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Transport in Nanochannels and Nanoporous Materials

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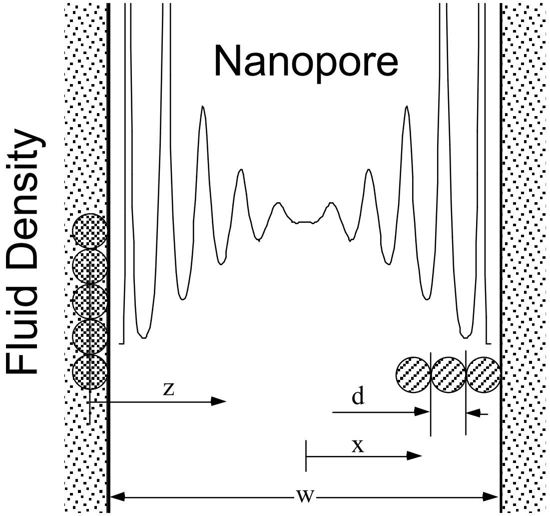
Fundamentals of Nanofluidics (LDRD)



Problem Description:

Continuum models fail to account for molecular physics of structured surface layers.

Molecular Dynamics (MD) simulations are too slow to address nanometer-to-millimeter domains of engineering interest.

Technical Approach:

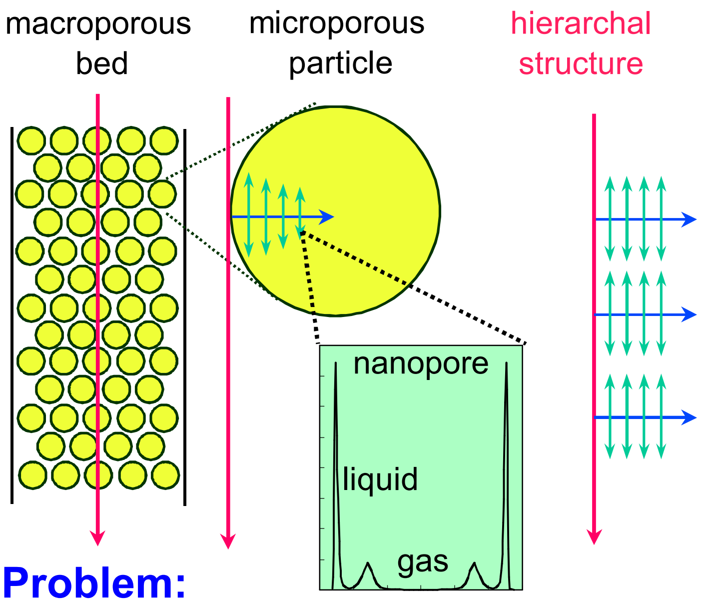
- Use Density Functional Theory (DFT) to model molecular-scale physics.
- Derive "wall functions" for incorporation of DFT physics into continuum models.
- Relate transport properties to DFT variables.
- Use DFT inputs to solve continuum transport equations.
- Validate with existing MD simulations and data.

Applications: NanoChannels & NanoMaterials enable new and enhanced functionality

- DHS: MicroChemLab devices, electrokinetic pumps
- DP: gas storage, supercapacitors, getters
- Energy/Water: H_2 & CH_4 storage, membrane filtration

Team: Bob Nilson (8755), Stewart Griffiths (8700), Aili Ting (8757), Greg Wagner (8757)

Multiscale Modeling of Transport in Hierarchal Nanoporous Materials (ESRF)



Problem:

- Optimal nanoporous materials entail a hierarchal pore network having --
  - •nanopores for surface area and functionality
  - •micropores for transport
- Requires multiscale hierarchal modeling as well as atomistic physics

Approach:

- Use DFT and MD to understand single-pore physics
- Incorporate DFT results into continuum-like models of multiscale, multiphase transport in complex materials.
- Use models to optimize storage capacity and rates of discharge/recharge for gas storage and electrical energy storage.

DP Applications:

- Gas Transfer Systems (H_2 storage)
- Double-layer super capacitors and batteries
- Getters for bulk gas and MEMS devices

Team Members:

R. H. Nilson, 8755
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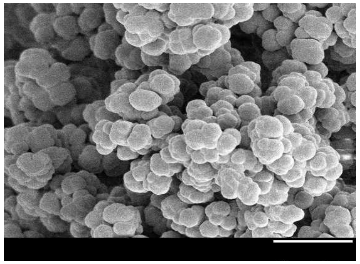
Intent & Applicability

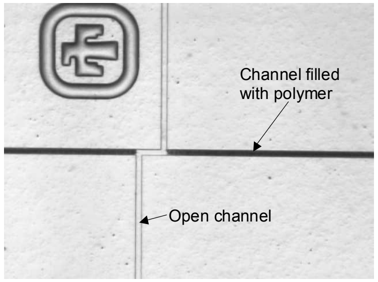


Technical Impact:

- Incorporate atomistic non-continuum physics into continuum-like models

Relevance to Mission: Enables invention and design of next generation systems

- DP: nanoporous materials for gas transfer systems, supercapacitors, pulsed-power energy supplies (radar, firing sets), getters
- Energy, Environment, Water: H_2 and CH_4 storage, capacitors & batteries for hybrid vehicles, catalytic beds and membranes, desalination & purification membranes
- DHS: Chem/Bio detection (Electroosmotic Flow, Separations, Pumps)



Connection to Experimental Studies & External Community:

- Sandia CA Microfluidics & Biosystems groups are largely experimental
- initiated LDRD project on Synthesis of Nanoporous Materials with University of Illinois, Evans Capacitor, Protonex Corp.
- initiated MSRF project on Characterization of Nanoporous Materials with LLNL (aerogels)
- NSF/Sandia projects on “Liquid Motion in NanoEnvironments” by Yu Qiao at UCSD and “Wall Mediated Transport” by K.S. Breuer at Brown

Density Functional Theory (DFT) seeks density distributions minimizing free energy

Define free energy functional

- ρ = fluid density
- V = external "field" of solid
- γ = chemical potential
- U = L-J fluid/fluid interaction
- $\Delta\psi$ = hard sphere repulsion
- Φ = electrical interaction

$$\Omega[\{\rho\}] = \sum_i \int \rho_i(\mathbf{r}) \left(F[\rho_i(\mathbf{r})] + V(\mathbf{r}) - \gamma_i \right) d\mathbf{r}$$

$$F[\rho_i(\mathbf{r})] = kT \ln\left[\Lambda^3 \rho_i(\mathbf{r})\right] + \frac{1}{2} U_i(\mathbf{r}) + \Delta\psi_i(\mathbf{r}) + \Phi_i$$

$$U_i(\mathbf{r}) = -4 \sum_j \varepsilon_{LJ} \int \rho_j(\mathbf{r}') \left[\left(\frac{\sigma}{s}\right)^6 - \left(\frac{\sigma}{s}\right)^{12} \right] d\mathbf{r}'$$

$$\Phi_i(\mathbf{r}) = q_i \phi(\mathbf{r}) + \Delta\Phi_i^{\text{short range}}$$

Apply Variational Principle

$$\frac{d\Omega}{d\rho_i} = 0$$

Yields expression involving

- DFT adjustment to local chemical potential, $\Delta\gamma$
- Σs over surrounding density field

$$\frac{\rho_i(\mathbf{r})}{\rho_i^0} = \exp\left(-\frac{q_i \phi_i(\mathbf{r}) - \gamma_i^0 - \underline{\Delta\gamma_i(\mathbf{r})}}{k_B T} \right)$$

$$\underline{\Delta\gamma_i(\mathbf{r})} = U_{LJ_i}(\mathbf{r}) + V_i(\mathbf{r}) + \Delta\psi_{hs_i}(\bar{\rho}(\mathbf{r})) + \Delta\Phi_i^{\text{short range}}$$

Discretize and Solve

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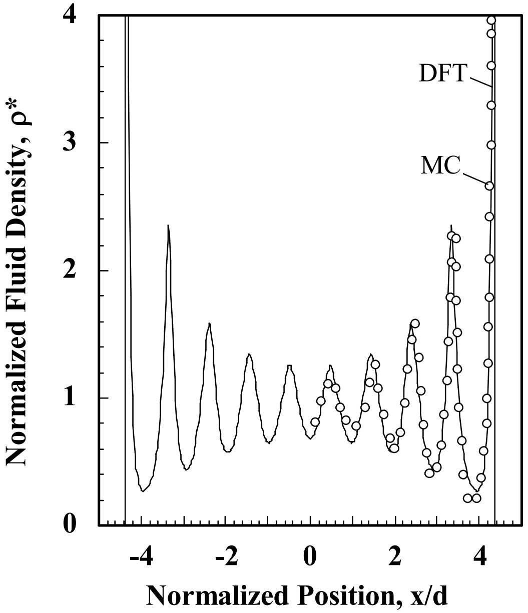
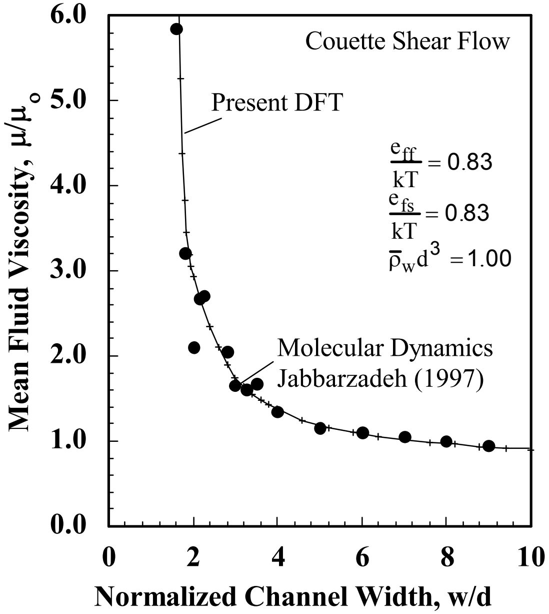
DFT results agree with Monte Carlo and Molecular Dynamics Simulations



Density Profiles across Nanochannels



Viscosity Variation with Channel Size

Chapman-Enskog model provides local viscosity.

$$\mu = \mu(\hat{\rho}, T, M)$$

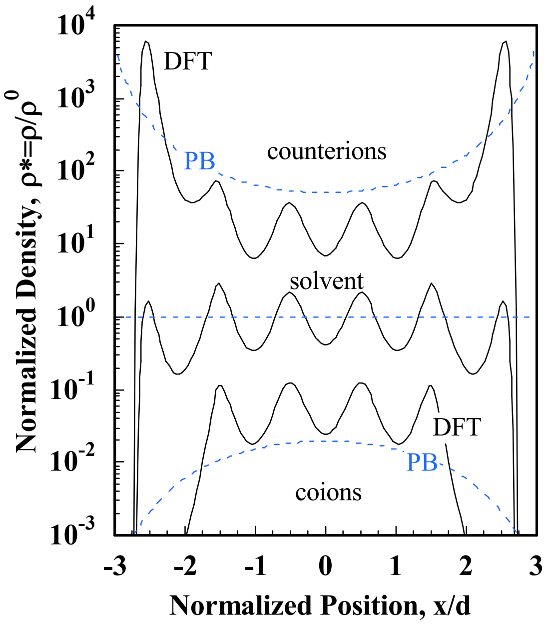
$$\hat{\rho} = \frac{1}{V}\int_V \rho \, d\mathbf{r}$$

Solve continuum equation for velocity field.

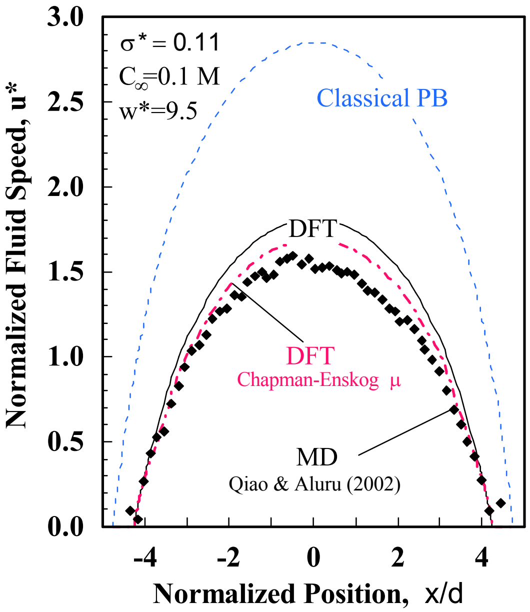
$$\frac{\partial}{\partial x}\left(\mu \frac{\partial u_z}{\partial x}\right) = F_z$$

Equilibrium profiles not disturbed for u<100 m/s

Modeling of Electric Double Layers: DFT vs. classical Poisson-Boltzmann (PB) model



DFT predicts fewer counterions in channel center



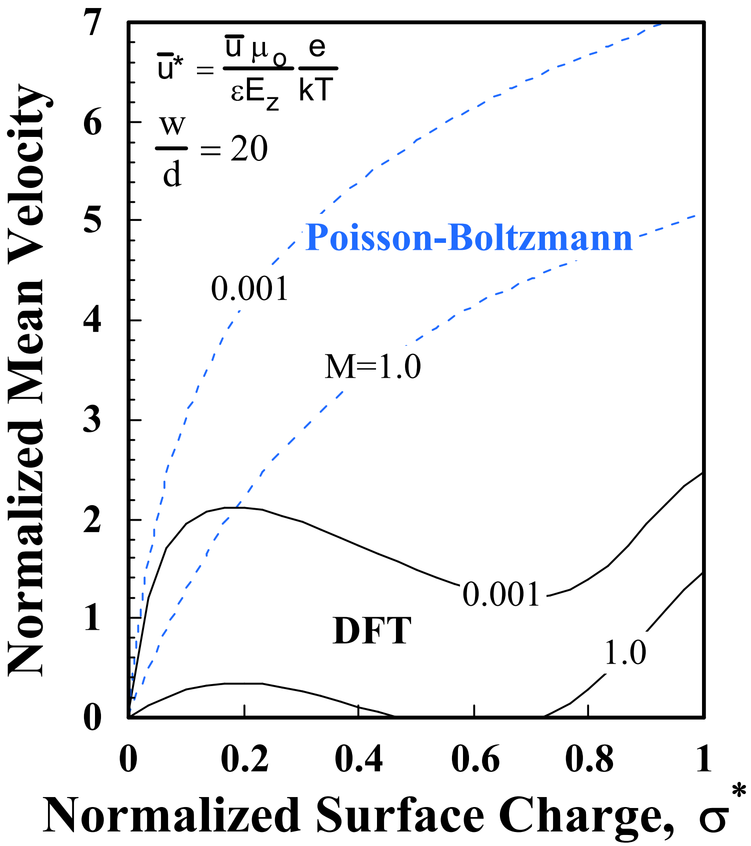
DFT predicts slower electroosmotic speeds

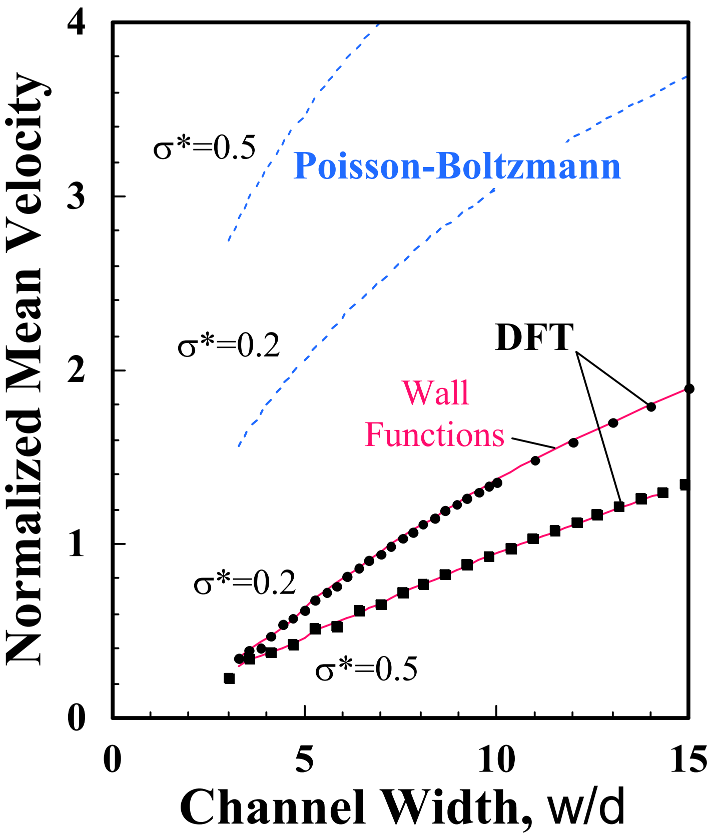
Electroosmotic motion is produced by action of axial electric field, E_z, on local charge density in fluid

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

- Ion distributions, ρ_i, computed from DFT

Electroosmotic Flow:
Disparity between DFT and PB increases with increasing charge and decreasing channel size





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“Wall Functions” based on DFT can be easily introduced into continuum codes

Transport is driven by velocity, **u**, and by gradients in species chemical potential, γ_i

$$\nabla \cdot \left(\rho_i \mathbf{u} - \upsilon_i \rho_i \nabla \gamma_i\right) = 0$$

Classical chemical potential depends on electric field and density

$$\gamma_i = \gamma_i^o + z_i e \phi + kT \ln \rho_i$$

DFT chemical potential includes additional terms that comprise wall functions, $\Delta\gamma_i$

- computed from DFT solution

$$\gamma_i = \gamma_i^o + z_i e \phi + kT \ln \rho_i + \underline{\Delta\gamma_i}$$

$$\underline{\Delta\gamma_i(r)} = U_{LJ_i}(r) + V_i(r) + \Delta\psi_{hs_i}(\bar{\rho}(r)) + \Delta\Phi_i^{elec}$$

“Wall Functions” derived from DFT are relatively insensitive to channel width

Hard sphere repulsions and Lennard Jones interactions

- produce an oscillatory correction
- common to all species

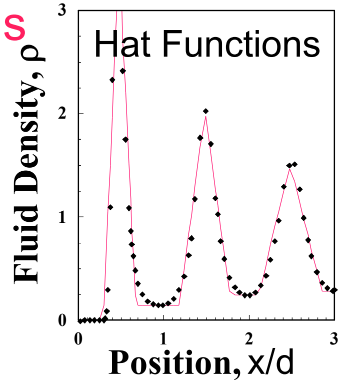
Non-coulombic electrical interactions

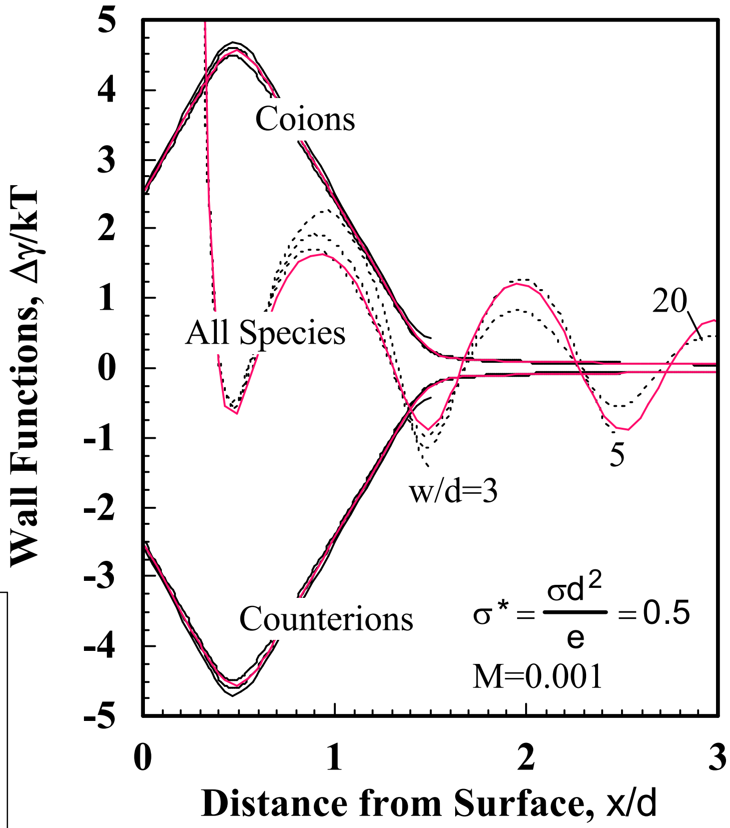
- opposite signs for counterions and coions

Wall functions computed for w/d=10 are applicable to all channels w/d>3

Approximate wall functions

- coarse-grained
- based on “hat” functions
- match mean and peak
- computed “on the fly”
- needed for transients & supercapacitor





Gas Storage Systems: DFT provides density profiles for use in modeling of transient pore condensation

Pore condensation process

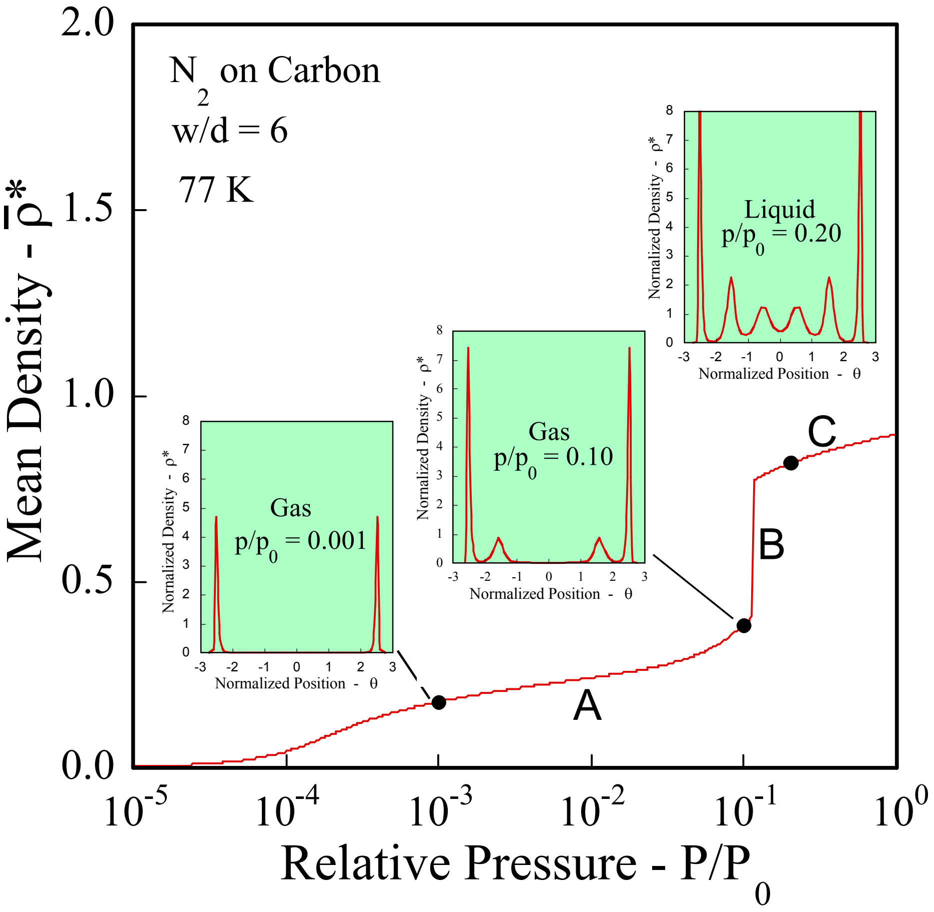
- adsorbed layer formation (A)
- condensation jump (B)
- liquid densification (C)

Mean pore density $\bar{\rho}(P,T;w)$ serves as EOS for quasi-1D modeling

Density profiles used to compute gas & liquid flow

- velocity profiles (gas & liquid)
- mass transport coefficients, J

$$\overline{\rho u} = -J\frac{dP}{dx} \qquad J = J(P,T;w)$$



Gas Storage Systems: "Compact" DFT-based models enable multiscale modeling of hierarchal media

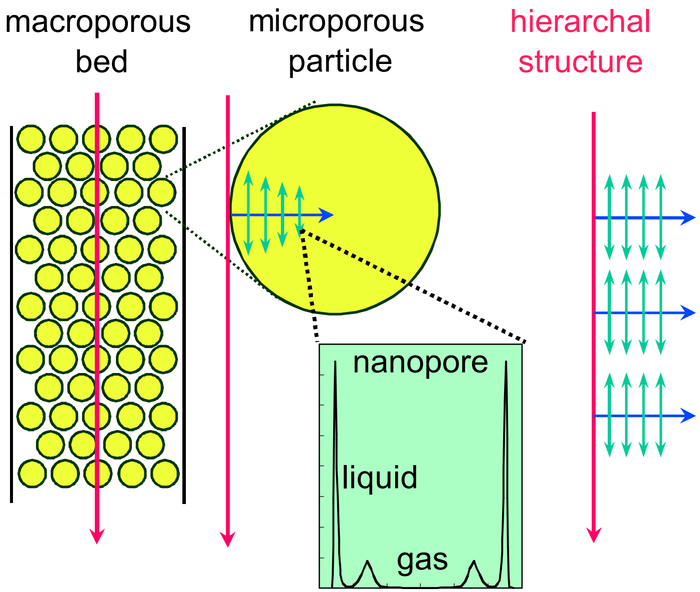
Quasi-1D model of gas/liquid flow based on DFT inputs:

$$\frac{d\bar{\rho}}{dt} = -\frac{d}{dx}\left(\overline{\rho u}\right)$$

$$\underline{\left[\frac{d\bar{\rho}}{dP}\right]_{DFT}} \frac{dP}{dt} = \frac{d}{dx}\left(\underline{J}\,\frac{dP}{dx}\right)$$

Viscous flow from DFT is blended with low-pressure Knudsen-like asymptote for adsorbing walls

$$J = \underline{J_{\text{viscous}(L+G)}} + J_{\text{free molecular}(G)}$$



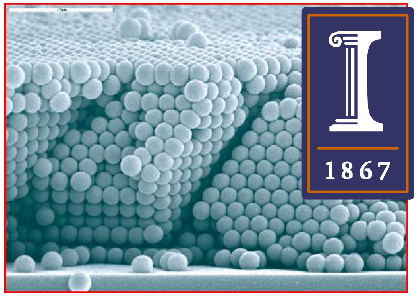
Similar approach should work for modeling EDL supercapacitors

- begin with 2D modeling of single-pore ion transport using DFT & wall functions
- distill to quasi-1D if needed (gradients in ion concentration and electric potential)

Complementary LDRD project addresses synthesis of optimized nanoporous materials

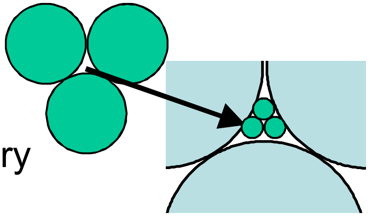
With University of Illinois (UIUC)

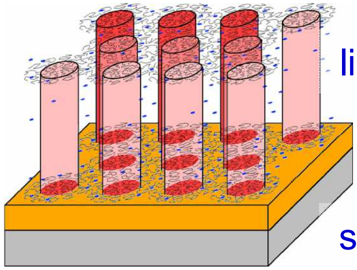
- Drs. Paul Braun & Eric Luijten & students



Material synthesis and functionalization

- templating by self-assembly
- liquid crystal, block copolymer, colloids
- combined techniques for hierarchical and dendritic topologies



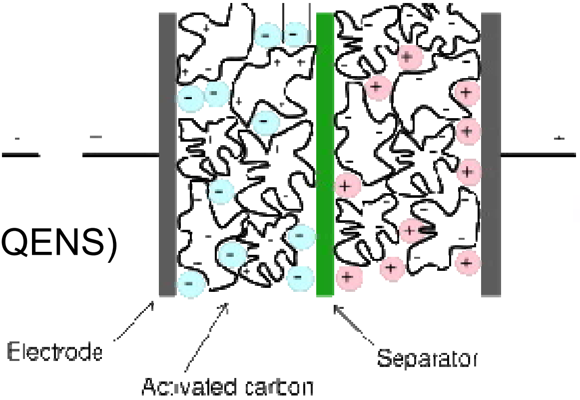


Material characterization

- x-ray diffraction, TEM, porosimetry

Transport model validation by comparison with measured --

- adsorption isotherms
- gas uptake rates
- capacitor charge/discharge rates
- quasi-elastic neutron scattering (QENS)



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Summary of Accomplishments and Future Directions

Nanofluidics (LDRD)

- developed new DFT approach for incorporation of atomistic physics into continuum modeling
  - seconds to minutes - not hours to days for MD
- implemented via wall functions applicable in any continuum code
- demonstrated impact on nano-to-macro scale flows
- optimized performance of “Autogeneous” Separations and Electrokinetic Pumps

Multiscale Transport in Nanoporous Materials (ESRF)

- extended DFT-to-Continuum methodology to gas/liquid flows
  - including free molecular flow
- developed efficient fully-coupled non-iterative algorithm for solving transport equations in hierarchal media (nano, micro, macro)

Future Directions

- apply to charge/discharge of EDL supercapacitors (approx. wall functions)
- experimental validation (pore condensation & capacitors)
- computational optimization of hierarchal materials (submitted LDRD proposal)
- filtration processes, catalytic membranes, protein separations (LDRD proposal)

Journal Articles and Presentations

Journal Articles

- "Influence of atomistic physics on electroosmotic flow: an analysis based on Density Functional Theory," ***Journal of Chemical Physics***, 125 (16): No. 164510, 1-13, Oct 2006.
- "Charged Species Transport, Separation and Dispersion in Nano-Scale Channels: Autogenous Electric Field-Flow Fractionation", ***Analytical Chemistry***, 78 (23): 8134-8141, Dec 2006.
- "The efficiency of electrokinetic pumping at a condition of maximum work," ***Electrophoresis*** 26 (2) 351-361, Jan 2005.

Symposium Papers

- "Wall functions for incorporation of atomistic physics into continuum modeling of electroosmotic flow," ***Proceedings of Nanotech 2006***, Boston, ISBN 0-9767985-9-X, Vol. 3 (5) 503-506, May 2006.
- "Hybrid atomistic/continuum modeling of electroosmotic flow in nanoscale channels," ***Proceedings of MicroTAS 2005***, Boston, ISBN 0-9743611-1-9, Vol. 1, 235-237, October 2005.
- "Modeling nanoscale flows by combining density functional theory with classical continuum mechanics," ***8th US National Congress on Computational Mechanics***, (invited talk) Austin, July 24-28, 2005.

In Preparation

- "Incorporation of Atomistic Physics into Continuum Modeling of the Electric Double Layer", for ***Journal of Colloid and Interface Science***.

End of Presentation

Slides beyond this point are backup material.

Approach: combine Density Functional Theory with classical continuum mechanics

Density Functional Theory (DFT) provides a rigorous description of molecular physics

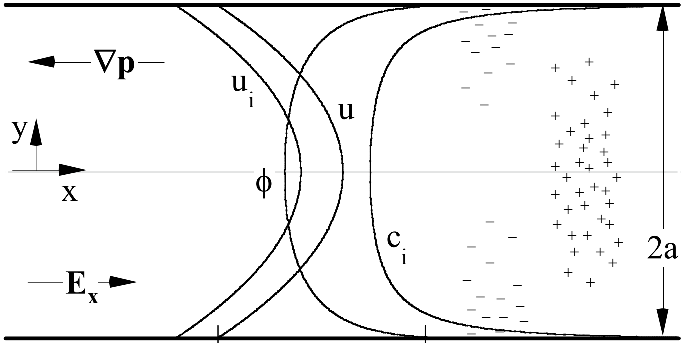
- same inputs as MD (intermolecular potentials)
- integral equations yield continuous density distributions
- facilitates formulation of compact “wall-function” and “layer averaged” models
- CPU times measured in seconds rather than hours or days for MD

Constitutive models relate transport properties to DFT density and energy distributions

Continuum model of fluid flow and transport incorporates atomistic physics through --

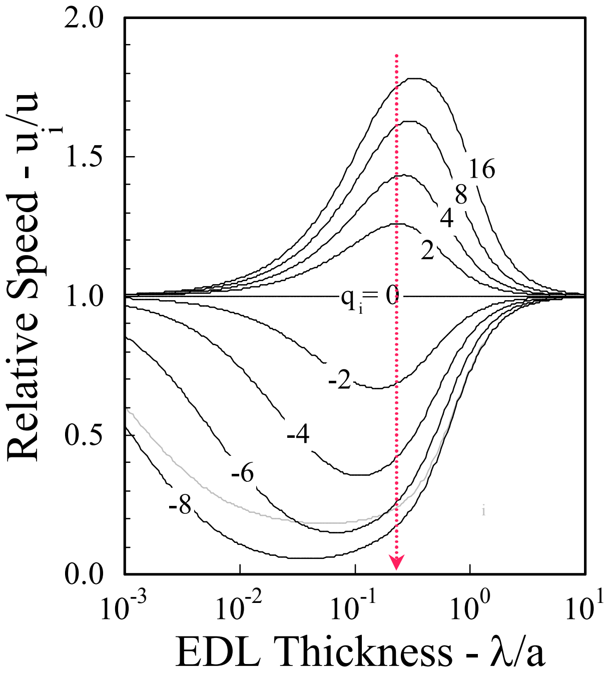
- DFT distributions of chemical and ion species
- wall functions: electrochemical potential functions derived from DFT
- transport properties

Application: “Autogenous” Separation of charged species in nanochannels



Intrinsic potential field within EDL produces transverse separation of charged species

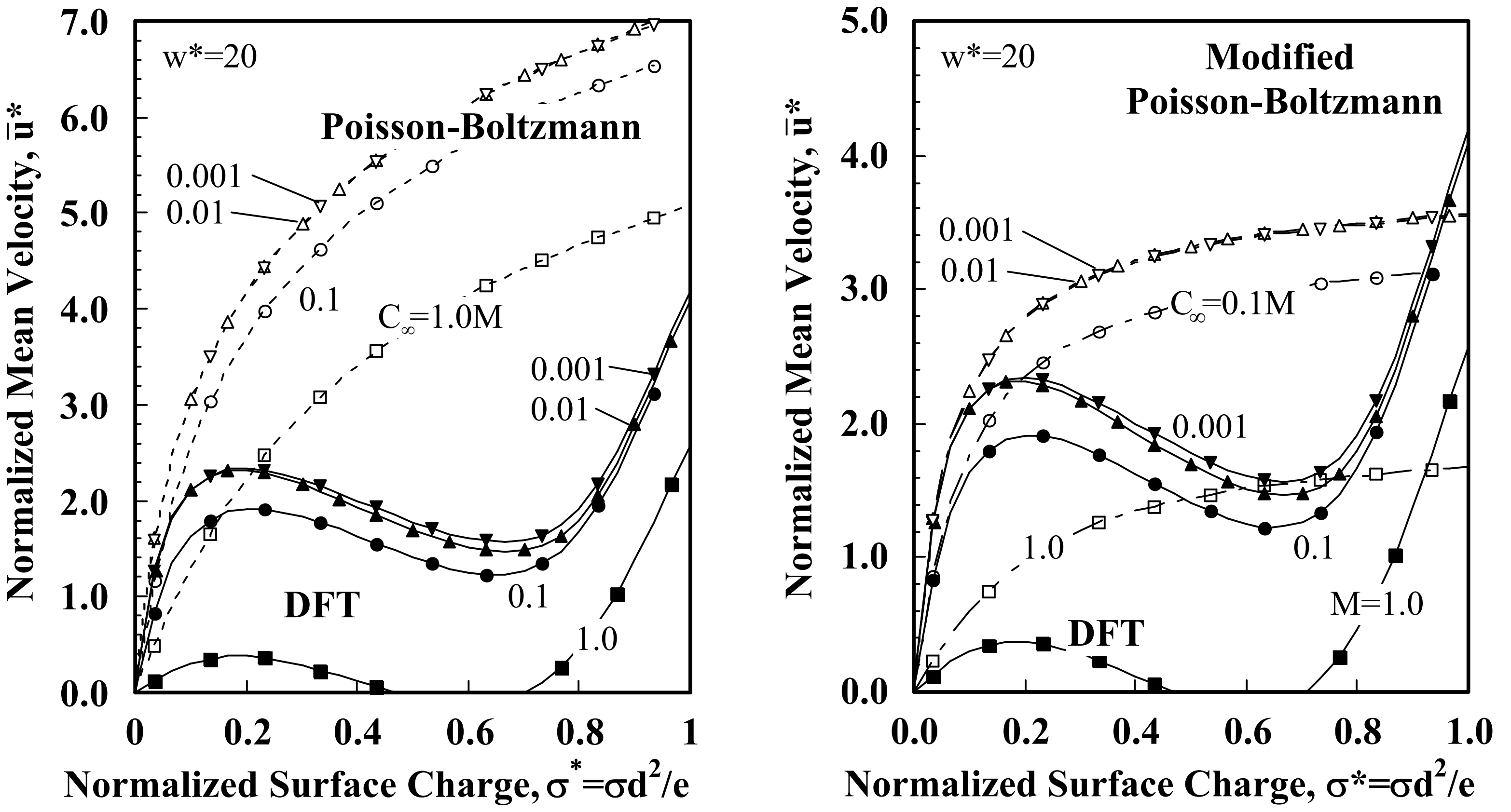
- counterions near wall advect slowly
- coions in center advect fastest
- produces axial separation
- only works when channel width is comparable to EDL thickness



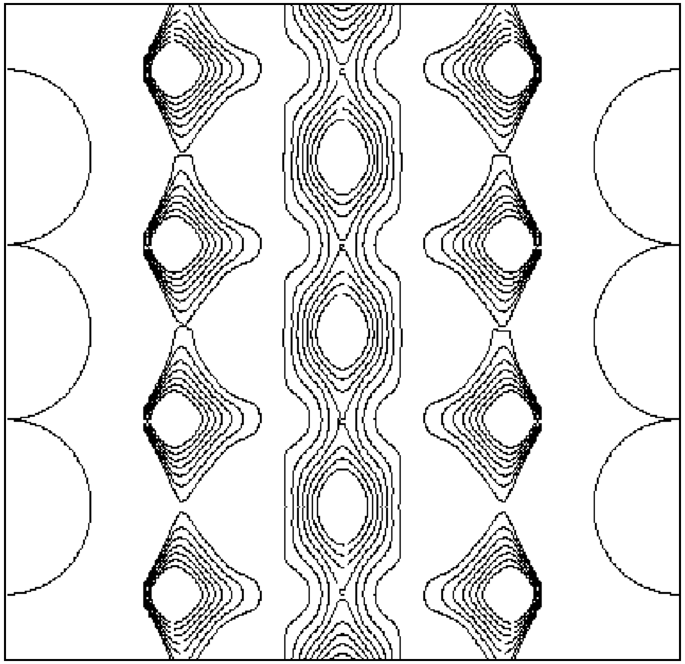
Showed that --

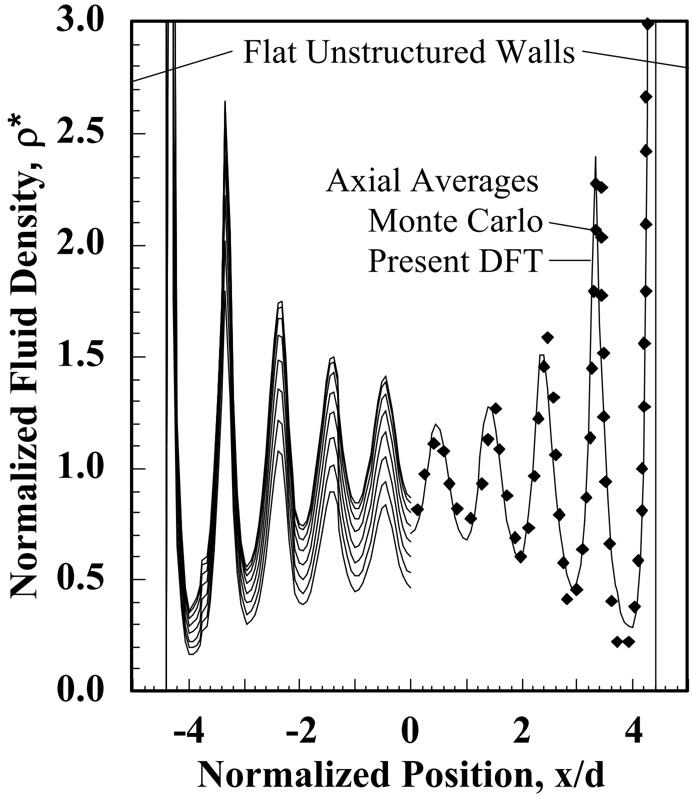
- unique identification is possible for pressure-driven flow
- non-unique for electroosmotic flow due to electromigration

Classical vs. Modified Poisson-Boltzmann: Modified PB shifts location of no-slip BC



Two-Dimensional DFT: Axial average of 2D calculation is consistent with 1D result





Modeling of Gas Storage Systems: Model is completed by blending viscous flow from DFT with low-pressure Knudsen asymptote

$$\frac{d\bar{\rho}}{dt} = -\frac{d}{dx}(\rho u)$$

$$\left[\frac{d\bar{\rho}}{dP}\right]_{\mathrm{DFT}} \frac{dP}{dt} = \frac{d}{dx}\left(J \frac{dP}{dx}\right)$$

Two forms of asymptotic blending:

- Blend viscous gas/liquid flow with free molecular gas flow

$$J = J_{\text{viscous}(G+L)} + J_{\text{free molecular}(G)}$$

- Separate treatment of gas and liquid flows

$$J = J_{\text{viscous}(L)} + \left(J_{\text{viscous}(G)} + J_{\text{free molecular}(G)}\right)$$

Working on low pressure asymptote for adsorbing walls