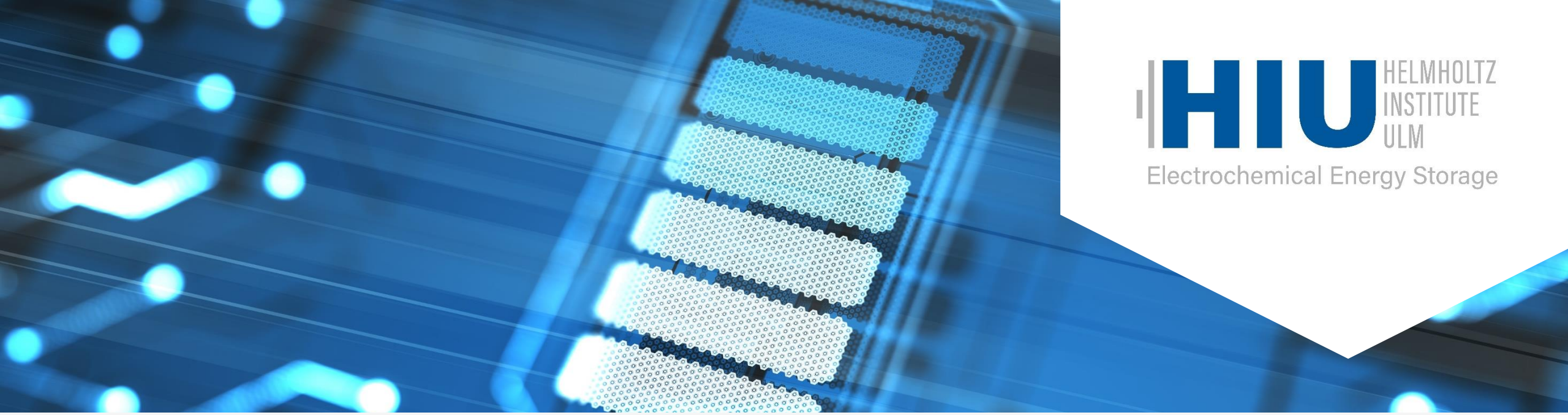


HIU HELMHOLTZ INSTITUTE ULM
Electrochemical Energy Storage

Max Schammer, Franziska Kilchert, Constantin Schwetlick, Arnulf Latz, and Birger Horstmann

From bulk thermodynamics to nano-structuring near electrified interfaces

A holistic continuum approach for battery electrolytes incorporating solvation effects

DLR Deutsches Zentrum für Luft- und Raumfahrt e.V.
German Aerospace Center
Institute of Technical Thermodynamics - Computational Electrochemistry

KIT Karlsruhe Institute of Technology
ulm university universität ulm
SW
DLR

Multi-Scale Continuum Modeling of Highly Correlated Electrolytes

Highly Concentrated Electrolytes & Ionic liquids

- exciting (fundamental)
- relevant (applied)

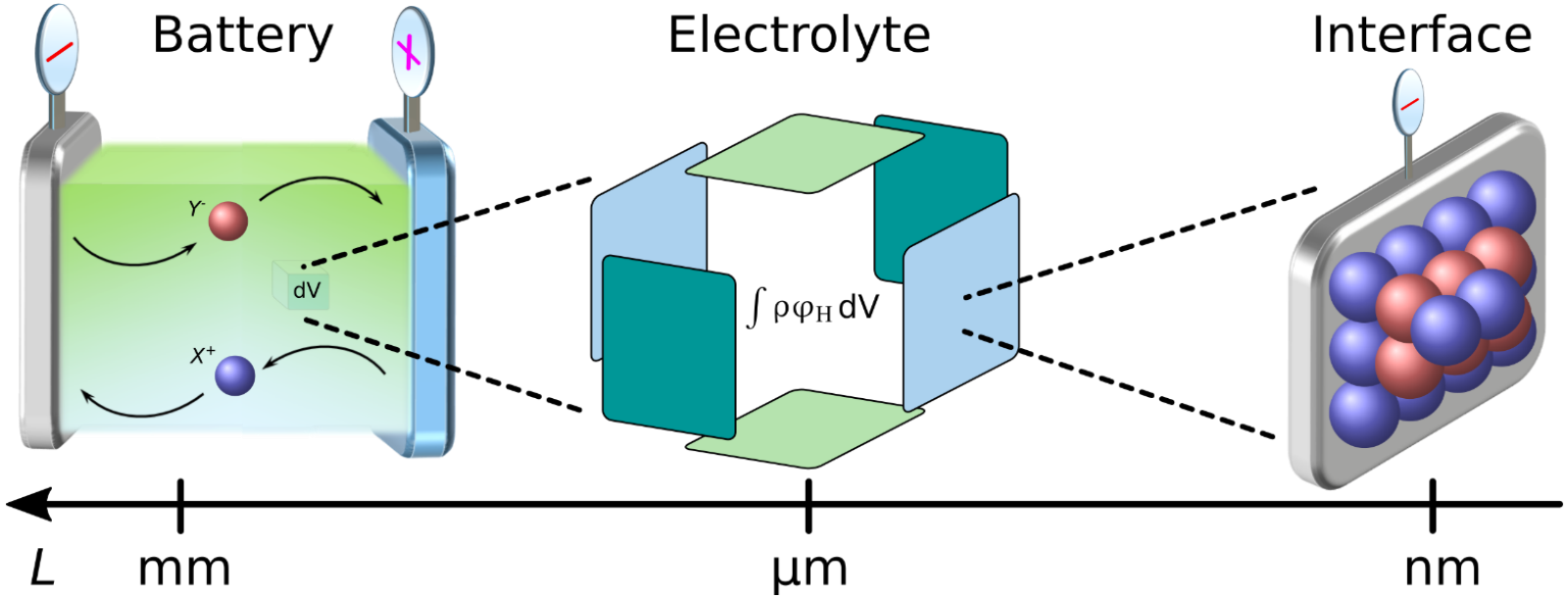
Goal

Holistic framework

- multiple length scales
- Cell & EDL simulations

Compatibility

- Experiments
- Atomistic Simulations



Framework of Rational Thermodynamics

Rational Thermodynamics

Thermodynamic Consistency

- 2nd axiom of TD

Rigorous Foundation

- Balancing Laws, …

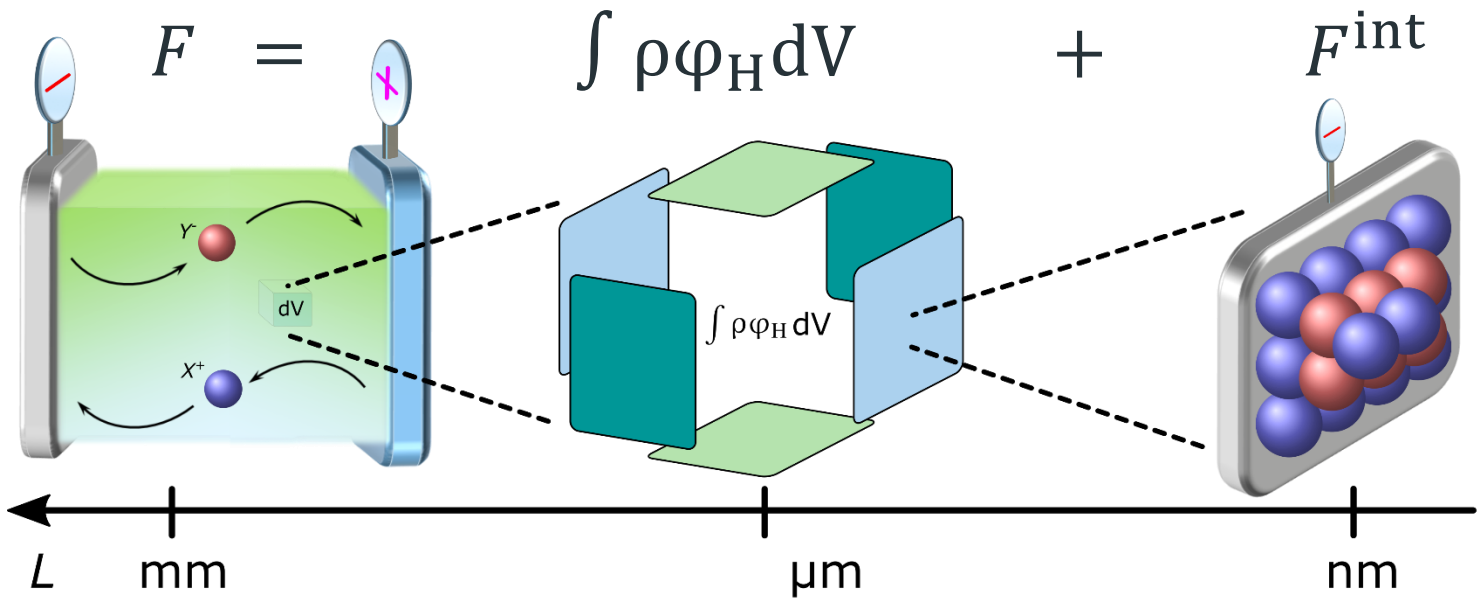
Focal Quantity: Free energy F

- Constitutive Equations

Onsager Formalism

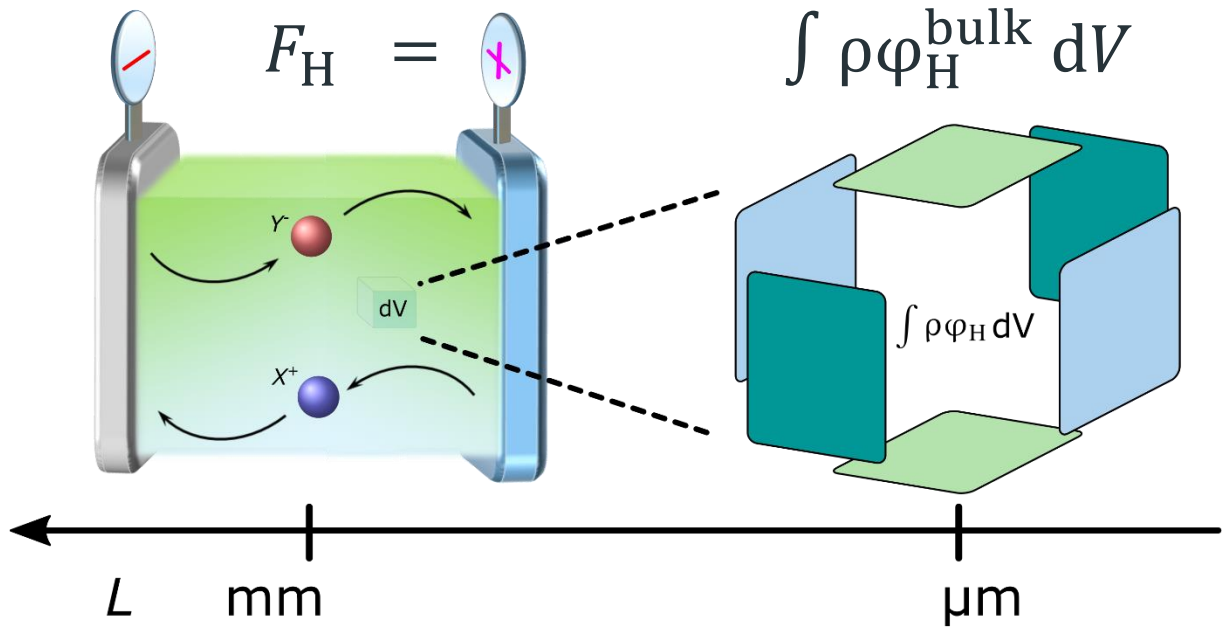
Thermodynamic Fluxes

Transport Parameters



Multi-Scale Modeling of Ionic Liquids

Overview Bulk Transport Theory



Basic Continuum Assumption

Ion size $r_{ion}^3 \ll dV$

➢ Neglect particle nature

Ion-ion correlations $\ell_{int}^3 \ll dV$

➢ Neglect ion correlations

Free energy density $\rho\varphi_H$

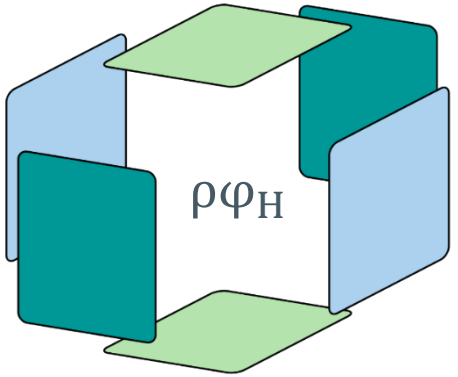
Derivation of Theory Based Electrolyte Model*

Modeling Free Energy Density

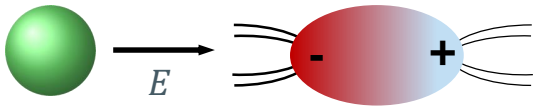
$$F = F^{\text{bulk}}(\rho_\alpha, D, \kappa, T) = \int \rho\varphi_{\text{H}}\,\mathrm{d}V$$

$$\rho\varphi_{\text{H}} = \frac{1}{2} E\,D + \frac{\mathcal{K}}{2}(1 - \Sigma_\alpha c_\alpha \nu_\alpha^0)^2 + \Sigma_\alpha \rho_\alpha \mathcal{C}_\alpha\,\Delta T + \frac{k_{\text{B}} T}{N_{\text{A}}} \Sigma_\alpha c_\alpha \ln(\nu_\alpha c_\alpha)$$

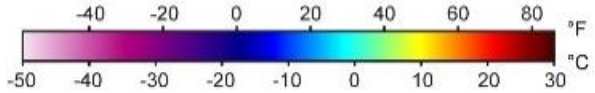
electrical | mechanical | heat capacity | entropy



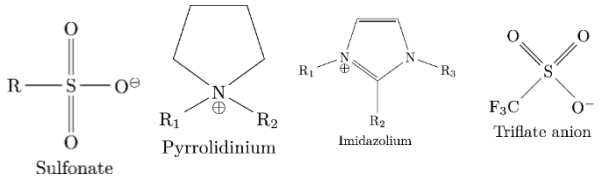
D: **Polarization**

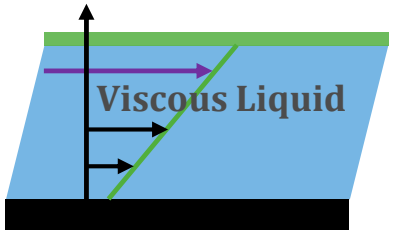


T: **Temperature**



ρ_α: **Multi-component**





Thermodynamic Derivatives Constitutive equations

Chemical Potentials $\mu_\alpha = \frac{\partial(\rho\varphi_{\text{H}})}{\partial c_\alpha}$, Stress Tensor σ, …

*M.Schammer, B.Horstmann, A. Latz. *Journal of The Electrochemical Society* 168.2 (2021): 026511.

Electrolyte Transport: Migration, Diffusion, Convection*

Constraints Reduce Description

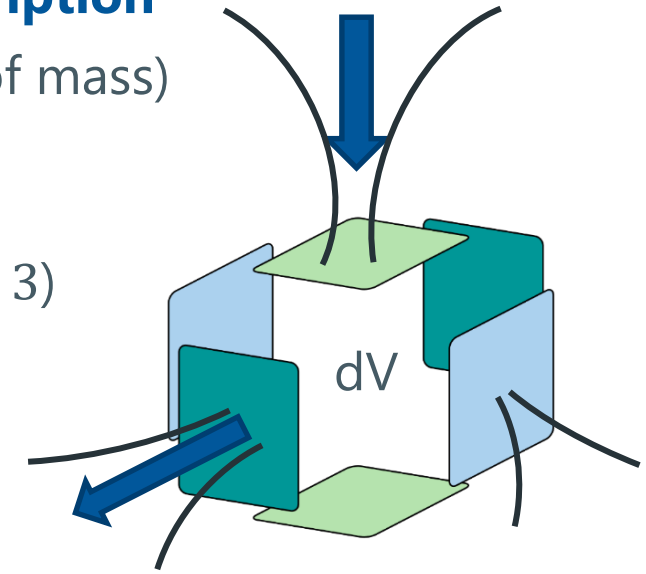
- $\sum_{\alpha=1}^{N} M_\alpha \mathcal{N}_\alpha = 0$ (Center of mass)
- $\sum_{\alpha=1}^{N} c_\alpha \nu_\alpha = 1$

Transport Equations ($\alpha \geq 3$)

$$\partial_t \varrho = -\nabla \mathcal{J} - \nabla(\varrho \mathrm{v})$$
$$\partial_t c_\alpha = -\nabla \mathcal{N}_\alpha - \nabla(c_\alpha \mathrm{v})$$

Fluxes ($\alpha \geq 3$)

- $\mathcal{N}_\alpha = \frac{\tau_\alpha}{F}\mathcal{J} - \sum_{\beta=3}^{N} \mathcal{D}_{\alpha\beta} \nabla \mu_\beta$
- $\mathcal{J} = -\kappa \nabla \phi - \frac{\kappa}{F z_2} \nabla \mu_2 - \sum_{\beta=3}^{N} \frac{\kappa \tau_\beta}{F} \nabla \mu_\beta$



Incompressibility

- $\nabla \mathrm{v} = -\sum_\alpha \nu_\alpha \nabla \mathcal{N}_\alpha$
- $\nabla \mathrm{v}^{\mathrm{vol}} = 0$

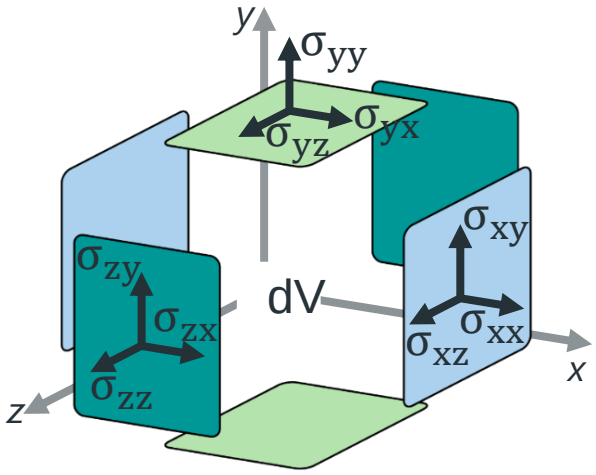
$(\mathrm{v}^{\mathrm{vol}} = \sum_\alpha c_\alpha \nu_\alpha \mathrm{v}_\alpha)$

Surface Forces

- $\rho \dot{\mathrm{v}} = \nabla \sigma$

Stress Tensor σ

Molar volumes $\nu_\alpha(p)$



Forces

- $\nabla \mu_\alpha = \sum_\beta \theta_{\alpha\beta} \nabla(\ln c_\beta) - \nu_\alpha \varrho \nabla \Phi + \nu_\alpha \nabla \tau$

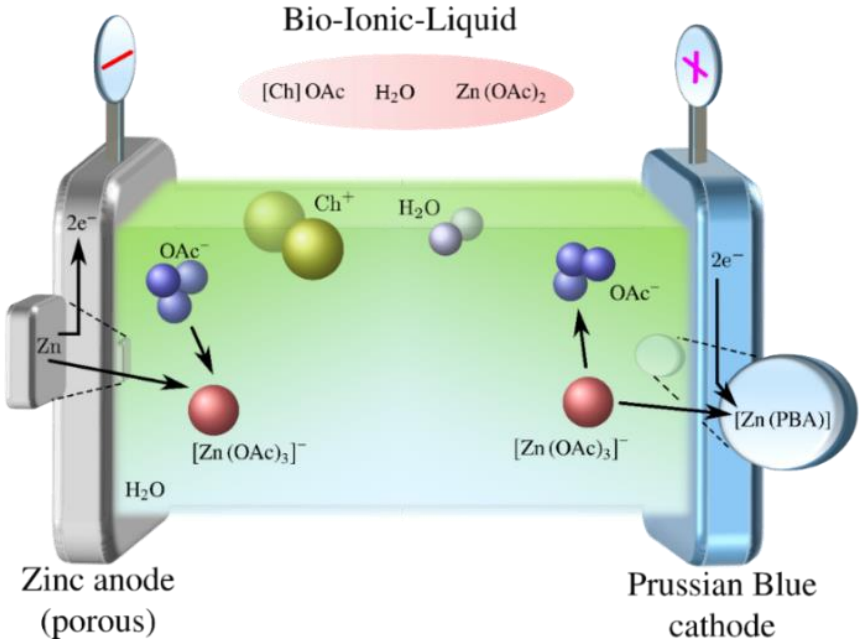
*M.Schammer, B.Horstmann, A. Latz. *Journal of The Electrochemical Society* 168.2 (2021): 026511.

Validation Overview

Secondary Zinc Ion Battery[#]

Electrolyte Mixture

ChOAc / water / zinc acetate



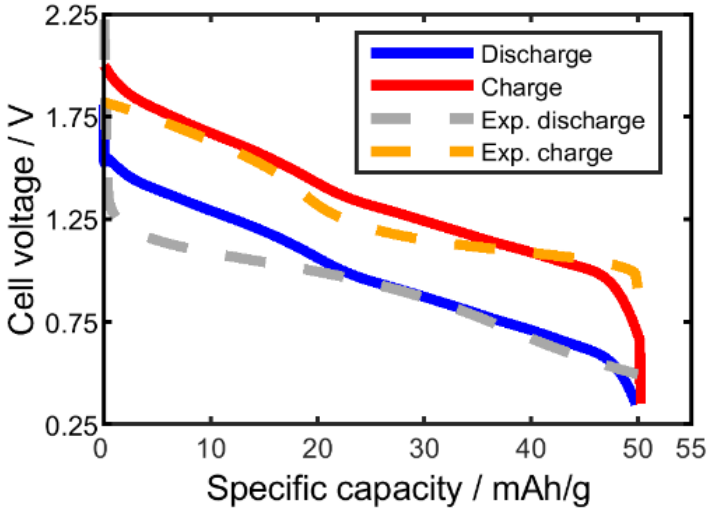
1D Cell Simulation*

Electroneutral theory

Two independent species

Capacity

Good agreement with experiment



[#]Z. Liu, F. Endres, *ACS Appl. Mater. Interfaces* 8, 12158–12164 (2016).
*M.Schammer, B.Horstmann, A. Latz. *Journal of The Electrochemical Society* 168.2 (2021): 026511.

eNMR experiment

Species mobilities

- $m_\alpha = \mathrm{v}_\alpha / E$
- Set up $\mathrm{v}|_{\mathrm{sample}} = 0$

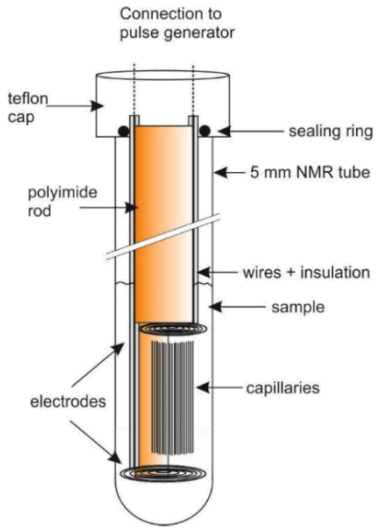
Theory

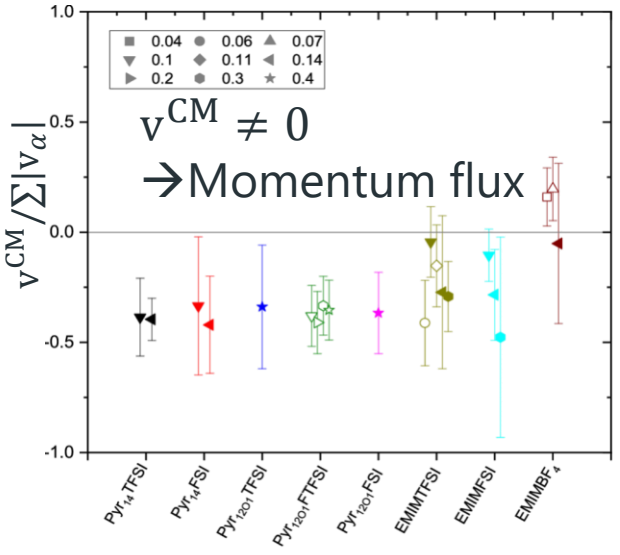
Incompressible IL mixtures

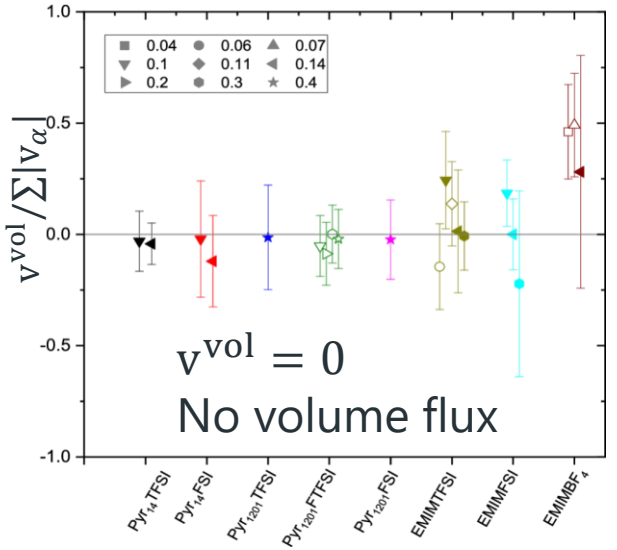
- CM: $\nabla \mathrm{v}^{\mathrm{CM}} = -\sum_\alpha \nu_\alpha \nabla \mathcal{N}_\alpha$
- Volume flux: $\nabla \mathrm{v}^{\mathrm{vol}} = 0$
- $t_\alpha E \kappa = F z_\alpha c_\alpha (E m_\alpha + \mathrm{v})$

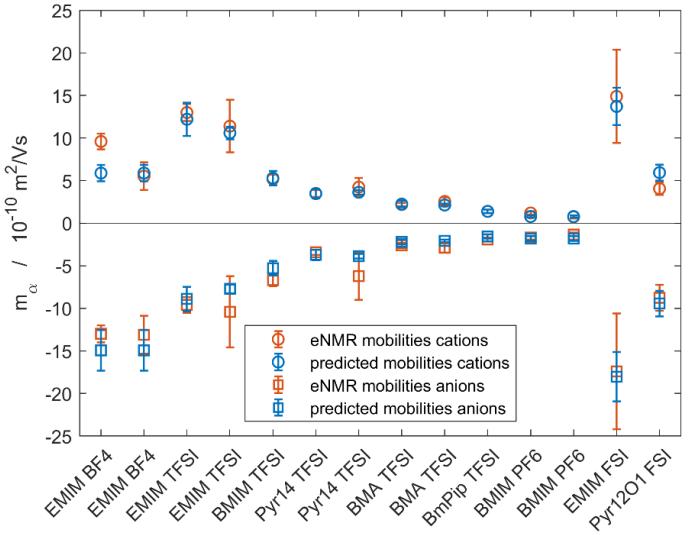
Mobilities $m_+/m_- = \nu_-/\nu_+$

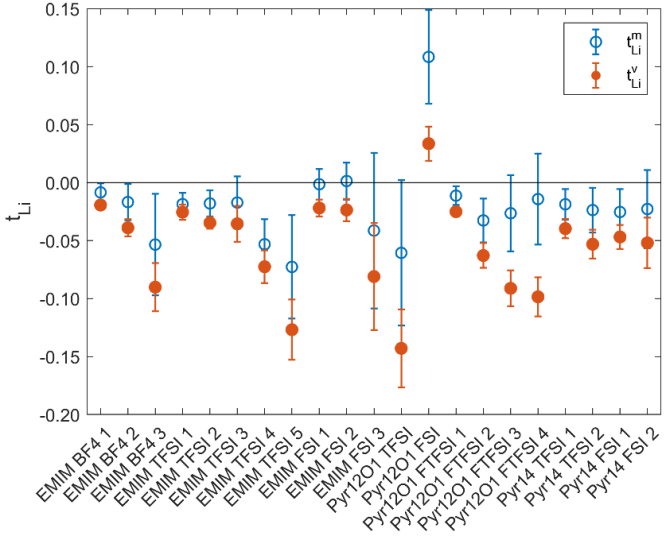
Frame dependent t_α







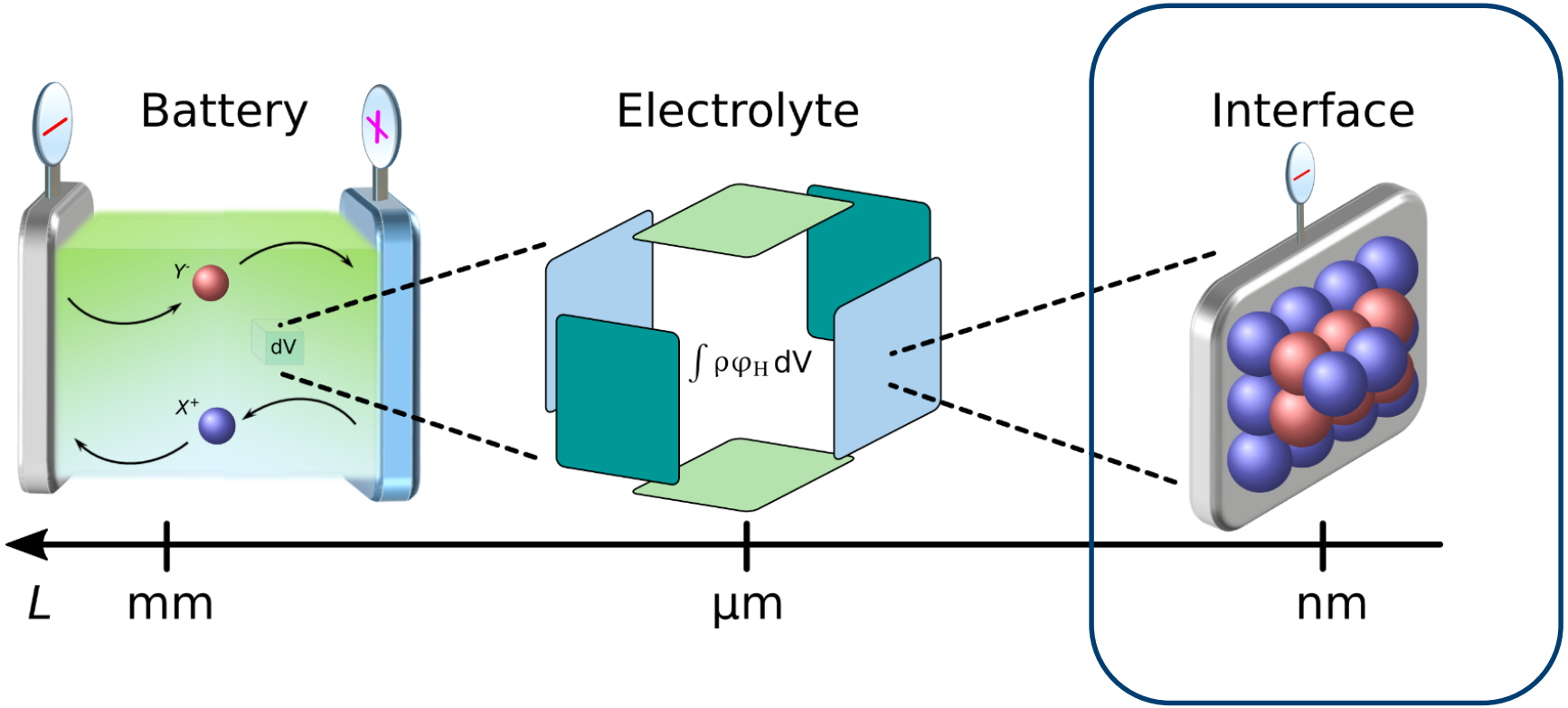




*F.Kilchert, M.Schammer, A.Latz, B.Horstmann, M.Schönhoff et al. *Submitted to PCCP*. (see arXiv:2209.05769v1)
#F.Kilchert, M.Schammer, A.Latz, B.Horstmann, M.Schönhoff et al., *J. Phys. Chem. Lett.* 2022, 13, 37, 8761–8767

Continuum Modeling: Non-local Interactions

Main Part Electrochemical Double Layer

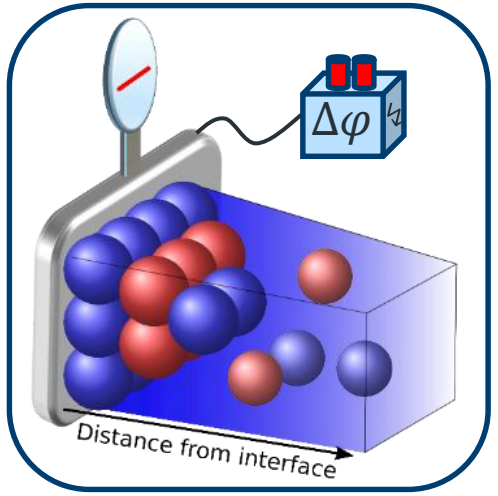


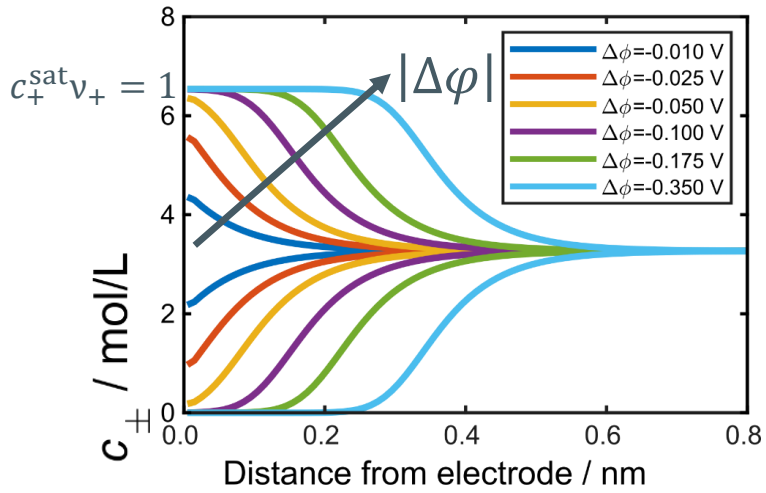
Motivation: Why is a bulk description of the EDL insufficient?

Binary IL PYR[1,4]TFSI

Equilibrium EDL Structures

- $\varrho = -\nabla^2 \Phi$
- $0 = \Phi - \gamma_+ \ln(c_-) + (1 - \gamma_+) \ln(c_+)$





Simulation results

Small $\Delta\varphi$ Exponential decay

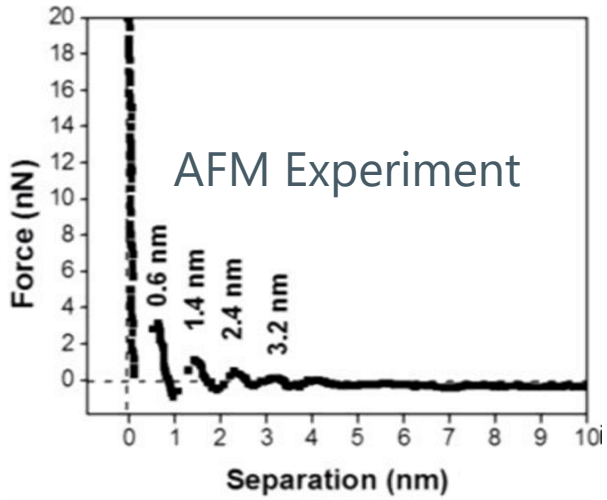
Larger $\Delta\varphi$ Charge saturation (“Crowding”)

Comparison

AFM Experiment

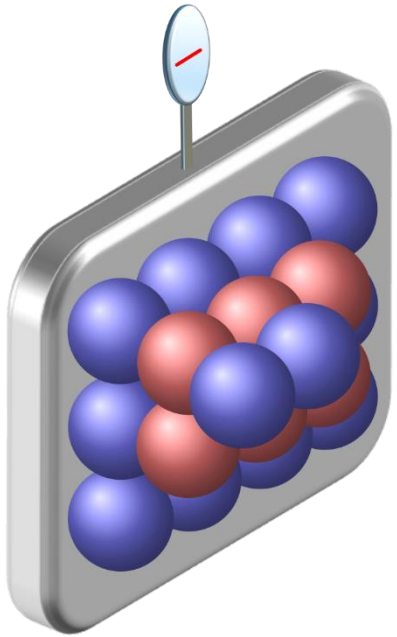
Layered structure over several nm

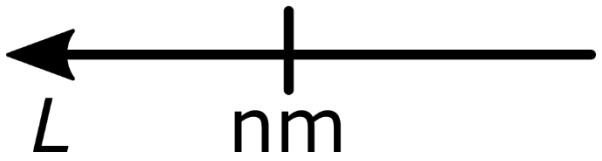
→ **Something is missing …**



*M. Schammer, B. Horstmann, & A. Latz, *Journal of The Electrochemical Society*, *168*(2), 026511 (2021).
#V. Hoffmann, M. Schammer, et al., *Phys. Chem. Chem. Phys.*, 2018,20, 4760-4771.

Multi-Scale Modeling of Ionic Liquids*,#



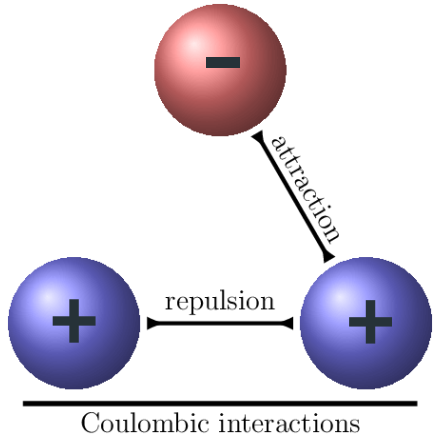


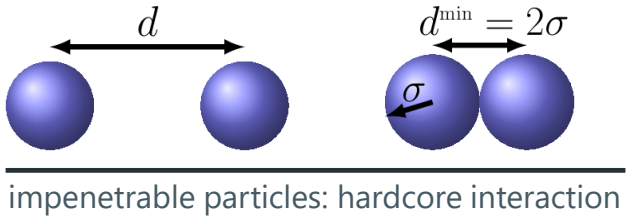
Length Scales

- Ion size $\mathcal{O}(r_{\mathrm{ion}}) \approx \mathrm{nm}$
- Ion correlations $\mathcal{O}(\ell_{\mathrm{int}}) \approx \mathrm{nm}$

➢ Hard Particles

➢ Short ranged ion correlations





*V. Hoffmann, M. Schammer, et al., *Phys. Chem. Chem. Phys.*, 2018,20, 4760-4771.
#M.Schammer, A.Latz, B.Horstmann, *J. Phys. Chem. B* 2022, 126, 14, 2761–2776

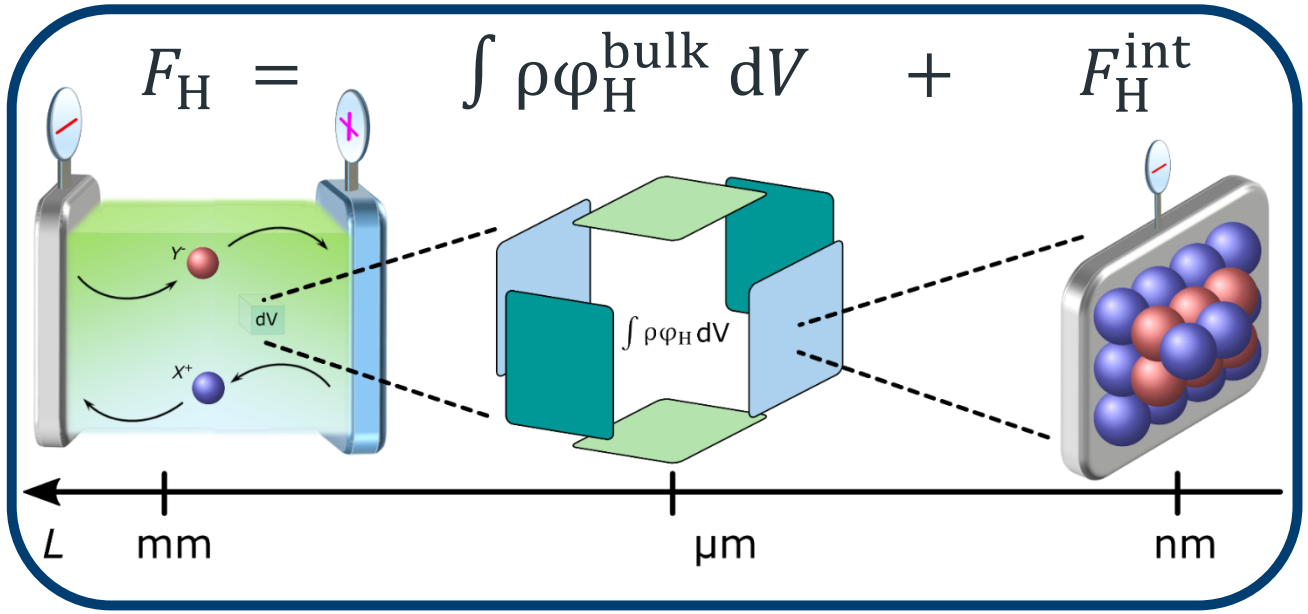
EDL: Nonlocal Molecular Interactions

Free Energy Functional

$$F_{\mathrm{H}}^{\mathrm{int}} = \Sigma_{\alpha,\beta} \iint \mathrm{d}y\mathrm{d}x \, \mathcal{F}_{\alpha\beta}(|x-y|)\, c_\alpha(x)\, c_\beta(y)$$

Transport

- $\mu_\alpha = \frac{\partial \rho \varphi_{\mathrm{H}}^{\mathrm{bulk}}}{\partial c_\alpha} + \frac{\delta F^{\mathrm{int}}}{\delta c_\alpha}$
- $\frac{\delta F^{\mathrm{int}}}{\delta c_\alpha} = \sum_\beta \int \mathrm{d}y \, \mathcal{F}_{\alpha\beta}(|x-y|)\, c_\beta(y)$



Equilibrium Equation ($\nabla\mu = 0$)

- $0 = \Phi - \gamma_+ \ln(c_-) + (1-\gamma_+)\ln(c_+) - \int \mathrm{d}x \, \mathcal{F}_{+-}(x-y)\varrho(x)$

EDL: Model for interaction potential

Interaction Potential

- $\mathcal{F}_{\alpha\beta}(\ell_{\mathrm{int}}, \mathcal{V}^0) = \mathcal{V}^0 \cdot \mathcal{S}(\ell_{\mathrm{int}})$

Two novel parameters (at least)

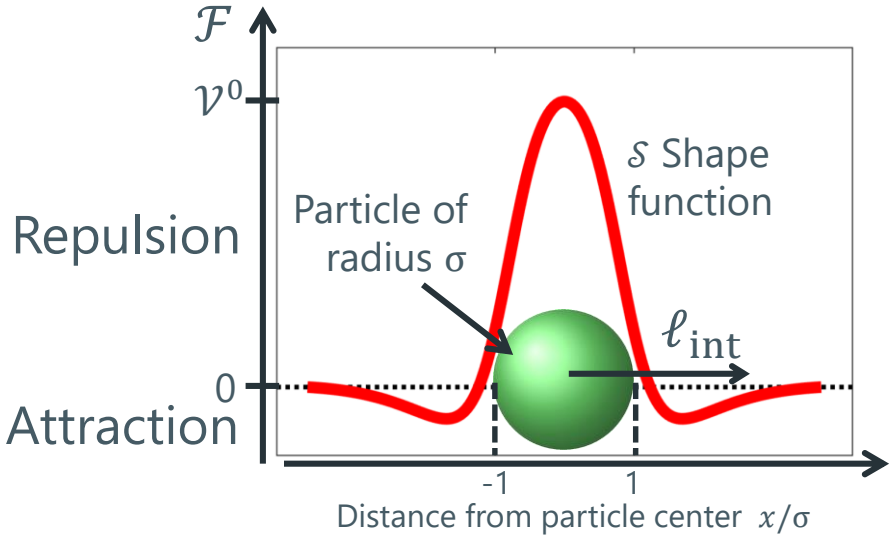
- Correlation length ℓ_{int}
- Interaction strength $\mathcal{V}^0$

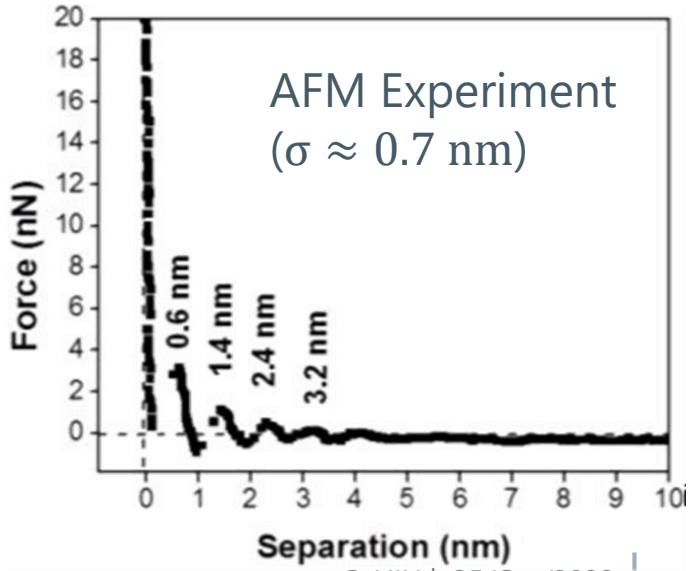
Shape function $\mathcal{S}(\ell_{\mathrm{int}})$

Model for hard particles

Experiment $\ell_{\mathrm{int}} \approx \sigma$

Gauss shape $\mathcal{S}(\ell_{\mathrm{int}}) = \exp(-[x/\ell_{\mathrm{int}}(\sigma)]^2)$

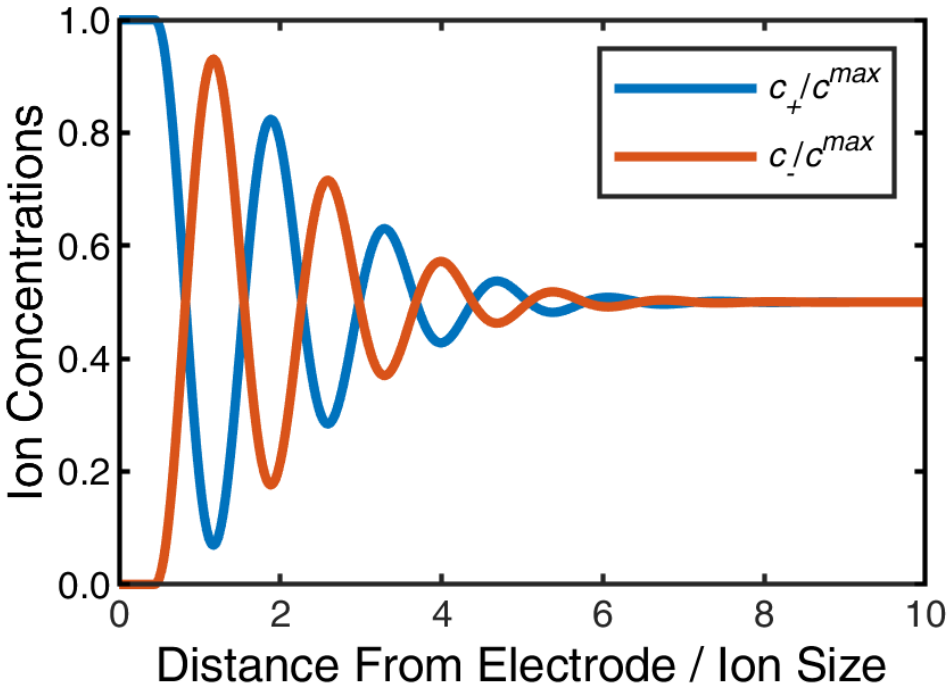


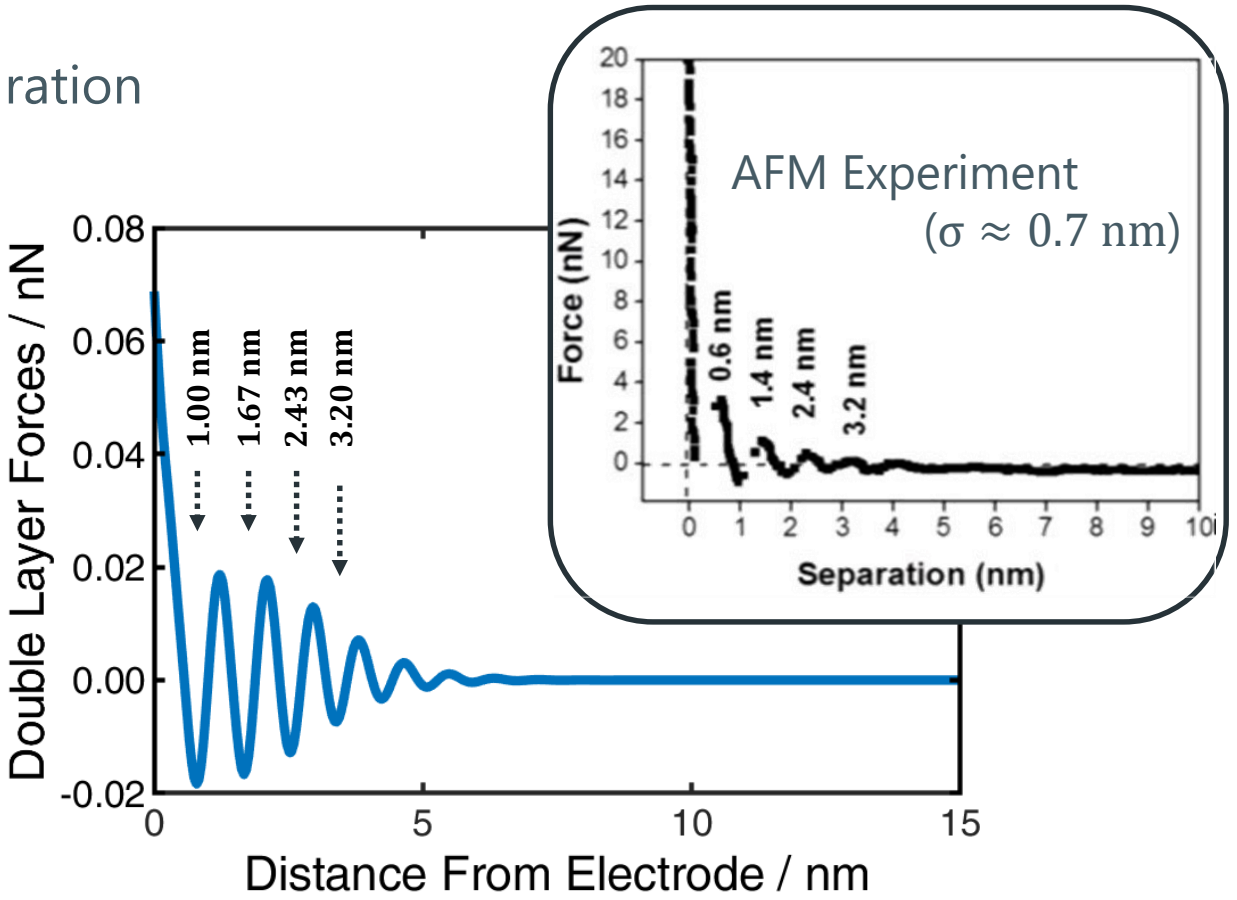


Gauss Model for Hardcore Particles

Overscreening

Layered long-range ordering with decay and saturation





Influence of Interaction Energy

Different Screening Profiles

- Room temperature ($k_B T \approx 250$ meV)

$\nu^0 \ll RT$

- Exponential Decay

$\nu^0 \approx RT$

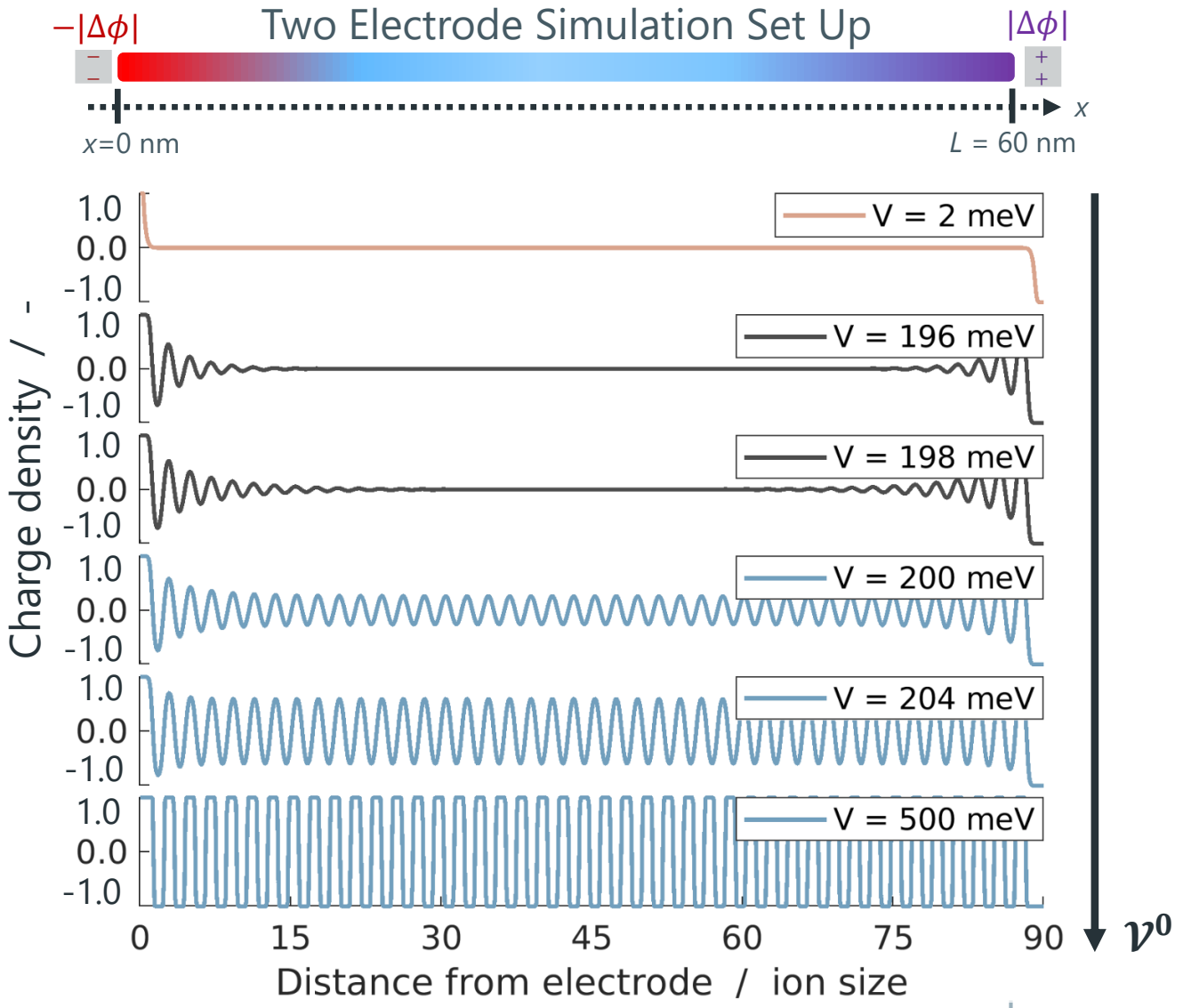
- Damped charge oscillations

$\nu^0 > RT$

Oscillations

- Bulk nano-structuring
- Phase Separation

Parametrization ???



Parameterization: Asymptotic Analysis

Small potentials $\Phi \ll RT/F$

Short-ranged $\mathcal{F}_{\alpha\beta}$

- $F_{\mathrm{H}}^{\mathrm{int}} \approx \ \Sigma_{n=0}\Sigma_{\alpha\beta}\Gamma_{\alpha\beta}^{2n}\int \mathrm{dy}\, c_\alpha\, \nabla^{2n} c_\beta$

First two perturbation modes

- $\Gamma_{+-}^{0} = \mathcal{V}^0/E_{\mathrm{th}}$
- $\Gamma_{+-}^{2} = 2\mathcal{V}^0 E_{\mathrm{el}}/\pi E_{\mathrm{th}}^2$

Three competing energy scales

- $E_{\mathrm{th}} = k_{\mathrm{B}}T$
- $E_{\mathrm{el}} = (ez_+)^2/(4\pi\varepsilon_0\varepsilon_{\mathrm{R}}a)$
- $E_{\mathrm{int}} = \mathcal{V}^0(\varepsilon_{\mathrm{R}}, T)$

First order stationary state

- $0 = \Phi\ + \hat{\varepsilon}_{\mathrm{R}} \cdot \varrho$
- $\varrho = -\nabla^2\Phi$

Dielectric operator

- $\hat{\varepsilon}_{\mathrm{R}}(\Gamma_{+-}^{2\mathrm{n}})|_{n=0,1} = 1 - \frac{\mathcal{V}^0}{E_{\mathrm{th}}} - \frac{2\mathcal{V}^0 E_{\mathrm{el}}}{\pi E_{\mathrm{th}}^2} \cdot \nabla^2$

→ BSK Theory*

Can be solved analytically

- $\varrho \propto \exp(-kx) = \exp(-k_{\mathbb{R}}x) \cdot \cos(k_{\mathbb{C}}x)$

Wave number $k(E_{\mathrm{th}}, E_{\mathrm{el}}, \mathcal{V}^0)$

- Determines EDL structure

*Bazant, M., Storey, B., Kornyshev, A. *Physical review letters* 106.4 (2011): 046102.

Analysis of Screening Phases

Competing energy scales

$\varrho \propto \exp(-k_{\mathbb{R}} x) \cdot \cos(k_{\mathbb{C}} x)$

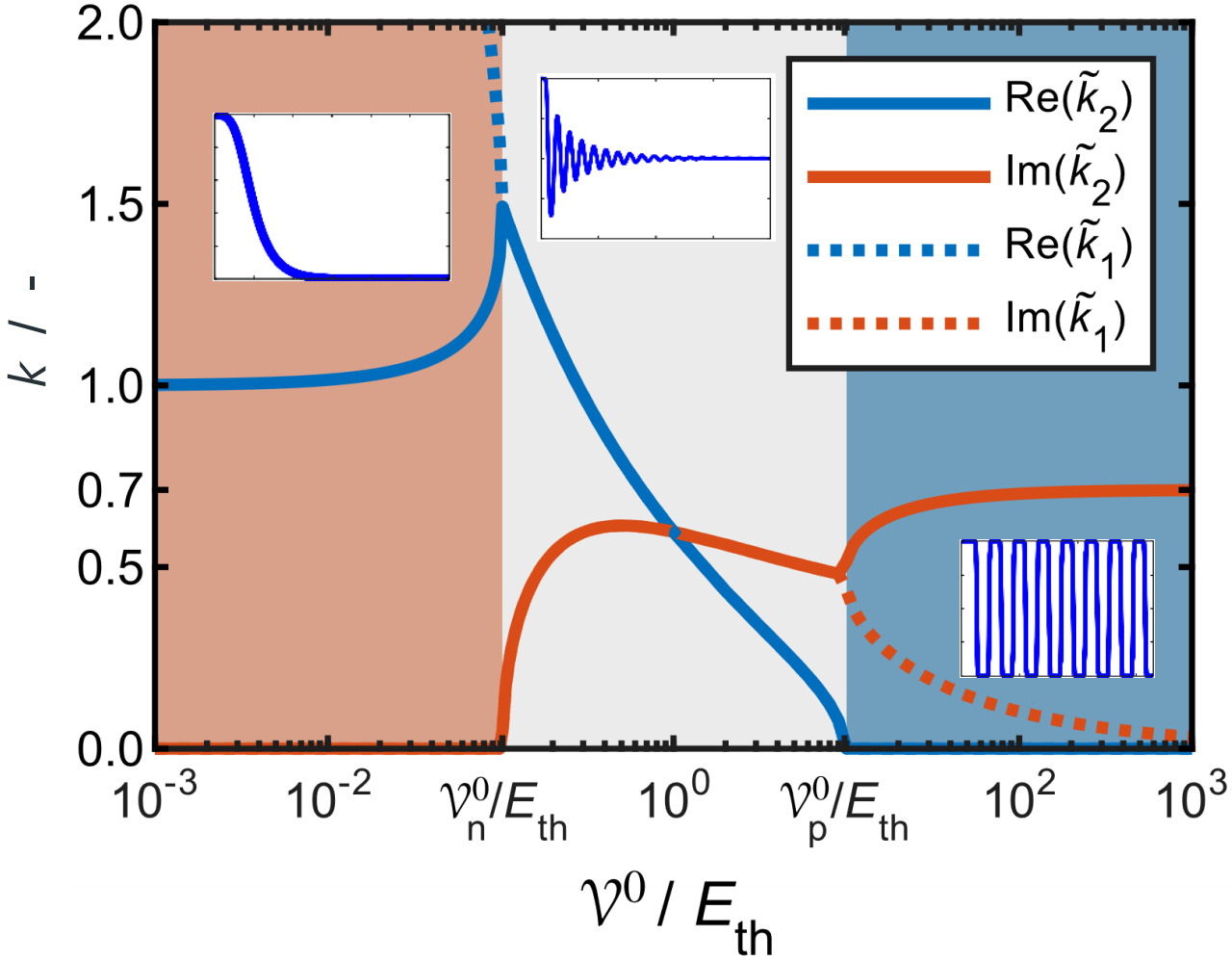
$k(E_{\mathrm{th}}, E_{\mathrm{el}}, \mathcal{V}^0)$

Three Screening Phases

- Exponential damping
- Damped oscillations
- Oscillations

Phase Boundaries

- $\mathcal{V}^0_{\pm} = E_{\mathrm{th}} + 4E_{\mathrm{el}}/\pi \pm \sqrt{2E_{\mathrm{el}}(2E_{\mathrm{el}}/\pi + 2E_{\mathrm{th}})/\pi}$



Comparison: Two EDL Descriptions

Integral Description

$$\varrho = -\nabla^2 \Phi$$
$$0 = \Phi - \gamma_+ \ln(c_-) + \gamma_- \ln(c_+) - \int \mathrm{d}x \mathcal{F}(x,y)\varrho(x)$$

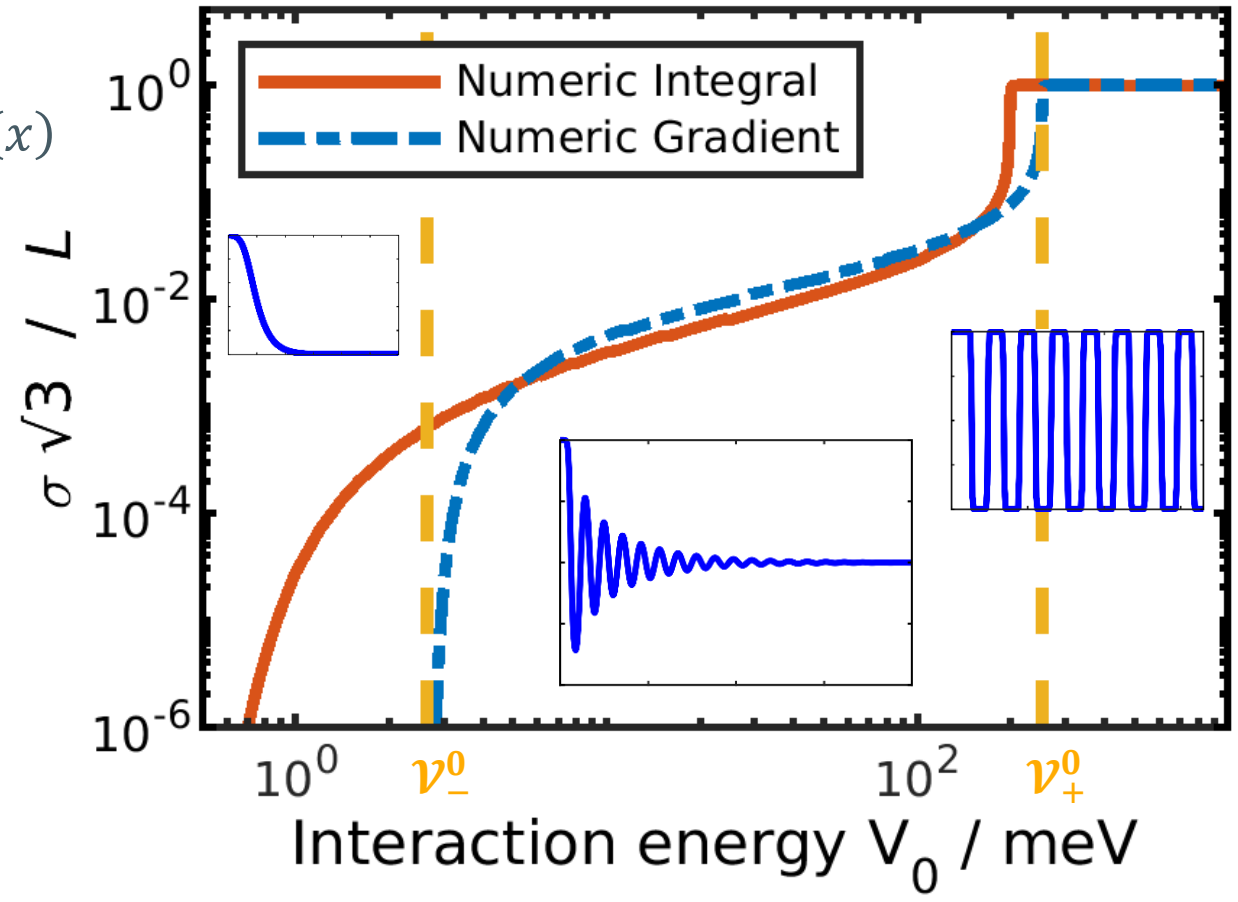
Gradient description (first order)

$$\varrho = -\nabla^2 \Phi$$
$$0 = \Phi + \hat{\varepsilon}_\mathrm{R}(E_\mathrm{th}, E_\mathrm{el}, \mathcal{V}^0, \nabla^2) \cdot \varrho$$

Comparison

Variance of peak number

- $\sigma^2 = \frac{\sum_i \varrho_i^{\mathrm{peak}} \cdot \left(x_i^{\mathrm{peak}}\right)^2}{\sum_j \varrho_j^{\mathrm{peak}}}$



A Roadmap from DFT to Non-equilibrium Thermodynamics

DFT

Determines force fields for MD

MD

Determines $g(r)$ for LST

LST $h(r) = g(r) - 1$

Total correlation function determines $c^{(2)}(r)$

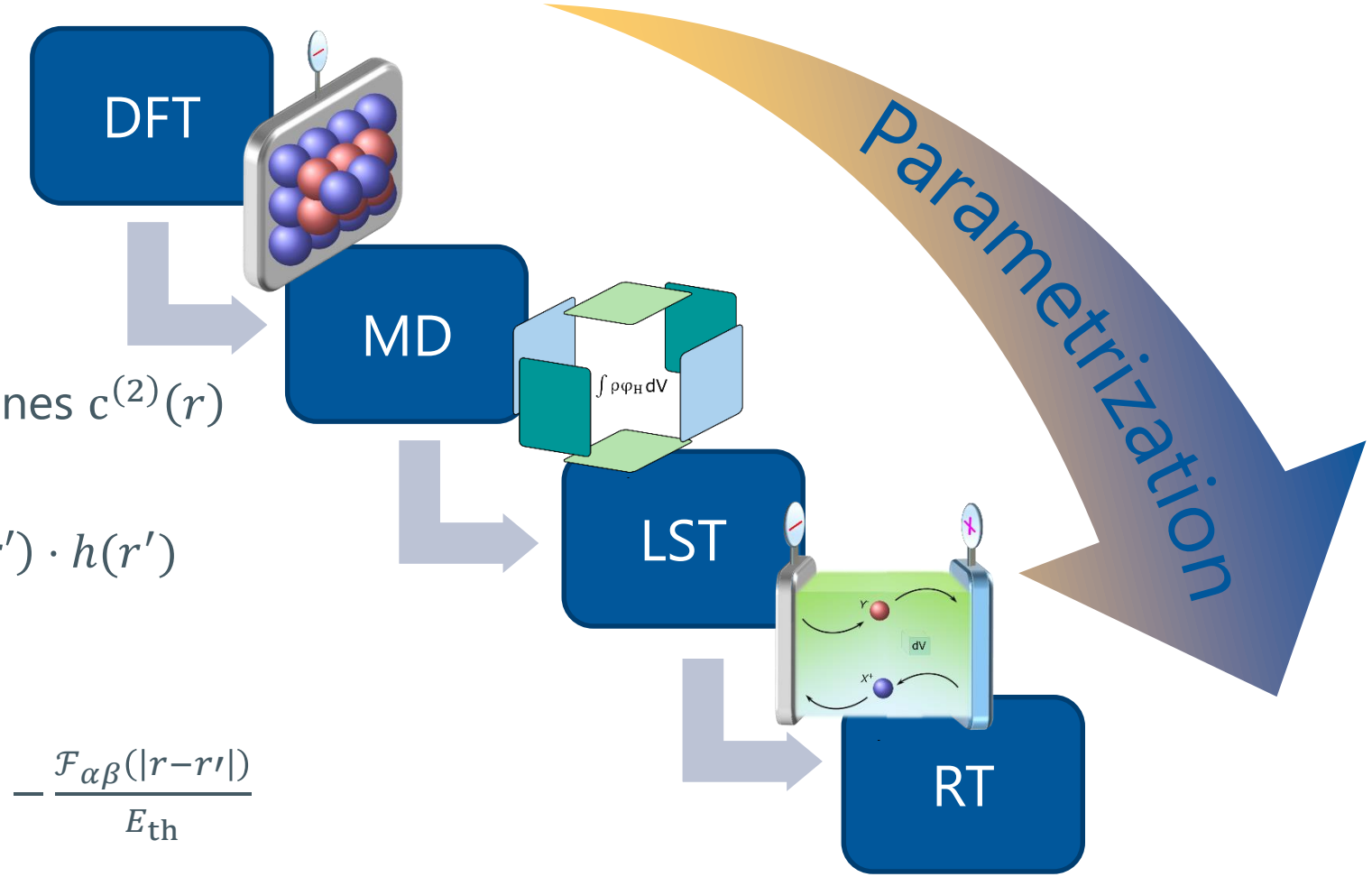
Ornstein-Zernike relation

- $h(r) = c^{(2)}(r) + \rho^{b} \int dr' c^{(2)}(r, r') \cdot h(r')$

Direct pair correlation function

Determines F^{int}

- $c^{(2)}_{\alpha\beta}(r, r') = -\frac{1}{E_{\text{th}}} \frac{\delta^2 F^{\text{int}}}{\delta c_\beta(x) \delta c_\alpha(y)} = -\frac{\mathcal{F}_{\alpha\beta}(|r - r'|)}{E_{\text{th}}}$



IL + solvent mixtures

EDL Structure

Neutral Solvent

Salt in IL

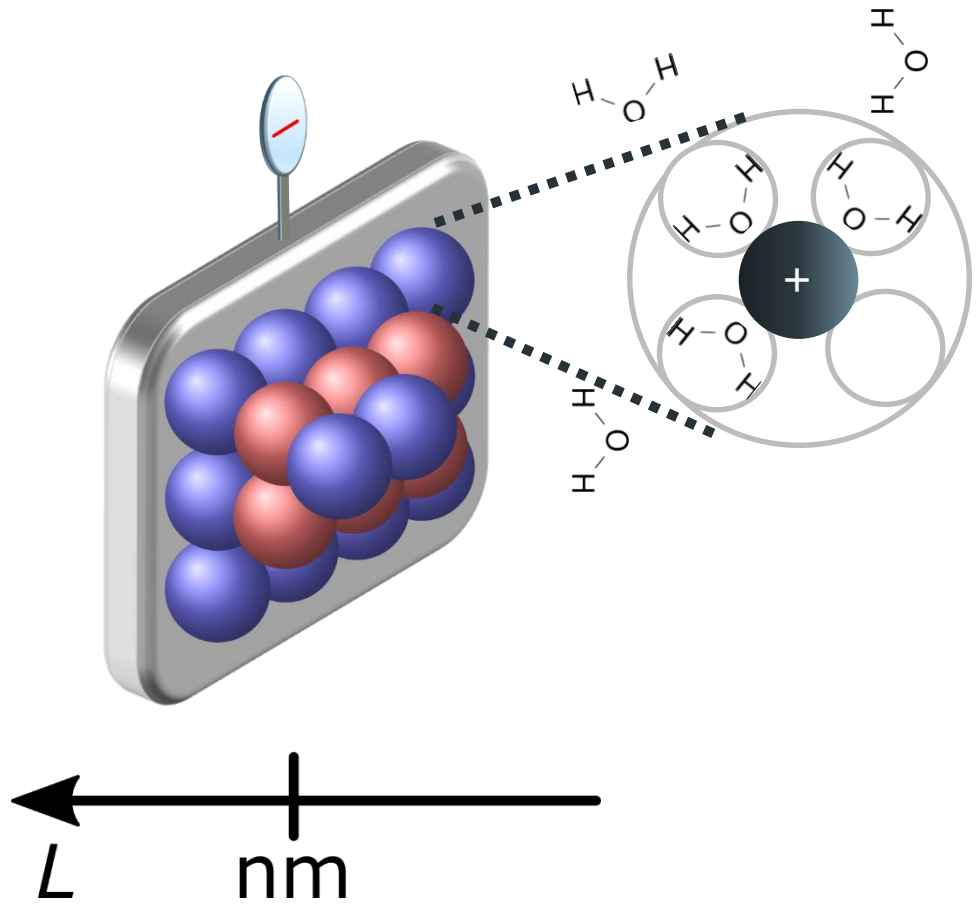
Solvation $\rho\varphi_{\mathrm{H}} = \rho\varphi_{\mathrm{H}}^{\mathrm{bulk}} + \rho\varphi_{\mathrm{H}}^{\mathrm{solv}}$

- Modified statistics $N_0^{\mathrm{free}} = N_0 - \sum_{\alpha=\pm} \tilde{\lambda}_\alpha \lambda_\alpha^{\mathrm{m}} N_\alpha$
- Binding Energy (novel parameter) E_{solv}

$$\rho\varphi_{\mathrm{H}}^{\mathrm{solv}} = RT\, \Sigma_{\pm} \lambda_\alpha^{\mathrm{m}} c_\alpha \left(\tilde{\lambda}_\alpha [\tilde{E}_{\mathrm{solv}} + \ln \tilde{\lambda}_\alpha] + \left(1 - \tilde{\lambda}_\alpha\right) \ln[1 - \tilde{\lambda}_\alpha] \right)$$

Solvent Coordination number (variable)

- $\tilde{\lambda}_\alpha(c_\pm, \Phi) \in [0; 1]$



Motivation: Influence of Minor Additive on EDL Structure

Neutral Solvent (water)

Solvent pushed out of EDL

"Dilute limit"

- EDL perturbation

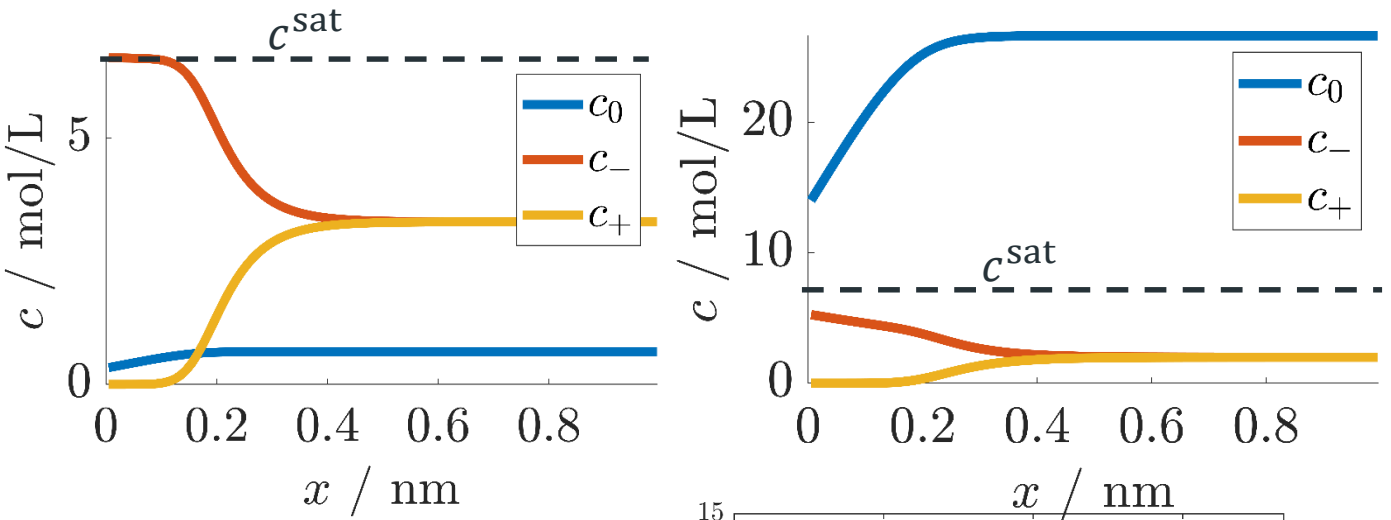
Salt Additive[#] (AgTFSI)

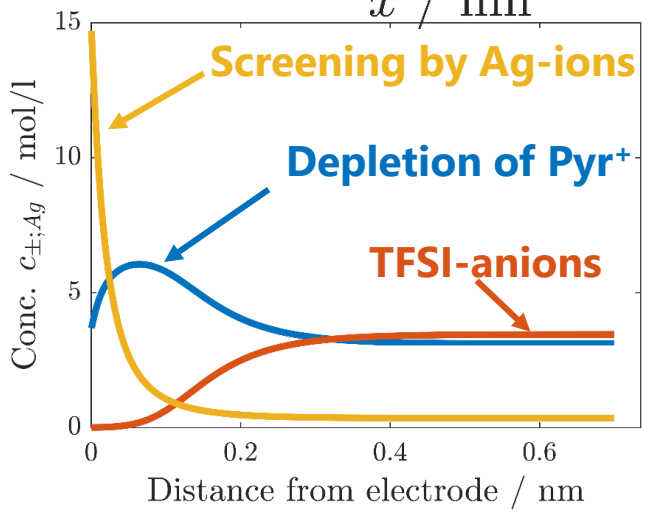
Theory

Critical Bulk Concentration

- $c_{\mathrm{AgTFSI}}^{\mathrm{critical}} \approx 0.04\ \mathrm{M}$
- Perturbation of EDL

Agreement with experiment[#]





[#]F. Endres, M. Schammer, et al., *Phys. Chem. Chem. Phys.*, 2018,20, 4760-4771.

Solvation

Incorporate Solvation

PyrTFSI with water

Simulation $\lambda_\alpha^{\mathrm{m}} = 8$

“Free” solvent

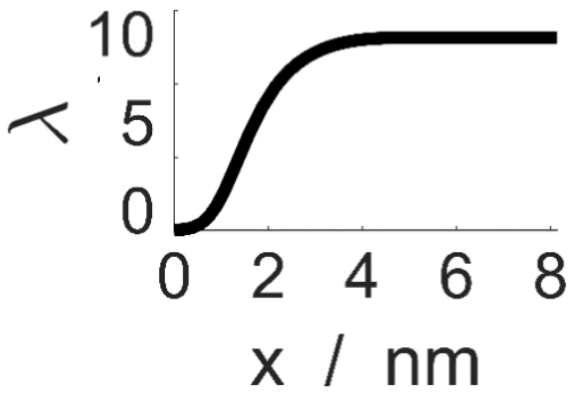
- pushed out of EDL

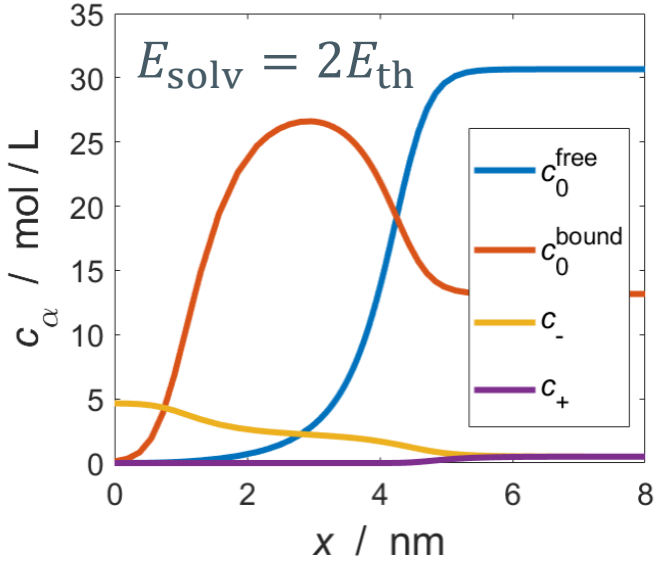
Solvent

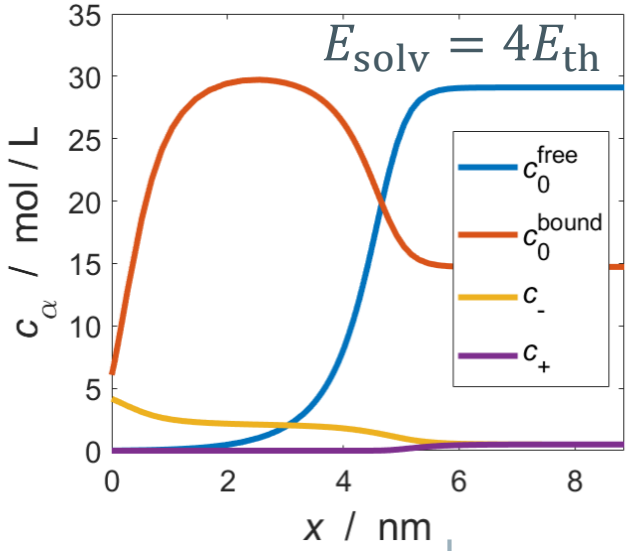
- Near Electrode: No solvation
- Near Bulk: Ions pull solvent into EDL

Influence of Binding Energy

- EDL perturbation
- More solvent pulled into EDL







Comparison with MD

MD Simulation[#]

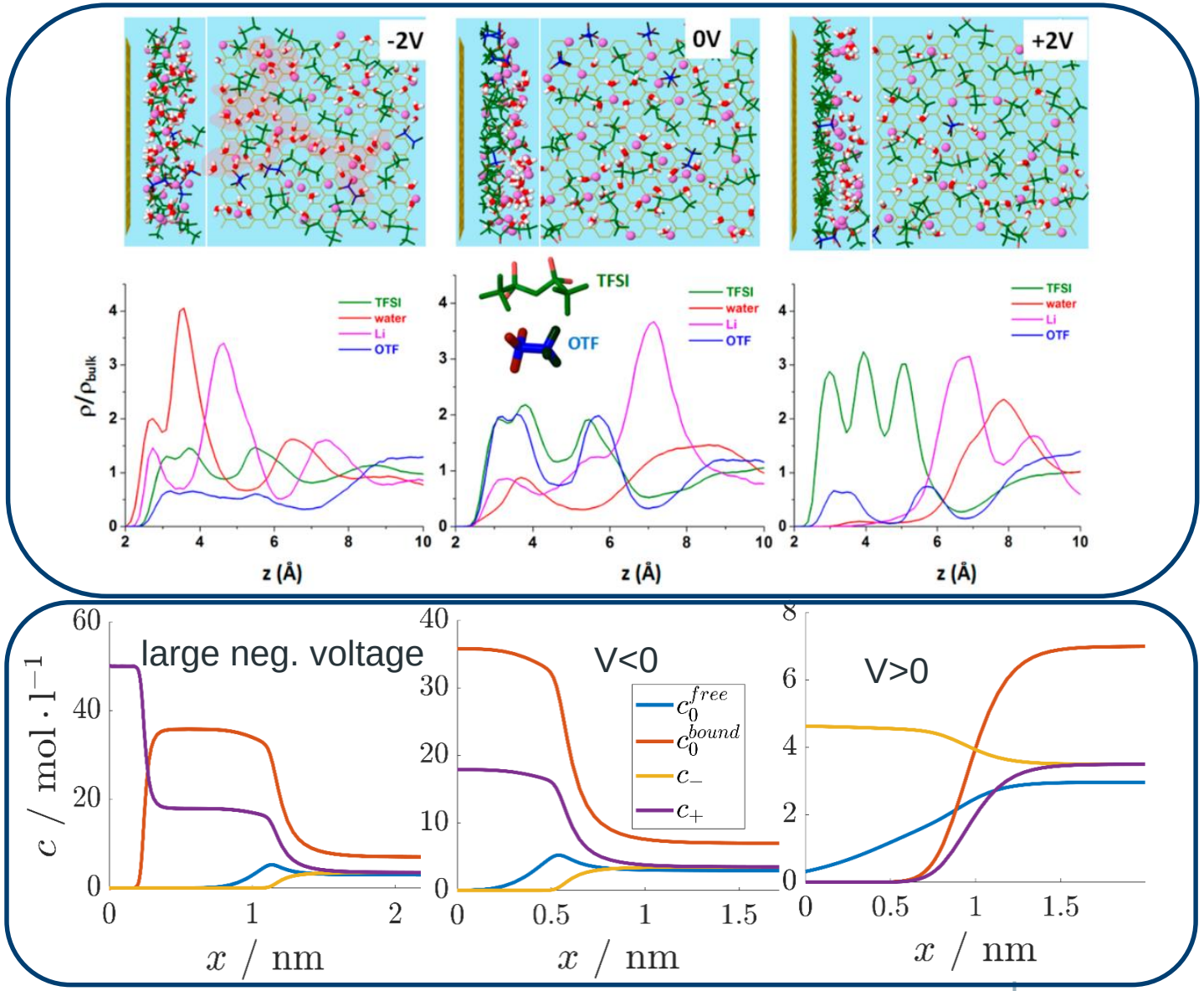
- Water in LiTFSI / OTF
- Influence of interface potential

[#]Vatamanu, J. and Borodin, O. *J. Phys. Chem. Lett.* 2017, 8, 4362−4367

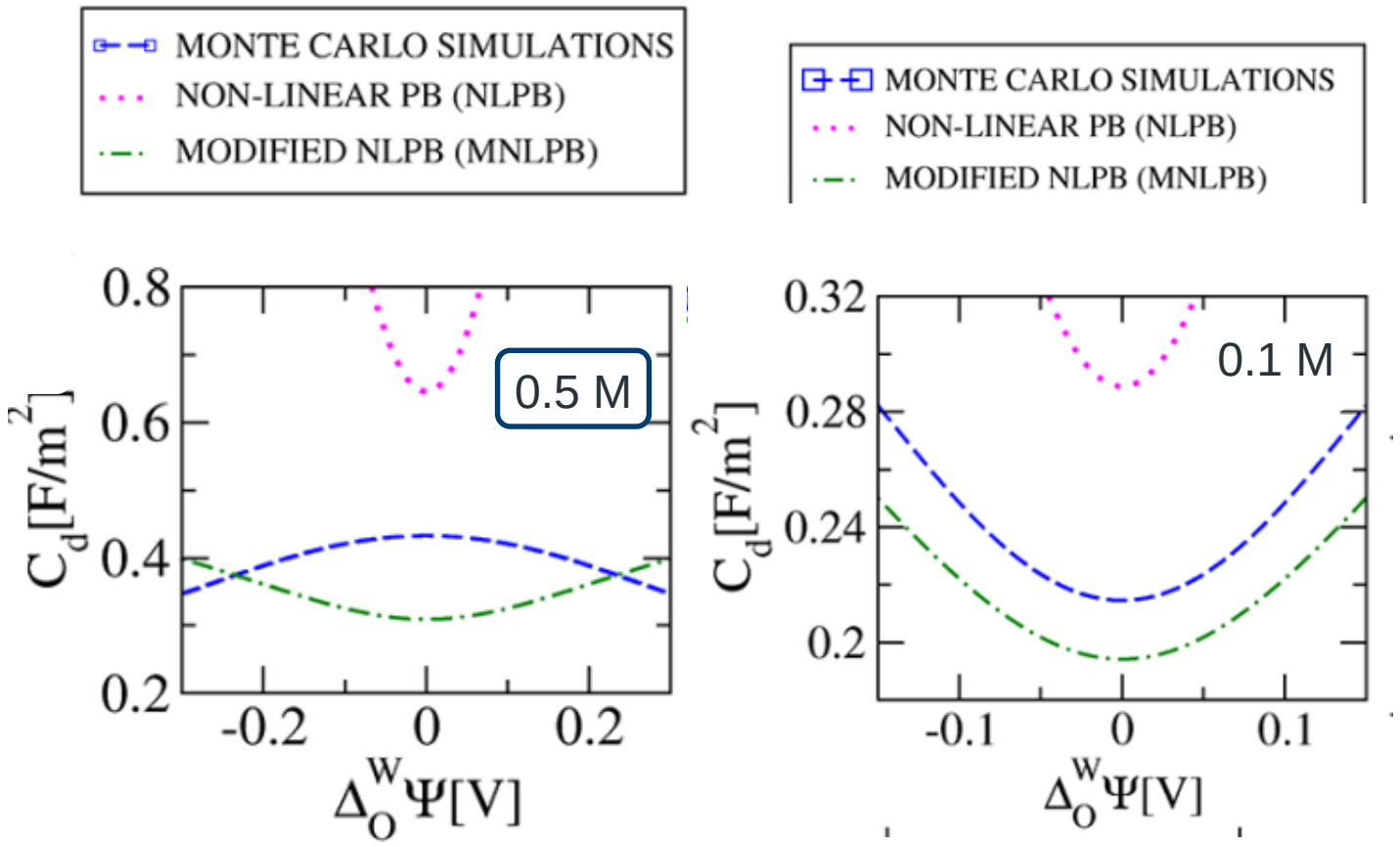
Continuum Simulation

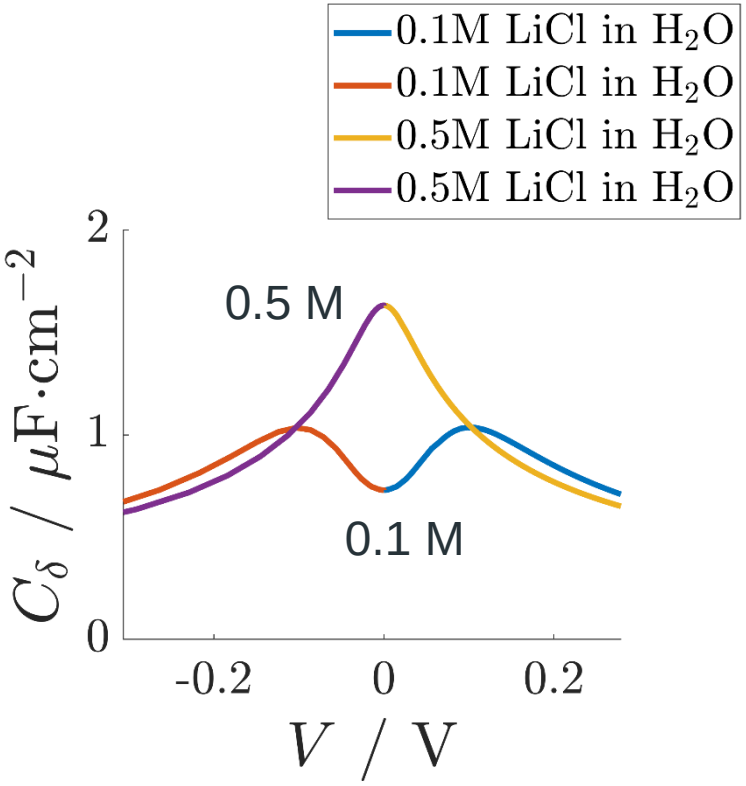
Assumption

- Water in LiTFSI
- strong Li-H_20 binding
- no TFSI-H_20 binding



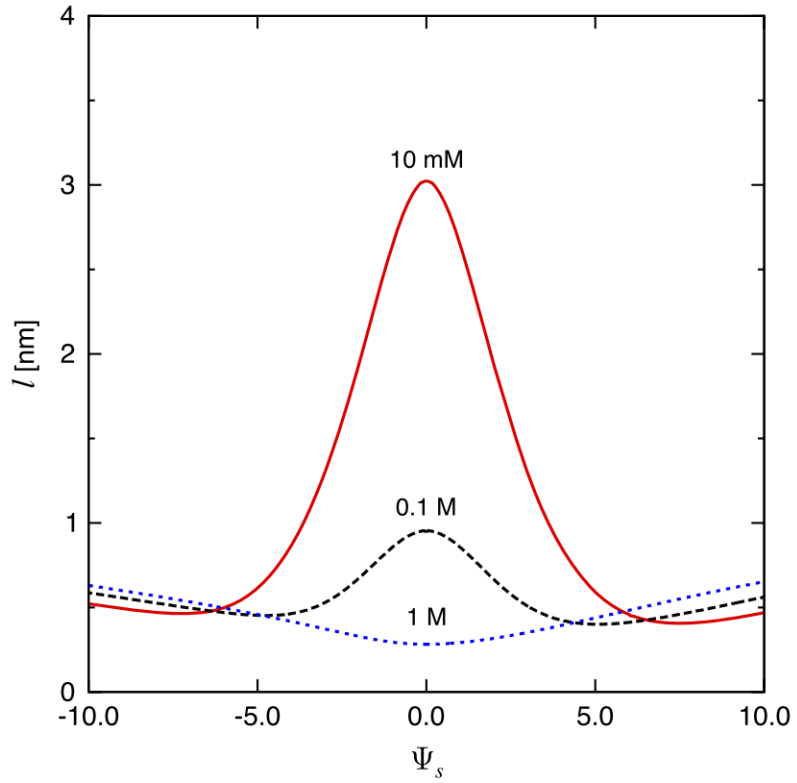
Comparison with LiCl in water: Differential Capacity

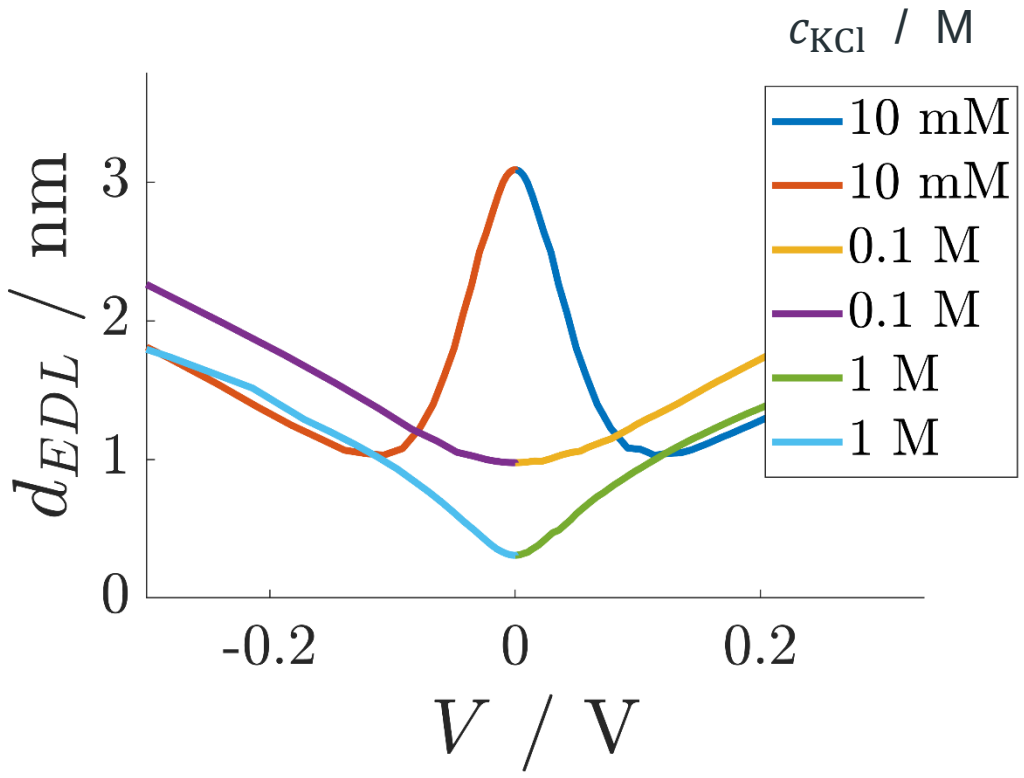




Guerrero-García, G. et al. *J. Chem. Theory Comput.* 2013, 9, 1−7

Comparison with KCl in water: Double Layer Thickness





Nakayama, Y. and Andelman, D. *J. Chem. Phys.* 2015, 142, 044706

Conclusions: Holistic Multi Scale Framework

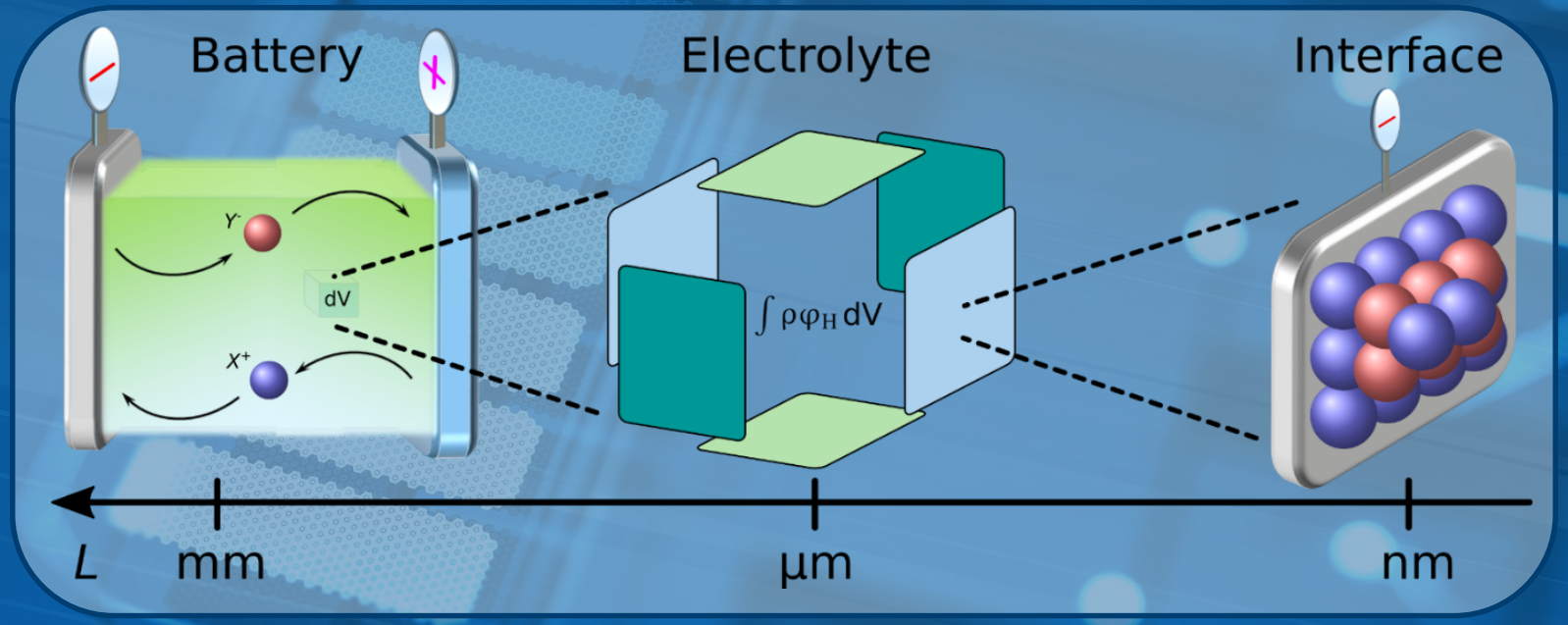
DFT → MD → non-equilibrium thermodynamics → phase-field theory

Rigorous methodology

- Bulk Transport
- EDL structure formation
- Outlook: Solvation

Experiments and Validation

- Battery Dynamics
- Transport Parameters
- AFM



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 814464

THANKS FOR LISTENING.

Coarse Graining: A Recipe for Atomistic Parametrization?

Free Energy Functional

$$F_{\mathrm{H}}^{\mathrm{int}} = \iint \mathrm{d}y\mathrm{d}x\, \mathcal{F}_{\alpha\beta}(|x-y|)\, c_\alpha(x)\, c_\beta(y)$$

Interaction Potential

$$\mathcal{F}_{\alpha\beta} = \mathcal{V}^0 \cdot \mathcal{S}_{\alpha\beta}(\ell_{\mathrm{int}})$$

Limit $\ell_{\mathrm{int}} \to 0$

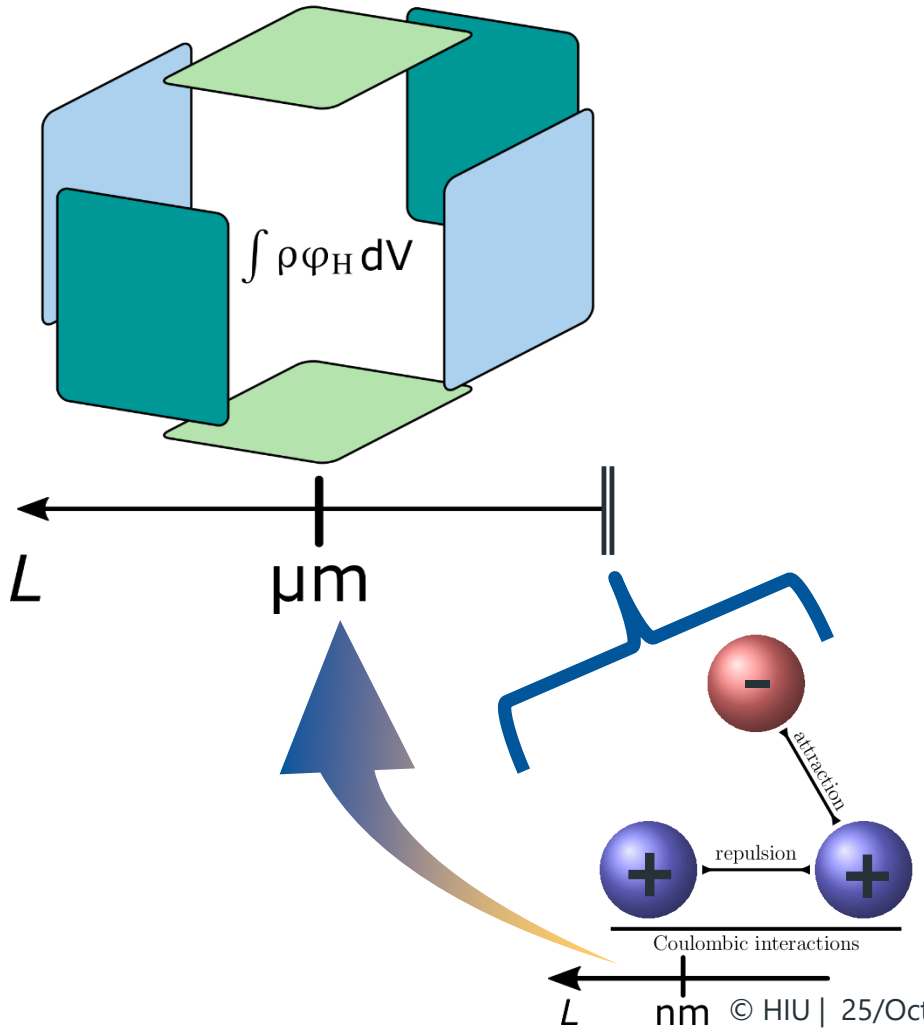
- Delta Distribution
- $\mathcal{S}_{\alpha\beta}(|x-y|) = \chi_{\alpha\beta}^{\mathrm{coarse}} \cdot \delta(|x-y|)$

Local free energy

$$\rho\varphi_{\mathrm{H}}^{\mathrm{coarse}} = \mathcal{V}^0 \chi_{\alpha\beta}^{\mathrm{coarse}} c_\alpha\, c_\beta$$

Example

Flory Huggins $\rho\varphi_{\mathrm{H}}^{\mathrm{Flory}} = RT\chi_{\alpha\beta}^{\mathrm{Flory}} c_\alpha \nu_\alpha c_\beta \nu_\beta$



Solvation Model

Define one species as solvent (c_0), this can form solvation shells around the other species.

- We modify the statistics to reflect solvation. Two contributions are included:
  - Reduction of free solvent molecules by $c_0^{bound} = \sum_{\alpha \geq 1} \lambda_\alpha c_\alpha$
  - Exchanges in the solvent shell of each ion-species
- λ_α is a local variable in the range $[0, \lambda_\alpha^m]$

A distinguishable macrostate is defined by $\{c_0, c_\alpha, \lambda_\alpha\}$

Add binding energy of the form $\sum_{\alpha \geq 1} E_\alpha \lambda_\alpha c_\alpha$ to the free energy

Validation of Analytical Approach

Hard Particles

Dominant Interaction

- $\mathcal{V}^0 \gg E_{\mathrm{th}}, E_{\mathrm{el}}$

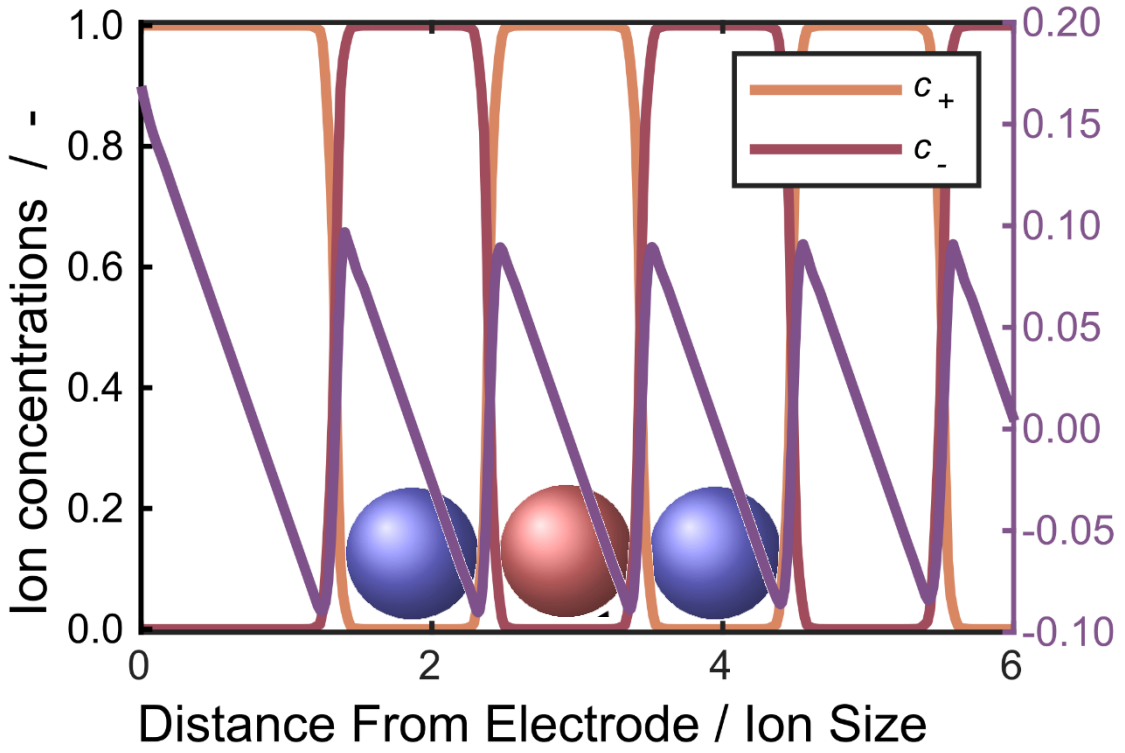
Phase separation

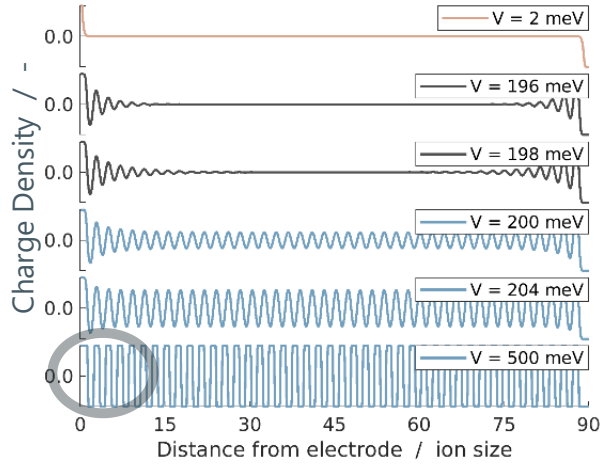
Pure Ion Layers

Nanostructured bulk

- Layers ≈ ion size

→ **“Particles”**





Transference Numbers: Reference Frame*,#

Fluxes depend on reference frame

- $\mathrm{v}^{\Psi} = \sum_{\alpha=1}^{\mathrm{N}} \psi_{\alpha} \mathrm{v}_{\alpha}$
- $\mathcal{N}_{\alpha}^{\Psi} = c_{\alpha}\left(\mathrm{v}_{\alpha} - \mathrm{v}^{\Psi}\right)$

Onsager Matrix

Transport Parameters

Transference Numbers

Specific current contribution

- $\mathcal{J}_{\alpha}^{\Psi} = \mathcal{N}_{\alpha}^{\Psi} / F\tilde{z}_{\alpha}^{\Psi}$
- $t_{\alpha}^{\Psi} = \mathcal{J}_{\alpha}^{\Psi} / \mathcal{J}^{\Psi} = \mathcal{N}_{\alpha}^{\Psi} / \mathcal{J}^{\Psi} F z_{\alpha}$

Reduced set of independent parameters

Flux constraint

- $\sum_{\alpha=1}^{N} \psi_{\alpha} \mathcal{N}_{\alpha}^{\Psi} / c_{\alpha} = 0$

Charge continuity

- $F \sum_{\alpha=2}^{N} \mathcal{N}_{\alpha}^{\Psi} \tilde{z}_{\alpha}^{\Psi} = \mathcal{J}^{\Psi}$

Transference Numbers

- $\sum_{\alpha=2}^{N} t_{\alpha}^{\Psi} = 1$
- N-2 independent parameters $t_3^{\Psi}, \ldots, t_N^{\Psi}$

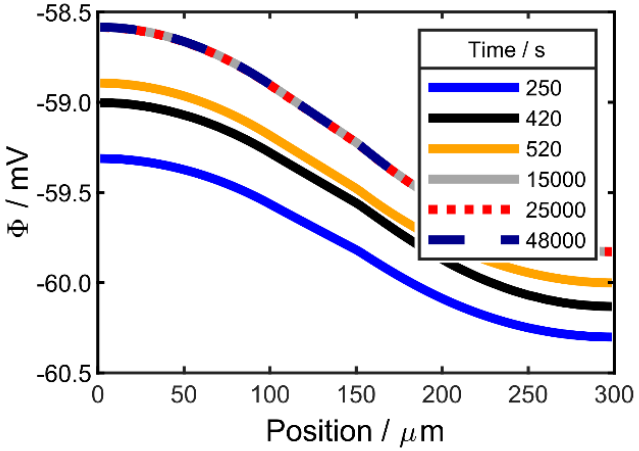
*F.Kilchert, M.Schammer, A.Latz, B.Horstmann, M.Schönhoff et al. *Submitted to PCCP*. Available on arxiv
#F.Kilchert, M.Schammer, A.Latz, B.Horstmann, M.Schönhoff et al., *J. Phys. Chem. Lett.* 2022, 13, 37, 8761–8767

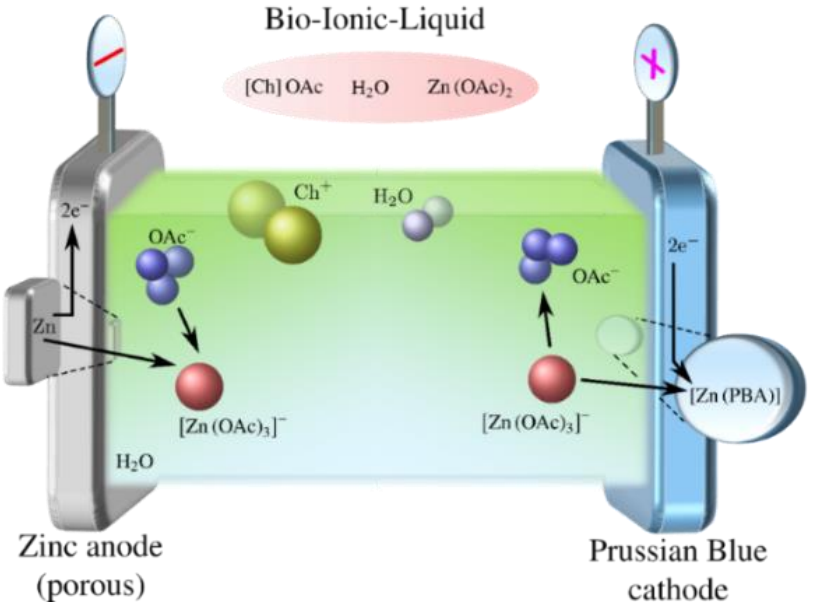
Transport Effects*

Potential drop towards cathode

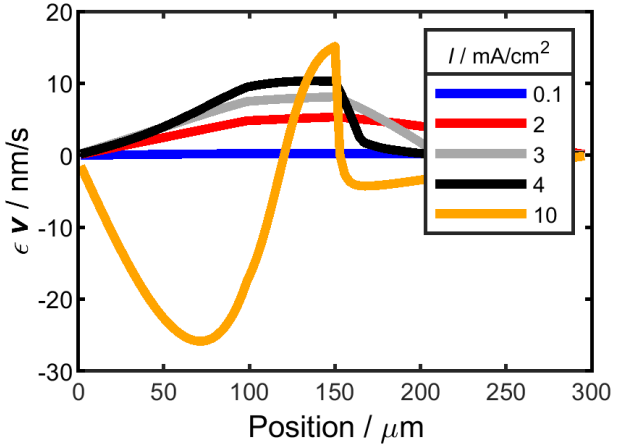
- Potential drop towards cathode
- Migration to Anode

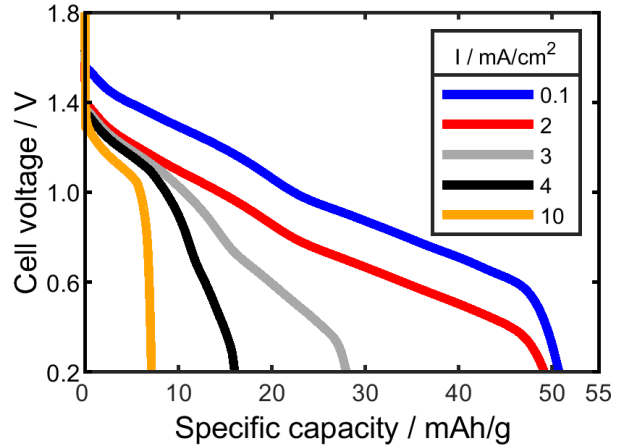
→ Competes with diffusion

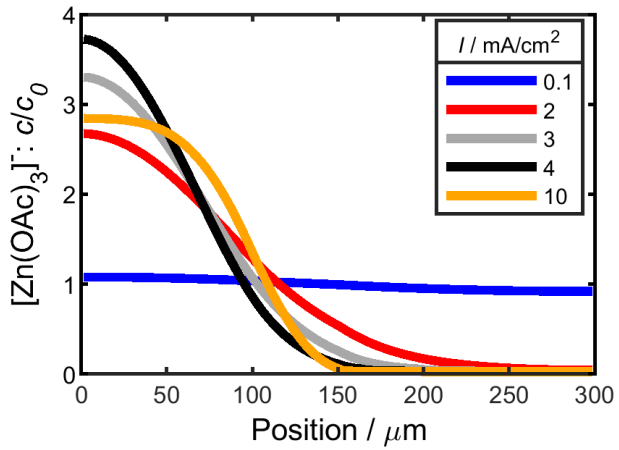




Enhanced Discharge Dynamics







*M.Schammer, B.Horstmann, A. Latz. *Journal of The Electrochemical Society* 168.2 (2021): 026511.

Transference Numbers: Reference Species

Constraints reduce parameters

Flux constraint

- $\sum_{\alpha=1}^{N} M_\alpha \mathcal{N}_\alpha = 0$

Charge continuity

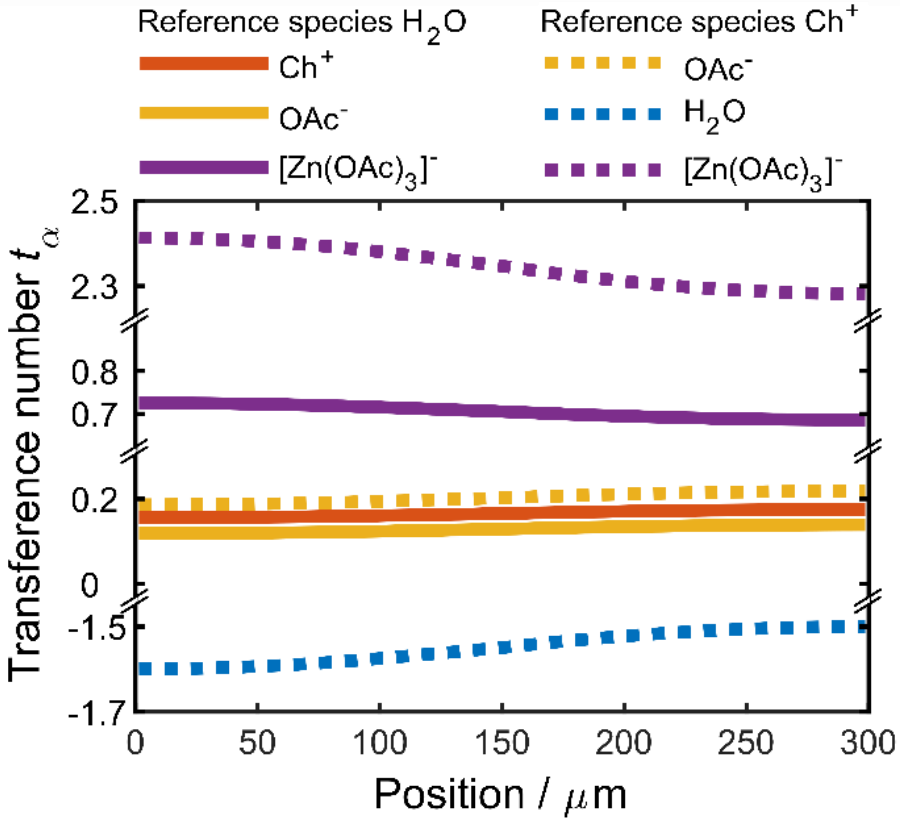
- $\sum_{\alpha=2}^{N} \mathcal{N}_\alpha F \tilde{z}_\alpha = \mathcal{J}$

Transference Numbers

- Follow from Onsager Matrix
- $\sum_{\alpha=2}^{N} t_\alpha = 1$
- N-2 independent parameters $t_3, \ldots, t_N$

Influence of reference species $\alpha = 1$

- Sign and Magnitude



*M.Schammer, B.Horstmann, A. Latz. *Journal of The Electrochemical Society* 168.2 (2021): 026511.

Parametrization: Asymptotic Analysis of EDL Structure

Near Electrode

- **Large potentials** $\Phi \gg RT/F$
- Charge saturation: Box profile

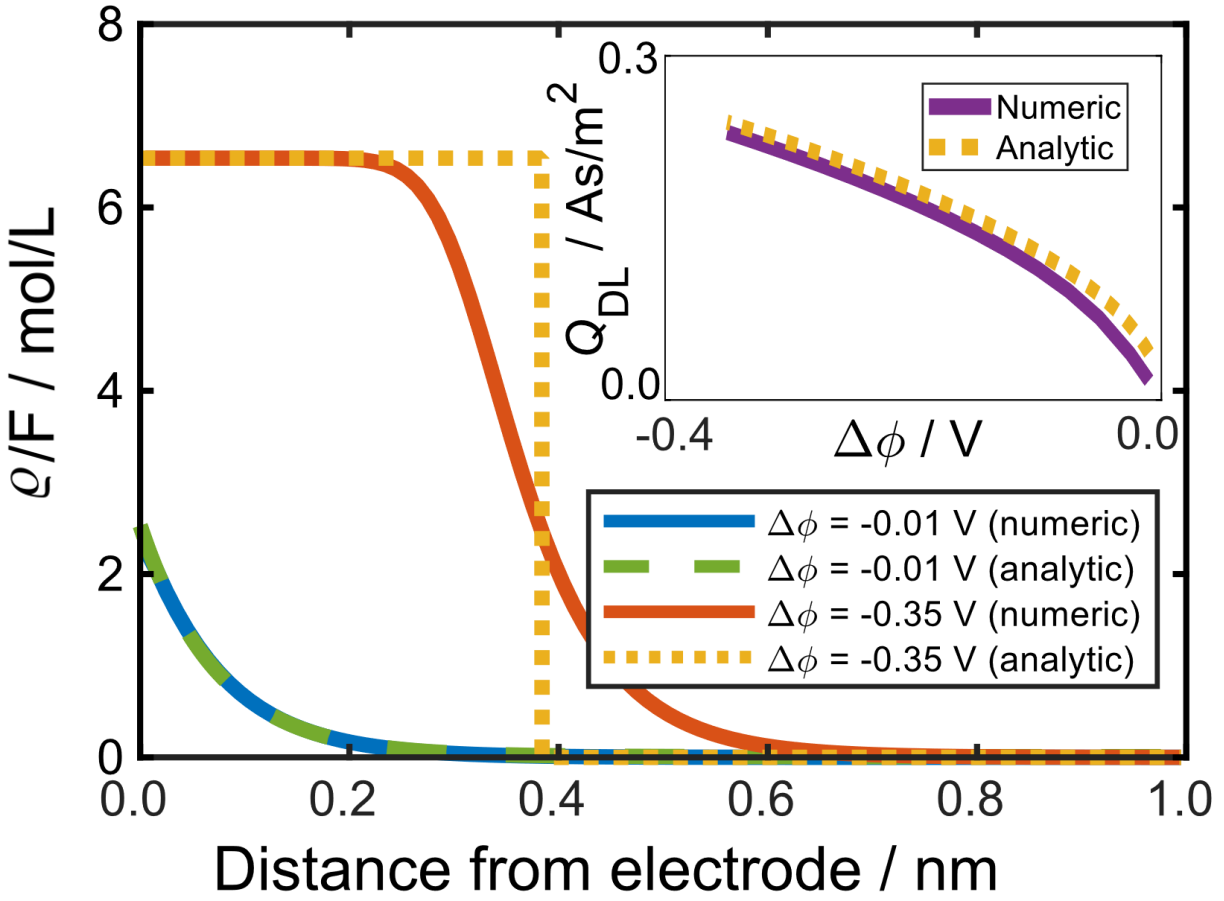
$$L_{\mathrm{EDL}} = \sqrt{2a^3|\Delta\phi|\gamma_+ \varepsilon_0\varepsilon_\mathrm{r}/(ez_+)^2}$$

Bulk Region

- **Small potentials** $\Phi \ll RT/F$
- Exponential decay

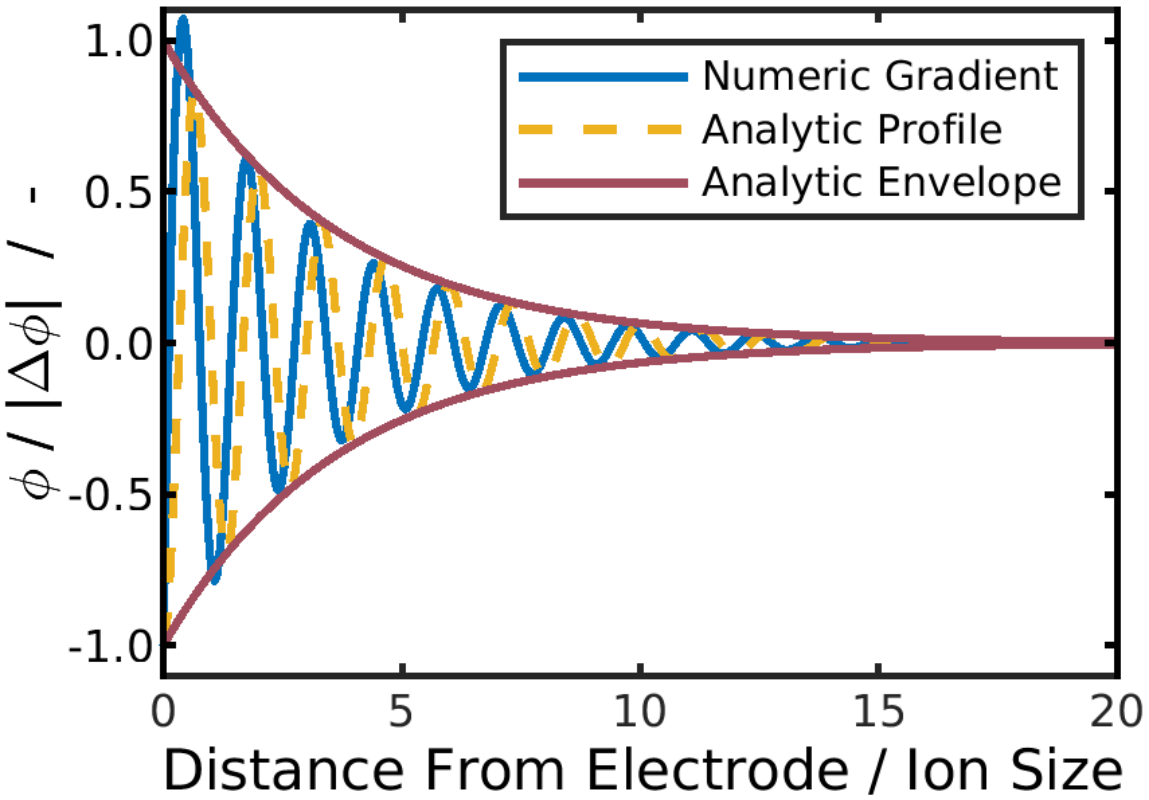
$$\Phi = \Delta\phi \cdot e^{-x/L_\mathrm{D}}$$

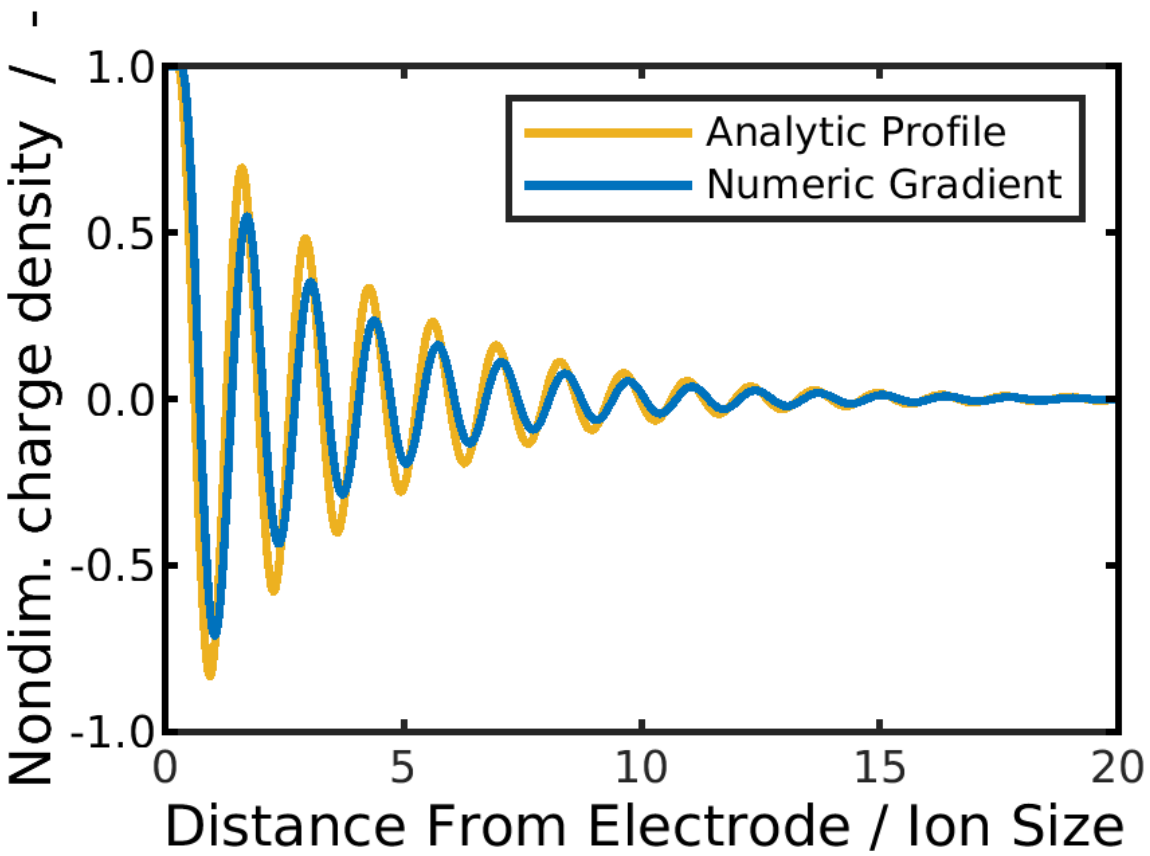
- Debye-length $L_\mathrm{D}(a, \epsilon_\mathrm{r}, T, \gamma_\alpha)$



Validation of Analytic Approach

Numeric results vs. Analytic prediction





Bilder Sammler