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Temperature Control and Measurement of Flow Enhancement for Confined Nonequilibrium Fluids

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Numerical Aspects of Nonequilibrium Dynamics – IHP, Paris, 25-28 April 2017

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Outline

- Flow enhancement in confined fluids
  - High slip systems (e.g. water in carbon nanotubes or graphene sheets)
  - Errors in simulation via nonequilibrium molecular dynamics (NEMD) methods
  - How to reduce errors: (a) NEMD, and (b) using equilibrium MD
- Temperature control for confined fluids
  - Pros and cons (errors) in thermostatting a confined fluid either directly, or through the walls
  - Compromise scheme that both freezes walls and thermostats it (?)
- Application: non-mechanical external pumping by rotating electric fields
- Conclusions

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Part 1

Measurement of Slip

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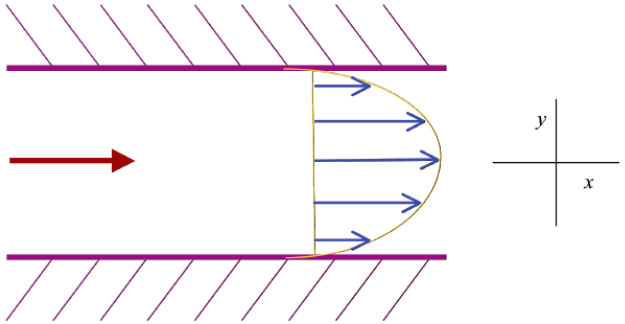
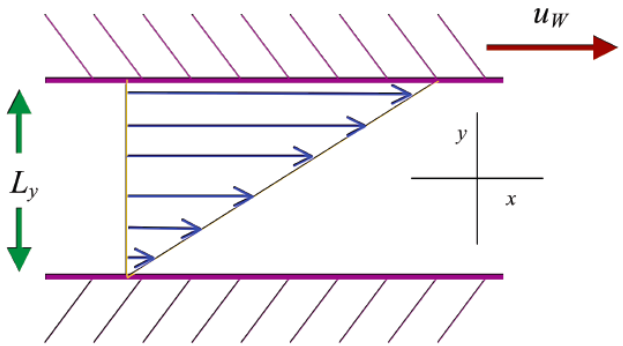
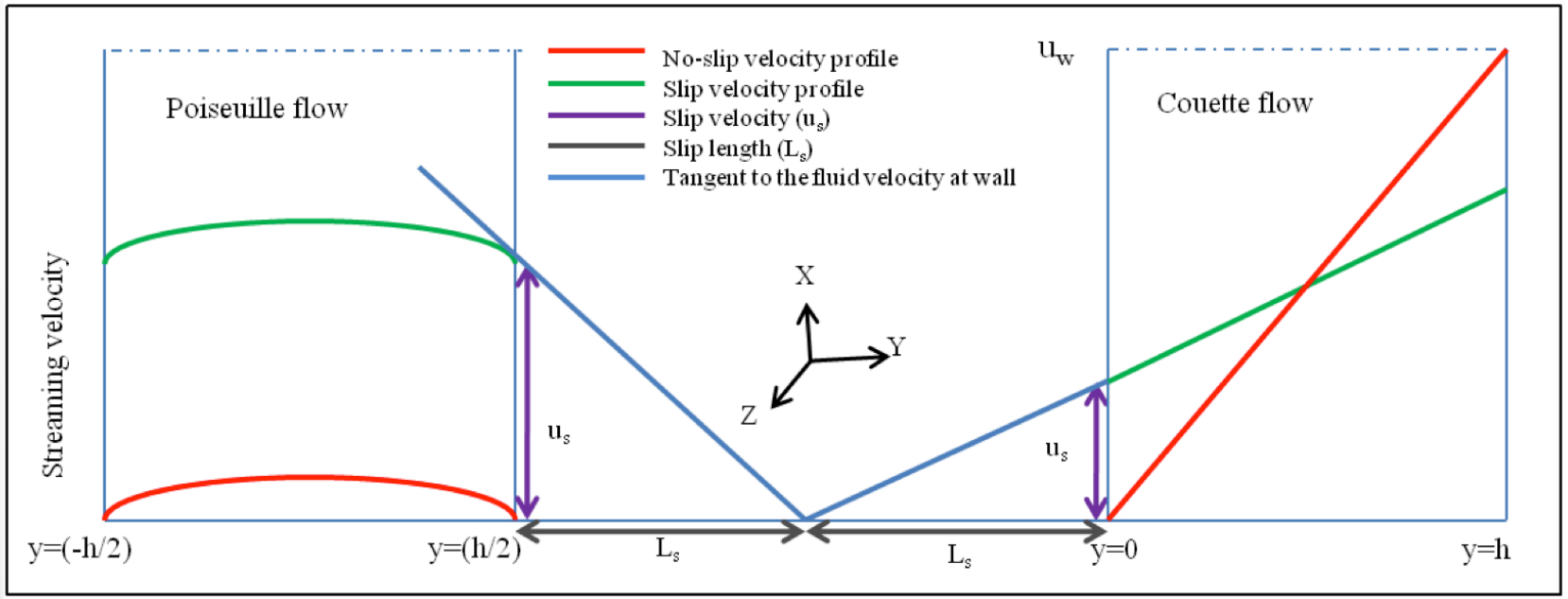
What is slip?







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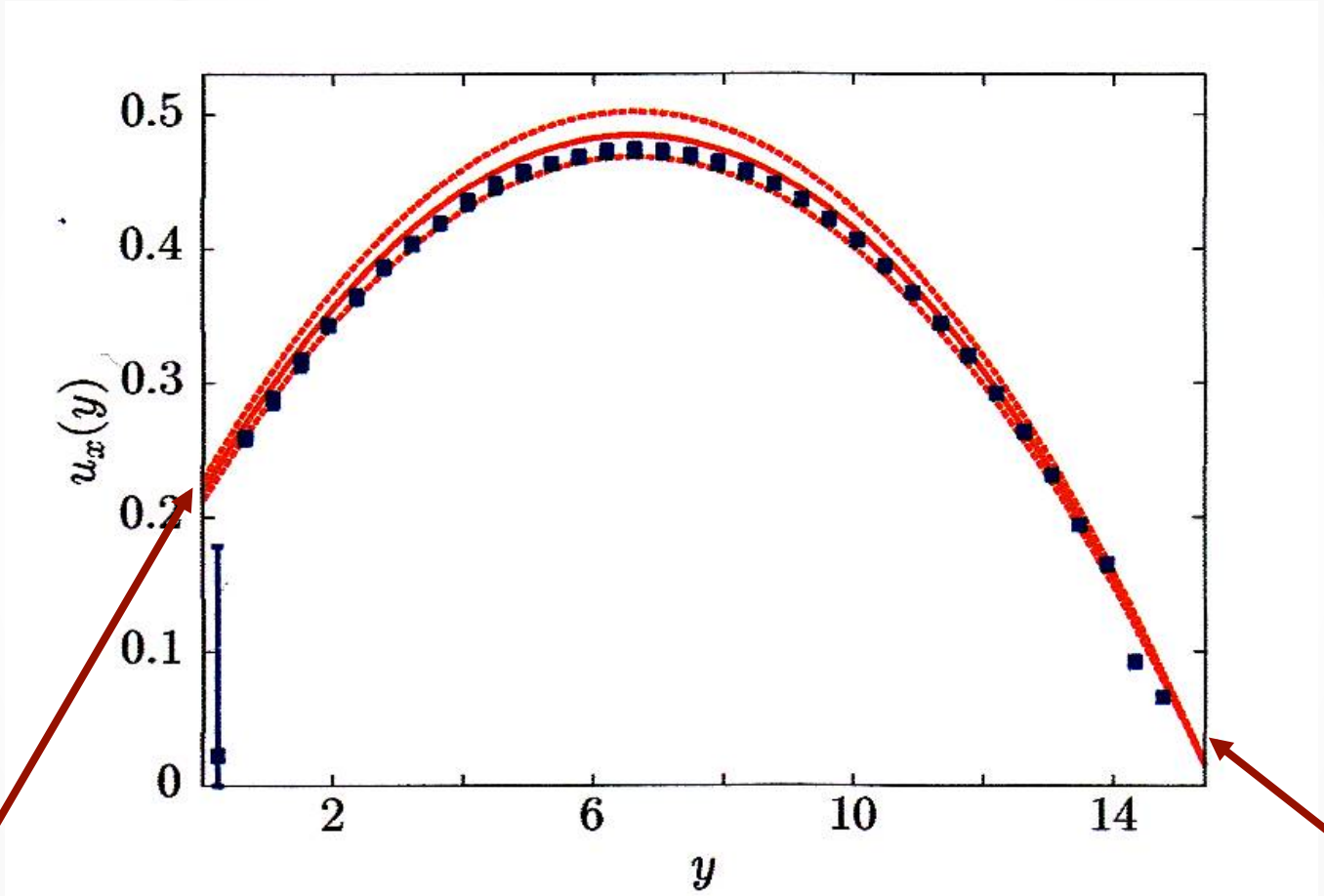
Example: Poiseuille flow NEMD simulation



'hydrophobic' wall

'hydrophilic' wall

Hansen, Todd & Daivis, Phys. Rev. E **84**, 016313 (2011)

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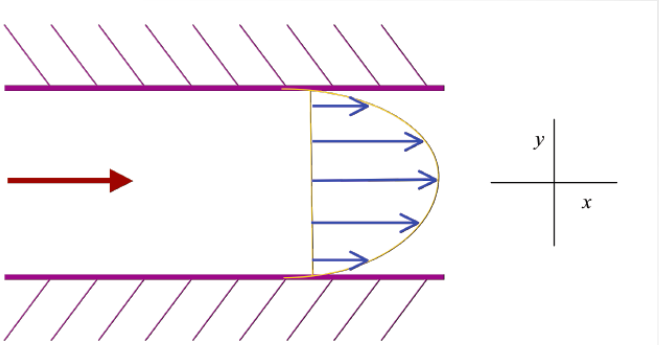
Slip

- Low slip systems (e.g. hydrophilic confinement):
  - Slip lengths small compared to channel width/ diameter
  - No noticeable difference between classical flow predictions based on hydrodynamic theory and simulation/experimental results
- High slip systems (e.g. hydrophobic confinement):
  - Slip lengths large compared to channel width/ diameter
  - Significant differences between classical flow predictions based on hydrodynamic theory and simulation/experimental results

Slip and flow enhancement

1. Planar Poiseuille flow



$$u_x(y) = \frac{\rho F_e}{2\eta_0}\left[\left(\frac{h}{2}\right)^2 - y^2\right] + u_s$$

Streaming velocity prediction with slip

$$\varepsilon = \frac{Q_{slip}}{Q_{no-slip}} = \left(1 + \frac{6l_s}{h}\right)$$

Flow enhancement, ε

where Q_{slip} = observed flow rate, $Q_{no\text{-}slip}$ = classical no-slip prediction flow rate

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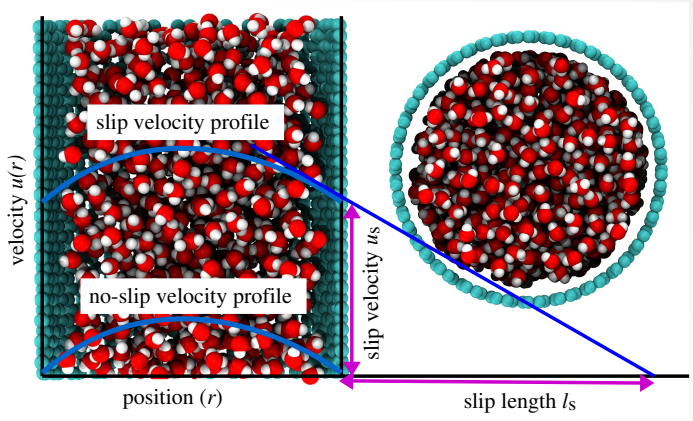
Slip and flow enhancement

2. Hagen-Poiseuille flow



$$u_z(r) = \frac{\rho F_e}{4\eta_0}\left[\left(\frac{d}{2}\right)^2 - r^2\right] + u_s$$

Streaming velocity prediction with slip

$$\varepsilon = \frac{Q_{slip}}{Q_{no-slip}} = \left(1 + \frac{8l_s}{d}\right)$$

Flow enhancement, ε

where Q_{slip} = observed flow rate, $Q_{no\text{-}slip}$ = classical no-slip prediction flow rate

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Controversy for high slip systems

- Experimental results
  - Majumder *et al*. (2005): l_s ~ 39,000-68,000 nm (flow enhancement of 44,000 – 77,000) for 7 nm diameter CNT
  - Holt *et al*. (2006): l_s ~ 140-1400 nm for 1.3-2 nm CNTs
  - Overall, l_s data scattered over 5 orders of magnitude (10 nm – 485,000 nm) for CNTs of diameter 0.81-10 nm and still no consensus has been reached.

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Controversy for high slip systems

- NEMD simulation results
  - Thomas *et al.* (2008) reassessed available flow area in earlier experiments and found l_s ~ 105 – 30 nm (flow enhancement 433 to 47) for CNTs 1.66 – 4.99 nm diameter
  - Errors resulted from fitting of parabolic velocity profiles, assumptions of water viscosity and fitting constraints (e.g. unconstrained fits result in 40% lower slip for small strain rates)
  - NEMD simulation studies show variation of l_s from ~ 1 nm to 5000 nm

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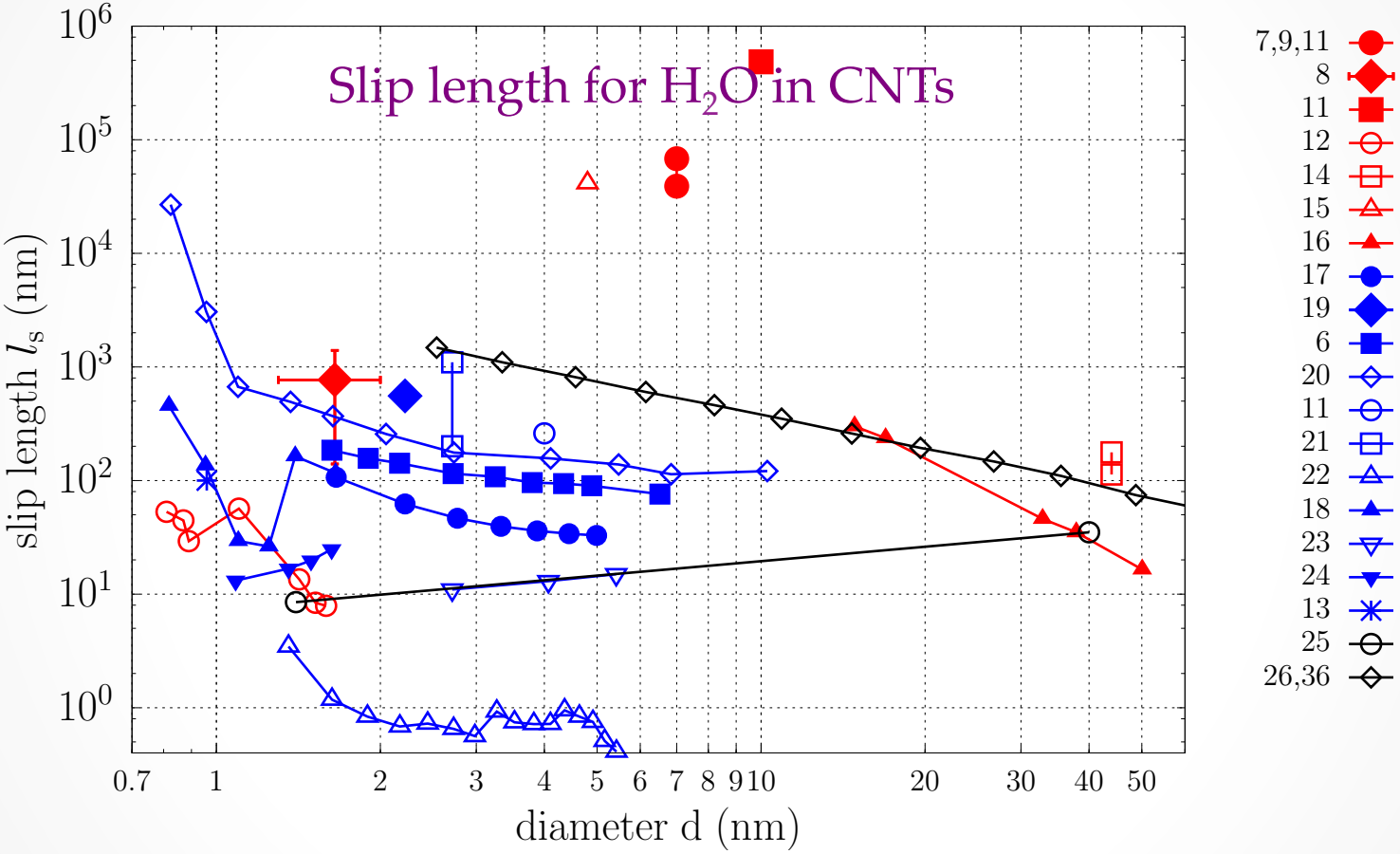
Controversy for high slip systems



Experiment – red; Simulation – blue; Theory - black

Kannam, Daivis & Todd, MRS Bulletin **42**, 283–288 (2017)

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Where does the controversy stem from in NEMD simulations?

- Largely due to questionable extrapolation of slip velocity from velocity profile data
- Compounded for high-slip systems where velocity profile (for Poiseuille flow) is 'plug-like', i.e. flat.
- Other issues include assumption of zero-shear viscosity (η_0), water-CNT model used, electrostatic force handling (e.g. Ewald vs Wolf), density profiles, thermostatting, etc.

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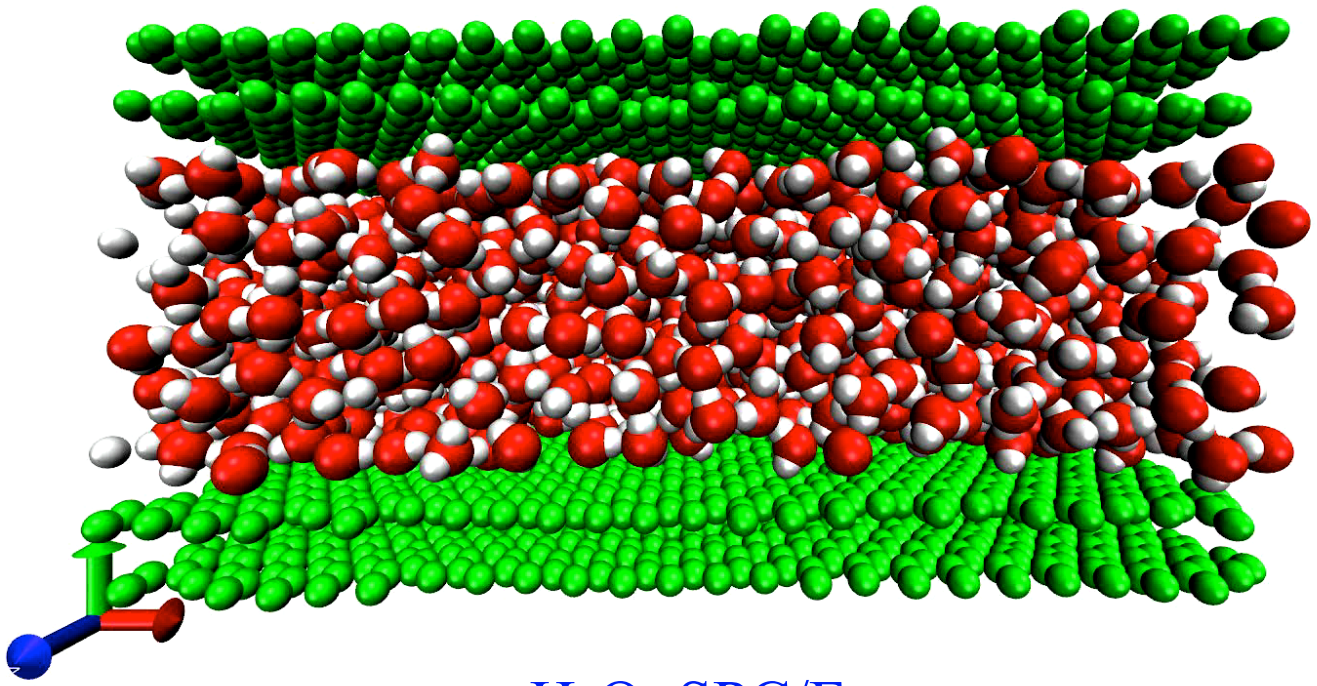
Example 1: H_2O flowing in graphene nanochannels undergoing Couette flow



H_2O: SPC/Fw

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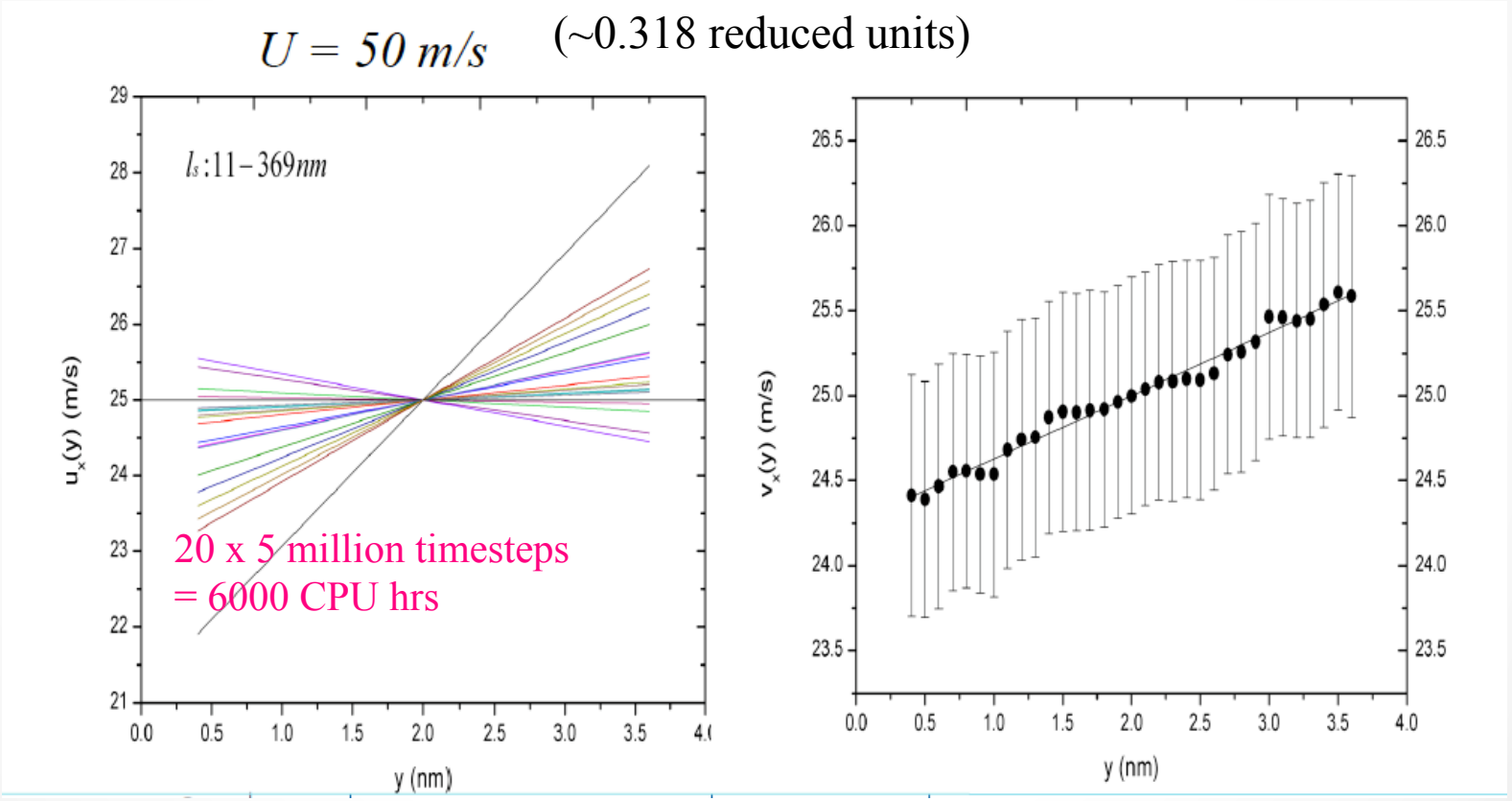
Example 1: H_2O flowing in graphene nanochannels undergoing Couette flow

$U = 50\ m/s$ (~0.318 reduced units)



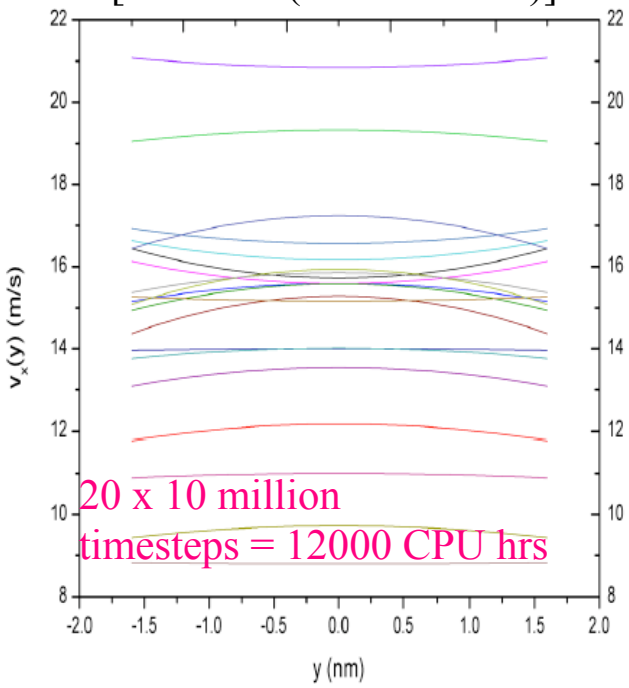
Couette: H_2O, L_s (EMD) = 60 ± 6 nm; NEMD = 61 nm

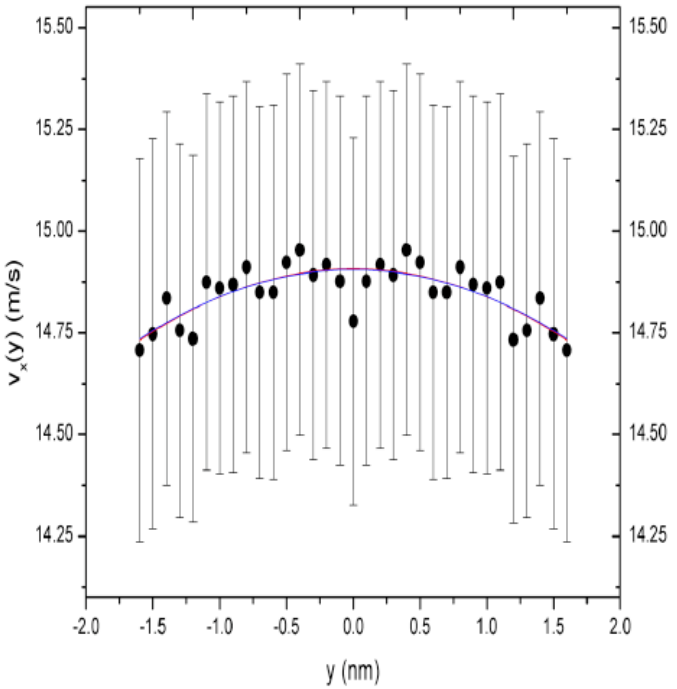
Kannam et al, J. Chem. Phys. **136**, 024705 (2012).

Example 2: H_2O flowing in graphene nanochannels undergoing Poiseuille flow

$F_x = 1.0 \times 10^{11}$ m/s^2

[~ 0.0015 (reduced units)]





Poiseuille: H_2O, L_s (EMD) = 60 ± 6 nm; NEMD = 53 nm

Kannam et al, J. Chem. Phys. **136**, 024705 (2012).

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Observations from NEMD simulation of Poiseuille flow

1. Average slip velocity 14.7±0.4 m/s
2. Average velocity difference from from centre to wall very small (<0.25 m/s)
3. Strain rate (velocity gradient) at wall very small and variation large among different fits
4. Some fits are inverted parabola, due to statistical fluctuations resulting from very weak strain rates
5. Weak strain rates still higher than typical experimental strain rates, and represent lowest viable NEMD rates (reasonable temperatures of ~ 300K achievable via thermostatting walls)
6. Use of higher external forces (hence higher strain rates) makes relating to experimental data unreliable and also results in excessive heating
7. How then can we make reliable estimates of slip velocity by extrapolation when data is so noisy?

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Strategies for NEMD data

1. P1 – 'raw' method.
   - Simply compute l_s for each simulation run separately and then average:
   - WON'T WORK!
   - Inverted parabola yield undefined slip lengths, hence would discard actual data, resulting in selective bias that would reduce the average value of l_s.

2. P2 – Average first, then fit using errors as weights.
   - Results in slip lengths of 60 ± 9, 46 ± 3 and 130 ± 21 nm for external field strengths (F_e) of 1.00, 1.25 and 1.50 $\times$ 10^{11} ms^{-2}
   - Strong field dependence unrealistic in linear regime (as will be seen later)
   - Also results in fit-estimates of η_0 that do not compare well with known value of η_0 (from independent equilibrium MD, Green-Kubo calculations)
   - Suggests method is naïve and error prone

Strategies for NEMD data

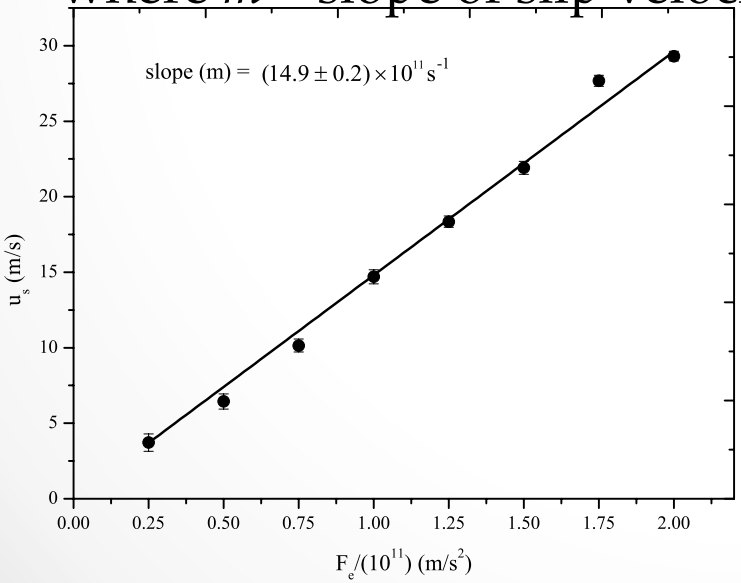
3. P3 – use the definition of the slip length (Navier 1823)

$$l_s = \frac{\eta_0}{\xi_0}; u_s = l_s \left. \frac{\partial u_x}{\partial y} \right|_{y=h/2}$$

which leads to

$$l_s = \frac{2m\eta_0}{\rho h}; \xi_0 = \frac{2m}{\rho h}$$

where m = slope of slip velocity vs. field strength plot



Kannam et al, J. Chem. Phys. **136**, 024705 (2012).

Leads to $l_s = 63 \pm 4$ nm

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Strategies for NEMD data

4. P4 – Use of independent viscosity to constrain velocity fit profiles

- Thomas & McGaughey (2008) found that unconstrained fit to velocity profiles result in 100% deviation in l_s and η_0 from the known actual values

- Use of accurate η_0 computed via independent Green-Kubo equilibrium MD instead to constrain the fit (rather than allowing η_0 to be a free fitting parameter) leads to a value of $\eta_0 = 62 \pm 5$ nm.

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Strategies for NEMD data

5. P5 – Use of of flow enhancement

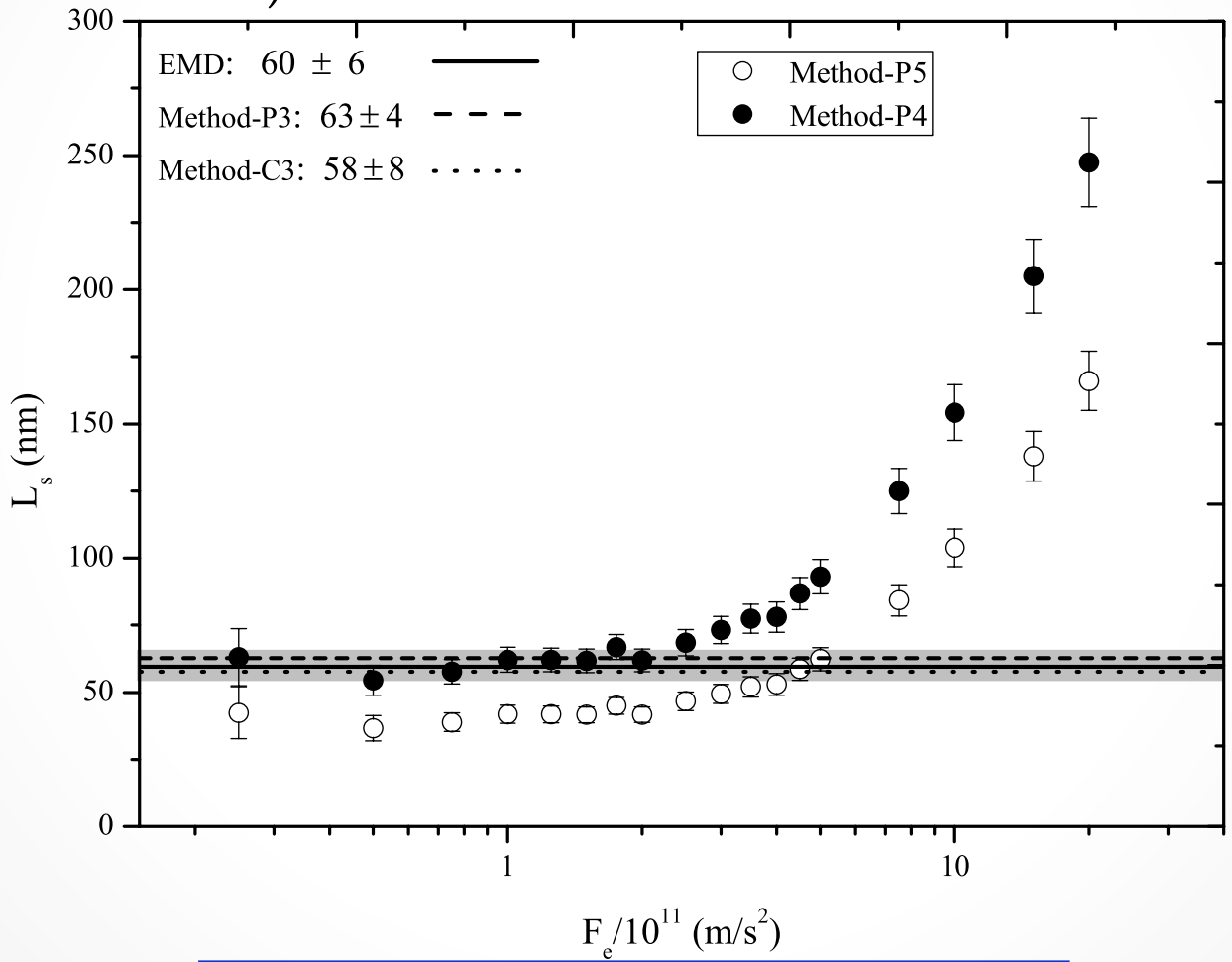
$$\varepsilon = \frac{Q_{slip}}{Q_{no-slip}} = \left(1 + \frac{6l_s}{h}\right)$$

Q_{slip} obtained by counting number of water molecules crossing a fixed plane in the streaming direction, i.e. we measure the flow rate directly without any assumption or approximation.

Advantage of this method is it does not suffer from sensitivity of streaming velocity profiles

Strategies for NEMD data

Comparison of all NEMD methods + equilibrium method (to be discussed next)



Kannam et al, J. Chem. Phys. **136**, 024705 (2012).

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Equilibrium Method to Compute Slip

- Designed to be able to predict slip velocity for highly confined fluids
- Makes use of constitutive equation for frictional force between solid-fluid to form relevant time correlation functions (TCFs)
- From TCFs extract friction coefficient
- From friction coefficient and fluid viscosity predict slip velocity and slip length for a nonequilibrium system
- Model is valid in weak to moderate-field regime
- Computationally less expensive and procedurally simpler than NEMD

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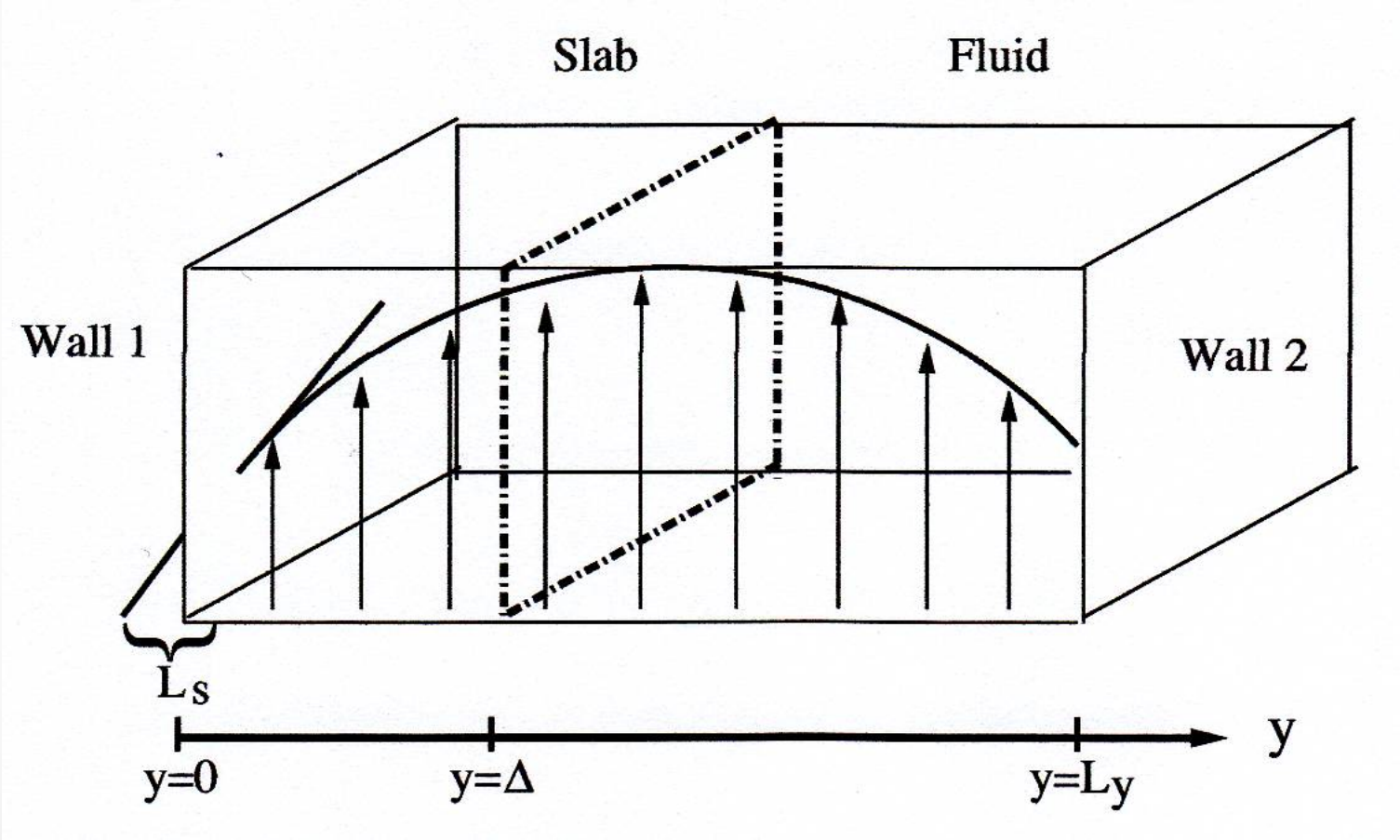
Model: geometry



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Model: Time Correlation functions

$$\tilde{C}_{u_S F'}(s) = -\tilde{\zeta}(s)\tilde{C}_{u_S u_S}(s)$$

with

$$C_{u_S u_S}(t) \equiv \langle u_S(0) u_S(t) \rangle; \quad u_W(t) = 0 \quad (equilibrium)$$

$$C_{u_S F'}(t) \equiv \langle u_S(0) F'(t) \rangle$$

Hansen, Todd & Daivis, Phys. Rev. E **84**, 016313 (2011)

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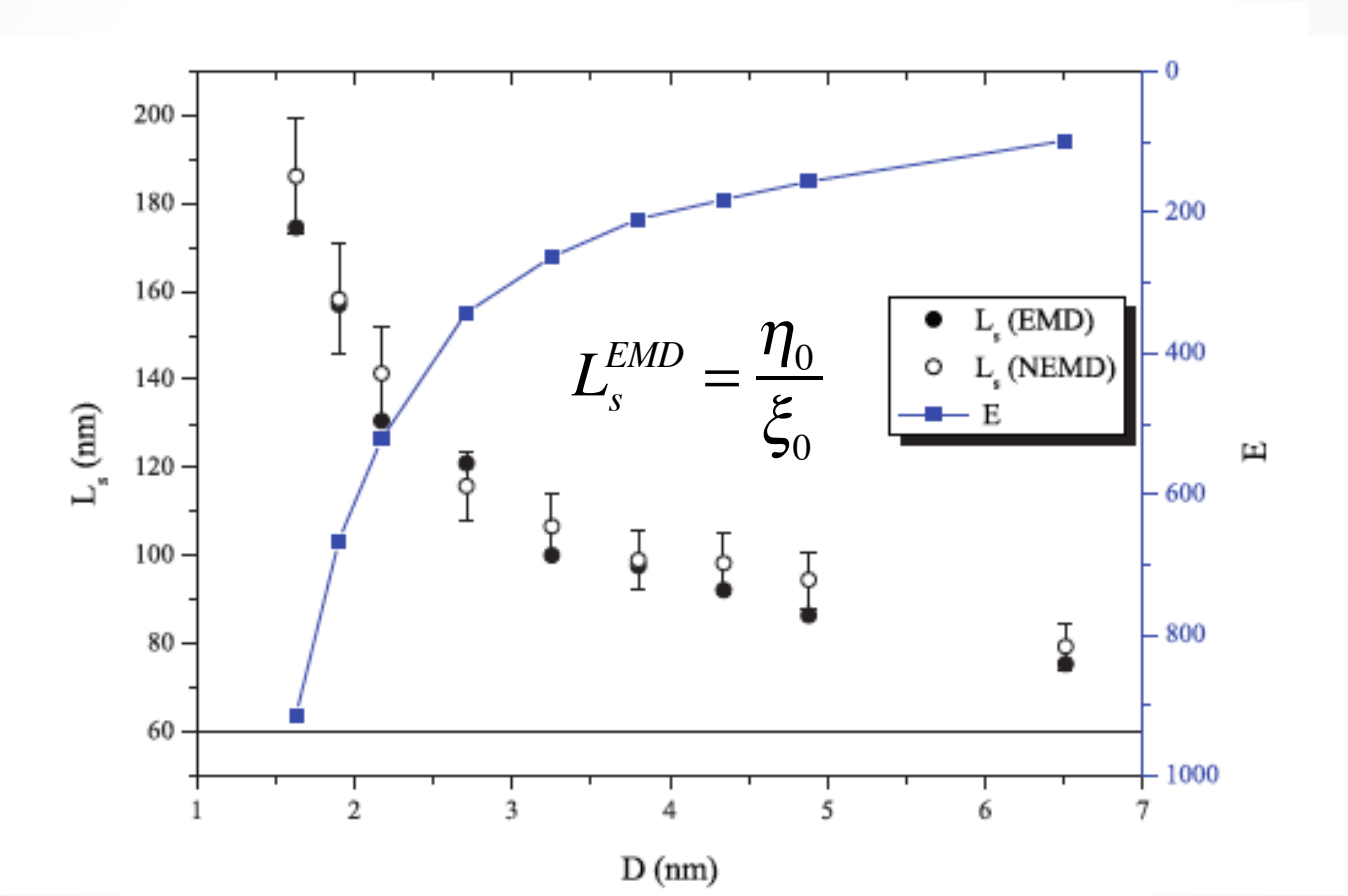
Comparison: H_2O flowing in carbon nanotubes



Kannam et al, J. Chem. Phys. **138**, 094701 (2013)

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Part 2

Temperature Control for Nanofluidic Systems

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Temperature control

- As nanofluidics becomes a serious technology, measurement and control of temperature becomes a serious challenge in both laboratory and simulation work

- For NEMD simulation, there are two strategies one could use:

  1. Thermostat the fluid molecules directly
  2. Thermostat only the wall atoms and allow heat to dissipate through the walls

- We ask: which is preferable, or does it even matter?

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Thermostat (e.g. Poiseuille flow with wall thermostat)

- Most basic form of microscopic equations of motion for single-component atomic fluid:

$$\left.\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i^{\phi} + \mathbf{F}_i^{H} - \alpha \mathbf{p}_i\end{aligned}\right\} wall \qquad \left.\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i^{\phi} + \mathbf{F}^{ext}\end{aligned}\right\} fluid$$

  - Wall atoms can vibrate about their tethering sites
  - Fluid atoms evolve only under Newton's equations with an external applied field (e.g. gravity) that acts in much the same way as a pressure gradient
  - Fluid flow generated by the external field
  - Heat is conducted out of the fluid (unthermostatted) through the walls (thermostatted)

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Temperature control

- It turns out it *does* matter what to thermostat
  - Preferable to thermostat walls and allow heat generated in the fluid to dissipate through the walls
  - Models Nature more faithfully and generates physically realistic heat fluxes (thermostatting fluid produces no heat flux)

- Why not just thermostat the fluid directly?
  - Would have the advantage of being able to freeze walls, hence making simulations faster and also adding rigidity to walls so unwanted permeation of fluid atoms into walls does not occur
  - Particularly important for realistic and geometrically complex atomic wall structure

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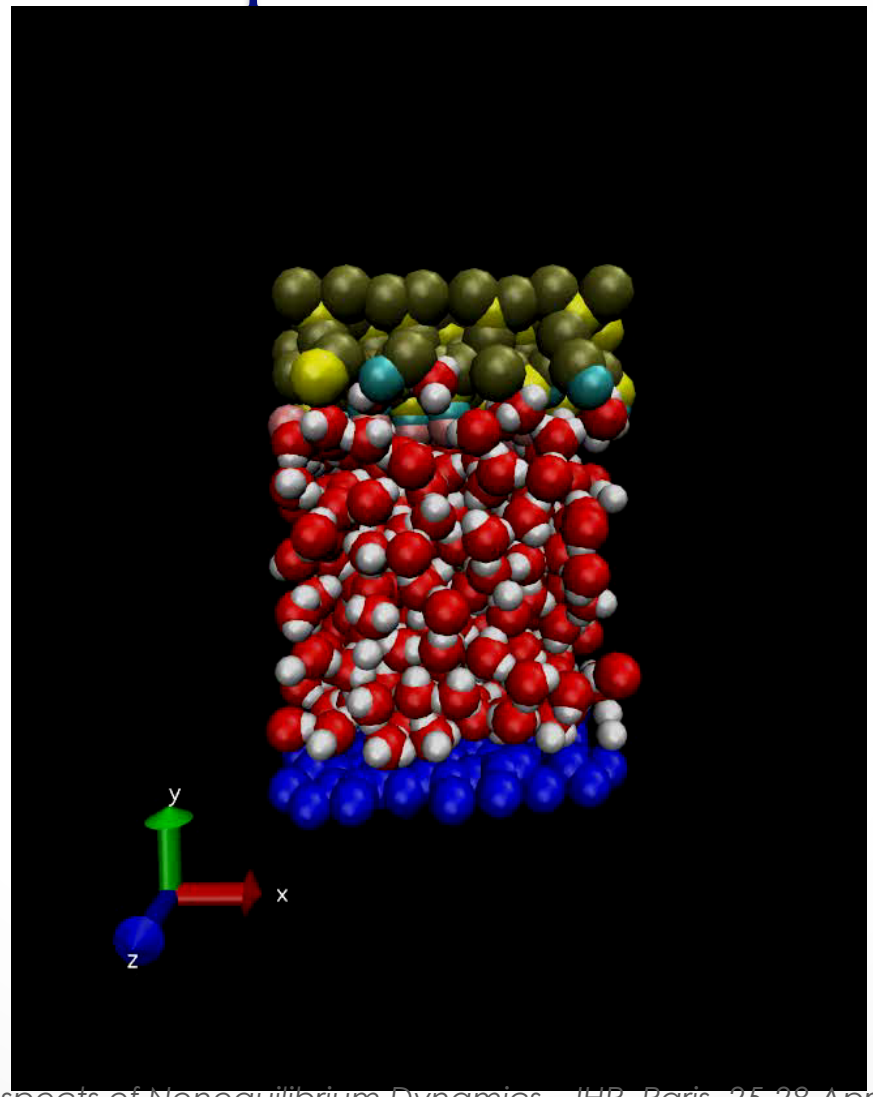
Temperature control: water permeation



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Temperature control

- Previous studies (Bernardi *et al.*, J. Chem. Phys. **132**, 244706 (2010)) show that freezing walls and thermostatting liquid under flow conditions can lead to undesirable and unphysical side-effects such as:
  - Anomalies in the shear stresses
  - Anomalies in the resulting streaming velocities
  - Anomalies in the fluid densities
  - Reduction in fluid slip at walls

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Temperature control

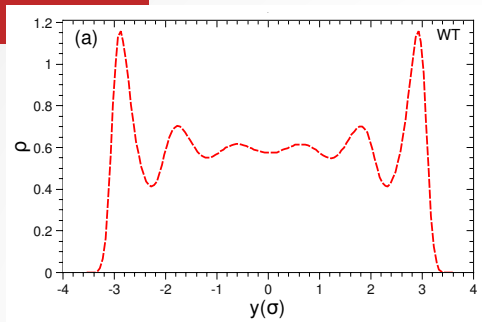
Unthermostatted fluid

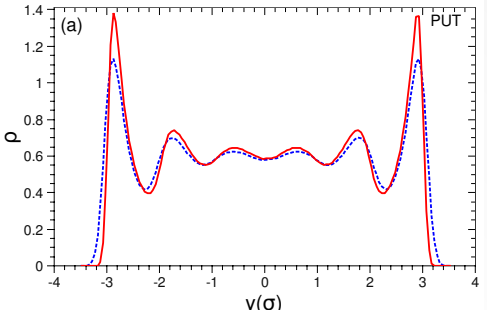
Thermostatted fluid

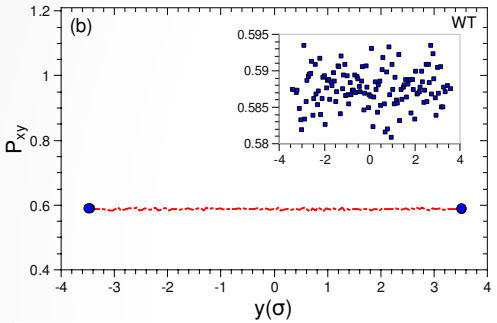
Bernardi, Todd & Searles, J. Chem. Phys. **132**, 244706 (2010)

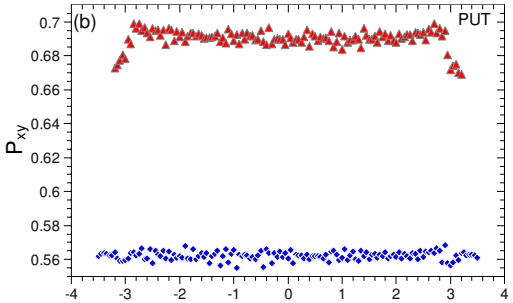
Blue: vibrating walls thermostatted at $T = 1.0$; fluid thermostatted at $T = 2.5$

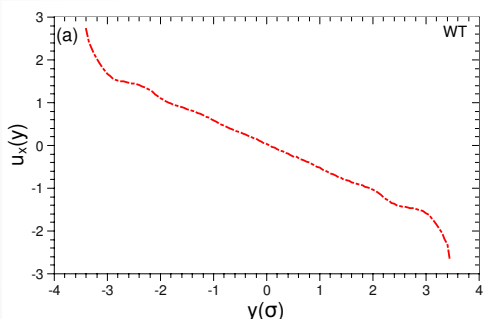
Red: frozen walls; fluid thermostatted at $T = 2.5$

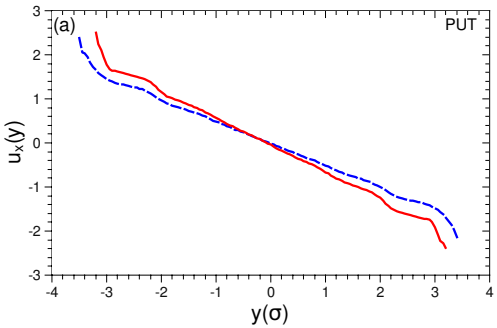


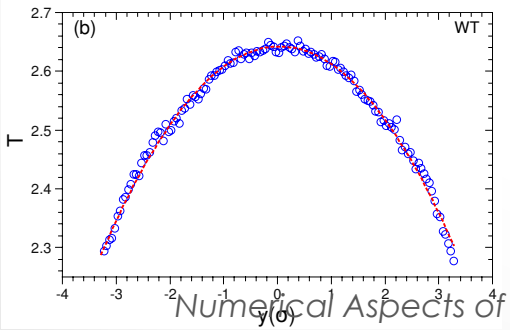


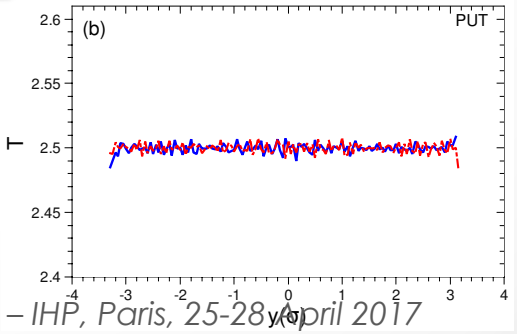












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Temperature control

- Propose a new way to combine the best of both worlds, i.e.
  - Freeze walls, **and**
  - Thermostat the walls
  - Absolutely no thermostat applied directly to the fluid!
- Introduce *'virtual particles'* tethered by harmonic potential to the walls
  - Virtual particles *interact only with fluid molecules*
  - They are 'invisible' to wall atoms and can pass straight through them
  - Carry no charge but have mass and momentum
  - VPs are *not* stiff, but rather 'loosely' bound and do not behave as a barrier (wall)

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NEMD simulation

- Water confined to realistic hydrophobic (high slip) and hydrophilic (low slip) surfaces
- Simulation details
  - System geometry
  - Interaction potentials
  - Equations of motion – apply either a uniform gravity-like field or an external rotating electric field
- Some results and comparison with Extended Navier-Stokes (ENS) equations to show coupling of molecular rotation with linear translational motion

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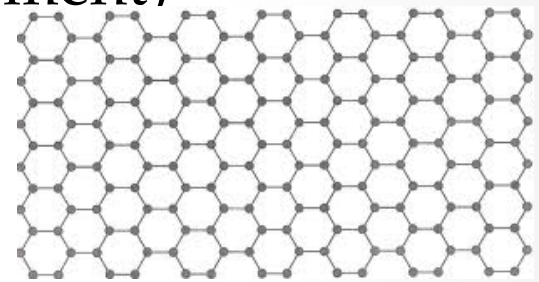
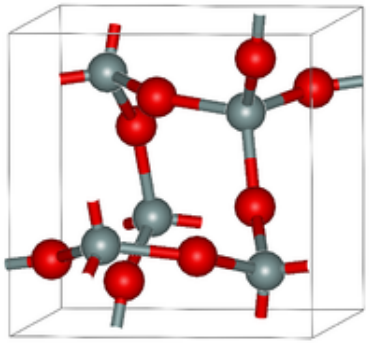
Simulation system and geometry

- SPC/E water molecules (good agreement with experimental viscosity and dipole moment)
- Hydrophobic surface: graphene



- Hydrophilic surface: β-cristobalite
  - Polymorph of silica (SiO_2)
  - Tetrahedral (diamond) structure
  - Well investigated
  - Hydroxylate unsaturated oxygens with hydrogen



- Entire system is electrically neutral

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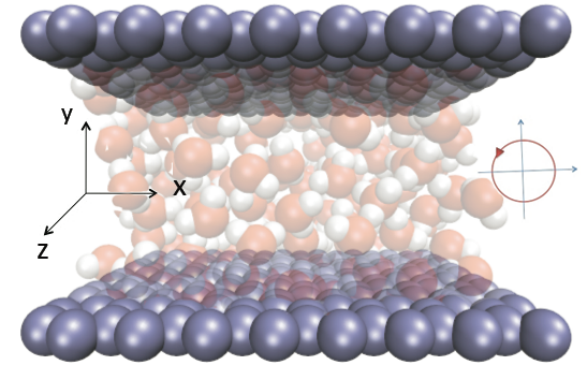
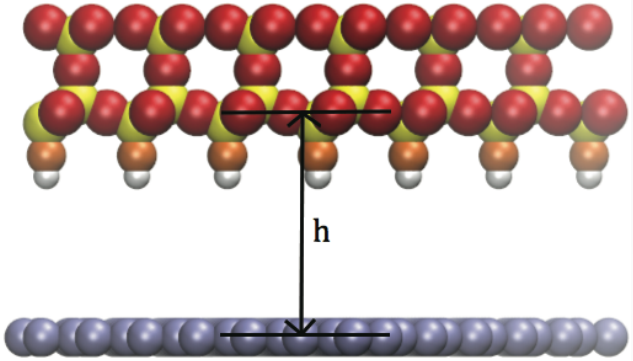
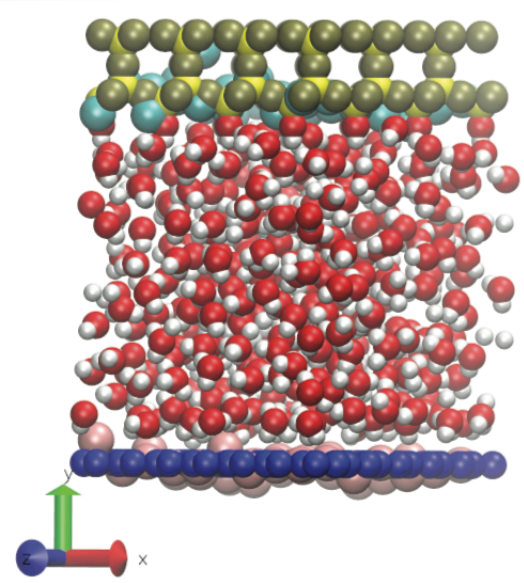
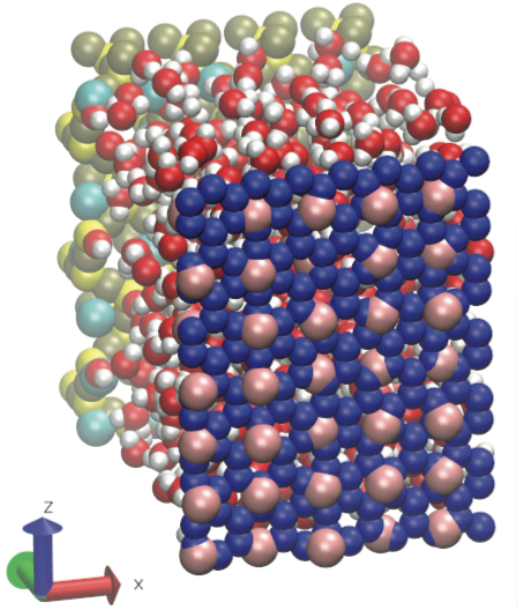
Simulation system and geometry









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Equations of motion for water molecules and virtual wall particles

$$\left.\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_i}\\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{F}_{ext}\end{aligned}\right\} \quad water \qquad \left.\begin{aligned}\dot{\mathbf{r}}_i &= \frac{\mathbf{p}_i}{m_{VP,i}}\\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - k\left(\mathbf{r}_i - \mathbf{r}_{i0}\right) - \alpha\mathbf{p}_i\end{aligned}\right\} \quad VPs\left(1\mathrm{D}\ or\ 3\mathrm{D}\right)$$

where

$$\mathbf{F}_i = -\sum_{\substack{j=1\\ j\neq i}}^{N} \nabla\phi\left(r_{ij}\right); \qquad \phi\left(r_{ij}\right) = \sum_{i=1}^{N}\sum_{j>i} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \sum_{i=1}^{N}\sum_{j>i}\frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$

and

$$\mathbf{F}_{ext} = m_i\mathbf{g}\ (\text{gravity-like}) \quad \text{or} \quad q_i\mathbf{E}_i\ (\text{electric field})$$

$$\mathbf{E}_i = E\left(\cos\omega t, \sin\omega t, 0\right) \qquad \boldsymbol{\tau}_{\mathrm{H_2O}} = \sum_{i\in \mathrm{H_2O}} \left(\mathbf{r}_i - \mathbf{r}_{CM}\right)\times q_i\mathbf{E}_i$$

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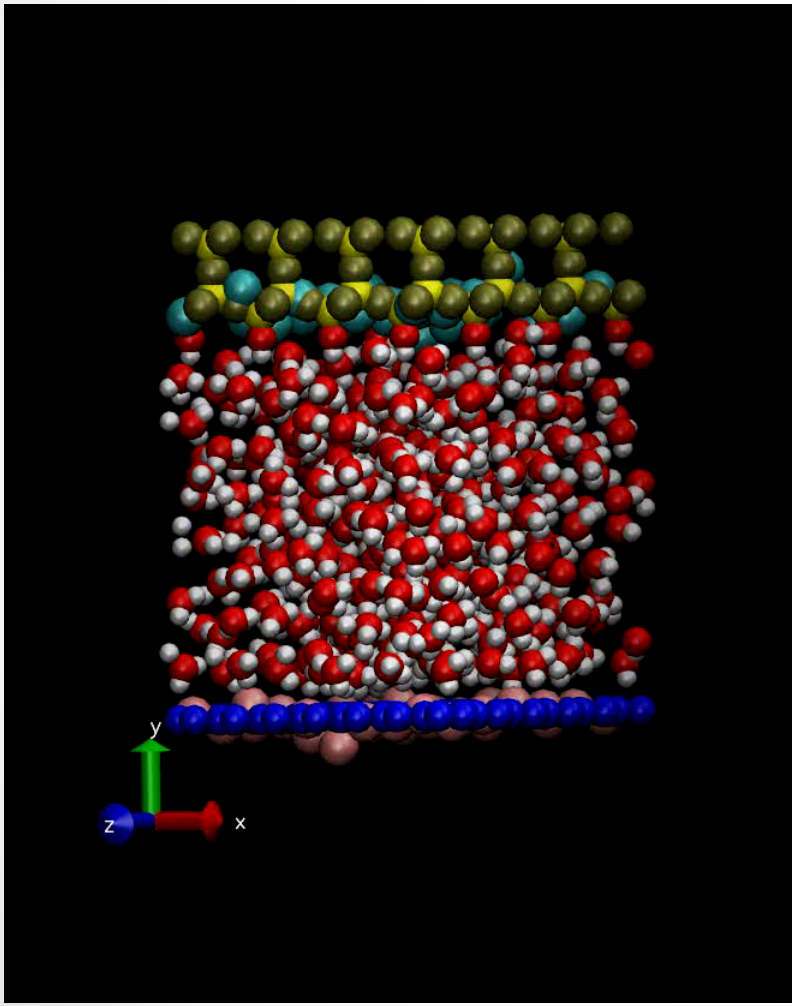
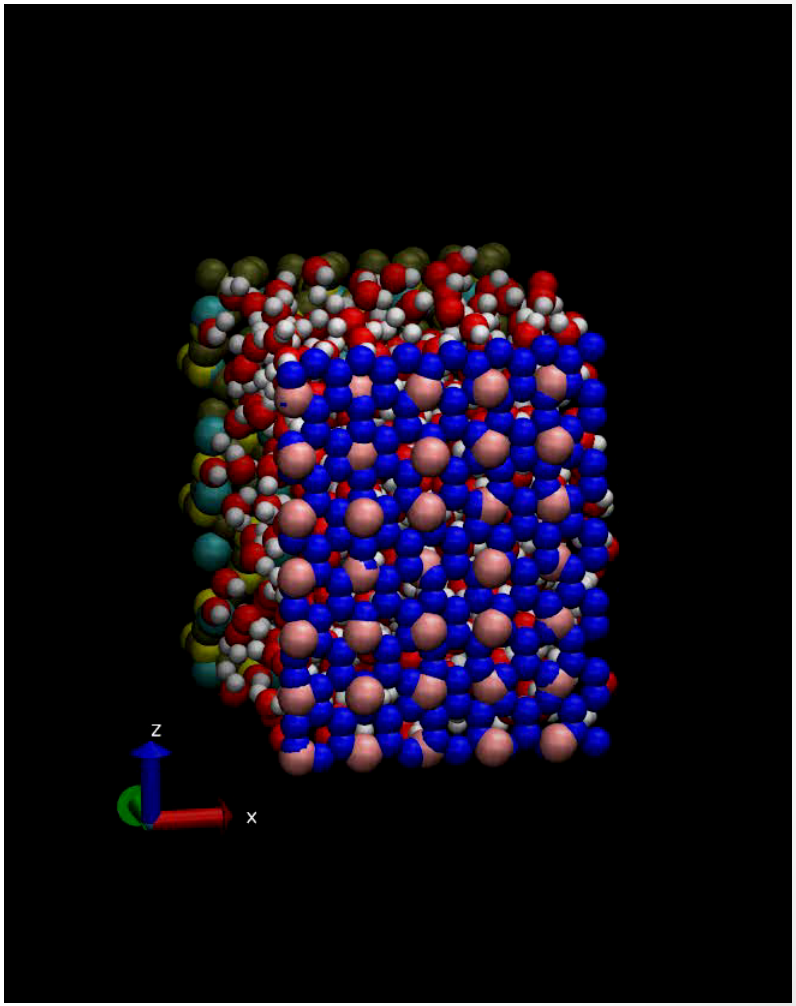
Temperature control





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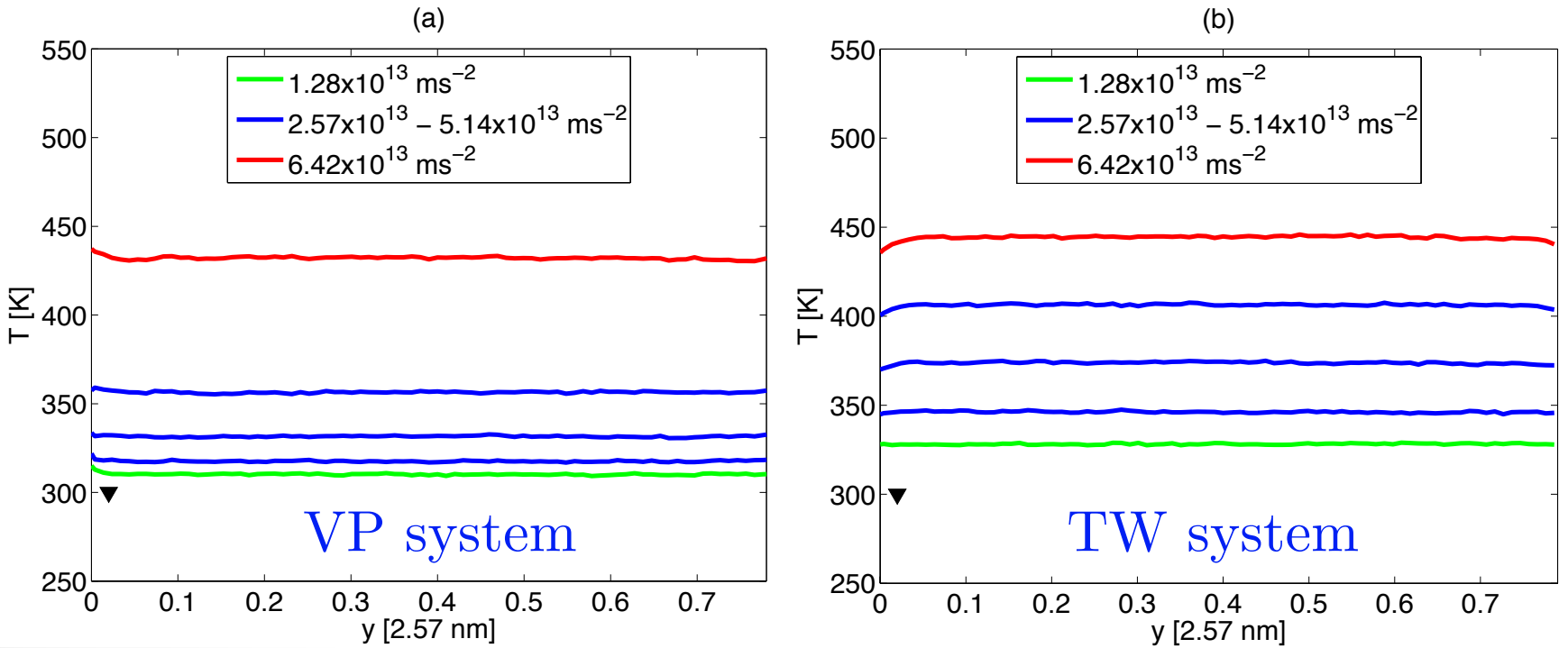
Temperature control

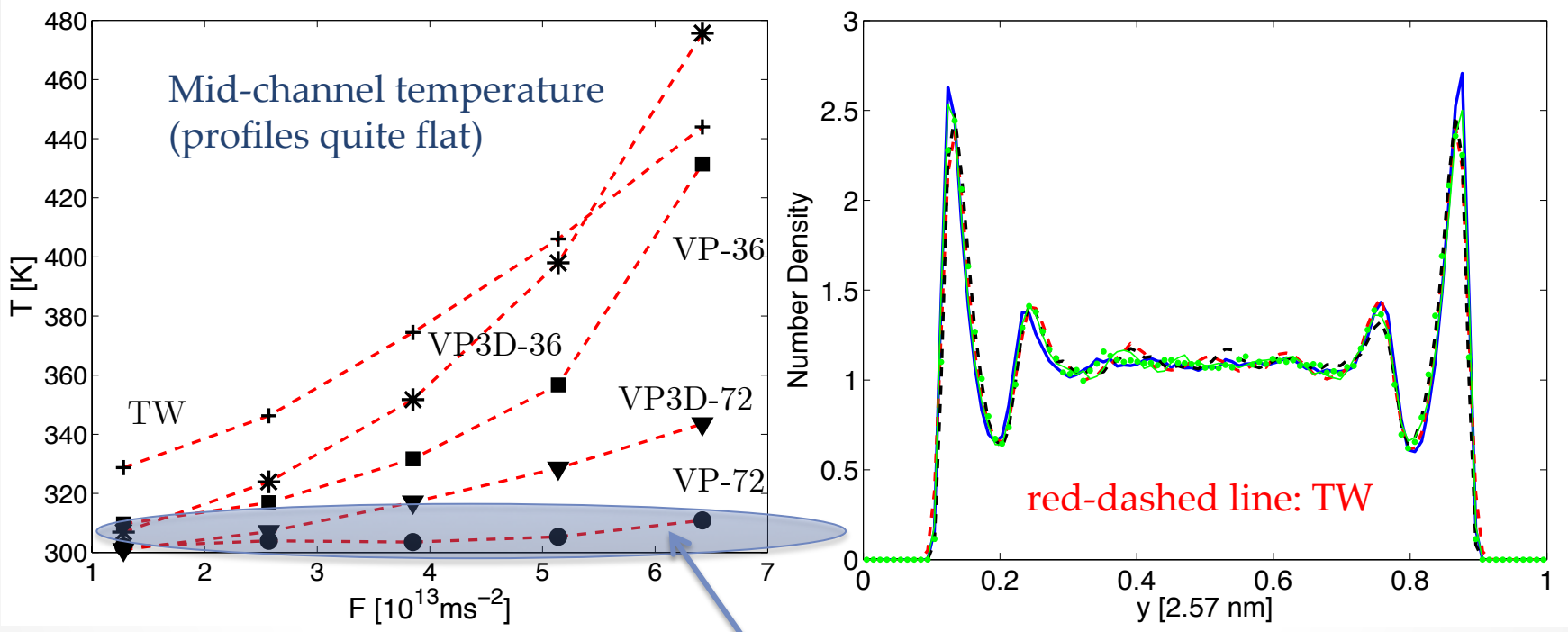


SPC/E water – graphene system

De Luca *et al.*, J. Chem. Phys. **140**, 054502 (2014)

Temperature control

SPC/E water – graphene system



$\sigma_{VP} = \sigma_O = 0.3166$ nm
$\varepsilon_{VP} = \varepsilon_O = 0.6502$ kJ/mol
$k_{VP} = 0.431$ Nm^{-1}
$d_{gv} = 0.63$ Å

Temperature control similar to directly thermostatting liquid without side-effects!

De Luca *et al.*, J. Chem. Phys. **140**, 054502 (2014)

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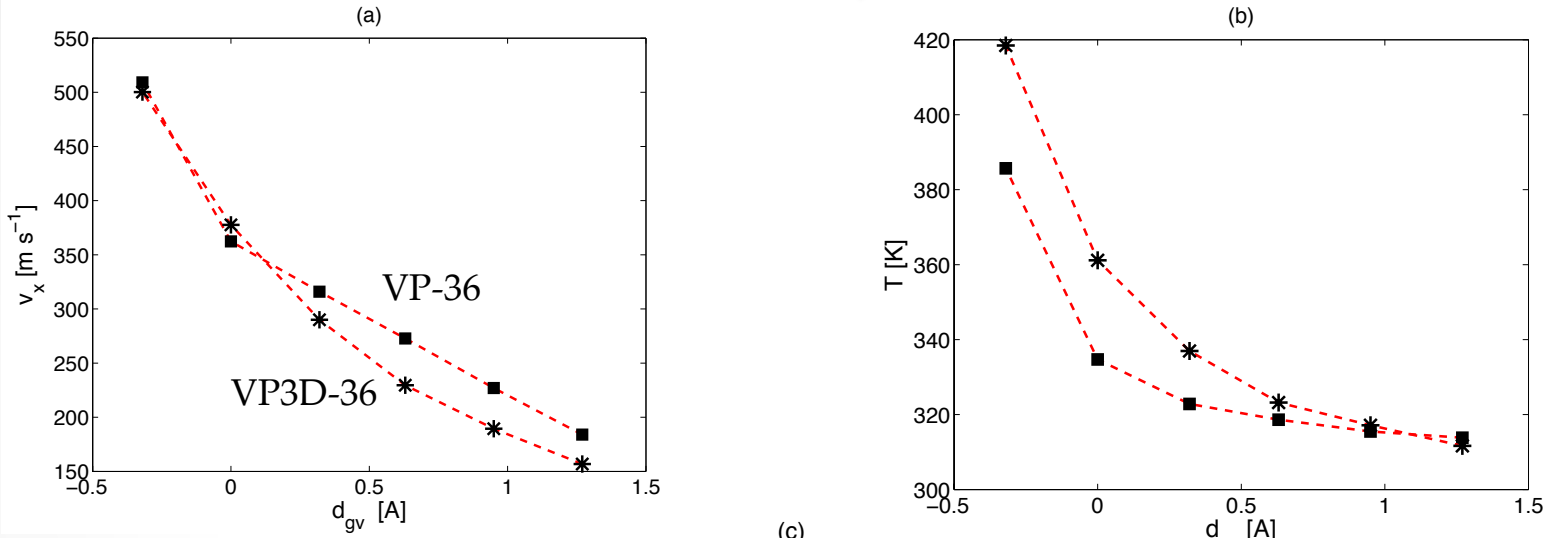
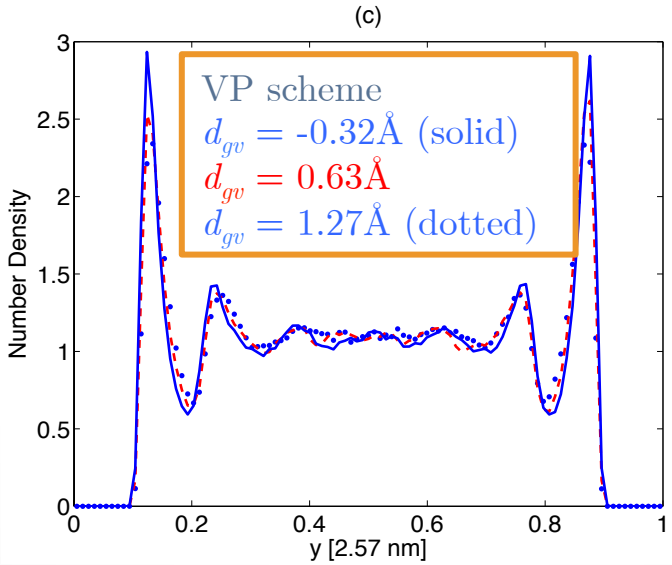
Slip velocity, temperature, density vs VP plane position





$\sigma_{VP} = \sigma_O = 0.3166$ nm
$\varepsilon_{VP} = \varepsilon_O = 0.6502$ kJ/mol
$k_{VP} = 0.431$ Nm^{-1}
$g = 2.56 \times 10^{13}$ ms^{-2}

De Luca *et al.*, J. Chem. Phys. **140**, 054502 (2014)

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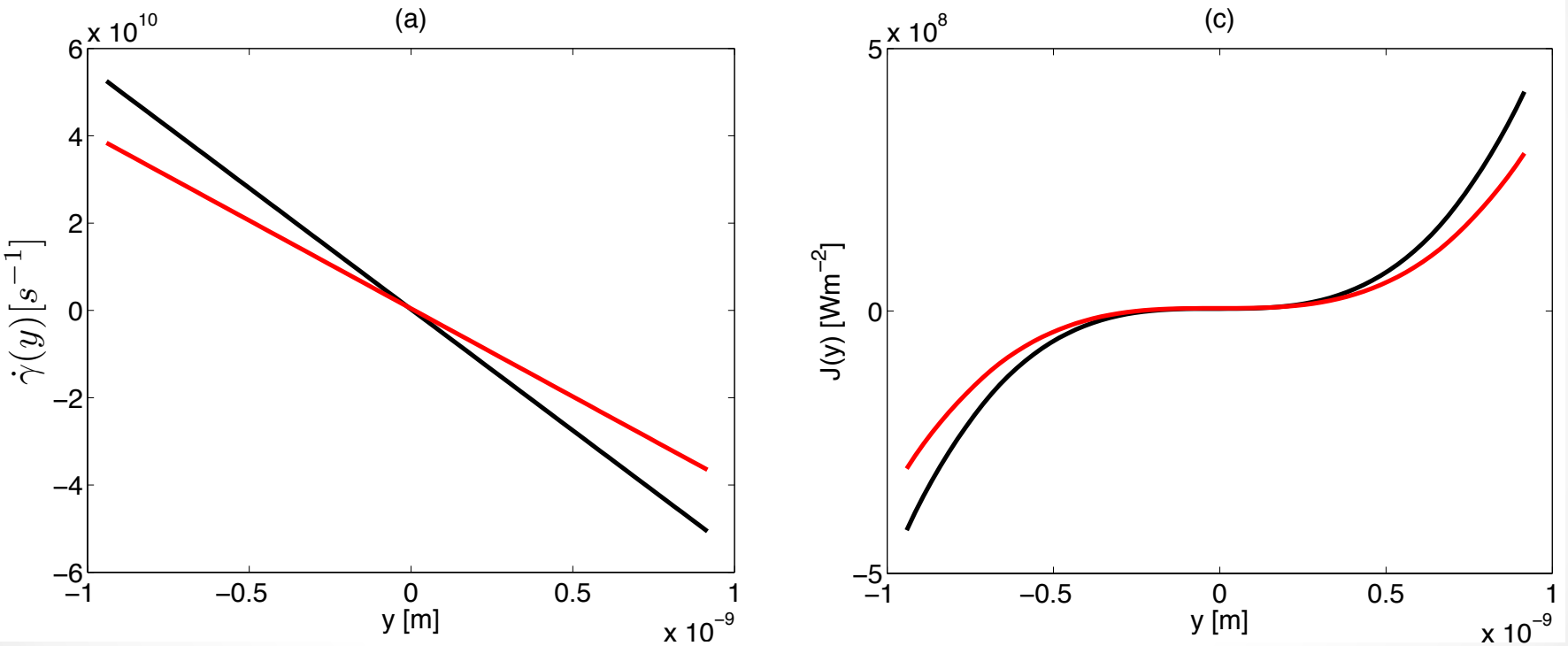
Strain rate, heat flux



TW: black; T ~ 350K

VP: red; T ~ 318K

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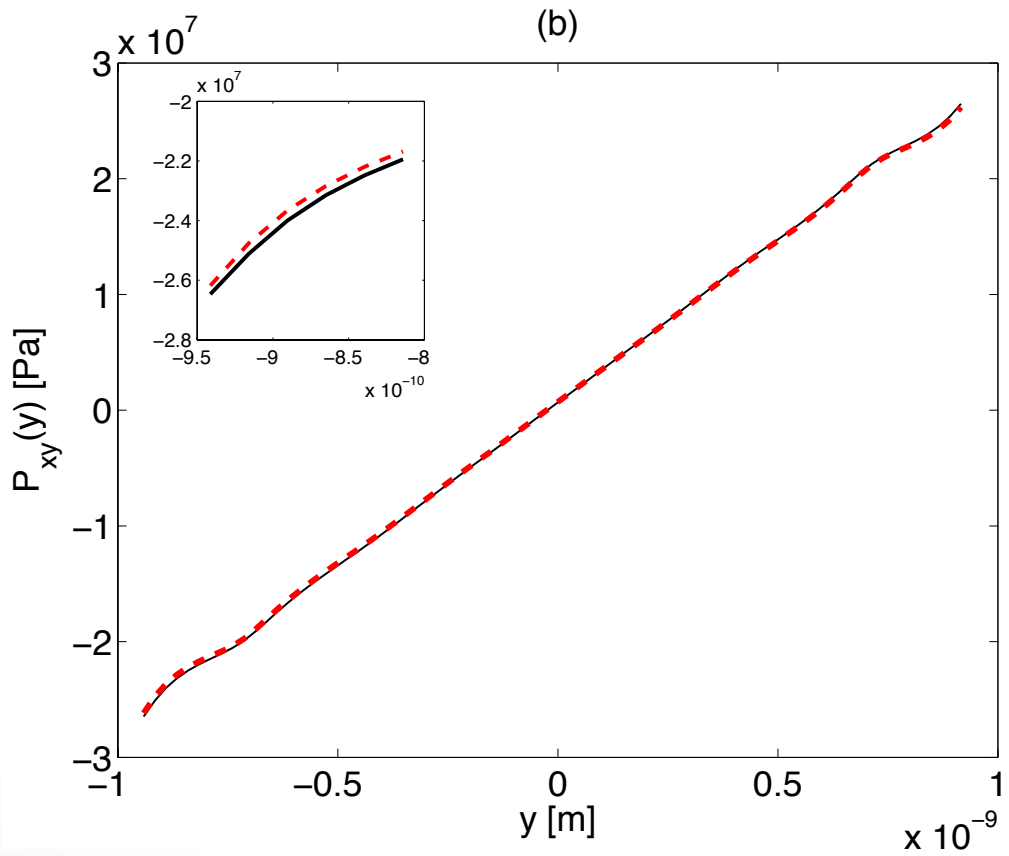
Stress profile



TW: black; T ~ 350K

VP: red; T ~ 318K

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Thermal resistance (Kapitza resistance)

TABLE I. Temperature jump, strain rate, shear stress, heat flux, and thermal boundary resistances as a function of d_{gv}. The point y_0 at which the properties are evaluated is close to the interface. Reference parameters and external field are indicated in the text.

d_{gv} (10^{-9} m)	ΔT (K)	$\gamma(y_0)$ (10^{11} s^{-1})	$P_{xy}(y_0)$ (10^{7} Pa)	$J_{qy}(y_0)$ (10^{9} Wm^{-2})	R (10^{-8} m^2KW^{-1})
0.127	14	0.41	3.04	0.4	3.5
0.095	15	0.4	3.04	0.39	3.9
0.063	19	0.42	3.04	0.41	4.6
0.032	23	0.45	3.04	0.43	5.3
0	35	0.53	3.04	0.51	6.8
−0.032	86	0.85	3.03	0.82	10.4

Experimental/simulation values in the range $R \sim (2 \times 10^{-8} - 2 \times 10^{-9})$ m^2KW^{-1}

$$R \equiv \frac{\Delta T}{J_q} = \frac{T_f - T_w}{J_q}$$

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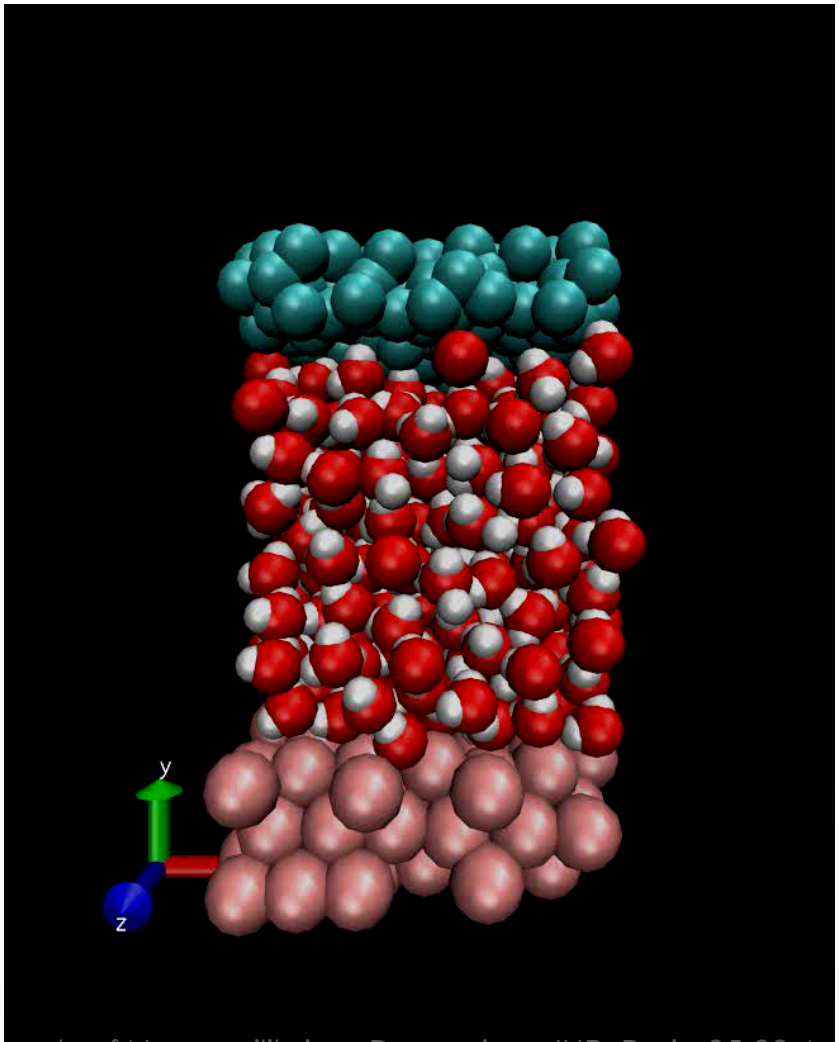
Application: Flow generation via rotating electric field



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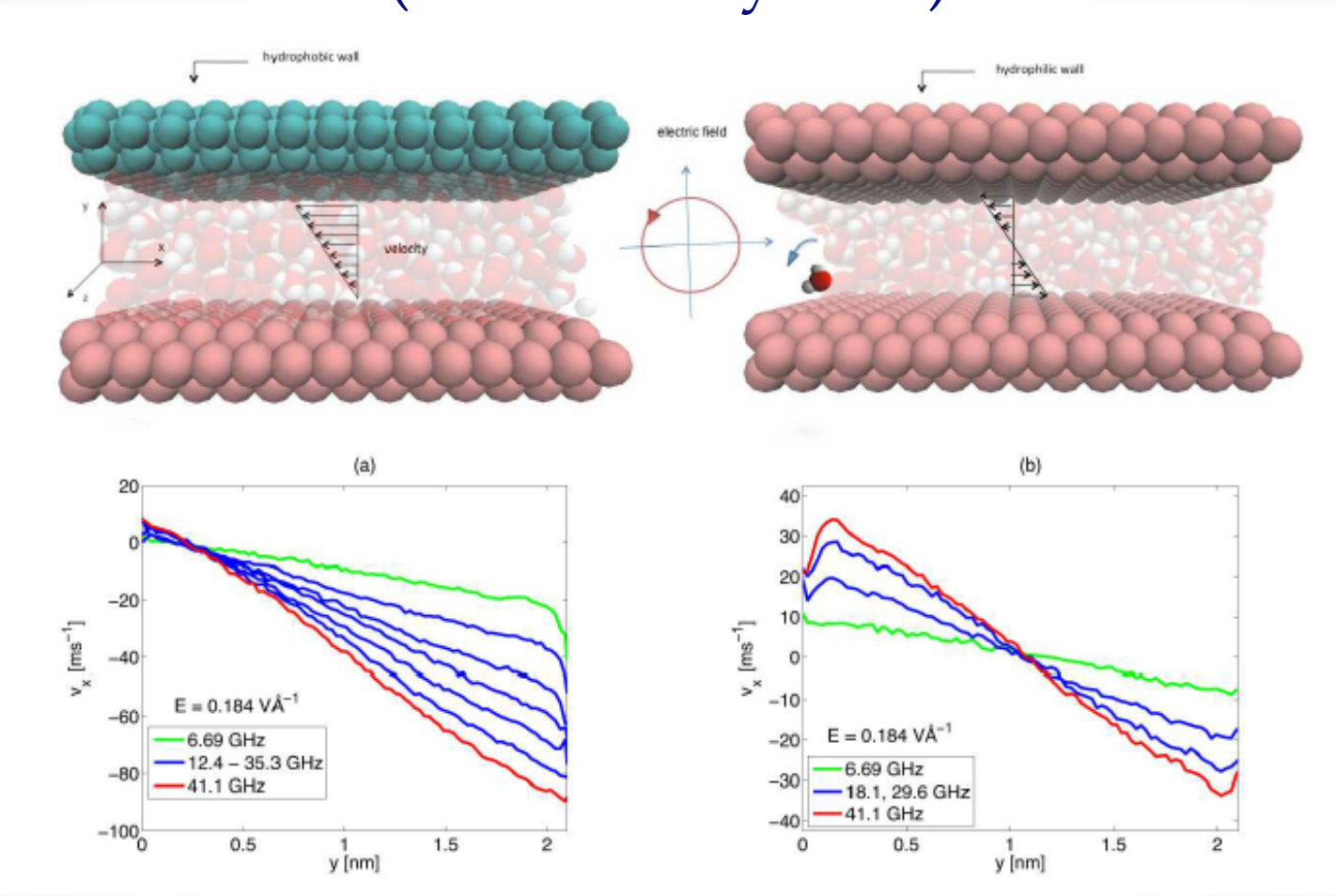
NEMD Simulation Results (Idealised system)



De Luca *et al*, J. Chem. Phys. **138**, 154712 (2013)

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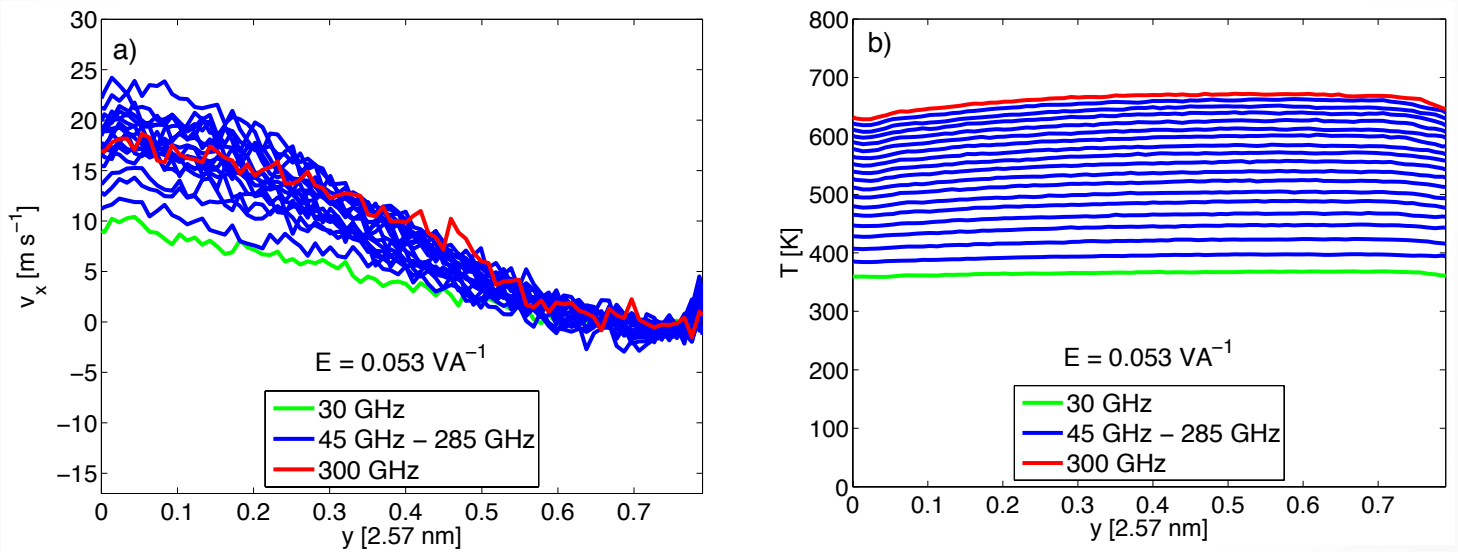
NEMD Simulation Results (asymmetric graphene-silica system)



De Luca *et al*, Langmuir **30**, 3095 (2014)

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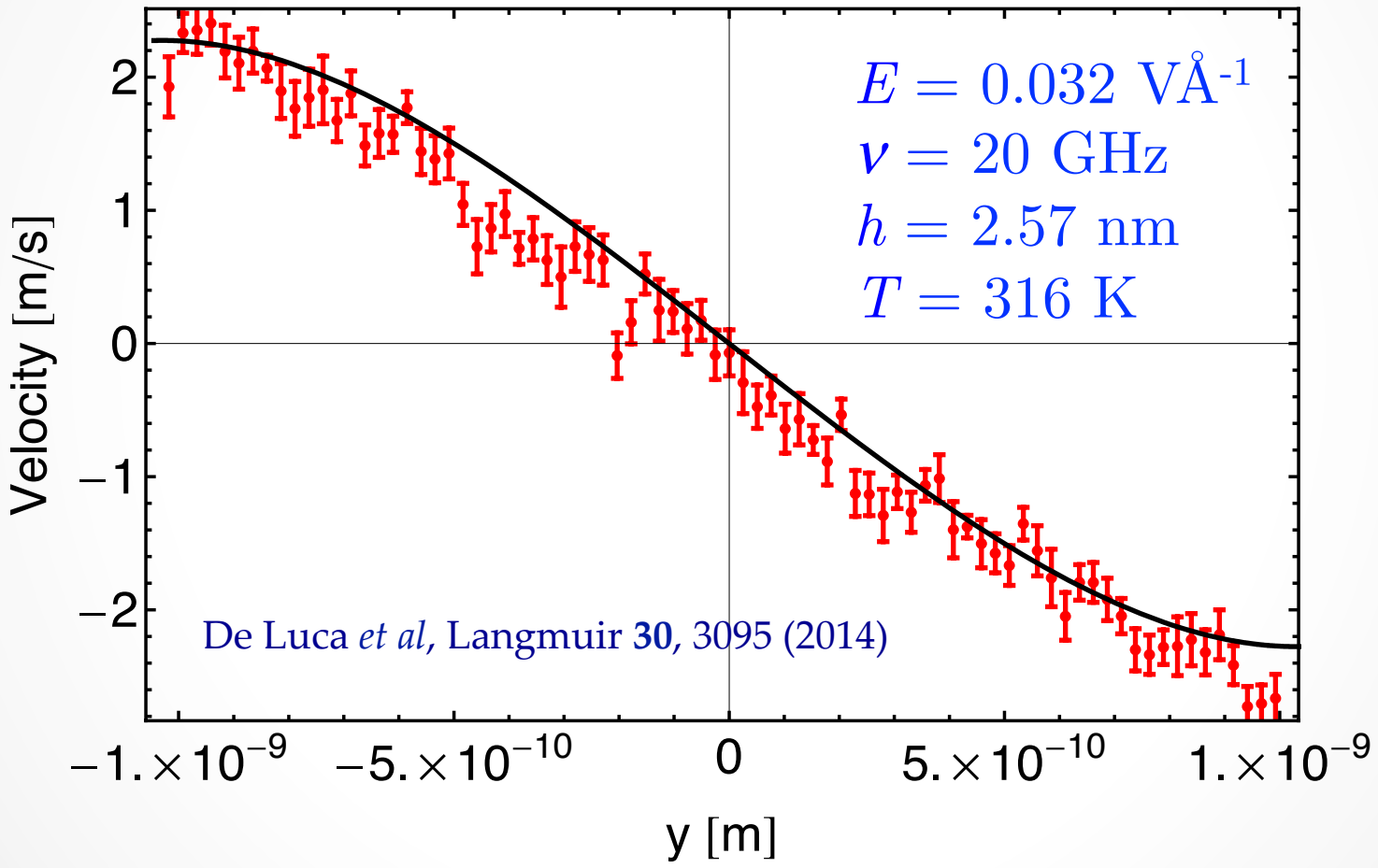
Comparison with continuum theory

Bonthuis *et al.*, Phys. Rev. Lett. **103**, 144503 (2009)
Bonthuis *et al.*, Langmuir **26**, 12614 (2010)



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Conclusions

Flow Enhancement Simulations

- Direct NEMD needs careful analysis and excellent statistics to make reasonable predictions
- Equilibrium MD methods based on time correlation functions more accurate, reliable and valid in linear (experimental) regime

Temperature Control Simulations

- Thermostatting confined fluid directly a questionable simulation strategy that results in several sources of error
- 'Virtual particle' thermostat allowing rigid walls to co-exist with unthermostatted fluid enables thermostatting of complex wall-fluid systems and may be a useful NEMD simulation scheme to control temperature for confined fluids

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  - National Computing Infrastructure
  - Swinburne Supercomputer Cluster

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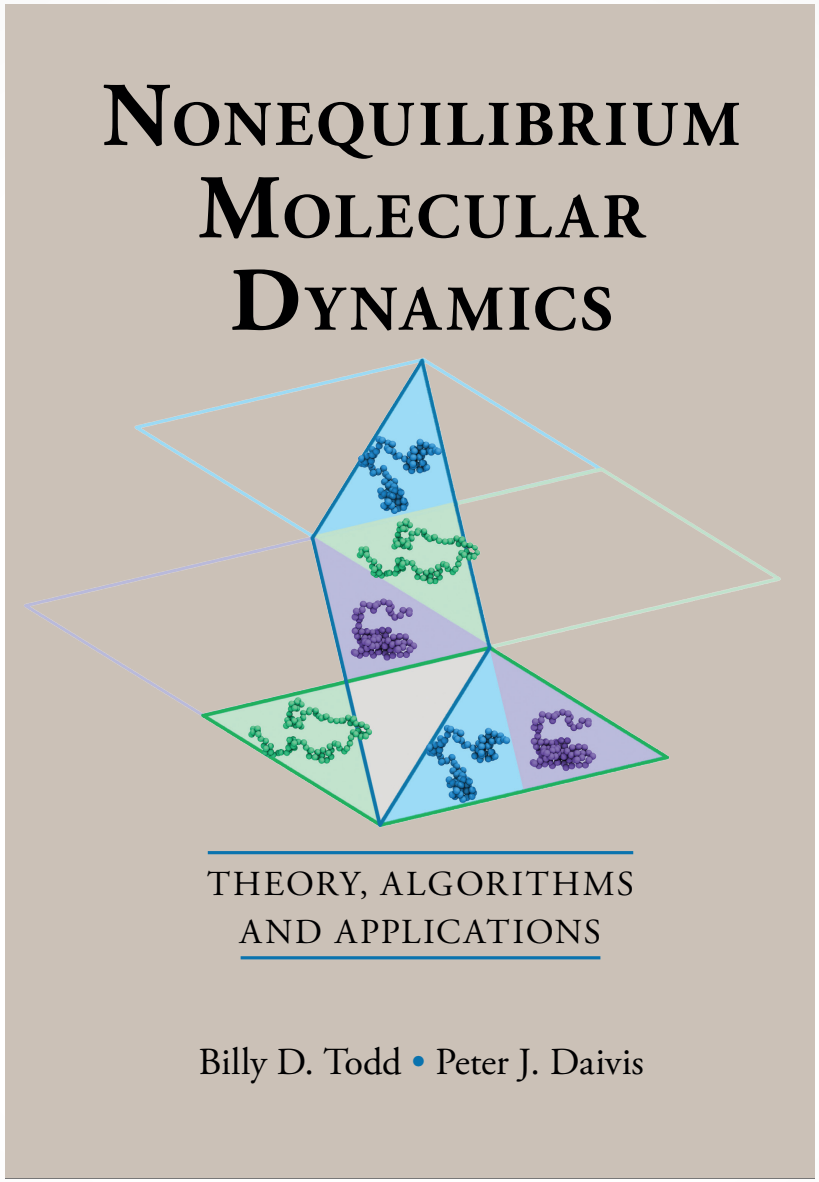

Cambridge University Press, 2017