Dielectric response with short-ranged electrostatics

Possible ways to assess error (maybe)

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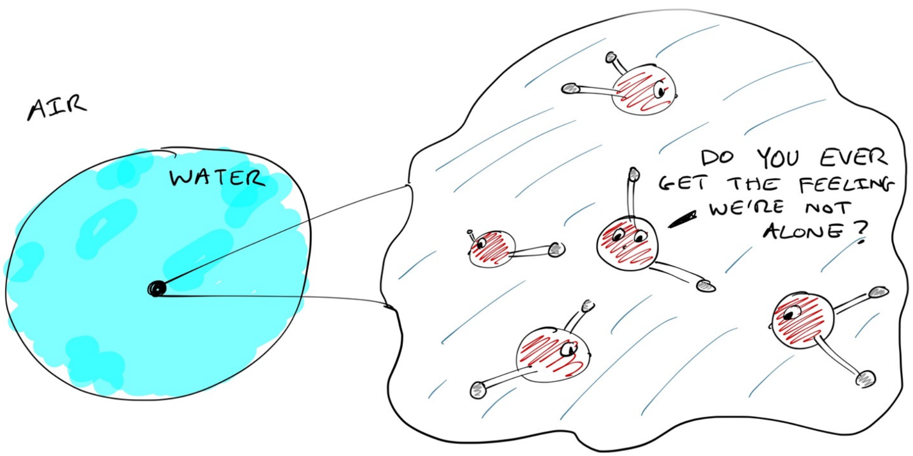
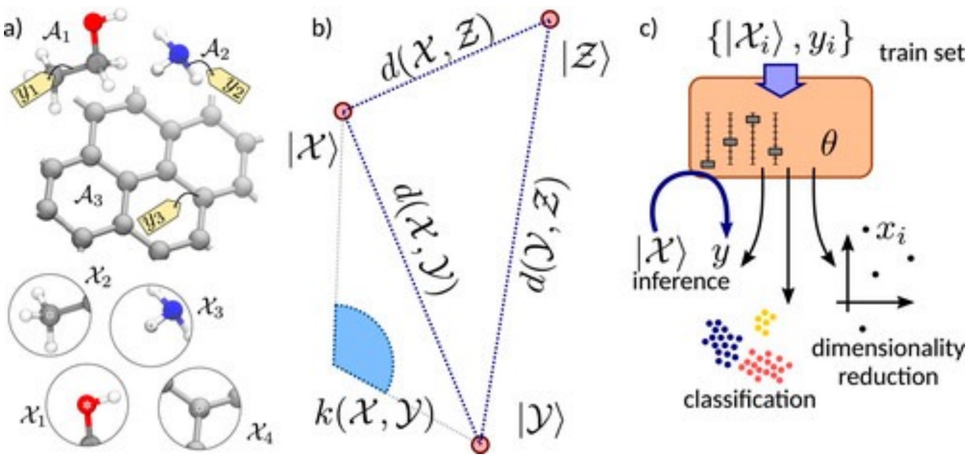
University of Cambridge
CECAM Workshop, June 2022



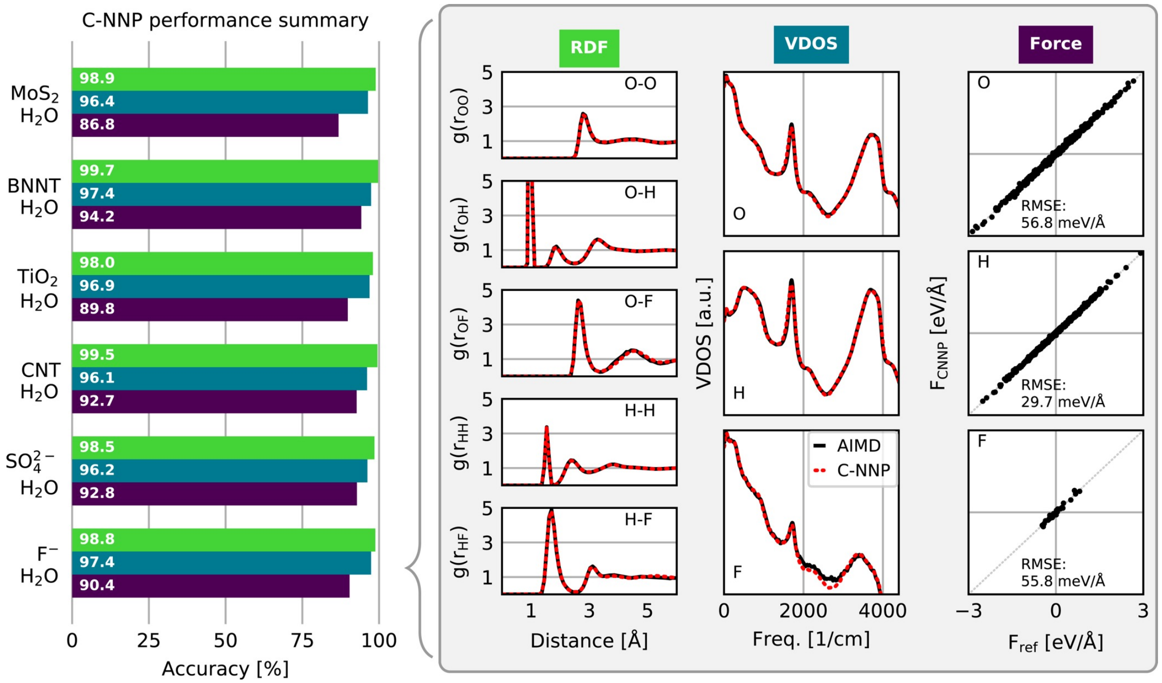
Cox, PNAS **117**, 19746 (2020)

By and large, short-ranged potentials are uncannily good



Ceriotti, JCP **150**, 150901 (2019)

By and large, short-ranged potentials are uncannily good



Schran *et al.*, PNAS **118**, e2110077118 (2021)

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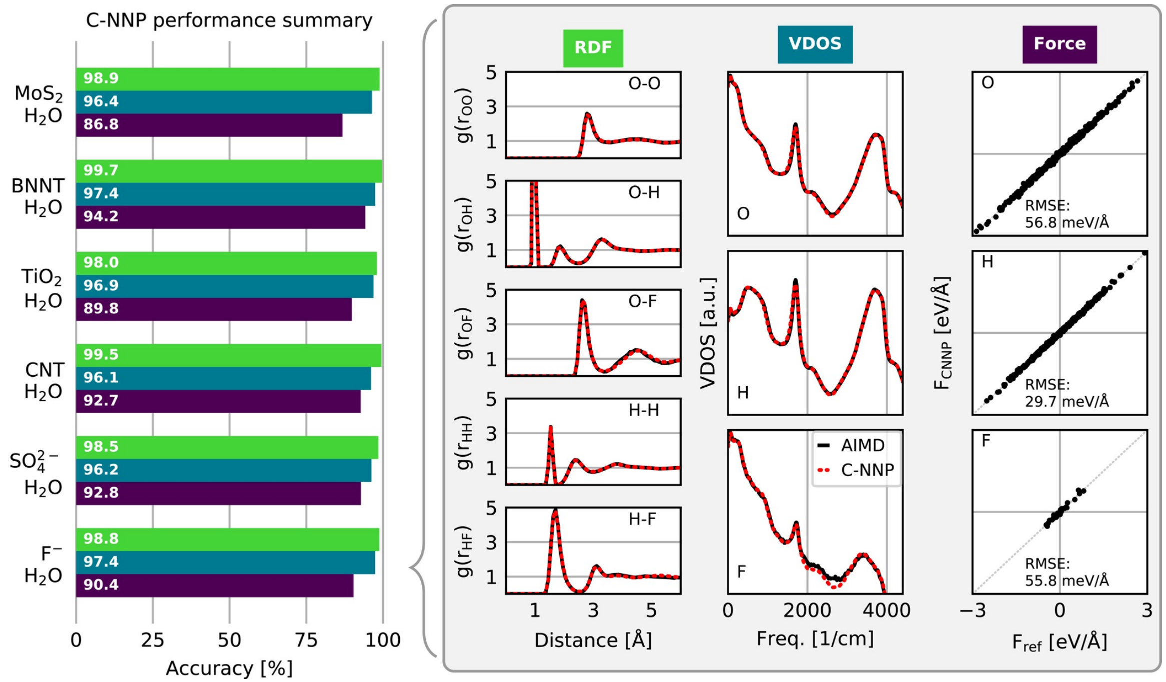


Can we use liquid state theory to understand the impact of treating systems with long-ranged interactions in a short-ranged fashion?

Schran *et al.*, PNAS **118**, e2110077118 (2021)

Some initial results

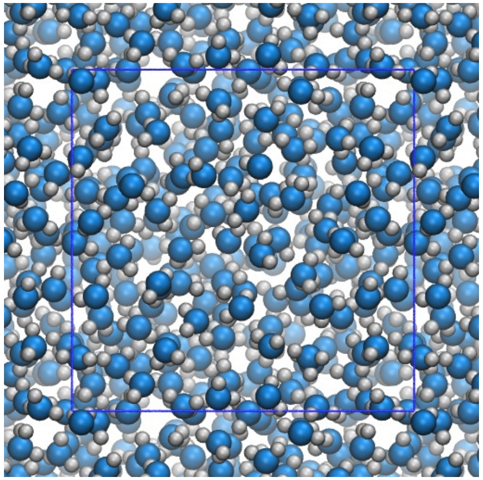
Take SPC/E water, and replace Coulomb interaction with something short-ranged:

$$1/r \to \mathrm{erfc}(\kappa r)/r$$

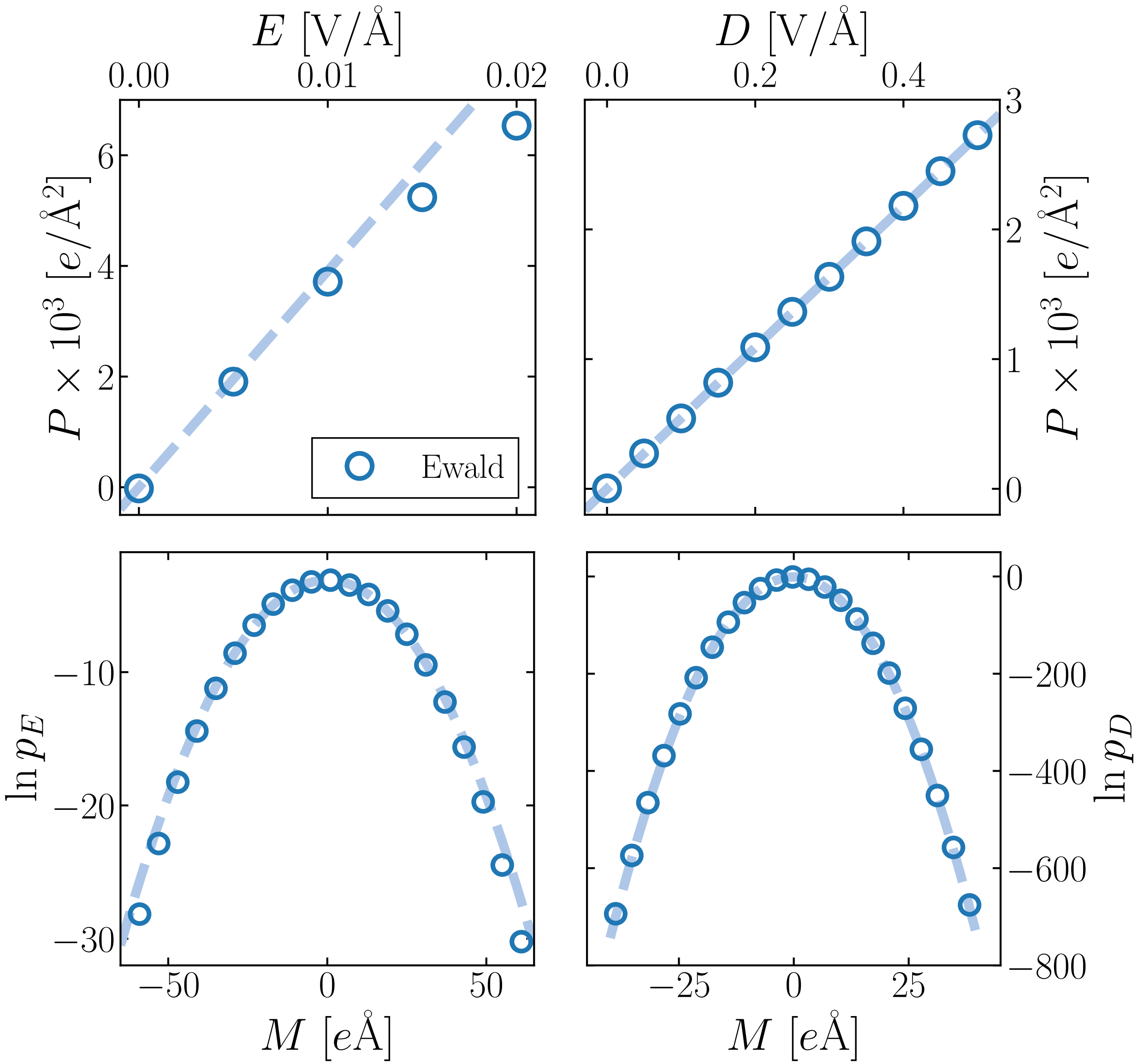
“Strong coupling approximation” (SCA)

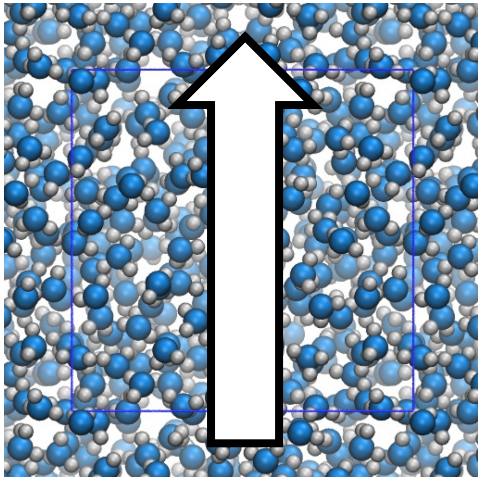
κ^{-1} = 4.5 Å found to recover radial distribution function.

Only consider bulk (no interfaces) for now.



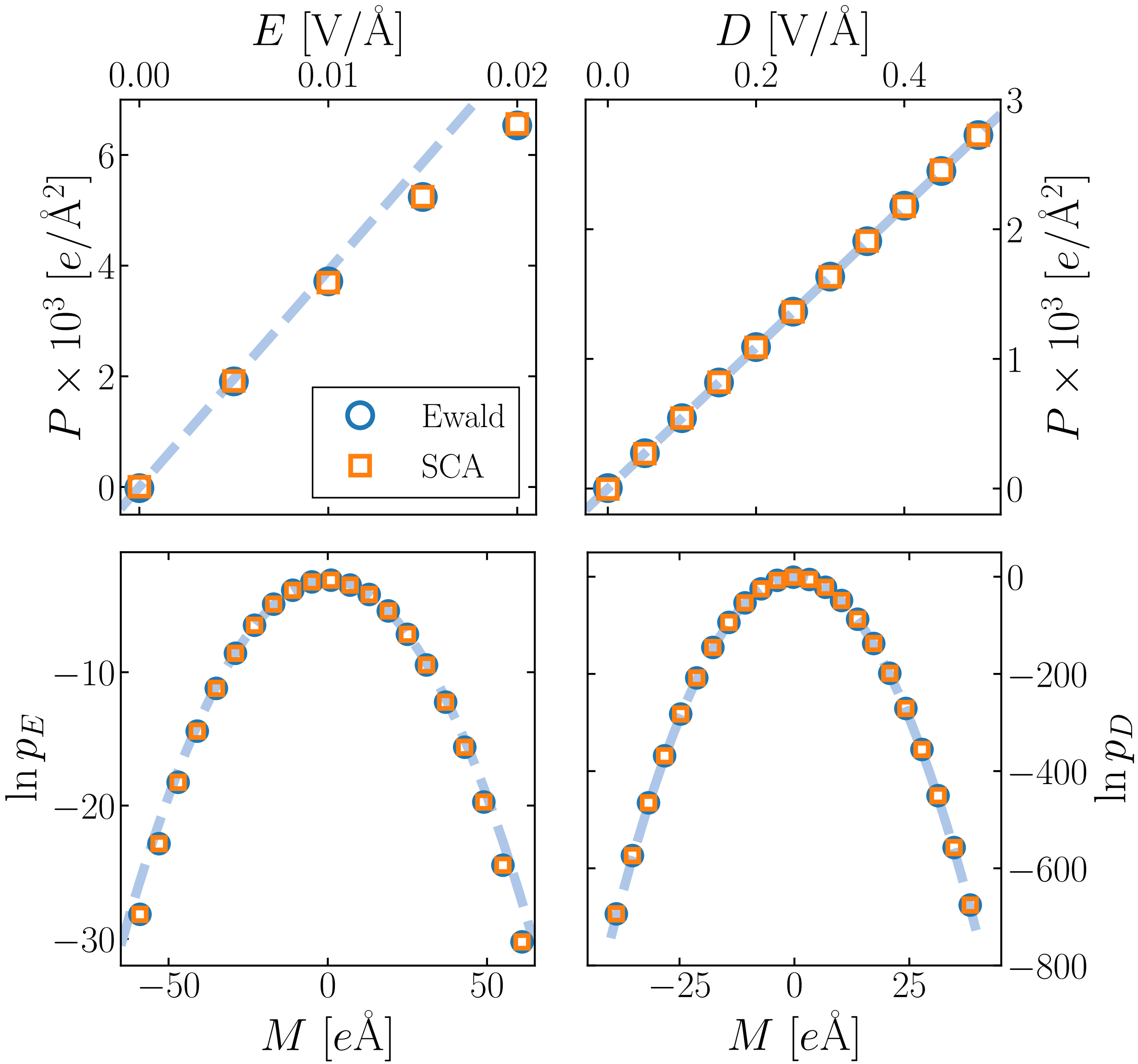
Some initial results

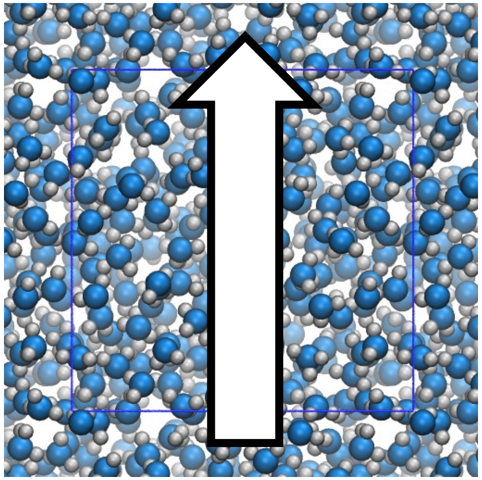




E or D

Some initial results





What about the dielectric constant?

$$h(1,2) = h_S(R) + \underbrace{h_\Delta(R)}_{\text{short-ranged}}(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2) + \underbrace{h_D(R)}_{\text{here be dragons}}[3(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\mathbf{R}}_{12})(\hat{\boldsymbol{\mu}}_2 \cdot \hat{\mathbf{R}}_{12})]$$

Madden & Kivelsen, Adv. Chem. Phys. **56**, 467 (1984)

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Dielectric const. is material property: **independent of system size/shape**

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Dielectric const. is material property: **independent of system size/shape**

Consider an *infinite* system – not what we simulate

$$\frac{(2\epsilon+1)(\epsilon-1)}{9y\epsilon} = 1 + \frac{4\pi\rho}{3}\int_0^\infty \mathrm{d}r\, r^2 h_\Delta(r)$$

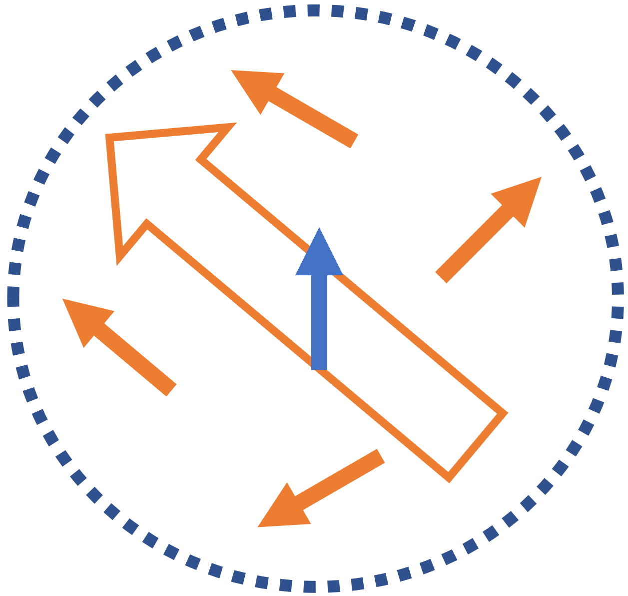
By construction, short-ranged correlations are accurate

Dielectric constant is the same

Madden & Kivelsen, Adv. Chem. Phys. **56**, 467 (1984)

SR correlations

$$G_{\mathrm{K}}(r) = \langle \boldsymbol{\mu}_1 \cdot \mathbf{M}_v(r) \rangle / \mu^2$$



Kirkwood, J. Chem. Phys. **7**, 911 (1939)
Caillol, J. Chem. Phys. **96**, 7039 (1992)

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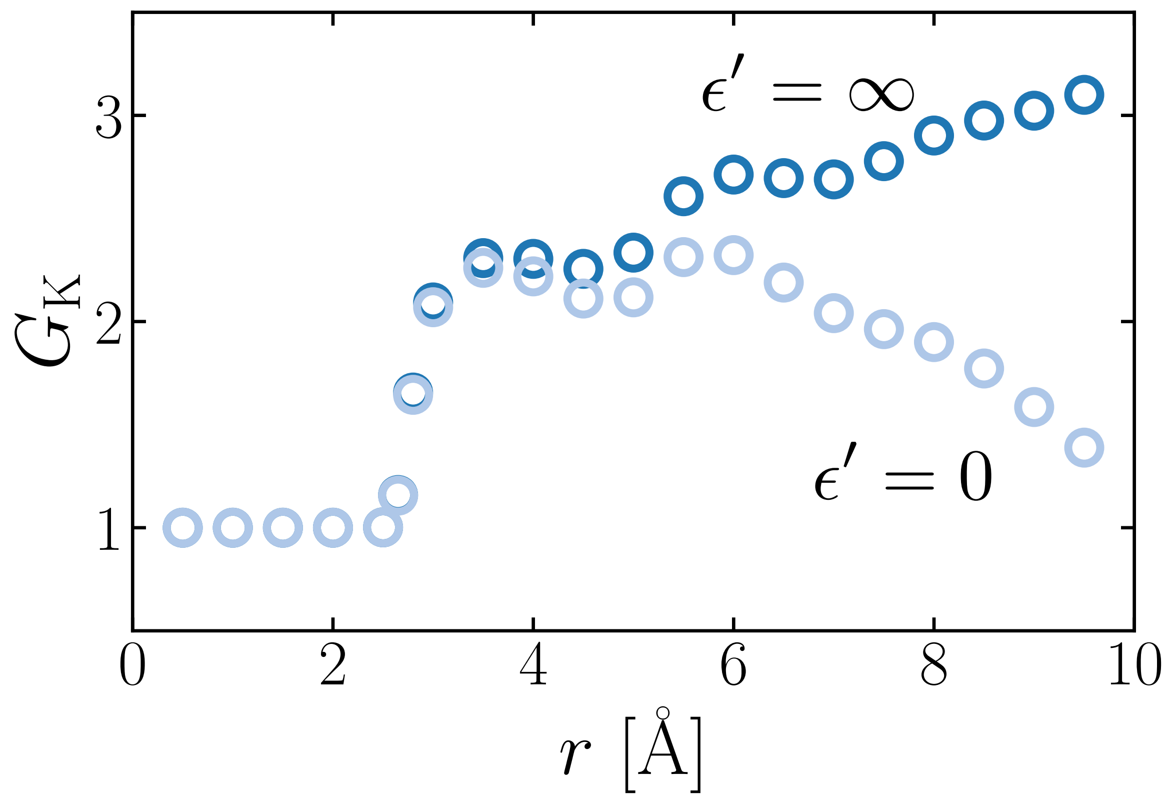

$$h_{\Delta}(r) \sim \frac{1}{3y\rho} \frac{(\epsilon - 1)^2}{\epsilon} \frac{2(\epsilon' - \epsilon)}{\epsilon(2\epsilon' + \epsilon)} \frac{1}{L^3}$$

Caillol, J. Chem. Phys. **96**, 7039 (1992)

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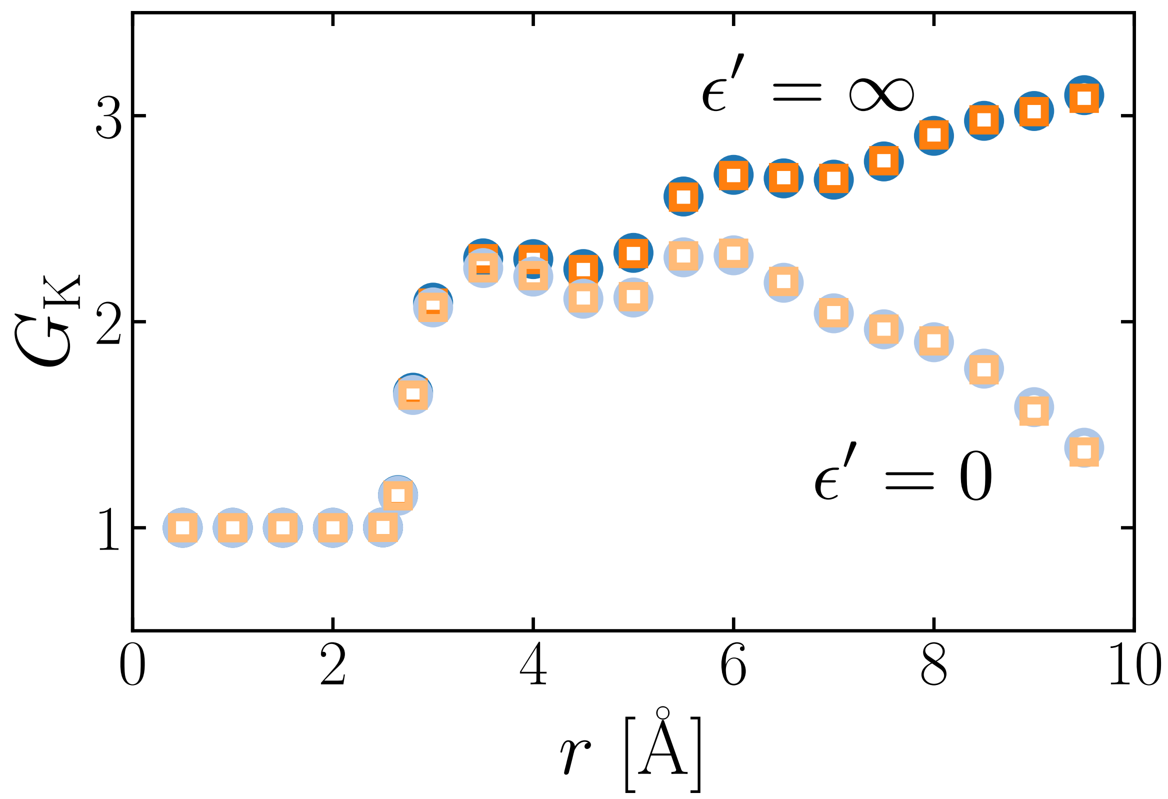

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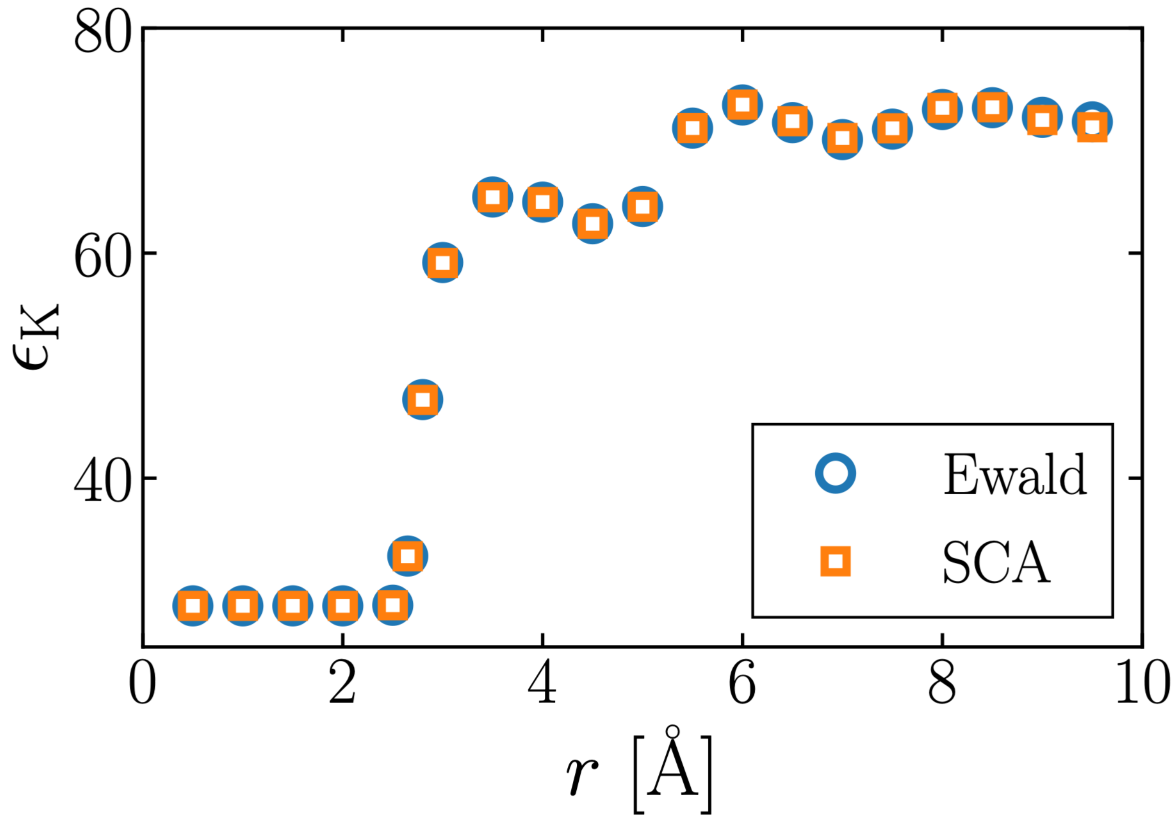
Caillol, J. Chem. Phys. **96**, 7039 (1992)

Confirmation: dielectric constant is unchanged

$$\epsilon = 71.7$$



Zhang, Hutter, Sprik, J. Phys. Chem. Lett. **7**, 2696 (2016)

Madden & Kivelson, Adv. Chem. Phys. **56**, 467 (1984)

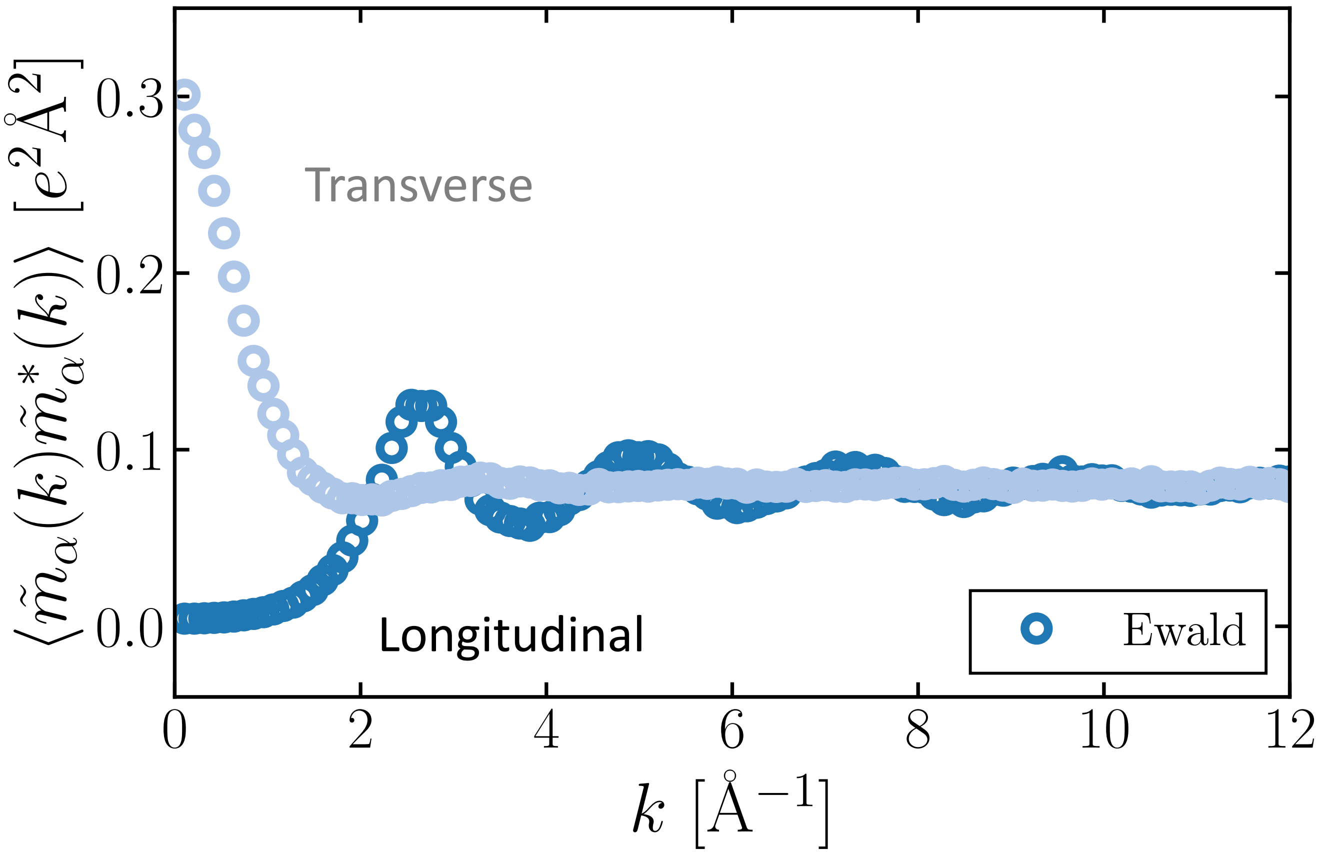
All is well with bulk?

"Transverse"

$$\lim_{\mathbf{k}\to\mathbf{0}} 4\pi\chi^{(0)}_{xx}(\mathbf{k}) = \epsilon - 1$$

"Longitudinal"

$$\lim_{\mathbf{k}\to\mathbf{0}} 4\pi\chi^{(0)}_{zz}(\mathbf{k}) = \frac{\epsilon - 1}{\epsilon}$$



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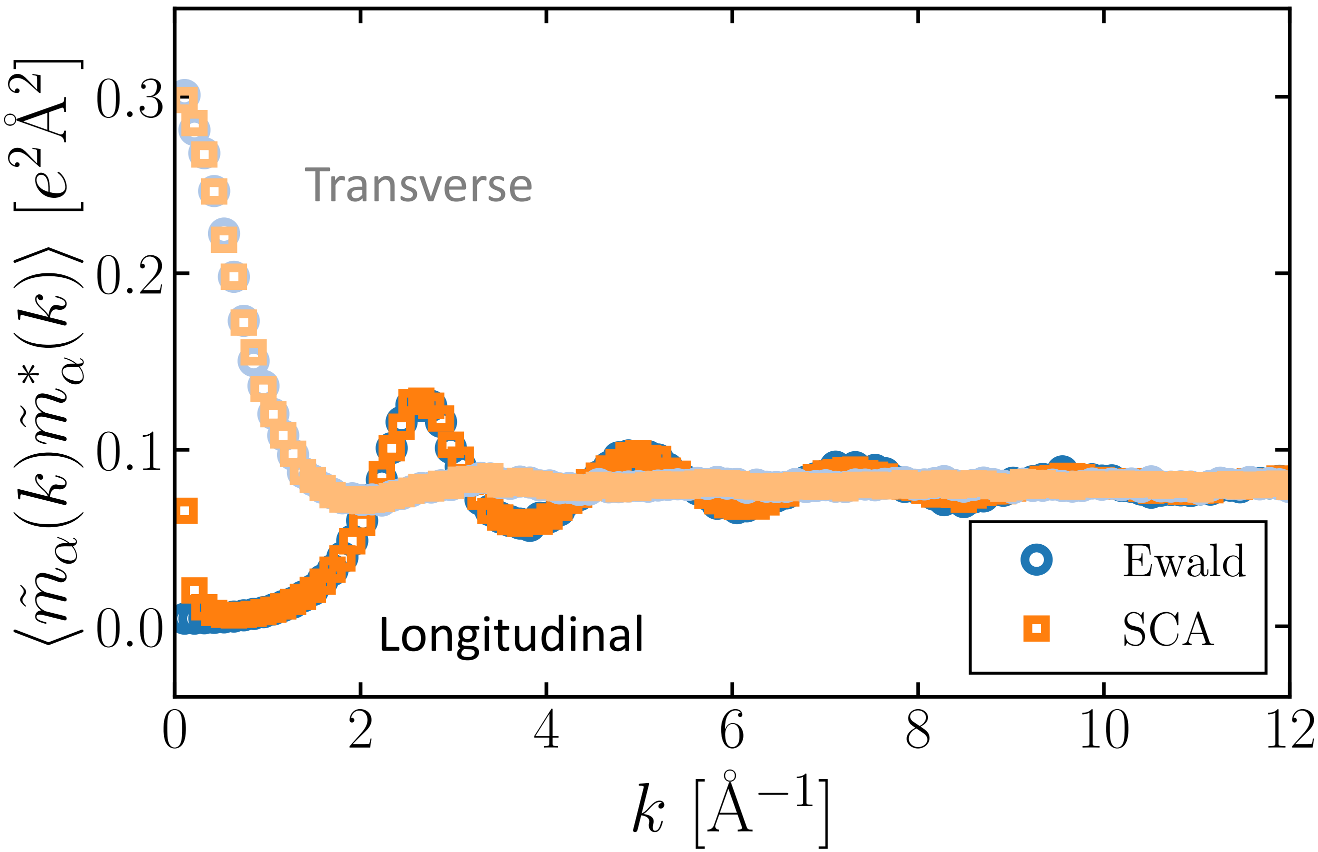

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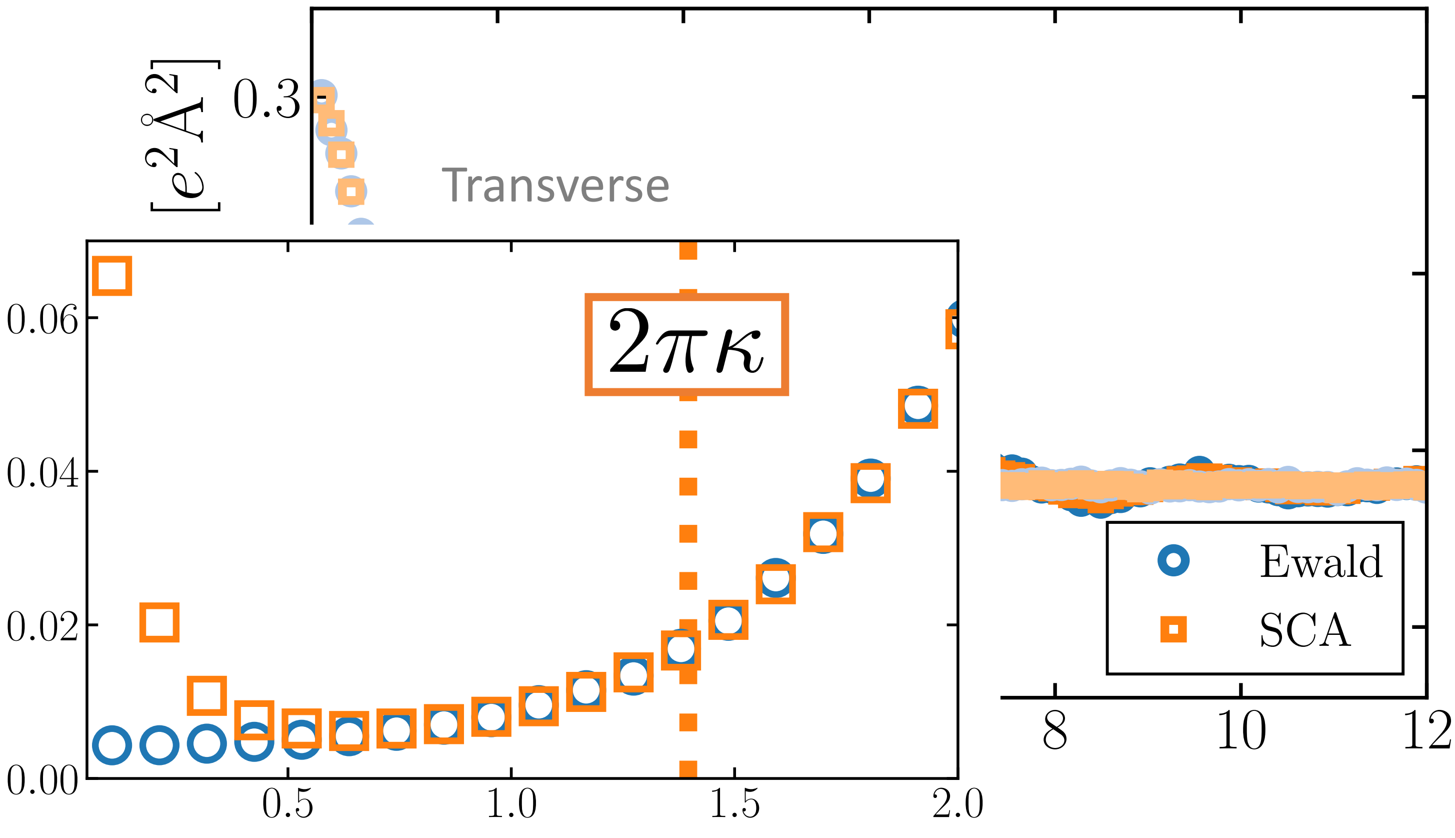


Consider infinite system again (LR electrostatics)

$$\mathbf{E}(\mathbf{k}) = \mathbf{E}^{(0)}(\mathbf{k}) - 4\pi\hat{\mathbf{k}}\hat{\mathbf{k}} \cdot \mathbf{P}(\mathbf{k})$$

$$4\pi\mathbf{P}(\mathbf{k}) = \boldsymbol{\chi}(\mathbf{k}) \cdot \mathbf{E}(\mathbf{k}) \quad 4\pi\mathbf{P}(\mathbf{k}) = \boldsymbol{\chi}^{(0)}(\mathbf{k}) \cdot \mathbf{E}^{(0)}(\mathbf{k})$$

$$\boldsymbol{\chi}^{(0)}(\mathbf{k}) = \underline{\left[\mathbf{1} + 4\pi\hat{\mathbf{k}}\hat{\mathbf{k}} \cdot \boldsymbol{\chi}(\mathbf{k})\right]^{-1}} \cdot \underline{\boldsymbol{\chi}(\mathbf{k})}$$

Exploit phenomenology: $\lim_{\mathbf{k}\to\mathbf{0}} \boldsymbol{\epsilon}(\mathbf{k}) = \epsilon\mathbf{1}$

$$\lim_{\mathbf{k}\to\mathbf{0}} 4\pi\chi_{xx}^{(0)}(\mathbf{k}) = \lim_{\mathbf{k}\to\mathbf{0}} 4\pi\chi_{yy}^{(0)}(\mathbf{k}) = \epsilon - 1,$$

$$\lim_{\mathbf{k}\to\mathbf{0}} 4\pi\chi_{zz}^{(0)}(\mathbf{k}) = \frac{\epsilon - 1}{\epsilon}$$

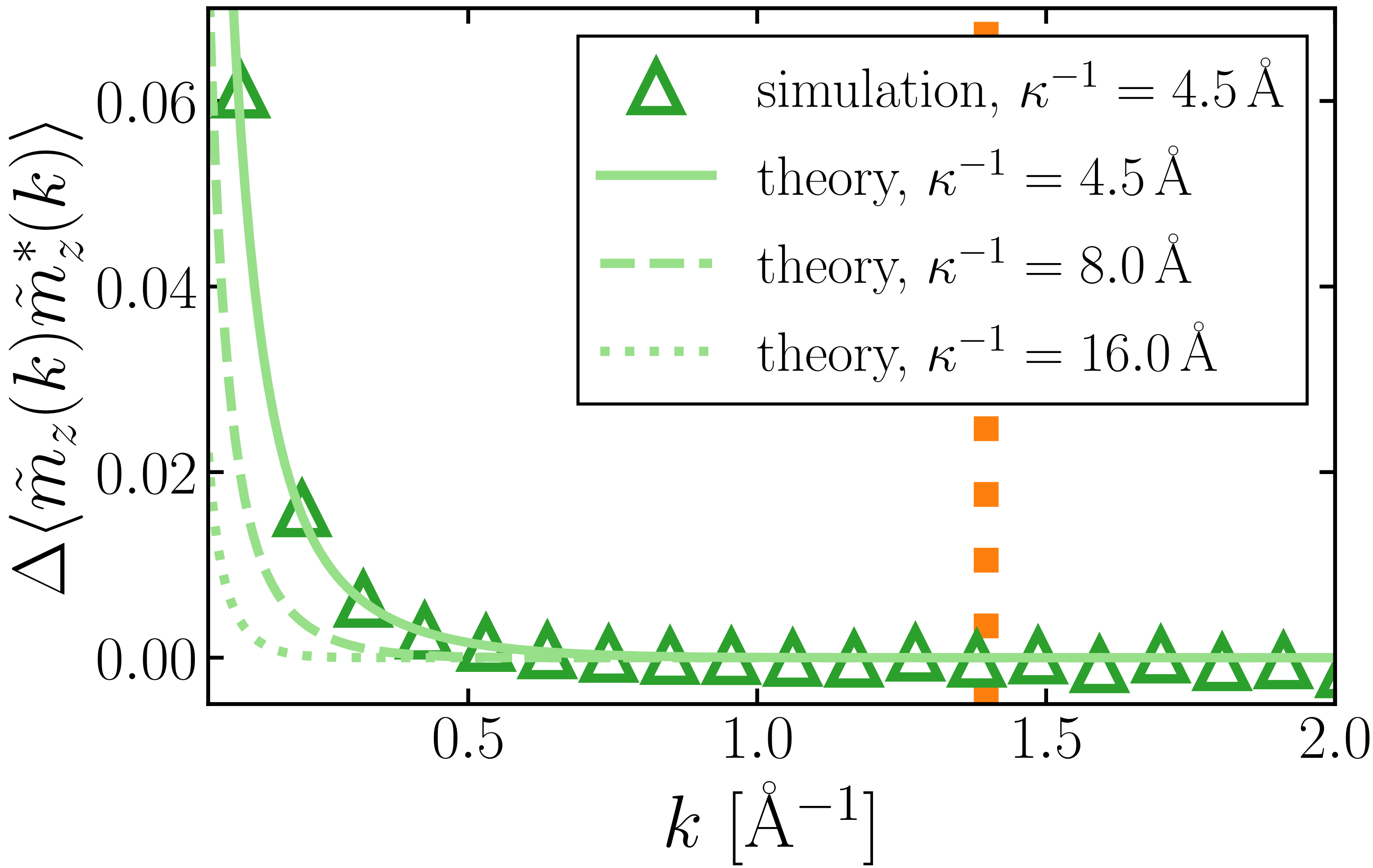
Consider infinite system again (SR electrostatics)

$$\boldsymbol{\chi}^{(0,\mathrm{SCA})}(\mathbf{k}) = \Big[\mathbf{1} + 4\pi[1 - \exp(-k^2/4\kappa^2)]\hat{\mathbf{k}}\hat{\mathbf{k}} \cdot \boldsymbol{\chi}(\mathbf{k})\Big]^{-1} \cdot \boldsymbol{\chi}(\mathbf{k})$$

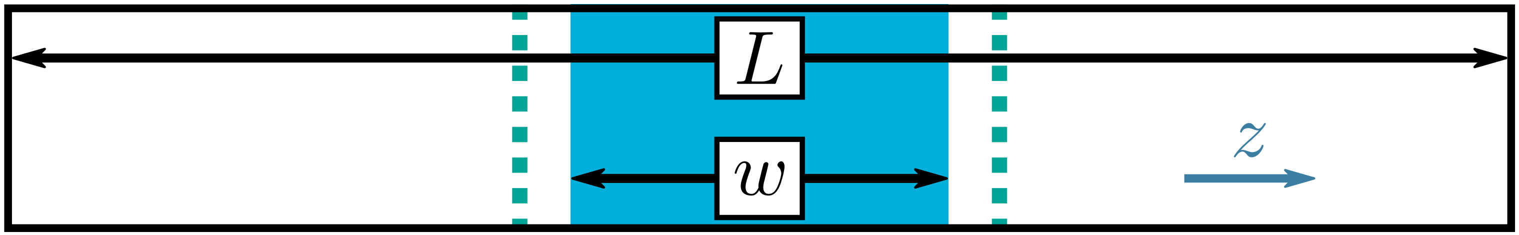
Assume weak k-dependence at low k: $4\pi\boldsymbol{\chi}(\mathbf{k}) \approx (\epsilon - 1)\mathbf{1}$

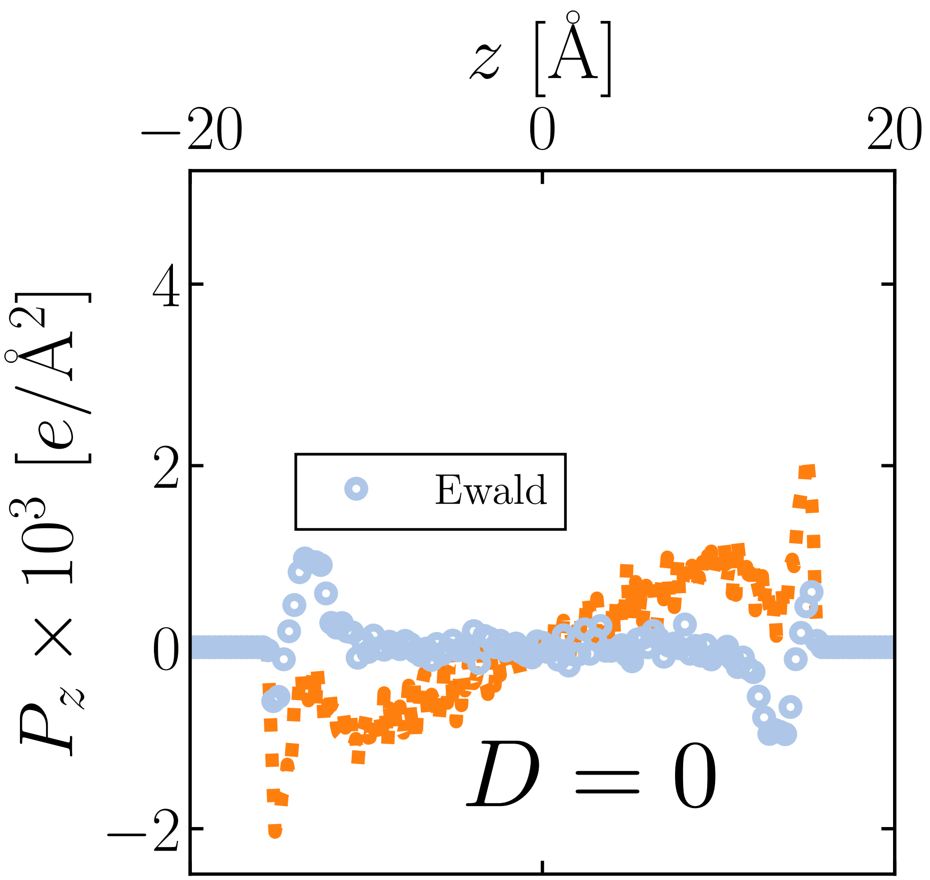
$$\begin{aligned} 4\pi\Delta\chi_{zz}(\mathbf{k}) &= 4\pi\left[\chi_{zz}^{(0,\mathrm{SCA})}(k) - \chi_{zz}^{(0)}(k)\right] \\ &= \frac{(\epsilon-1)^2}{\epsilon}\left[\epsilon\,\mathrm{e}^{k^2/4\kappa^2} - (\epsilon - 1)\right]^{-1} \end{aligned}$$

Comparison b/t theory and simulation



Interfaces





Local molecular field theory

Full system: $$U(\mathbf{r}^N) = \sum_{\langle i,j \rangle} u_0(r_{ij}) + U_1(\mathbf{r}^N)$$

Singlet density:

$$\rho^{(1)}(\mathbf{r})$$

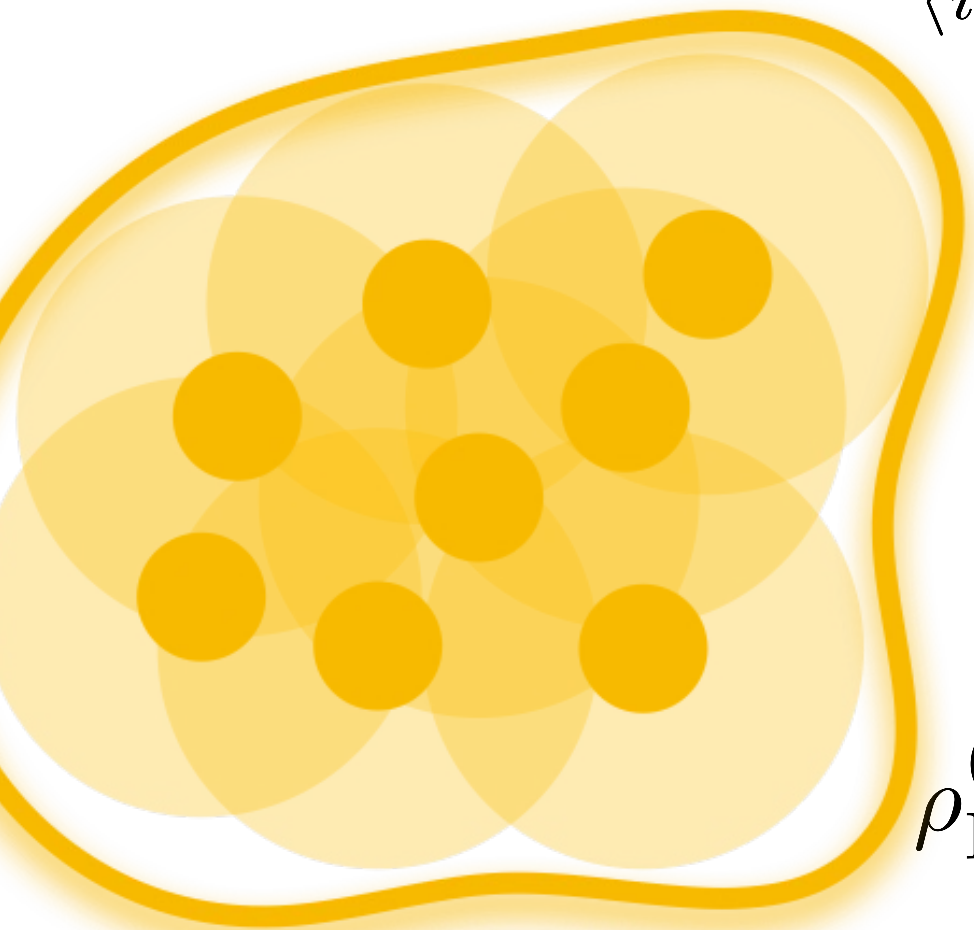
Conditional singlet density:

$$\rho^{(1)}(\mathbf{r}|\mathbf{r}') = \frac{\rho^{(2)}(\mathbf{r},\mathbf{r}')}{\rho^{(1)}(\mathbf{r})}$$

See e.g., Rodgers & Weeks, J. Phys. Condens. Matter **20**, 494206 (2008)

Local molecular field theory

Mimic system: $$U_{\mathrm{R}}(\mathbf{r}^N) = \sum_{\langle i,j \rangle} u_0(r_{ij}) + \sum_i \phi_{\mathrm{R}}(\mathbf{r}_i)$$



Singlet density:

$$\rho_{\mathrm{R}}^{(1)}(\mathbf{r}) = \rho^{(1)}(\mathbf{r})$$

Conditional singlet density:

$$\rho_{\mathrm{R}}^{(1)}(\mathbf{r}|\mathbf{r}') = \rho^{(1)}(\mathbf{r}|\mathbf{r}')$$

See e.g., Rodgers & Weeks, J. Phys. Condens. Matter **20**, 494206 (2008)

LMFT is *not* a simple mean field theory

$$w = u_0 + u_1$$

Range separation

YBG hierarchy

$$-k_{\mathrm{B}}T\nabla \ln \rho^{(1)}(\mathbf{r}) = \nabla\phi(\mathbf{r}) + \int d\mathbf{r}'\, \rho(\mathbf{r}'|\mathbf{r})\nabla w(|\mathbf{r}-\mathbf{r}'|)$$

$$-k_{\mathrm{B}}T\nabla \ln \rho_{\mathrm{R}}^{(1)}(\mathbf{r};\phi_{\mathrm{R}}) = \nabla\phi_{\mathrm{R}}(\mathbf{r}) + \int d\mathbf{r}'\, \rho(\mathbf{r}'|\mathbf{r};\phi_{\mathrm{R}})\nabla u_0(|\mathbf{r}-\mathbf{r}'|)$$

Take the difference

$$\nabla\phi_{\mathrm{R}}(\mathbf{r}) = \nabla\phi(\mathbf{r}) + \int d\mathbf{r}'\, \rho_{\mathrm{R}}(\mathbf{r}';\phi_{\mathrm{R}})\nabla u_1(|\mathbf{r}-\mathbf{r}'|)$$
$$+ \int d\mathbf{r}'\, \left[\rho(\mathbf{r}'|\mathbf{r};\phi) - \rho_{\mathrm{R}}(\mathbf{r}'|\mathbf{r};\phi_{\mathrm{R}})\right]\nabla u_0(|\mathbf{r}-\mathbf{r}'|) + \int d\mathbf{r}'\, \left[\rho(\mathbf{r}'|\mathbf{r};\phi) - \rho(\mathbf{r}';\phi)\right]\nabla u_1(|\mathbf{r}-\mathbf{r}'|)$$

Integrate

$$\phi_{\mathrm{R}}(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}'\, \rho_{\mathrm{R}}(\mathbf{r}';\phi_{\mathrm{R}})u_1(|\mathbf{r}-\mathbf{r}'|) + C$$

LMFT for electrostatics

$$1/r \equiv \underbrace{\mathrm{erfc}(\kappa r)/r}_{v_0(r)} + \underbrace{\mathrm{erf}(\kappa r)/r}_{v_1(r)}$$

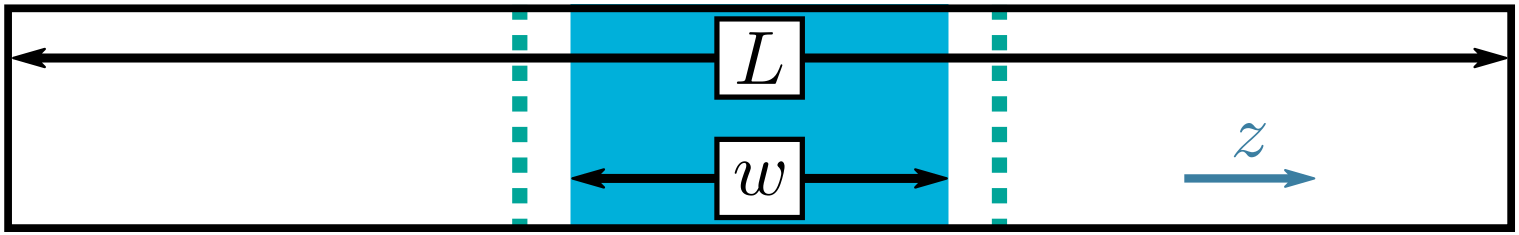
Ewald-like separation

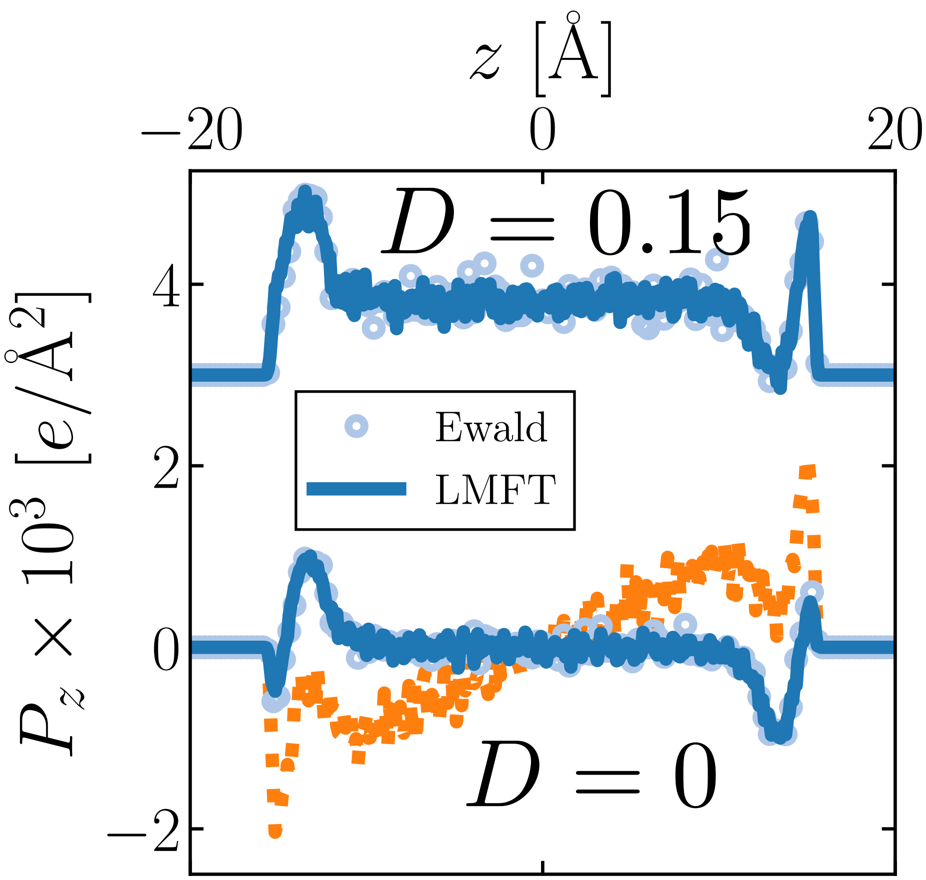
Splitting chosen on physical grounds, rather than efficiency

$$\mathcal{V}_{\mathrm{R}}(\mathbf{r}) = \mathcal{V}(\mathbf{r}) + \int \mathrm{d}\mathbf{r}' \underbrace{n_{\mathrm{R}}(\mathbf{r}')}_{\text{charge density in mimic system}} v_1(|\mathbf{r} - \mathbf{r}'|)$$

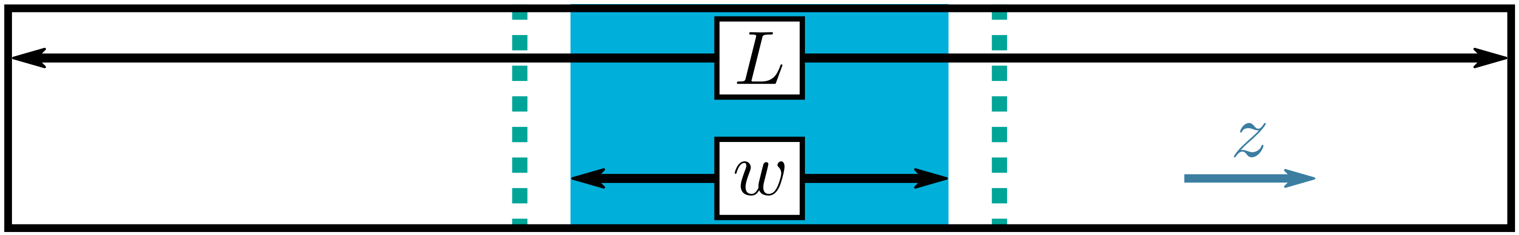
“Strong coupling approximation” (SCA) ignores second term

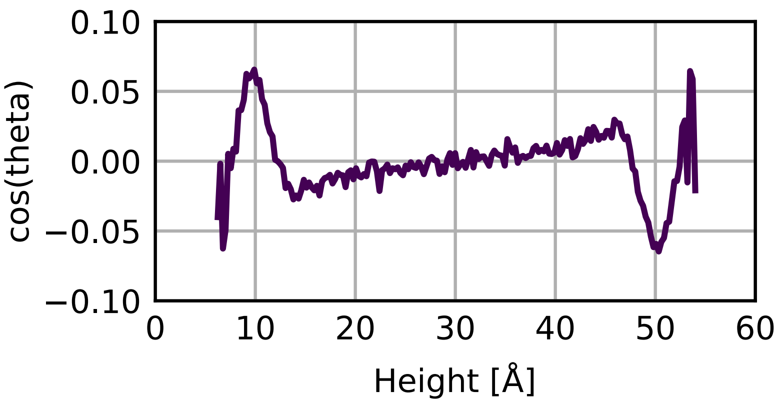
Interfaces – response



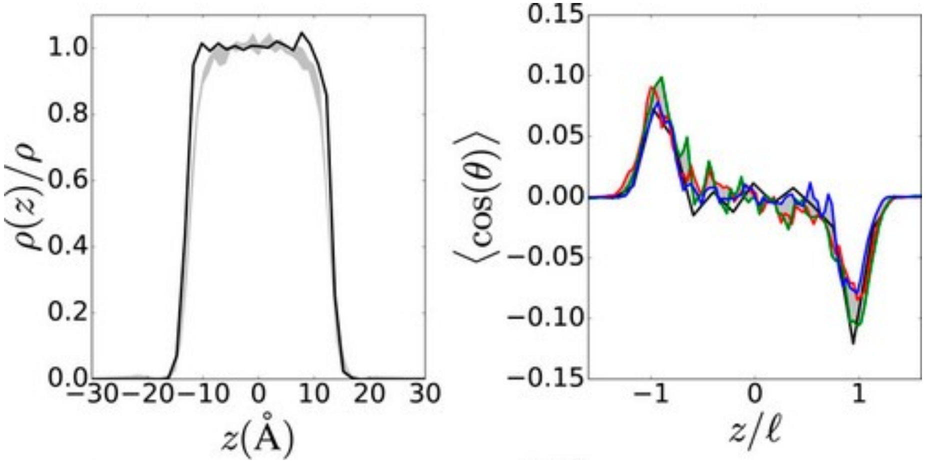


Relevance for MLPs



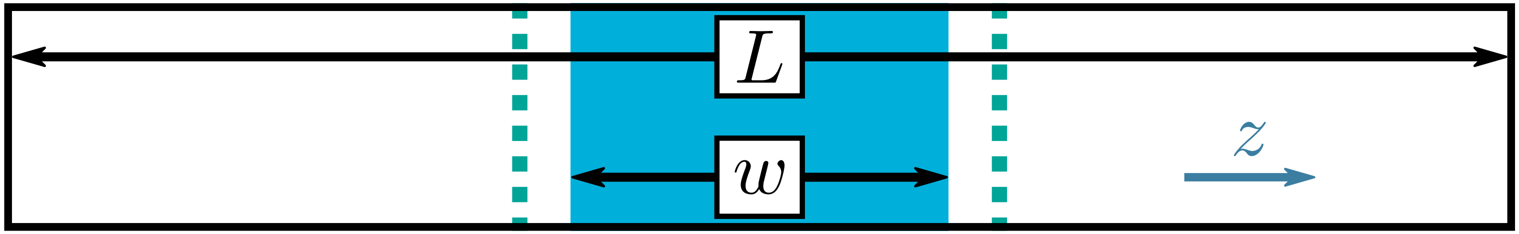


From Christoph Schran

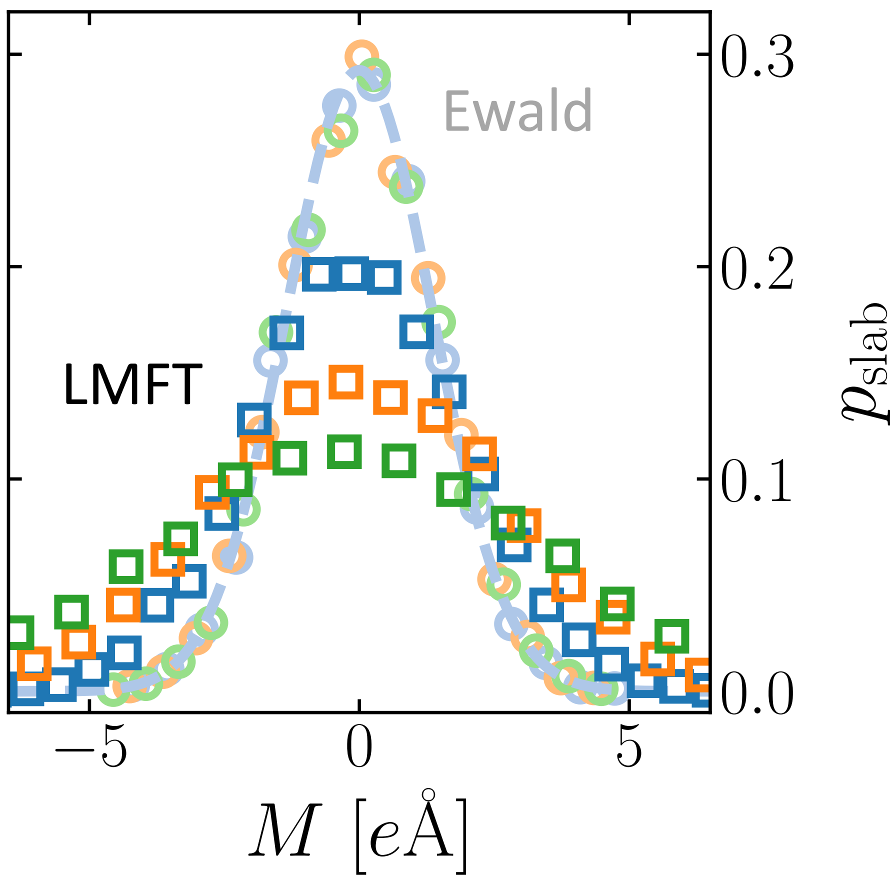


Niblett *et al.*, J. Chem. Phys. **155**, 164101 (2021)

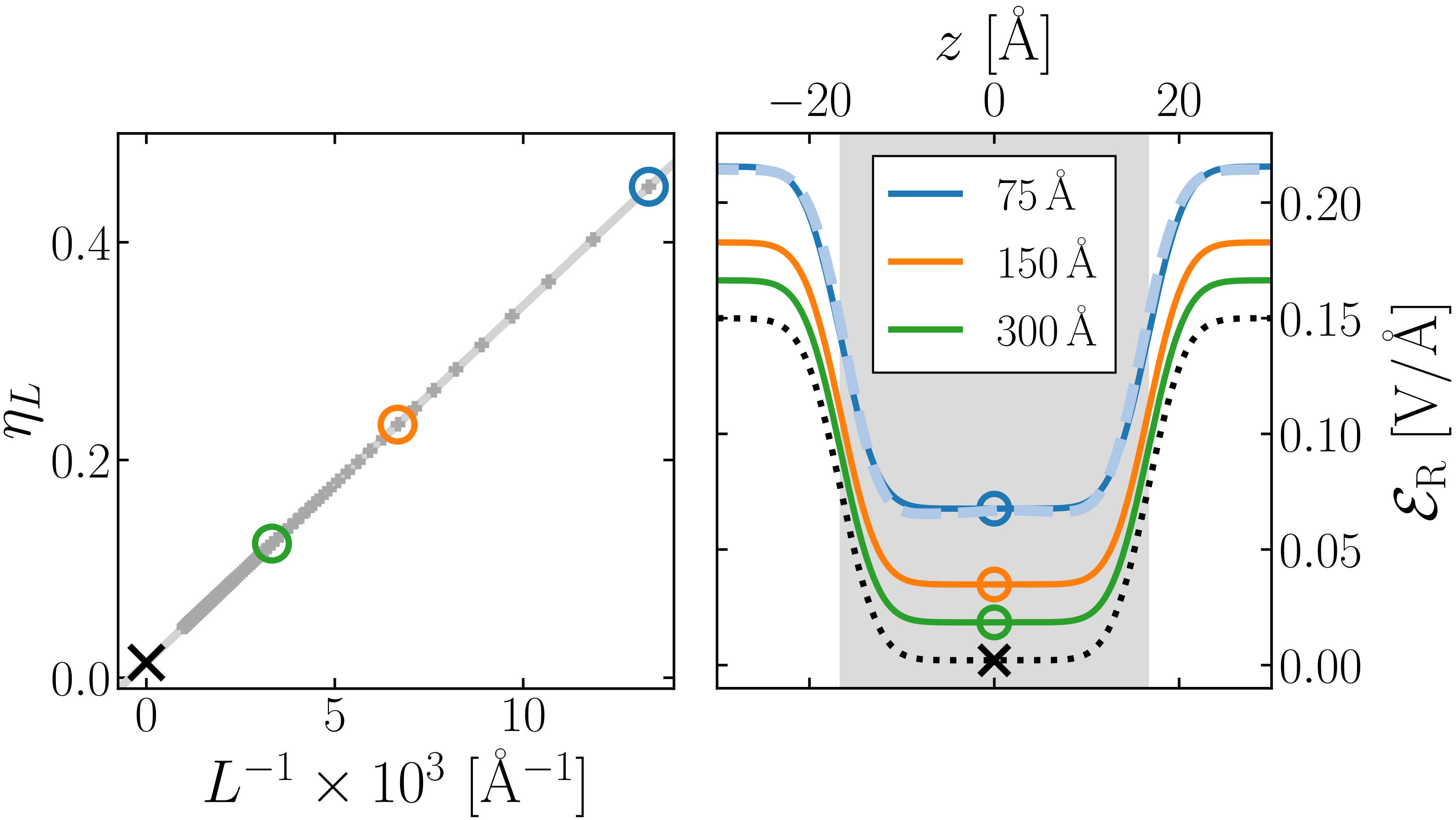
Interfaces – fluctuations



L = 75 Å
L = 150 Å
L = 300 Å

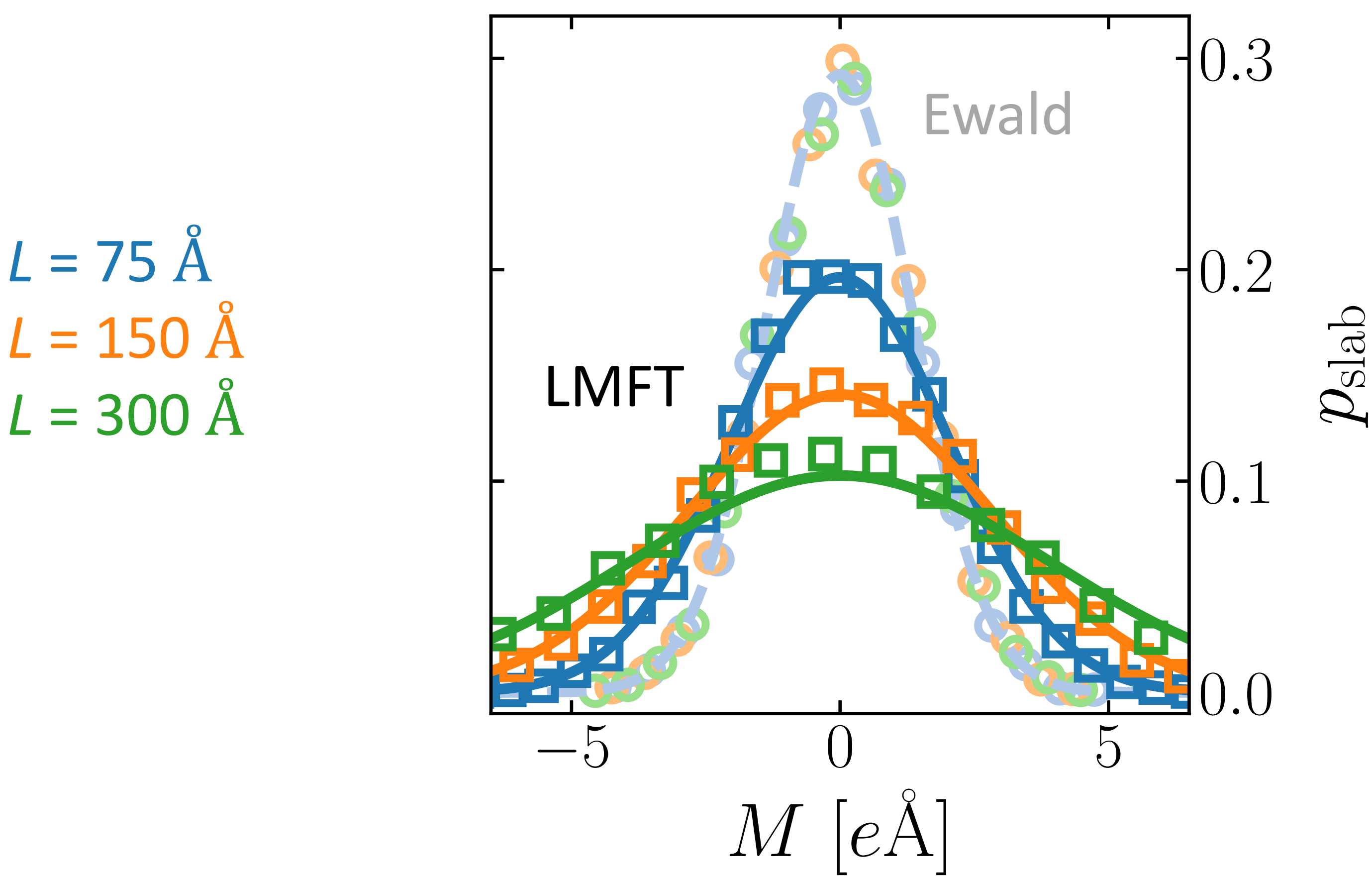


Interfaces – LMFT + DCT predicts observed behavior



Interfaces – LMFT + DCT predicts observed behavior

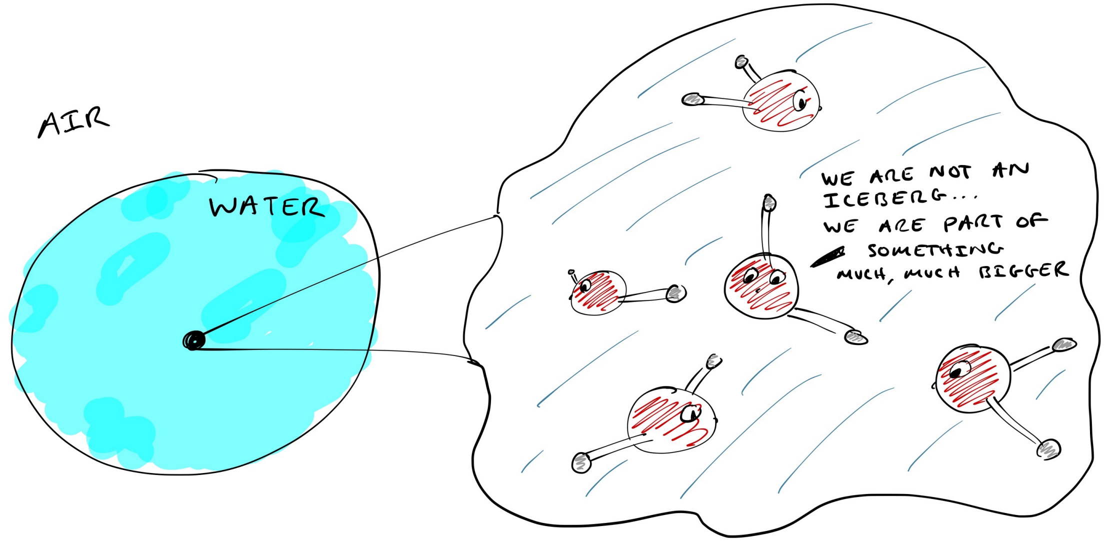
$$\lim_{L\to\infty} 4\pi\chi^{(0)}_{\mathrm{R},zz} = \epsilon - 1$$



Summary

- **Physical**: It is useful to consider short-ranged systems as having the same dielectric constant.
- **Practical**: Short-ranged potentials are much better for dielectric properties than we would naively expect.
- **Conceptual**: Local molecular field theory provides a useful framework for understanding the properties of short-ranged systems.

Thanks!



Michiel Sprik
Rob Jack
Tom Sayer
Christoph Schran

SJ Cox, PNAS **117**, 19746 (2020)

THE ROYAL SOCIETY

MATERIALS AND MOLECULAR MODELLING HUB