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Classical Density Functional Theory of Electrolyte Solutions

Amalie L. Frischknecht

Sandia National Laboratories

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Electrolytes Near Surfaces

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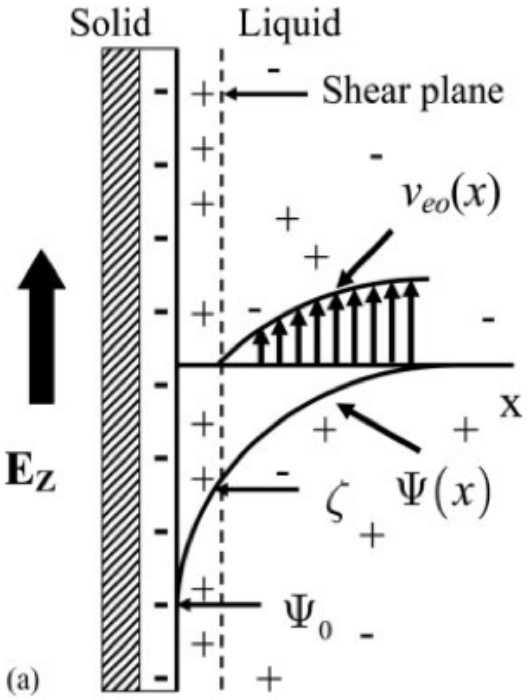
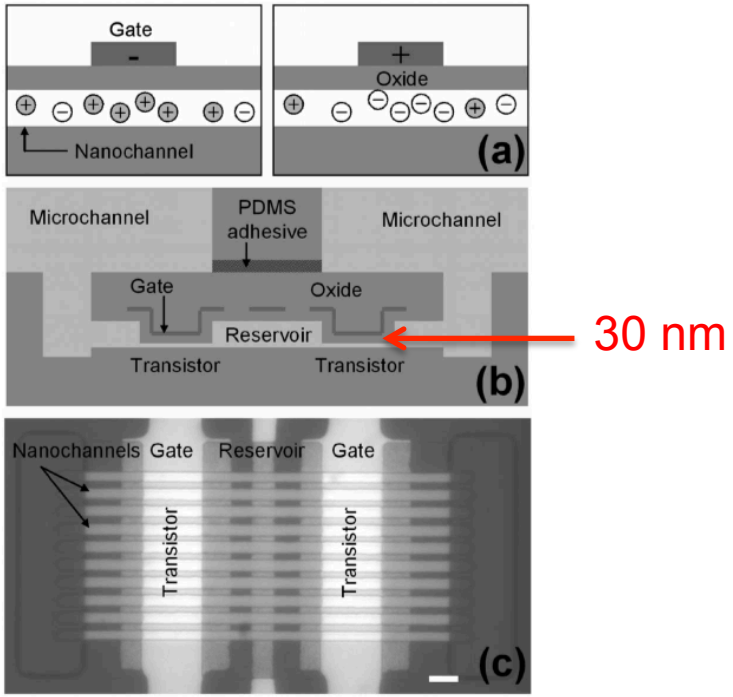
form double layer



details important in nanochannels



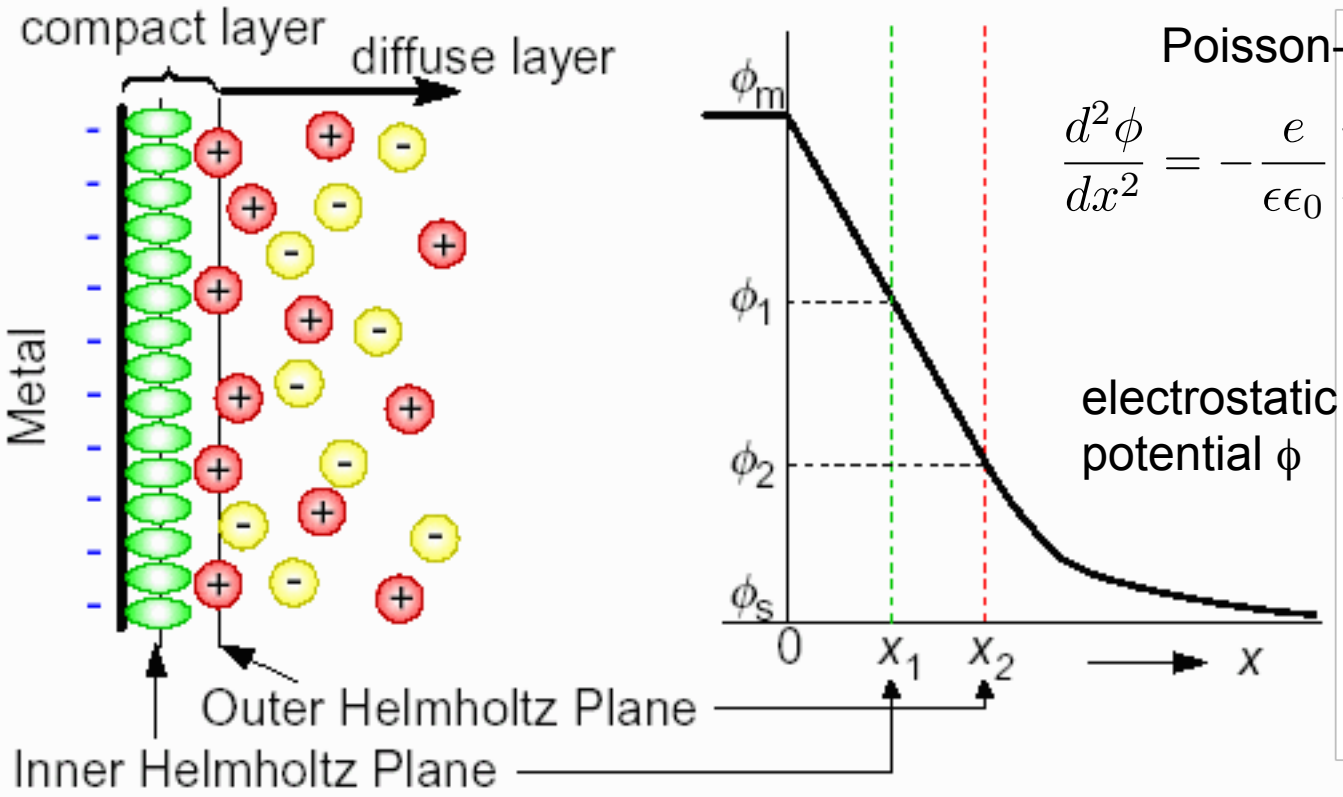
typical Debye lengths from 1-100 nm

Yuan, Z., Garcia, A. L., Lopez, G. P. & Petsev, D. N. *Electrophoresis* **28,** 595–610 (2007).

Karnik, R., Castelino, K. & Majumdar, A. *Appl. Phys. Lett.* **88,** (2006).

Classical Theory

Gouy-Chapman-Stern theory (GCS)



Poisson-Boltzmann eqtn

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon\epsilon_0}\sum_i z_i\rho_i^0 \exp\left(\frac{-z_i e\phi}{kT}\right)$$

electrostatic potential ϕ

$$\phi(z) = \frac{4kT}{e}\tanh^{-1}\left(\tanh\left(\frac{\phi_w e}{4kT}\right)\exp[-\kappa(z-d)]\right) \qquad \kappa = (2\rho_0 e^2/\epsilon kT)^{1/2}$$

size of diffuse layer depends on: potential, concentration, temperature

Physics Missing from GCS Theory

- finite size ions
- ion-ion correlations
- ion-ion interactions
- ion-electrode interactions
  - specific adsorption
- polarization

path forward

build up from simple models

simulations (MC, MD)

advanced theory

classical density functional theory

Outline of the Talk

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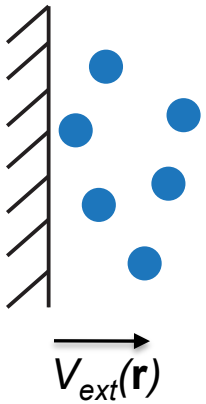
- classical density functional theory for electroytes
- application to charged nanoparticles
  - compare to MD simulations
- extension to steady-state diffusion
- application to flow in nanochannels
  - compare to Poisson-Nernst-Planck (PNP) theory

Classical Density Functional Theory



$$\rho_0(\mathbf{r}) = \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle$$ equilibrium density

- suppose have open system, temp T, volume V, chem potential μ
- grand potential energy:

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int d\mathbf{r}\rho(\mathbf{r})\left[V_{ext}(\mathbf{r}) - \mu\right]$$

Variational principle: can show

$$\Omega[\rho(\mathbf{r}) \neq \rho_0(\mathbf{r})] > \Omega[\rho_0(\mathbf{r})] \equiv \Omega$$

which implies: $$\left.\frac{\delta\Omega[\rho(\mathbf{r})]}{\delta\rho(\mathbf{r})}\right|_{\rho_0} = 0$$

Issue: we don't know the form of F. Approximate it.

Basic Structure of a cDFT

- model for the fluid
- expression for Helmholtz free energy
  - can contain multiple additive terms
  - e.g. excluded volume, van der Waals, Coulomb, etc.
- minimize grand free energy

$$\frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} + V_{ext}(\mathbf{r}) - \mu = 0 \longrightarrow$$ integral equations to solve for ρ(r)

Example: ideal gas

$$\beta F^{id}[\rho] = \int d\mathbf{r}\rho(\mathbf{r}) \left(\ln(\lambda^3 \rho(\mathbf{r})) - 1\right)$$

$$\rho(\mathbf{r}) = \lambda^{-3} \exp[-\beta(V_{ext}(\mathbf{r}) - \mu)]$$ Boltzmann dist.

$$\lambda = \sqrt{\frac{\beta h^2}{2\pi m}}$$ de Broglie wavelength, not important (absorb into $e^{\beta\mu}$)

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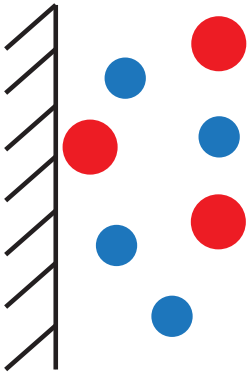
Hard Sphere Fluids



- mixture of hard spheres
  - can have different sizes
- near a hard wall

state of the art: "White Bear" functional, Roth et al, 2002

excess Helmholtz free energy

$$F_{hs}\left[\rho_\alpha(\mathbf{r})\right] = kT \int d\mathbf{r}\, \Phi[n_\gamma(\mathbf{r})]$$

$$\Phi = -n_0 \ln\left(1-n_3\right) + \frac{n_1 n_2 - n_{V1}\cdot n_{V2}}{1-n_3} + \left(n_2^3 - 3n_2 n_{V2}\cdot n_{V2}\right)\frac{n_3 + (1-n_3)^2\ln(1-n_3)}{36\pi n_3^2 (1-n_3)^2}$$

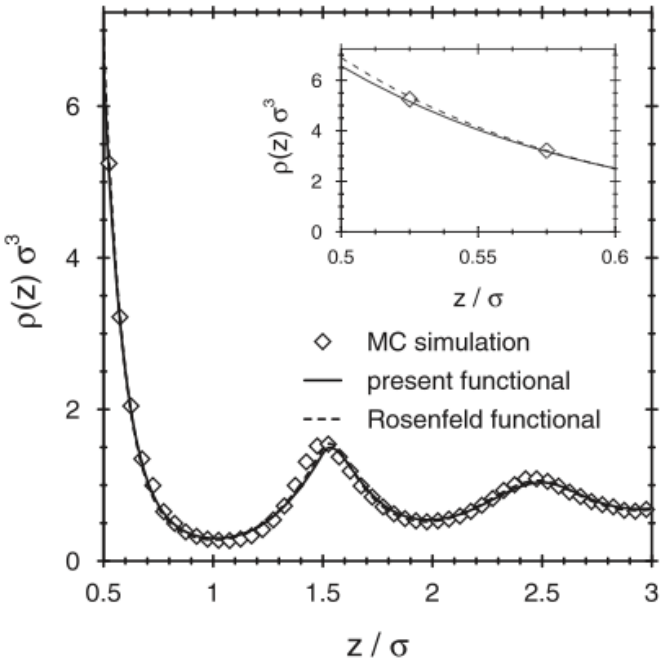
weighted densities

$$n_\gamma(\mathbf{r}) = \sum_\alpha \int d\mathbf{r}'\, \rho_\alpha(\mathbf{r})\omega_\alpha^{(\gamma)}(\mathbf{r}-\mathbf{r}'),$$

$$\omega_\alpha^{(2)}(\mathbf{r}) = \delta(R_\alpha - |\mathbf{r}|) \qquad \omega_\alpha^{(3)}(\mathbf{r}) = \theta(R_\alpha - |\mathbf{r}|)$$

$$\omega_\alpha^{(0)}(\mathbf{r}) = \frac{\omega_\alpha^{(2)}(\mathbf{r})}{4\pi R_\alpha^2} \qquad \omega_\alpha^{(1)}(\mathbf{r}) = \frac{\omega_\alpha^{(2)}(\mathbf{r})}{4\pi R_\alpha}$$

$$\omega_\alpha^{(V2)}(\mathbf{r}) = \frac{\mathbf{r}}{r}\delta(R_\alpha - |\mathbf{r}|) \qquad \omega_\alpha^{(V1)}(\mathbf{r}) = \frac{\omega_\alpha^{(V2)}(\mathbf{r})}{4\pi R_\alpha}$$



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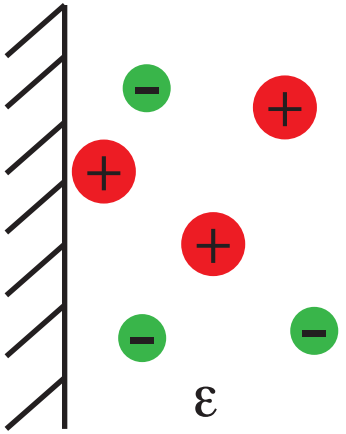
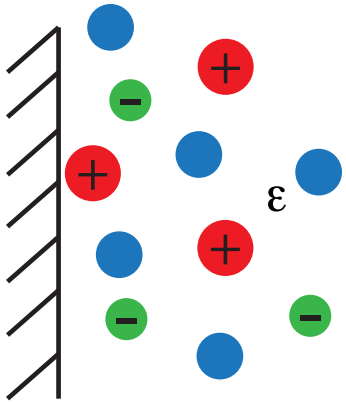
Application of DFT to the Double Layer

- first done in 1987 (Boyle et al)
- seminal papers by Tang, Scriven, Davis, et al.
- other important work by D Henderson, D Gillespie, etc.



Primitive Model (PM)

- ions as charged hard spheres
- continuous dielectric medium for solvent
- charged hard surface (wall)

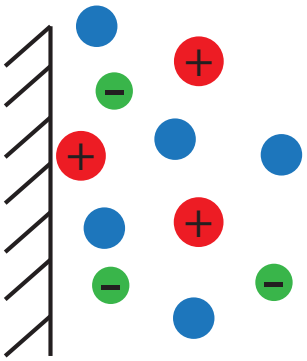


Semi-primitive model (SPM)

- charged hard spheres
- neutral charged solvent, dielectric ε
- charged hard wall

- also called 3-component model (3CM)

Free-energy for the Double-Layer



$$F[\rho_\alpha] = F^{id}[\rho_\alpha] + F^{hs}[\rho_\alpha] + F^{MF}[\rho_\alpha] + F^{corr}[\rho_\alpha]$$

$$F^{MF}[\rho_i] = \frac{1}{2}\sum_i \int d\mathbf{r} z_i e \rho_i(\mathbf{r})\phi(\mathbf{r})$$

$$\phi(\mathbf{r}) = \sum_j \int d\mathbf{r}' \rho_j(\mathbf{r}') \frac{z_j e}{\epsilon kT|\mathbf{r}-\mathbf{r}'|}$$

mean-field electrostatics

where ϕ satisifes Poisson's eq with appropriate BCs

$$F^{corr}[\rho_i] = -\frac{1}{2}kT\sum_{ij}\int d\mathbf{r}d\mathbf{r}'\rho_i(\mathbf{r})\rho_j(\mathbf{r}')\Delta c_{ij}(|\mathbf{r}-\mathbf{r}'|)$$

$$\Delta c_{ij}(|\mathbf{r}-\mathbf{r}'|) = c_{ij}(r) + \frac{z_i z_j e^2}{\epsilon kT|\mathbf{r}-\mathbf{r}'|} - c_{ij}^{HS}(r)$$

ion correlation term

obtain from integral eq. theory of bulk state (MSA)

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Residual Equations to Solve

solve $R_i = 0$

$$R_1 = \ln \rho_\alpha(\mathbf{r}) + V(\mathbf{r}) - \mu_\alpha + \int \sum_\gamma \frac{\partial \Phi}{\partial n_\gamma}(\mathbf{r}')\omega_\alpha^{(\gamma)}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' + \sum_\beta \int d\mathbf{r}'\rho_\beta(\mathbf{r}')u_{\alpha\beta}(\mathbf{r}-\mathbf{r}') - \sum_\beta \int d\mathbf{r}'\rho_\beta(\mathbf{r}')\Delta c_{\alpha\beta}(\mathbf{r}-\mathbf{r}') + Z_\alpha\phi(\mathbf{r})$$

$$R_2 = n_\gamma(\mathbf{r}) - \sum_\alpha \int d\mathbf{r}'\, \rho_\alpha(\mathbf{r})\omega_\alpha^{(\gamma)}(\mathbf{r}-\mathbf{r}')$$

$$R_3 = \nabla^2\phi - \frac{4\pi}{T^*}\sum_\alpha q_\alpha\rho_\alpha \qquad T^* = 4\pi k_B T\epsilon\epsilon_0 d/e^2$$

T* characterizes strength of Coulomb interactions

Bjerrum length: $l_B \equiv \frac{e^2}{4\pi kT\epsilon\epsilon_0} = \frac{d}{T^*}$

where electrostatic energy = kT

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Numerical Solution

- inexact Newton's method for residual equations: **Ax = b**
- divide matrix into physics-related blocks:

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$$

- solve by Schur complement method:

$$S = A_{22} - A_{21} A_{11}^{-1} A_{12}$$

$$Sx_2 = (b_2 - A_{21} A_{11}^{-1} b_1)$$

$$x_1 = A_{11}^{-1}(b_1 - A_{12} x_2)$$

subblock A_{22} is relatively dense:

$$\begin{array}{c} \\ R_2 \\ R_1 \\ R_3 \end{array} \begin{array}{c} \begin{array}{ccc} n & \rho & \phi \end{array} \\ \left(\begin{array}{c|cc} I & \hat{B}(\sigma/2) & 0 \\ \hline \hat{B}(\sigma/2) & B(\sigma/2) & D \\ 0 & D & M \end{array} \right) \end{array}$$

Heroux, M. A., Salinger, A. G. & Frink, L. J. D. *Siam J Sci Comput* **29,** 2059–2077 (2007)
Frischknecht, A. L., Halligan, D. O. & Parks, M. L. *J Chem Phys* **141,** 054708 (2014)

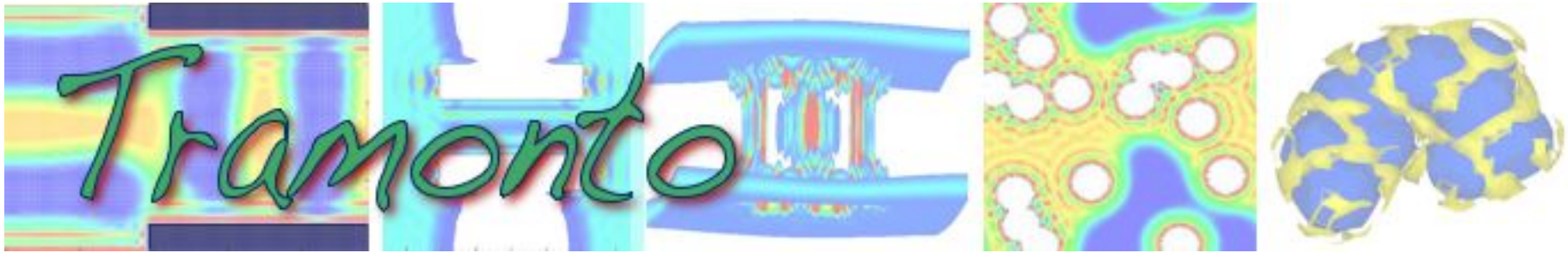
Implementation: Tramonto

http://software.sandia.gov/tramonto

3D parallel fluids-DFT code
primarily developed by: Laura Frink, Andy Salinger, Mike Heroux, Mike Parks

code strategies:

- solve by collocation on 3D Cartesian mesh, real space
- precalculate integration stencils (e.g. for delta funcs)
- Poisson's eq: finite elements
- inexact Newton's methods
  - use analytic Jacobian
  - Trilinos



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- application to charged nanoparticles
  - compare to MD simulations
- extension to steady-state diffusion
- application to flow in nanochannels
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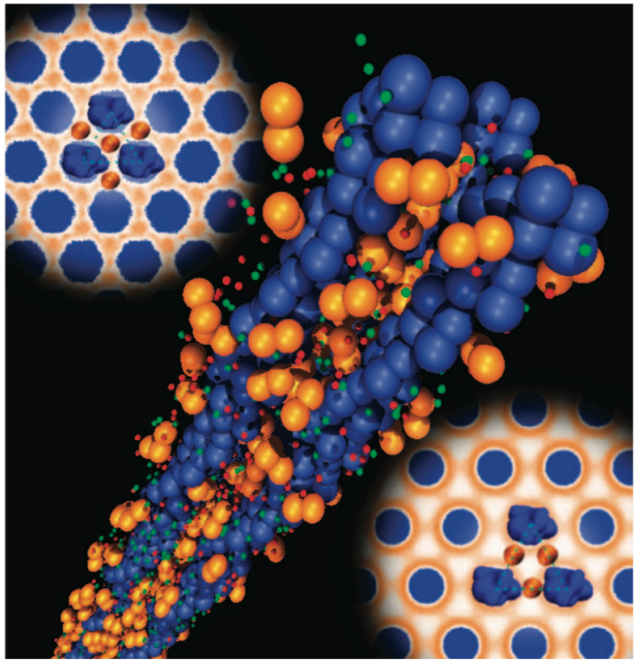
Why Charged Nanoparticles?

- Control over assembly
  - Manipulate individual NPs as well as assembled membranes
- Dispersion vs aggregation
  - bio systems
  - colloidal systems
  - nanofluidics



Wong, G. C. L. & Pollack, L. *Annu Rev Phys Chem* **61,** 171–189 (2010).

DFT vs MD simulations

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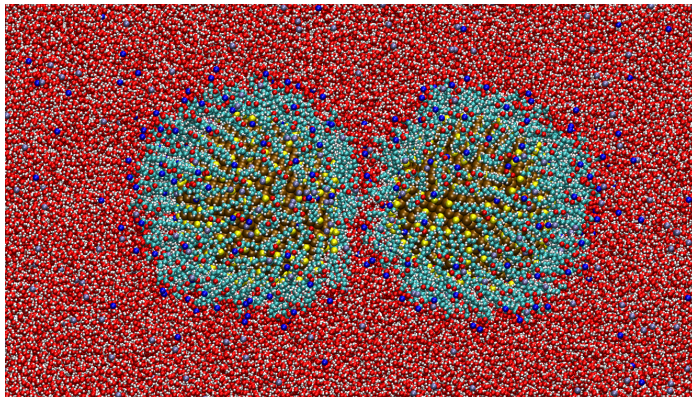
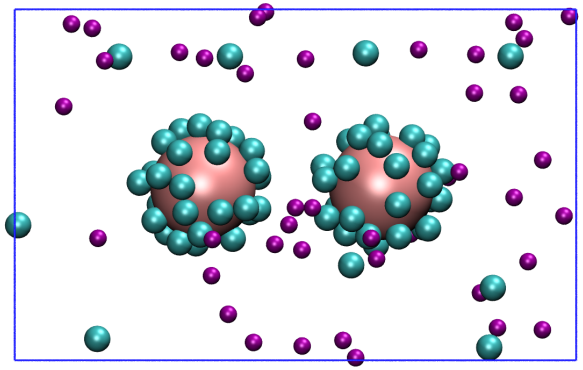
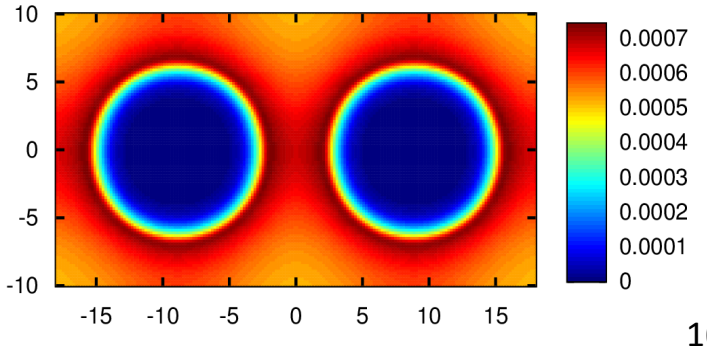
- Atomistic molecular dynamics
  - 4nm decanethiol-coated in water ⇒ $7x10^5$ atoms
  - Can simulate a handful of parameters



- Coarse-grained molecular dynamics (CGMD)
  - Charged 4nm “NPs” with counterions and coions in neutral fluid⇒$2x10^4$ particles

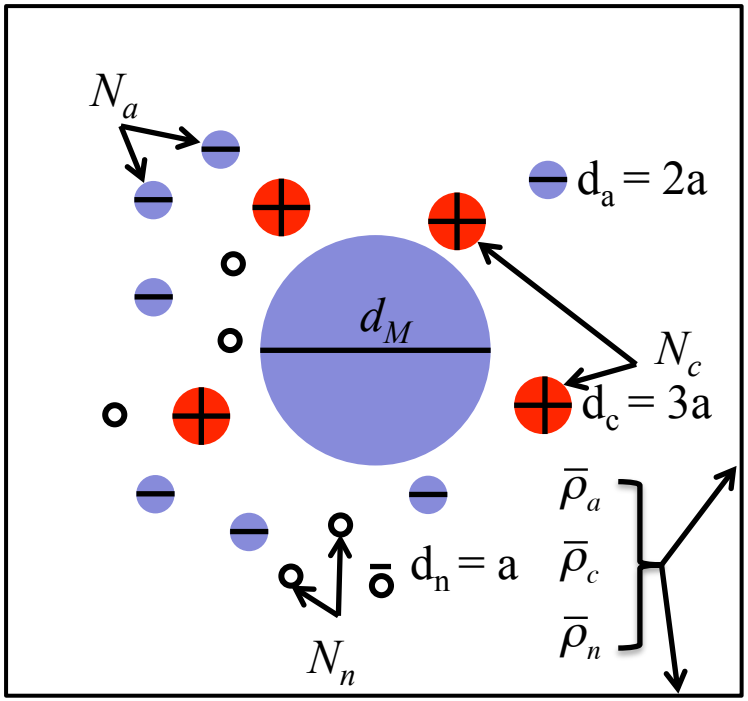


- Classical DFT
  - 10X faster
  - Efficiently use 10X more cores
  - Free energy (FE) functional F[ρ(r)]



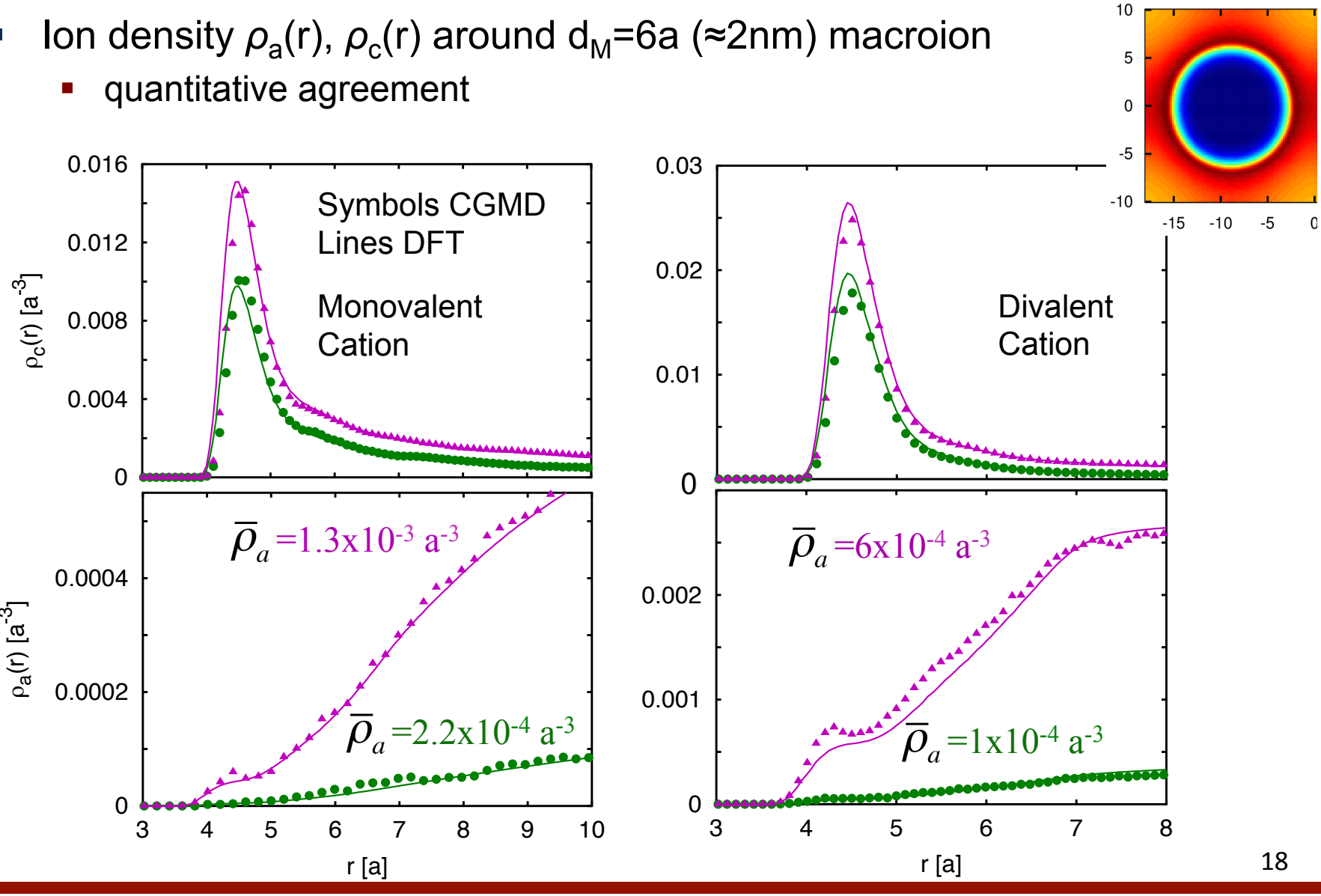
Model

- Nanoparticle diameter d_M, negative charge $q_M = \pi d_M^2 \sigma_M$
- cations $d_c = 3a$, charge $q_c = 1e, 2e, 3e$
- anions $d_a = 2a$, charge $q_a = -1e$
- neutral particles $d_n = a$ (=0.285nm)
- Bjerrum length
  $\ell_B = 2.5a = 0.71$ nm
- Moderate coupling $3 < g < 300$
  $$g = 2q_c^3 \ell_B^2 q_M / (e^4 d_M^2)$$
- Interactions
  - DFT – hard-sphere
  - CGMD – cut & shifted 12-6 $\varepsilon = k_B T$



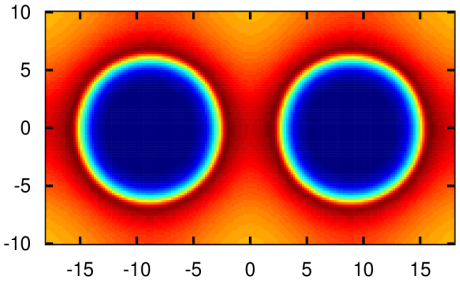
DFT vs MD: density profiles

- Ion density $\rho_a(r)$, $\rho_c(r)$ around d_M=6a (≈2nm) macroion
  - quantitative agreement

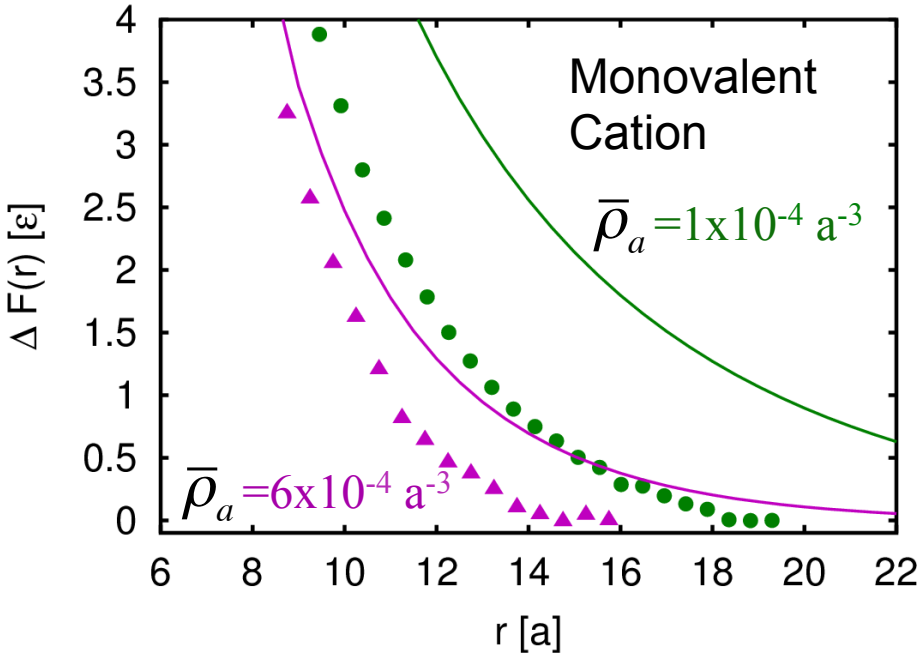


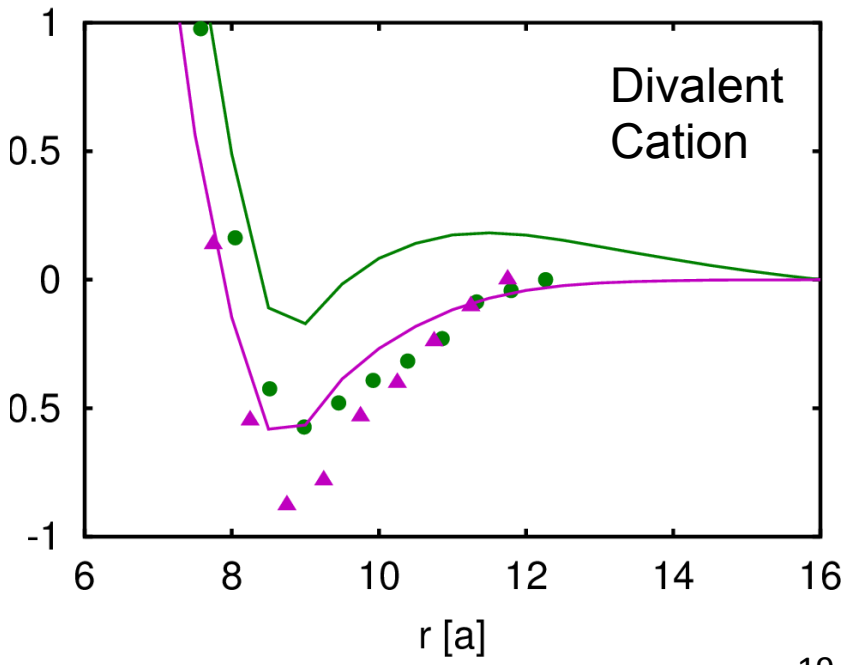
DFT vs MD: Free Energy

- Macroion-macroion interaction free energy
  - Qualitative agreement
  - Correct trends and order of magnitude for well depth



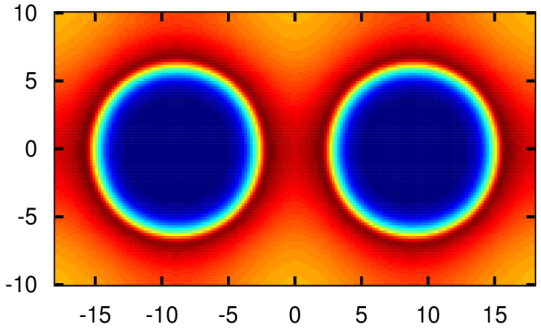
Symbols CGMD
Lines DFT

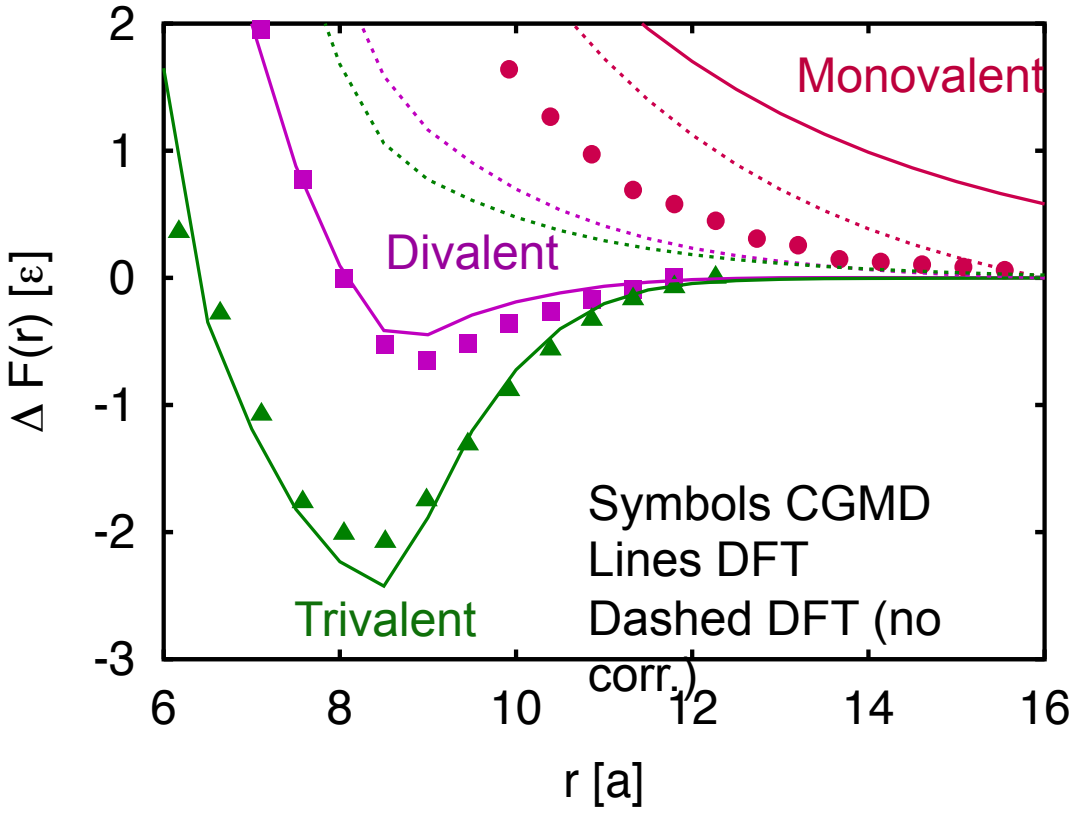




Ion Valence / Ion Correlations

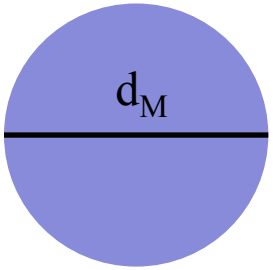
- Ion valence increases coupling *g*
- Ion correlations drive attractive interactions
  - DFT ion correlation term produces attraction

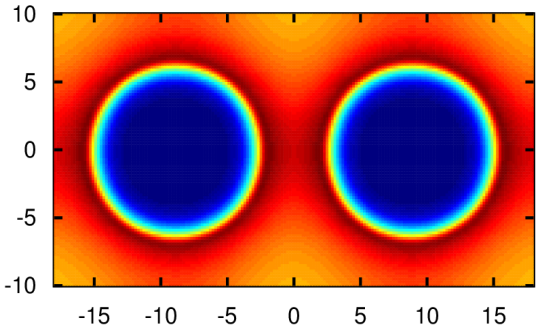


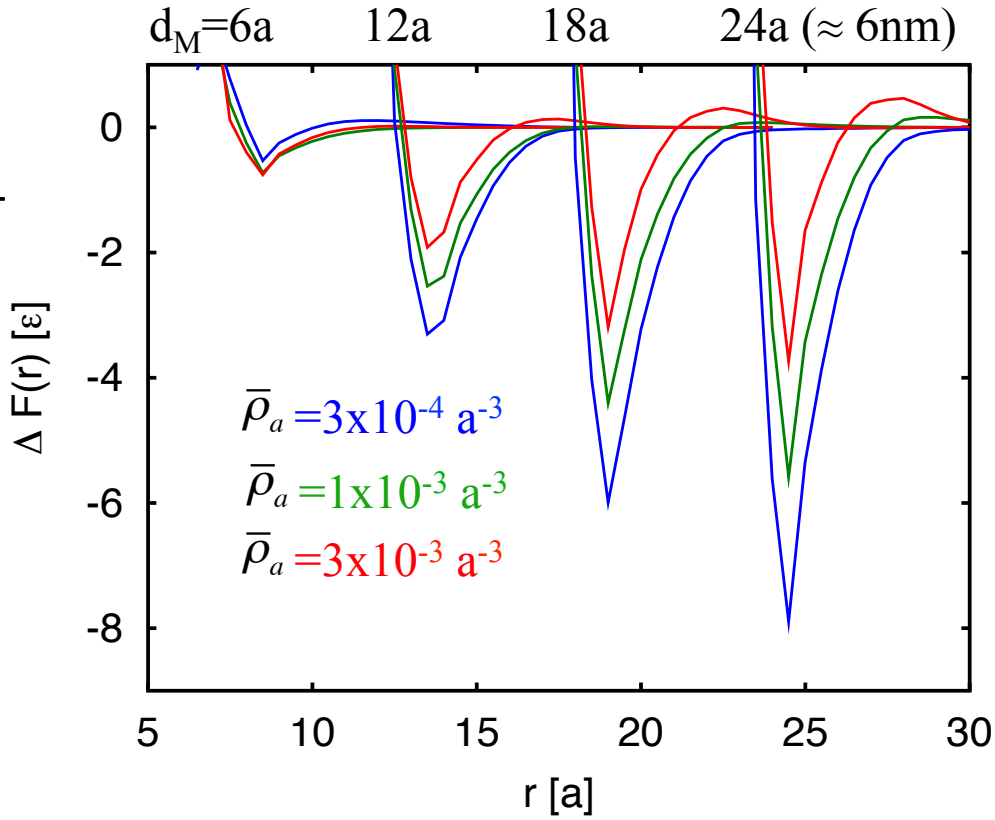


Effect of Macroion Diameter

- Depth of minimum ΔF_{min} increases with d_M
- ΔF_{min} and variation depend on ion density
- $8\ kT$ minimum leads to aggregation
- Costly for CGMD, enabled by DFT model

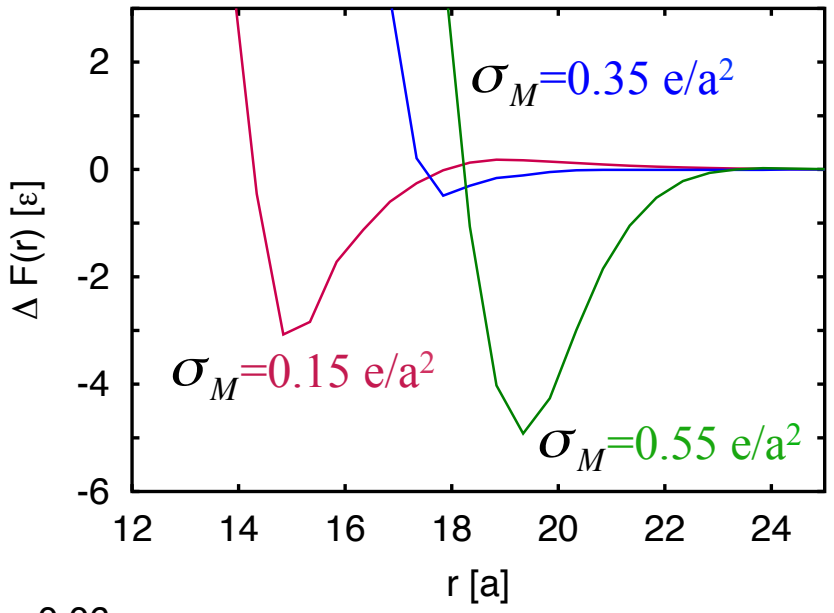


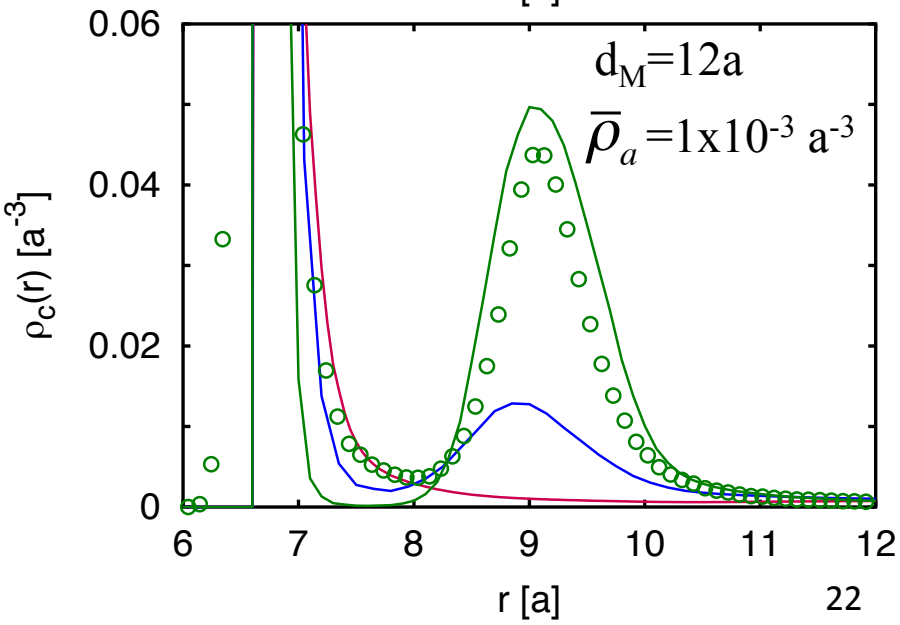




Counterion Layering

- Both minimum depth ΔF_{min} and location vary
  - Larger equilibrium separation with increasing σ_M
- Secondary counterion peak shows layering
  - Weak interaction from small secondary peak
  - Deep minimum from large secondary peak
  - Secondary peak occurs in CGMD & DFT





K. M. Salerno, A. L. Frischknecht, and M. J. Stevens, *J Phys Chem B* 120, 5927 (2016)

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Steady-State Transport

chemical potential varies: $\mu(\mathbf{r})$
add steady-state drift-diffusion equation

$$\mathbf{J}_\alpha(\mathbf{r}) = -D_\alpha \rho_\alpha(\mathbf{r}) \nabla \beta\mu_\alpha(\mathbf{r}) \qquad \nabla \cdot \mathbf{J}_\alpha = 0$$

$$\beta\mu_\alpha(\mathbf{r}) = \ln \rho_\alpha(\mathbf{r}) + \frac{\delta \beta F^{ex}}{\delta \rho_\alpha(\mathbf{r})} + z_\alpha \phi(\mathbf{r})$$

steady-state Poisson-Nernst-Planck (PNP) theory

assume point particles so $\beta\mu_\alpha(\mathbf{r}) = \ln \rho_\alpha(\mathbf{r}) + z_\alpha \phi(\mathbf{r})$

$$\nabla \cdot \left(D_\alpha \nabla \rho_\alpha(\mathbf{r}) + \frac{D_\alpha e z_\alpha}{kT} \rho_\alpha(\mathbf{r}) \nabla \psi(\mathbf{r}) \right) = 0$$

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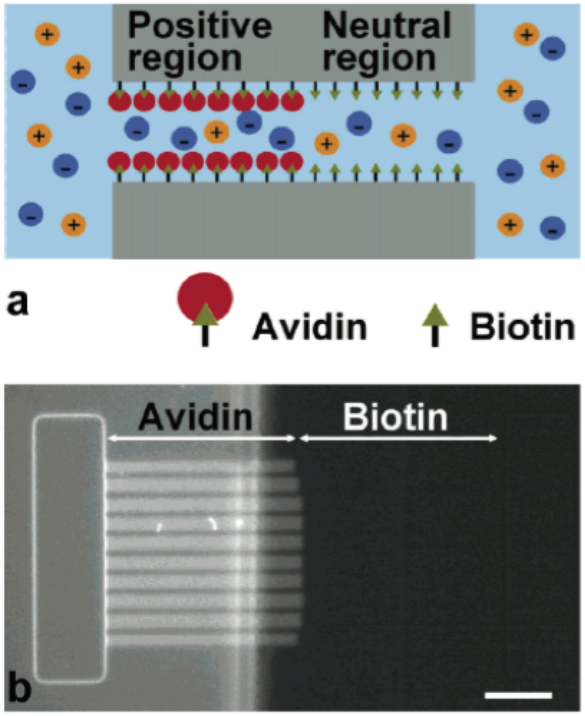
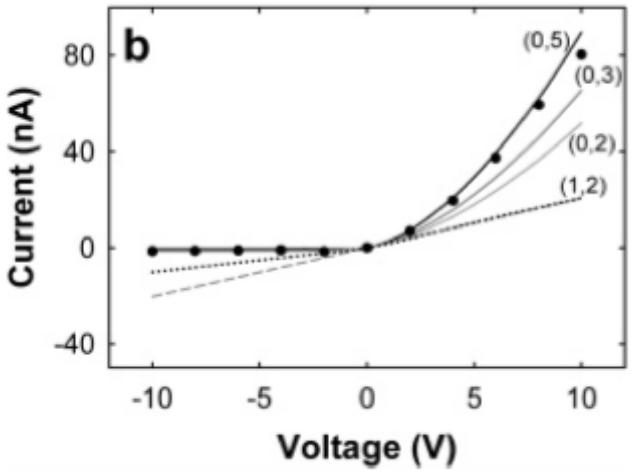
Steady-State Transport in Nanofluidics



30 nm channels

channel acts like a diode



Karnik, R., et al., *Nano Lett* **7,** 547–551 (2007)

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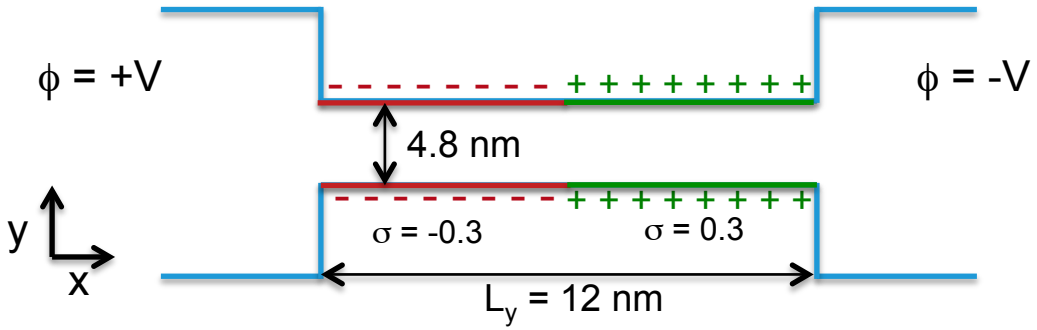
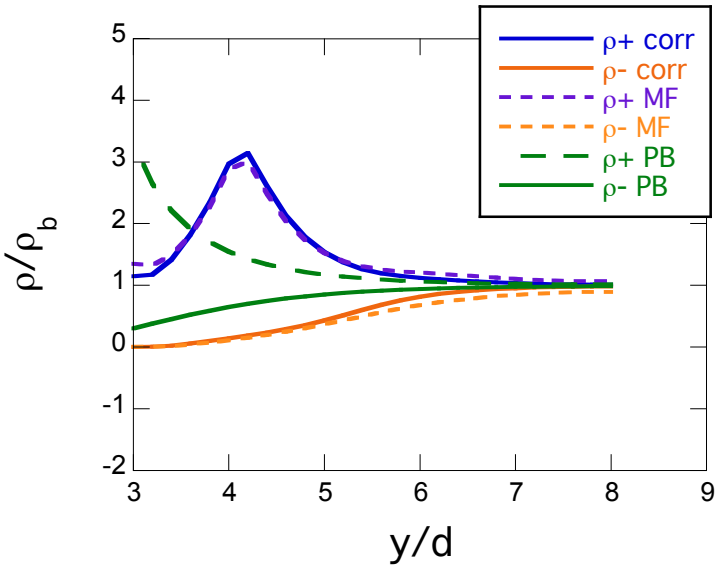
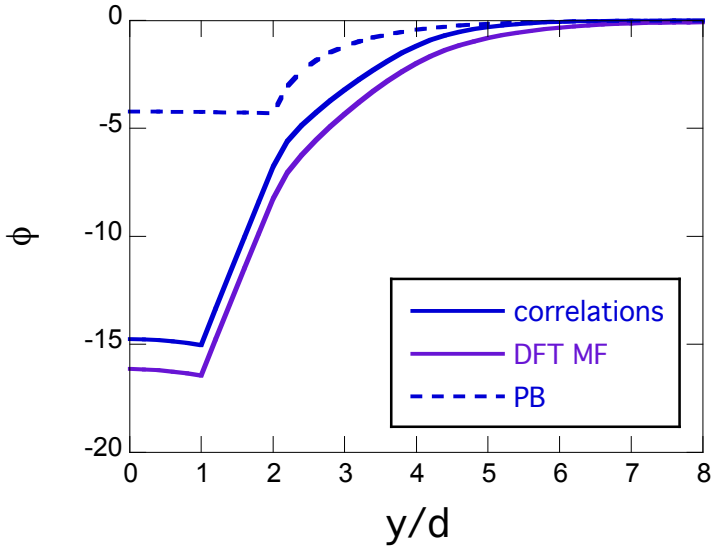
Transport in Nanochannels

monovalent ions
d+ = .6 nm, d- = .3 nm
concentration 1M



density profiles and ϕ across the channel





ion size important; correlations less important

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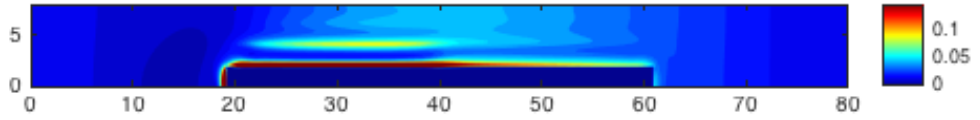
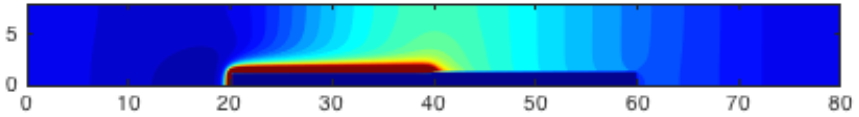
2D Densities and Fluxes

$\Delta\phi = 40$ ($\approx$ 1V)

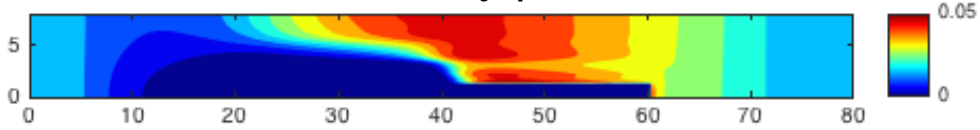
cation density ρ_+, DFT



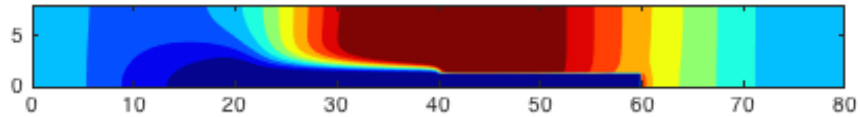
cation density ρ_+, PNP



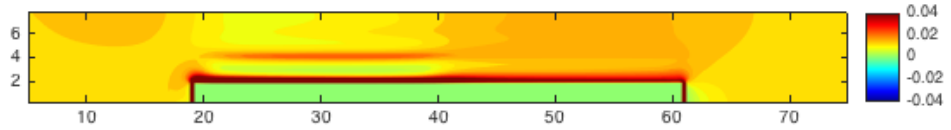
anion density ρ_-, DFT



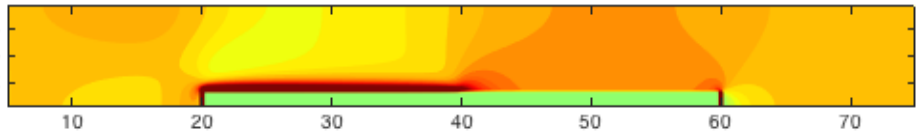
anion density ρ_-, PNP



cation flux $J_{x,+}$, DFT



cation flux $J_{x,+}$, PNP



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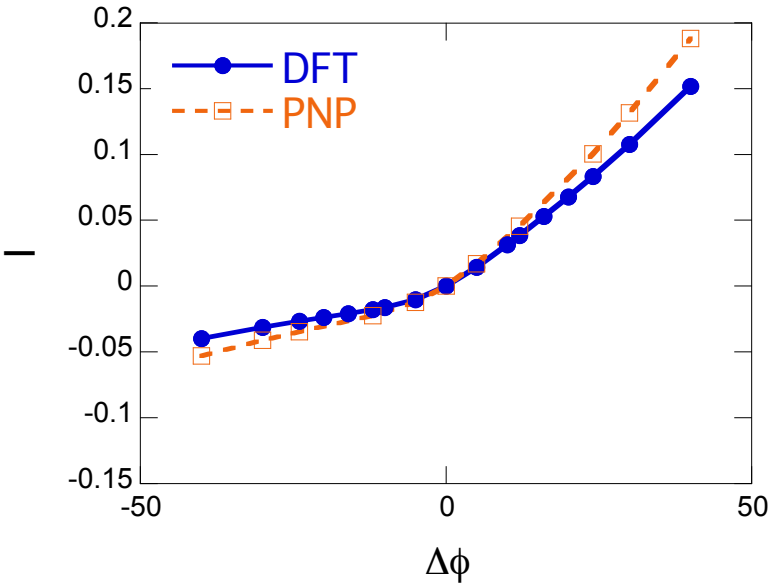
Current Rectification



DFT current is lower than PNP
need to test further

Conclusions

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- DFT often accurate molecular model
  - faster than particle simulations
  - direct calculation of free energies, phase diagrams

- DFT goes beyond Poisson-Boltzmann/PNP
  - more accurate at high ion concentration
  - more accurate at high surface density
  - includes finite ion size, ion correlations

K. M. Salerno, A. L. Frischknecht, and M. J. Stevens, *J Phys Chem B* 120, 5927 (2016)

J. Cheung et al., in preparation

Acknowledgments

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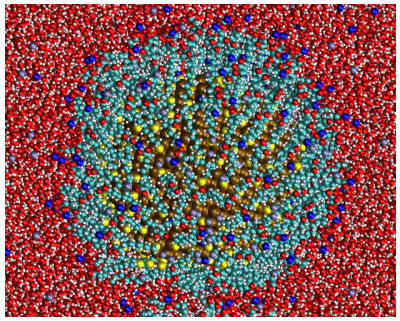
CM4

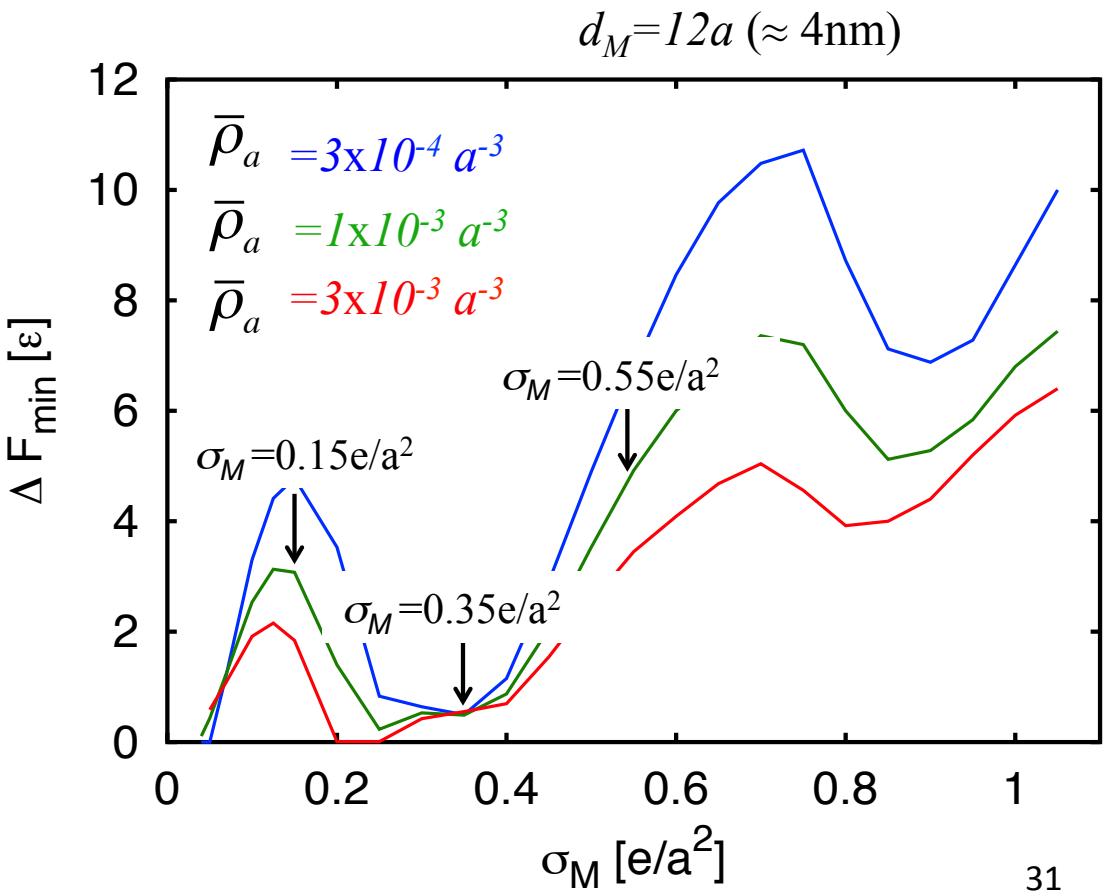
U.S. DEPARTMENT OF ENERGY | Office of Science

Collaboratory on Mathematics for Mesoscopic Modeling of Materials (CM4)

Macroion Surface Charge

- Interaction minimum ΔF_{min} depends on surface charge σ_M
  - NP full coverage
    $4.7\ e/nm^2 \approx 0.35\ e/a^2$
  - Nonmonotonic in σ_M
  - Varies widely





Parallel Scaling

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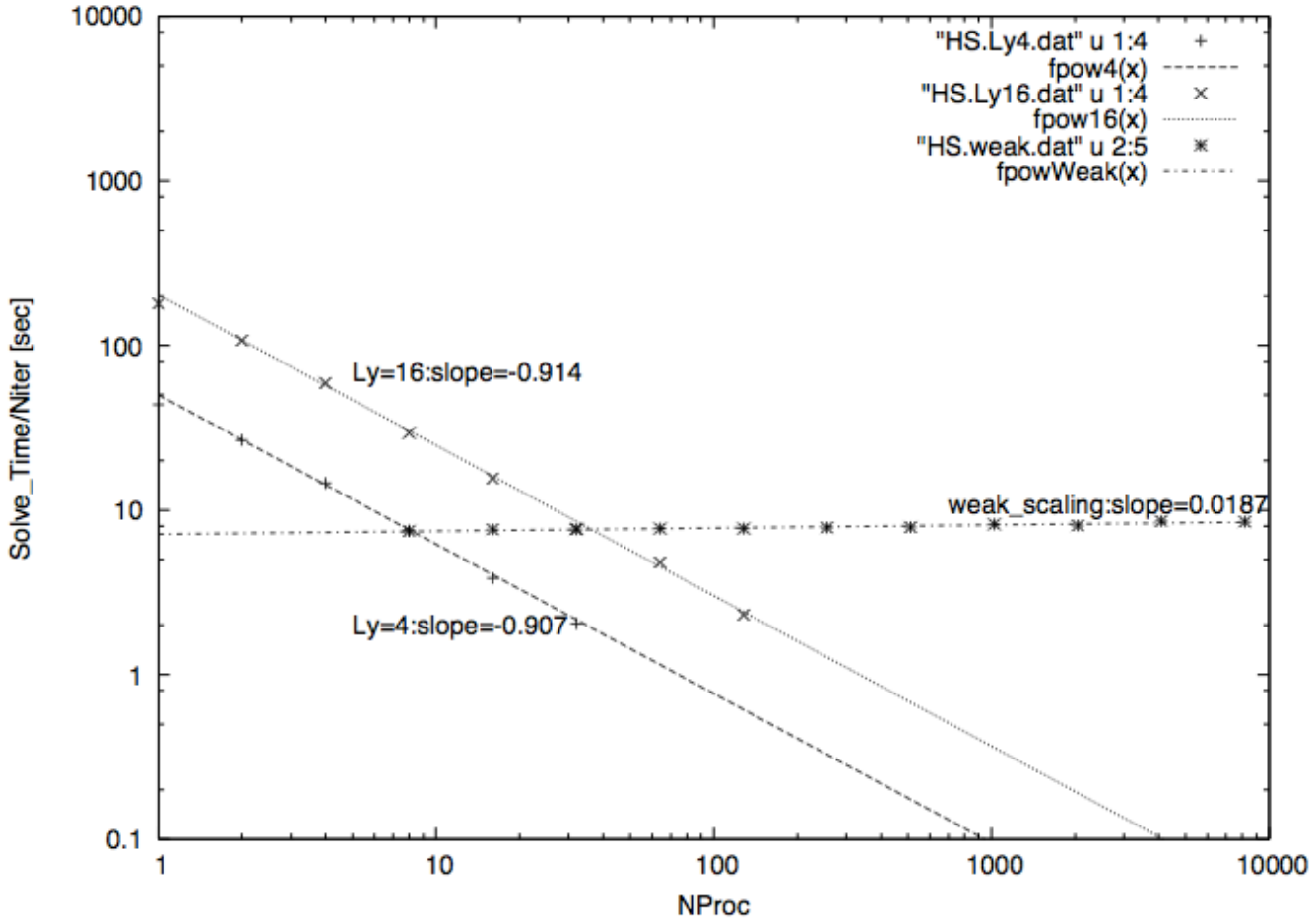
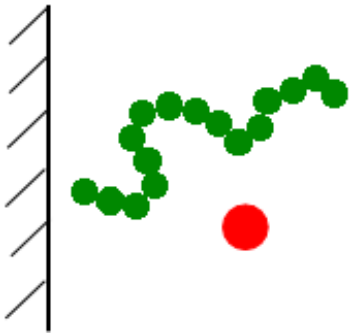
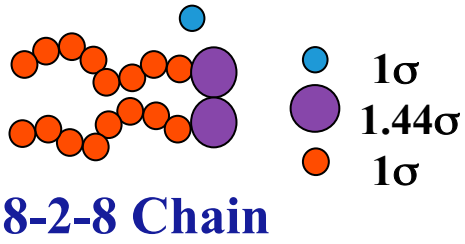
1 component HS system



Models/Physics in Tramonto

basic elements:
- spherical fluid particles
- surfaces





8-2-8 Chain

- hard-sphere fluids
  - 3 different versions of FMT
- mean-field attractive interactions
  - Lennard-Jones, exponential, Yukawa
- bonded molecules
  - 2 classes of functionals: CMS; iSAFT
  - polymers, linear or branched
- charged systems
- diffusive transport
- arbitrary surface geometries

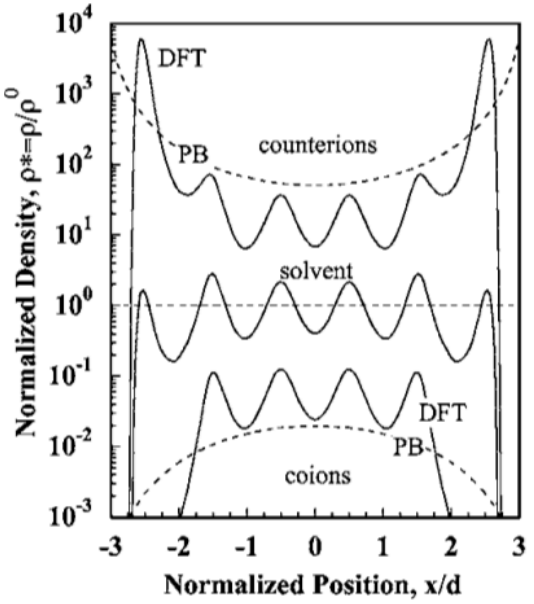
Application to EOF

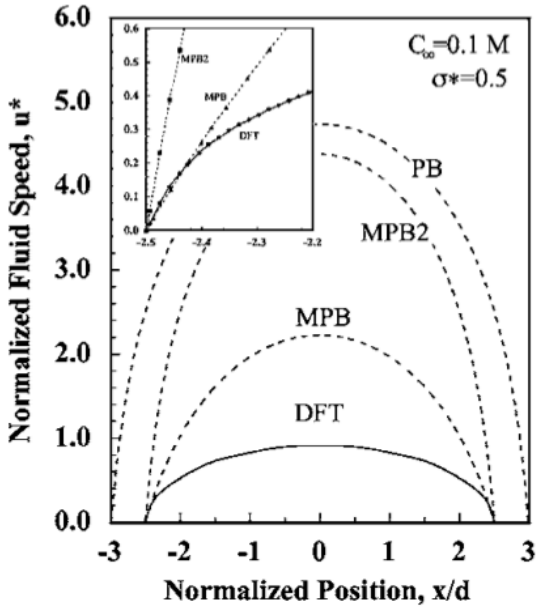
consider steady-state electro-osmotic flow in a channel aligned along *z*

$$\frac{\partial}{\partial x}\left(\mu\frac{\partial u_z(x)}{\partial x}\right) = -\rho_e E_z$$

$$\rho_e(x) = \sum_i z_i e \rho_i(x)$$

obtain ρ_e from DFT

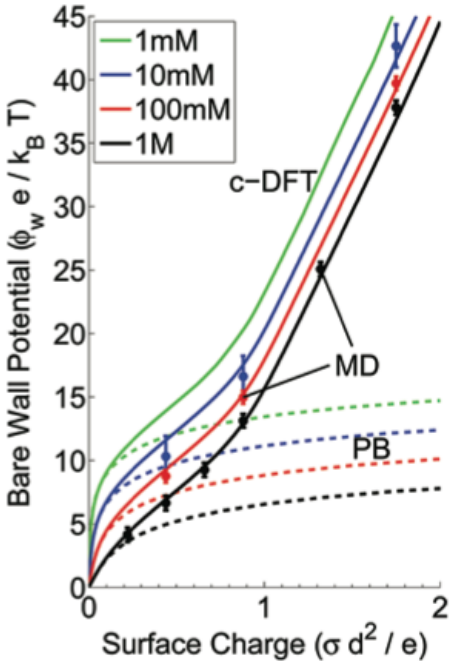


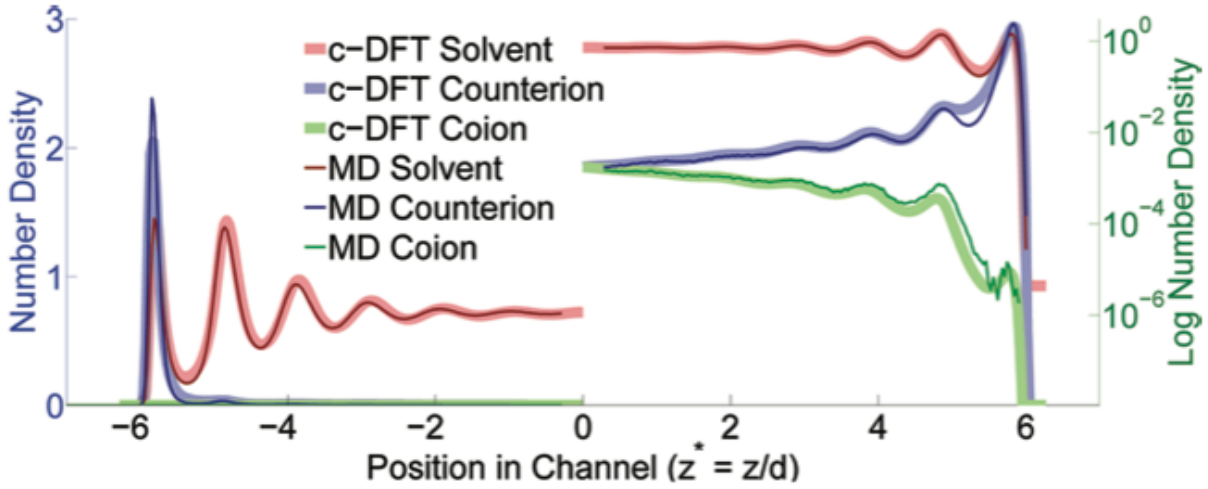


Nilson, R. H. & Griffiths, S. K. Influence of atomistic physics on electro-osmotic flow: An analysis based on density functional theory. *J Chem Phys* **125,** 164510 (2006).

Comparison of DFT with MD, PB

1:1 electrolyte in water, 300K, LJ interactions





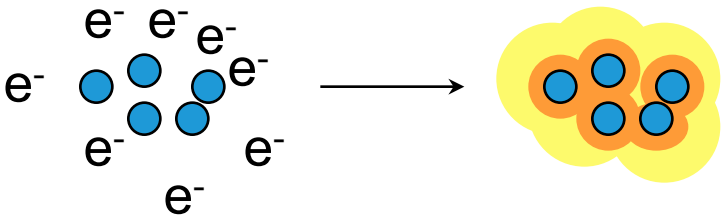
93 mM, surface charge 0.44

Jonathan W. Lee, Robert H Nilson, Jeremy A. Templeton, Stewart K Griffiths, Andy Kung, and Bryan M. Wong, J *Chem Theory Comput* **8,** 2012–2022 (2012).

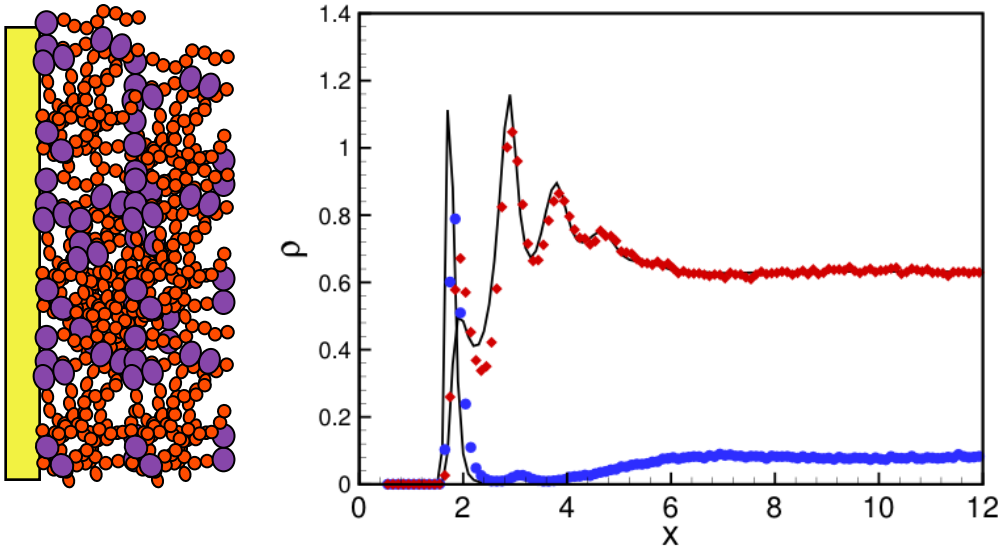
Relation to Electronic Structure DFT

$$\Omega[\rho(r)] : V(r) \rightarrow \rho(r)$$

External field — Density profile



Electronic Structure
(Closed system with N-electrons)



Fluid Structure
(Often open system with fixed chemical potential)

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