

# *Fluid Flow in Nanoconfined Geometries*

**Ali Beskok**

*Professor & Chair*

*Mechanical Engineering Department*

*(214) 768-1403*

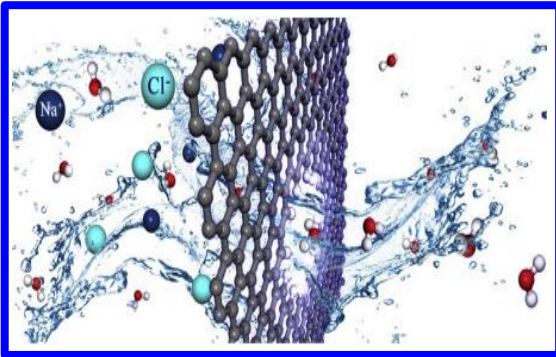
**abeskok@smu.edu**



# Motivation

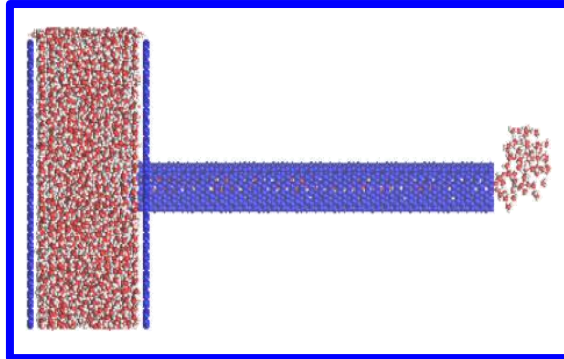
- Nanofluidics often refers to study and application of fluid motion through and around nanosized objects with a characteristic length scale in the range of 0-100 nm.
- Understanding liquid and gas flows in nanoscale systems is of fundamental importance for a variety of applications.

## ❑ Water Desalination

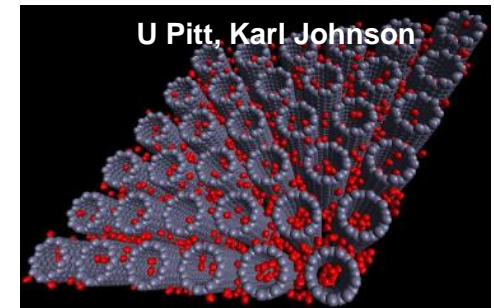


Wang et al. (2014)

## ❑ Nanopumping



Vijayaraghavan and Wong (2014)



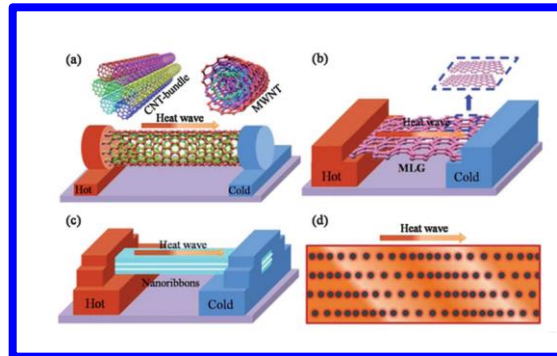
Adsorbed Hydrogen gas on CNT

## ❑ Energy Storage

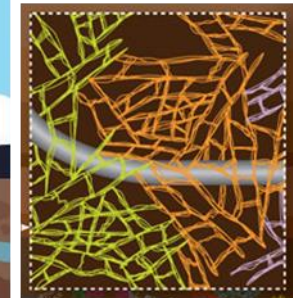
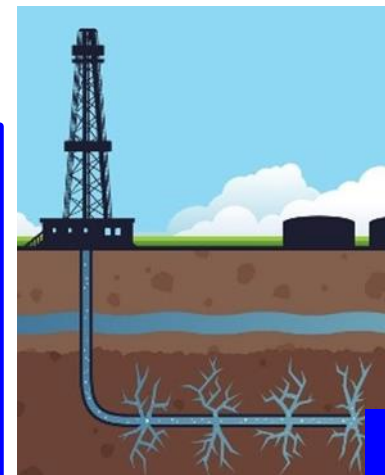


<http://www.anglia.com>

## ❑ Heat management



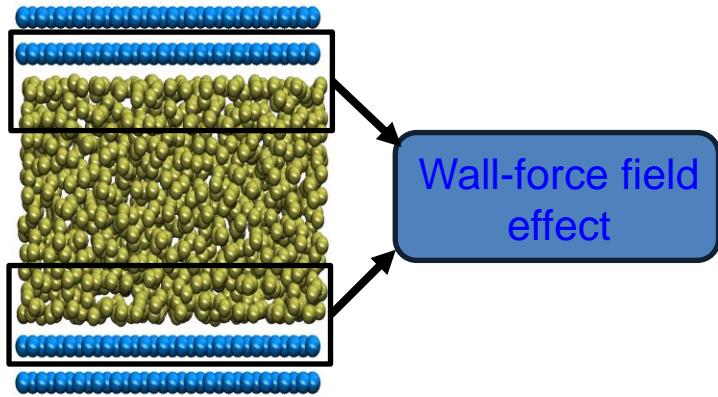
Sun et al. (2012)



Gas Recovery from Shale Reservoirs

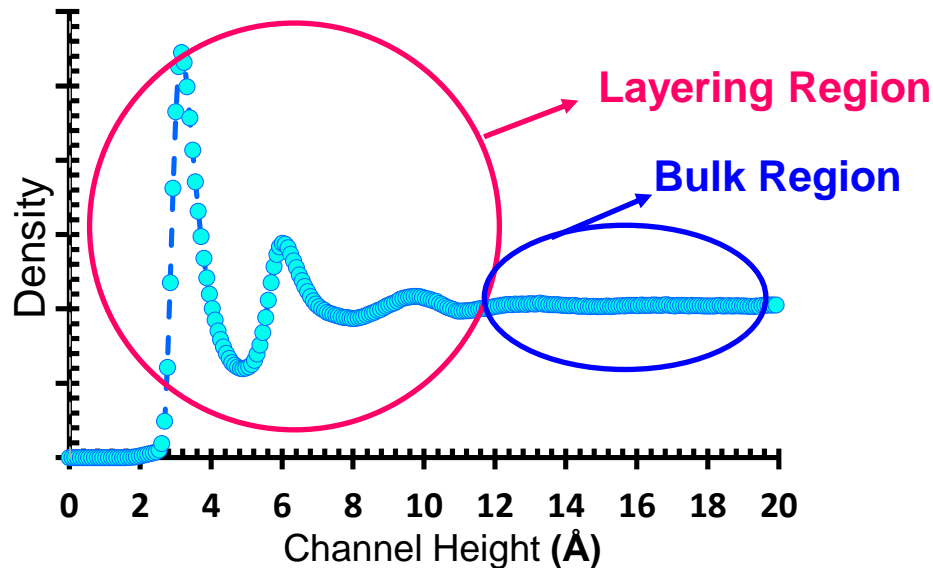
# Motivation

In nanoscale confinements, interplay between interfacial and bulk phenomena is significant due to the small size and wall force field effects.



- Well-established continuum flow models may fail
- Hydrodynamic properties could be significantly different than their macroscopic counterparts (i.e., density layering, viscosity, thermal conductivity, etc.)
- Classical no-slip boundary condition may no longer exist.

## □ Density Layering



# Van der Waals Interactions of Argon in Platinum Nanochannels. No Flow Case

# Molecular Dynamics Simulations

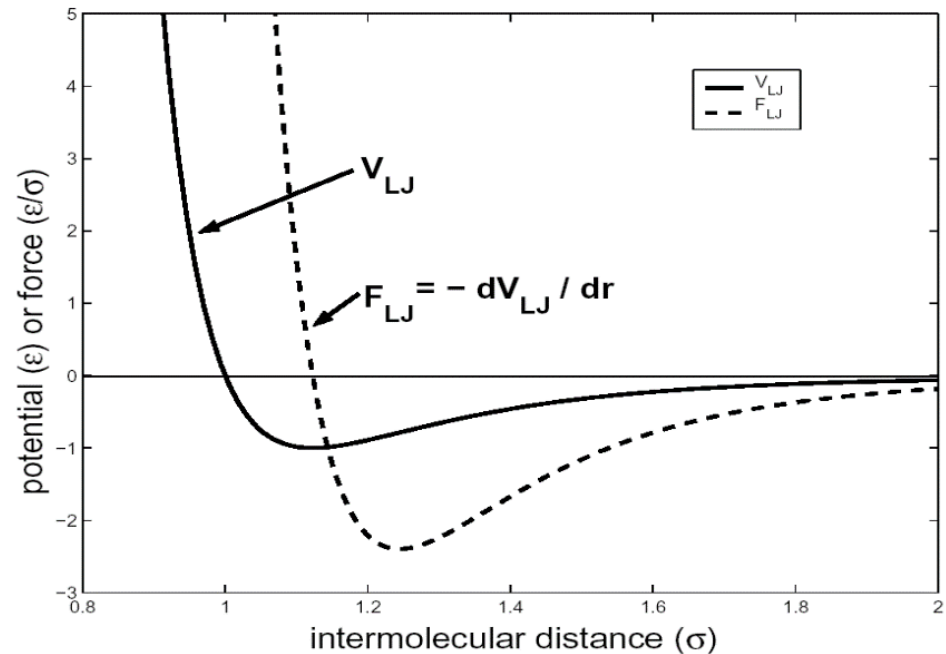
- Model **van der Waals** interactions via Lennard-Jones potential.

$$V_{LJ} = 4\epsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)$$

$r$ : inter atomic distance

$\sigma$ : molecular diameter

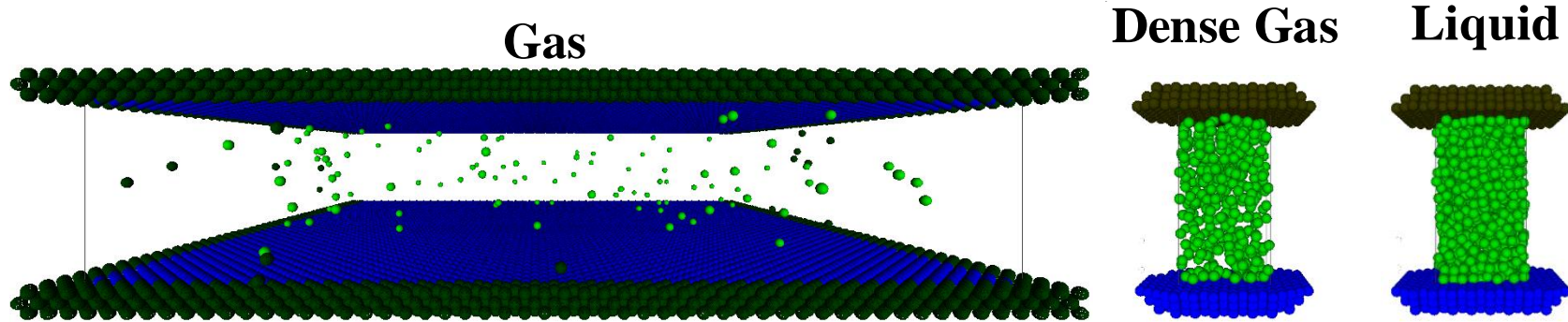
$\epsilon$ : depth of potential well  
(energy parameter)



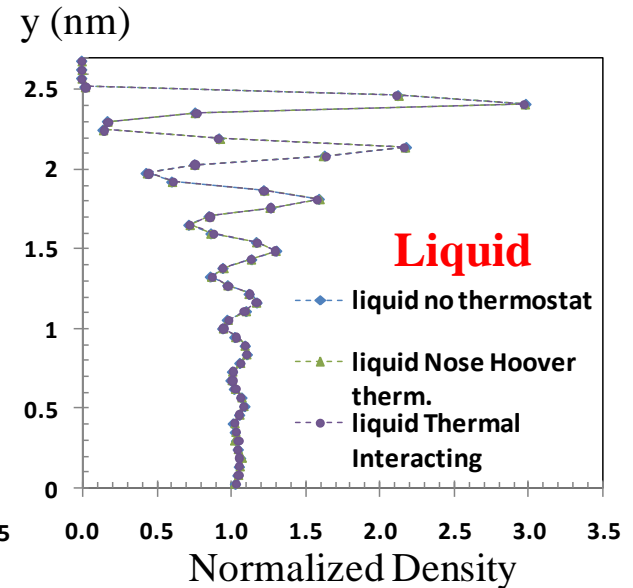
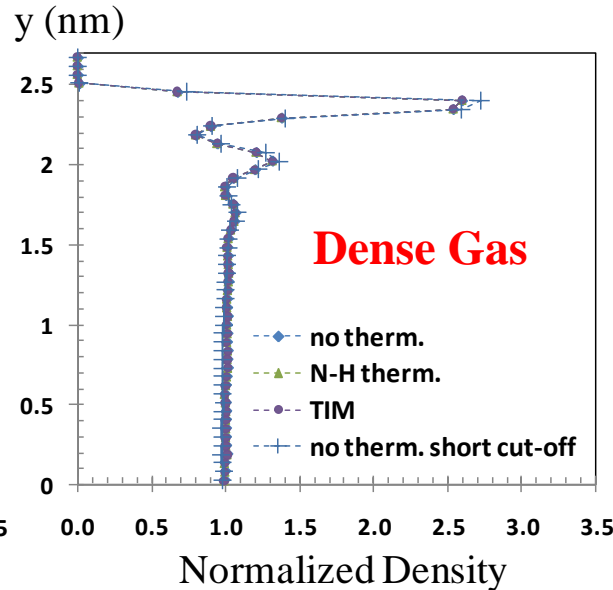
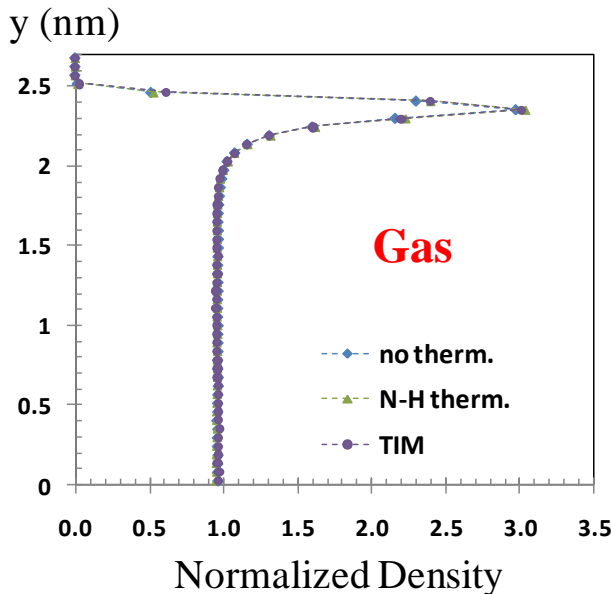
- Lennard Jones potential for fluid/fluid and fluid/wall interactions.
- **Smart Wall Algorithm is used to calculate surface gas interactions\***.
- For gas flows computational domains are on the order of a mean free path in the streamwise and lateral directions.



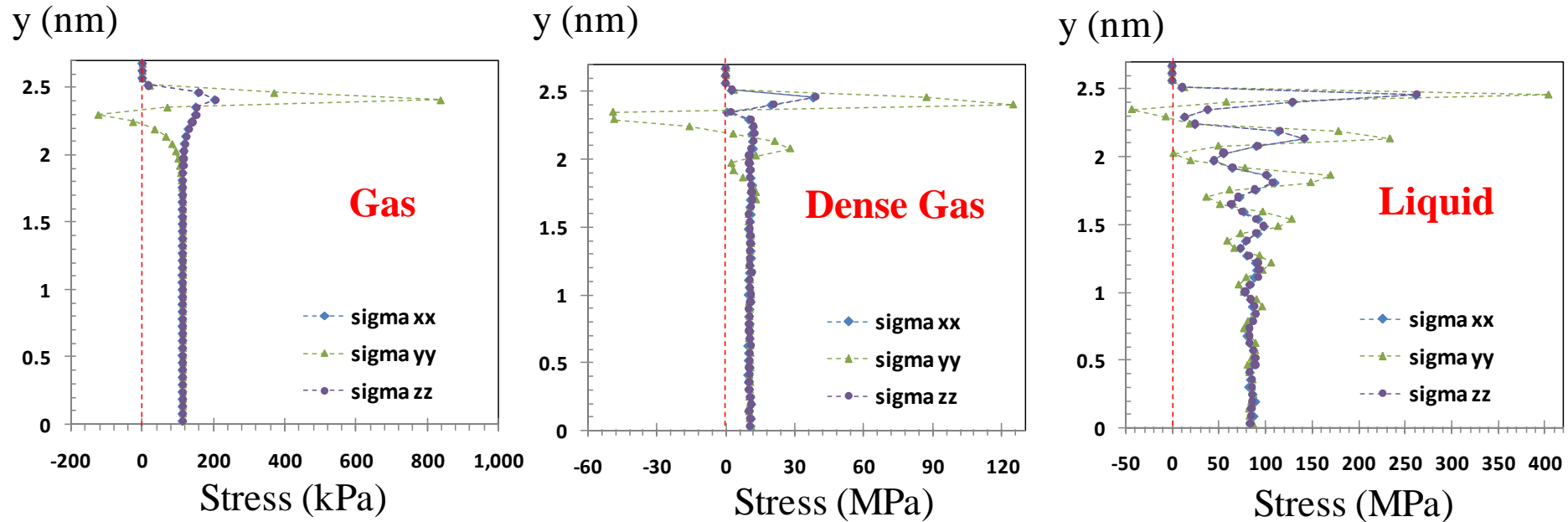
# Nano-Confinement in Static Fluids



- ❑ Equilibrium MD simulations are performed with thermostat free domains.
- ❑ Near surface density and stress variations are investigated for static fluids.



# Normal Stress Profiles



$$S_{kl} = \frac{1}{Vol} \left\langle \sum_i^N m^i (V_k^i - \bar{V}_k^i)(V_l^i - \bar{V}_l^i) + \frac{1}{2} \sum_{i,j}^N (r_k^j - r_k^i) f_l^{i,j} \right\rangle \text{ Irving-Kirkwood}$$

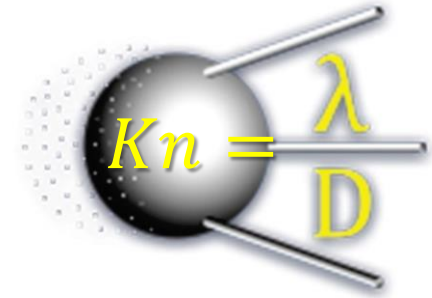
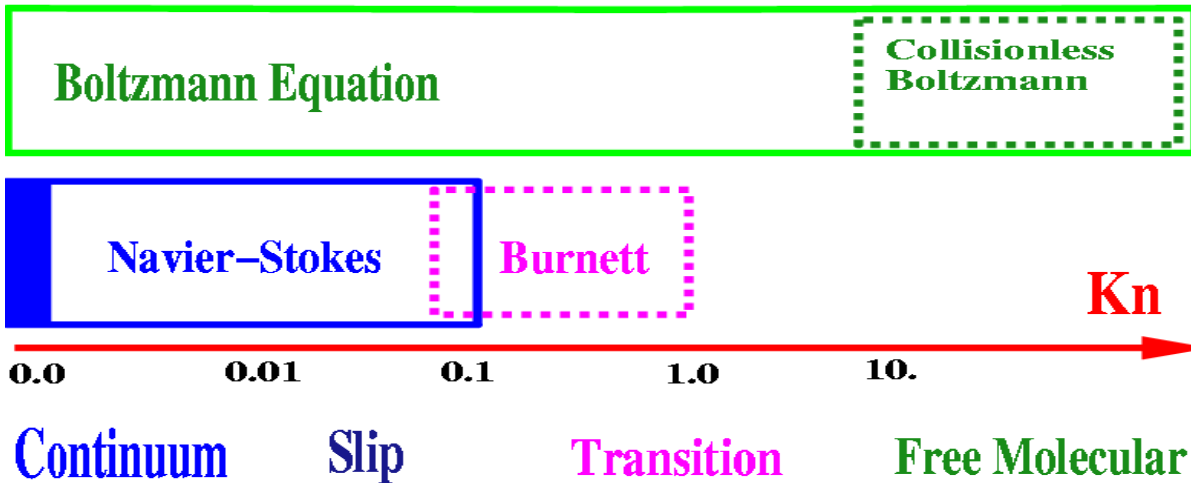
- ❑ Normal stresses in the near wall region are anisotropic due to the surface effects, while they are isotropic in the bulk region.
- ❑ Surface virial is a measure of the surface force effects.
- ❑ MD predicts the thermodynamic state of gas, dense gas and liquid states.

# Shear and Force Driven Nanochannel Gas Flows

Argon Flow in Platinum Nanochannels

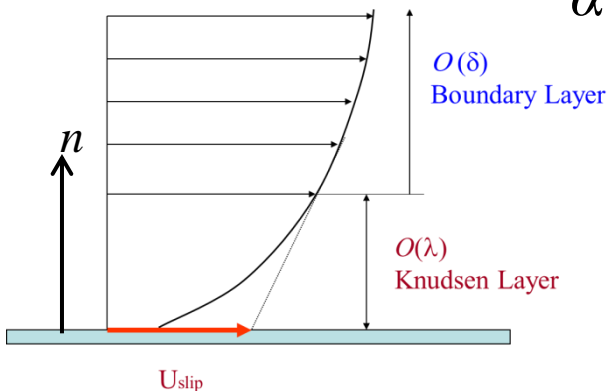


# Characterization of Gas Transport



$$U_{gas}^* - U_{wall}^* = \frac{2 - \alpha}{\alpha} Kn \frac{\partial U^*}{\partial n^*} \quad \text{Maxwell 1879}$$

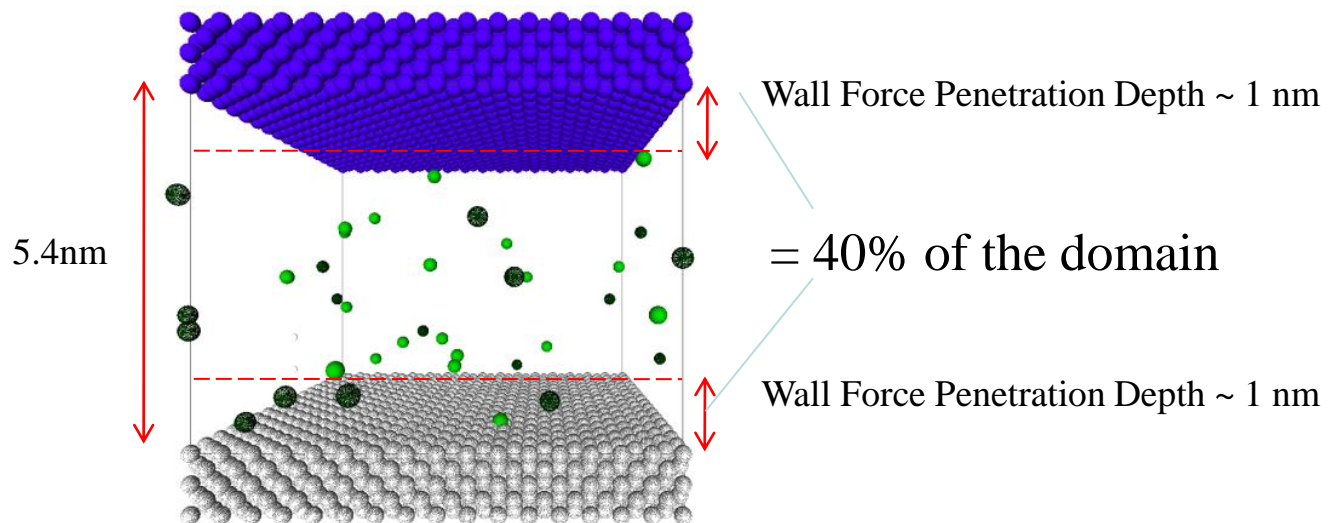
$\alpha$  is the Tangential Momentum Accommodation Coefficient



$$U_{gas}^* - U_{wall}^* = \frac{2 - \alpha}{\alpha} \left( \frac{Kn}{1 + Kn} \right) \frac{\partial U^*}{\partial n^*}$$

## Are rarefied and nano-scale gas flows at given Knudsen and Mach numbers *dynamically similar*?

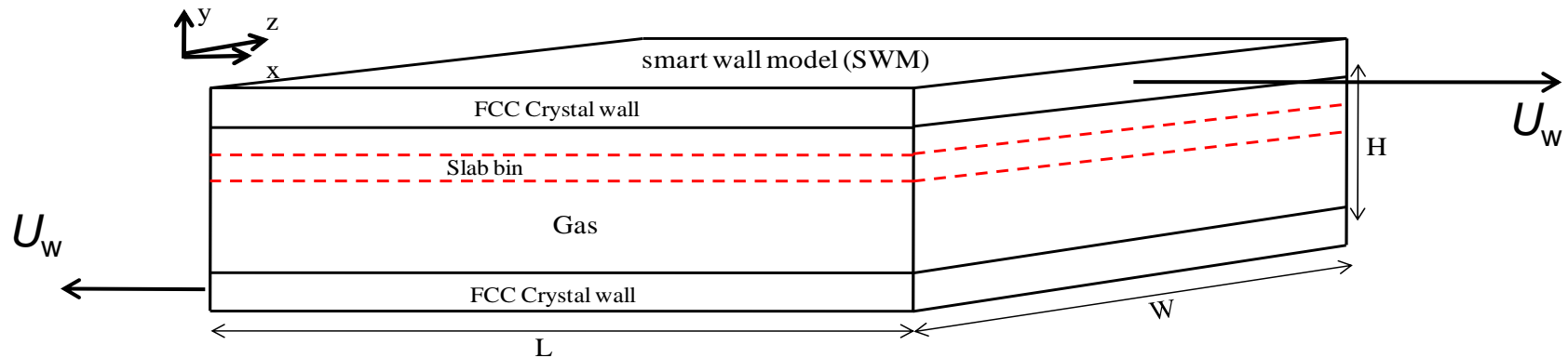
Most previous work on nano-scale gas flows neglect the *wall force field effects*...



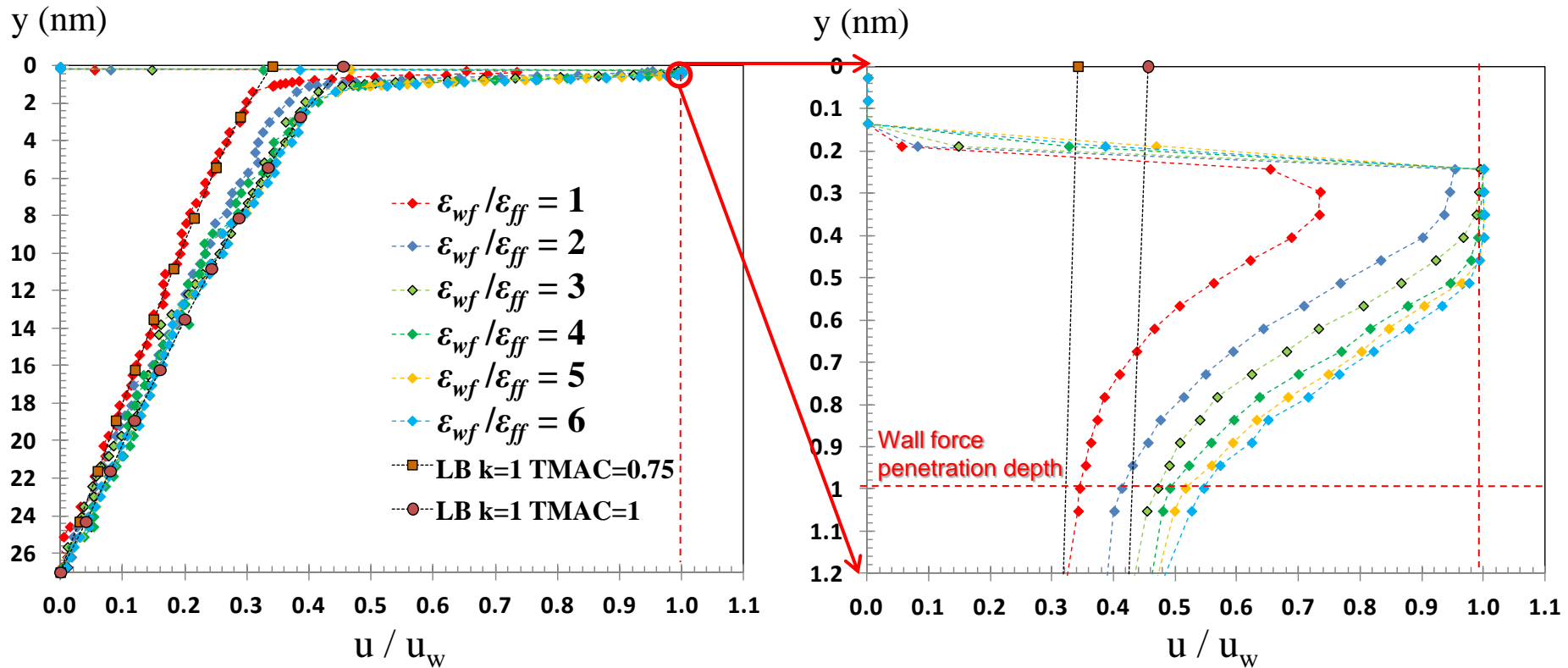
# 3D Nano-Channel Couette Flow

**Objective:** Investigate *wall force field effects* in nano confinements as a function of **Kn** and surface-gas interaction strength ratio ( $\epsilon_{wf}/\epsilon_{ff}$ )

$$k = \left( \frac{\sqrt{\pi}}{2} \right) Kn$$



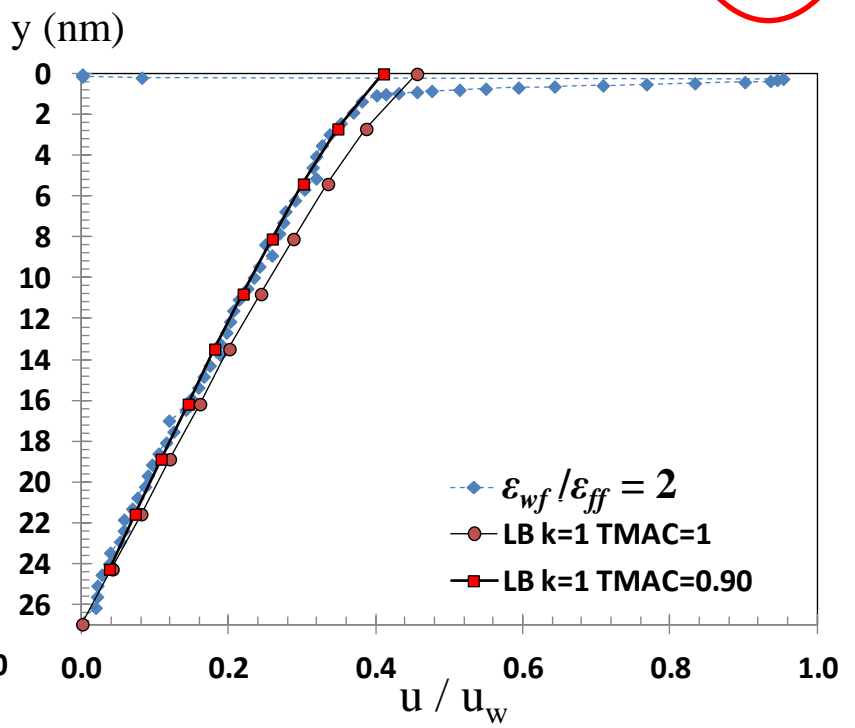
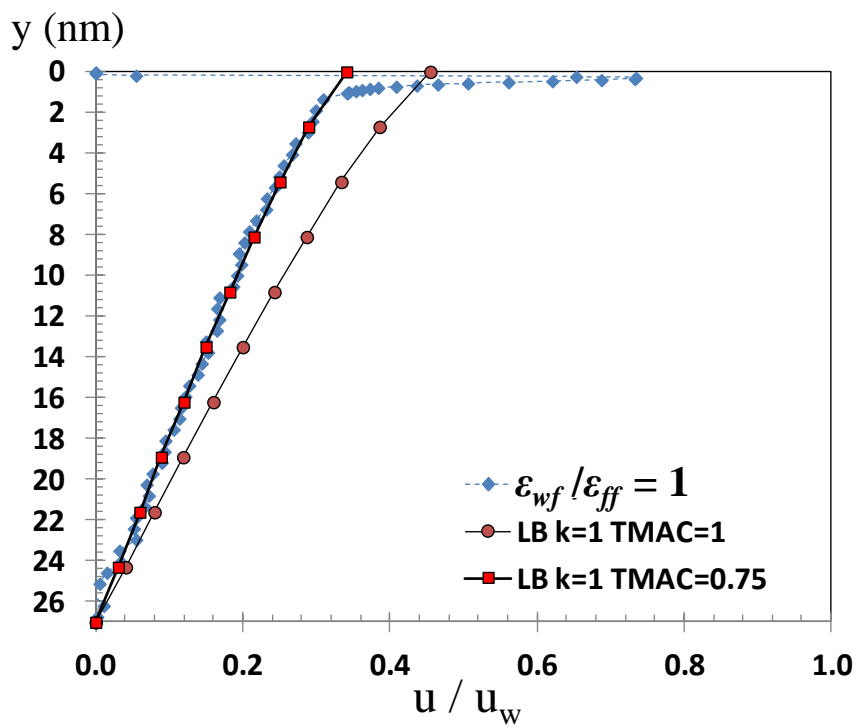
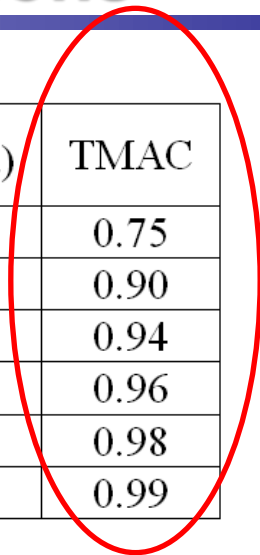
# Velocity Profiles for Couette Flow (Kn=1)



- Velocity profile in the bulk region matches KT prediction.
- Deviations are within the wall force penetration depth ( $B=3\sigma/h$ )
- $\epsilon_{wf}/\epsilon_{ff}$  dependency of the velocity profiles are observed.
- Velocity profiles reach the wall velocity for  $\epsilon_{wf}/\epsilon_{ff} \geq 3$ .

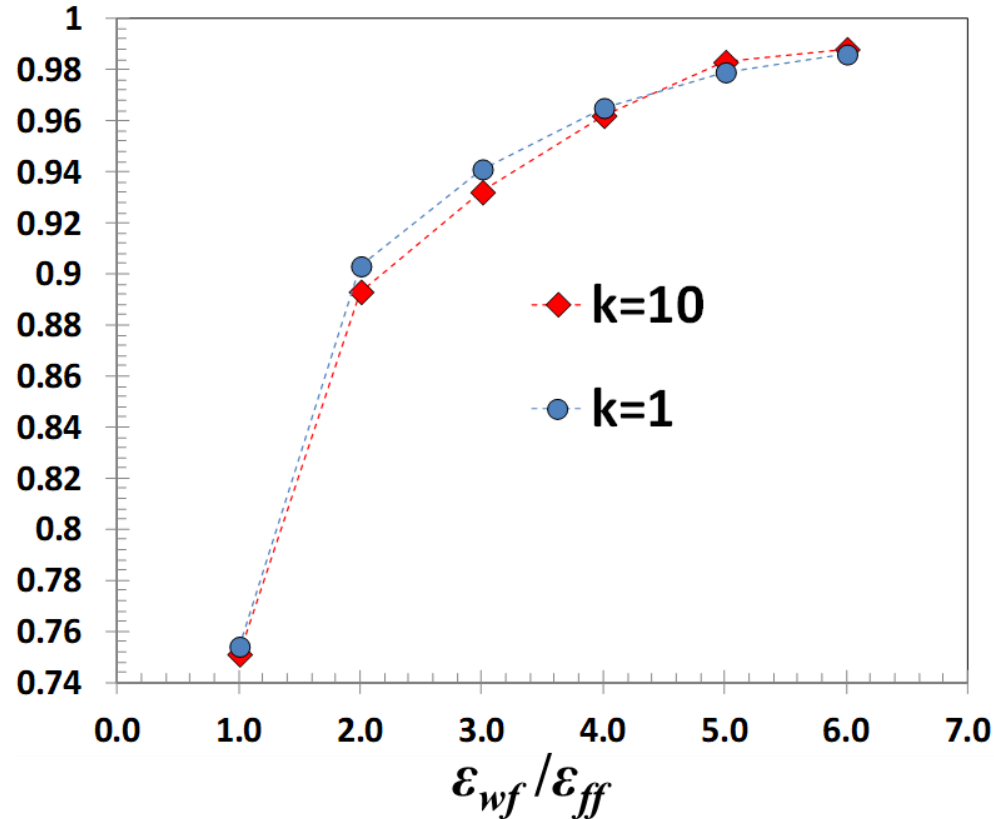
# Various $\epsilon_{wf}/\epsilon_{ff}$ at $k=1$ : TMAC Predictions

$\epsilon_{wf}/\epsilon_{ff}$	# molecules	$\rho_{bulk}$ (kg/m <sup>3</sup> )	k	$\tau_{\infty}$ (kPa)	$\tau_{k=1}$ (kPa)	$\tau_{MD}$ (kPa)	TMAC
1	4,500	1.89	1.01	-23.97	-15.70	-9.51	0.75
2	4,700	1.87	1.02	-23.78	-15.62	-12.85	0.90
3	5,500	1.84	1.03	-23.42	-15.45	-13.77	0.94
4	10,000	1.90	1.00	-24.15	-15.66	-14.61	0.96
5	22,000	1.88	1.01	-23.89	-15.50	-15.02	0.98
6	36,000	1.85	1.03	-23.51	-15.25	-15.03	0.99



# Variation of TMAC with $\epsilon_{wf}/\epsilon_{ff}$

TMAC



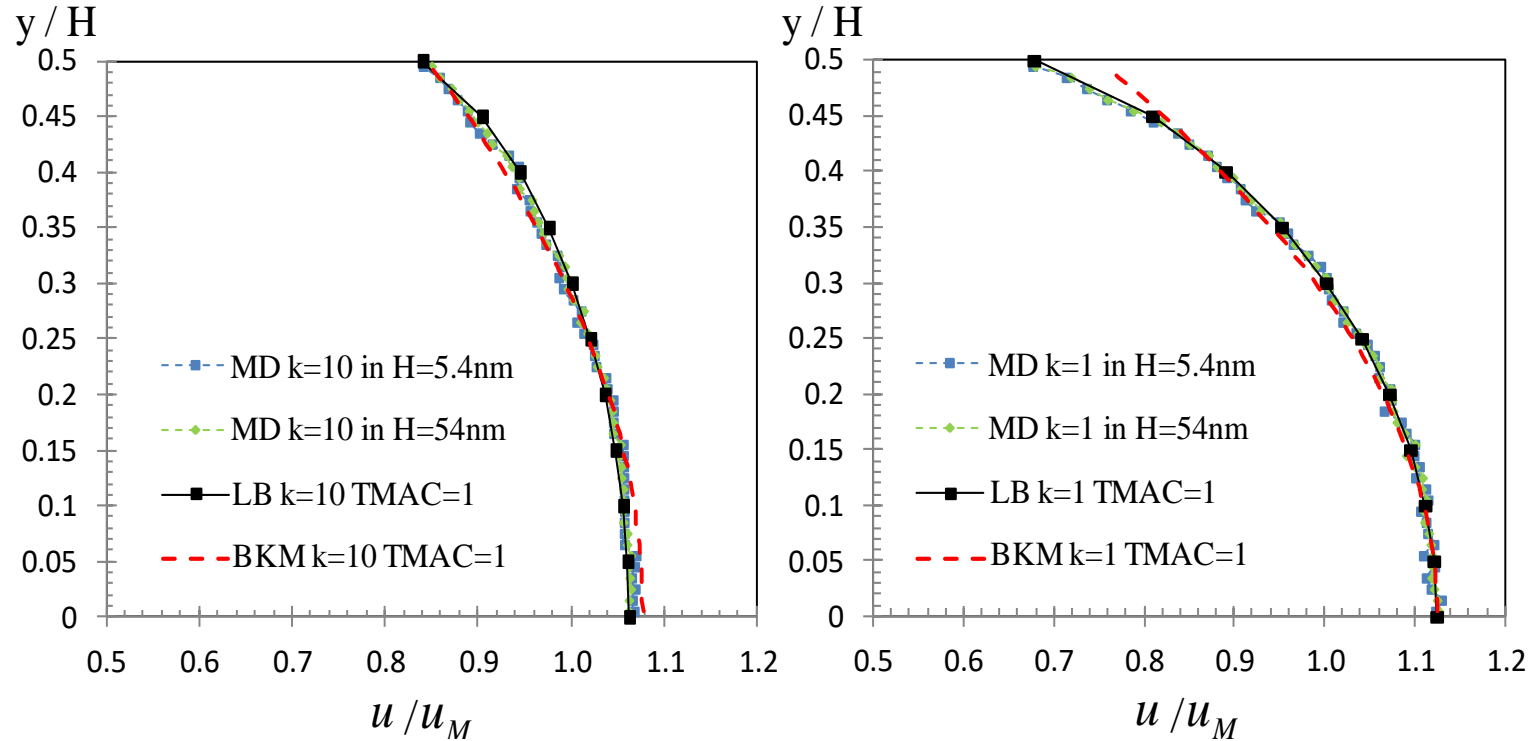
- ❑ Comparing KT based shear stress with MD calculated values allows determination of the TMAC ( $\alpha$ ).
- ❑ Surface gas interaction strength ( $\epsilon_{wf}/\epsilon_{ff}$ ) determines the TMAC, which is independent of  $Kn$ .



# Force Driven Gas Flows (with planar BCs)

BC: Diffuse reflection of molecules from an isothermal flat surface with Maxwell distribution.

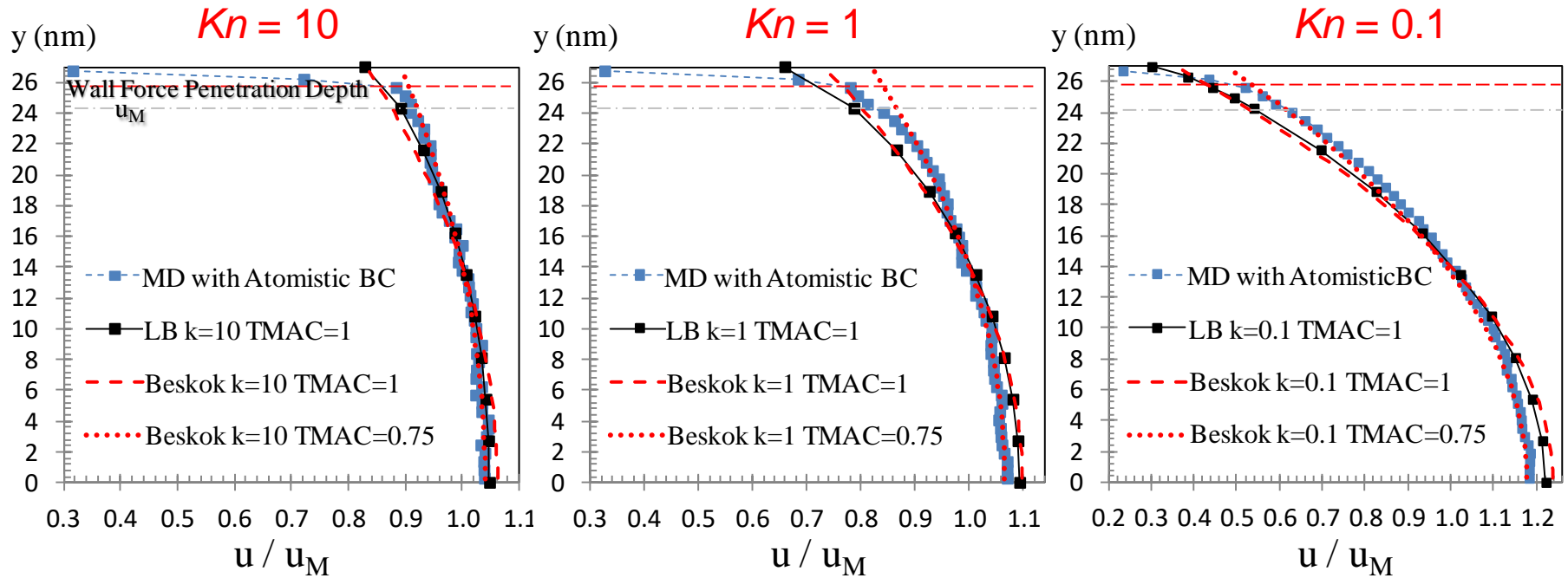
No atomic details or wall force field



$$U^*(y, Kn) \equiv \frac{U(x, y)}{\bar{U}(x)} = \left[ \frac{-\left(\frac{y}{H}\right)^2 + \left(\frac{y}{H}\right) + \left(\frac{2-\alpha}{\alpha}\right) \frac{Kn}{1+Kn}}{\frac{1}{6} + \left(\frac{2-\alpha}{\alpha}\right) \frac{Kn}{1+Kn}} \right]$$

□ MD verifies Boltzmann solution & BKM for  $\alpha=1$

# Force Driven Gas Flows ( $h=54\text{nm}$ , $\epsilon_{wf}/\epsilon_{ff}=1$ )

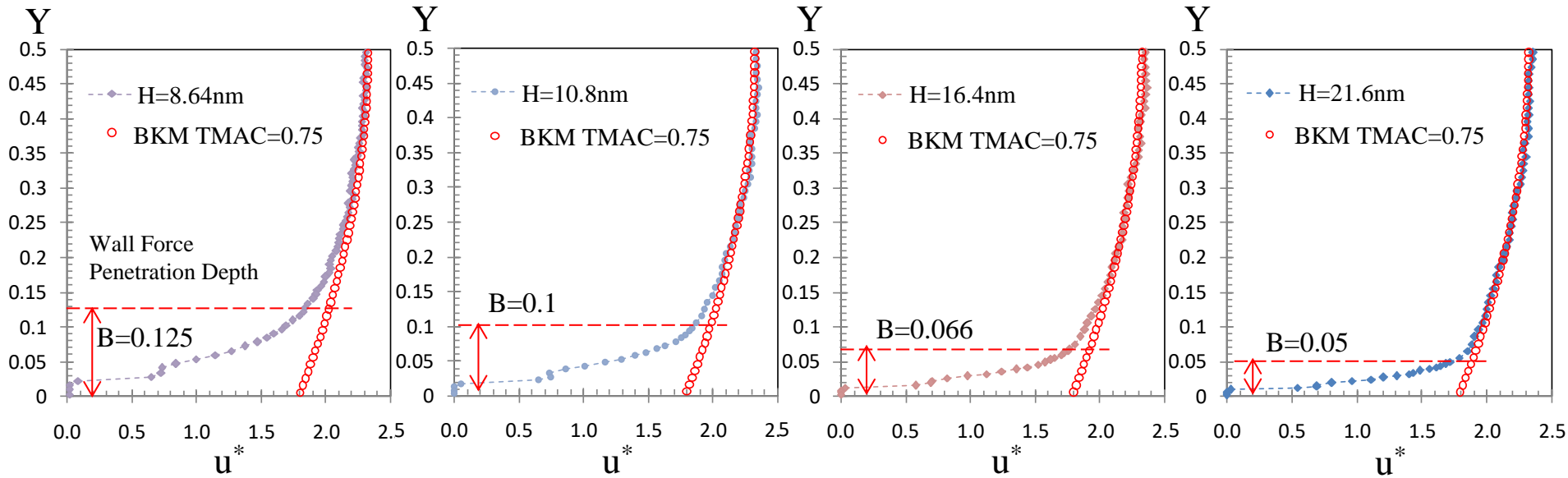


## ATOMISTIC WALLS

$$U^*(y, Kn) \equiv \frac{U(x, y)}{\bar{U}(x)} = \left[ \frac{-\left(\frac{y}{H}\right)^2 + \left(\frac{y}{H}\right) + \left(\frac{2-\alpha}{\alpha}\right) \frac{Kn}{1+Kn}}{\frac{1}{6} + \left(\frac{2-\alpha}{\alpha}\right) \frac{Kn}{1+Kn}} \right]$$

- ❑ In large channels KT match MD with atomistic walls if proper TMAC value is used.

# Velocity Profiles (Kn=1)



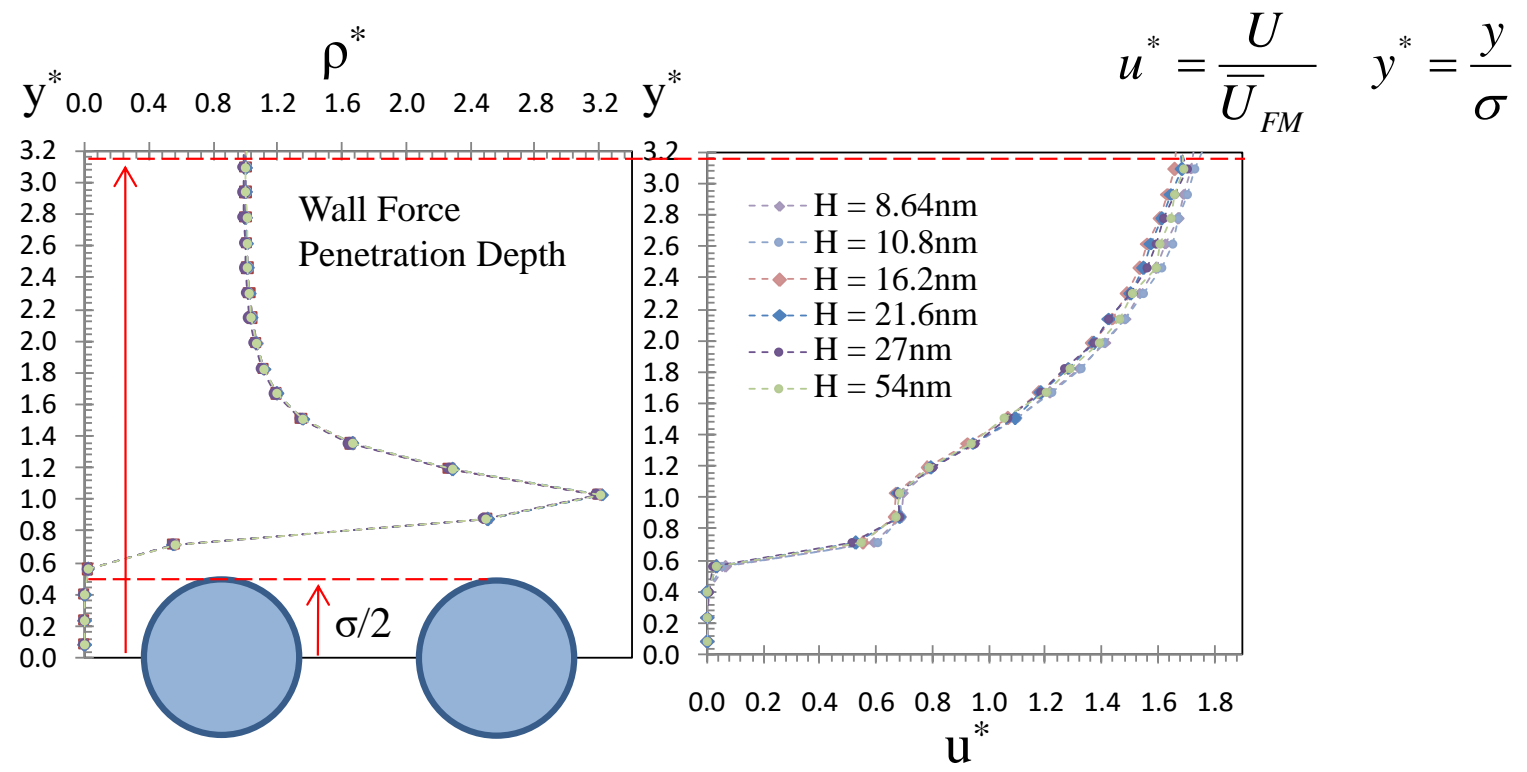
$$u^* = \frac{U}{\overline{U}_{FM}} \quad Y = \frac{y}{h}$$

$$B = \frac{\text{Wall force penetration length } (\sim 3\sigma)}{\text{Channel height}}$$

Velocity profiles show two distinct regions

- Bulk flow region can be determined using KT in channels as small as 8nm (but needs TMAC value as the boundary condition!)
- Near-wall region deviates from KT, which varies as a function of  $B=3\sigma/h$ .

# Near Wall Behavior ( $Kn=1, \epsilon_{wf}/\epsilon_{ff}=1$ )



Normalized density and velocity profiles are identical for  $Kn=1$  flows for different height channels and pressures

- Near wall region shows a **universal behavior** for constant surface properties and Knudsen number  $\rightarrow$  *Law of the nano-wall*

# Observations for Gas Flows

- ❑ *Wall force penetration length* emerges as an important length scale in nano-confined gas flows in addition to the channel dimension and gas mean free path.

$$B = \frac{\text{Wall force penetration length}}{\text{Channel height}}$$

- ❑ For  $B \rightarrow 0$ , nanoscale flows can be predicted using kinetic theory.
  - ❑ Dynamic similarity is valid, but TMAC is not known
  - ❑ TMAC is determined by gas/wall interaction strength, and independent of  $Kn$ .
- ❑ For finite  $B$ , transport in the near wall region cannot be ignored
- ❑ Near-wall density and velocity distributions depend on the wall-fluid interaction and  $Kn \rightarrow$  “*law of the nano-wall*”.

## Acknowledgements:

NSF Grant No. DMS 0807983 & ACS PRF #54562-ND9

## References:

*Microscale Thermophysical Engineering*, 8:4, 43-77, 1999  
*Communications on Computational Physics*, 7(5): 977-993, 2010  
*Microfluidics Nanofluidics*, 11:5 611-622, 2011  
*Microfluidics Nanofluidics*, 11:3 269-282, 2011  
*Microfluidics Nanofluidics*, 13, 789–798, 2012  
*Physics of Fluids*, 26, 052003, 2014  
*Microfluidics and Nanofluidics*, 18, 1365–1371, 2015  
*Microfluidics and Nanofluidics*, 20:46, 2016

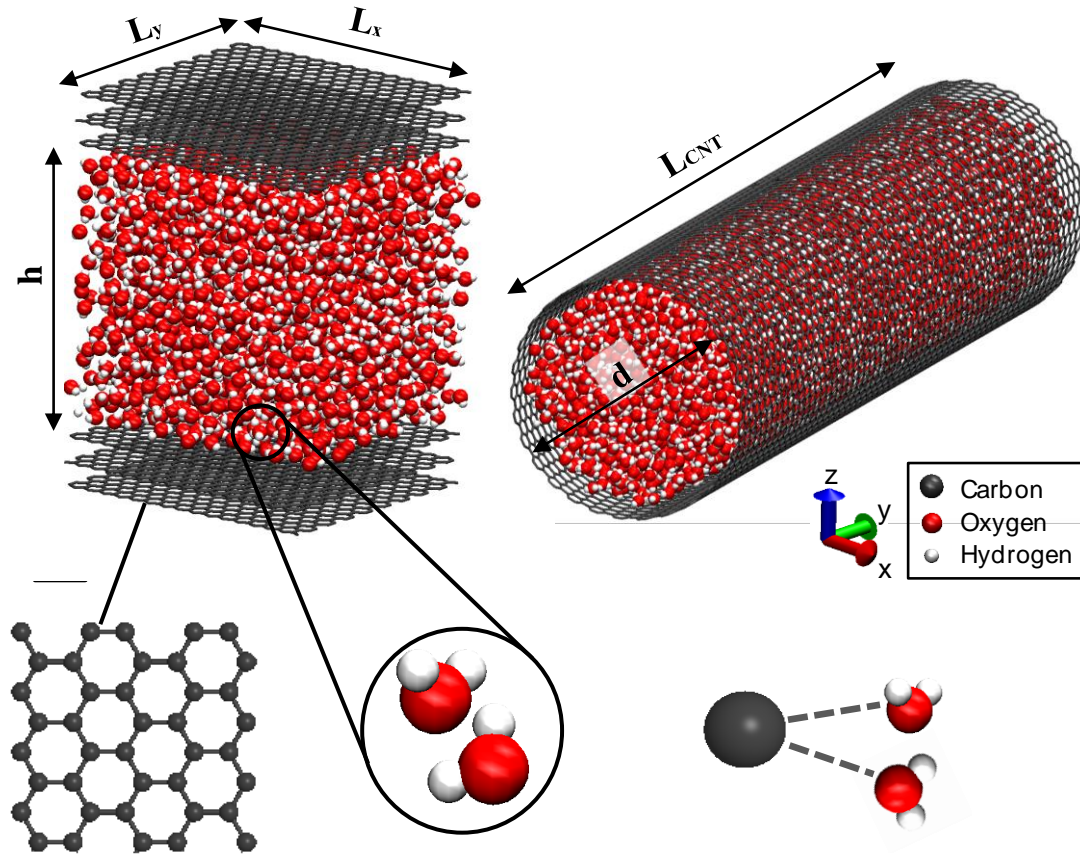


Assoc. Prof. Murat Barisik, IZTECH

# Force-driven Deionized Water Flow in Carbon-based Nanochannels



## □ Molecular Model: Water Graphene / CNT



### Carbon

- AIREBO
- Neutral/Charged  
Stuart et al. (2000)

### Water

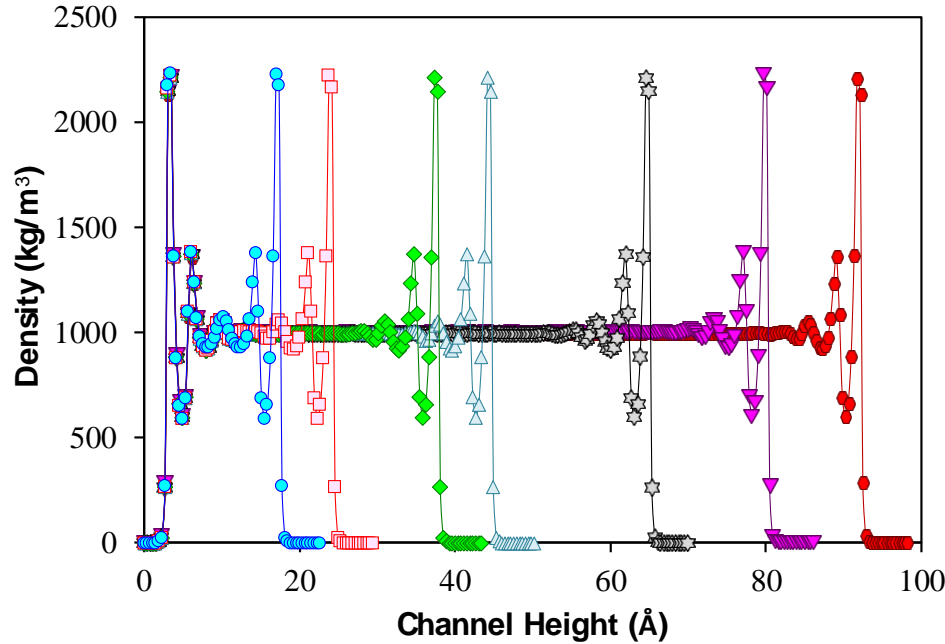
- TIP4P/2005 Model  
Abascal et al. (2005)

### Carbon - Water

- Experimental Contact angle calculations  
Werder et al. (2017)

# Force-driven Water Flow through Uncharged CNTs and Graphene Channels

## □ Density Distributions



**Fixing Thermodynamic State**

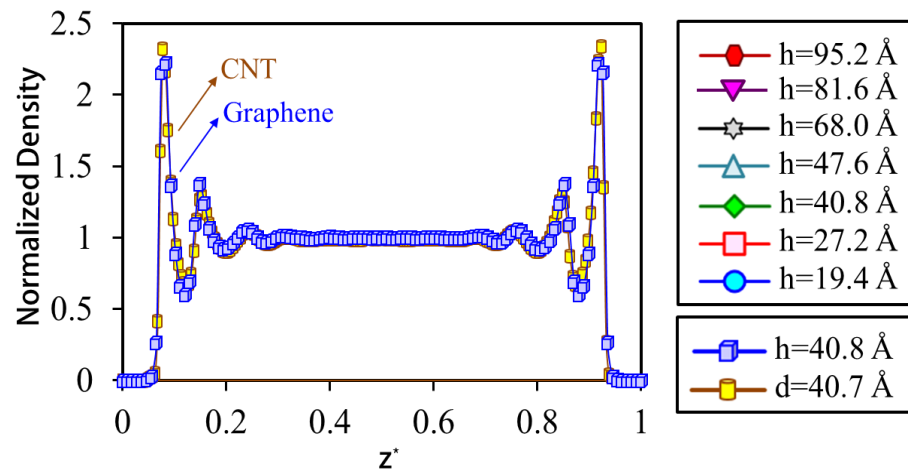
$T = 300 \text{ K}$  and  $\rho_{\text{bulk}} = 997.2 \text{ kg/m}^3$

---

$\mu_{\text{TD}} = 858 \text{ }\mu\text{Pa}\cdot\text{s}$

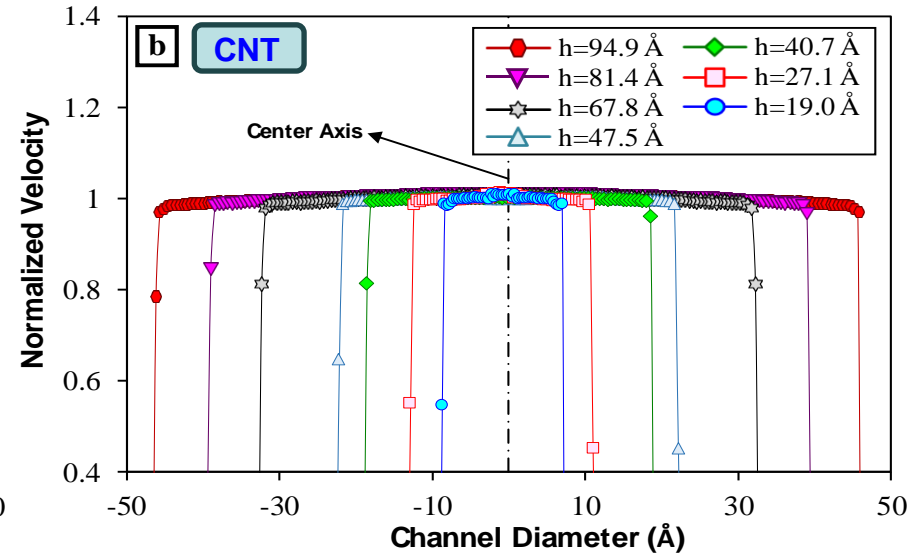
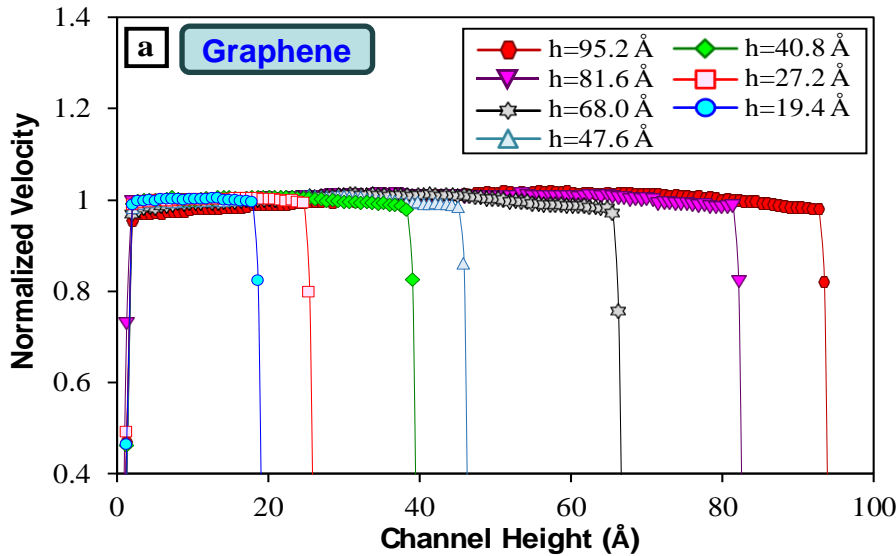
## □ At Fixed Thermodynamic State

- Average density of liquid in nanoscale confinements is always lower than the desired thermodynamic value due to the density oscillations. This effect diminishes with increasing the channel heights.
- Water in carbon confinements presents three distinct density peaks. First peak is located approximately  $3.15 \text{ }\text{\AA}$  away from the solid wall.
- Water density profiles in CNTs and graphene nanochannels are similar to each other for similar channel/tube sizes.



# Force-driven Water Flow through Uncharged CNTs and Graphene Channels

## Velocity Profiles



- Nearly plug-like velocity profiles that are independent of the channel size are observed.
- Due to hydrophobic nature of carbon, there is weak interfacial resistance, resulting large slip length and fast water transport.

• Conservation of linear momentum in integral form

$$\tau_w = \frac{F}{2A} = \frac{fV}{2A} = \frac{fAh}{2A} \rightarrow \tau_w = \frac{fh}{2}$$

Navier-type slip condition at the interface

$$u_s = \beta \frac{du}{dz}$$

Constitutive law for Newtonian fluids

$$\tau_w = \mu \frac{du}{dz}$$

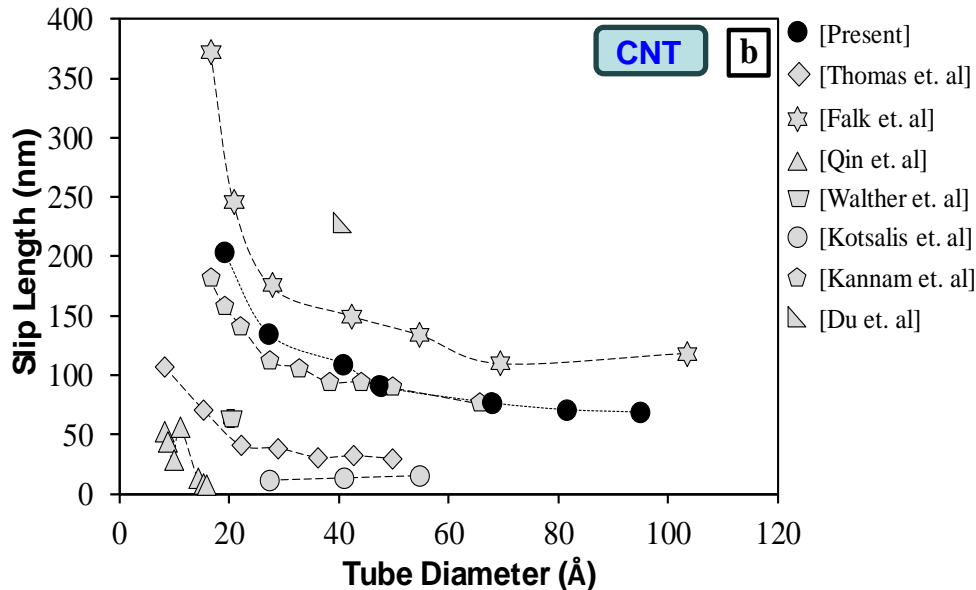
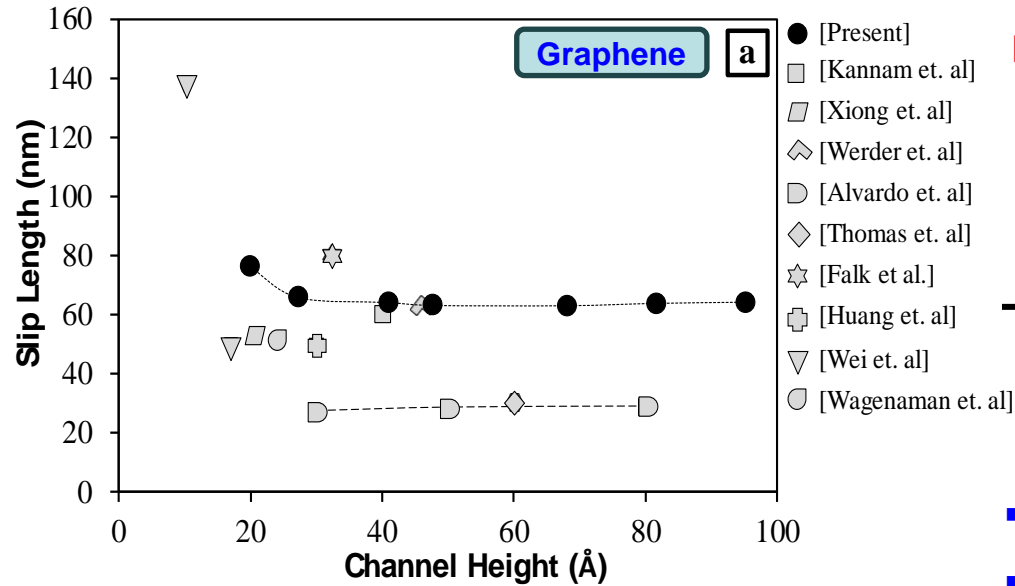
MD average velocity



Slip Length:

$$\beta = \frac{2\mu u_s}{fh} = \frac{2\mu \bar{u}}{fh}$$

# Force-driven Water Flow through Uncharged CNTs and Graphene Channels



## Slip Lengths

- To quantify SLIP:

Plug-flow Method

$$\beta = \frac{2\mu_{TD}\bar{u}_G}{fh}$$

Graphene

$$\beta = \frac{2\mu_{TD}\bar{u}_{CNT}}{fR}$$

CNT

- For channels larger than 2nm,  $\beta \approx 64$  nm.
- CNTs curvature affects  $\beta$  for  $d < 6$  nm, above which,  $\beta \approx 64$  nm.
- Discrepancies in the literature are due to:
  - Different interaction parameters used between liquid-solid interface
  - Using different water models
  - Not fixing the thermodynamic state

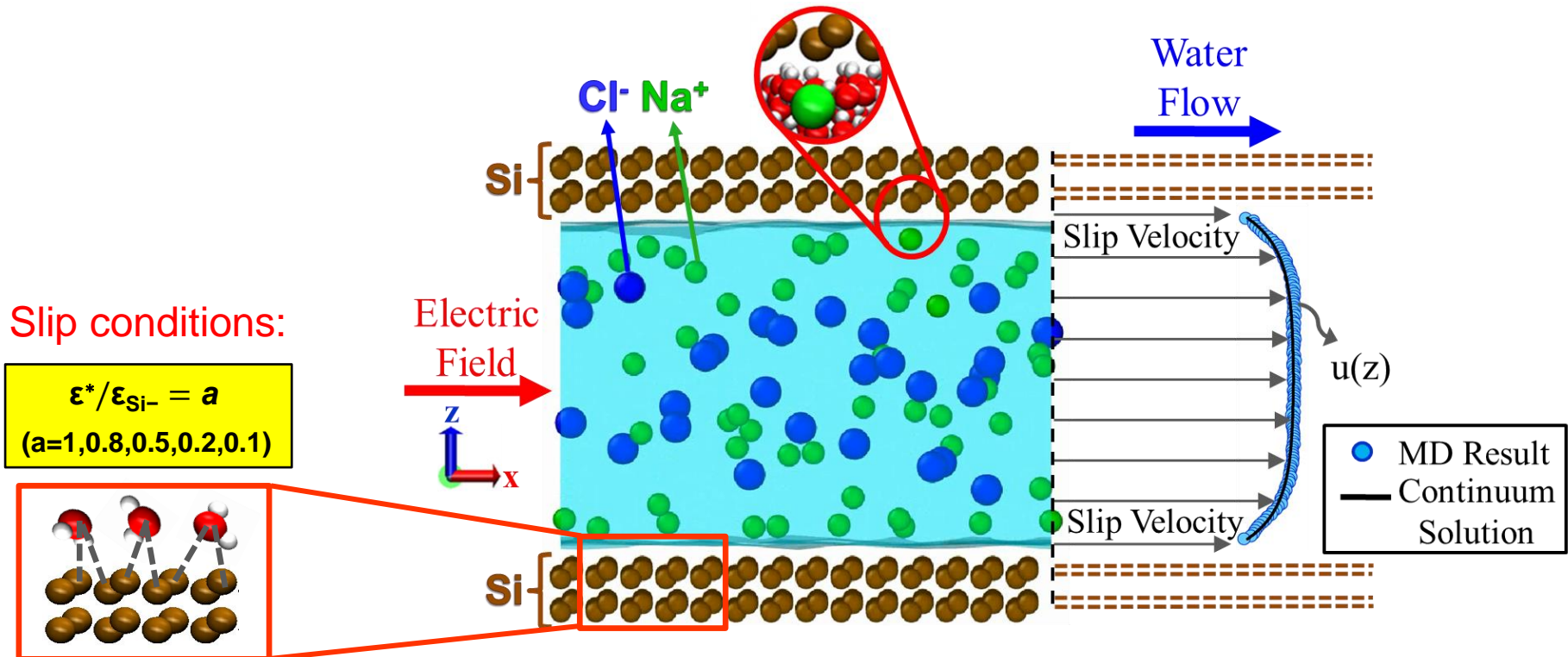
# Molecular and Continuum Transport Perspectives in Electroosmotic (EO) Slip Flows

# EOF Simulations of NaCl Solution in Silicon Nano-Channels

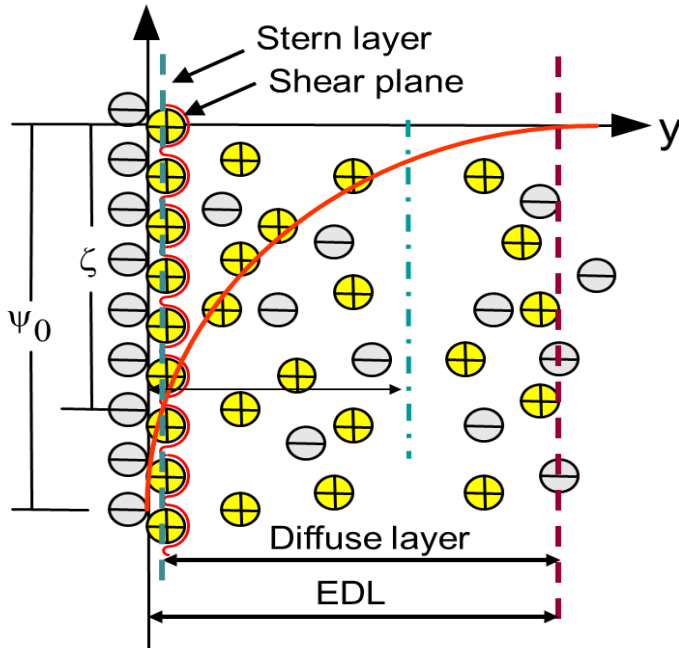
We perform electroosmotic flow simulations (EOF) for a 3D system consisting of aqueous NaCl solution confined in charged silicon nano-channels under realistic electrochemical conditions.

## Objectives

- To investigate the effects of *slip length* and *viscosity* variations on EOF.
- To compare nano-scale electroosmotic slip flow simulations with analytical continuum solutions with velocity slip.







## □ Electrical Double Layer (EDL):

### Stern Layer

- Shield the surface charge with counter-ions
- One ionic diameter thick
- Immobilized ions

### Zeta Potential ( $\zeta$ )

### Diffuse Layer

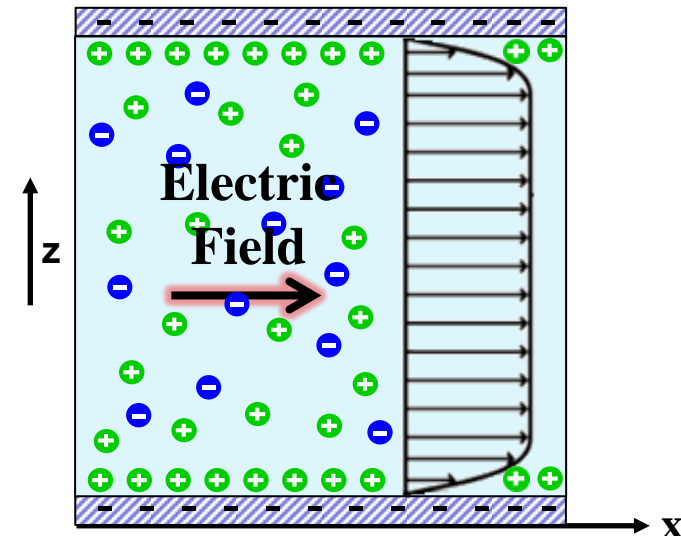
- Outside Stern layer
- Boltzmann distribution
- Net charge (counter ions)

### Electroosmotic Flow

□ **Electroosmotic Flow (EOF):** When an externally electric field is applied, ions in the Diffuse layer drag water molecules through electric field direction and creates an electric field driven flow.

**Why Important?**

- Creating flow with externally applied electric field instead of large pressure drops
- Pumping without moving mechanical components



## Governing Continuum Equations in Electrokinetic Transport Theory:

□ **Poisson-Boltzmann Equation (PB):** For an electrolyte solution with N different ionic species, PB equation determines the electrokinetic potential within the electrolyte

$$\nabla^2 \psi = -\frac{\rho_e}{\epsilon_0 \epsilon_r} = -\frac{F}{\epsilon_0 \epsilon_r} \left[ \sum_{i=1}^N v_i c_{i0} \exp\left(-\frac{v_i F \psi}{RT}\right) \right]$$

Poisson Equation

□ **Navier-Stokes Equation (NS):** Velocity profile in the stream wise direction for

$$\frac{du^2}{dz^2} = -\frac{\rho_e}{\mu} E_x$$

- Steady
- Incompressible
- Fully developed
- Electroosmotic flow
- No pressure gradient

Combining NS and PB equations, one can obtain a relationship between EO velocity and electrokinetic potential

$$\frac{du^2}{dz^2} = \frac{\epsilon_0 \epsilon_r}{\mu} E_x \frac{d\psi^2}{dz^2}$$

**NO INFORMATION ABOUT SLIP**

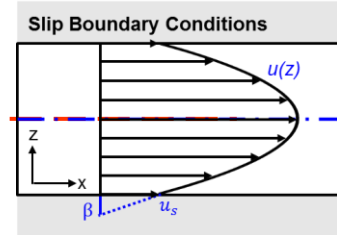
# Theory: Poisson-Boltzmann and Stokes Equations with Slip Correction

## Boundary conditions

- Navier-type slip condition at the interface
- Symmetry at the channel center

$$u_s - u_w = \beta \frac{du}{dz}$$

$$\frac{du}{dz} = 0 \text{ and } \frac{d\psi}{dz} = 0$$



## Solution of momentum equation with a Navier-type slip condition

$$u(z) = \frac{\epsilon_0 \epsilon_r}{\mu} E_x \left[ \psi(z) - \zeta + \beta \frac{d\psi}{dz} \Big|_{z=0} \right]$$

**Slip modified EOF in nanochannels requires**

- Solution of PB Equation ( $\psi(z)$ )
- Electrokinetic potential on the wall ( $\zeta$ )
- The gradient of electrokinetic potential on the wall ( $\frac{d\psi}{dz} \Big|_{z=0}$ )

$$\psi(z) = \frac{4\zeta}{\alpha} \left[ \tanh^{-1} \left[ \tanh \left( \frac{\alpha}{4} \right) \exp(-\omega z) \right] \right]$$

$$\frac{d\psi}{dz} = \frac{4\zeta}{\alpha} \left[ \frac{\omega \tanh \left( \frac{\alpha}{4} \right) \exp(-\omega z)}{\tanh^2 \left( \frac{\alpha}{4} \right) \exp(-2\omega z) - 1} \right]$$

Ionic energy parameter:  $\alpha = \frac{Fv\zeta}{RT}$

Debye Hückel parameter:  $\omega = \frac{1}{\lambda_D} = \sqrt{\frac{\sum_{i=1}^N v_i^2 F^2 c_{i0}}{\epsilon_0 \epsilon_r RT}}$

# Theory: Poisson-Boltzmann and Stokes Equations with Slip Correction

□ PB-S Eqn with slip correction between  $z=0$  and  $z=h/2$ :

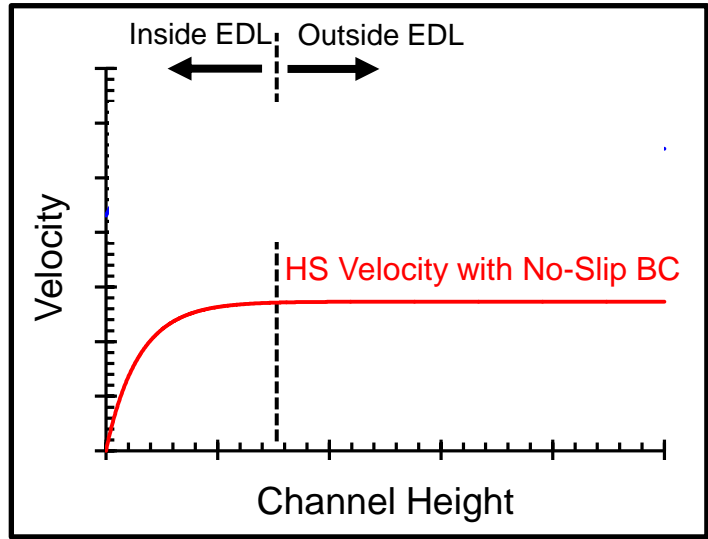
$$u(z) = u_{HS} \left\{ 1 - \frac{4}{\alpha} \left[ \tanh^{-1} \left( \tanh \left( \frac{\alpha}{4} \right) \exp(-\omega z) \right) - \frac{\beta}{\lambda_D} \left( \frac{\tanh \left( \frac{\alpha}{4} \right)}{1 - \tanh^2 \left( \frac{\alpha}{4} \right)} \right) \right] \right\}$$

Helmholtz-Smoluchowski Velocity

No-slip BC ( $\beta=0$ )

Outside EDL ( $\psi(z)=0$ )

$$u_{HS} = -\frac{\epsilon_0 \epsilon_r \zeta}{\mu} E_x$$



EOF velocity with and without slip

★ Based on this equation, we can predict EOF velocity profiles if we know the Slip Length and Apparent Viscosity.

➤ OUTSIDE EDL ( $\psi(z)=0$ )

$$\frac{u_{HSslip}}{u_{HS}} = 1 + \frac{4\beta}{\alpha\lambda_D} \left( \frac{\tanh \left( \frac{\alpha}{4} \right)}{1 - \tanh^2 \left( \frac{\alpha}{4} \right)} \right)$$

This equation shows that slip contribution in EOF is independent from the channel height. Hence, it is theoretically possible to observe slip enhanced EOF in nano/micro-channels by

- Choosing a hydrophobic channel with large slip length ( $\beta$ )
- Increasing the ionic concentration to reduce Debye length ( $\lambda_D$ )

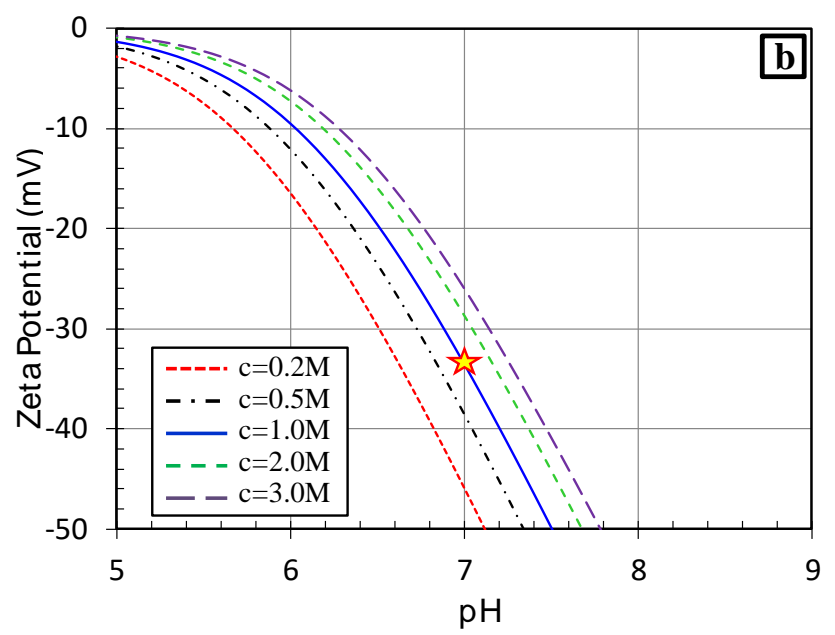
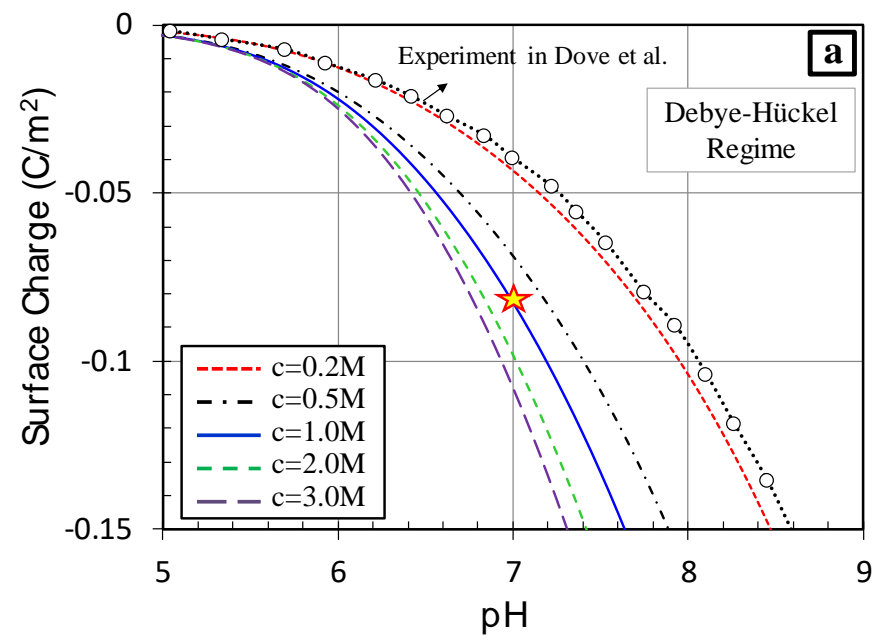
# Theory: Determination of Realistic Electrochemical Conditions

## Surface charge density & zeta potential

- Ionic Concentration
- pH of the solution
- Surface chemistry

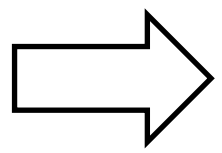
~~Arbitrary~~

Charge Regulation Model  
(Triple Layer Theory)



## In our MD Simulations, we pick

- $c=1 M$
- $pH=7$
- Silica Surface Chemistry

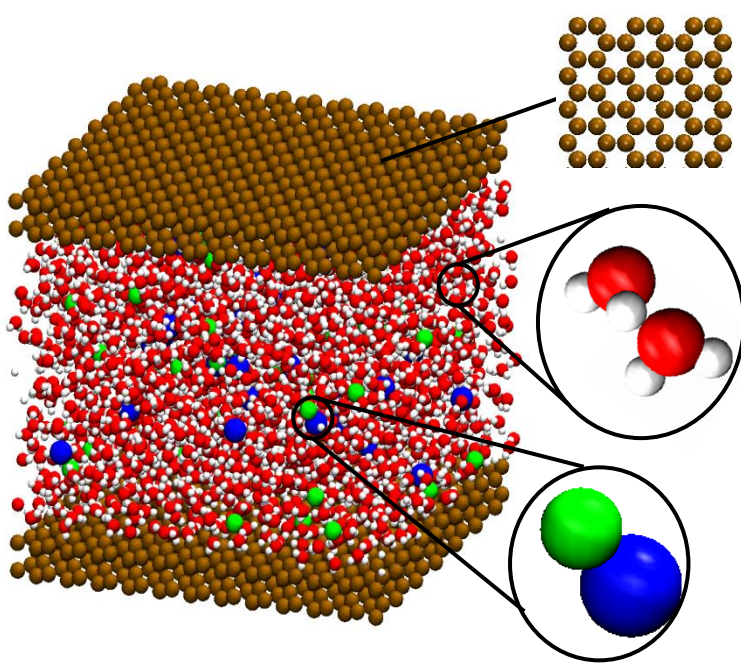



**Electrochemical Conditions**

→  $\sigma_s = -0.082 C/m^2$

→  $\zeta = -33 mV$

## Model: NaCl solution – Silicon System

<span style="color: blue;">●</span>	Chloride
<span style="color: green;">●</span>	Sodium
<span style="color: brown;">●</span>	Silicon
<span style="color: red;">●</span>	Oxygen
<span style="color: white;">●</span>	Hydrogen

### Silicon <111>

- GROMACS
- Negatively Charged

### Water

- SPC/E Model

### Sodium and Chloride

- Quantum Chemical Calculations

### Dissimilar Atoms

- Lorentz-Berthelot Rule

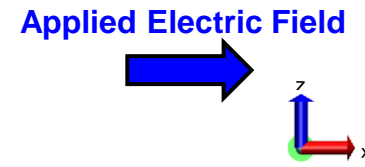
$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$$

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

## Channel Size

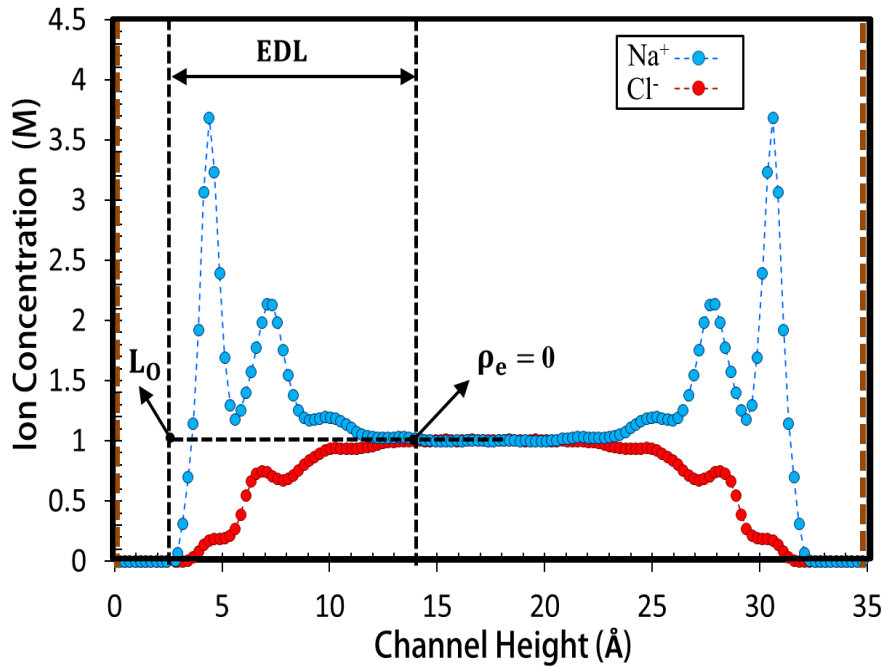
- Continuum-like behavior
- Solid-liquid interface phenomena
- No EDL overlapping

3.49 nm

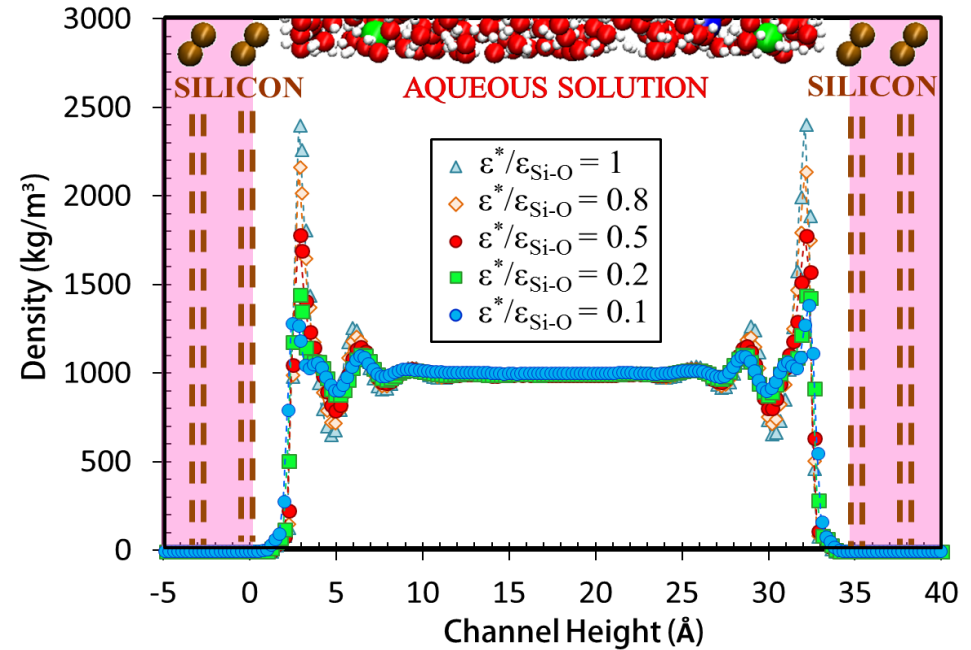




## Ion Distribution



## Density Distribution



- Total number of 50Na<sup>+</sup> and 28Cl<sup>-</sup> results surface charge of  $\sigma = -0.082 \text{ C/m}^2$  and  $c = 1 \text{ M}$  bulk ionic concentration.

- EDL Thickness

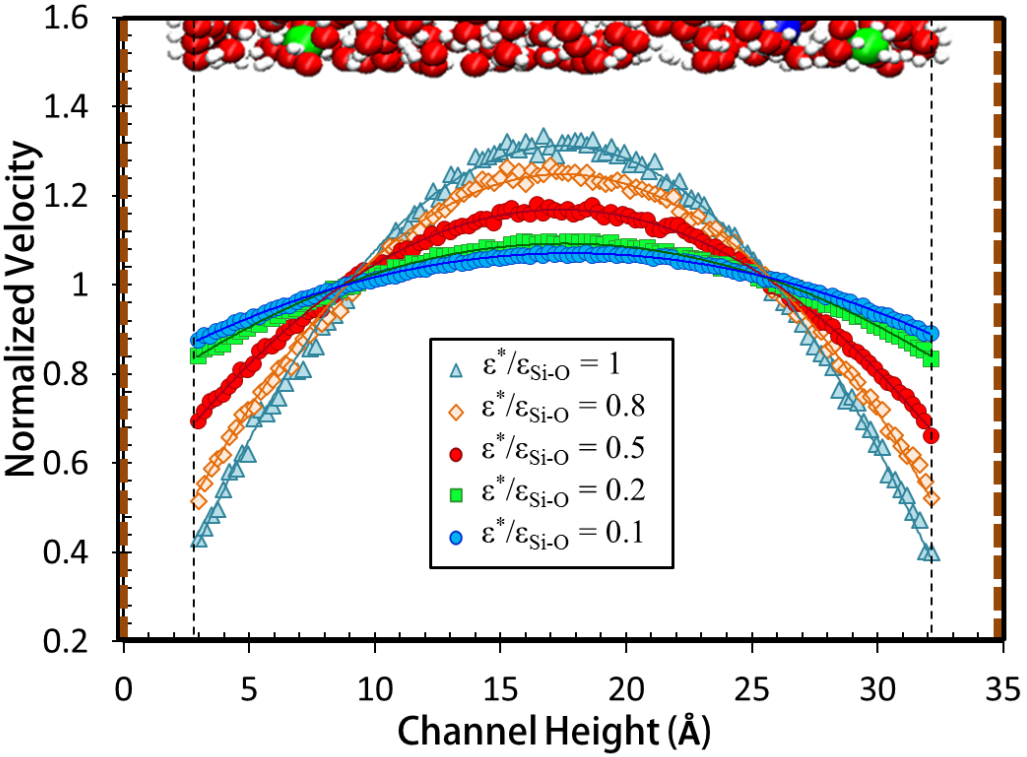
Graphically  $\sim 1.1 \text{ nm}$

Analytically  $\sim 4.5 \lambda_D$

- Thermodynamic state is fixed at  $T = 300 \text{ K}$  and  $\rho_{\text{bulk}} = 997.2 \text{ kg/m}^3$
- Magnitude of first density peak increases with increased epsilon ratio, accumulating more water molecules near silicon walls.

# Force-Driven Flow Simulations: Viscosity and Slip Length

## Velocity Profiles



### With reduced $\epsilon^*/\epsilon_{Si-O}$ ratio

- Liquid-wall interaction strength at interface decreases
- The velocity profiles become less parabolic with larger slip length

- MD predicted parabolic velocity profiles

Polynomial Fitting

$$u(z) = Az^2 + Bz + C$$

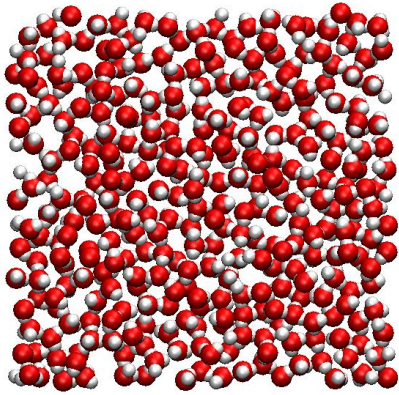
- Poiseuille flow with slip correction for 1D, incompressible, steady, fully-developed, and force driven flow

$$u(z) = \frac{fh^2}{2\mu} \left( -\left(\frac{z}{h}\right)^2 + \left(\frac{z}{h}\right) + \left(\frac{\beta}{h}\right) \right)$$

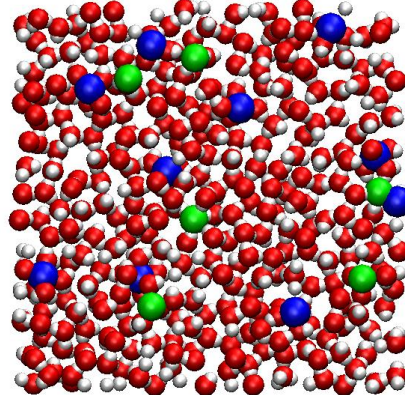
Viscosity:  $\mu = -\frac{f}{2A}$  and  $\mu = -\frac{fh}{2B}$

Slip Length:  $\beta = \frac{2C\mu}{fh}$

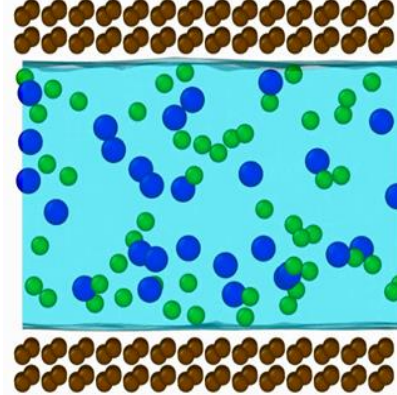
## □ Viscosity of Water in Different Conditions



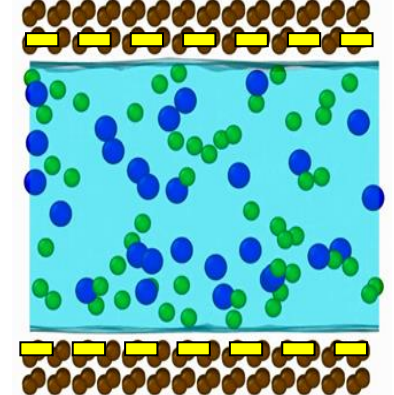
▪ Deionized Water without Wall



▪ Ionic Solution without Wall



▪ Ionic Solution in Uncharged Channel



▪ Ionic Solution in Charged Channel

## □ Viscosity

- Viscosity of deionized water model increases nearly 26% with addition of 1M NaCl.
- Inclusion of walls does not significantly alter the apparent viscosity of the ionic solution for channel height of 3.5 nm.
- Comparing with the neutral case, surface charge results in viscosity enhancement as well as reduction in the slip lengths.

## Slip Length

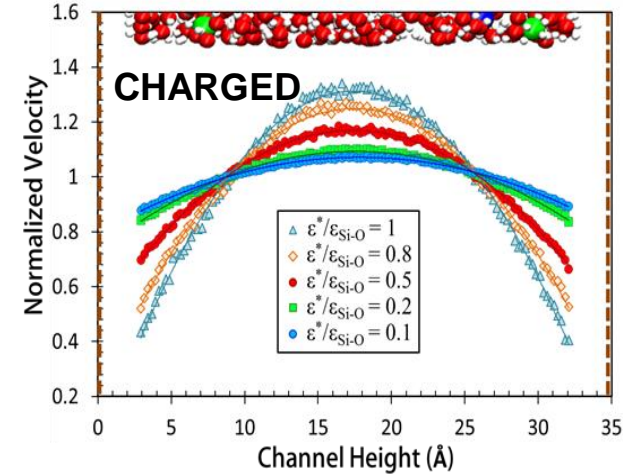
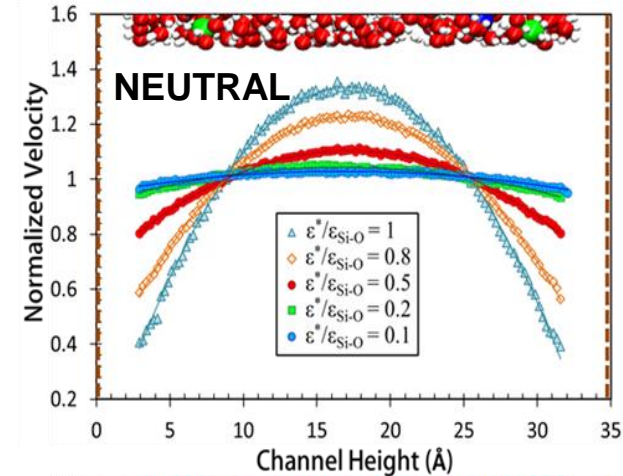
	Charged Nano-channel		Neutral Nano-channel	
	Viscosity ( $\mu\text{Pa}\cdot\text{s}$ )	Slip Length (nm)	Viscosity ( $\mu\text{Pa}\cdot\text{s}$ )	Slip Length (nm)
$\epsilon^*/\epsilon_{\text{Si-O}} = 1$	944.5	0.33	923.7	0.38
$\epsilon^*/\epsilon_{\text{Si-O}} = 0.8$	943.9	0.54	925.0	0.72
$\epsilon^*/\epsilon_{\text{Si-O}} = 0.5$	943.8	1.06	916.4	1.91
$\epsilon^*/\epsilon_{\text{Si-O}} = 0.2$	948.8	2.19	-	-
$\epsilon^*/\epsilon_{\text{Si-O}} = 0.1$	948.0	2.79	-	-

$\mu = 945 \mu\text{Pa}\cdot\text{s}$

$0.33 \leq \beta \leq 2.79 \text{ nm}$

Force-driven flow simulations of 1 M NaCl solution in both electrically neutral and charged ( $\sigma_s = -0.082 \text{ C/m}^2$ ) silicon nanochannels at various  $\epsilon^*/\epsilon_{\text{Si-O}}$  ratio.

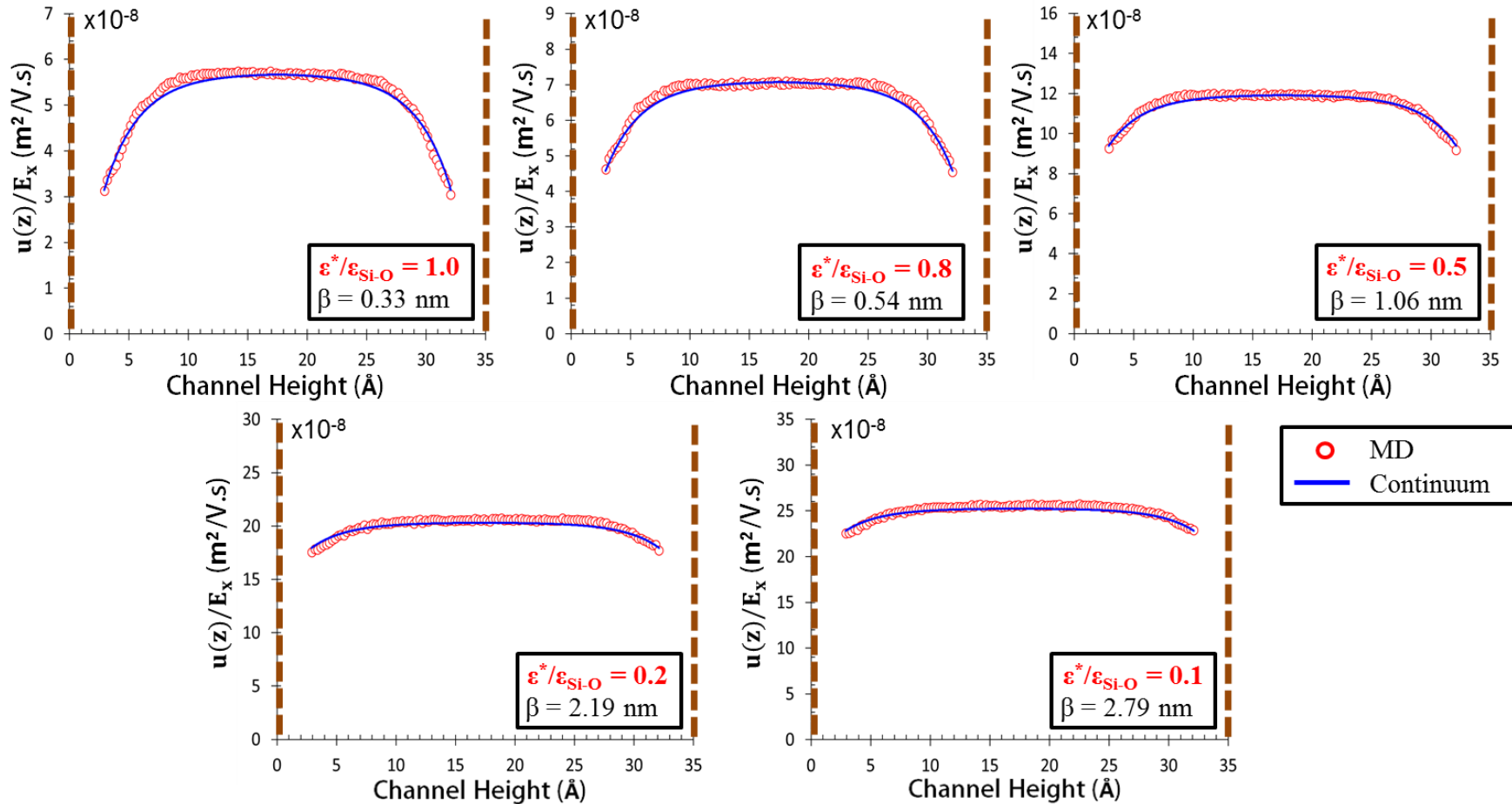
- Comparing with the neutral case, surface charge velocity profiles results in larger parabolic component
- Surface charge reduces the slip length
- With increased  $\epsilon^*/\epsilon_{\text{Si-O}}$  ratio, slip values decrease while apparent viscosities remain constant.




# Electroosmotic Flow Simulations vs Analytical Solutions of PB-S Equation

## Electroosmotic Mobilities

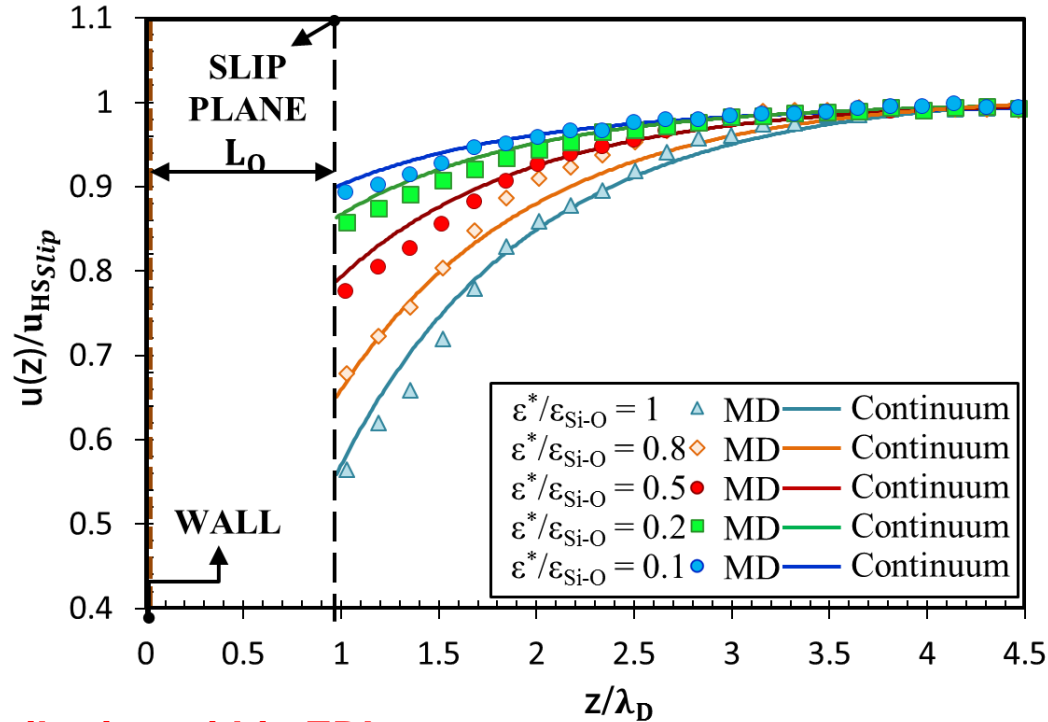
To compare simulation results for different  $\epsilon^*/\epsilon_{\text{Si-O}}$  ratios, velocity profiles are normalized by applied electric field.




 EOF simulations of **1M** NaCl solution in negatively charged ( $\sigma = -0.082 \text{ C/m}^2$ ) silicon channels



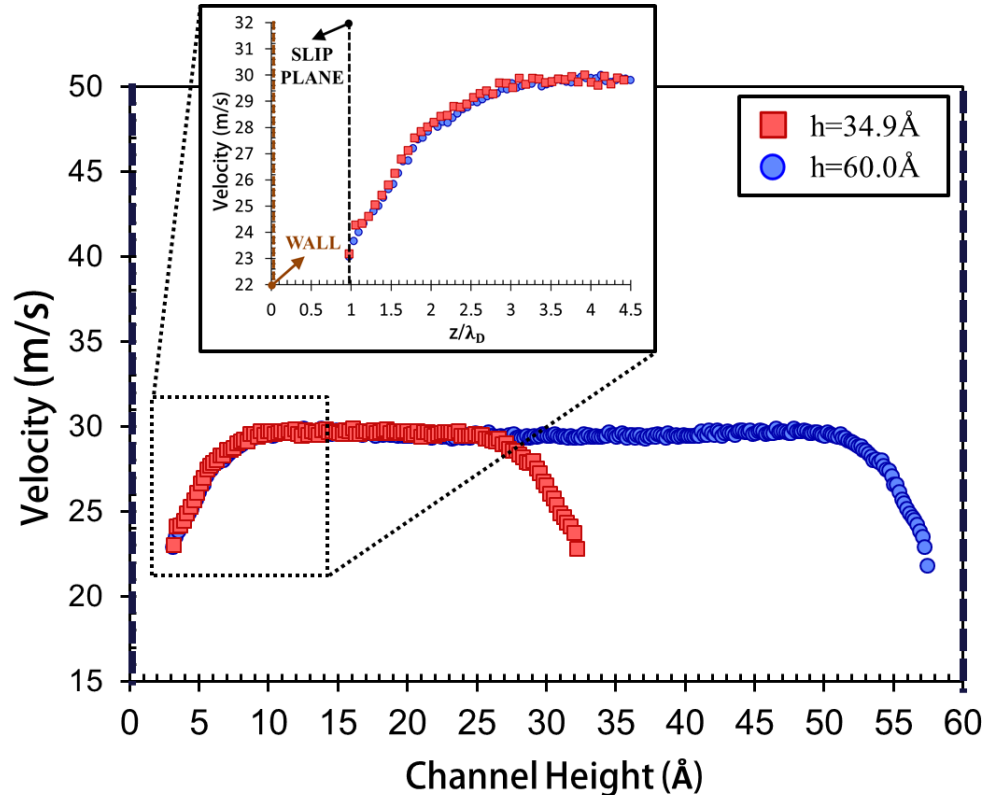
- **Velocity Profiles:** normalized by the slip-modified Helmholtz-Smoluchowski velocity



## EO velocity distribution within EDL

- The electrokinetic potential reaches to zero and the EOF reach its maximum value beyond  $z/\lambda_D > 4.5$ .
- Velocity gradients within the EDL are greatly reduced with increased slip length.
- Normalized velocity profiles show increased velocity slip by reduced  $\epsilon^*/\epsilon_{Si-O}$  ratio.
- Comparison of the MD results and continuum predictions show reasonable agreements.

## Comparison of different channel heights



## EO velocity distribution within EDL

- Enhanced EOF is a function of slip-length normalized by Debye length ( $\beta^* = \beta/\lambda_D$ ).
- It is theoretically independent from the channel height.

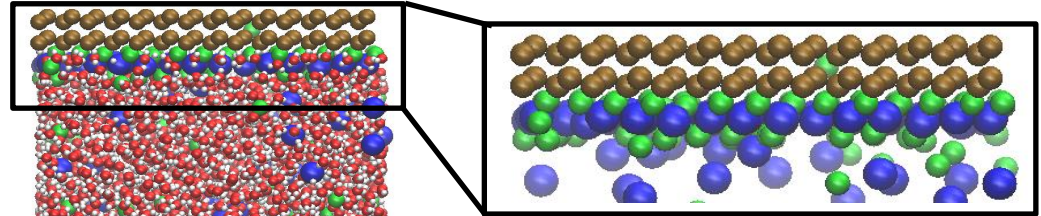
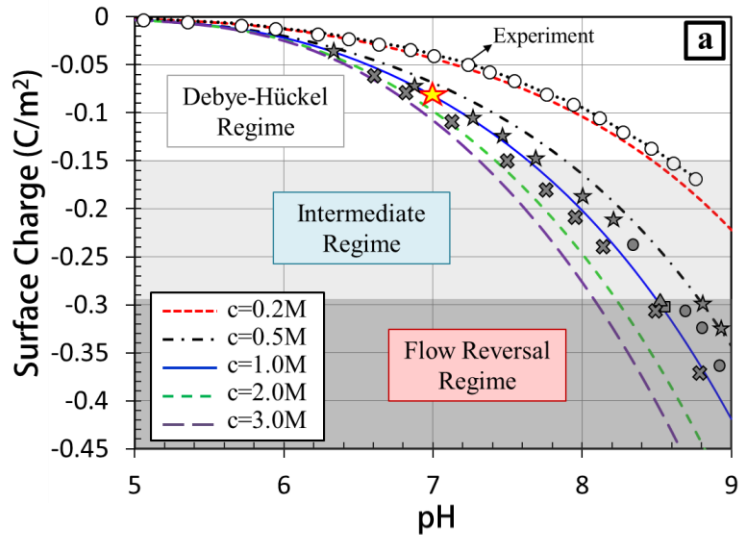
$$\frac{u_{HSslip}}{u_{HS}} = 1 + \frac{4\beta}{\alpha\lambda_D} \left( \frac{\tanh\left(\frac{\alpha}{4}\right)}{1 - \tanh^2\left(\frac{\alpha}{4}\right)} \right)$$

## Comparing EOF simulations for two different channel heights (h=3.5nm and h=6nm)

- The velocity profiles show similar slip behavior in the near wall region for both channel sizes, with a constant bulk flow velocity.
- This result verifies size independency of the electroosmotic slip flow.

# What Happens at Higher Surface Charges?

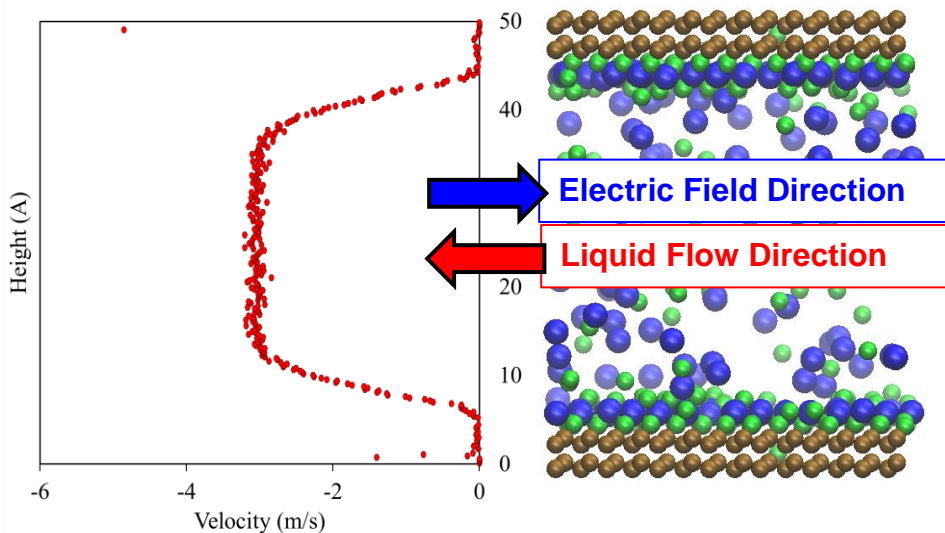
## Charge Inversion and Electroosmotic Flow Reversal



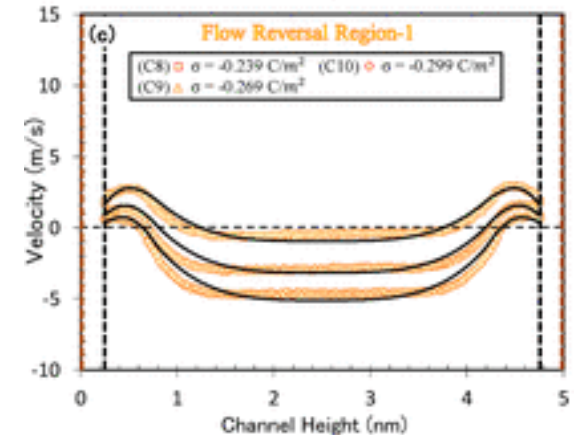
**Charge Inversion:** Excessive adsorption of counterions at the Stern layer, exceeding the net charge of the surface.

**Crowding:** More than one layer of counterions shielding the surface, which dominates charge inversion, and results in co-ion excess outside these layers

### Flow Reversal

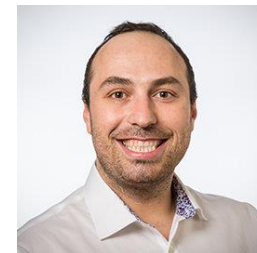


### MD predictions vs Poisson-Fermi Equation for charge inversion & flow reversal





- Excellent agreements between the MD results and analytical solutions of EOF in the Debye-Hückel regime are observed, when the slip lengths and viscosities are obtained from MD simulations.
- The velocity profile in the EDL shows finite slip at the first water density layer of the walls, followed with a typical viscous flow profile in the EDL that reaches the Helmholtz–Smoluchowski (HS) velocity in the bulk flow region.
- HS velocity increases due to velocity slip, which is a property of the water–surface interactions and the surface charge.
- The analytical model shows normalization of the slip length with the Debye length instead of the channel height, implying, slip enhancement in EOFs is independent of the channel height. This means that EOF slip can be measured experimentally in microchannels...



Resch Prof. Alper Celebi, Vienna Technical Univ

**THANK YOU**