SAND2013-5966C

Polarization as a field variable from molecular dynamics simulations: Applications to Electrical Double Layers

Kranthi Mandadapu, Jeremy Templeton & Jonathan Lee

Sandia National Laboratories, Livermore, CA, USA

"Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000."

Introduction

Macroscopic Electrostatics:

$$\nabla \quad = \rho_f^M$$

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

$\rho_f^M \rightarrow$ macroscopic free-charge density

$D \rightarrow$ macroscopic electric displacement

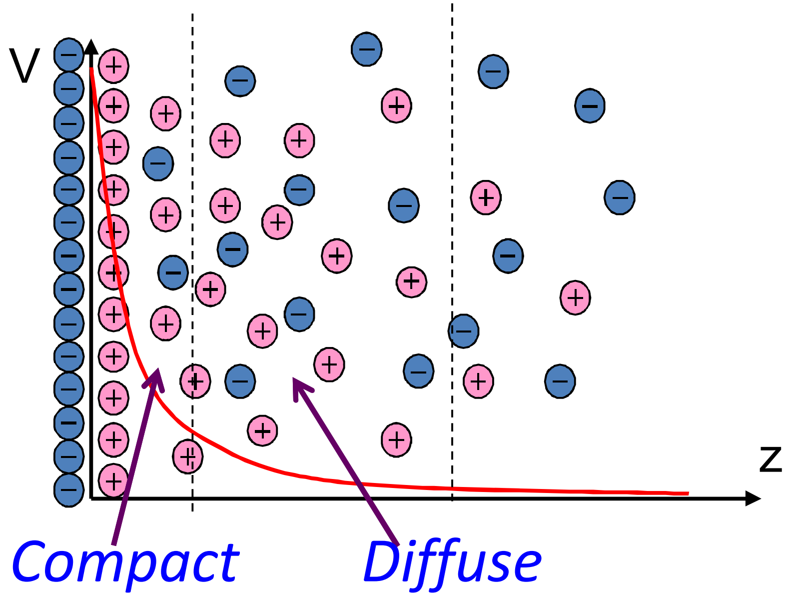
$E \rightarrow$ macroscopic electric field

$\varepsilon \rightarrow$ dielectric constant

$P \rightarrow$ macroscopic polarization

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

Electrical Double Layers

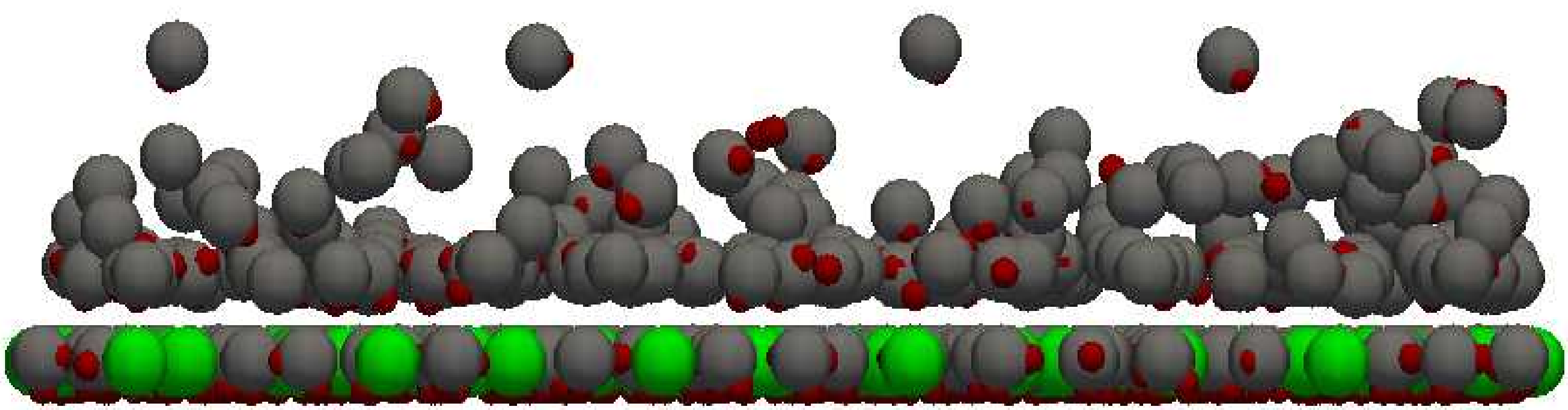


Models:

- Poisson-Boltzmann Theory
- Compact-Diffuse Layer Models
- Mean-Field Models

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

Compact Layer modeled by bulk dielectric constant



We need better polarization models to depict reality.

Today…

- Polarization interms of molecular positions and charges.

- Dielectric constant of bulk water

- Application to electrical double layers

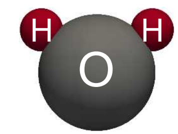
- At the interface
  - Water at the interface: Dipole and Quadrupole Moments

Microscopic-Macroscopic Connection

Microscopic: Macroscopic:

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

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



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

Coarse-graining Charge:

Phase-space distribution

$$\rho^M(\mathbf{x},t) = \int_{\mathcal{R}}\int_{\Gamma} \rho^m(\mathbf{x}',t)\ \ (\mathbf{x}-\mathbf{x}')\ \ \Gamma,t)\mathrm{d}\Gamma\,\mathrm{d}\mathbf{x}'$$

Coarse-graining function

Mandadapu et. al. (in prep); Irving and Kirkwood, 1950

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

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

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

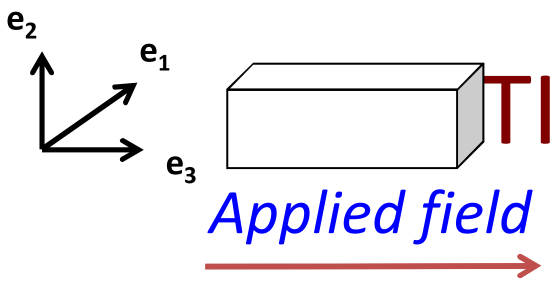
$$\frac{\partial}{\partial \mathbf{x}} \cdot \left[\underbrace{\int_{\Gamma} \sum_{n=1}^{N_m} \sum_{j=1}^{N_n} q_j^n \mathbf{x}_{jn} \Delta(\mathbf{x}-\mathbf{x}_n)\, f(\mathbf{\Gamma}, t)\mathrm{d}\mathbf{\Gamma}}_{\text{Macroscopic Dipole Moment}} - \underbrace{\int_{\Gamma} \sum_{n=1}^{N_m} \sum_{j=1}^{N_n}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

Order of Coarse Graining function Δ:

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

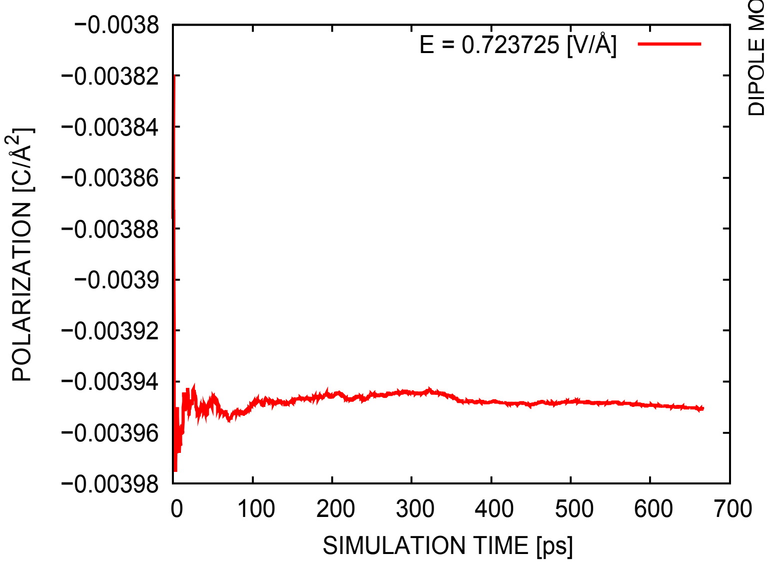
Irving and Kirkwood, 1950

Bulk Water- TIP3P(Validatio

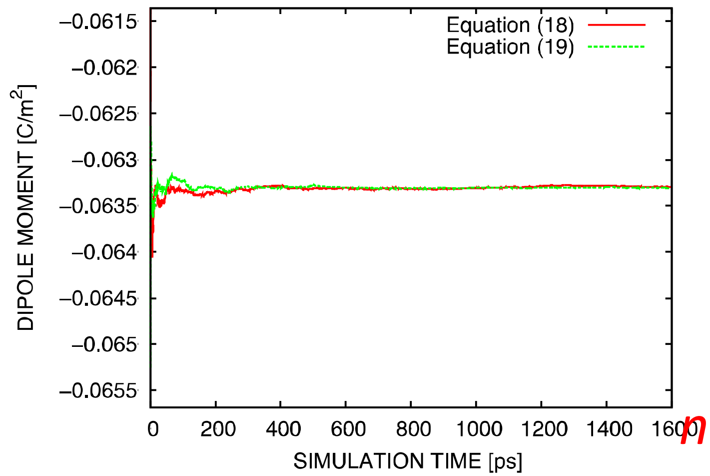


$$\Delta(z-z') = \begin{cases} \dfrac{1}{Al}\left(\dfrac{l-|z-z'|}{l}\right) & if\ |z-z'|<l \\ 0 & else \end{cases}$$

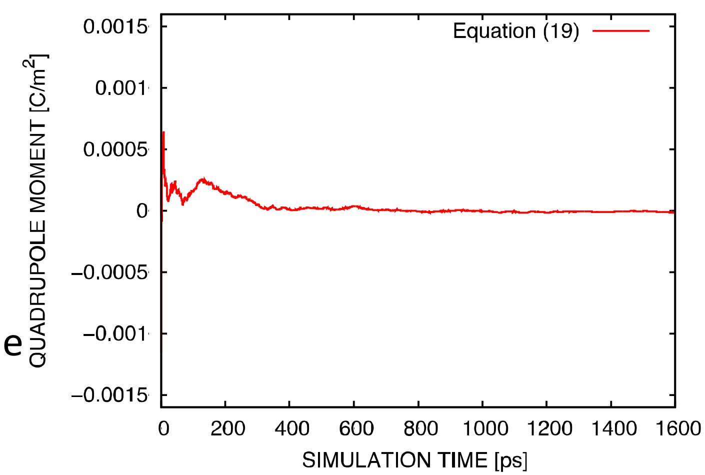
$$\Delta(z-z') = \begin{cases} \dfrac{1}{Al} & if\ |z-z'|<l \\ 0 & else \end{cases}$$



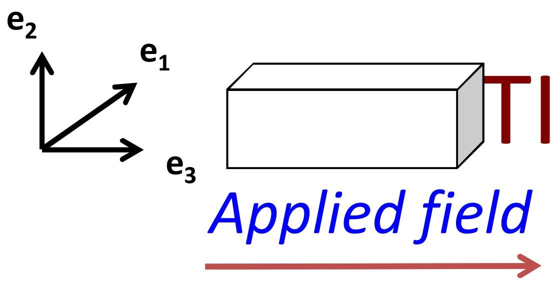
Polarization as a time average at the center of the simulation box for averaging length of 10 Angs



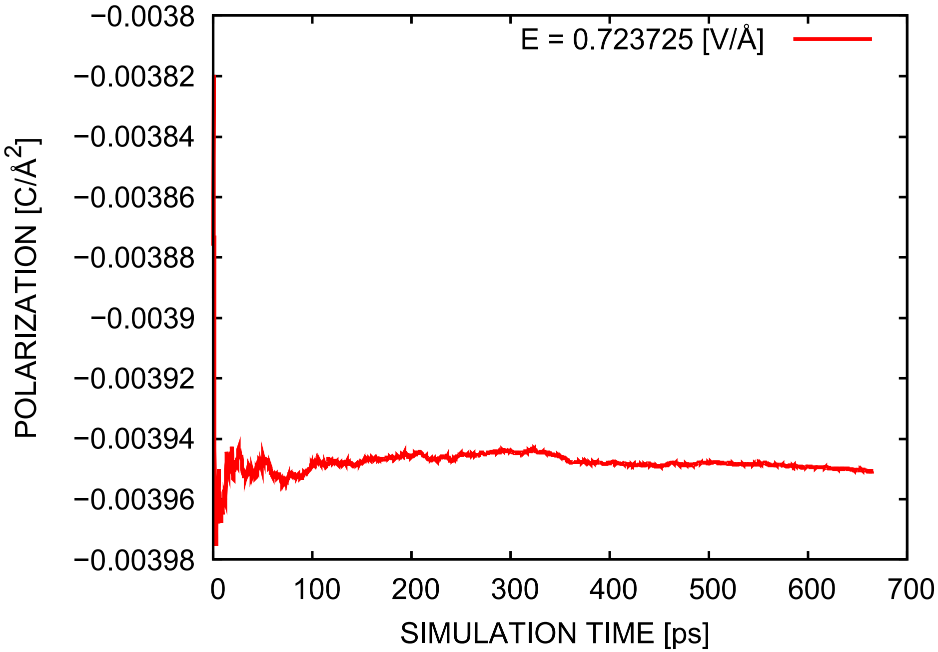
Quadrupole Moments are negligible in the bu !!!



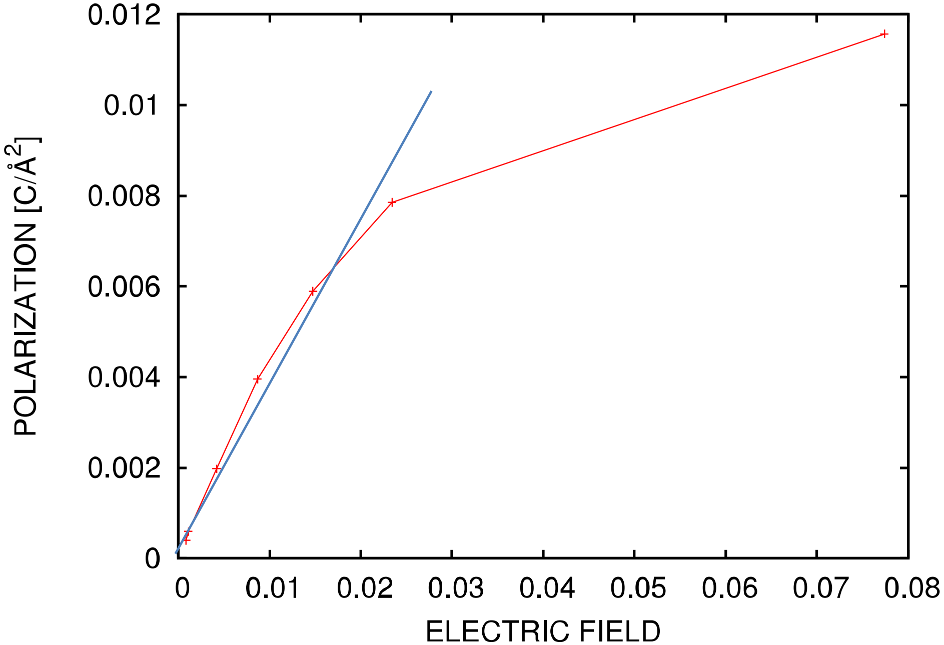
Bulk Water-TIP3P(Validation)



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



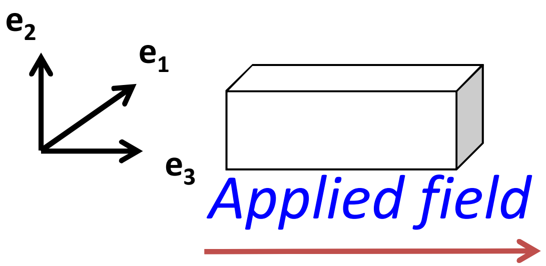
Polarization as a time average at the center of the simulation box for averaging length of 10 Angs



Polarization vs. Resultant electric field

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

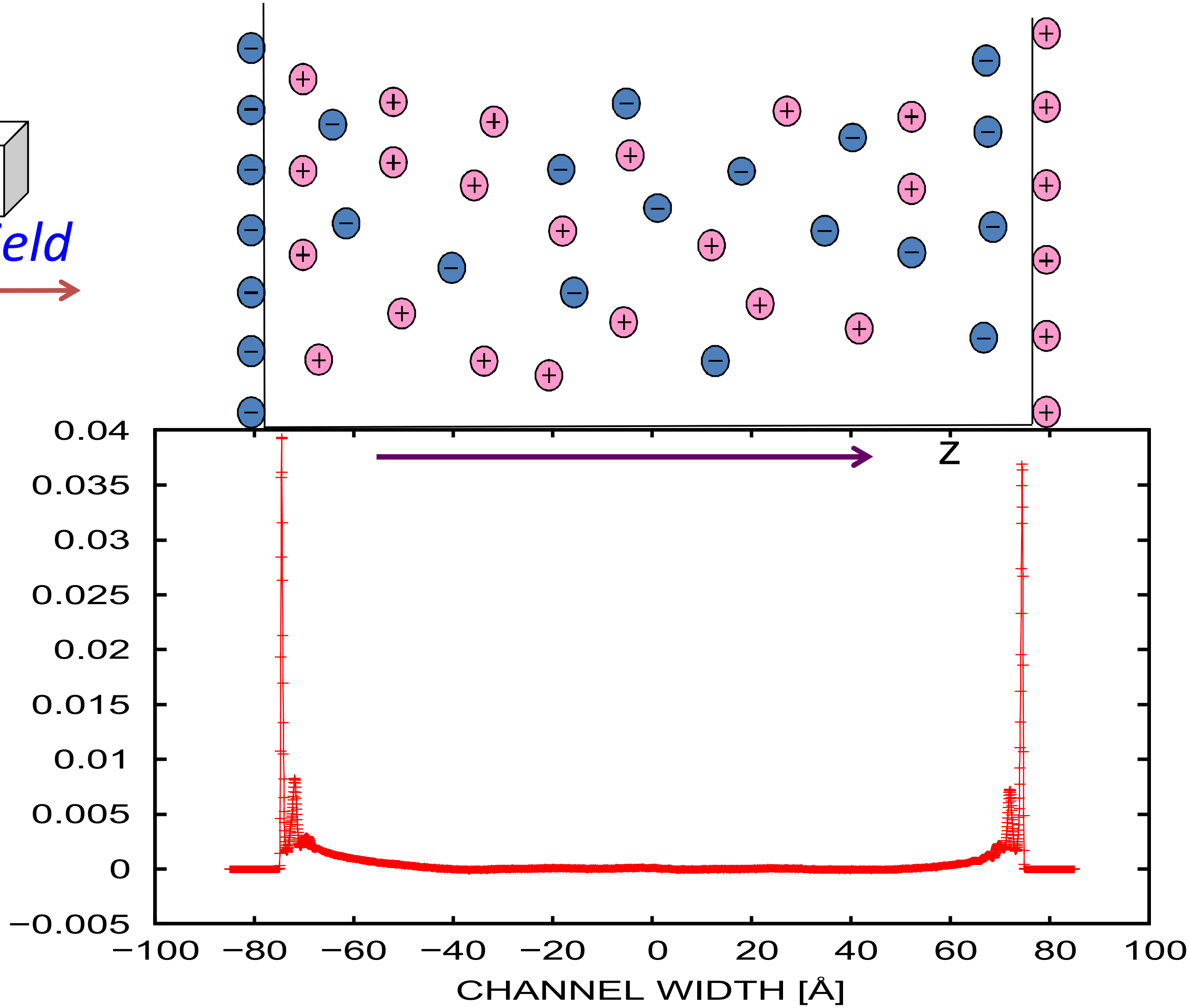
Electrical Double Layer – Water + KCl



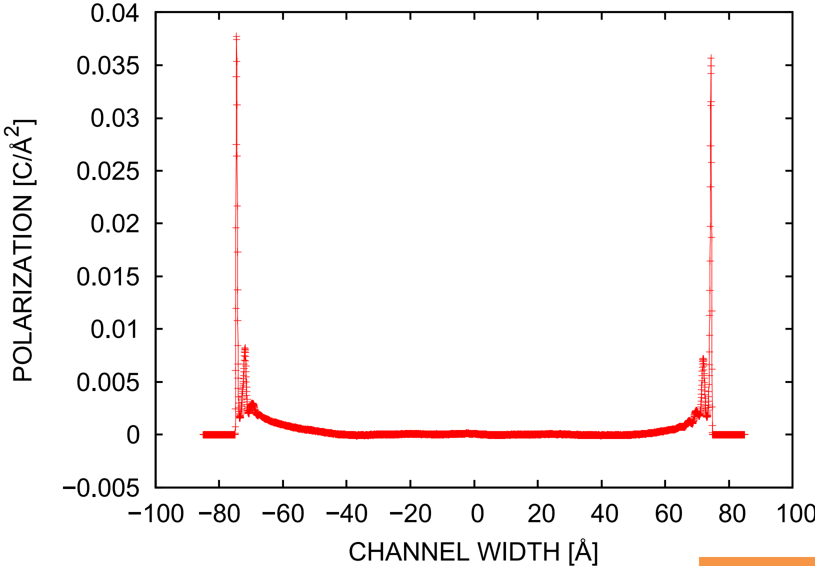
KCl conc: 100mM

Debye length : 1nm

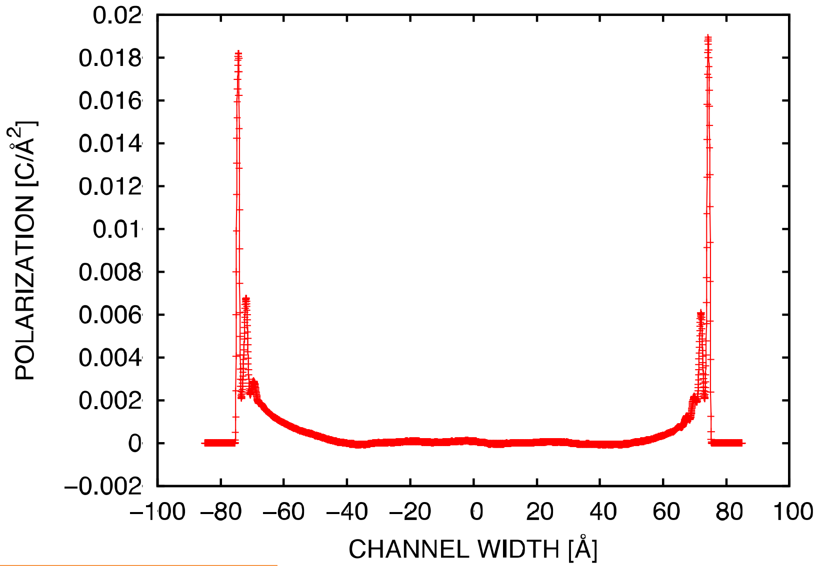
$$\Delta(z-z') = \begin{cases} \frac{1}{Al} & if\ |z-z'|<l \\ 0 & else \end{cases}$$



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

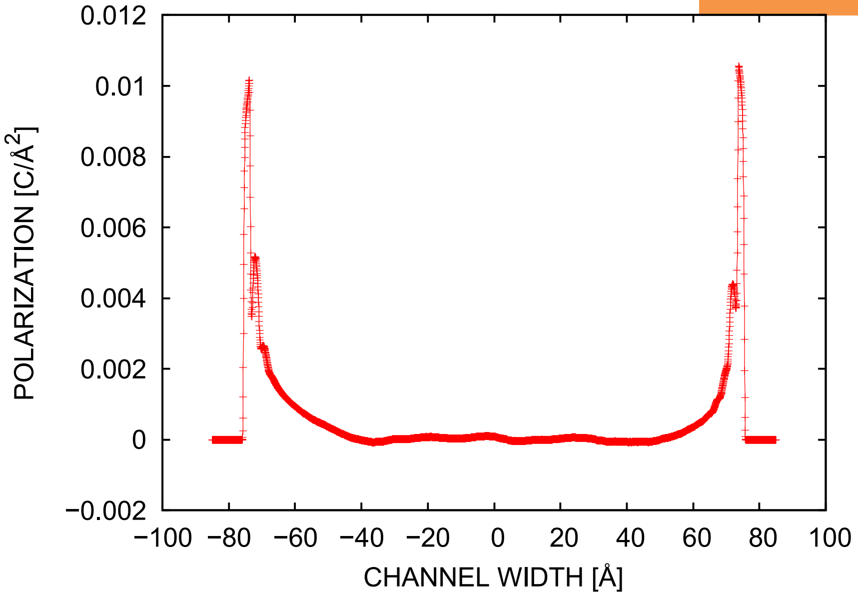


Averaging length = 0.1 Angs.

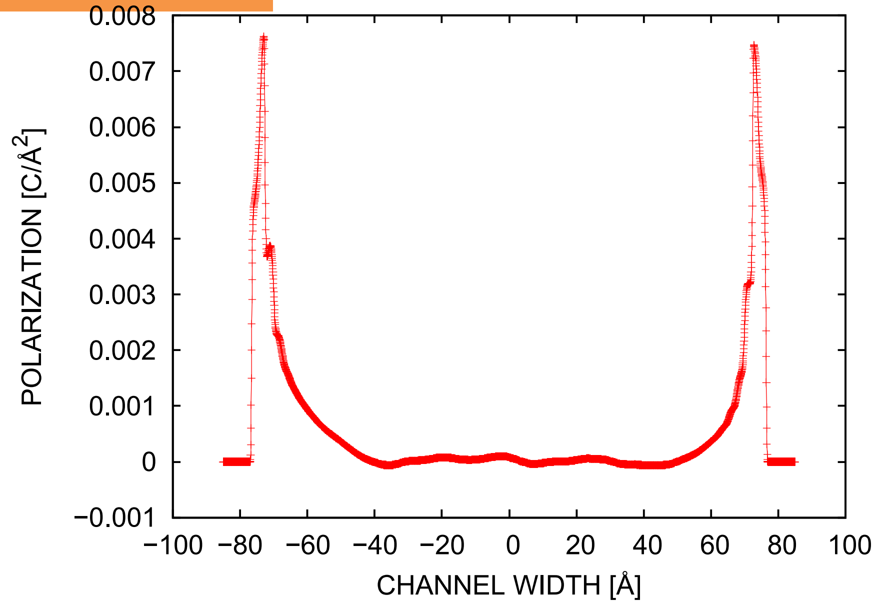


Averaging length = 0.5 Angs.

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

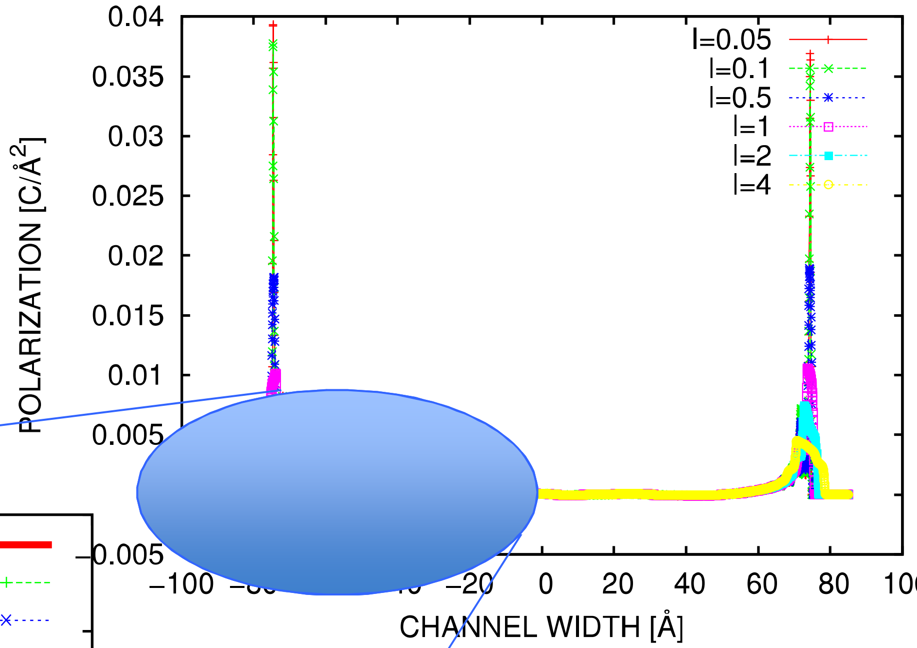


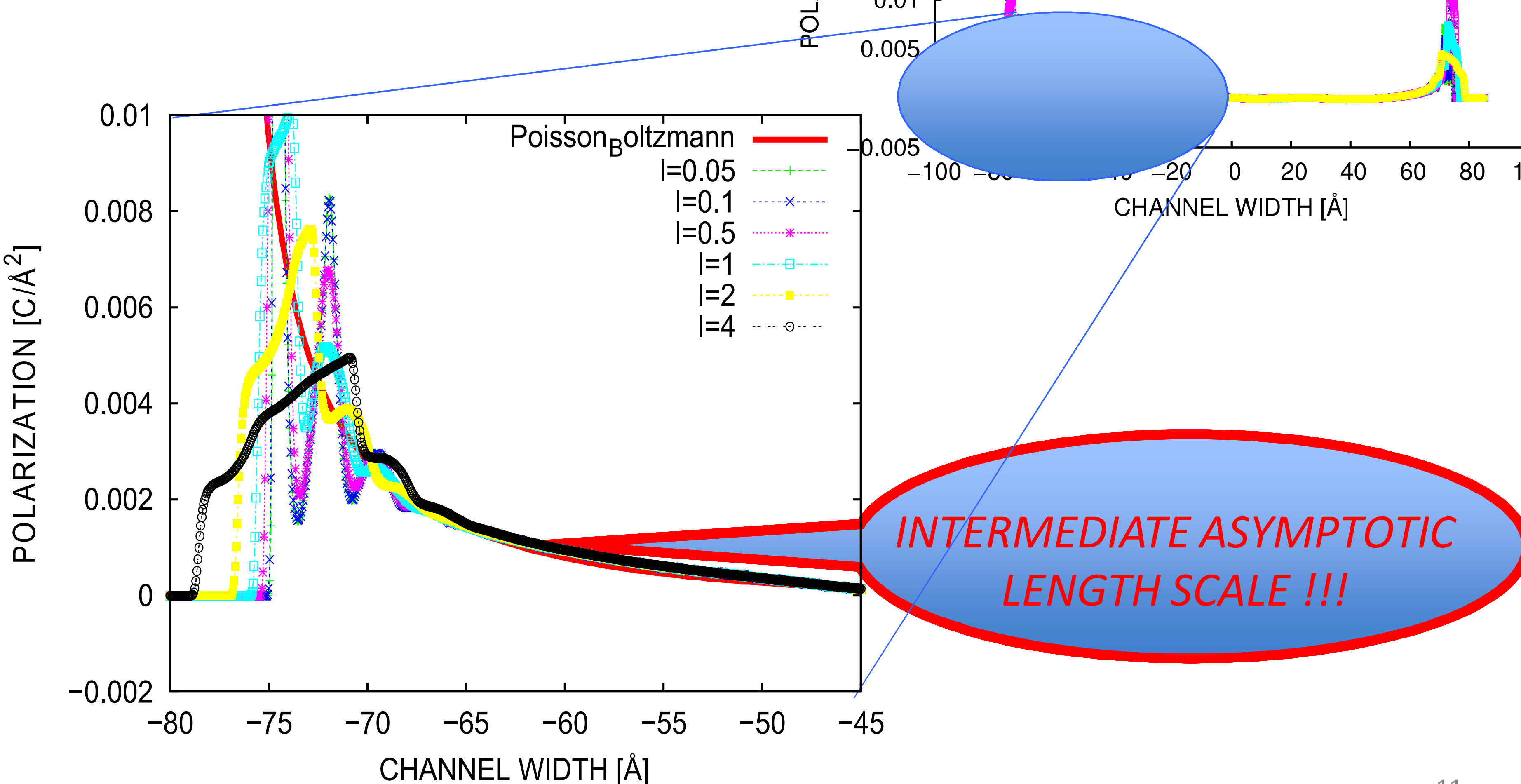
Averaging length = 1.0 Angs.



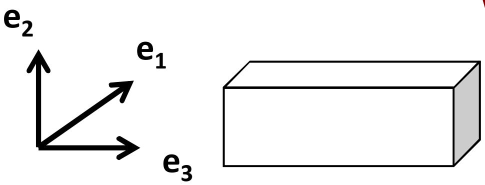
Averaging length = 2.0 Angs.

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



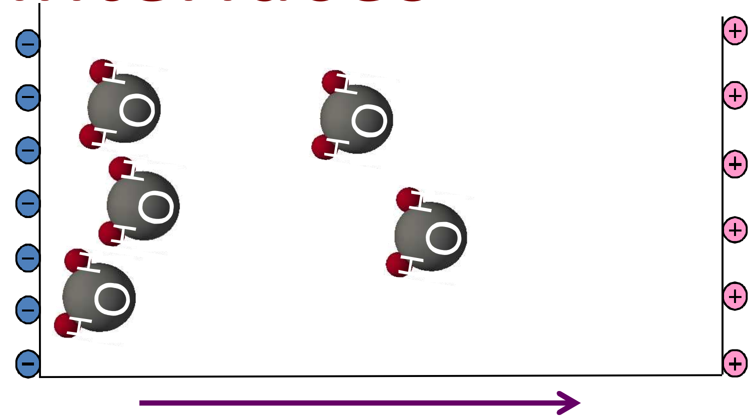


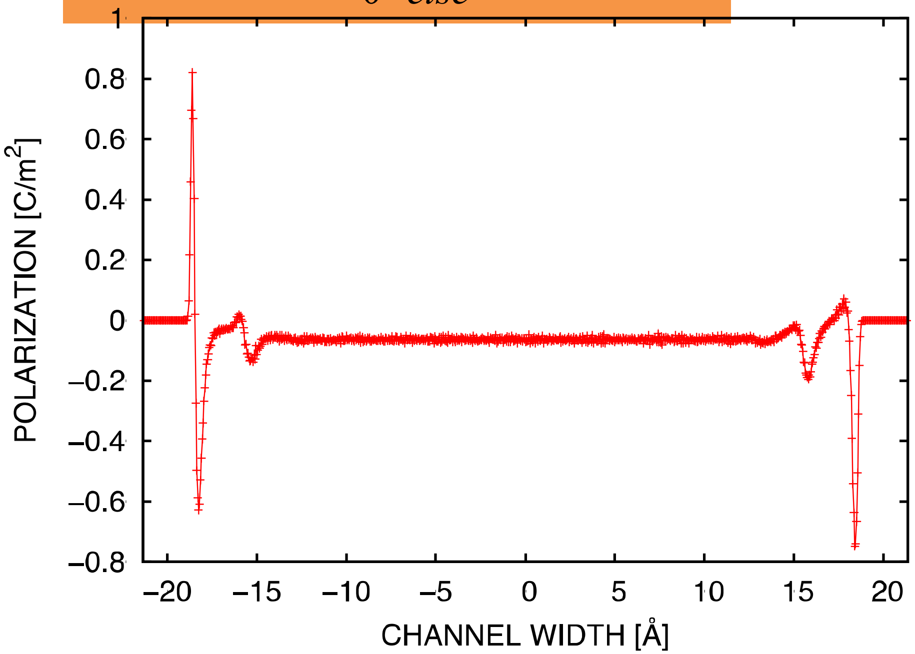
Water at the Interfaces

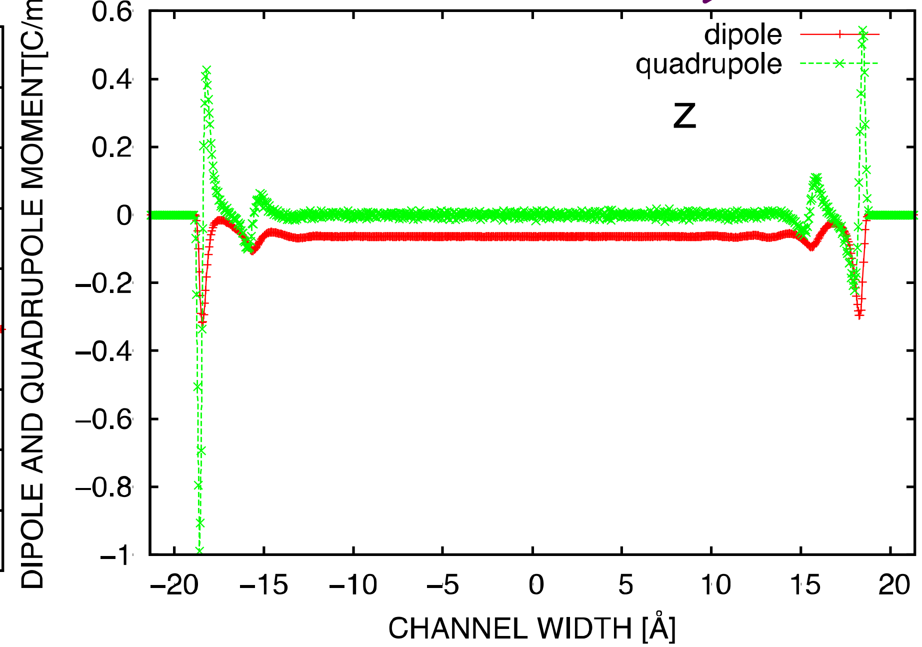


Applied field

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



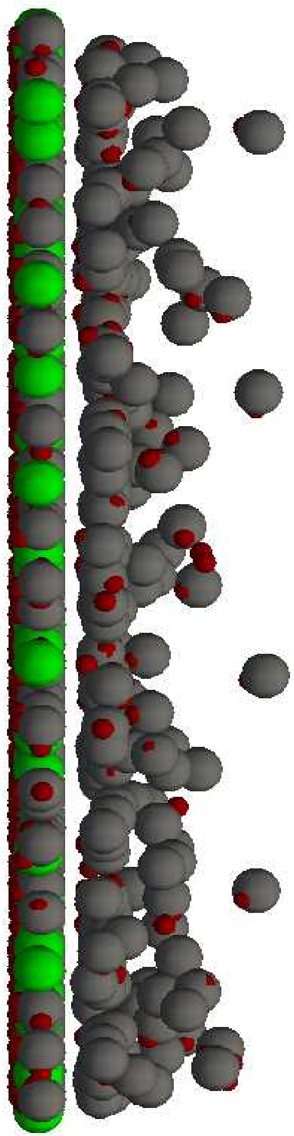


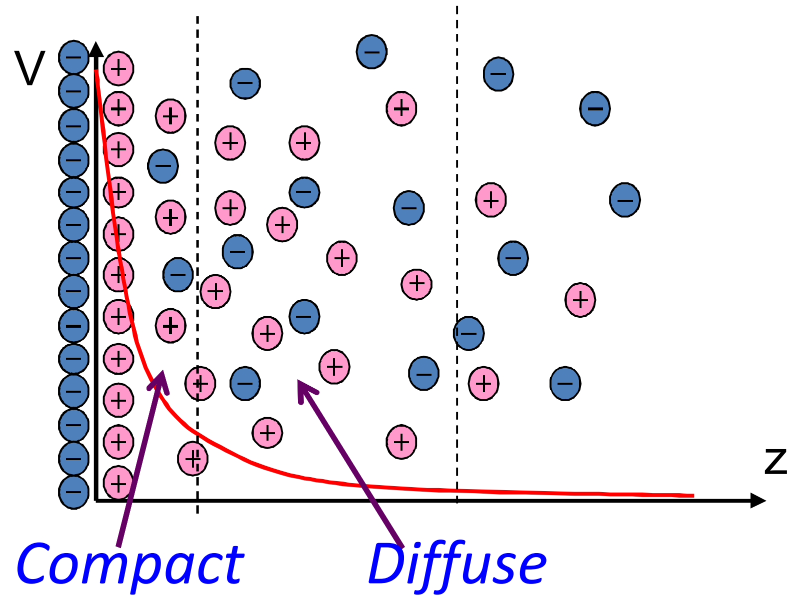


Dipole and Quadrupole Moments across the channel width for averaging length of 0.05 Angstroms.

Quadrupole Moments are NOT negligible at the interface !!!

New Models





$$D = \varepsilon_0 E + P$$

- Study polarization in compact layer and diffuse layers and identify intermediate asymptotic length scales
- Develop *new models*.

Acknowledgements

Dr. Jeremy Templeton	Sandia National Labs, Livermore
Dr. Jonathan Lee	Sandia National Labs, Livermore
Dr. Jonathan Zimmerman	Sandia National Labs, Livermore
Dr. Reese Jones	Sandia National Labs, Livermore

Thank You

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

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

$$\rho^m(\mathbf{x},t) \;=\; \sum_{j=1}^{N_f} \quad \sum^{N_m}$$

Macroscopic free charge

$$\sum_{n=1}^{N_m}\Big(\sum_{j=1}^{N_n} q_j^n$$

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

Irving and Kirkwood, 1950

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

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

Order of Coarse Graining function Δ:

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

Mandadapu et. al., in prep (2012)