

# Multiscale Simulation of Electroosmotic Transport Using Embedding Techniques

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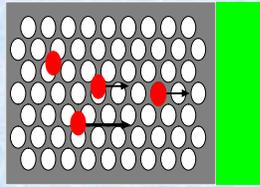
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## Outline

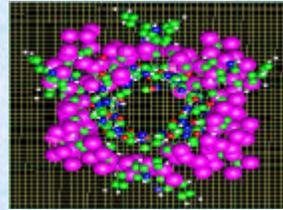
- ◆ **Overview: multiscale simulation methods for different applications**
- ◆ **Gas flow in micro/nanochannels**
  - Meshless Continuum-DSMC coupling
  - Simulation results
- ◆ **Ion transport in nanopores**
  - Parameterized multiscale simulation method
  - Simulation results
- ◆ **Electroosmotic transport in micro/nano channels**
  - Continuum and atomistic simulation methods
  - Multiscale simulation based on embedding techniques
    - Modified Poisson Boltzmann equation
    - Velocity embedding technique
- ◆ **Conclusions**

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## Overview: Multiscale Methods for Different Applications



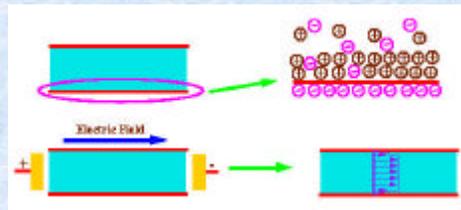
Gas Flows in Micro/Nano-fluidic Channels



Nanobiotechnology



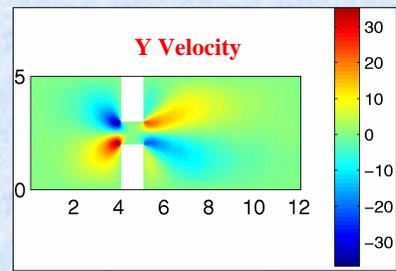
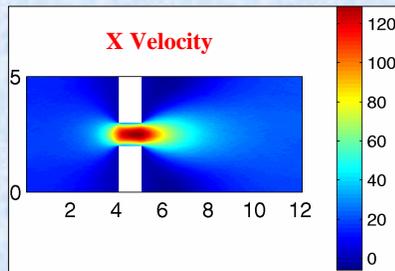
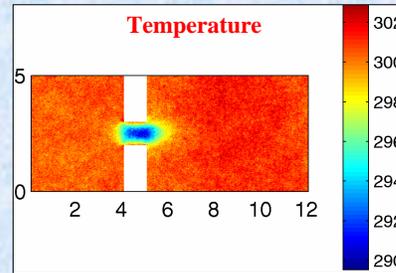
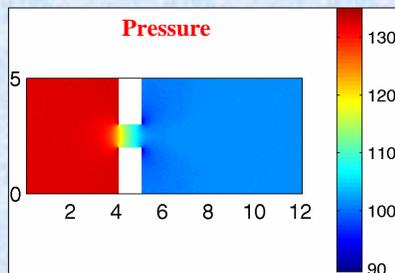
Nanoelectromechanical Systems (NEMS)



Nanoscale Liquid flows in the presence of charge

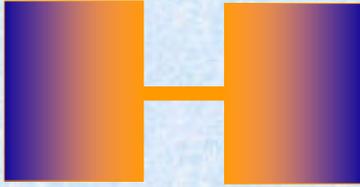
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## Gas flow in a 1mmX1mm Filter Element



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## Towards Multiscale Analysis



### Observations:

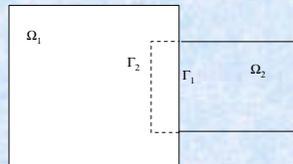
- MC required in the channel, and close to surfaces to capture rarefaction effects
- Input/output regions are approximately incompressible
- Combined continuum/molecular analysis

### Meshless Continuum-DSMC coupling

- **Meshless continuum: No need for meshing**
  - Can employ arbitrary shape for the interface
  - Can use arbitrary shaped continuum domains
- **Formulation and coding is easy**

*Aktas and Aluru, J. Comput. Phys. 178, 342, 2002*

## Alternating Schwarz Method



*Begin* :  $n = 0$ ;  $u_2^{(0)}|_{G_1}$  = initial condition

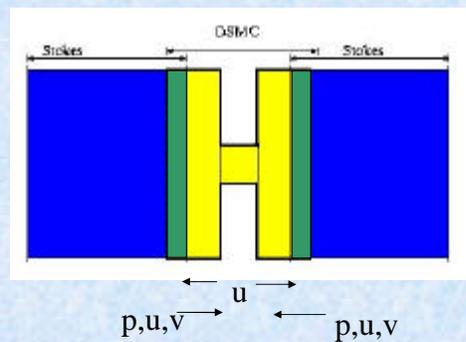
*Repeat* {  $n = n + 1$

Solve  $Lu_1^{(n)} = f_1$  on  $W_1$  with  $u_1^{(n)} = u_2^{(n-1)}$  on  $G_1$

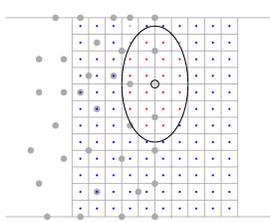
Solve  $Lu_2^{(n)} = f_2$  on  $W_2$  with  $u_2^{(n)} = u_1^{(n-1)}$  on  $G_2$

} until convergence

- Domain decomposition
- Scattered point interpolation between domains
- Dirichlet-Dirichlet boundary conditions
- Parallelism can be introduced



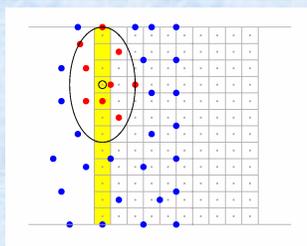
## Interpolation between domains



### DSMC to continuum interpolation

- Place kernel at each continuum node on the interface
- Find cells that are in cloud
- Calculate interpolation functions
- Interpolate solution to continuum nodes

$$u(x_{n_j}) = \sum_{i=1}^{NC} N_i(x_{n_j}) u_{n_i}$$

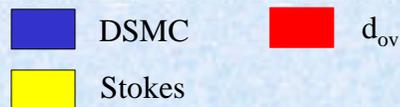
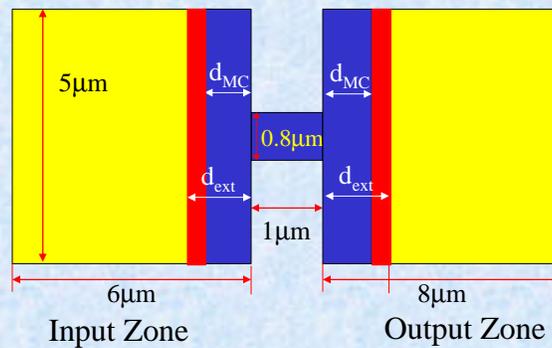


### Continuum to DSMC interpolation

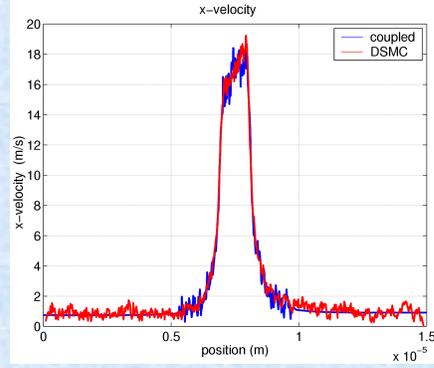
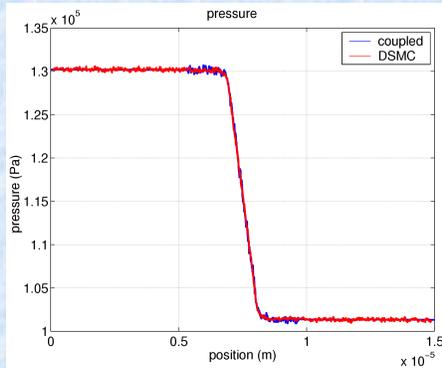
- Place kernel at each buffer cell
- Find nodes that are in cloud
- Calculate interpolation functions
- Interpolate solution to cell centers

$$u(x_{c_j}) = \sum_{i=1}^{NP} N_i(x_{c_j}) u_{n_i}$$

## Multi-Scale Analysis of Microfluidic Filters



## Stokes/DSMC Analysis of 0.2 x 1 mm filter

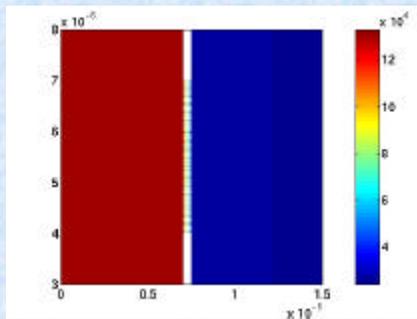


Channel length 1 mm, height 0.2 mm,  
input/output region height 5 mm

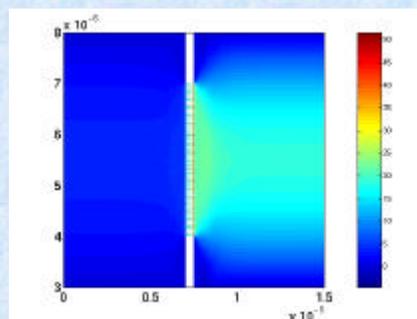
Expected Speedup:3.25  
Obtained Speedup:3.2

## Example: Filter Array

Pressure vs position



x-velocity vs position

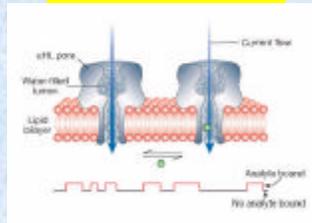


60 0.02 $\mu$ m filter elements in a 5 $\mu$ m membrane section

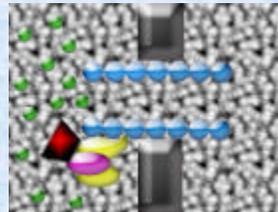
## Ion Channel based Nanopore Sensors

- ❑ Investigate carbon nanotube as nano-interface between Micro channels
- ❑ Single ion trapping and manipulation in CNTs, Detection of macromolecules

Natural Ion Channel



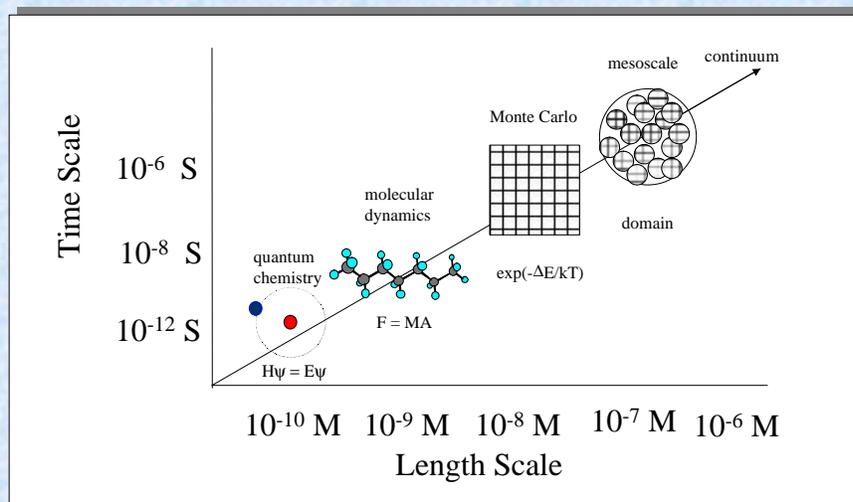
Artificial Ion Channel



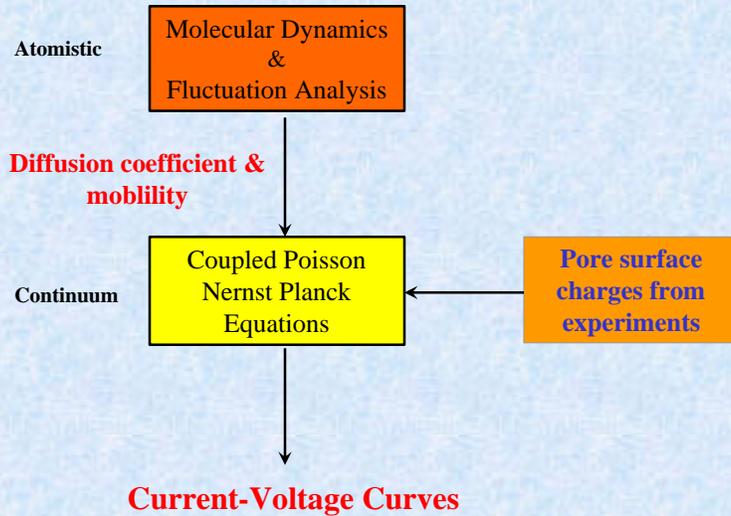
- ❑ Current flow changed by binding
- ❑ Frequency reveals concentration
- ❑ Amplitude reveals identity
- ❑ Durable only in a lab setting

- ❑ Goal: Functionality of ion channels in nanopores
- ❑ Successful experimental evidence for Gold Nanotubules for large diameters
- ❑ Carbon nanotubes are ideal for smaller diameters due to its excellent properties

## Scales in Simulations

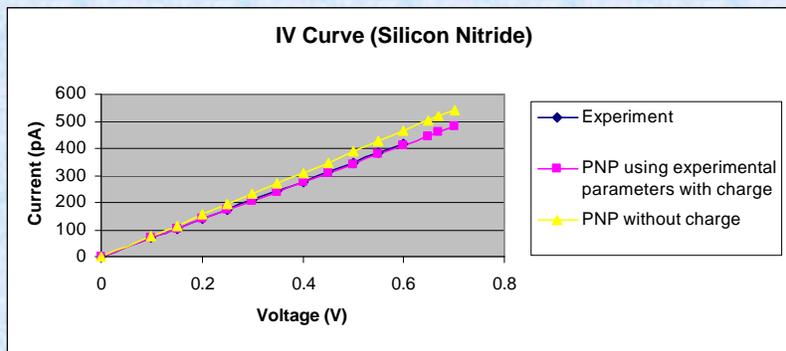


## Multiscale Approach



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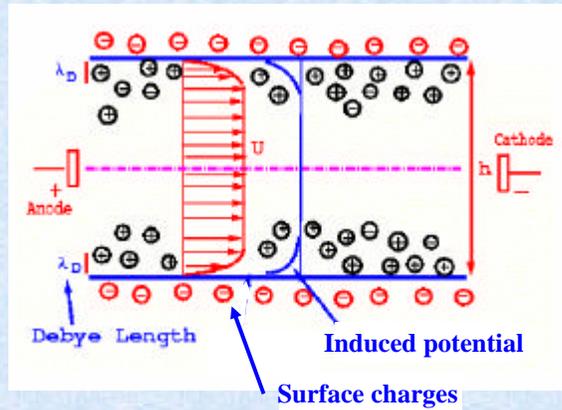
## Silicon Nitride Pore



- Silicon Nitride Pore, 8nm long, 2nm diameter
- 1M KCl
- With and without Surface charge of  $0.4 \text{ mol/dm}^3$
- IV current obtained using Multiscale solution

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## Electroosmotic Transport



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## Classical Continuum Theories

**Ion distribution: Poisson-Boltzmann equation**

$$\tilde{\mathcal{N}}^2 \mathcal{Y} = - \sum_i z_i c_i / e \quad c_i = c_{i,0} \exp\left(-\frac{z_i e \mathcal{Y}}{k_B T}\right)$$

**Fluid flow: Navier-Stokes equation**

$$\begin{aligned} \mathbf{r}(\mathbf{u} \times \tilde{\mathcal{N}}) \mathbf{u} &= m \tilde{\mathcal{N}}^2 \mathbf{u} - \tilde{\mathcal{N}} p + \tilde{\mathbf{f}} & \tilde{\mathbf{f}} &= -e \tilde{\mathcal{N}} \mathcal{Y} \sum_{i=1}^N z_i c_i \\ \tilde{\mathcal{N}} \times \mathbf{u} &= \mathbf{0} \end{aligned}$$

**Boundary conditions:**

$$\left. \frac{d\mathcal{Y}}{dn} \right| = \frac{s}{e}$$

$$\mathbf{u}|_{wall} = \mathbf{0}$$

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## Limitations of Continuum Theories

### ◆ Poisson-Boltzmann equation

- Ions are assumed to be infinitesimal and water is modeled as a continuum
- Accounts for only ion-ion electrostatic interactions in a mean-field fashion
  - Molecular ion - fluid (water) interactions are neglected
  - Molecular ion - Wall interactions are neglected
- Surface charge is assumed to be continuous

### ◆ Navier-Stokes equations

- State variables (e.g., density) do not vary significantly over intermolecular distance
- Usually assumes non-slip boundary conditions
- Assumes that viscosity depends on local properties (e.g., density) and can be described by a local and linear constitutive relation

## MD Simulation: Details

### □ Models

- **Water:** SPC/E model, i.e., water molecule is rigid, hydrogen and oxygen are point charges (O: -0.848e, H: +0.424e)
- **Ions ( $Na^+$  and  $Cl^-$ ):** modeled as point charge + Lennard-Jones atom
- **Wall:** each wall is made of four layers of Silicon atoms oriented in the <111> direction, and only the outmost layer is charged

### □ Force calculation

- ◆ Lennard-Jones interaction, electrostatic interaction and external electrical field

$$U_{LJ} = \frac{c_{12}}{r^{12}} - \frac{c_6}{r^6} \quad U_{Elec} = \frac{1}{4\pi\epsilon} \frac{q_i q_j}{r_{ij}} \quad \vec{F}_i = \vec{E} q_i$$

### □ Updating configuration

- ◆ Time step ranges from 1.0 to 2.0fs
- ◆ Temperature of system is regulated to 300K by Berendsen thermostat
- ◆ Wall atoms are frozen to their original position throughout the simulation

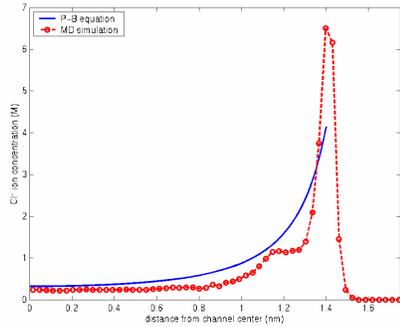
### □ Data analysis

- Binning method

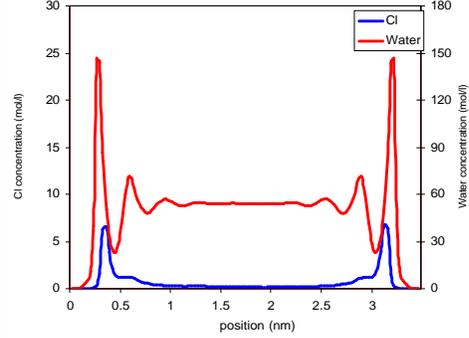
*Freund, J. Chem. Phys. 2002*

## Ion distribution ( $s > 0$ , counter-ion only)

**Channel width:** 3.49nm  
**Surface charge density:** +0.12C/m<sup>2</sup> (0.1e/wall atom, uniform charge distribution)  
**System:** water molecules (2246) and Cl<sup>-</sup> ions(32)



Cl<sup>-</sup> concentration profile across the channel

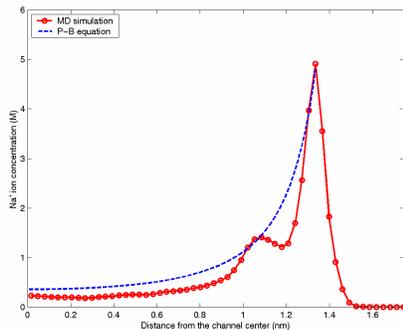


Correlation between Cl<sup>-</sup> concentration and water density profile across the channel

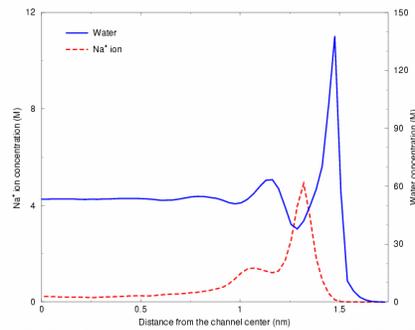
- ❖ molecular ion-wall interactions can influence the ion distribution near the channel wall significantly

## Ion distribution ( $s < 0$ , counter-ion only)

**Channel width:** 3.49nm  
**Surface charge density:** -0.12C/m<sup>2</sup> (uniform charge distribution)  
**System:** water molecules (2246) and Na<sup>+</sup> ion (32)



Na<sup>+</sup> concentration profile across the channel

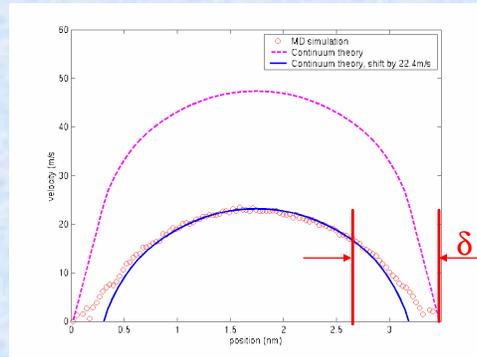


The Na<sup>+</sup> ion concentration peaks coincide with the water concentration valley

- ❖ The hydration effect of ion is more distinct for *smaller* ions
- ❖ The water structure near the channel wall can influence the ion distribution significantly

## Velocity profile: counter-ion only

**Channel width:** 3.49nm  
**Fluid:** water (2286) and Cl<sup>-</sup> ions (32),  
**Surface charge density:** +0.12 C/m<sup>2</sup>  
**External electrical field:** 0.55V/nm



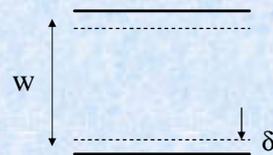
- ❖ The continuum flow theory using a constant viscosity seems to work fine in the central portion of the channel
- ❖ The near-wall region is an issue for the conventional continuum flow theory

Velocity profile across the channel

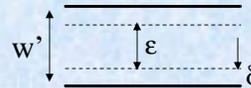
## Multiscale Simulation

### ◆ Embedding technique

- Do an MD simulation of a fine-scale problem
  - atomistic features are usually limited in certain small regions
- Embed the information into the continuum simulation of a bigger problem
- Computationally not very expensive and easy to implement



Original problem ( $w \gg \delta$ )



Fine scale problem ( $w \gg w'$ )

## Modified PB Equation

### ◆ Poisson-Boltzmann equation

$$\left\{ \begin{array}{l} \text{Poisson Equation} \quad \tilde{\nabla}^2 Y = - \sum_i z_i c_{0,i} / e \\ \text{Boltzmann distribution} \quad c_i = c_{0,i} \exp\left(-\frac{z_i F Y}{RT}\right) \end{array} \right.$$

At equilibrium, chemical potential of an ion must be *uniform* in the entire channel:  $m_i = z_i e Y + k_B T \log c_i = k_B T \log c_{0,i}$

(Only electrostatic interaction is considered)

To account for wall effects, we introduce an excess chemical potential  $f_{ex}$ :

$$m_i = z_i e Y + k_B T \log c_i + f_{ex,i} = k_B T \log c_{0,i}$$

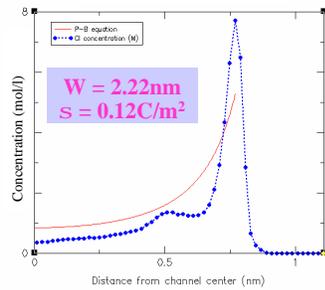
$$c_i = c_{0,i} \exp\left(-\frac{z_i F Y}{RT}\right) \exp\left(-\frac{f_{ex}}{RT}\right)$$

## Modified PB Equation

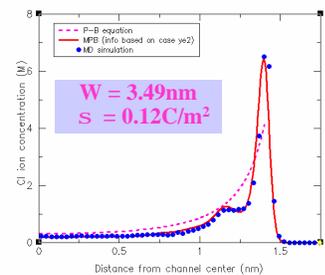
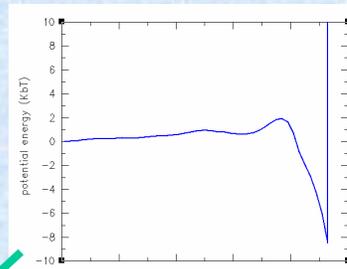
### Comments:

- The excess chemical potential is non-zero only at a position close to the channel wall
- Two possible ways to compute the excess chemical potential:
  - statistical mechanics approach: very difficult due to the extremely complicated interactions between fluid and ions near the channel wall
  - MD simulation
    - Do MD simulation in a small channel, obtain the ion distribution
    - Extract the excess chemical potential based on the modified Boltzmann distribution
    - Can use  $f_{ex}$  to compute ion distribution in a larger channel where MD simulation is much more expensive

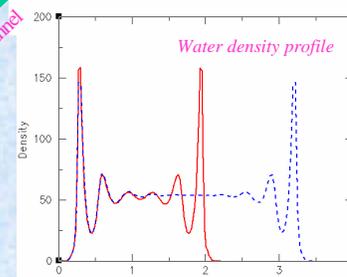
## Modified PB Equation: Results



Extract  $\phi_{ex}$



Apply  $\phi_{ex}$  to a wider channel



## Velocity Embedding Technique

### Embedding MD velocity in small channel into a larger channel

Integrating the governing equation from channel center:

$$\frac{d}{dz} \left( \frac{\rho}{m} \frac{du}{dz} \right) = -r_e E$$

For the small channel (center at point c):

$$m \frac{du}{dz} \Big|_{z=c} = \dot{Q}_{s=c}^z - r_e E ds$$

For the small channel (center at point c'):

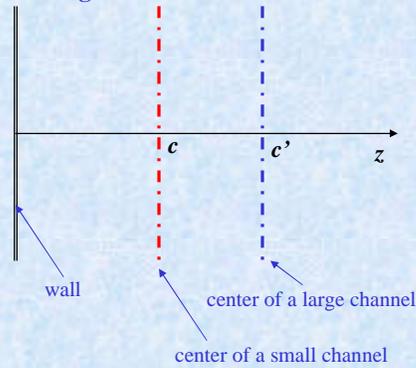
$$m \frac{d\bar{u}}{dz} \Big|_{z=c'} = \dot{Q}_{s=c'}^z - \bar{r}_e \bar{E} ds$$

$$\text{Since } \frac{d\bar{u}}{dz} \Big|_{z=c'} = \frac{du}{dz} \Big|_{z=c} = 0$$

$$\frac{d\bar{u}}{dz} \Big|_z = \frac{\dot{Q}_{s=c'}^z - \bar{r}_e \bar{E} ds}{\dot{Q}_{s=c}^z - r_e E ds} \frac{du}{dz} \Big|_z = F(z) \frac{du}{dz} \Big|_z$$

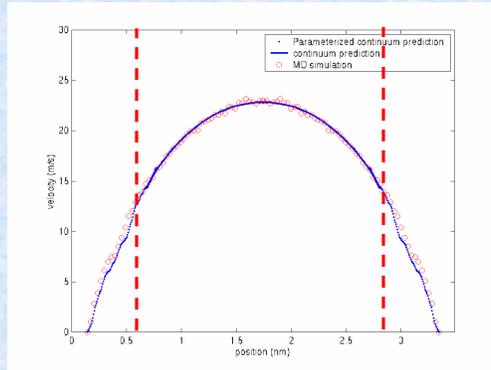
$$\bar{u}(z) = \int_0^z \frac{d\bar{u}}{ds} ds = \int_0^z F(s) \frac{du}{ds} ds = F(z) u(z) - \int_0^z \frac{dF(s)}{ds} u(s) ds$$

Qiao and Aluru  
J. Chem. Phys., 118, 4692, 2003



## Velocity Embedding Technique: Results

- Embedding MD velocity (channel width 2.22nm) near channel wall into the simulation of EOflow in a 3.49nm channel

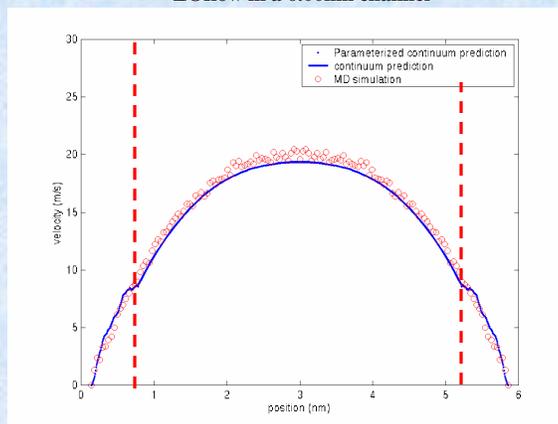


Comparison of velocity profile in a 3.49 nm channel

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## Velocity Embedding Technique: Results

- Embedding MD velocity (channel width 2.22nm) near channel wall into the simulation of EOflow in a 6.00nm channel



Comparison of velocity profile in a 6.00nm channel

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## Conclusions

- ❖ A meshless continuum – DSMC coupling method was developed to investigate the gas flow in micro-filters, and results shows good agreement with direct DSMC simulations
- ❖ A parameterized multiscale simulation method is proposed to investigate the ion transport in artificial nanopores, and the results shows good agreement with experimental results
- ❖ MD simulations of EO flow indicated that the classical Poisson-Boltzmann equation and Navier-Stokes equation can not predict the ion distribution and velocity profiles in nanochannels accurately
- ❖ A modified Poisson-Boltzmann equation is proposed to compute the ion distribution, and simulation results shows good agreement with MD simulation results
- ❖ A velocity embedding technique is proposed to compute the velocity distribution in an EO flow, and simulation results show good agreement with MD simulation results