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Classical Density Functional Theory: Applications to Nanocomposites and the Electrical Double Layer

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Sandia National Laboratories

CM4 Webinar

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Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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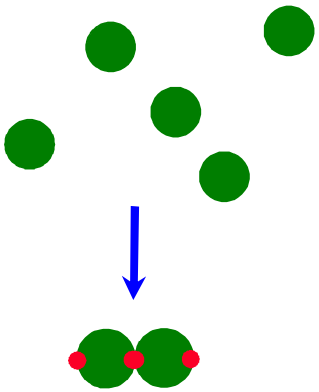
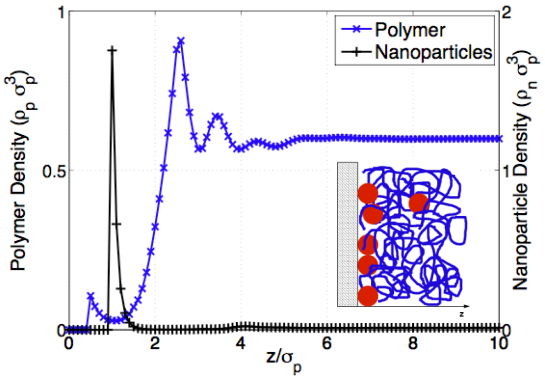
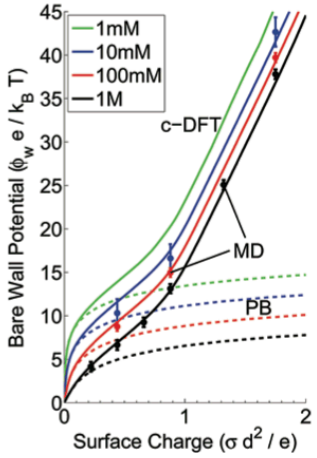
Outline

- classical density functional theory
- nanoparticle/polymer assembly
  - hard sphere systems
  - polymer-nanoparticle attractions
- electrical double layers
  - hard sphere systems
  - electroosmotic flow







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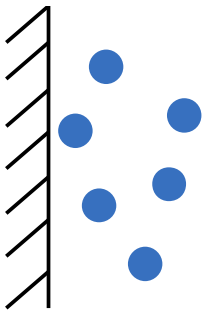
Basics



classical statistical mechanics for a fluid

goal is to calculate the free energy:

F for a canonical system (fixed V,T,n)
Ω for a grand canonical system (fixed V,T,μ)

many-body system: can't calculate *F* or Ω exactly

DFT: an approximate theory based on a variational principle

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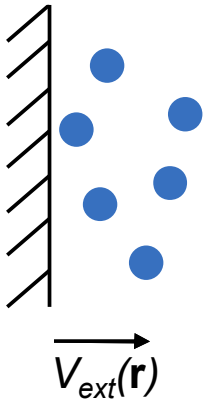
Foundation of DFT



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

- suppose have open system, temp T, volume V, chem potential μ
- can show Ω is a functional of ρ_0, $\Omega[\rho_0(\mathbf{r})]$
- Theorem: can show that $\rho_0(\mathbf{r})$ is uniquely given by $V_{ext}(\mathbf{r})$ (and vice versa)
  - then also, $F[\rho(\mathbf{r})]$ is a unique functional of $\rho(\mathbf{r})$
  - grand potential energy:

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

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Foundation of DFT, contd

Variational principle: can show

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

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

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

we have $$\frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} + V_{ext}(\mathbf{r}) - \mu = 0$$

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

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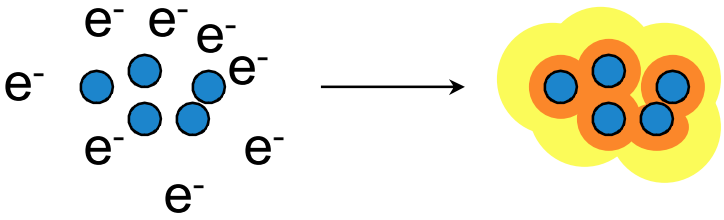
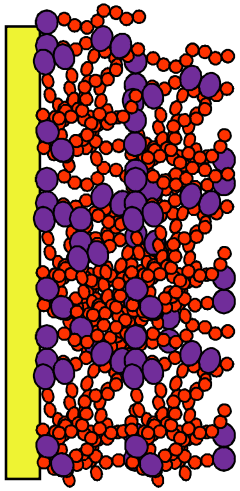
Relation to Electronic Structure DFT

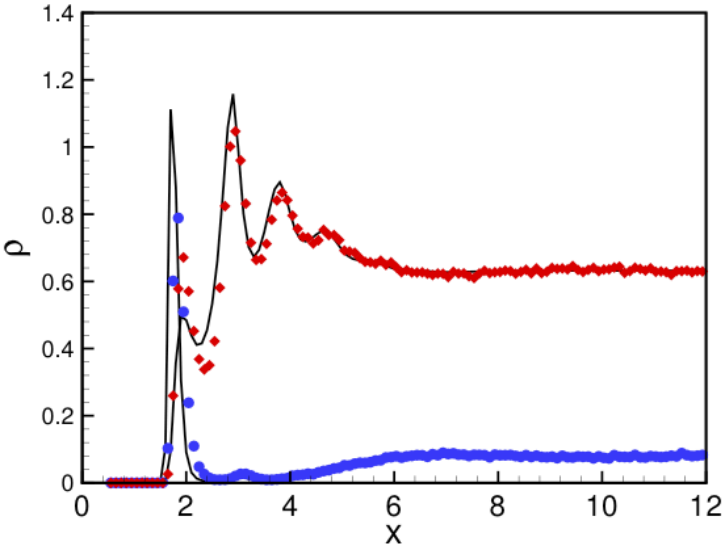
$$\Omega[\rho(r)] : V(r) \rightarrow \rho(r)$$

External field — Density profile



Electronic Structure
(Closed system with N-electrons)





Fluid Structure
(Often open system with fixed chemical potential)

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Basic Structure of a Fluids-DFT

- 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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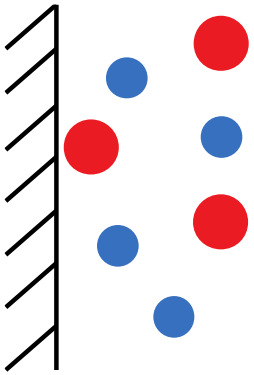
Hard Sphere Fluids



- 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

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

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

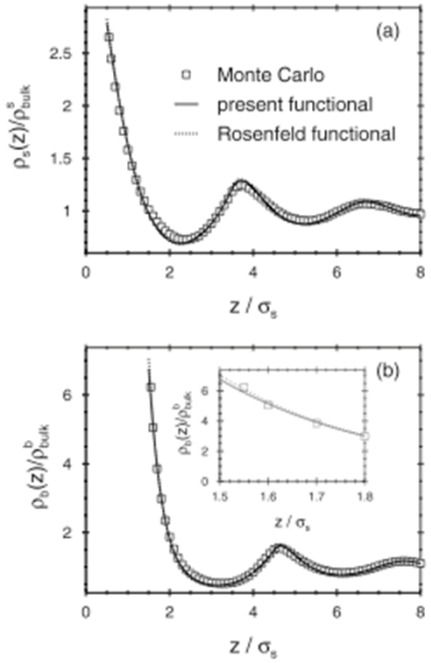
weighted densities

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

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

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

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



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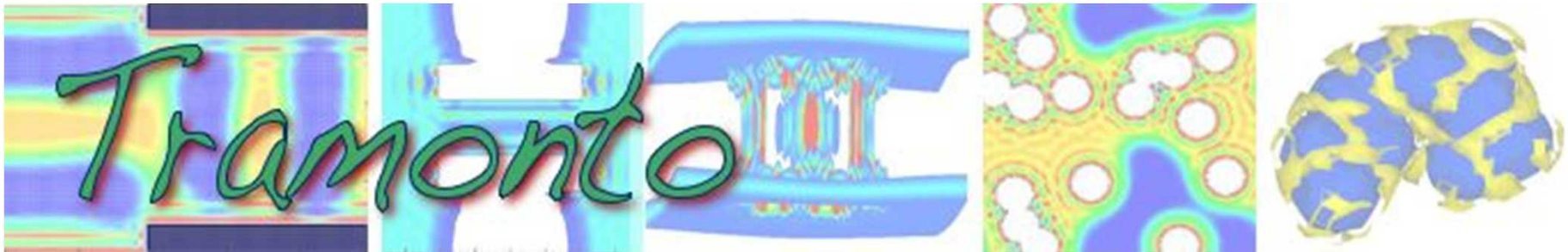
Implementation: Tramonto

http://software.sandia.gov/tramonto

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

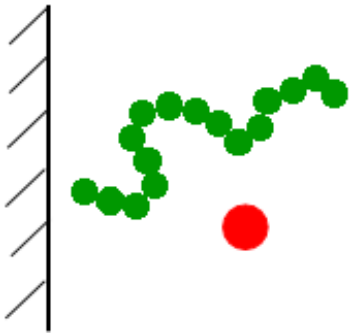
code strategies:

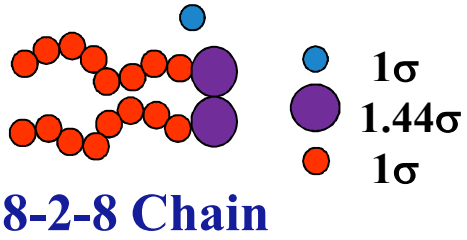
- solve by collocation on 3D Cartesian mesh, real space
- precalculate integration stencils (e.g. for delta funcs)
- Poisson's eq: finite elements
- solvers:
  - inexact Newton's methods
    - use analytic Jacobian
    - uses Trilinos
  - Picard iteration



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

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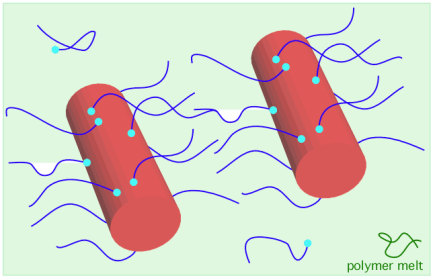
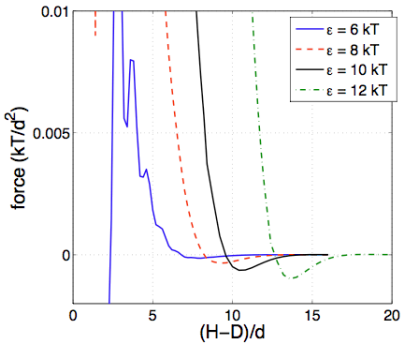
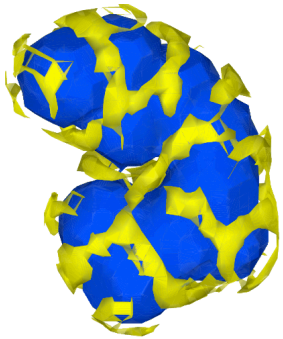
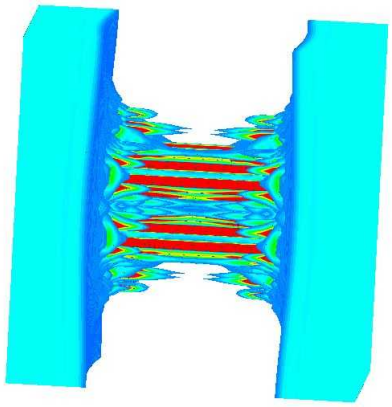
What can fluids-DFT do?

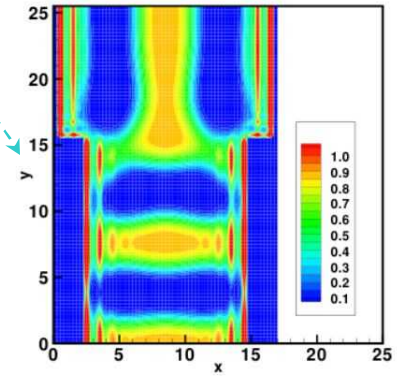
- forces between particles
- phase behavior
- solvation free energies
  - implicit solvent
- complex geometries
- complex chain architectures
- compare to simulation (e.g., MD, MC)

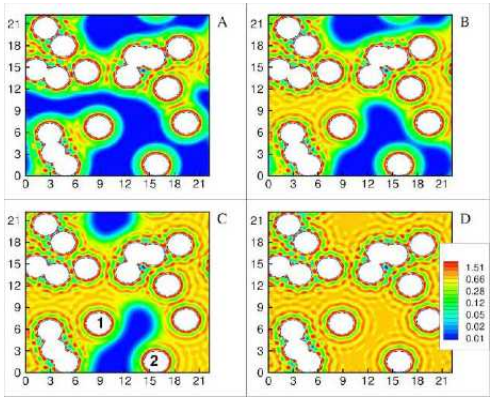


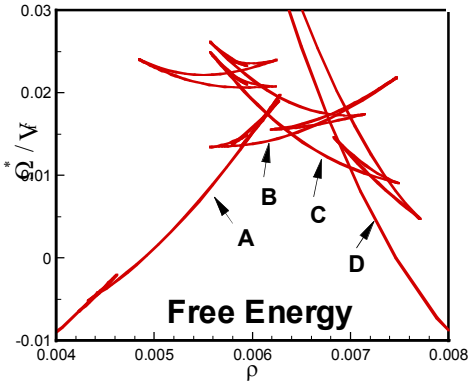












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Outline

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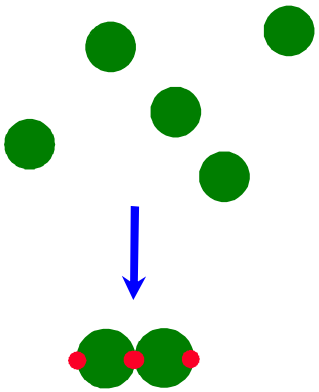
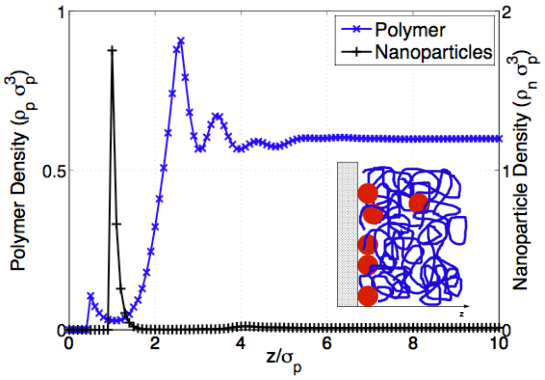
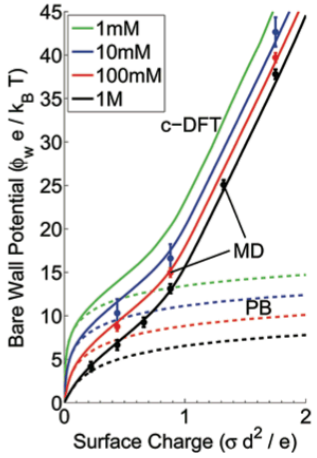
  - **hard sphere systems**
  - **polymer-nanoparticle attractions**
- electrical double layers
  - hard sphere systems
  - electroosmotic flow







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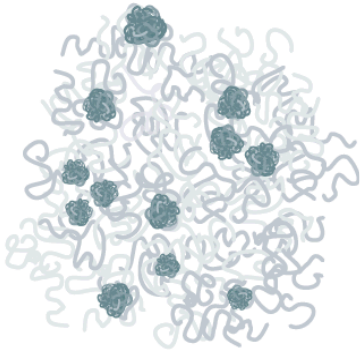
Interfacial Properties: Experiments

model athermal system: PS NPs in PS

NPs stay dispersed (for $R_{NP} < R_g$)



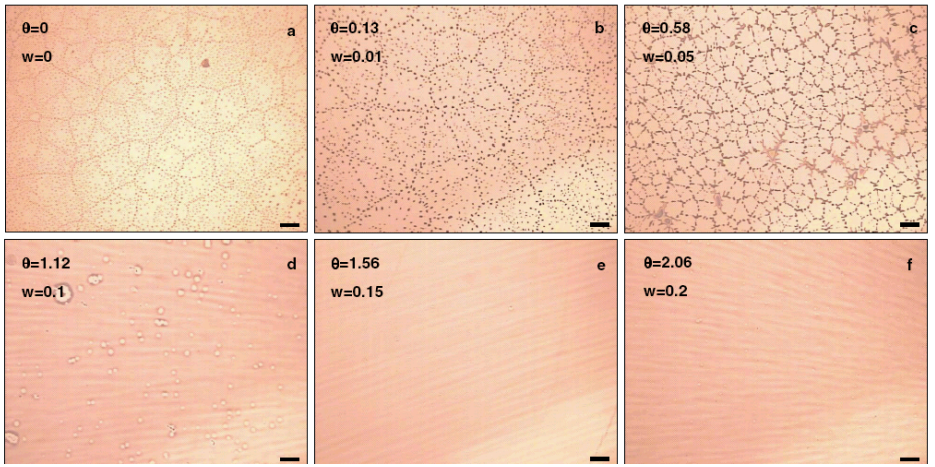
Mackay et al., Nature Mat., 2003

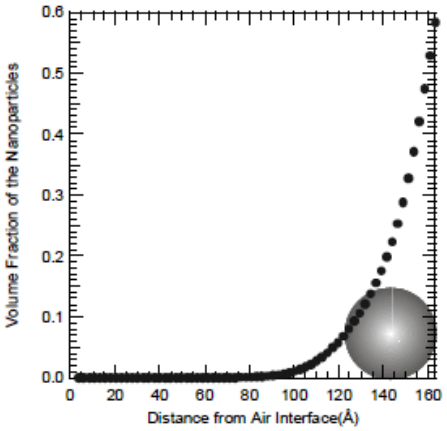
E. Harth, J. Am. Chem. Soc., 2002

PS nanoparticles blended with PS

40 nm thick film

NPs prevent dewetting!





- profile from neutron reflectivity
- nanoparticles segregate to surface

Krishnan et al. Langmuir (2005)

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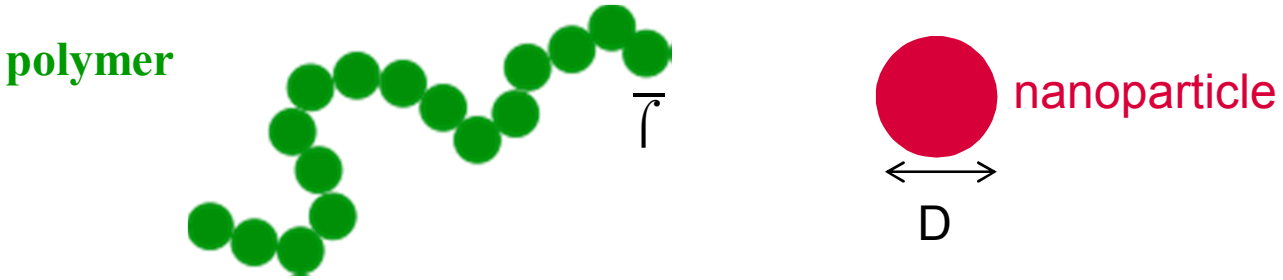
Coarse-Grained Models



- **polymers: freely-jointed, tangent chains**
- **athermal system:**
  - **model as hard spheres**
  - **only interactions are entropic**
- **attractions:**
  - **mean-field**
  - **simple forms (LJ; exponential)**

Kuhn length for PS: 1.485 nm

D = 2.0 ⟨r⟩ = 2.97 nm
D = 3.0 ⟨r⟩ = 4.45 nm

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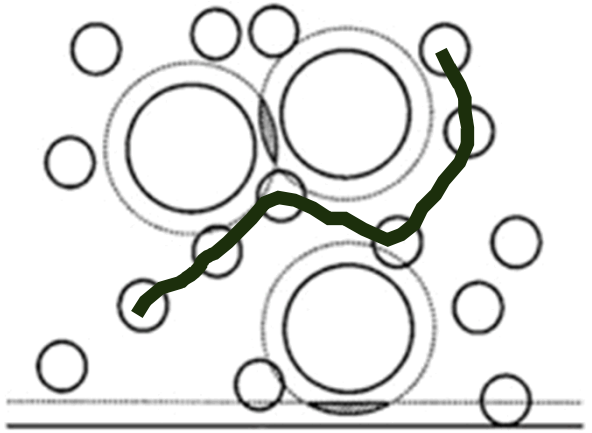
Physics of PNC Phase Behavior

hard sphere systems:
depletion attractions
(entropic)

- **between particles**
- **between particles & hard walls**



other contributions to equilibrium structure:

- **polymer configurational entropy**
- **enthalpic (van der Waals) interactions**

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Structure of a DFT: iSAFT

$$\Omega[\rho_\alpha(\mathbf{r})] = F[\rho_\alpha(\mathbf{r})] + \sum_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r})\,[V_\alpha(\mathbf{r}) - \mu_\alpha]$$

$$F = F^{id} + F^{hs} + F^{ch}$$

ideal gas part:

$$F^{id}[\rho_\alpha(\mathbf{r})] = kT \sum_\alpha \int d\mathbf{r}\rho_\alpha(\mathbf{r})\,[\ln \rho_\alpha(\mathbf{r}) - 1]$$

hard sphere functional:

$$F^{hs}[\rho_\alpha(\mathbf{r})] = kT \int d\mathbf{r}\Phi[n_\gamma(\mathbf{r})]$$

("White Bear" FMT, Roth et al., 2002)

chain bonding contribution:

$$F^{ch}[\rho_\alpha(\vec{r})] = kT \int d\vec{r}' \sum_{\alpha=1}^{m} \rho_\alpha^{seg}(\vec{r}') \sum_{\alpha}^{\{\alpha'\}} \left(-\frac{1}{2} \ln \int d\vec{r}'' \frac{\delta(|\vec{r}' - \vec{r}''| - \sigma^{\alpha\alpha'})}{4\pi(\sigma^{\alpha\alpha'})^2} y^{\alpha\alpha'}(\vec{r}', \vec{r}'') \rho_{\alpha'}^{seg}(\vec{r}'') + \frac{1}{2} \right)$$

minimize free energy

$$\frac{\delta\Omega}{\delta\rho(\mathbf{r})} = 0 \longrightarrow$$ equations to solve for ⟩ (r)

S. Tripathi and W.G. Chapman, *Phys. Rev. Lett.* **94**, 087081 (2005); *J. Chem. Phys.* **122**, 094506 (2005); S. Jain et al., *J. Chem. Phys.* **127**, 244904 (2007)

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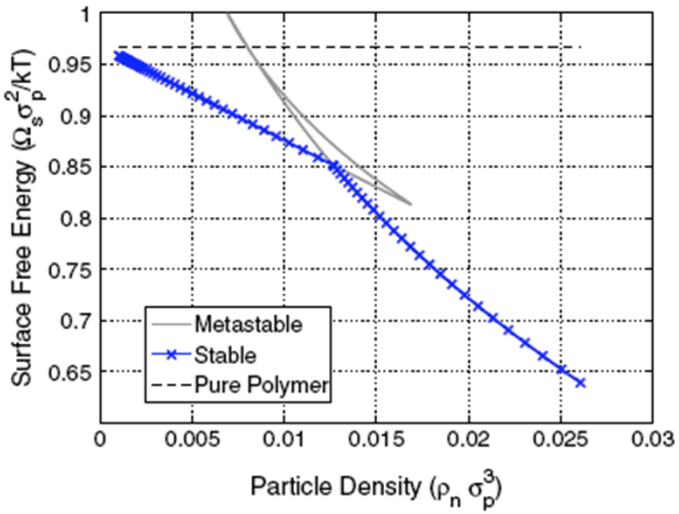
Athermal Blends: A Layering Phase Transition

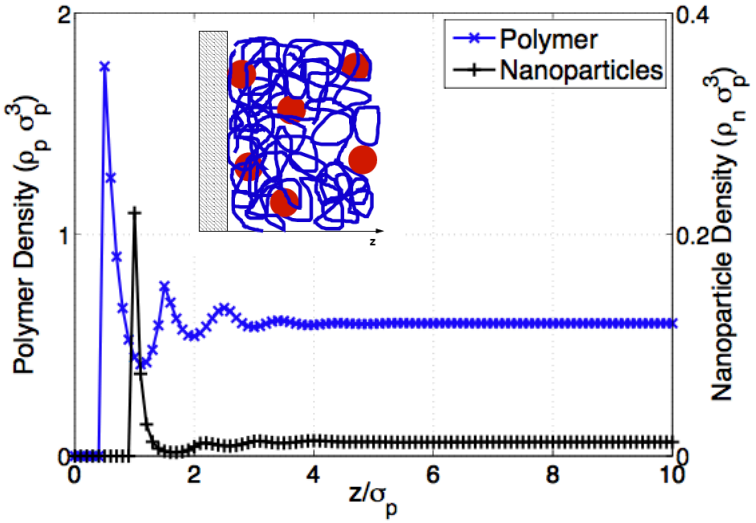


N = 40, D=2 ∫ H3nm

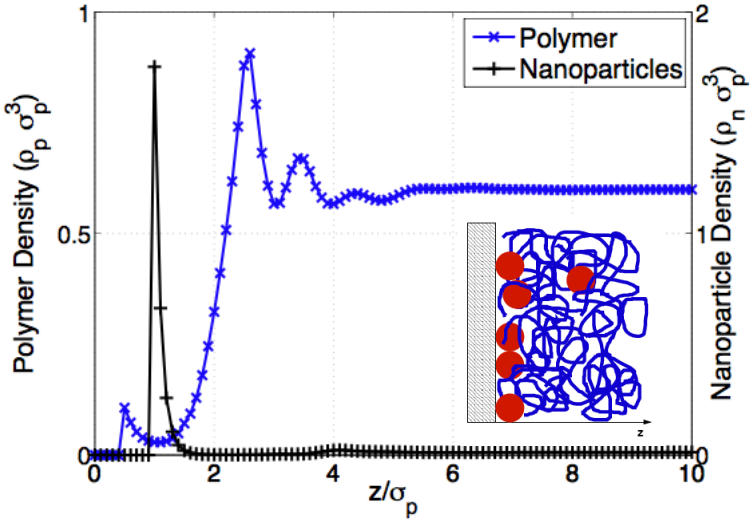
- fixed total packing fraction

$$\rho_p \sigma^3 + \rho_{np} \sigma_{np}^3 = 0.79$$

- first-order transition
- entropy-driven



typical fluid structure



NP layer, areal coverage 0.82

E. S. McGarrity et al., *Phys. Rev. Lett.*, **99**, 238302 (2007).

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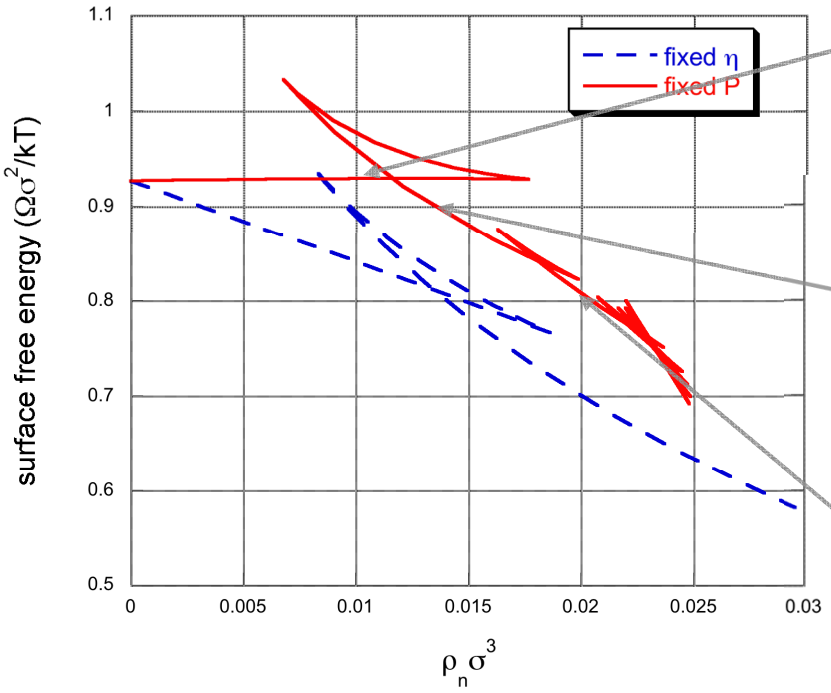
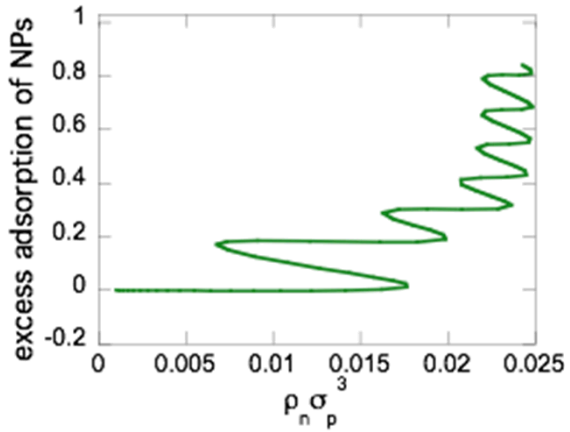
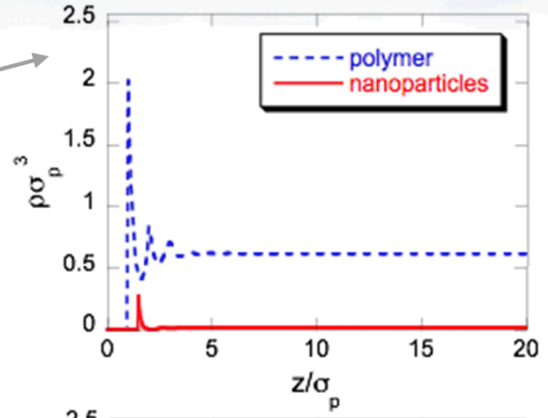
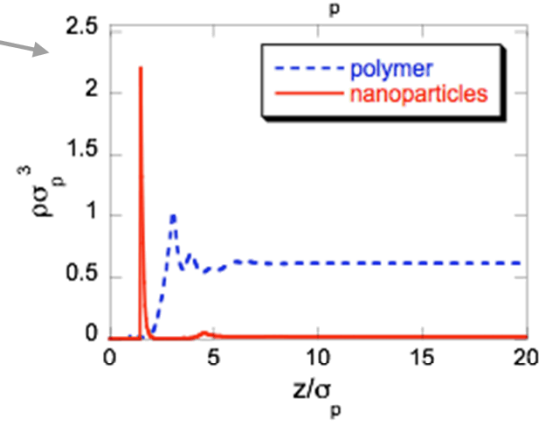
Constant pressure: still a transition

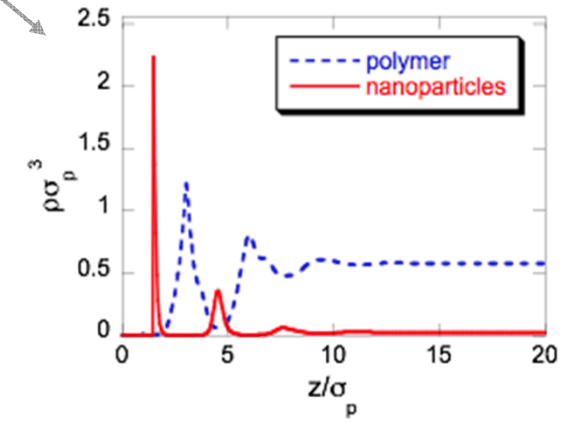
N=30, D=2 $\Gamma, | _0 = 0.37$







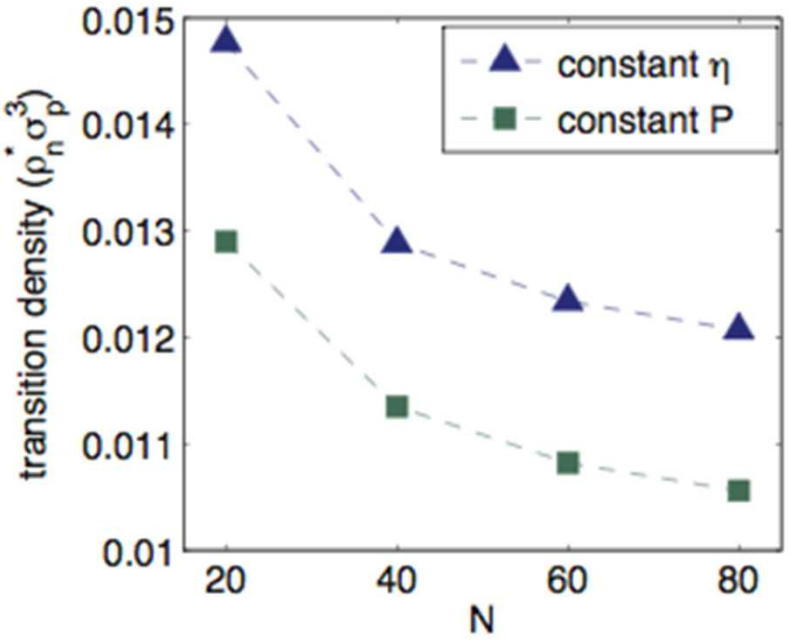




Balance of entropic terms

dependence on chain length

D = 2 ∫, | $_0 = 0.37$

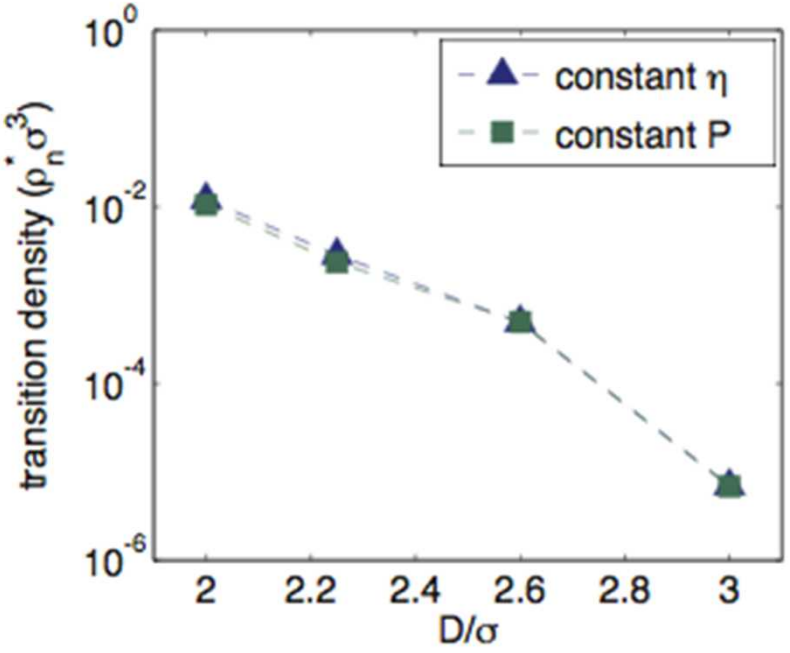


no transition for short chains

⟹ configurational entropy

dependence on NP size

N = 80, | $_0 = 0.37$



no transition for small particles

⟹ packing entropy

E. S. McGarrity et al., *J. Chem. Phys.*, **128**, 154904 (2008).

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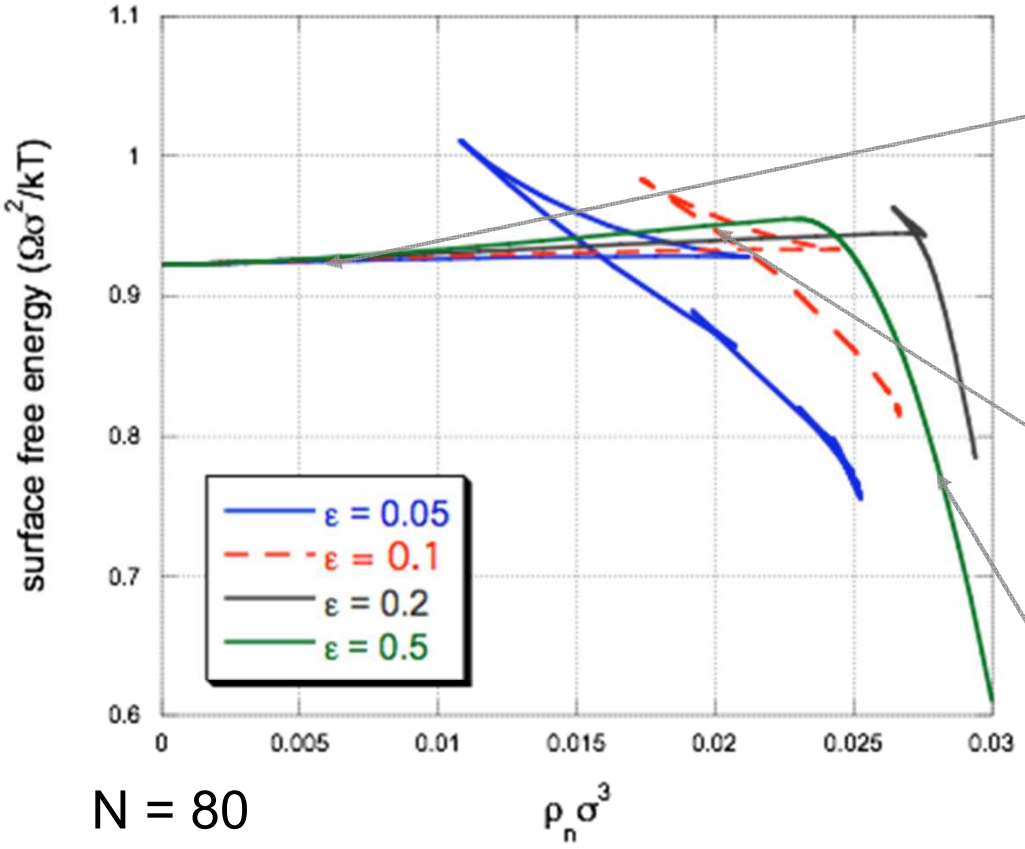
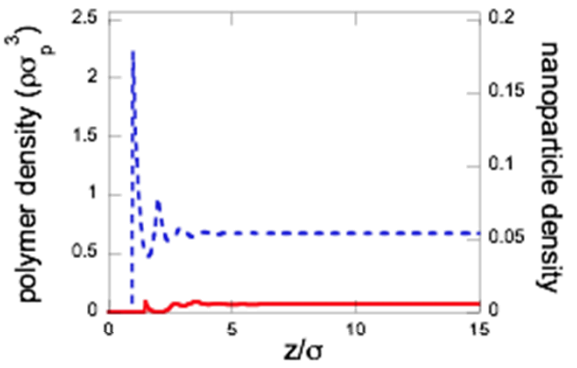
Effect of Attraction Strength

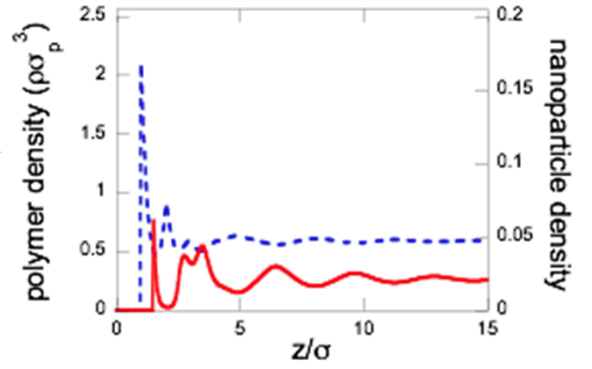
attractive potential $u_{np}(r) = -\epsilon e^{-(r-\sigma_{np})/\alpha}$

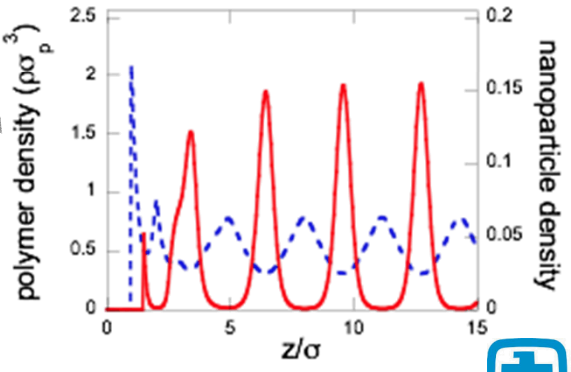


N = 80

σ_n = 2







- van der Waals loop vanishes at high ε
- transition becomes continuous

Frischknecht, A. L., Padmanabhan, V. & Mackay, M. E. *J Chem Phys* 136, 164904 (2012).

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Summary of NP Work

- modified iSAFT predicts NP surface segregation
  - first order phase transition
  - polymeric effect
  - entropy alone is sufficient to cause NPs to segregate to the surface
- transition still present for:
  - **constant pressure**
  - **monomer-particle attractive interactions**

E. S. McGarrity et al., *Phys. Rev. Lett.*, **99**, 238302 (2007).

E. S. McGarrity, A. L. Frischknecht, and M. E. Mackay, *J. Chem. Phys.*, **128**, 154904 (2008).

A. L. Frischknecht, V. Padmanabhan, M. E. Mackay, J. Chem. Phys., 136, 164904 (2012).

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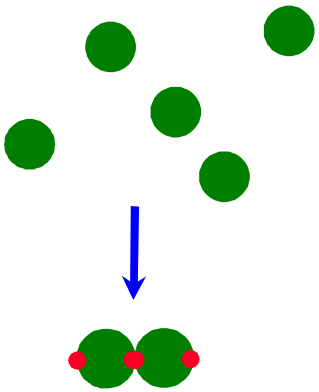
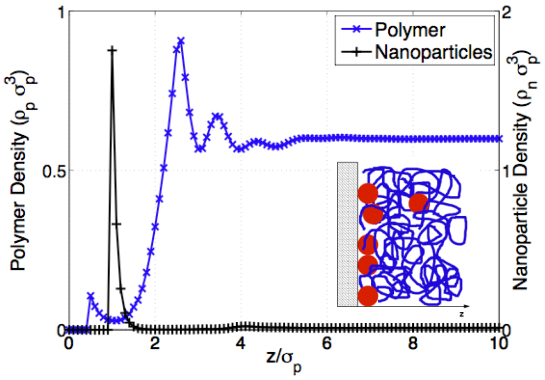
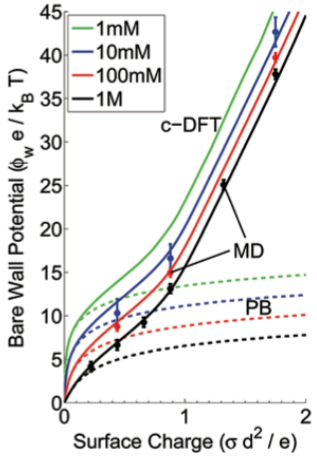
Outline

- classical density functional theory
- nanoparticle/polymer assembly
  - hard sphere systems
  - polymer-nanoparticle attractions
- **electrical double layers**
  - **hard sphere systems**
  - **electro-osmotic flow**







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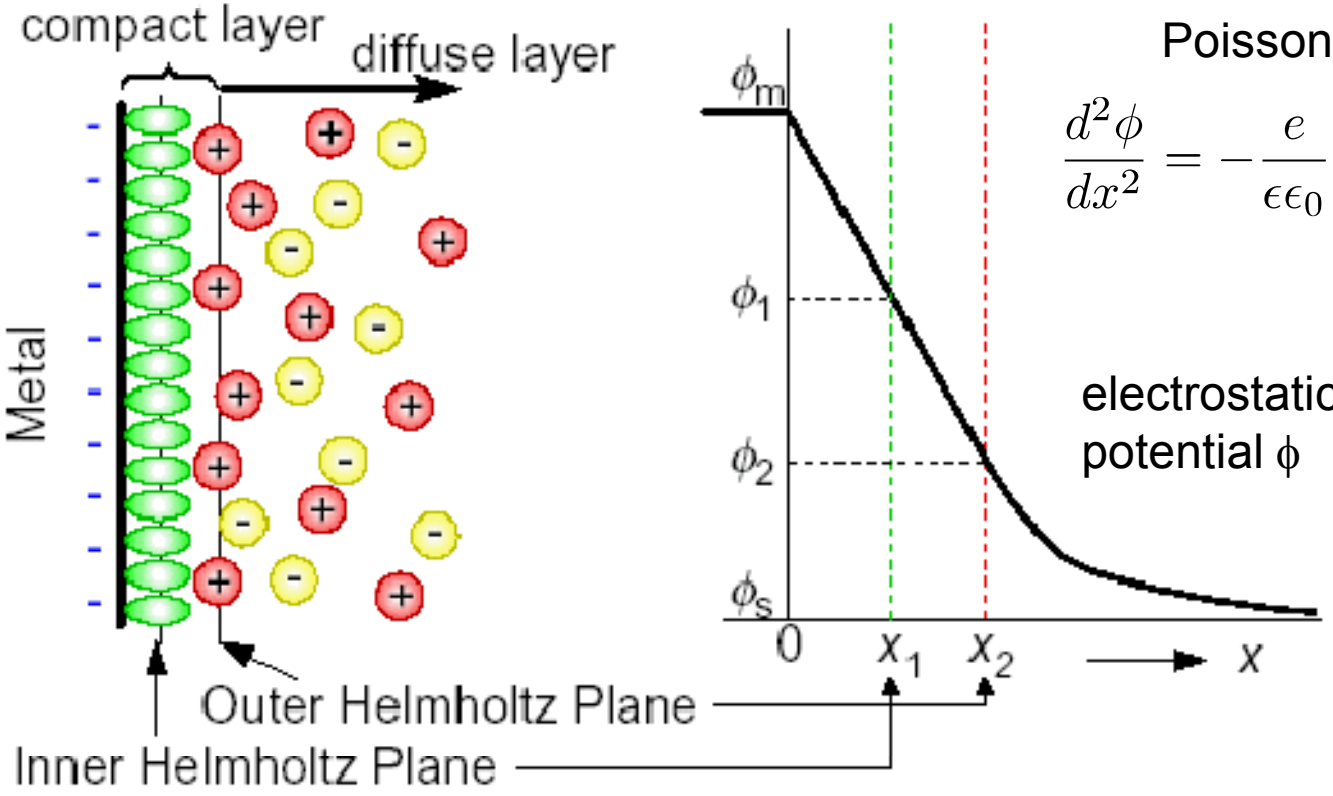
Classical Theory

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

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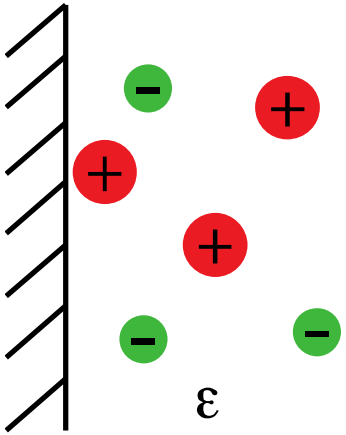
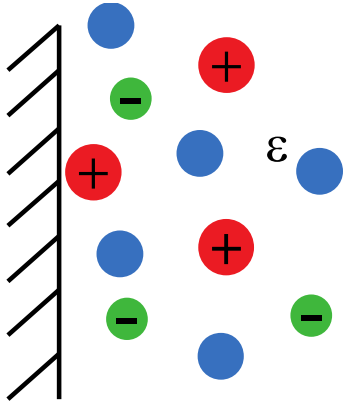
Application of DFT to the Double Layer

•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)
• if ions have same size, called restricted primitive model (RPM)



Semi-primitive model (SPM)
•charged hard spheres
•neutral charged solvent, dielectric ε
•charged hard wall

•also called 3-component model (3CM)

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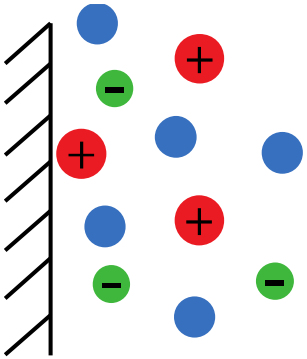
Free-energy for Double-Layer



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

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

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

mean-field electrostatics

where ϕ satisifes Poisson's eq with appropriate BCs

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

ion correlation term

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

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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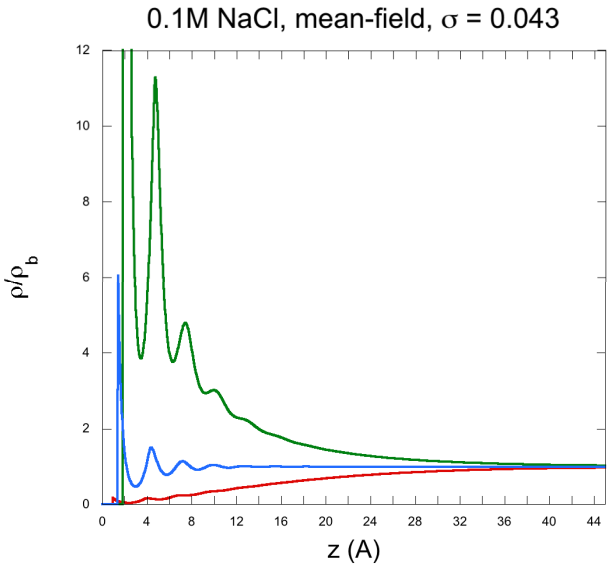
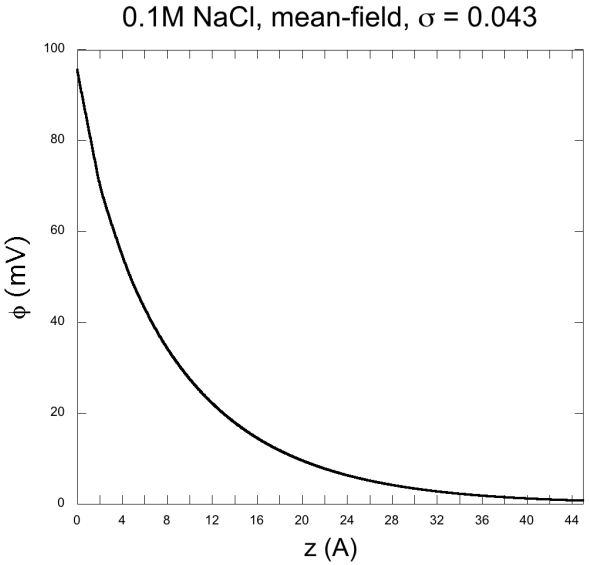
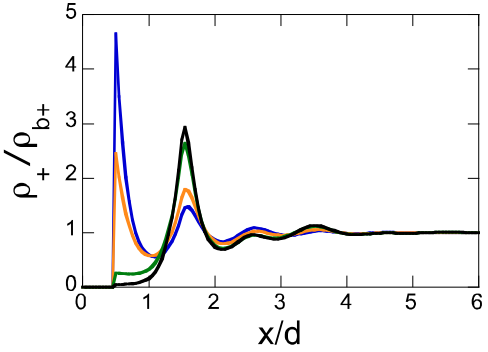
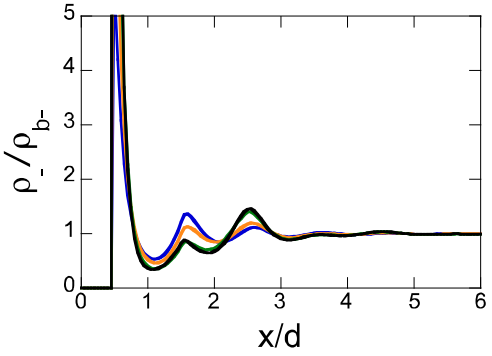
EDL from DFT



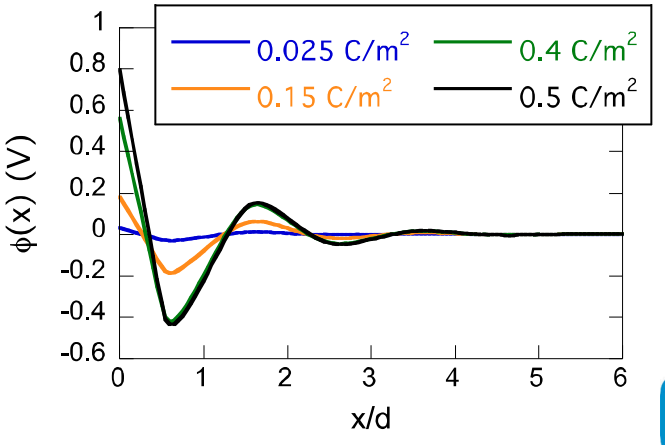
aqueous NaCl
T=300K
ε = 80







molten salt
T = 1400 K
ε = 10



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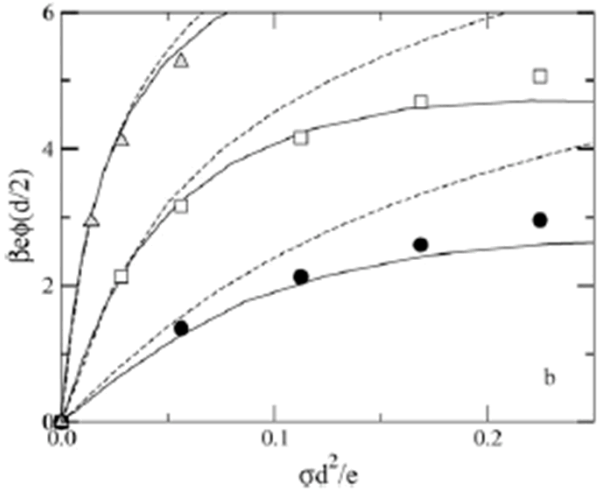
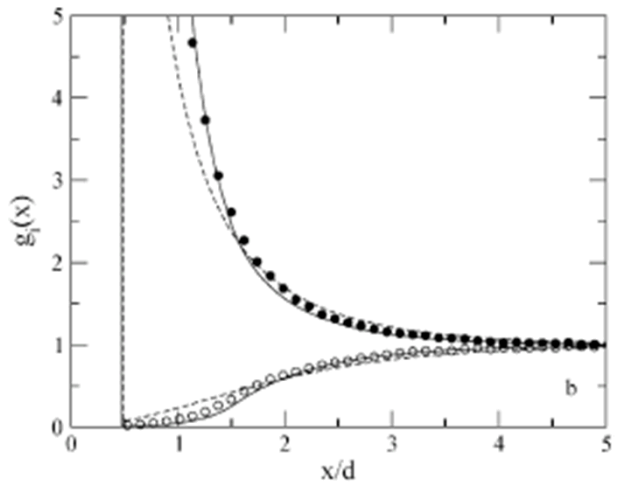
DFT Results: Primitive Model

Boda et al., J Chem Phys (2002) 116, 7170-7176

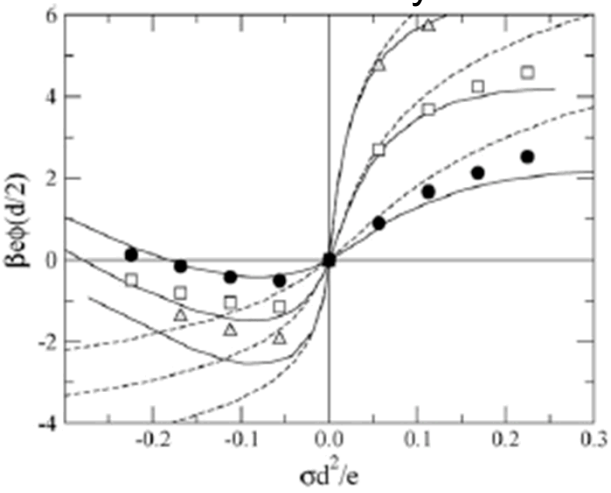
points = MC; solid lines = DFT; dashed lines = PB

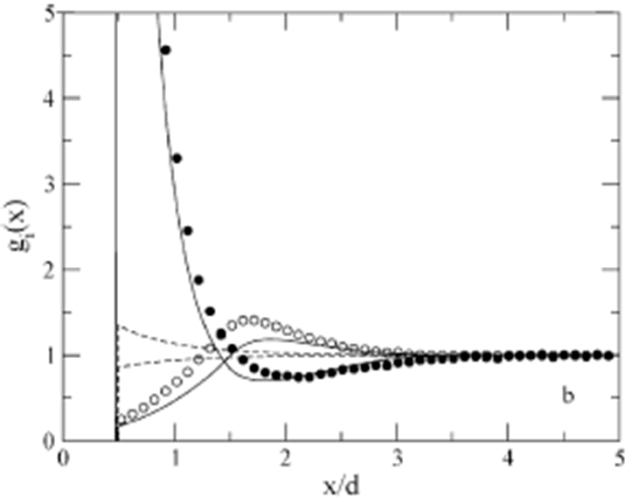
1:1 electrolyte





2:1 electrolyte





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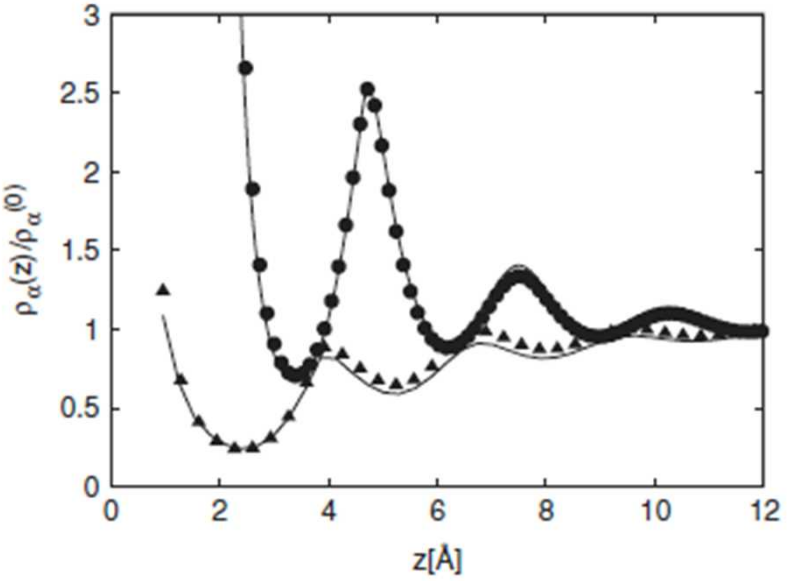
Semi-primitive model

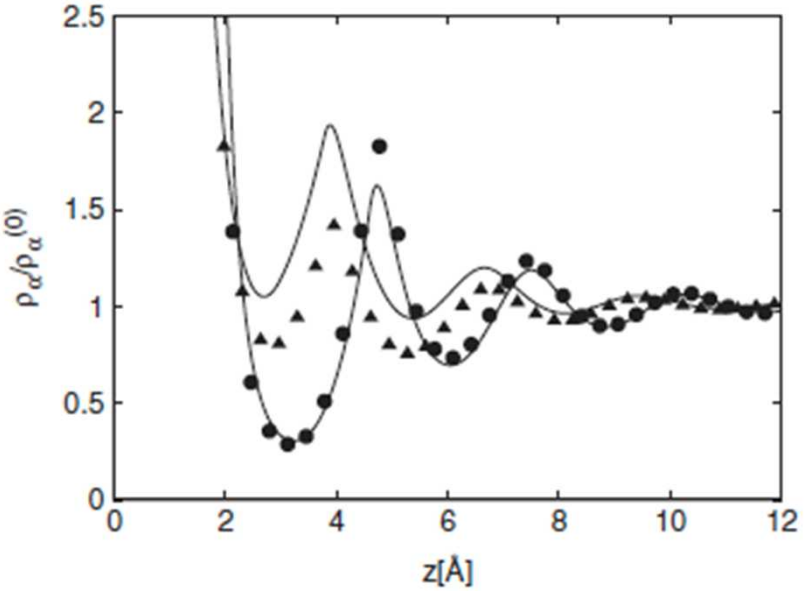
Oleksy and Hansen, Mol. Phys. (2006) 104, 2871-2883

- semi-primitive model
- all species have different sizes
- uses White Bear HS functional

1M NaCl, σ = 0.043



1M $CaCl_2$, σ = -0.087



also tabulate surface tensions, adsorptions

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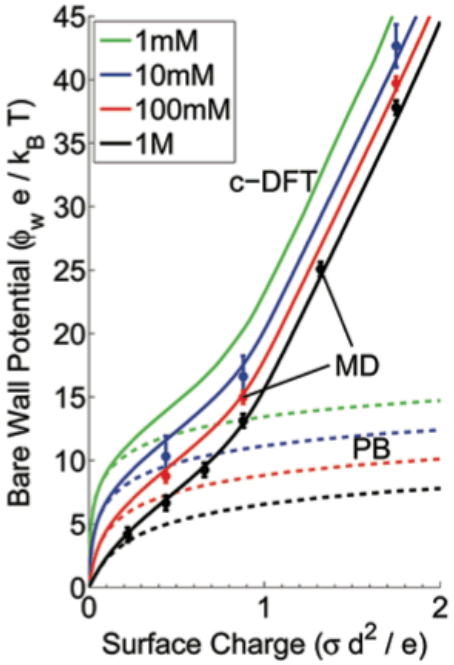
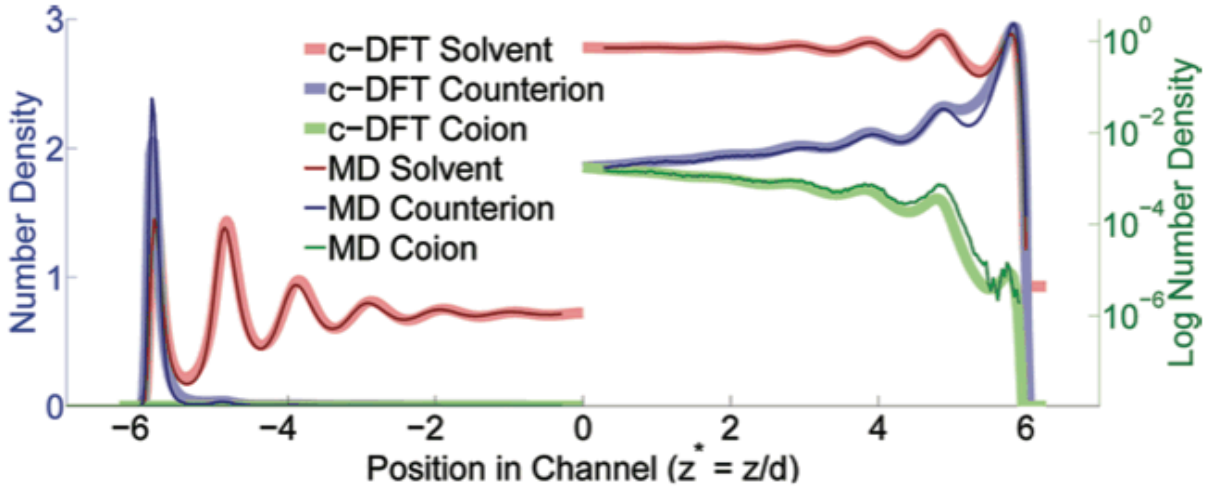
Comparison of DFT with MD, PB

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).

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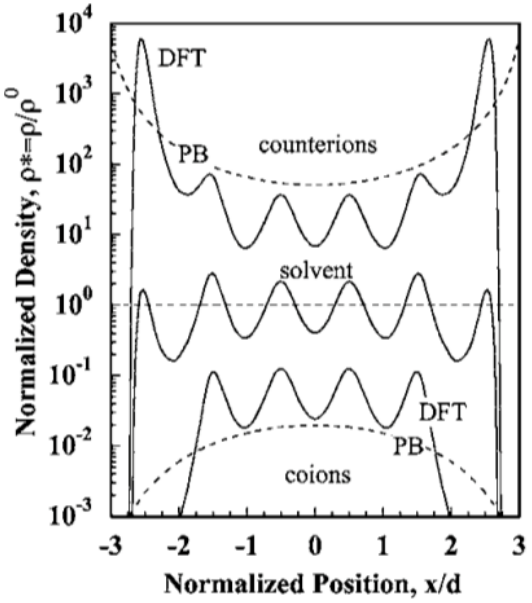
Application to EOF

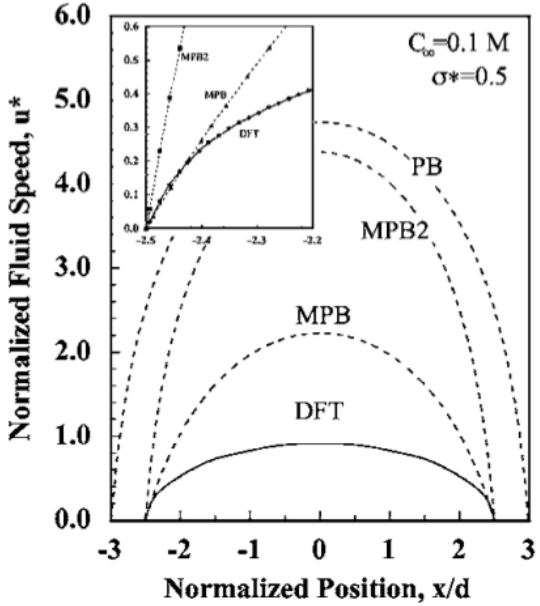
consider steady-state electro-osmotic flow in a channel aligned along *z*

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

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

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).

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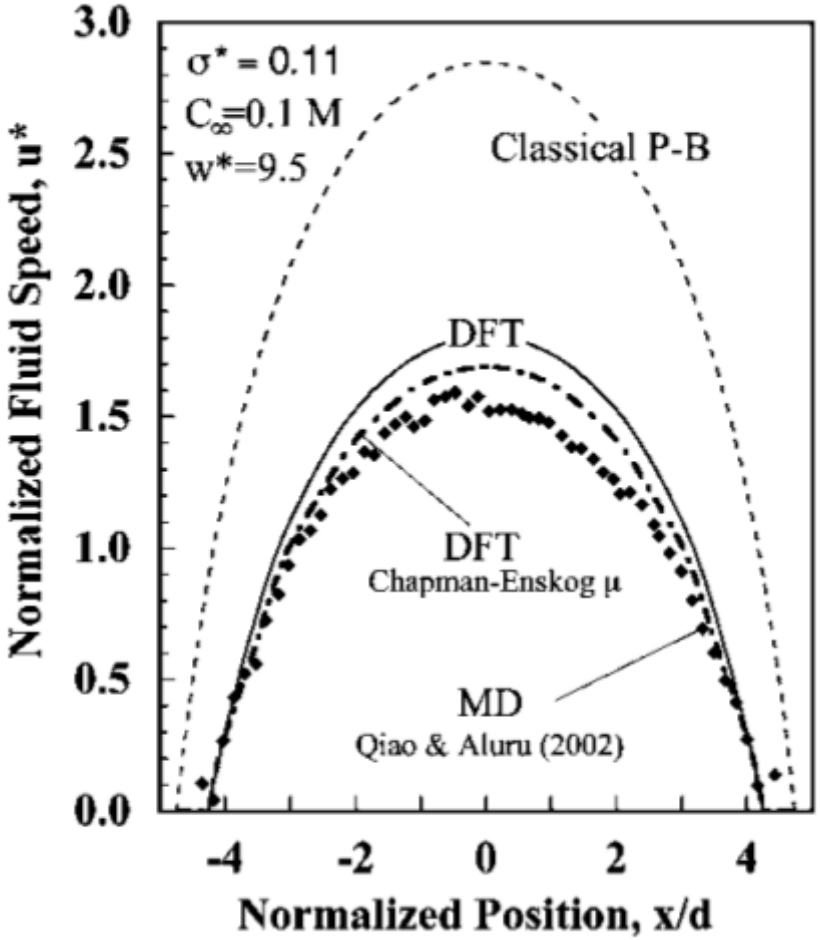
Comparison to MD



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).

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Conclusions

- DFT often accurate molecular model
  - faster than particle simulations
  - includes polymers, charges
- DFT goes beyond Poisson-Boltzmann
  - more accurate at high ion concentration
  - more accurate at high surface density
  - includes finite ion size, ion correlations

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Purdue

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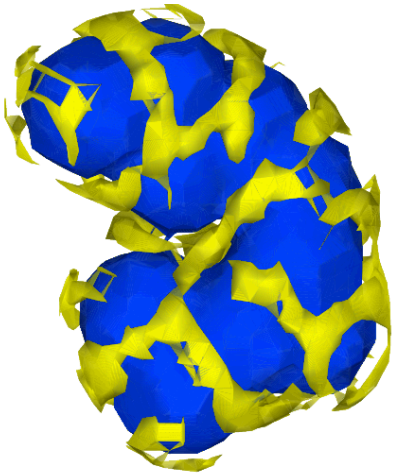
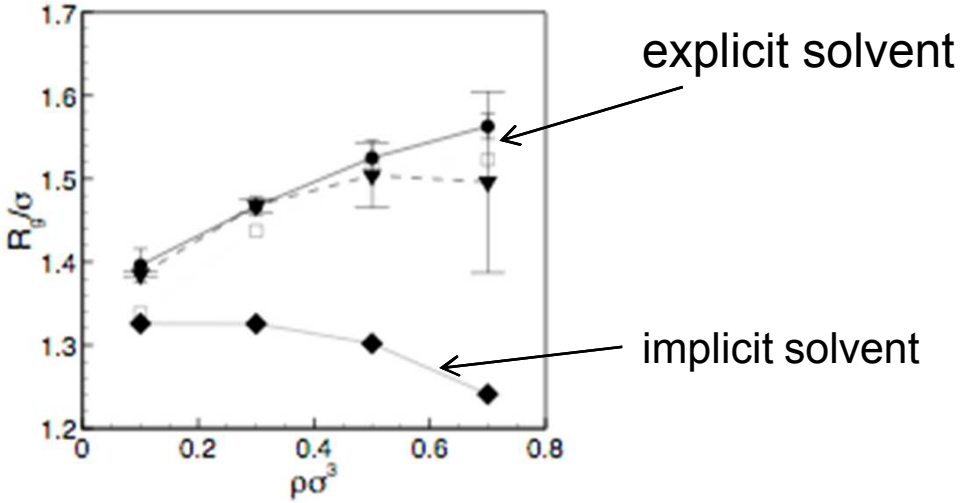
- LDRD
- ASC

Tramonto as a Solvent for Simulation

single chain polymer in LJ solvent

0. initial polymer configuration
1. polymer acts as external field for DFT
2. solve 3D DFT; calculate solvent potential of mean force on polymer
3. do MC step for new chain configuration; go back to 1.





L.J.D. Frink and M. Martin. Condens Matter Phys **8**, 271-280, (2005)

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