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Molecular Dynamics Simulations of Slip on Curved Surfaces

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EPSRC
Pioneering research and skills

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Outline

- Background to the project
- Introduction to slip
- Extracting the slip length with MD
  - Non-equilibrium method
  - Equilibrium method
- Curvature dependence

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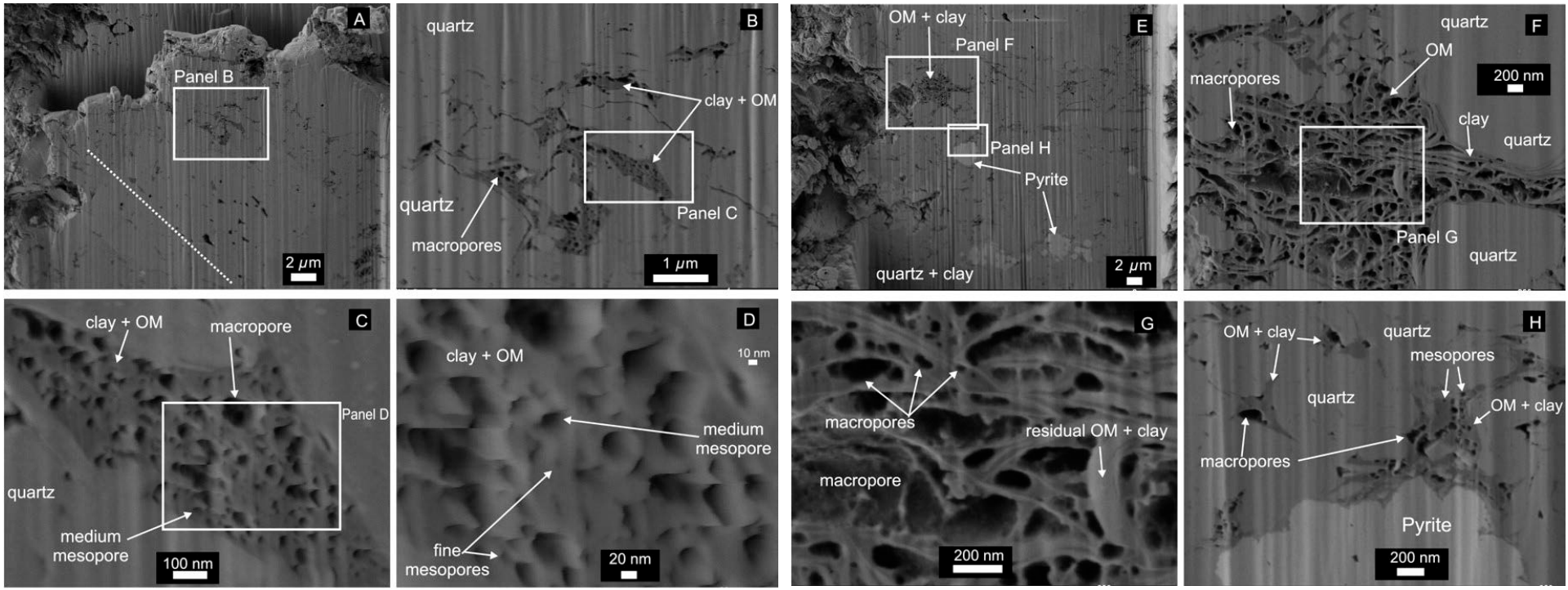
Intro – Gas Shale



FE-SEM images of Barnett gas shale
Chalmers, Bustin and Power. AAPG Bulletin. 96-6 (2012). 1099-1119.

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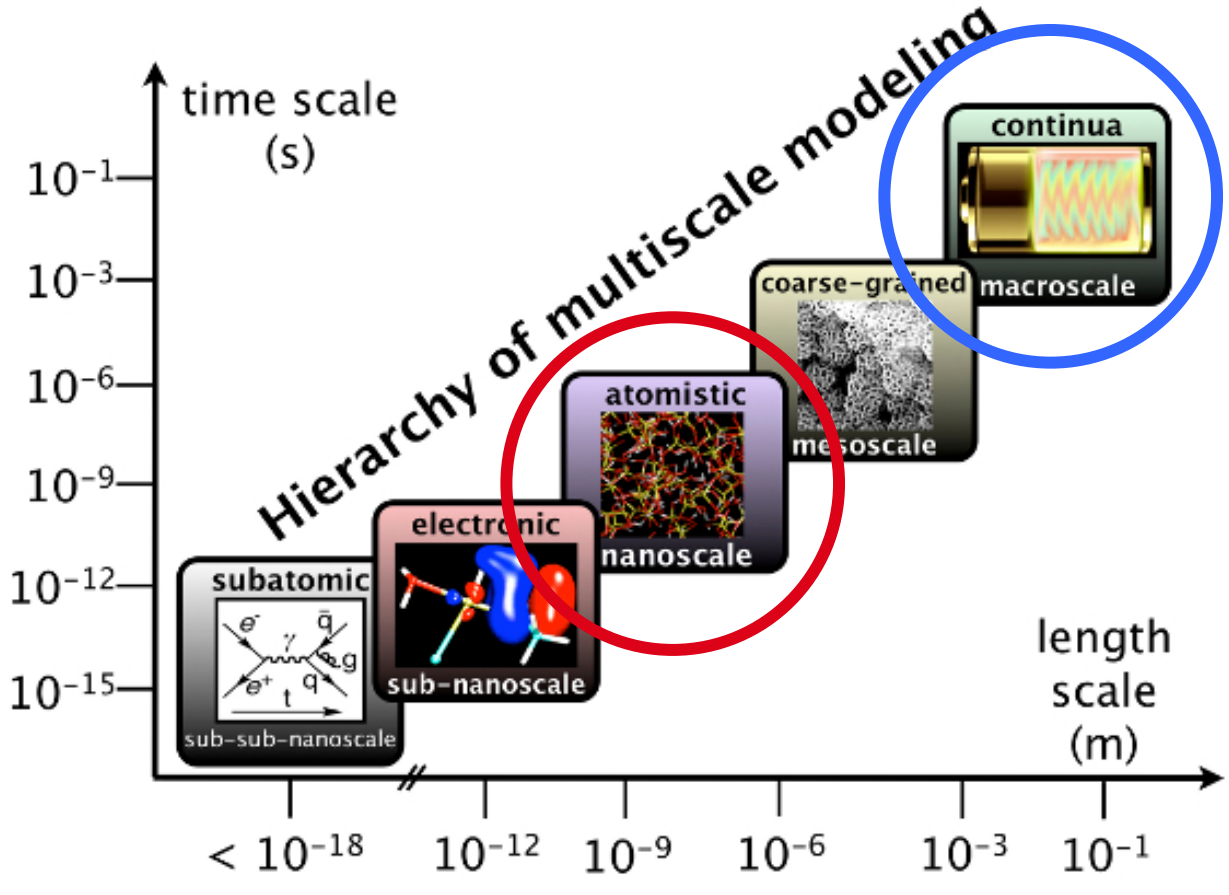
Intro – Methods



Helmholtz Institute Ulm. Karlsruhe Institute of Technology. http://www.hiu.kit.edu/104.php

Nanometre pores → MD (Molecular Dynamics - atomistic)

Interesting timescales → LB (Lattice Boltzmann - continua)

LB unable to exhibit nano-scale phenomena

LB requires modification for nano-pores.

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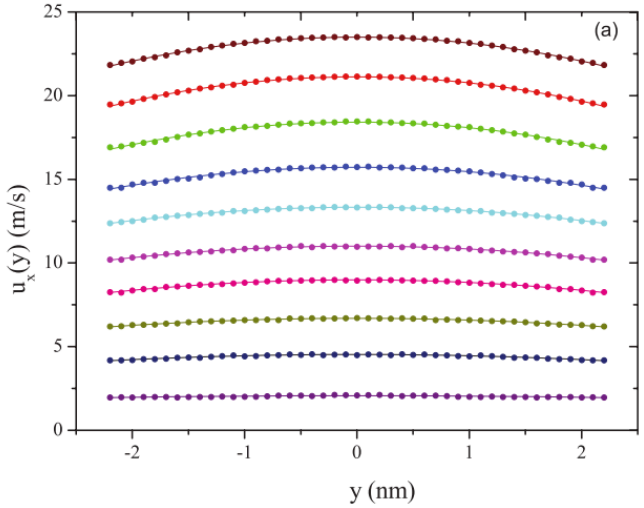
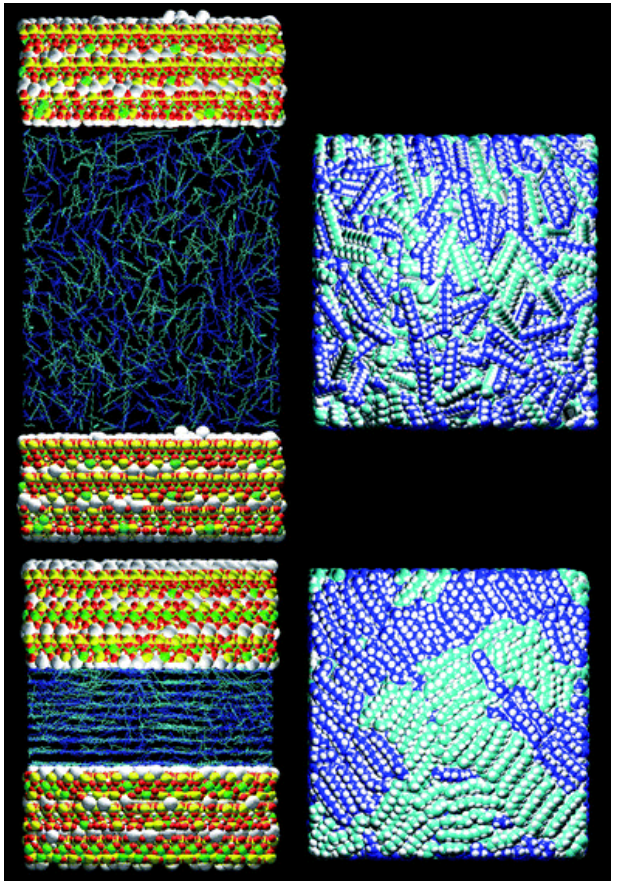
Nano-scale confinement phenomena

- Wave-like density distributions
- Elevated pressures due to wall attraction
- Molecular alignment and reorientation into solid like structures
- Slip



Velocity profile of water in graphene nanochannel with increasing body force (bottom to top). Kannam et. al. 2011

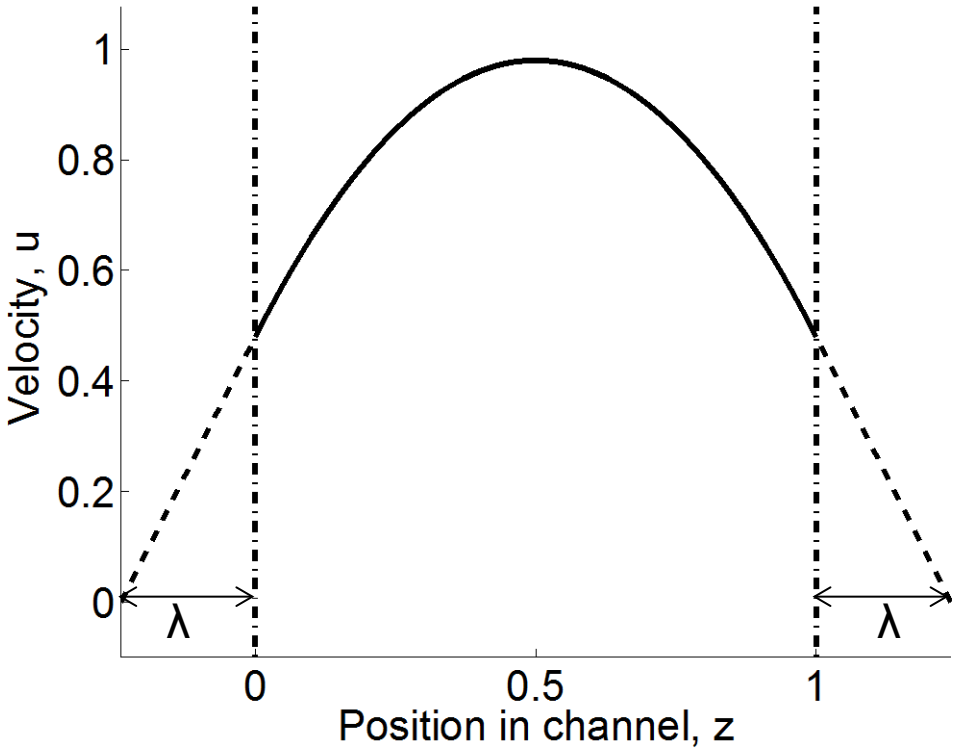


H, Docherty and P.T, Cummings (2010)

Slip and the slip length

- Usual assumption: no-slip
- Slip is non-negligible on the nano-scale
- No-slip assumption → vastly underestimate flow rates
- Slip quantified by slip length, λ:

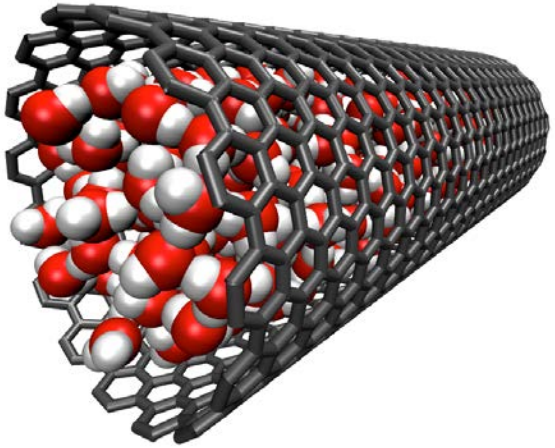
$$\lambda = \frac{u_{wall}}{\left.\frac{\partial u}{\partial z}\right|_{wall}}$$

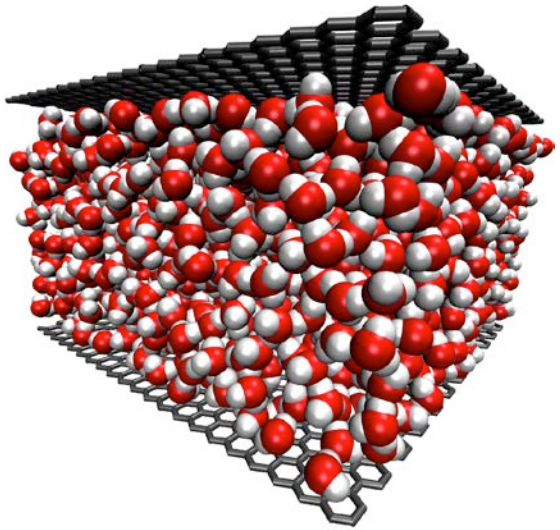


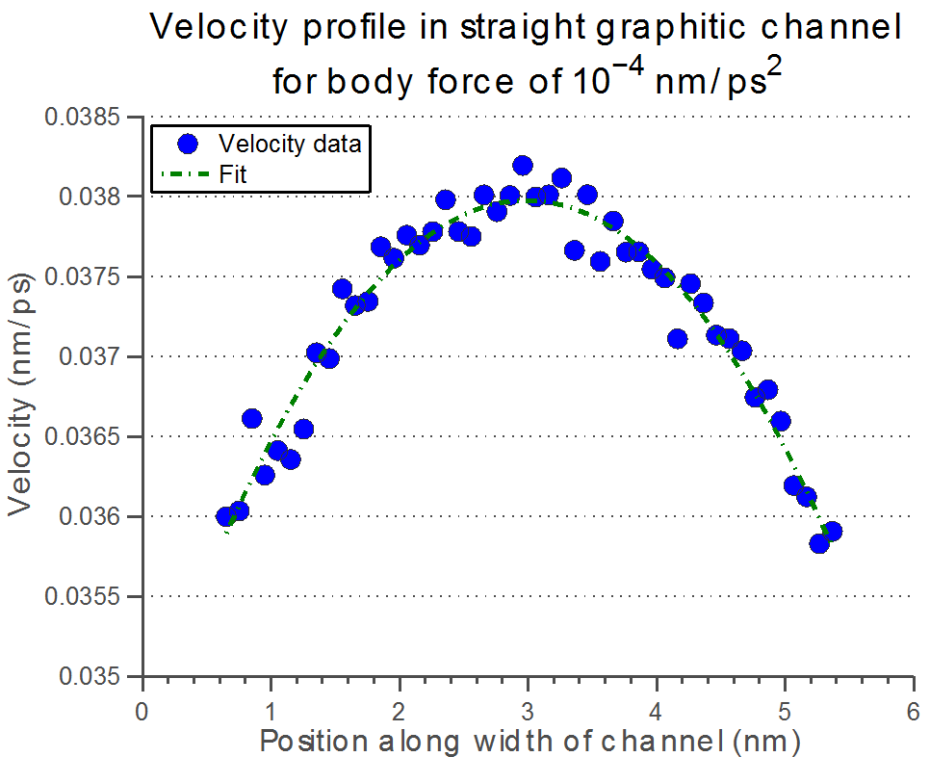
- Flow enhancement:

$$Q_{enhanced} = Q_{no-slip}(1 + 4\lambda / R)$$

Extracting slip length parameter - NEMD







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Extracting slip length parameter - EMD

- Green-Kubo expression is solved for the friction coefficient, C_F:

$$C_F = \frac{1}{Ak_BT}\int_0^\infty dt\left\langle F(t)F(0)\right\rangle_{equ}$$

- F(t): Tangential force acting along axial direction of surface; A: Area of surface; k_B: Boltzmann coefficient; T: Temperature
- Viscosity calculation from separate EMD simulation

$$\mu = \frac{V}{k_BT}\int_0^\infty dt\left\langle P_{\alpha\beta}(t_0)P_{\alpha\beta}(t_0+t)\right\rangle \qquad \lambda = \frac{\mu}{C_F}$$

Falk and Bocquet et. al. Nano Lett. 10 (2010). 40667-4073. Evolution of friction coefficient with confinement R, for water inside/outside CNT and between graphene sheets. EMD and NEMD.

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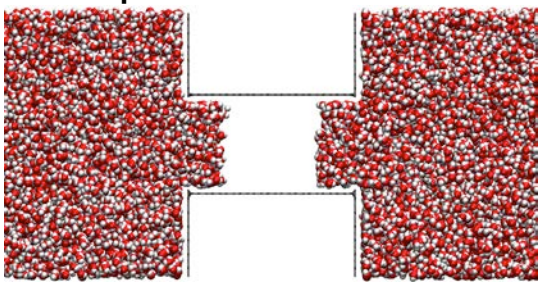
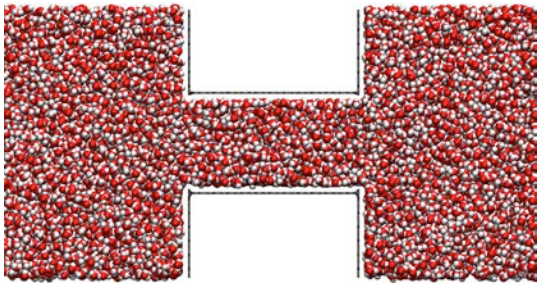
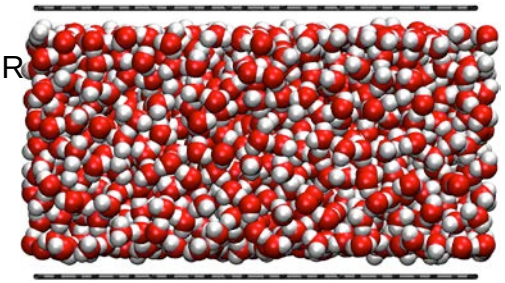
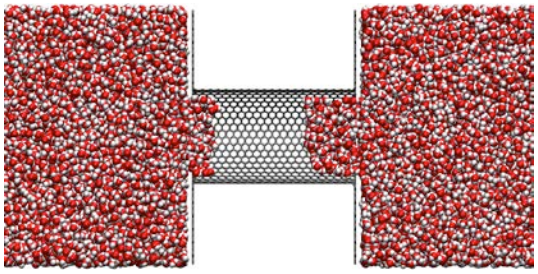
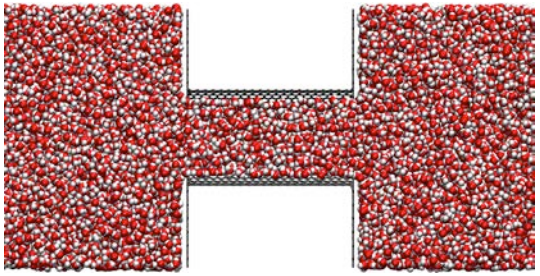
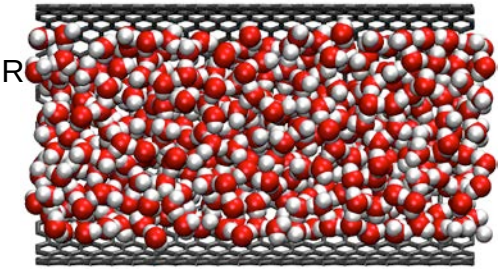
Equilibration process

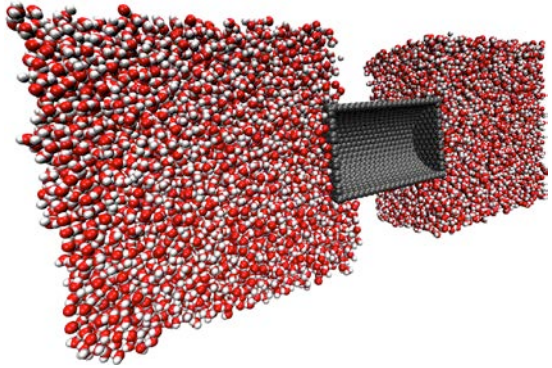
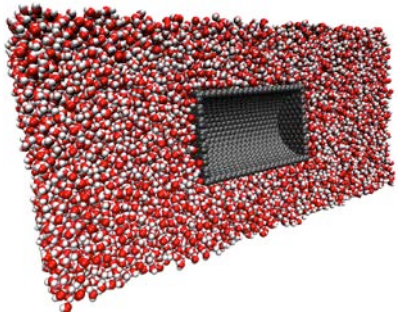
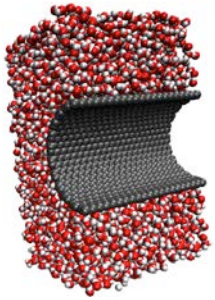
Slit pore

T_0  T_E  T_R 

Cylindrical pore – fluid inside

T_0  T_E  T_R 

Cylindrical pore – fluid outside

T_0  T_E  T_R 

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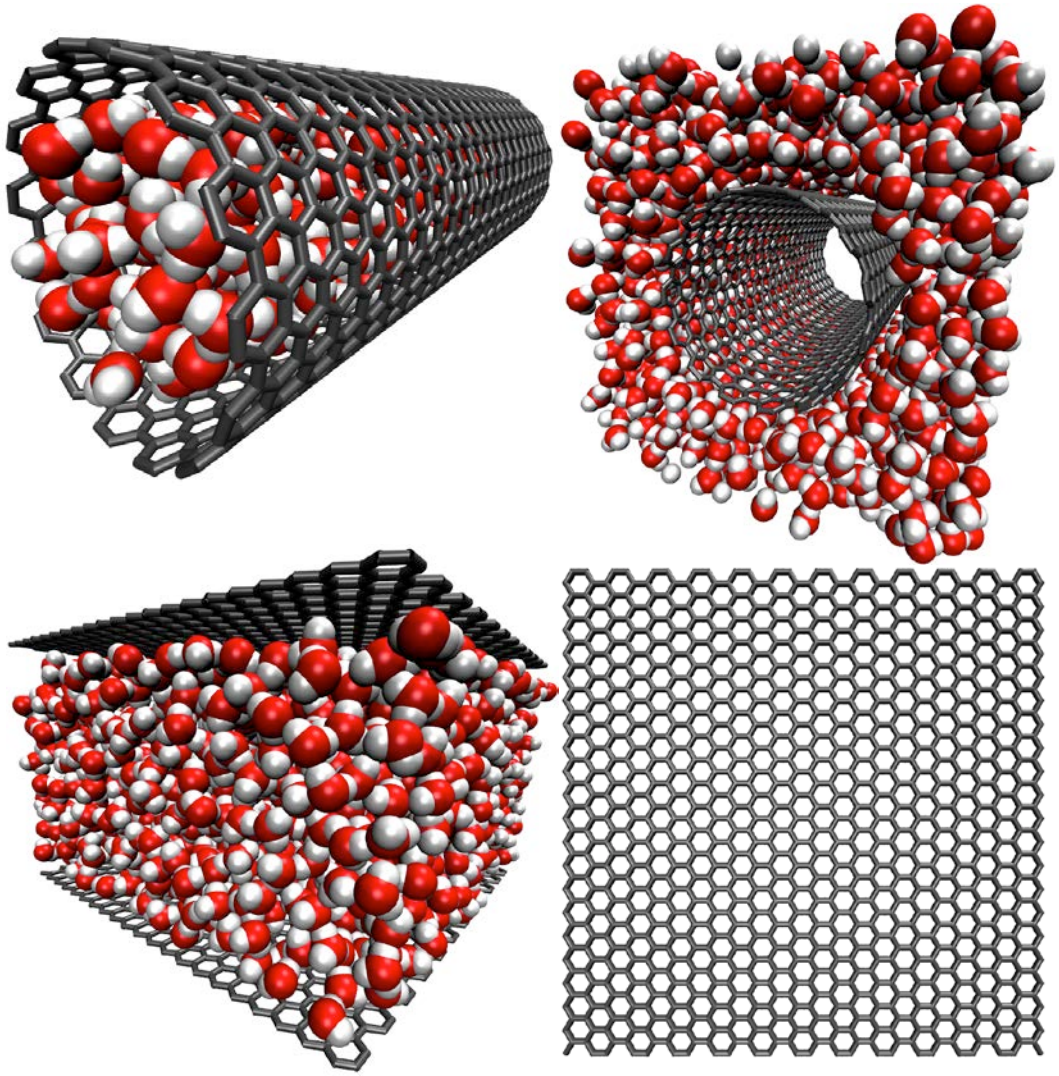
Simulated systems



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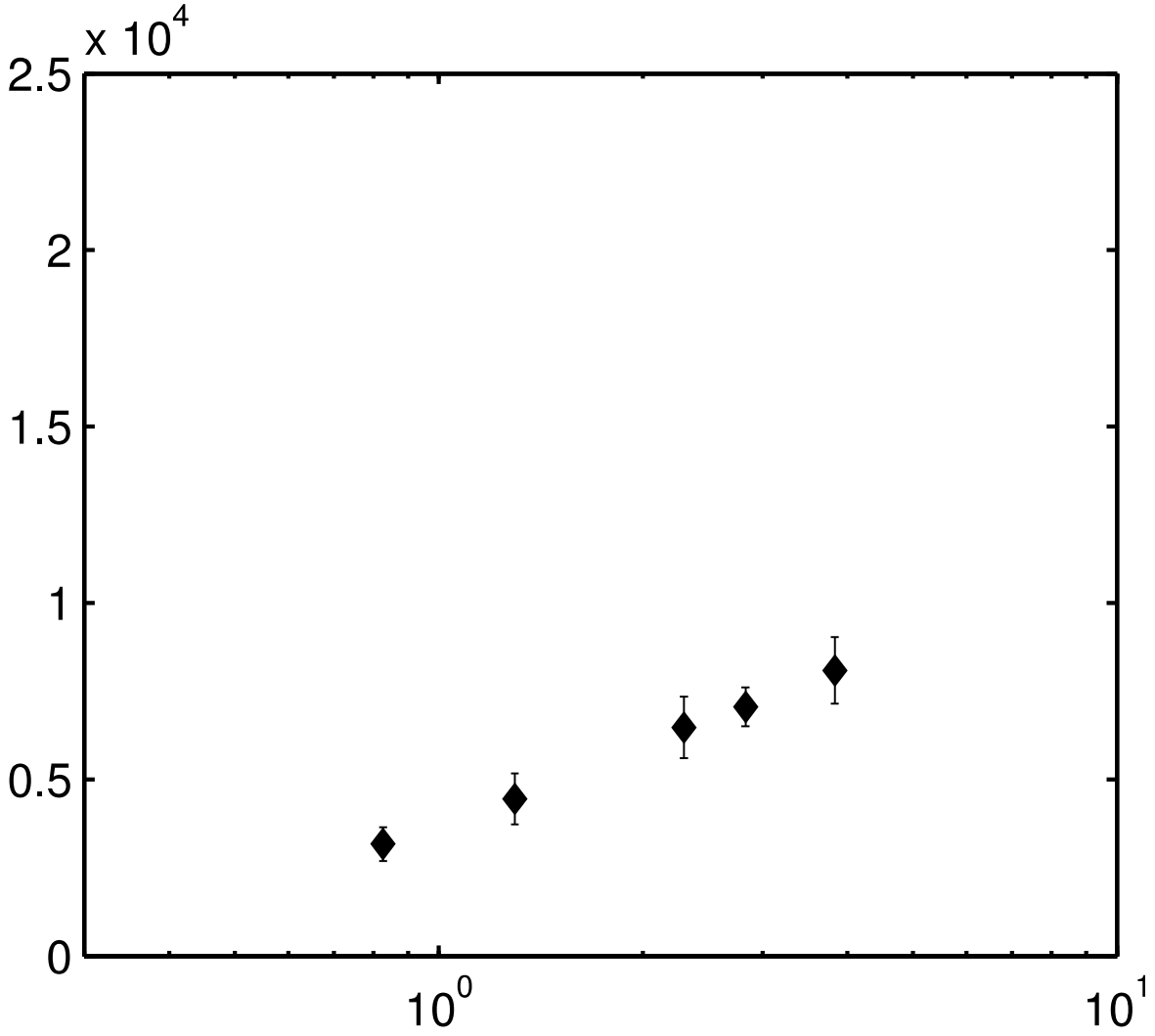
Friction coefficient variation with curvature



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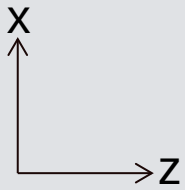
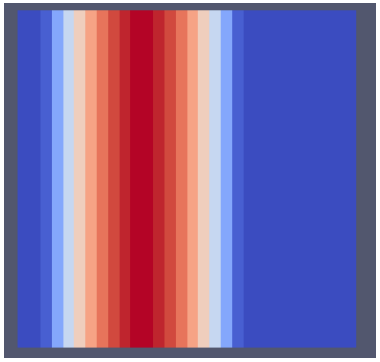
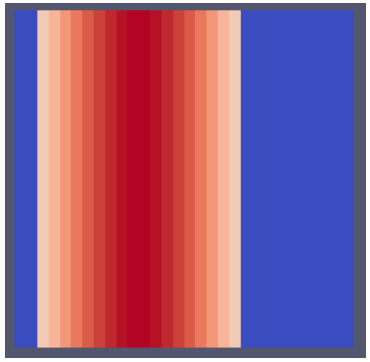
Lattice Boltzmann – Velocity boundary condition



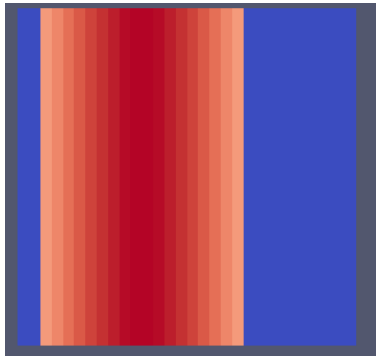


BF = (1.414e-4, 0, 0)

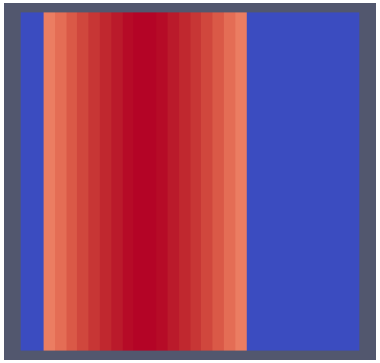
u_s = (0, 0, 0)



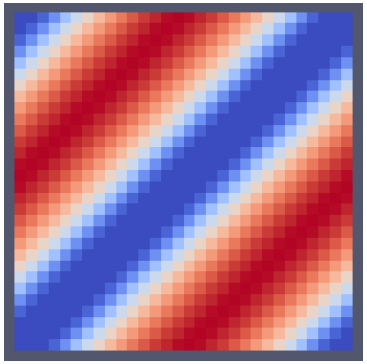
u_s = (0.1414, 0, 0)



u_s = (0.2828, 0, 0)

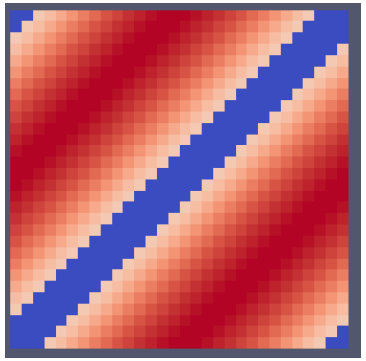


u_s = (0.4242, 0, 0)

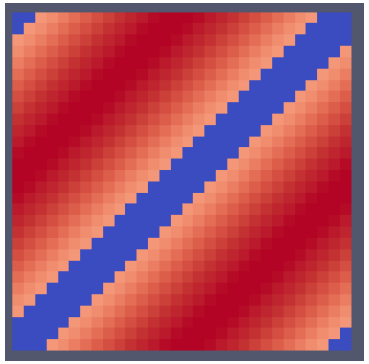


BF = (1e-4, 0, 1e-4)

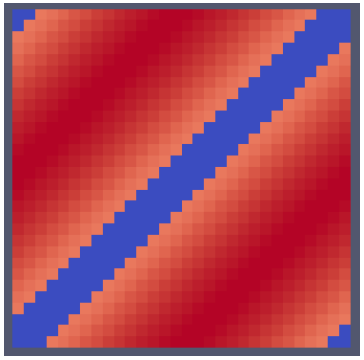
u_s = (0, 0, 0)



u_s = (0.1, 0, 0.1)



u_s = (0.2, 0, 0.2)



u_s = (0.2, 0, 0.2)

Conclusions and future work

- Geometry impacts slip length
- Slip larger for fluid inside a cylindrical pore compared to outside
- Slip approaches a constant value at large curvatures, for flow over both convex and concave surfaces.
- Next steps:
  - Increase statistical accuracy of MD slip data.
  - Perform same simulations with hydrocarbons.
- Other Work:
  - Lattice Boltzmann implementation of slip boundary condition in progress.
  - Streamline MD-LB process given surface-fluid interactions.

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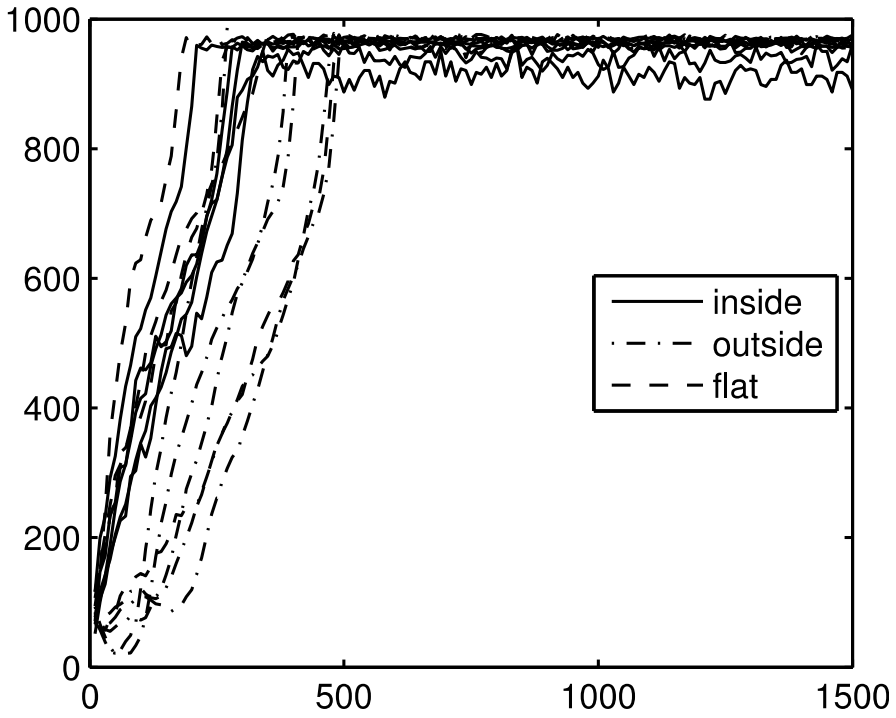
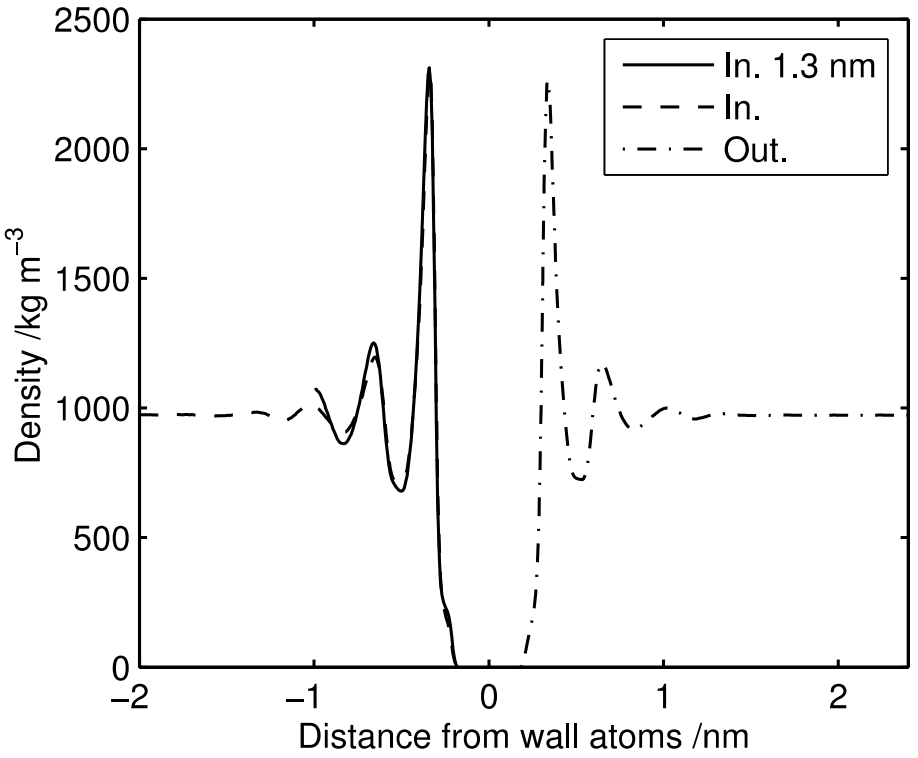
Density evolution and profiles





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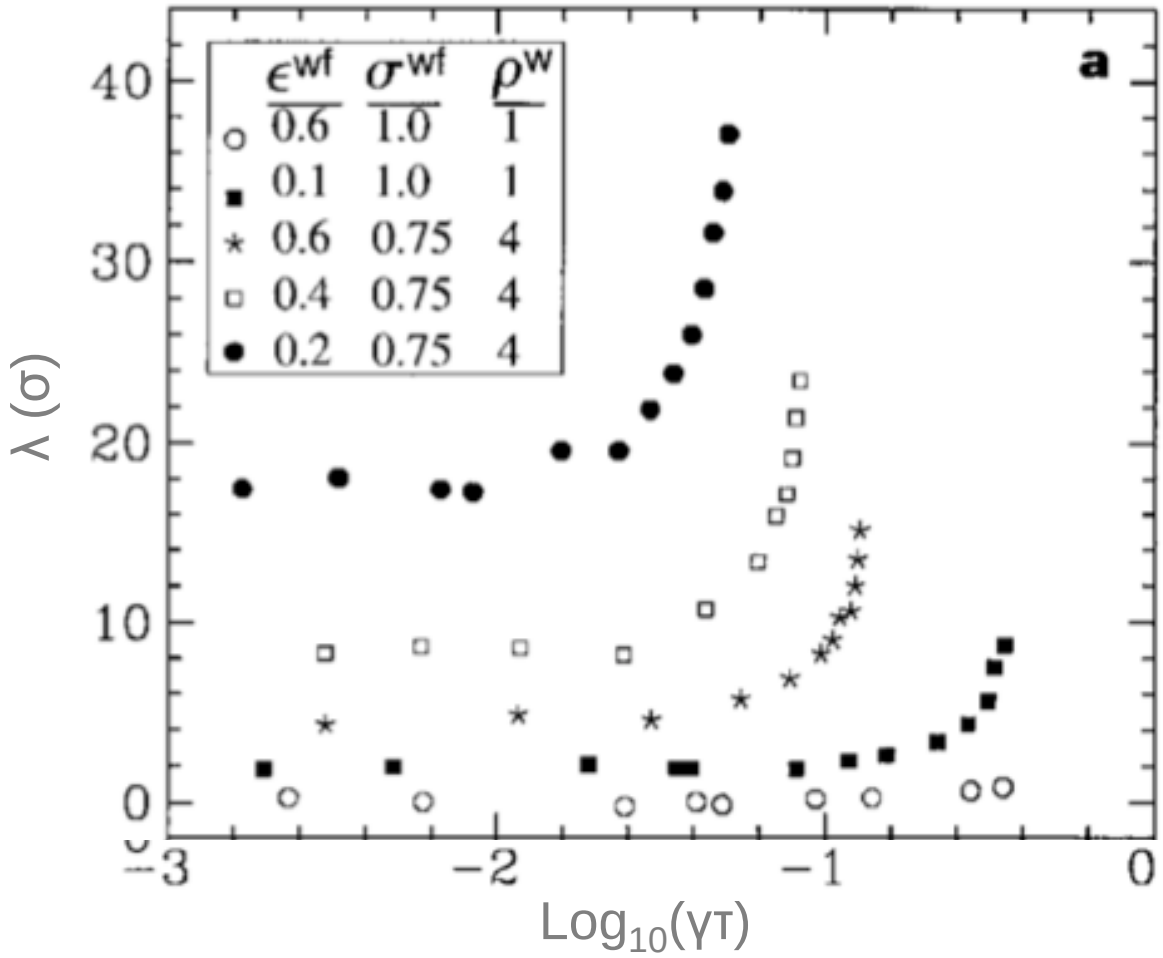
NEMD considerations



Critical body force for argon-graphene system = 10^{-4} nm/ps^2

Variation of slip length and viscosity as a function of shear rate. Thompson & Troian (1997). Nature 389.

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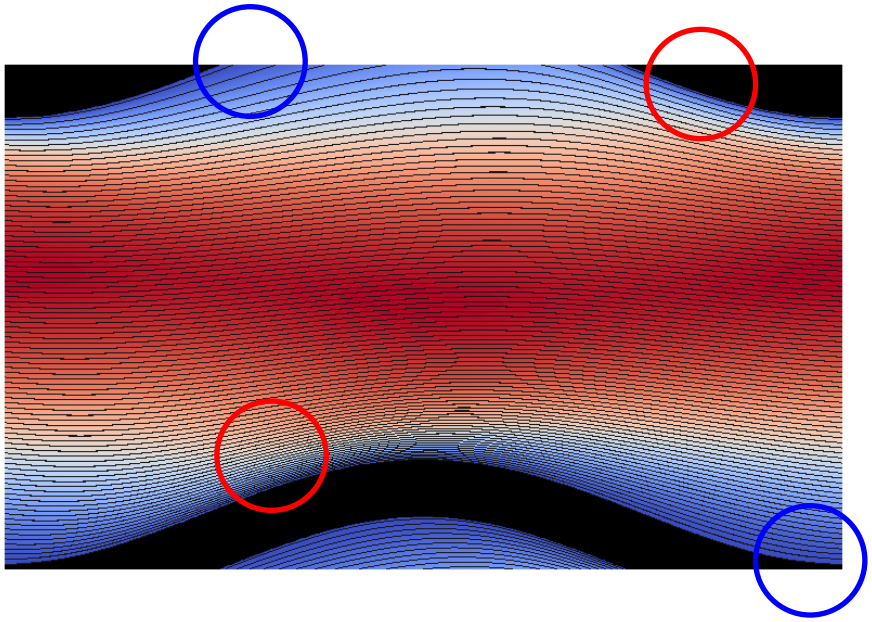
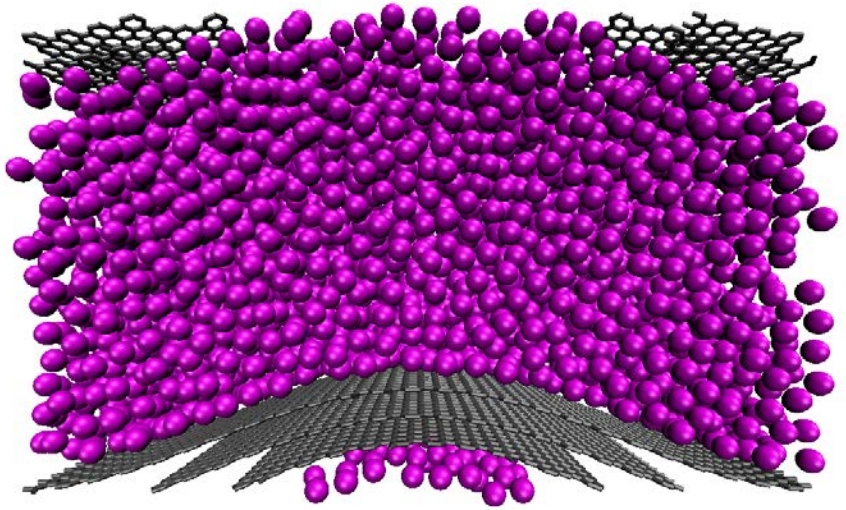
NEMD Issues





Maximum shear rate: $\dot{\gamma}_{max} \approx 2\,\dot{\gamma}_{straight}$

Minimum shear rate: $\dot{\gamma}_{min} \approx 0.2\,\dot{\gamma}_{straight}$

Also, shear rate varies by 0.5-2 times that of straight channel under same flow condition

Means even smaller body force required → unfeasible MD sims

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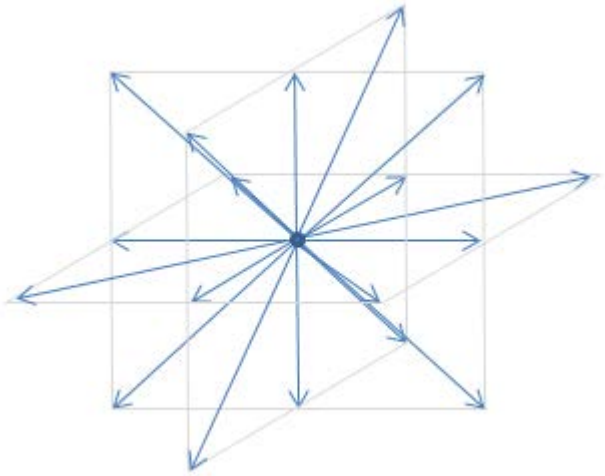
Lattice Boltzmann – Background

- In D3Q19, we have 19:
  - Velocity vectors, $\boldsymbol{e}_i$
  - Populations at each velocity, f_i
- Single relaxation time model

$$f_i(\boldsymbol{x}+\boldsymbol{e}_i dt, t+dt) = f_i(\boldsymbol{x},t) + \boldsymbol{S}[\, f_i^{eq}(\boldsymbol{x},t) - f_i(\boldsymbol{x},t)] + \boldsymbol{F}$$



- Multiple relaxation time model

$$\boldsymbol{f}'(\boldsymbol{x},t) = \boldsymbol{f}(\boldsymbol{x},t) + \boldsymbol{M}^{-1}\boldsymbol{S}\boldsymbol{M}[\, \boldsymbol{f}^{eq} - \boldsymbol{f}] + \boldsymbol{F}$$

- If we know all the local distribution functions, fi, we also know macroscopic quantities. Such as: density, momentum, energy flux, shear rate, pressure etc.

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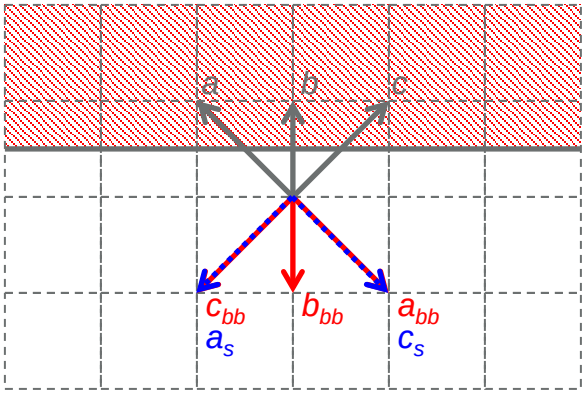
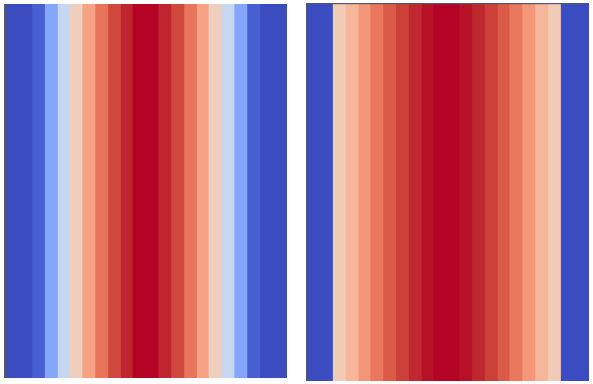
Lattice Boltzmann – Boundary Conditions

- Slip is implemented in the form of a new boundary condition.
- No-slip boundary condition is achieved via the bounce-back (bb) scheme.
  - Velocity populations are simple reversed (red).
- Specular reflection (s) boundary condition
  - Velocity populations are reflected completely (blue).
- Slip length can be set by varying ratio of bounce-back to specular reflections.





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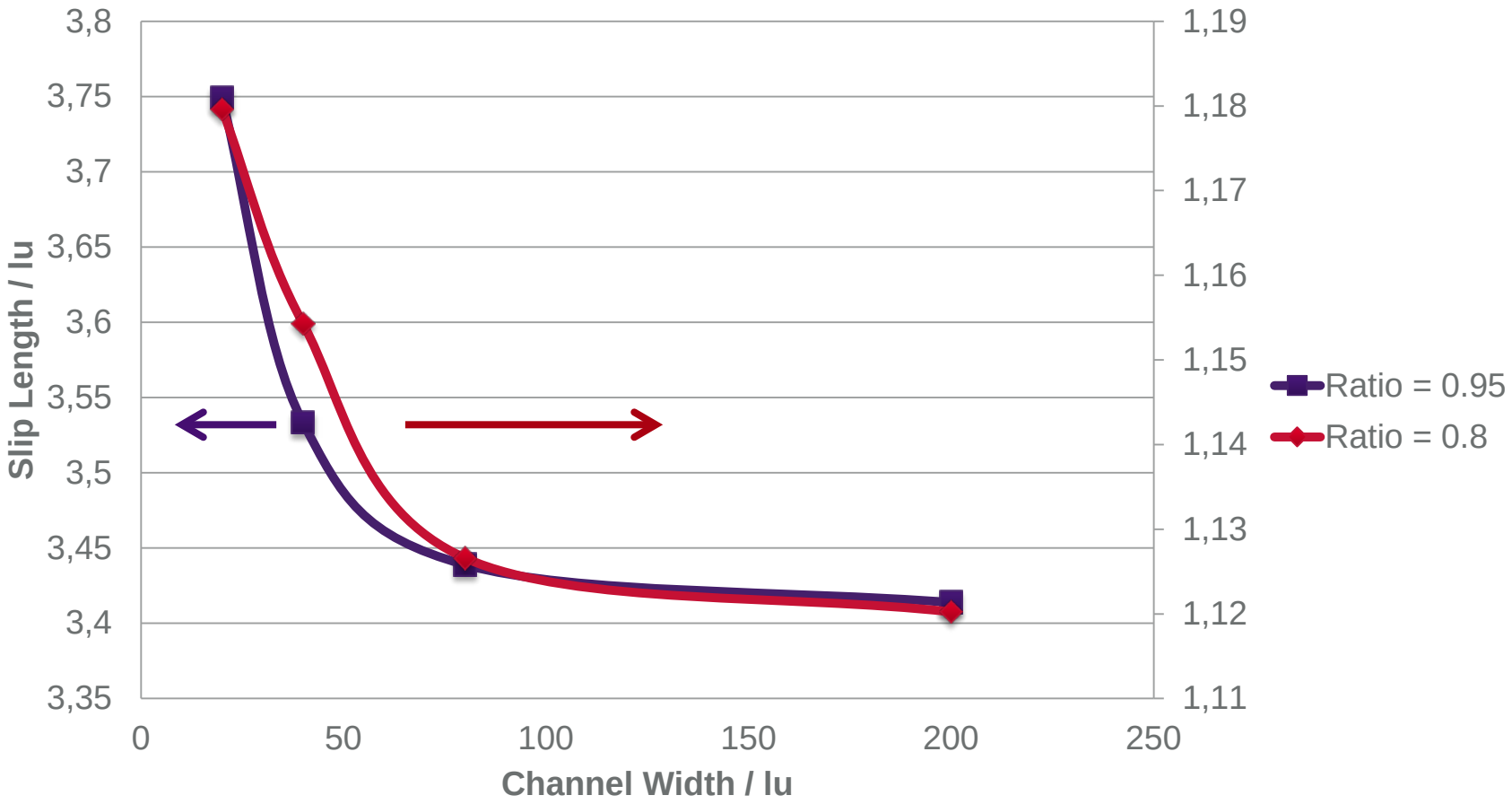
Lattice Boltzmann – Slip variation with channel width



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Lattice Boltzmann – Velocity Boundary Condition

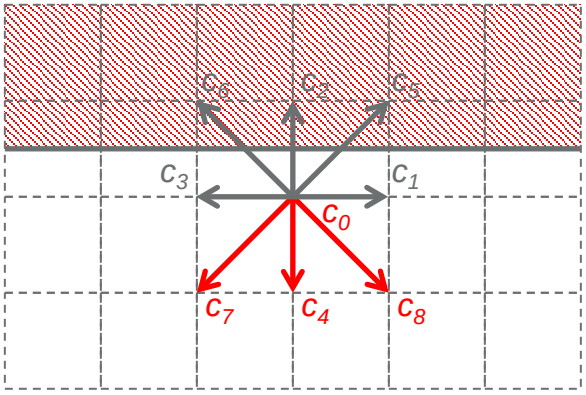
Density on node is calculated based on the unknowns and the perpendicular velocity (zero in all cases).

Unknown distributions found by assuming bounce back condition still valid for non-equilibrium part of distribution function.

Equilibrium distributions found by discretizing the Boltzmann distribution.

$$f_i = f_{-i} - f_{-i}^{(eq)} + f_i^{(eq)}$$

$$f_i^{(eq)}(\rho, \underline{v}) = \omega_i \rho \left[1 + \frac{\underline{c}_i \cdot \underline{v}}{c_s^2} + \frac{(\underline{c}_i \cdot \underline{v})^2}{c_s^2} - \frac{v^2}{2c_s^2} \right]$$



Hecht and Harting (2009). J. Stat. Mech. Implementation of on-site velocity boundary conditions for D3Q19 lattice Boltzmann simulations.

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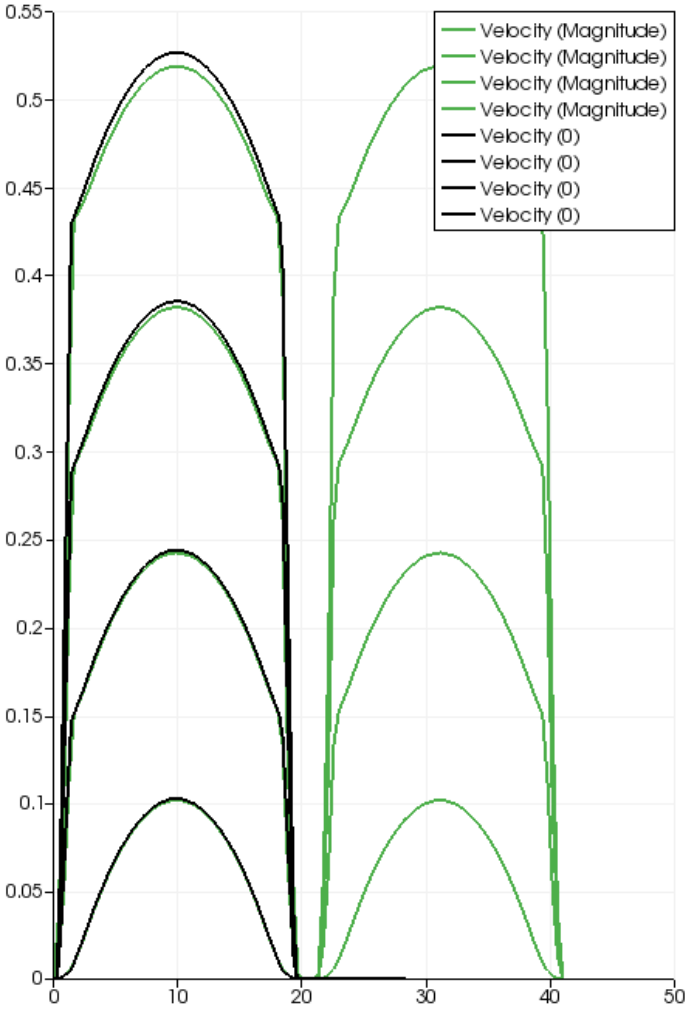
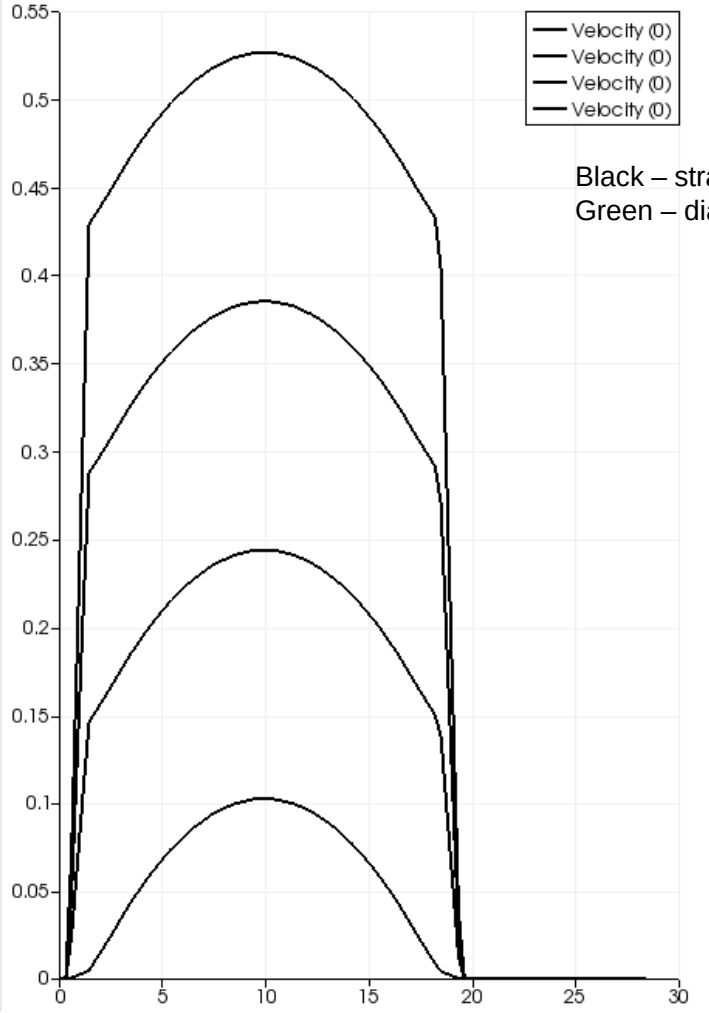
LB Velocity boundary condition





Black – straight channel
Green – diagonal channel

Conclusions and Future Work

- Slip in LB can be implemented easily for straight surfaces.
- Slip affects the distribution of velocities in complex geometries.
- Next steps:
  - Implement slip in LB for surfaces not aligned with the lattice.

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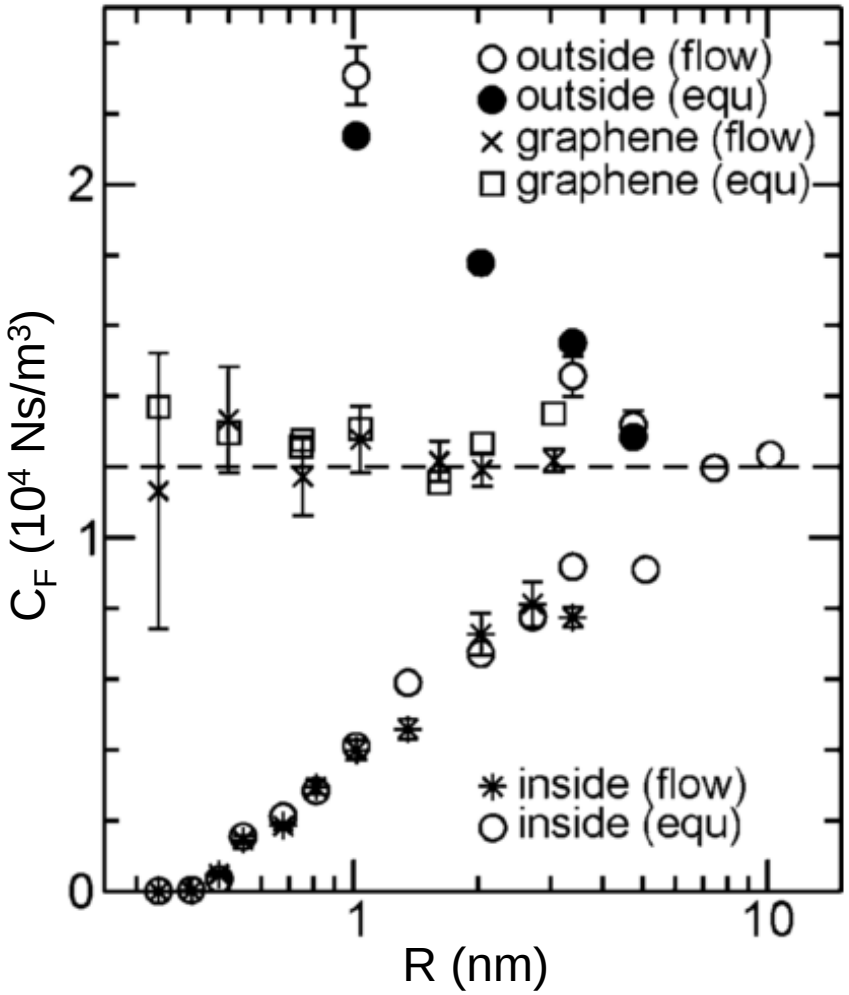
Suplementary slide – Falk & Bocquet



Falk and Bocquet et. al. Nano Lett. 10 (2010). 40667-4073. Evolution of friction coefficient with confinement R, for water inside/outside CNT and between graphene sheets. EMD and NEMD.