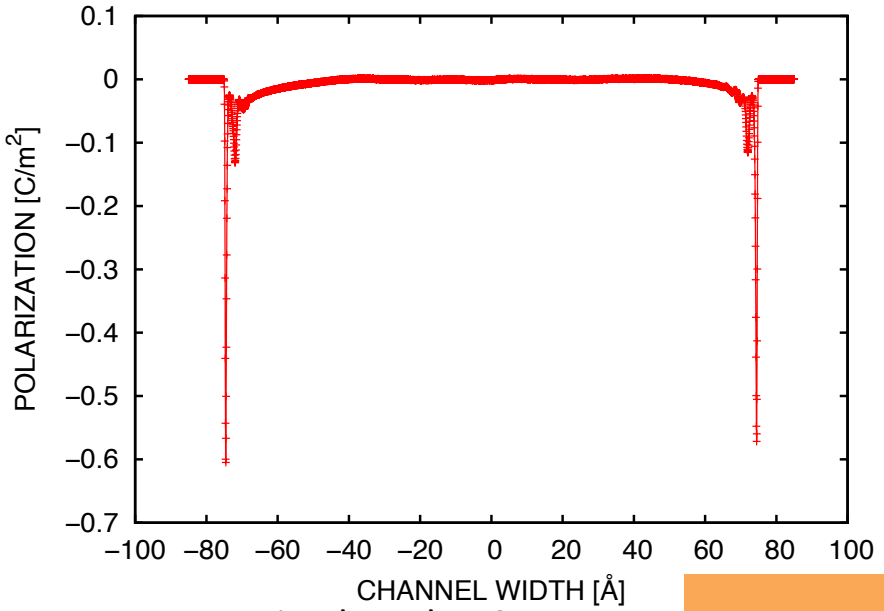
KCl concentration: 100mM

Debye length : 1nm

$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'| < l \\ 0 & else \end{cases}$$

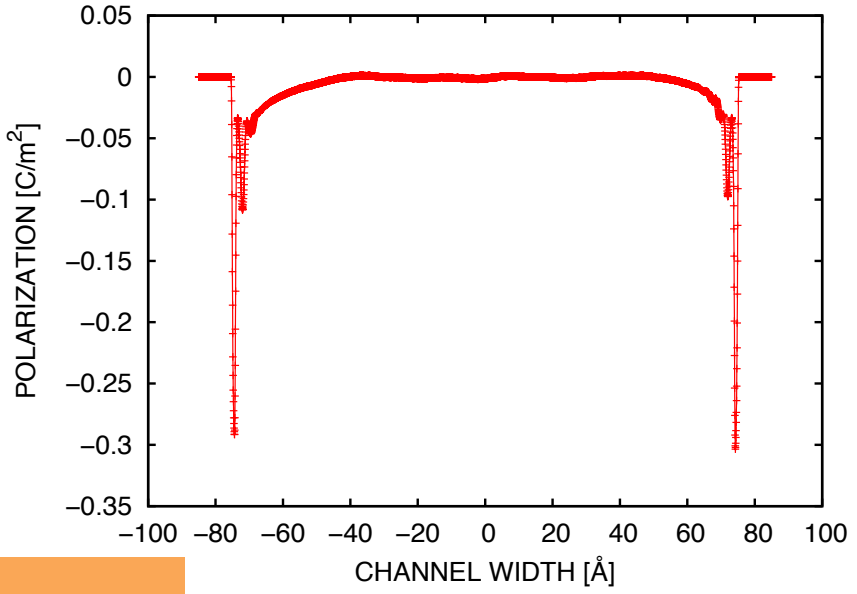


Polarization across the channel width for averaging length of 0.05 Angstroms.

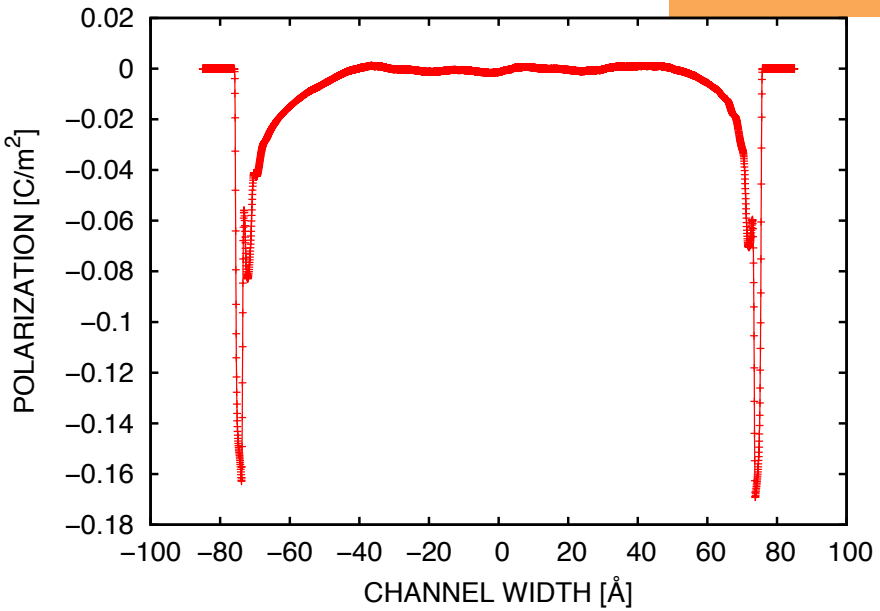


Averaging length = 0.1 Angs.

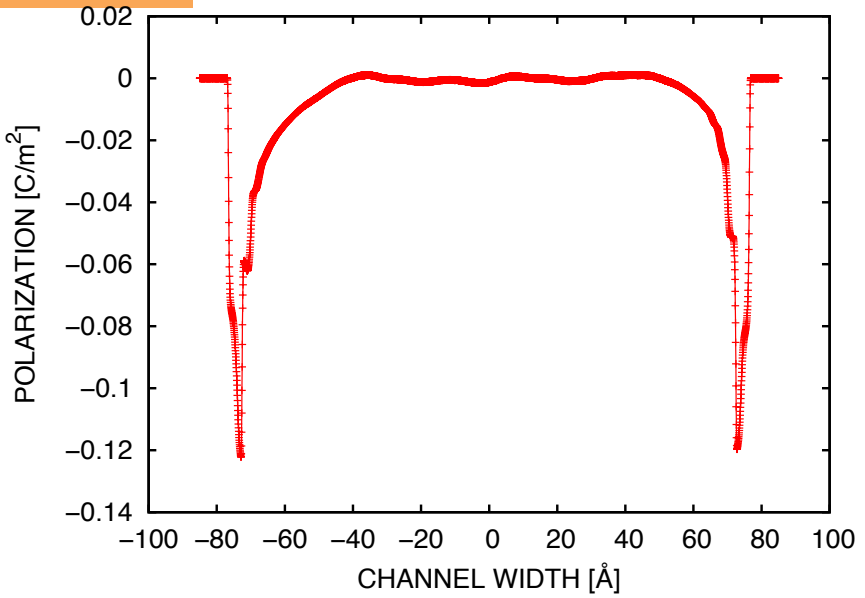
$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'|<l \\ 0 & else \end{cases}$$



Averaging length = 0.5 Angs.

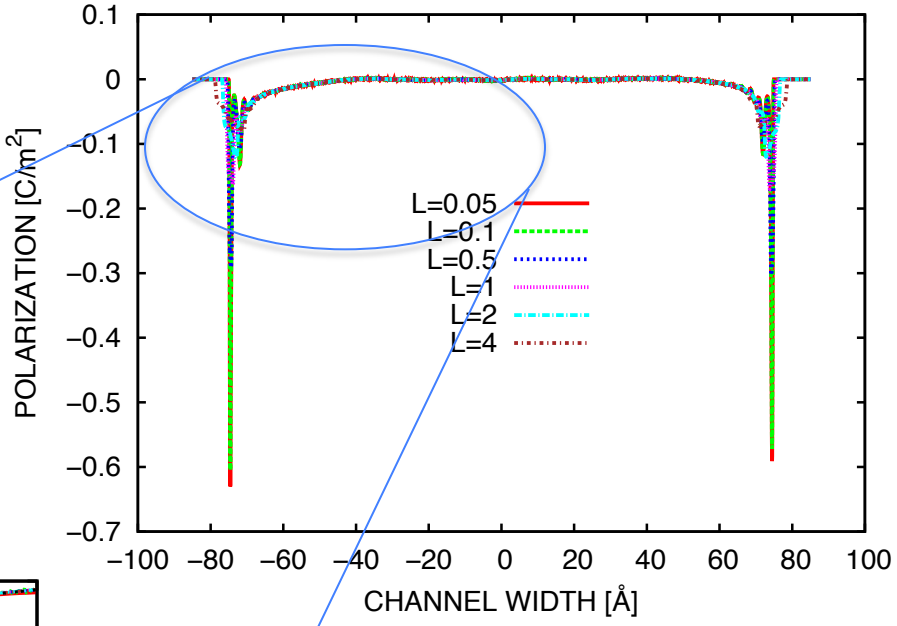


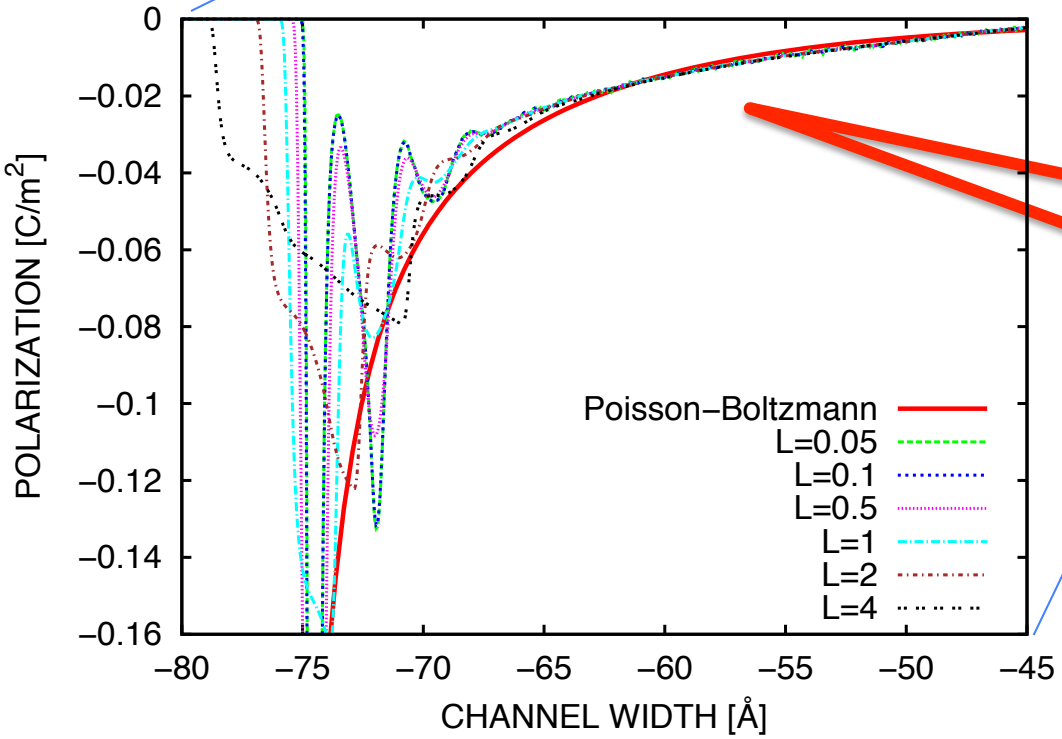
Averaging length = 1.0 Angs.



Averaging length = 2.0 Angs.

$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'| < l \\ 0 & else \end{cases}$$

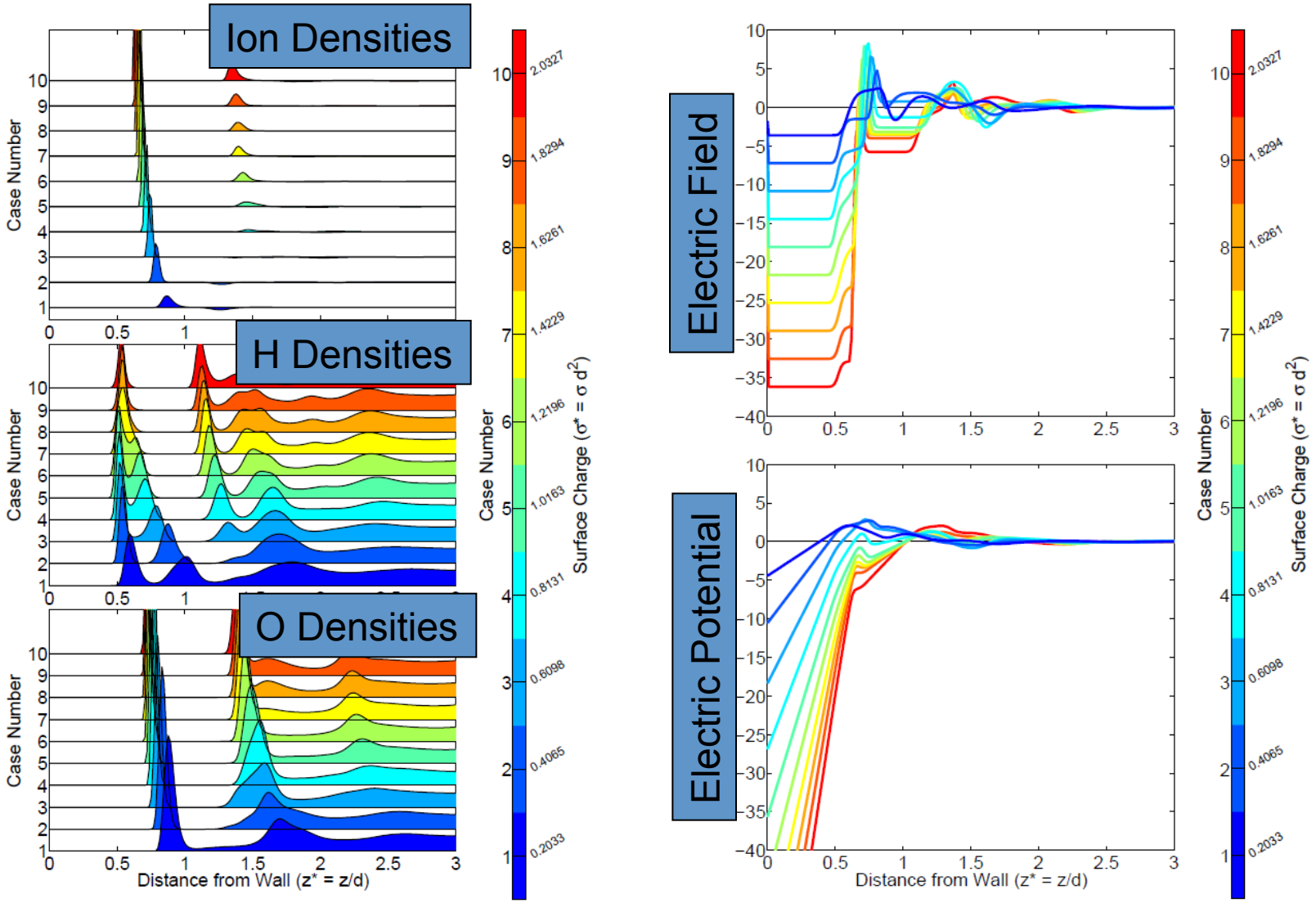




INTERMEDIATE ASYMPTOTIC LENGTH SCALE !!!

Barenblatt, Scaling (2003)

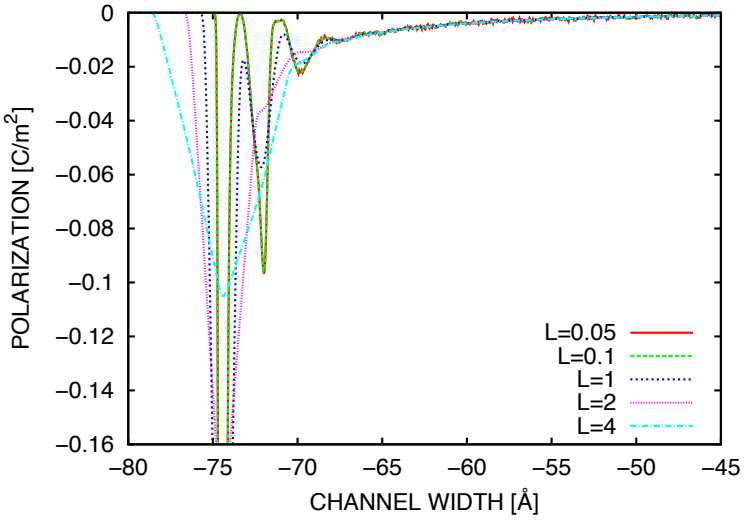
Electrical Double Layer – High Charge



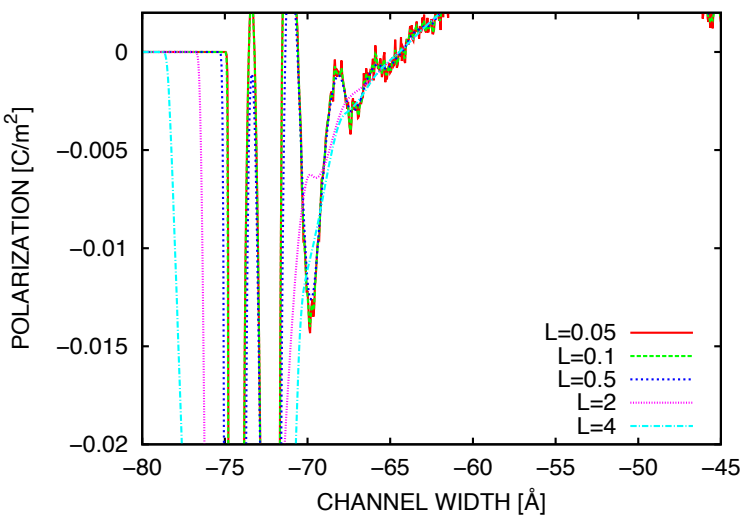
Lee, Templeton, Mandadapu, Zimmerman, J. Chem. Theor. Comp (2013)

Electrical Double Layer – Anode

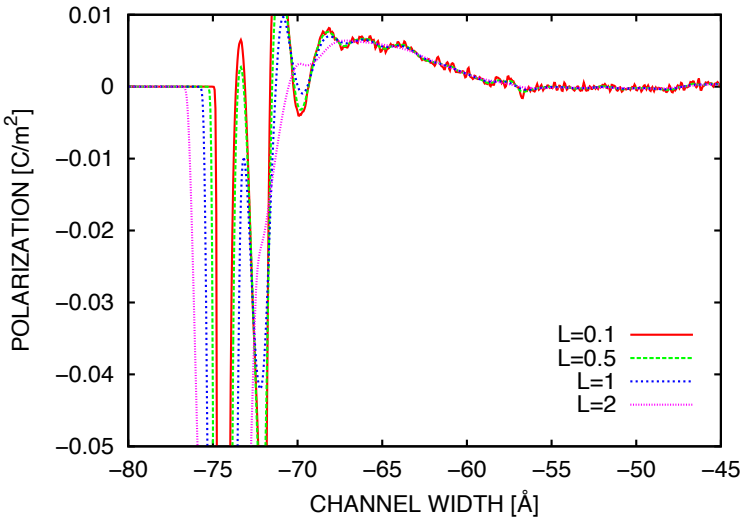
Case 1



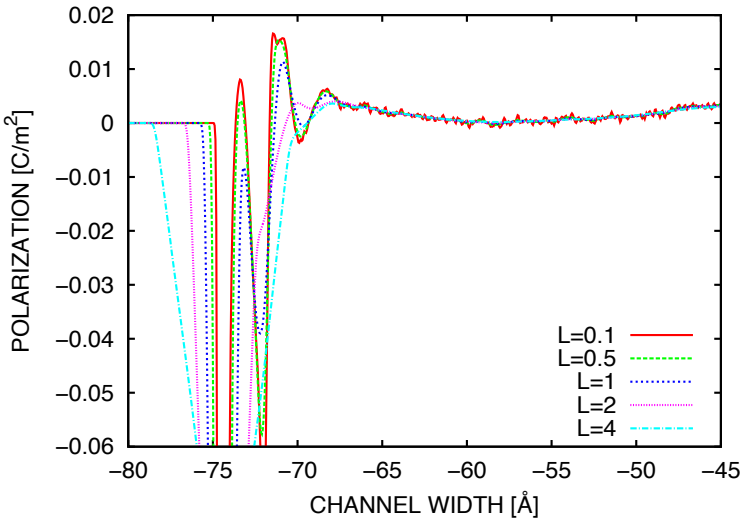
Case 3



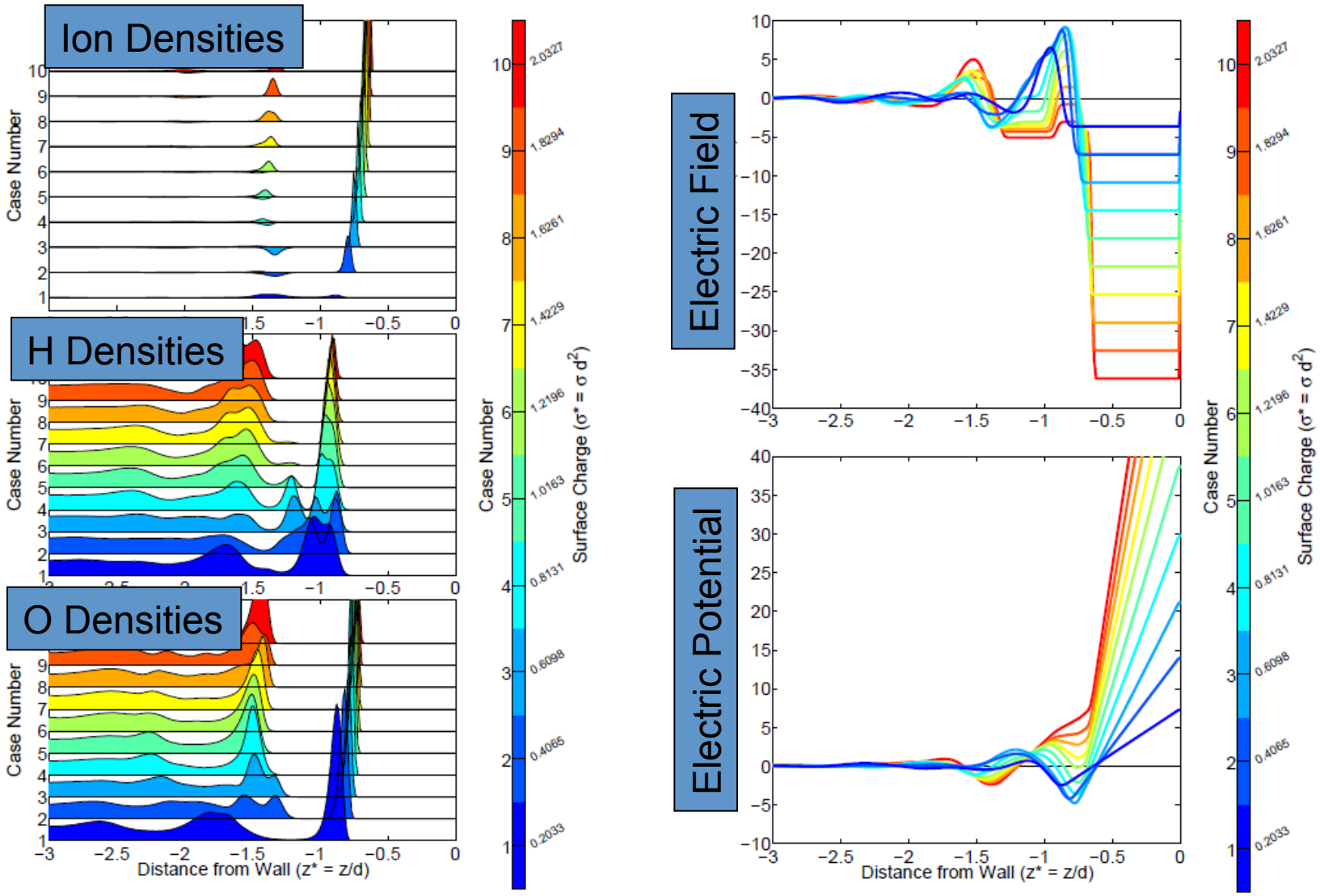
Case 5



Case 10



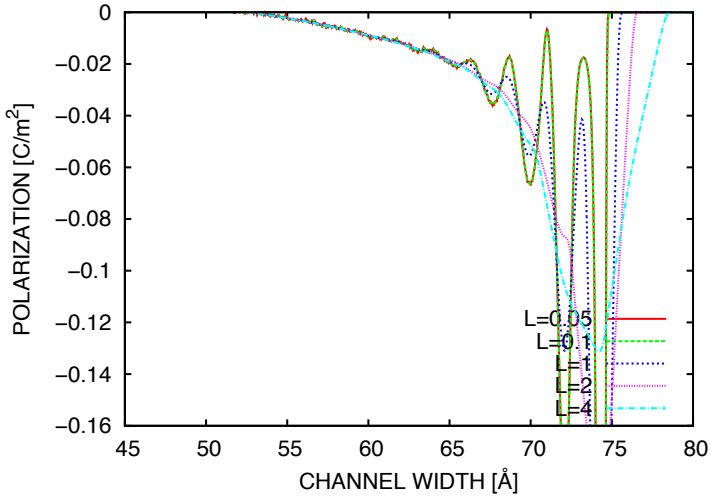
Electrical Double Layer – Cathode



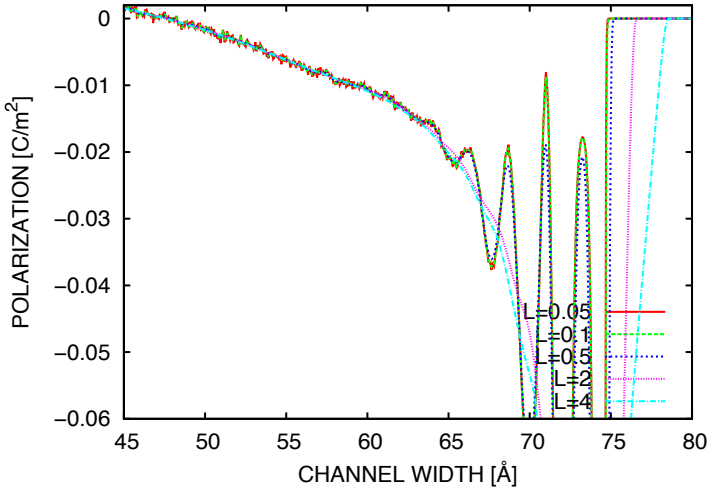
Lee, Templeton, Mandadapu, Zimmerman, J. Chem. Theor. Comp (2013)

Electrical Double Layer – Cathode

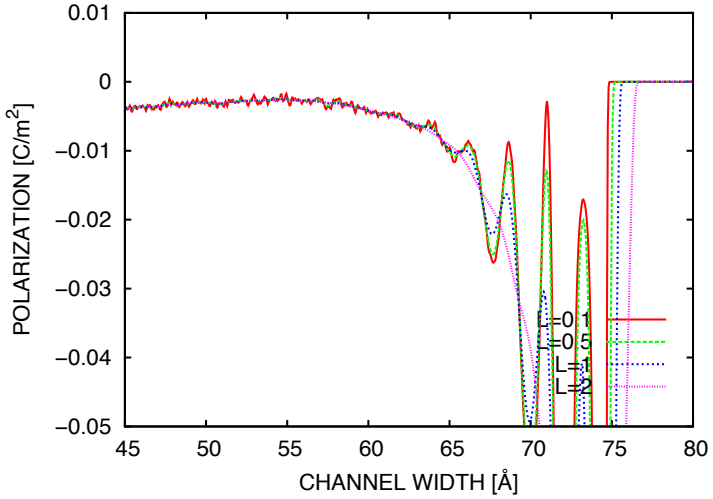
Case 1



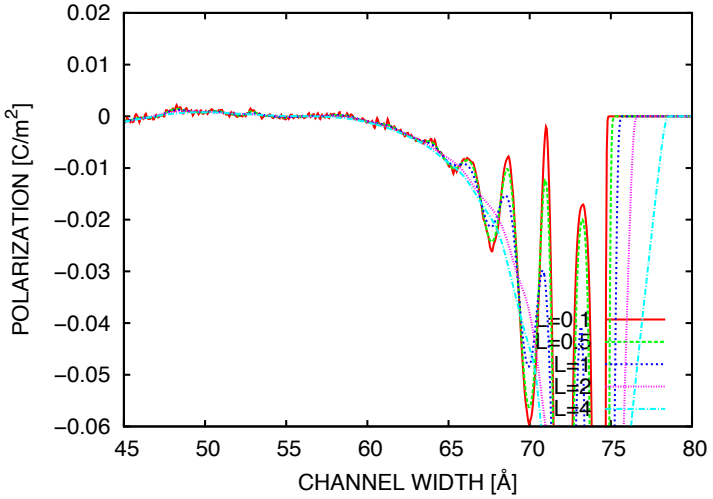
Case 3



Case 5

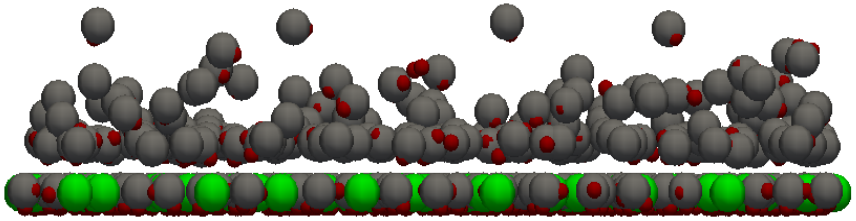


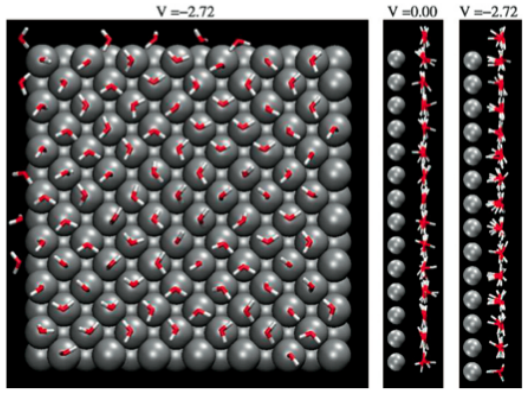
Case 10



Conclusions

- A theoretical and computational procedure in real space exists now for systematically calculating the moments that contribute to the total polarization vector.
- Intermediate asymptotic scales and therefore length scales of the diffuse layers can be found for various concentrations and surface charges.
- Quadrupole moments do not seem to be negligible at the interface.





Willard, Chandler (2008)

- Study polarization in stern, compact and diffuse layers.
- Develop *new models* by understanding hydrogen bonding networks.

Acknowledgements

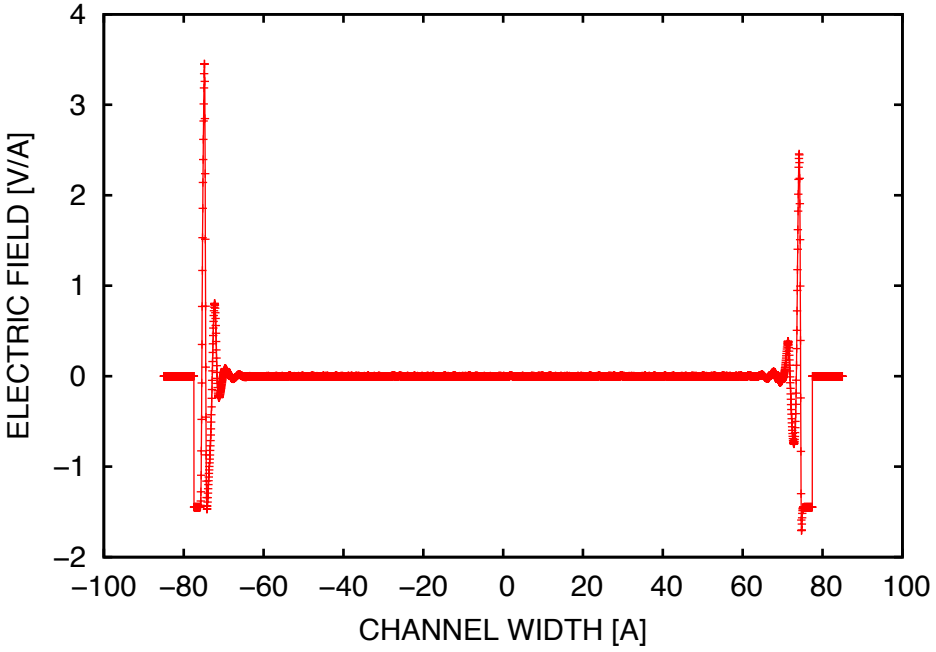
Funding: Sandia LDRD Program

K. K. Mandadapu, J. A. Templeton and J. W. Lee, Polarization as a field variable from molecular dynamics simulations.
The Journal of Chemical Physics (2013)

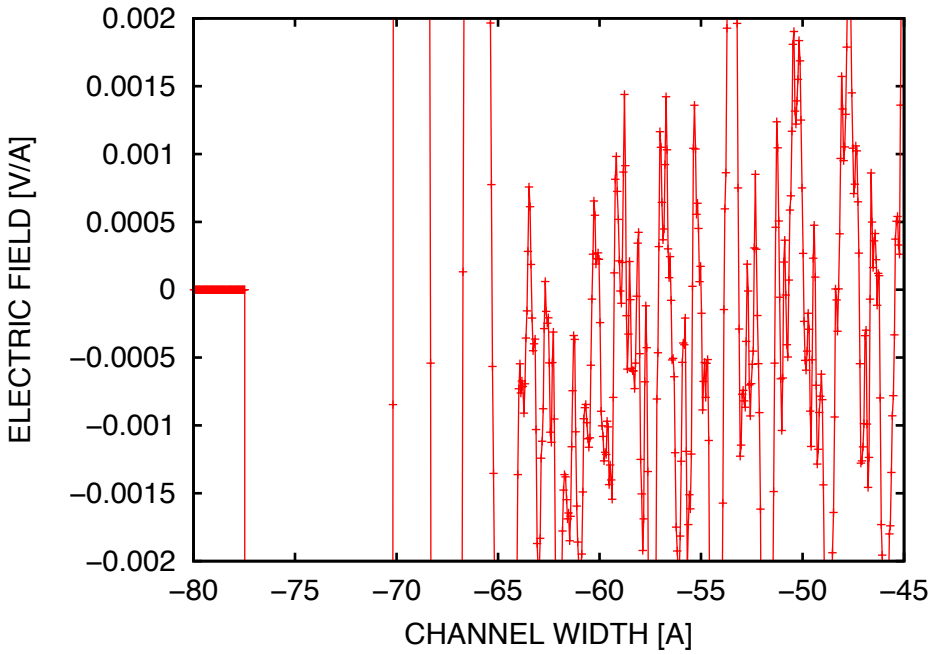
Computational software –
AtC package of LAMMPS.
Available to the public:
http://lammps.sandia.gov

Thank You

Advantages - Polarization



Electric field across the channel width using averages from 10 independent simulations using 10 million time steps.



Electric fields do not converge even for large number of timesteps !!!

Coarse-graining the microscopic electrostatic equation:

$$\int_{\mathcal{R}}\int_{\Gamma}\frac{\partial}{\partial \mathbf{x}'}\cdot\epsilon_0\mathbf{e}(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\mathrm{d}\,\mathbf{x}' \;=\; \int_{\mathcal{R}}\int_{\Gamma}\rho^m(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\,\mathrm{d}\mathbf{x}'$$

Macroscopic electric field

$$\frac{\partial}{\partial \mathbf{x}}\cdot\epsilon_0\mathbf{E}(\mathbf{x},t) \;=\; \int_{\mathcal{R}}\int_{\Gamma}\rho^m(\mathbf{x}',t)\Delta(\mathbf{x}-\mathbf{x}')\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}\,\mathrm{d}\mathbf{x}'$$

$$\frac{\partial}{\partial \mathbf{x}}\cdot\epsilon_0\mathbf{E}(\mathbf{x},t) = \int_{\Gamma}\left[\sum_{j=1}^{N_f}q_j\Delta(\mathbf{x}-\mathbf{x}_j)+\sum_{n=1}^{N_m}\left(\sum_{j=1}^{N_n}q_j^n\Delta(\mathbf{x}-\mathbf{x}_n)\right)\right]f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}+$$

$$\frac{\partial}{\partial \mathbf{x}}\cdot\left[\int_{\Gamma}\sum_{n=1}^{N_m}\sum_{j=1}^{N_n}q_j^n\mathbf{x}_{jn}\Delta(\mathbf{x}-\mathbf{x}_n)\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}-\int_{\Gamma}\sum_{n=1}^{N_m}\sum_{j=1}^{N_n}q_j^n\frac{\mathbf{x}_{jn}\otimes\mathbf{x}_{jn}}{2!}\cdot\frac{\partial}{\partial \mathbf{x}}\Delta(\mathbf{x}-\mathbf{x}_n)\,f(\mathbf{\Gamma},t)\mathrm{d}\mathbf{\Gamma}+\ldots\right]$$

Order of Coarse Graining function Δ:

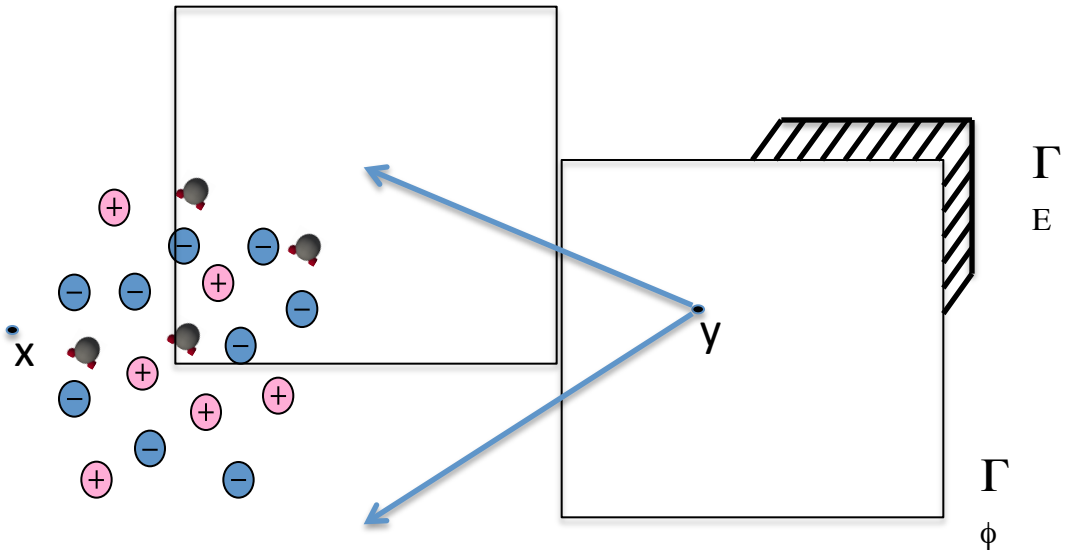
Macroscopic Dipole Moment

Macroscopic Quadrupole Moment

- Constant: gives only dipole moment
- Linear: gives up to quadrupole moment

Irving and Kirkwood, 1950

Descriptions of Scales



Microscale

Macroscale

$$\nabla \cdot \mathbf{e}(\mathbf{x}, t) = \frac{1}{\epsilon_0} \rho^m(\mathbf{x}, t)$$

$$\nabla \cdot \mathbf{D}(\mathbf{y}, t) = \rho_f^M(\mathbf{y}, t)$$