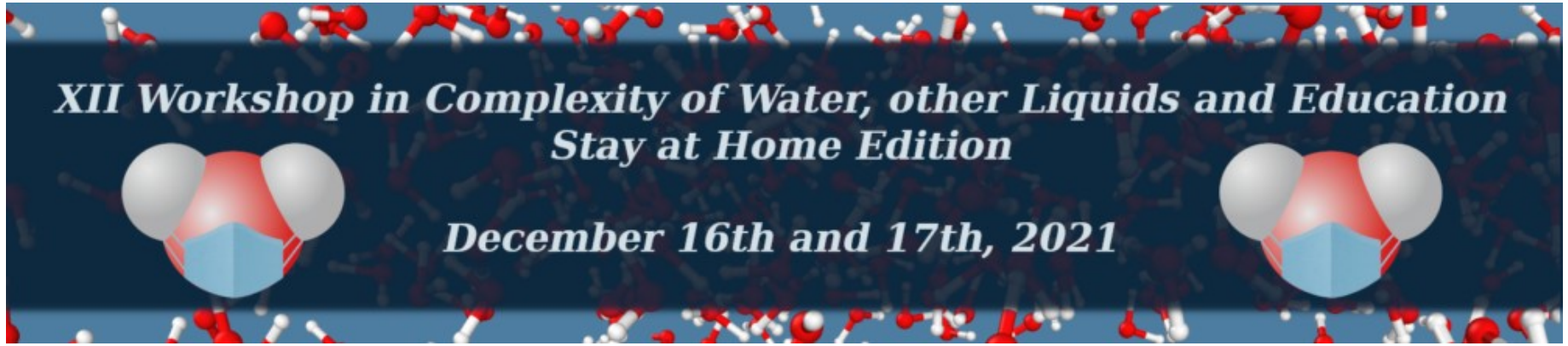

Real Ionic Solutions in the Functionalized Mean Spherical Approximation

DSc. Elvis do A. Soares, Prof. Nathalia S. Vernin, Prof. Mirella S. Santos and Prof. Frederico W. Tavares

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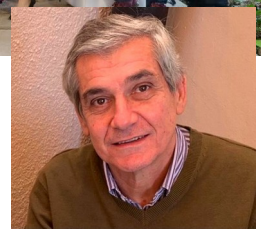
Applied Thermodynamics and Molecular Simulation
ATOMS
Termodinâmica Aplicada e Simulação Molecular

UFRJ

Rio de Janeiro, December 17, 2021

Universidade Federal do Rio de Janeiro

COPPE UFRJ



Applied Thermodynamics and Molecular Simulation

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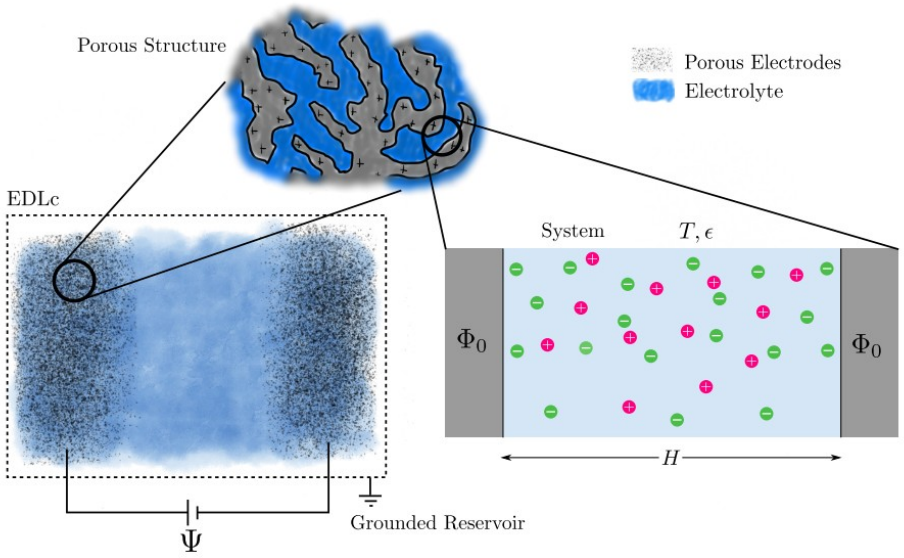
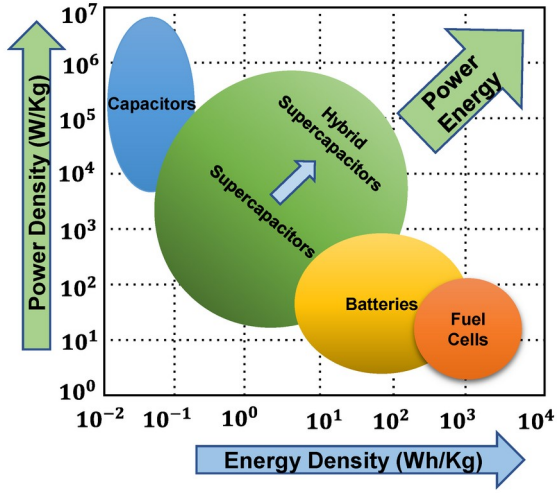
Pós-Doc - 2020

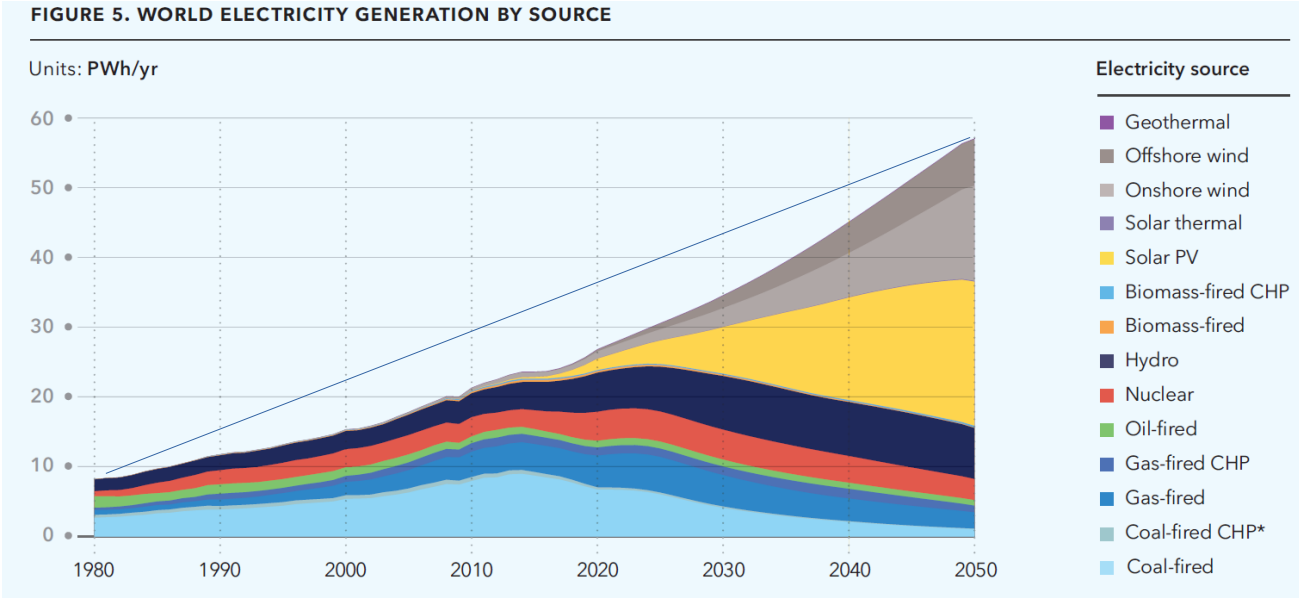
Instituto de Física UFRJ

Doutorado - 2017

Why Electrolytes?



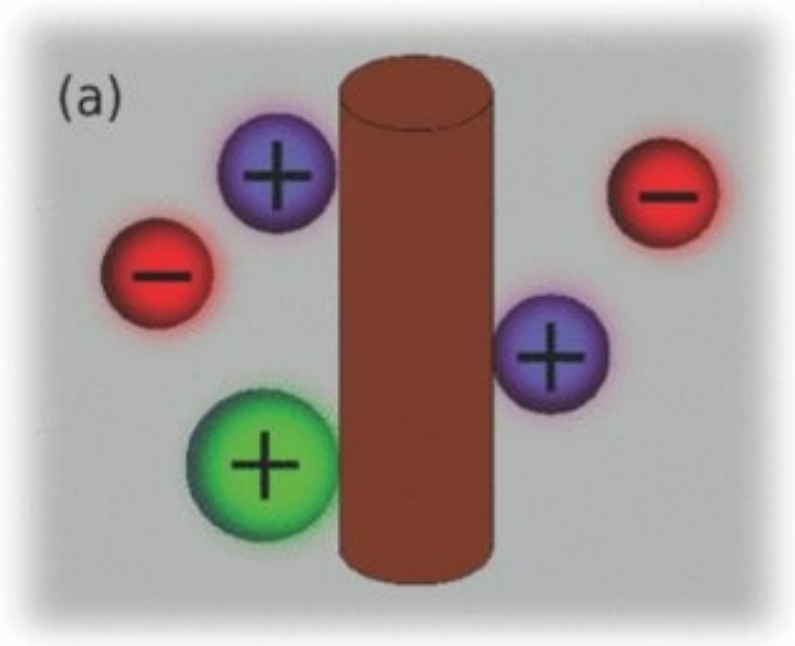




Cats, P., & van Roij, R. (2021). The Journal of Chemical Physics, 155(10), 104702.
Wayu, Mulugeta. (2021). Solids (2) 232-248.
https://eto.dnv.com/

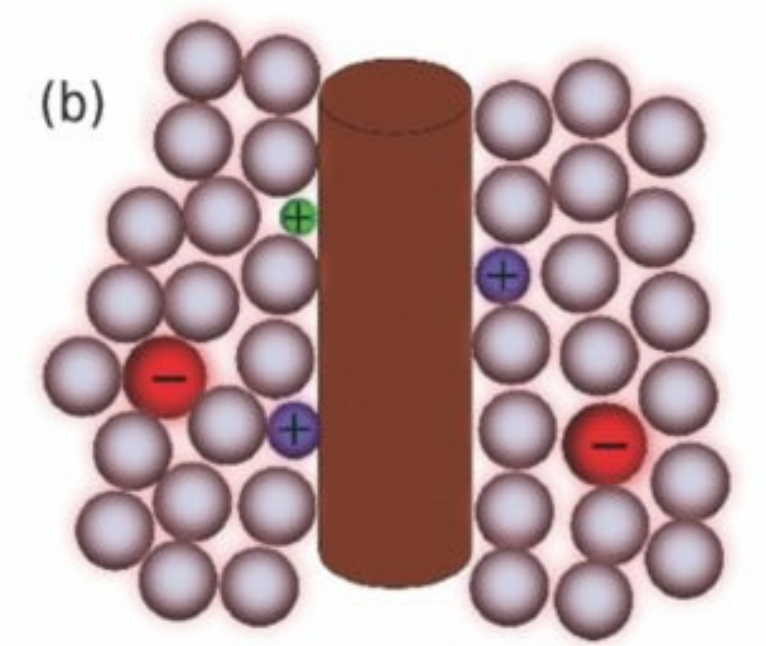
Electrolyte Solution Theories

Primitive Model



- Solvent is implicit (continuum medium)
- Hydrated size of ions
- Ion-ion interactions only

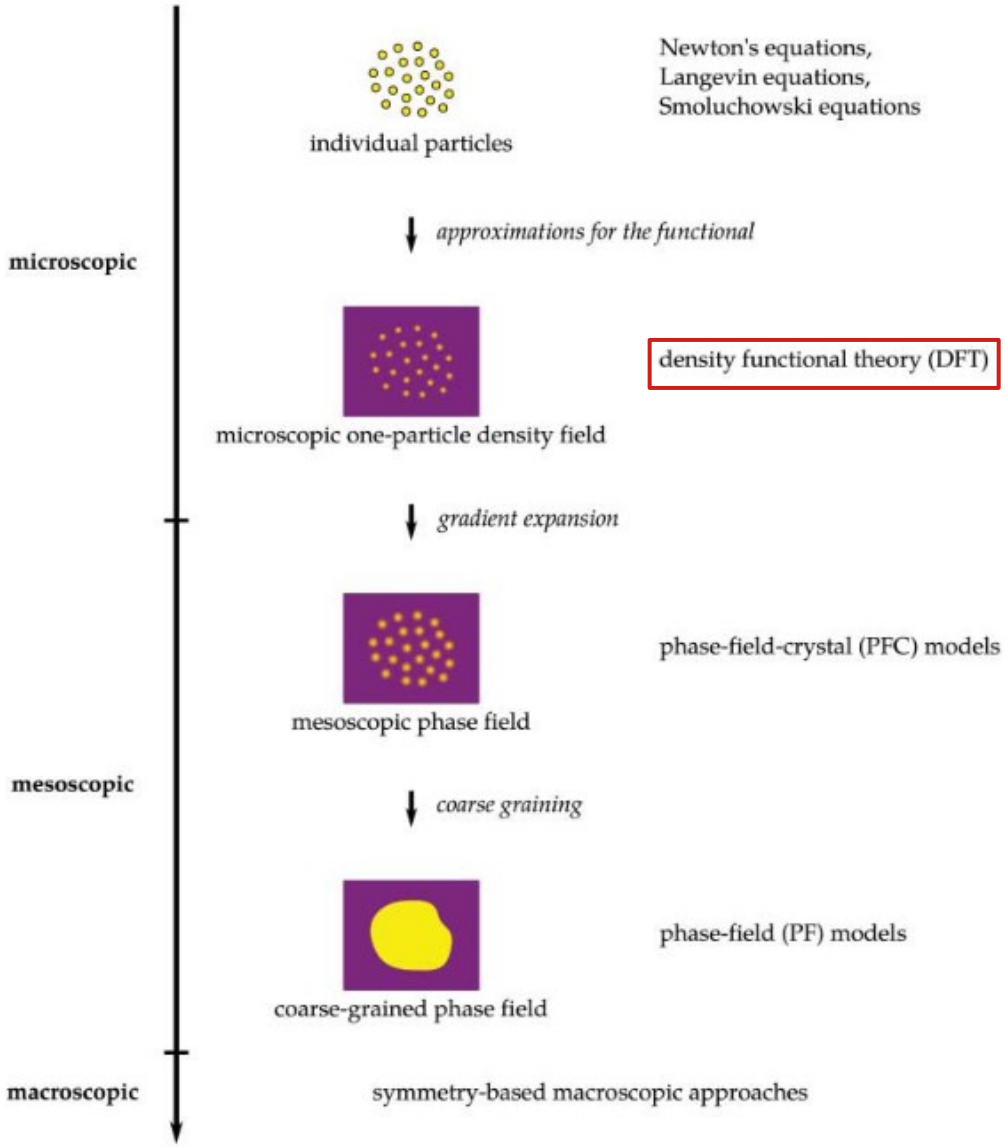
Non-primitive Model



- Solvent is explicit (particle)
- Pauli size of ions
- Ion-ion, Ion-solvent, solvent-solvent interactions

Kontogeorgis, G. M., & Folas, G. K. (2009). Thermodynamic models for industrial applications. John Wiley & Sons.
Ovanesyan, Z. et al (2014). The Journal of Chemical Physics, 141(22), 225103.

Classical Density Functional Theory *(DFT)*



Grand Potential functional

$$\Omega[\{\rho_k(\boldsymbol{r})\},\psi(\boldsymbol{r})] = F_{\mathrm{id}} + F_{\mathrm{exc}} + F_{\mathrm{coul}}$$
$$+\sum_i \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\,\left(V_i^{\mathrm{ext}}(\boldsymbol{r}) - \mu_i\right)\rho_i(\boldsymbol{r}) + \int_{\partial\mathcal{V}} \mathrm{d}\boldsymbol{r}\,\sigma(\boldsymbol{r})\psi(\boldsymbol{r})$$

Coulomb free-energy:

$$F_{\mathrm{coul}}[\{\rho_i(\boldsymbol{r})\},\psi(\boldsymbol{r})] = -\int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\left\{\frac{\epsilon_0\epsilon_r}{2}|\boldsymbol{\nabla}\psi(\boldsymbol{r})|^2 - \sum_i Z_i e\rho_i(\boldsymbol{r})\psi(\boldsymbol{r})\right\}$$

Thermodynamic equilibrium:

$$\left.\frac{\delta\Omega}{\delta\rho_i(\boldsymbol{r})}\right|_{V,\psi,\mu,T} = 0 \qquad \left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{V,\rho_i,\mu,T} = 0$$

Evans, R. (2009). Lectures at 3rd Warsaw School of Statistical Physics.
Evans, R. et al (2016). Journal of Physics: Condensed Matter, 28(24), 240401.
Wu, J., & Li, Z. Annual Review of Physical Chemistry, 58(1), 85-112. (2007)

Classical Density Functional Theory *(DFT)*

Density Profiles

$$\left.\frac{\delta\Omega}{\delta\rho_i(\boldsymbol{r})}\right|_{V,\psi,\mu,T} = k_B T \ln\left(\Lambda_i^3 \rho_i(\boldsymbol{r})\right) + Z_i e\psi(\boldsymbol{r}) + \frac{\delta F_{\text{exc}}}{\delta\rho_i(\boldsymbol{r})} + V_i^{\text{ext}}(\boldsymbol{r}) - \mu_i = 0$$

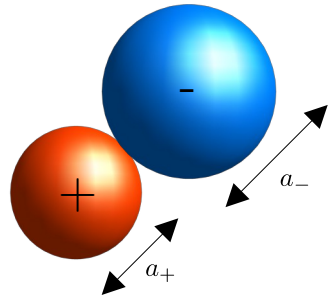
$$\rho_i(\boldsymbol{r}) = \rho_i^{(b)} \exp\left[-\beta Z_i e\psi(\boldsymbol{r}) + c_i^{(1),\text{exc}}(\boldsymbol{r}) + \beta V_i^{\text{ext}}(\boldsymbol{r}) + \beta\mu_i^{\text{exc}}\right]$$

Poisson Equation

$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{V,\rho_i,\mu,T} = \epsilon_0\epsilon_r \nabla^2\psi(\boldsymbol{r}) + \sum_i Z_i e\rho_i(\boldsymbol{r}) = 0$$

$$\left.\frac{\delta\Omega}{\delta\psi(\boldsymbol{r})}\right|_{\partial V,\rho_i,\mu,T} = -\frac{\epsilon_0\epsilon_r}{2}\hat{\mathbf{n}}(\boldsymbol{r})\cdot\boldsymbol{\nabla}\psi(\boldsymbol{r})\Big|_{\partial V} + \sigma(\boldsymbol{r}) = 0$$

Functionalized Mean Spherical Approximation (fMSA)



$$\beta F_{\mathrm{hs}}[\rho(\boldsymbol{r})] = \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \Phi_{\mathrm{FMT}}(\{n^{(\alpha)}(\boldsymbol{r})\})$$

$$\beta F_{\mathrm{ec}}[\rho(\boldsymbol{r})] = \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}\, \Phi_{\mathrm{MSA}}(\{q_i^{(0)}(\boldsymbol{r})\}) - \frac{1}{2}\sum_{i,j}\int_{\mathcal{V}} \mathrm{d}\boldsymbol{r} \int_{\mathcal{V}} \mathrm{d}\boldsymbol{r}'\, [\rho_i(\boldsymbol{r}) - \rho_i^{(b)}]\Delta c_{ij}^{(2),\mathrm{MSA}}(|\boldsymbol{r}-\boldsymbol{r}'|)[\rho_j(\boldsymbol{r}') - \rho_j^{(b)}]$$

Excess quantities

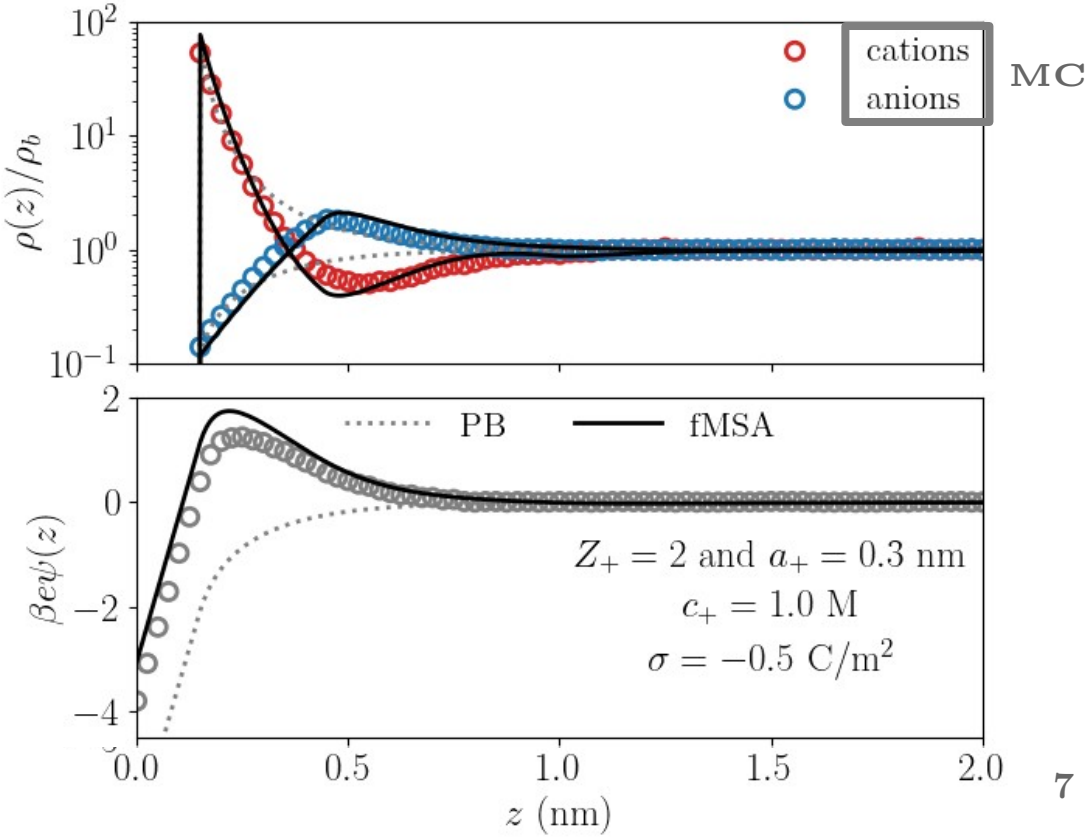
$$F_{\mathrm{exc}}[\rho(\boldsymbol{r})] = F_{\mathrm{hs}}[\rho(\boldsymbol{r})] + F_{\mathrm{ec}}[\rho(\boldsymbol{r})]$$

$$\mu_{\mathrm{exc}} = \mu_{\mathrm{hs}} + \mu_{\mathrm{ec}}$$

OZ MSA closure relation

$$g(r) = 0 \quad \text{for} \quad r < a$$

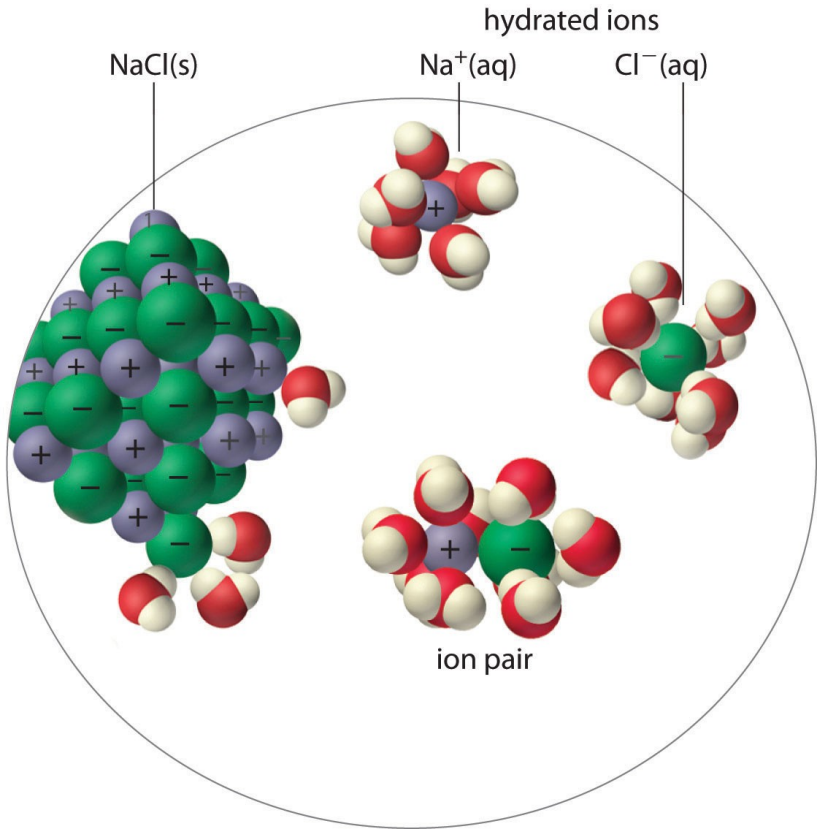
$$c(r) = -Z_i Z_j \frac{\lambda_B}{r} \quad \text{for} \quad r > a$$



Waisman, E., & Lebowitz, J. L. (1972).The Journal of Chemical Physics, 56(6), 3086-3093.
Levin, Y. (2002). Reports on Progress in Physics, 65(11), 1577-1632.
Roth, R., & Gillespie, D. (2016). Journal of Physics Condensed Matter, 28(24), 244006.

What are the problems with real electrolyte solutions?!

Hydrated Cation Radius



$$\beta\Delta G_{\mathrm{H}}^{(i)} = -\frac{\lambda_B}{a_B} Z_i^2 \left(1 - \frac{1}{\epsilon_r^{(w)}}\right)$$

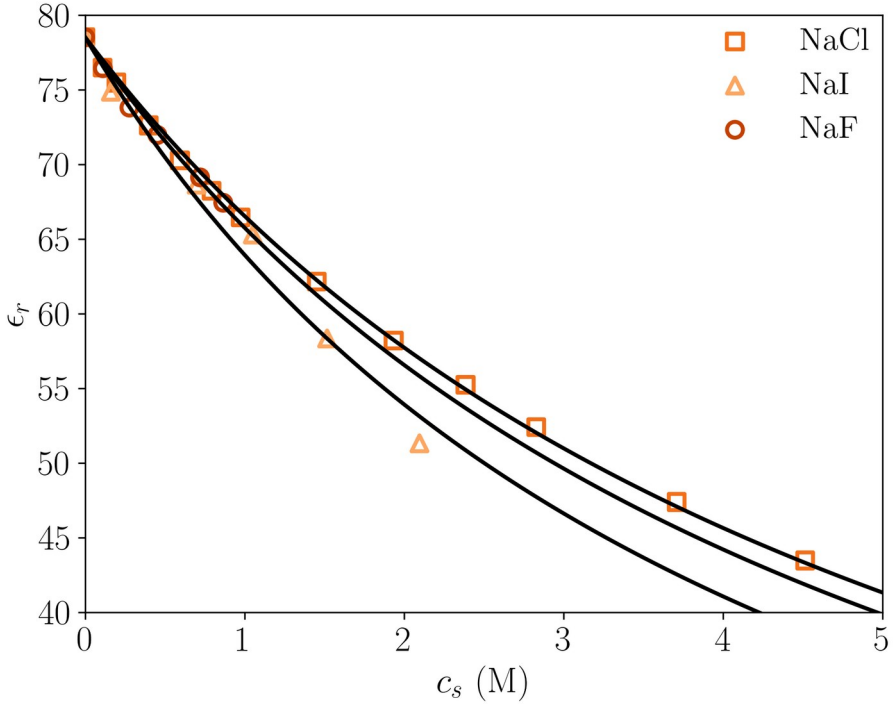
Ion	a_{P} (nm)	a_{B} (nm)	$-\Delta G_{\mathrm{H}}$ (kcal/mol)?
Li^+	0.12	0.285	114.6
Na^+	0.19	0.365	89.7
K^+	0.27	0.446	73.5
Cl^-	0.36	0.389	84.2
Br^-	0.39	0.420	78.0
I^-	0.43	0.468	70.0

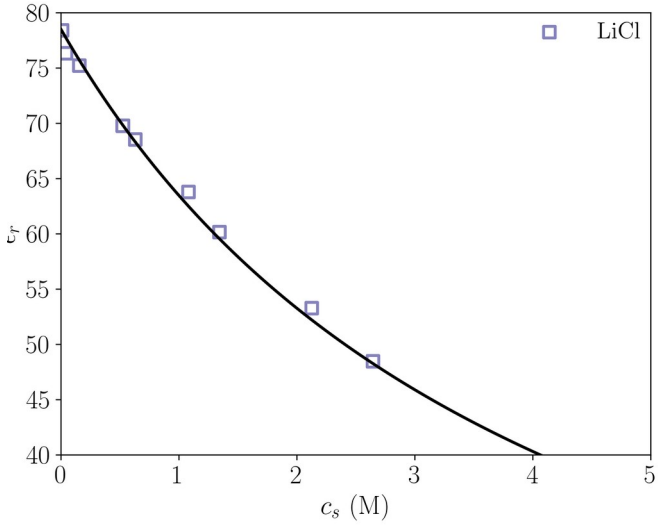
$$\mu_{\mathrm{exc}} = \frac{\partial \Phi_{\mathrm{FMT}}^{(b)}}{\partial \rho_i^{(b)}} + \frac{\partial \Phi_{\mathrm{MSA}}^{(b)}}{\partial \rho_i^{(b)}} + \frac{\partial \Phi_{\mathrm{FMT}}^{(b)}}{\partial a_+} \frac{\partial a_+}{\partial \rho_i^{(b)}} + \frac{\partial \Phi_{\mathrm{MSA}}^{(b)}}{\partial a_+} \frac{\partial a_+}{\partial \rho_i^{(b)}}$$

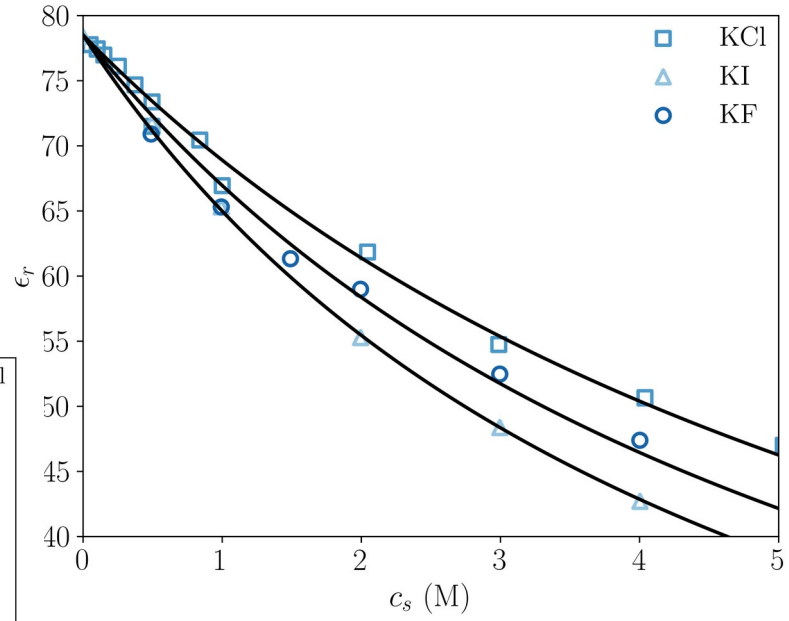
$$a^{(+)} = a_{\mathrm{P}}^{(+)} + \frac{\delta_H}{(1 + \alpha_H c_s)}$$

Robinson, R. A., & Stokes, R. H. (2002). Electrolyte solutions. Courier Corporation.

Water Electric Permittivity







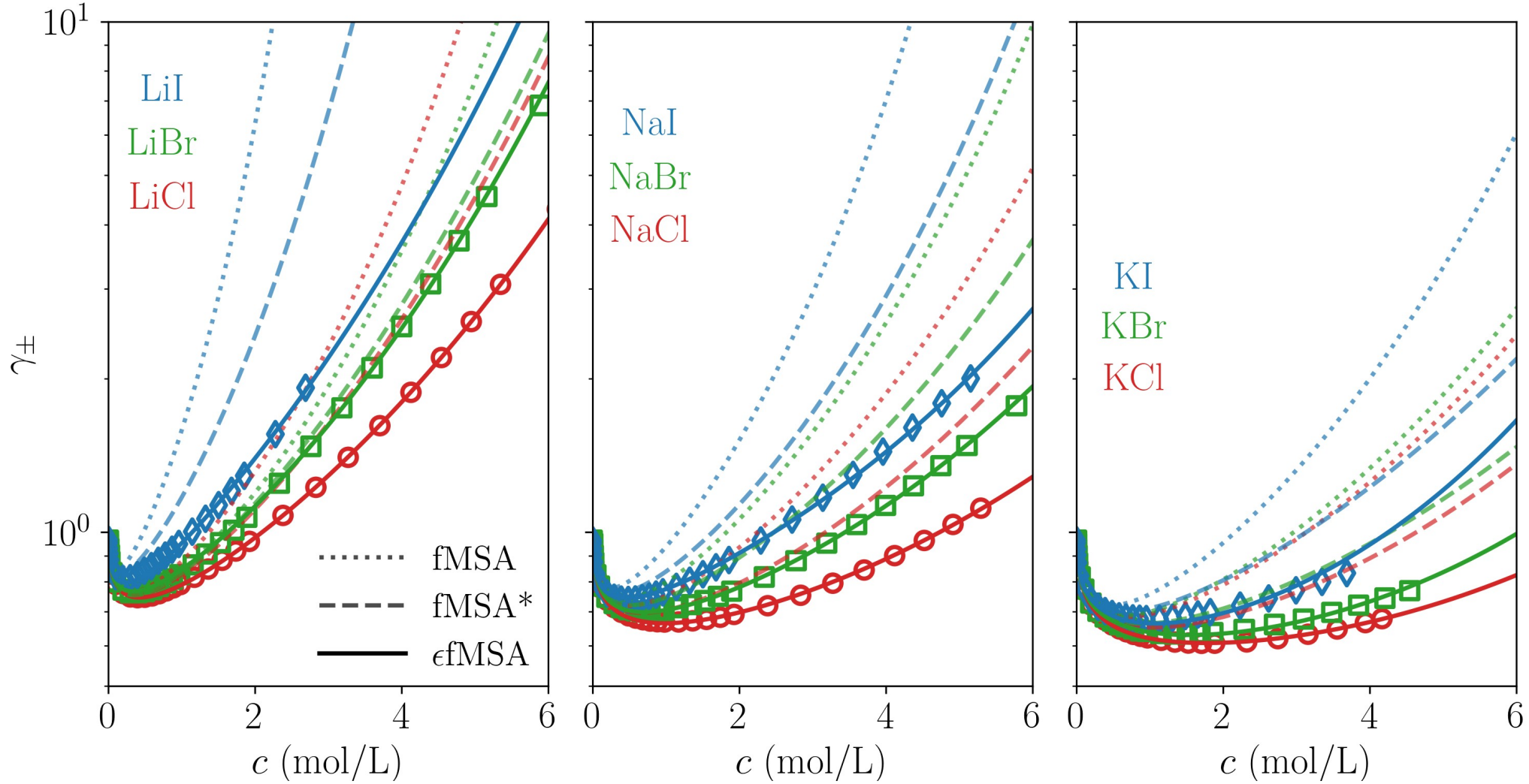
$$\epsilon_r(c_s) = \frac{\epsilon_r^{(w)}}{(1 + \sum_i \alpha_\epsilon^{(i)} x_i)}$$

$$\mu_{\text{exc}} = \frac{\partial \Phi^{(b)}_{\text{FMT}}}{\partial \rho_i^{(b)}} + \frac{\partial \Phi^{(b)}_{\text{MSA}}}{\partial \rho_i^{(b)}} + \frac{\partial \Phi^{(b)}_{\text{FMT}}}{\partial a_+} \frac{\partial a_+}{\partial \rho_i^{(b)}} + \frac{\partial \Phi^{(b)}_{\text{MSA}}}{\partial a_+} \frac{\partial a_+}{\partial \rho_i^{(b)}} + \frac{\partial \Phi^{(b)}_{\text{MSA}}}{\partial \epsilon_r} \frac{\partial \epsilon_r}{\partial \rho_i^{(b)}}$$

Zuber, A., Cardozo-Filho, L., Cabral, V. F., Checoni, R. F., & Castier, M. (2014). Fluid Phase Equilibria, 376, 116-123.

Activity Coefficient

$$\ln \gamma_{\pm} = \frac{1}{2}(\mu_{+}^{\mathrm{exc}} + \mu_{-}^{\mathrm{exc}})$$

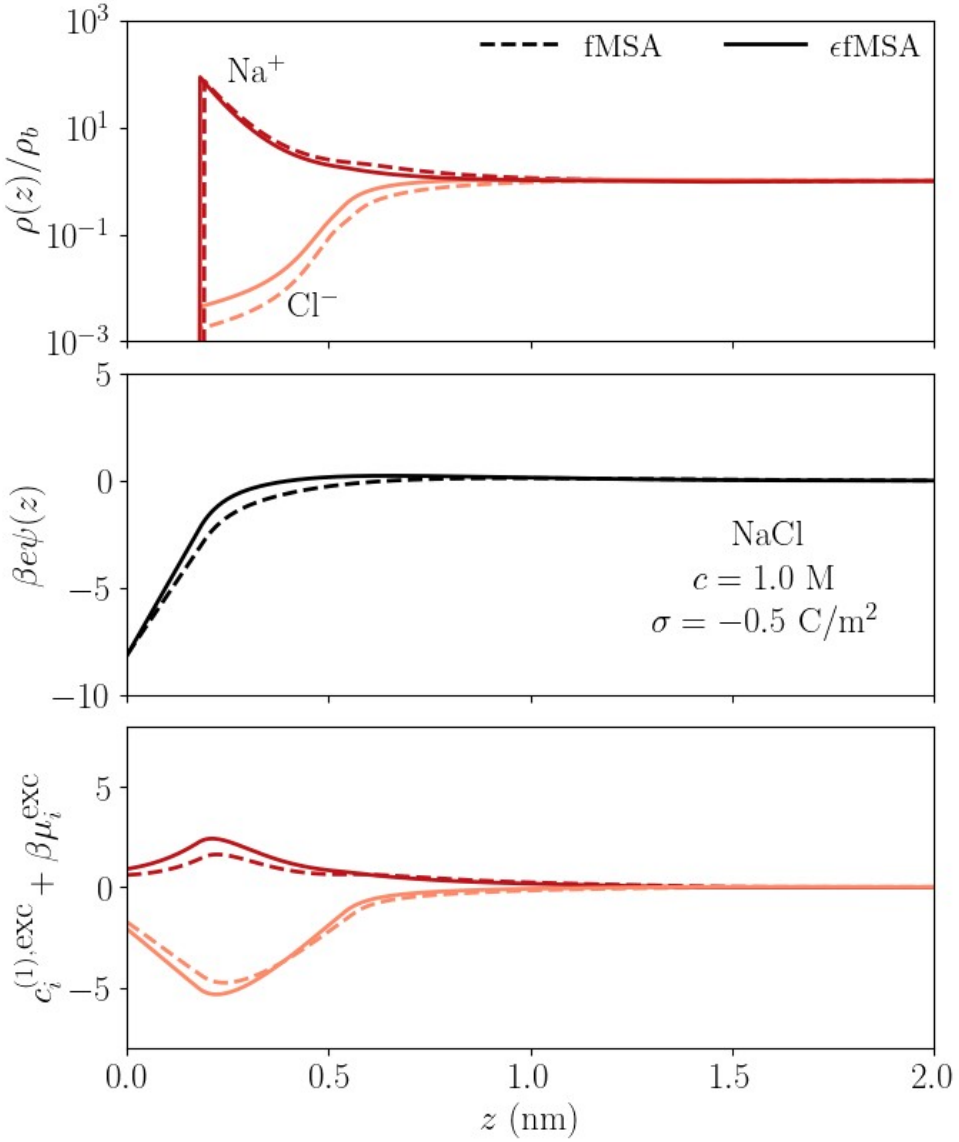


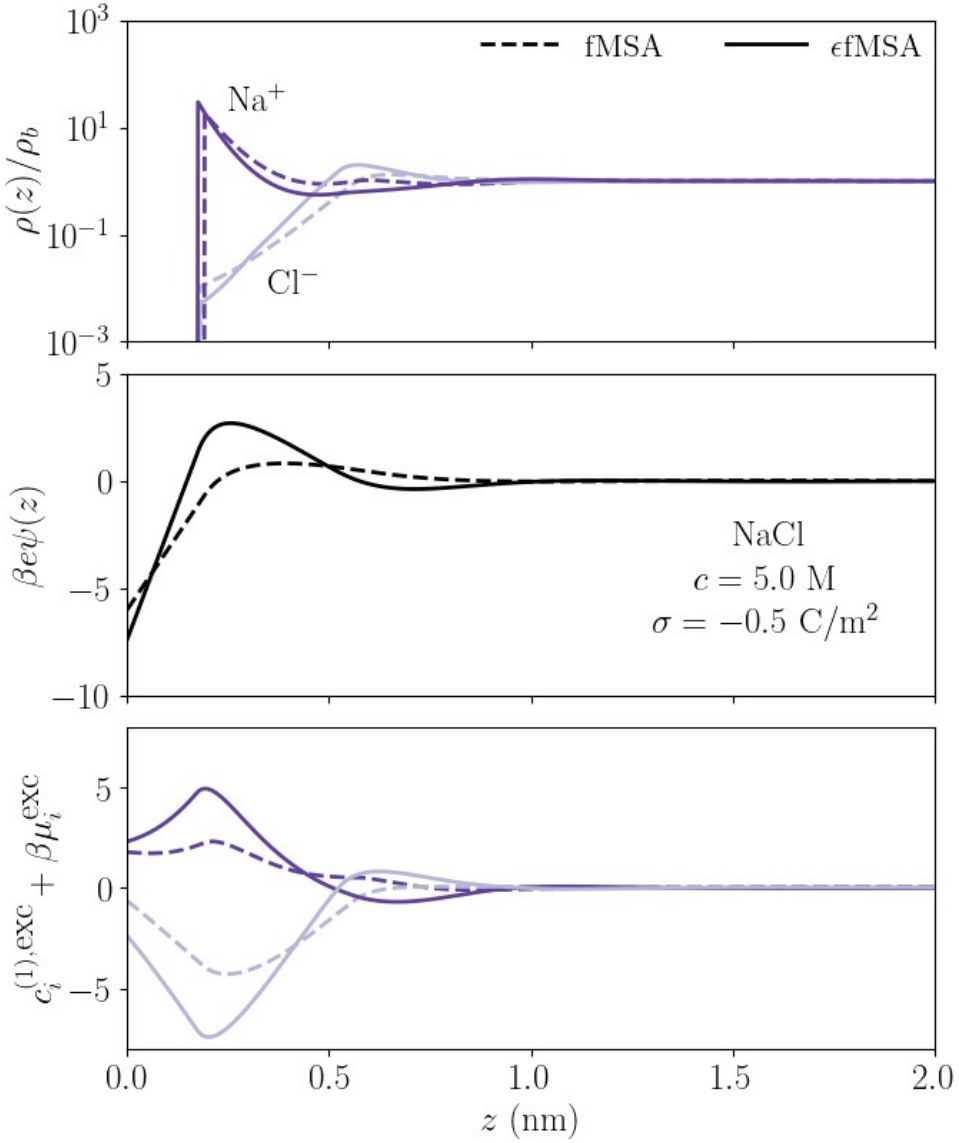
fMSA*: Using a_+ and ϵ_r values, but **without** μ_i^{exc} corrections

ϵfMSA: Using a_+ and ϵ_r values, **with** μ_i^{exc} corrections

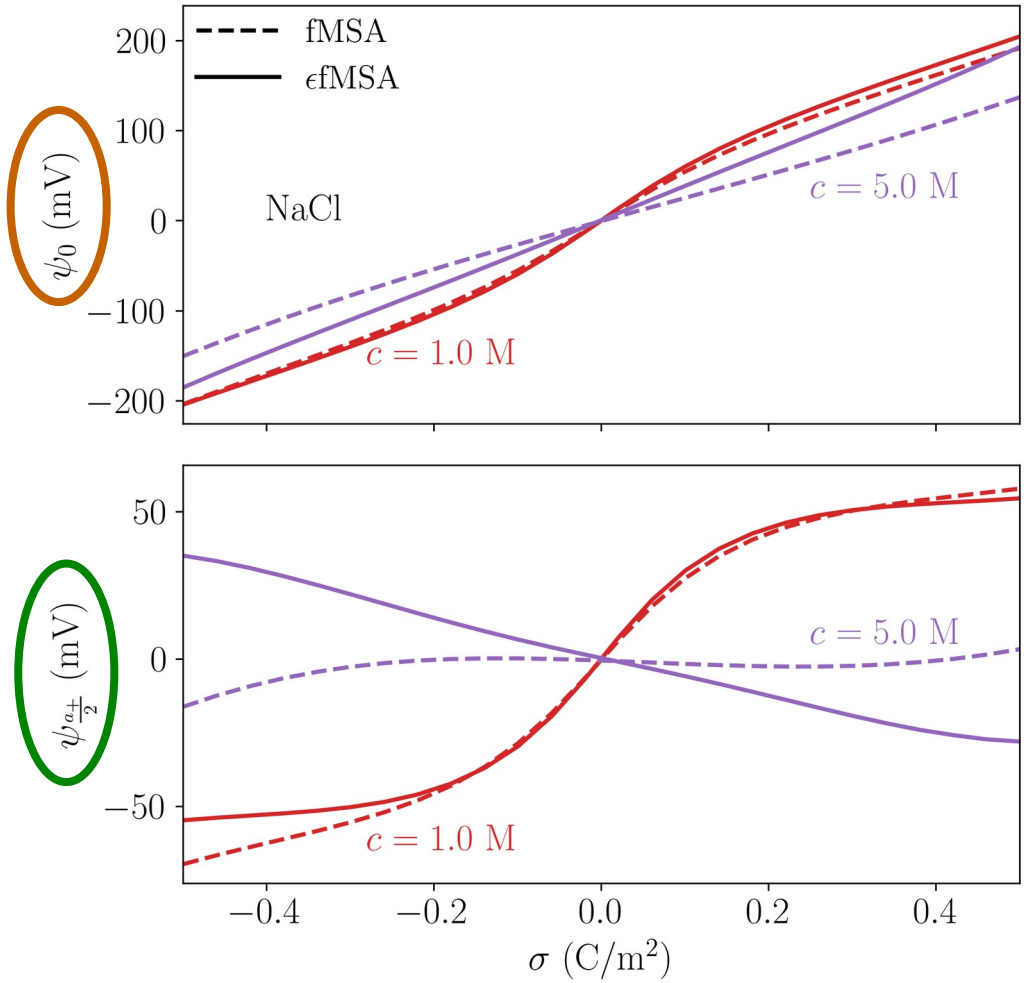
Profiles

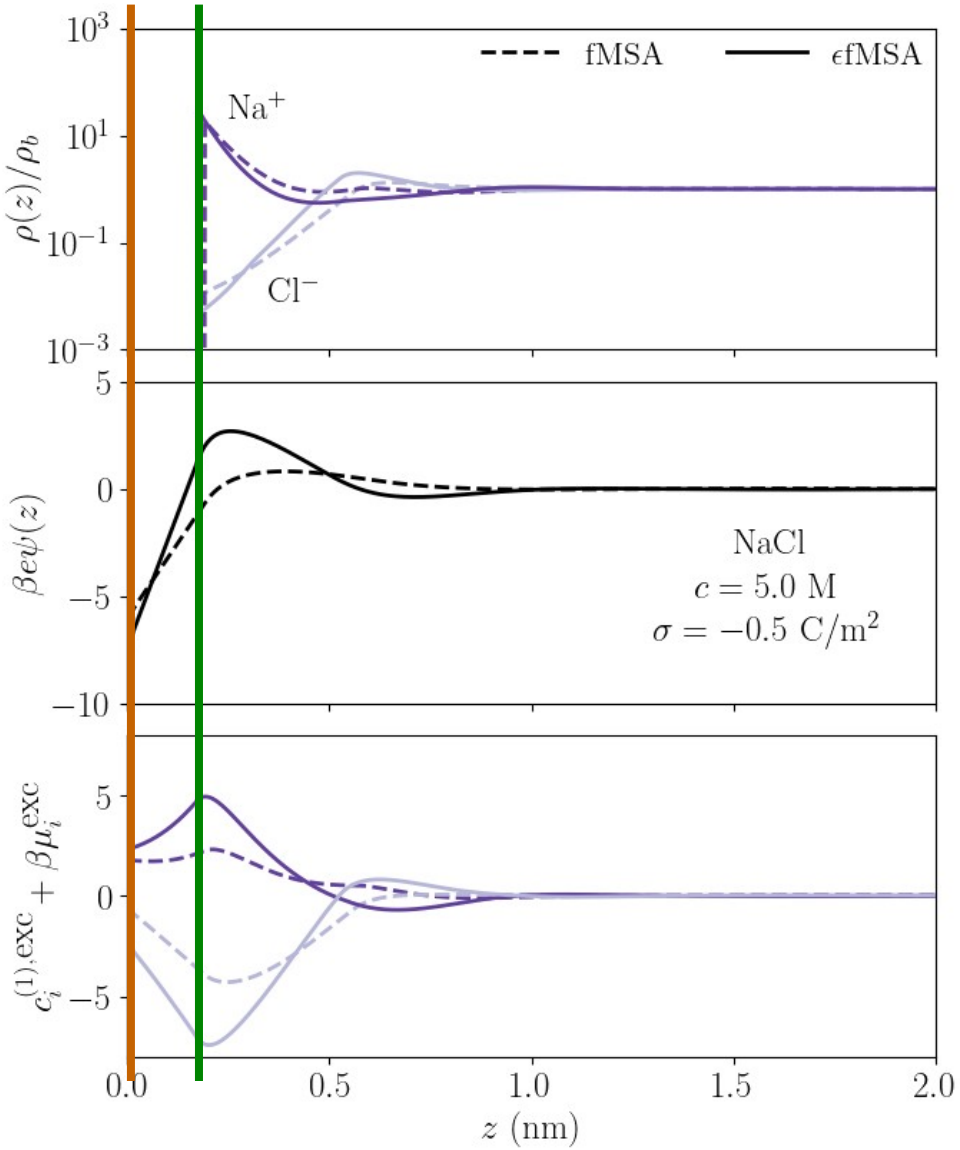
$$\rho_i(\boldsymbol{r}) = \rho_i^{(b)} \exp\Big[-\beta Z_i e\psi(\boldsymbol{r}) + c_i^{(1),exc}(\boldsymbol{r}) + \beta\mu_i^{exc}\Big]$$





Surface Electrostatic Potential





Conclusions

- We present electric permittivity and cation diameter correction to the well-known fMSA theory (εfMSA)
- **"DFT is not just about EOS but also about functional forms"**
- **To be Published:** Soares, E. do A., Vernin, N. S., Santos, M. S. & Tavares, F. W. Real Ionic Solutions in the Functionalized Mean Spherical Approximation: a density functional theory for electrolyte solutions.

- Extensions to 2:1 and 3:1 electrolytes, ion pairing interactions, solvent explicit systems, chain-like electrolytes (ionic liquids).

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Elvis Do Amaral Soares

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CAPES

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PETROBRAS