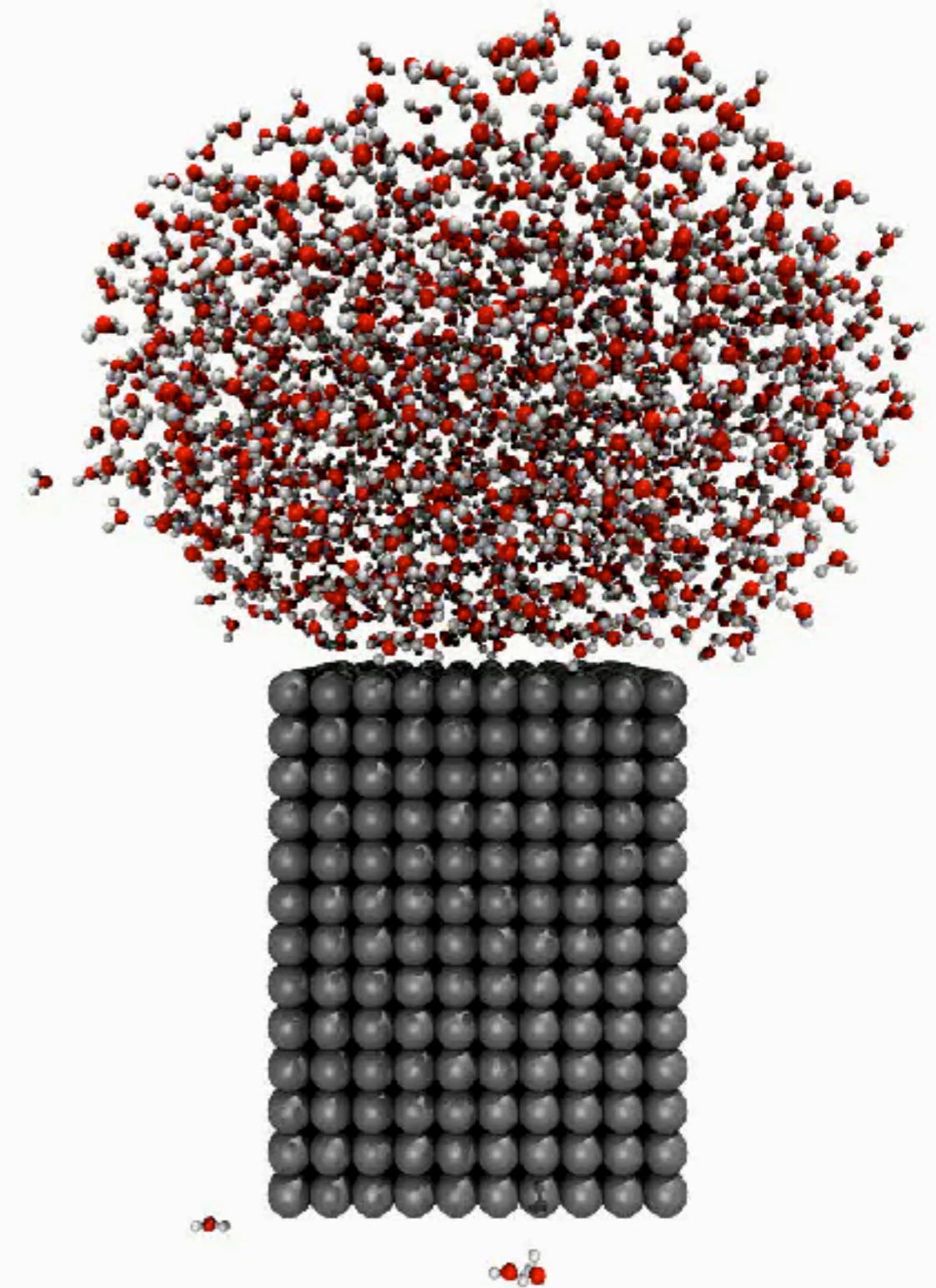


Molecular dynamics in engineering

Jason Reese

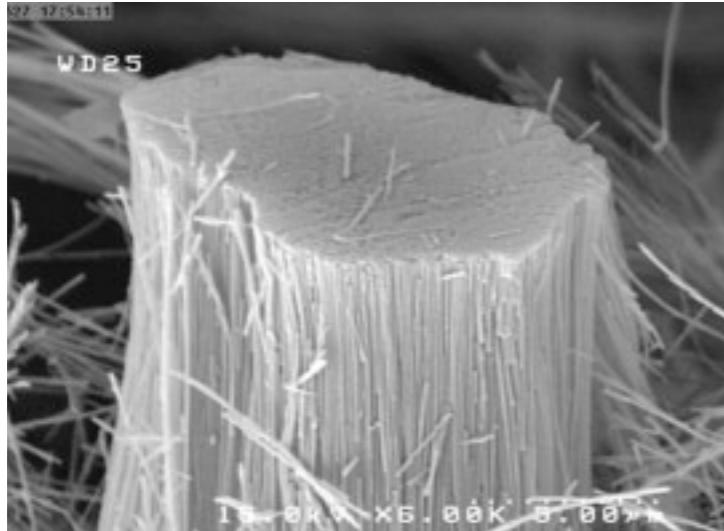
Matthew Borg

jason.reese@ed.ac.uk

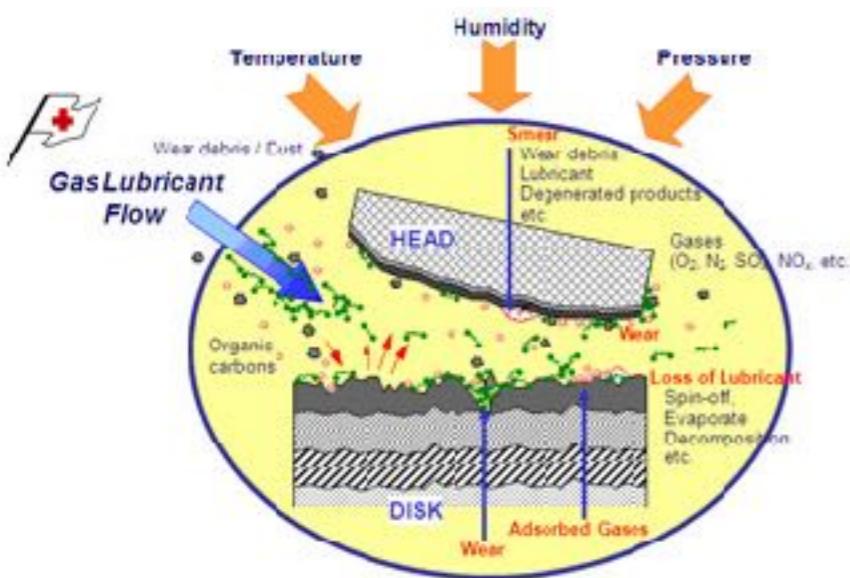


THE UNIVERSITY *of* EDINBURGH
School of Engineering

Multiscale flow technologies



nanotube membranes



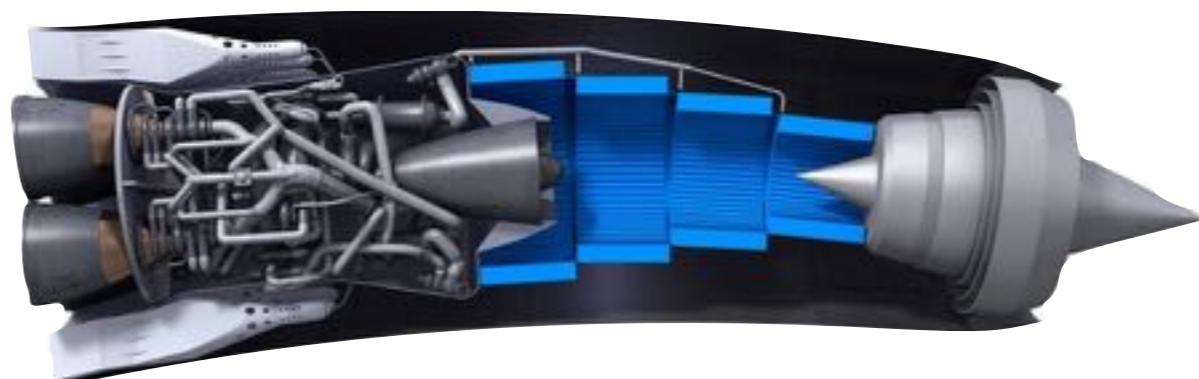
**flows through cracks
or bearings**



**high-speed,
high-altitude vehicles**

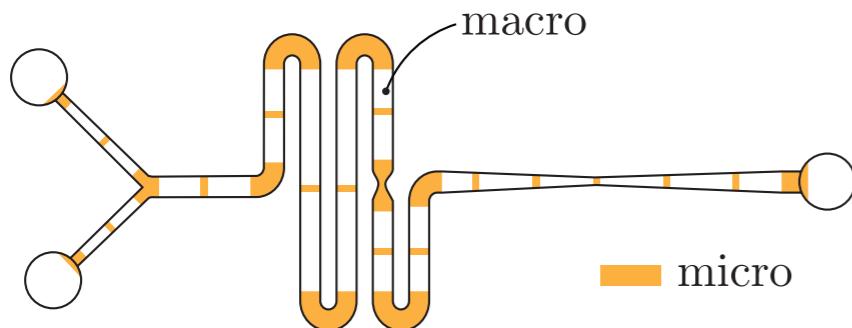


granular flows



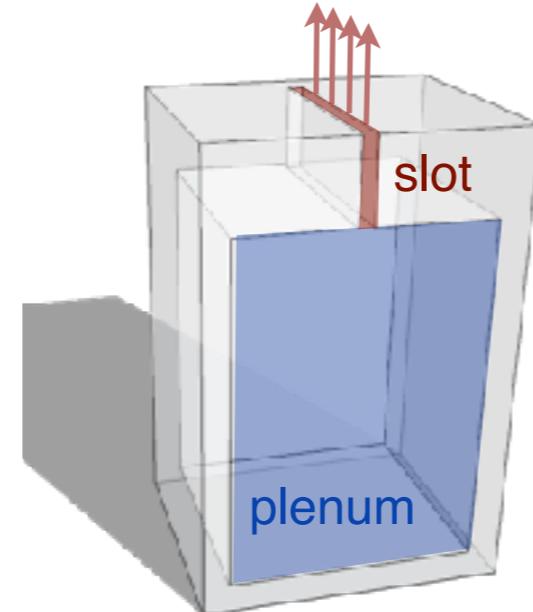
micro heat exchangers

Non-continuum flow examples



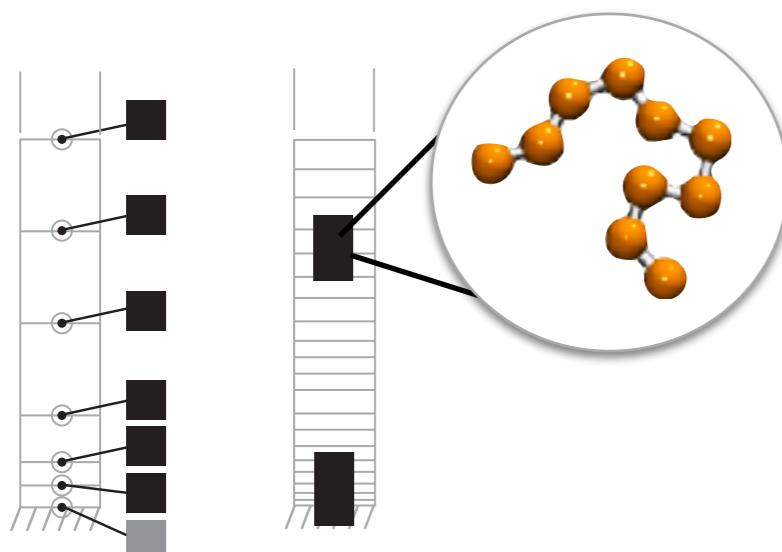
micro/nano channel networks

Stephenson, Lockerby, Borg & Reese (2014)
Microfluid. Nanofluid. **18**, 841-858



MEMS actuators

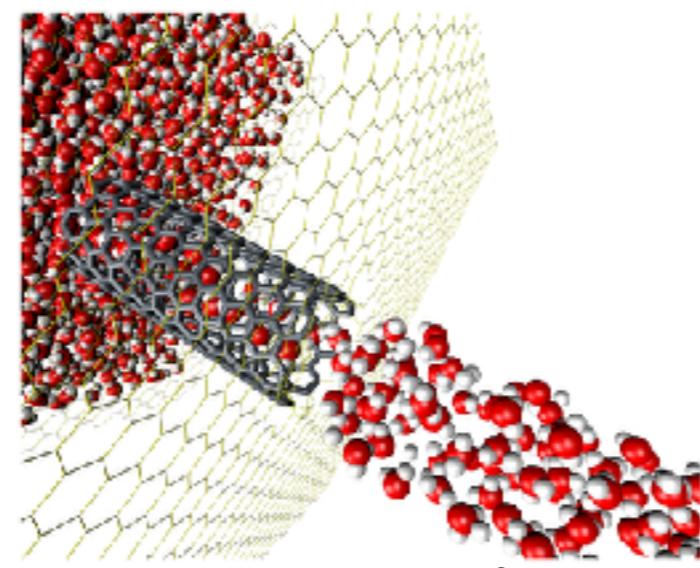
Lockerby, Duque-Daza, Borg & Reese (2013)
J. Comp. Phys. **237**, 344-365



non-Newtonian flows

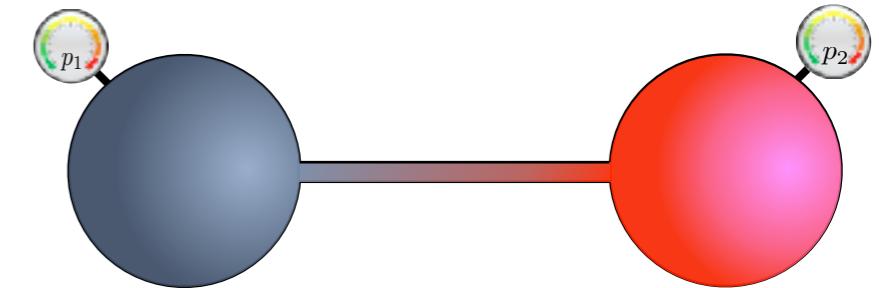
Borg, Lockerby & Reese (2013)
J. Comp. Phys. **255**, 149-165

Docherty, Borg, Lockerby & Reese (2014)
Int. J. Heat Fluid Flow **50**, 114-125



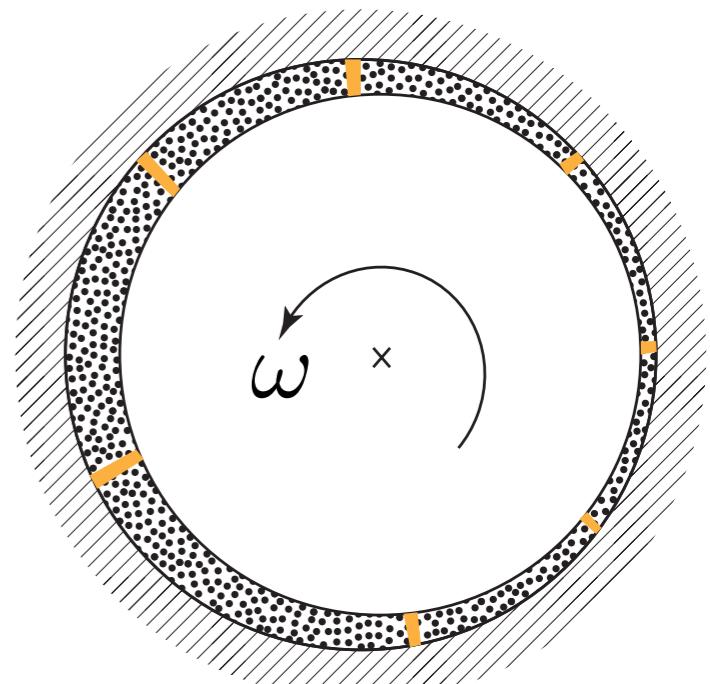
water transport in CNTs

Ritos, Borg, Lockerby, Emerson & Reese (2015)
Microfluid Nanofluid **19**, 997-1010



Knudsen pumps

Lockerby, Patronis, Borg & Reese (2015)
J. Comp. Phys. **284**, 261-272

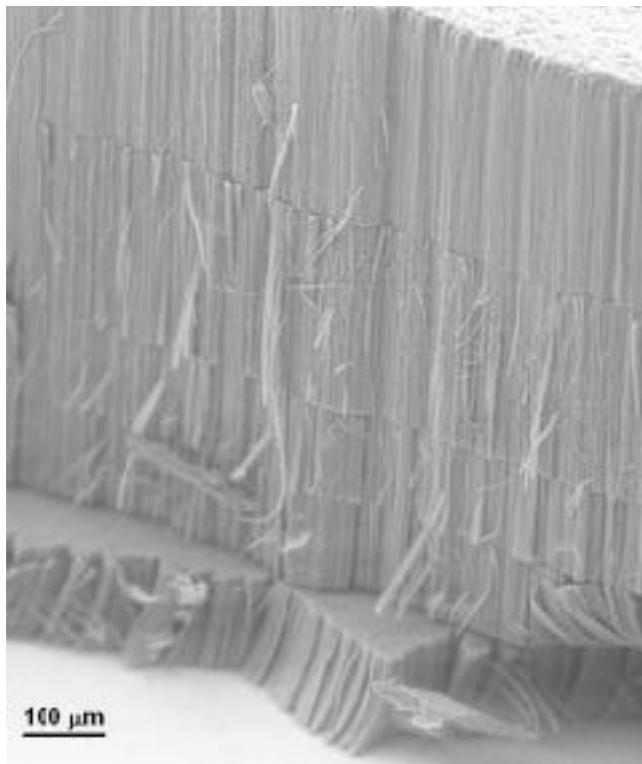


micro gas bearings

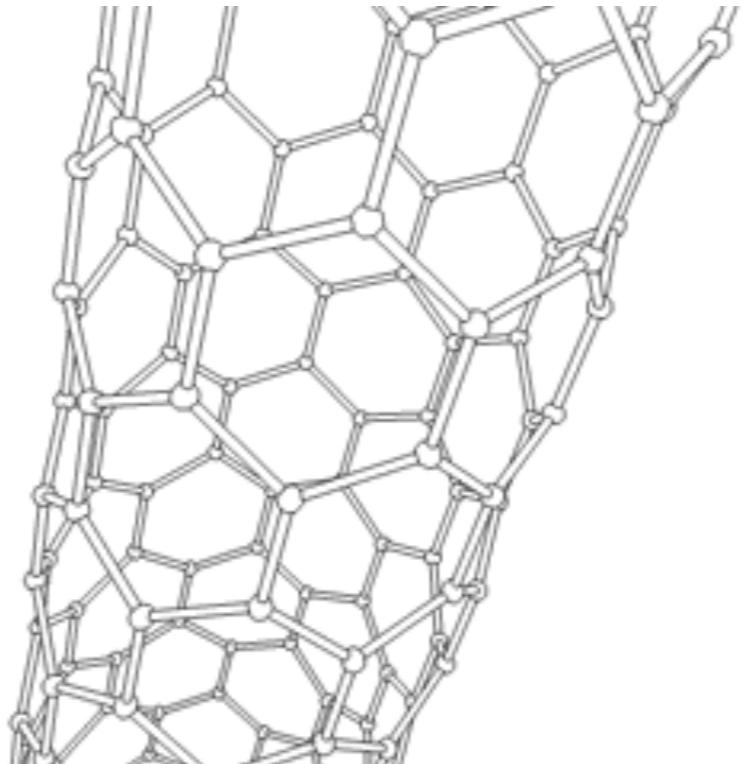
Patronis, Lockerby, Borg & Reese (2013)
J. Comp. Phys. **255**, 558-571

Desalination using nanotubes

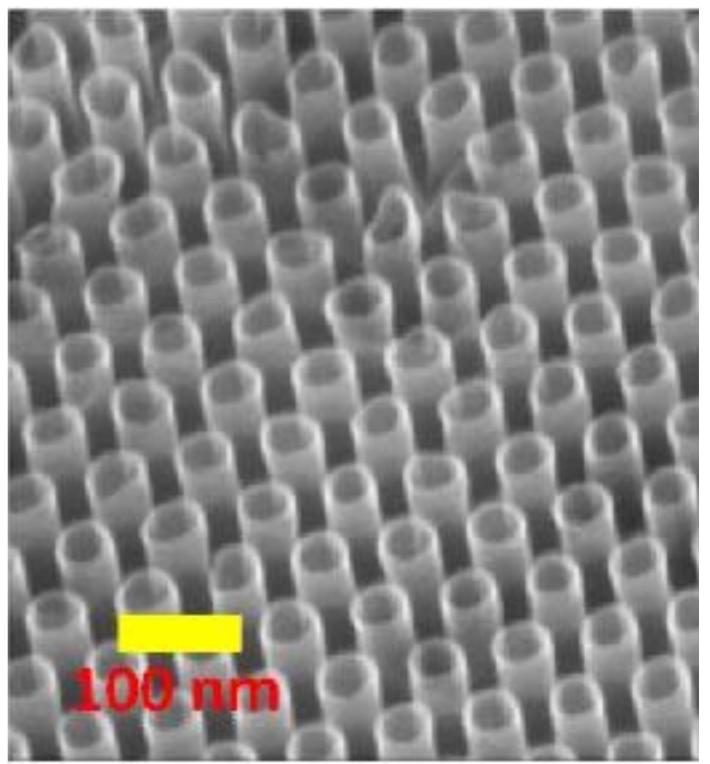
- ▶ by 2050, four billion people in 48 countries will lack sufficient water
- ▶ desalination (or water purification) mostly achieved through reverse osmosis (RO)
- ▶ could efficient new RO membranes be made using aligned nanotubes (e.g. CNTs)?
- ▶ “carpets” of aligned nanotubes can be grown on substrates
- ▶ small diameter nanotubes (e.g. 0.95 nm) could exclude Na^+ , Cl^- and other molecules
- ▶ fluid dynamics and performance prediction requires unusual simulation techniques



*layers of CNTs
grown in the lab*



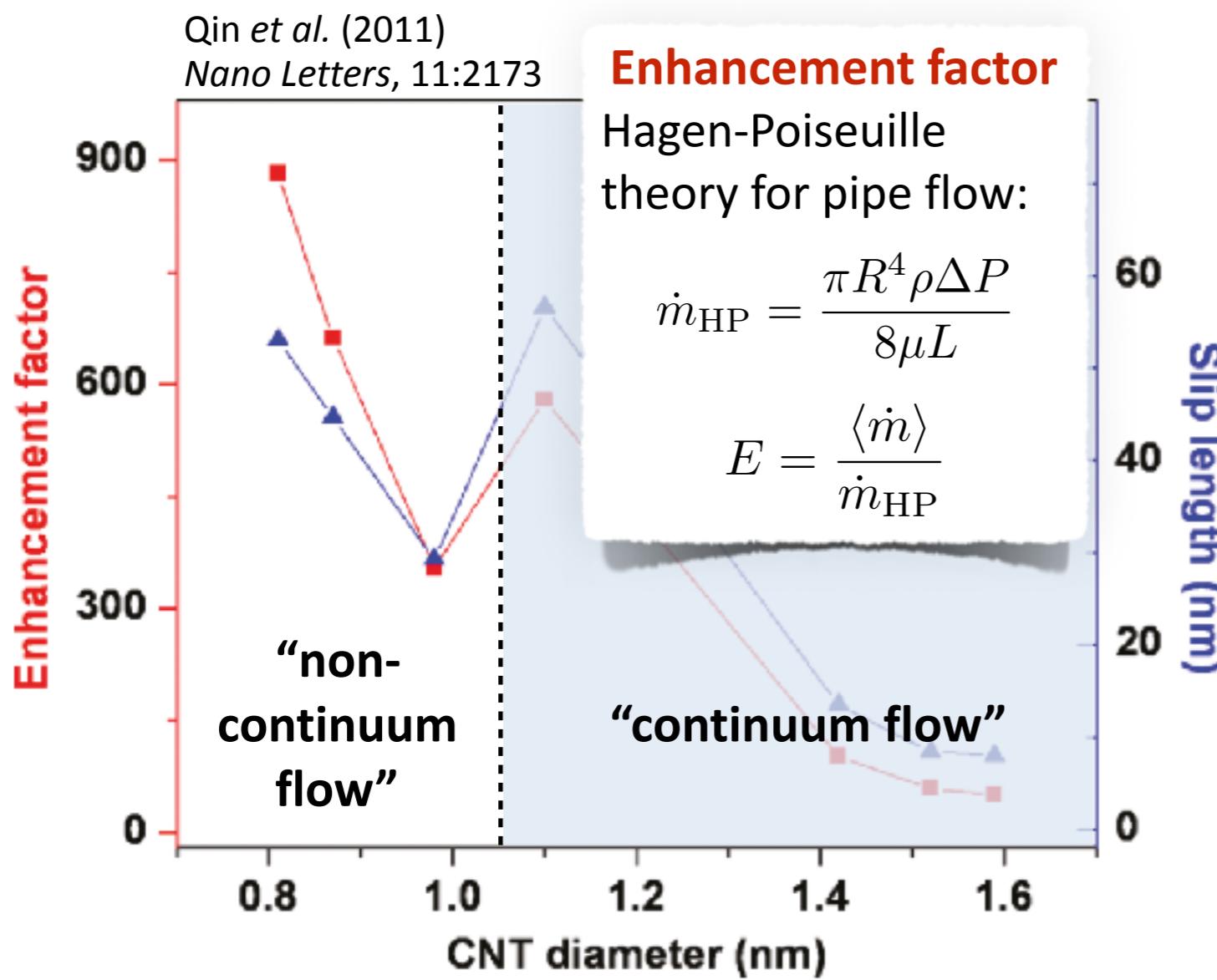
molecular structure of a CNT



aligned CNTs

What is the fluid dynamics problem?

- ▶ experiments on water flow in 1 mm-long CNTs of different diameters



- ▶ non-continuum flow cannot be captured by conventional fluid dynamics
 - slip at interfaces
 - density layering
 - non-linear constitutive behaviour
 - curvature-dependent surface friction
- ▶ non-continuum in gases can be indicated by the Knudsen number:

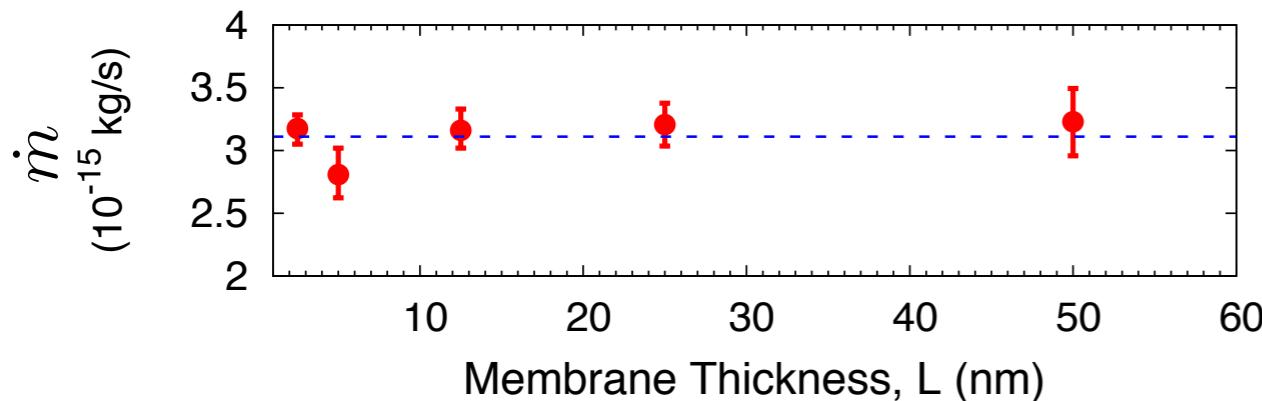
$$Kn = \frac{\lambda}{L} \approx \frac{1.3\mu}{L_p} \sqrt{RT}$$

molecular mean free path

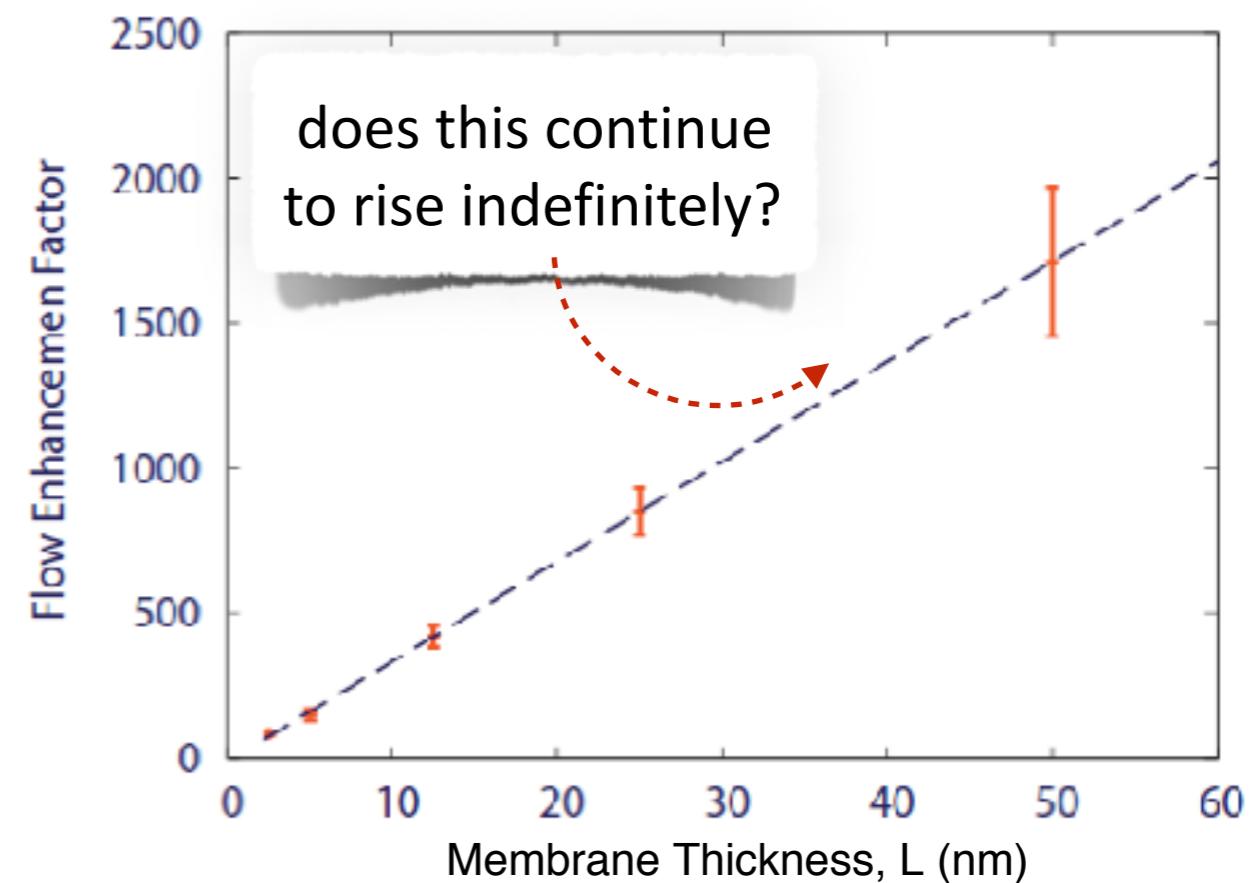
characteristic length

Non-continuum flow in slender CNTs

- ▶ pressure-driven water flow in (7,7) CNTs of 0.96 nm diameter
- ▶ constant flow rate, whatever the CNT length, for the same pressure difference
→ near-total slip? frictionless?



- ▶ a commonly-used measure is the *flow enhancement factor*
→ ratio of simulated flow rates to Hagen-Poiseuille pipe flow



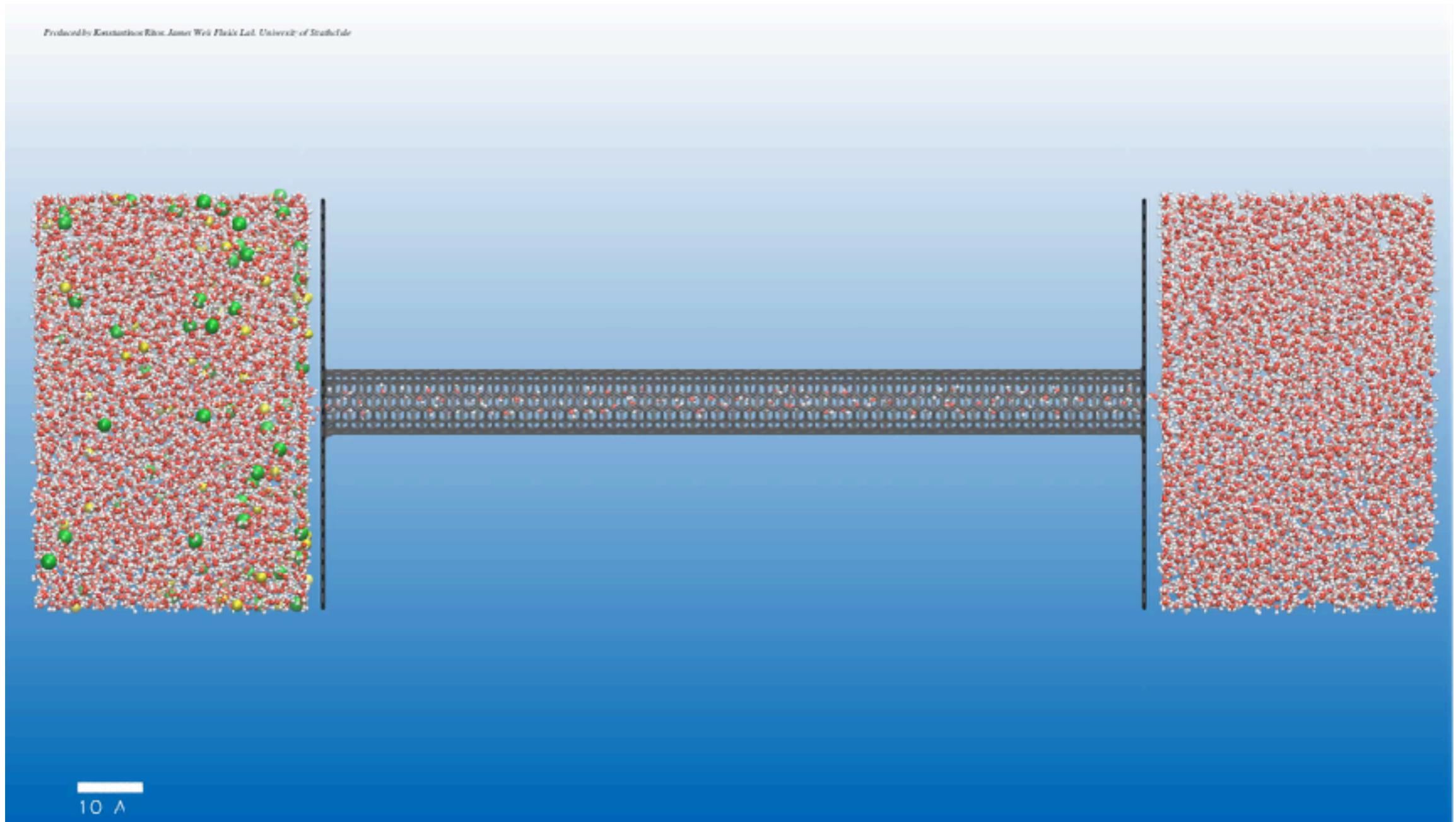
- ▶ flow enhancement factor
 - O(10) for CNTs of 2.5 nm length
 - O(1000) for CNTs 50 nm long
- ▶ what is going on?



Our open-source software base: OpenFOAM

- ▶ we use the C++ libraries and utilities of the open-source software OpenFOAM
- ▶ used by ~10,000 users (industrial/research) internationally
- ▶ models we developed are now incorporated into releases of OpenFOAM
 - ▶ Molecular Dynamics for gases and liquids: **mdFOAM+**
 - ▶ the direct simulation Monte Carlo technique for gases: **dsmcFOAM+**
 - ▶ high-speed, viscous, compressible flows on unstructured polyhedral meshes
 - ▶ velocity-slip and temperature-jump boundary conditions for gases
- ▶ latest version freely available to download at www.github.com/MicroNanoFlows/
- ▶ all our models and solvers work in arbitrary flow geometries and in parallel
- ▶ start from a flow system design in a CAD package (e.g. PTC Creo), export to meshing utility (e.g. GAMBIT) for meshing in, typically, hexahedral cells, then import to OpenFOAM

Molecular Dynamics for nanotube membrane



12,000 molecules (H_2O , Na^+ , Cl^- , C), $\Delta p=200 \text{ MPa}$
MD timestep is typically 1 fs, 12 CPU cores for 12 hours = 120 ps of 'problem time'

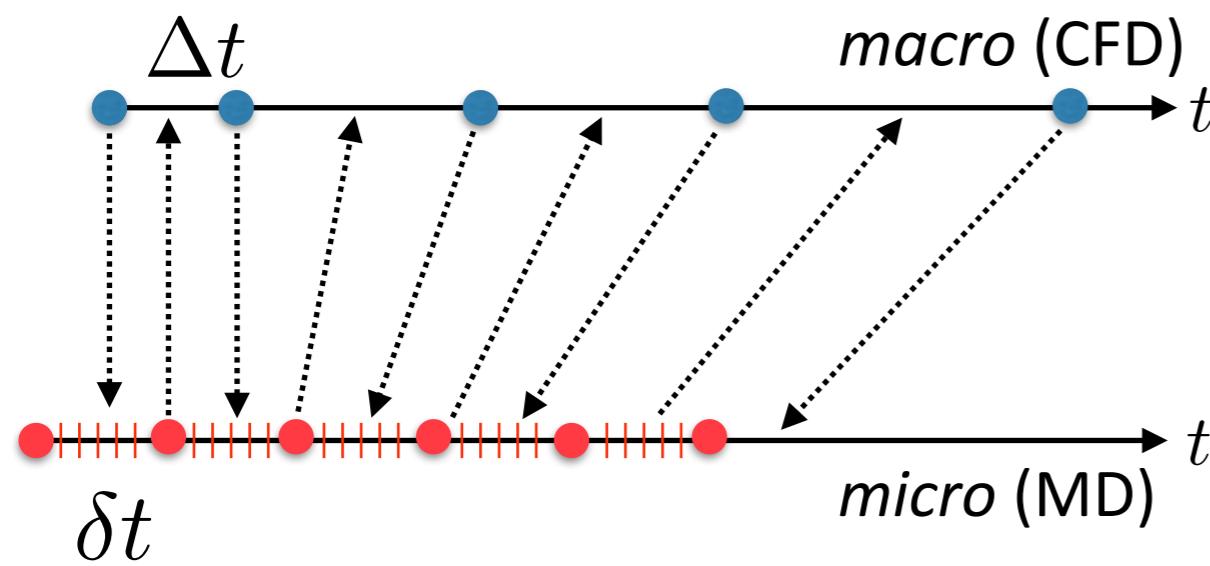
Hybrid methods: “best of both worlds”?

How can we simulate flow systems in which the length scales range from nanometres to millimetres (a difference of 10^6)?



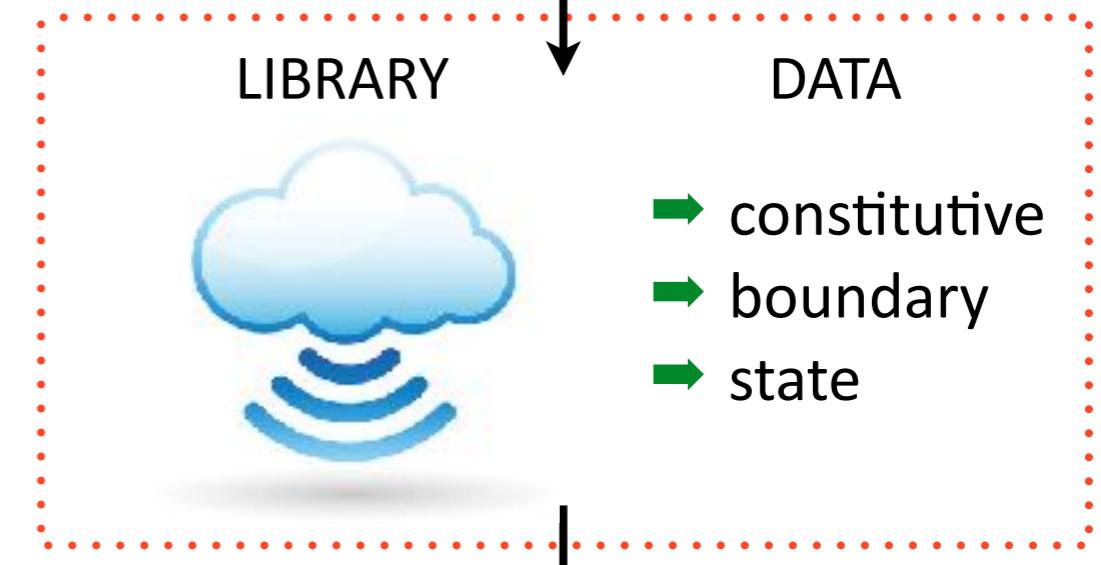
“combine the accuracy of molecular simulations, with the computational efficiency of fluid dynamics ...”

Two types of hybrid multiscale methods



Type A. Concurrent
(molecular-with-continuum)

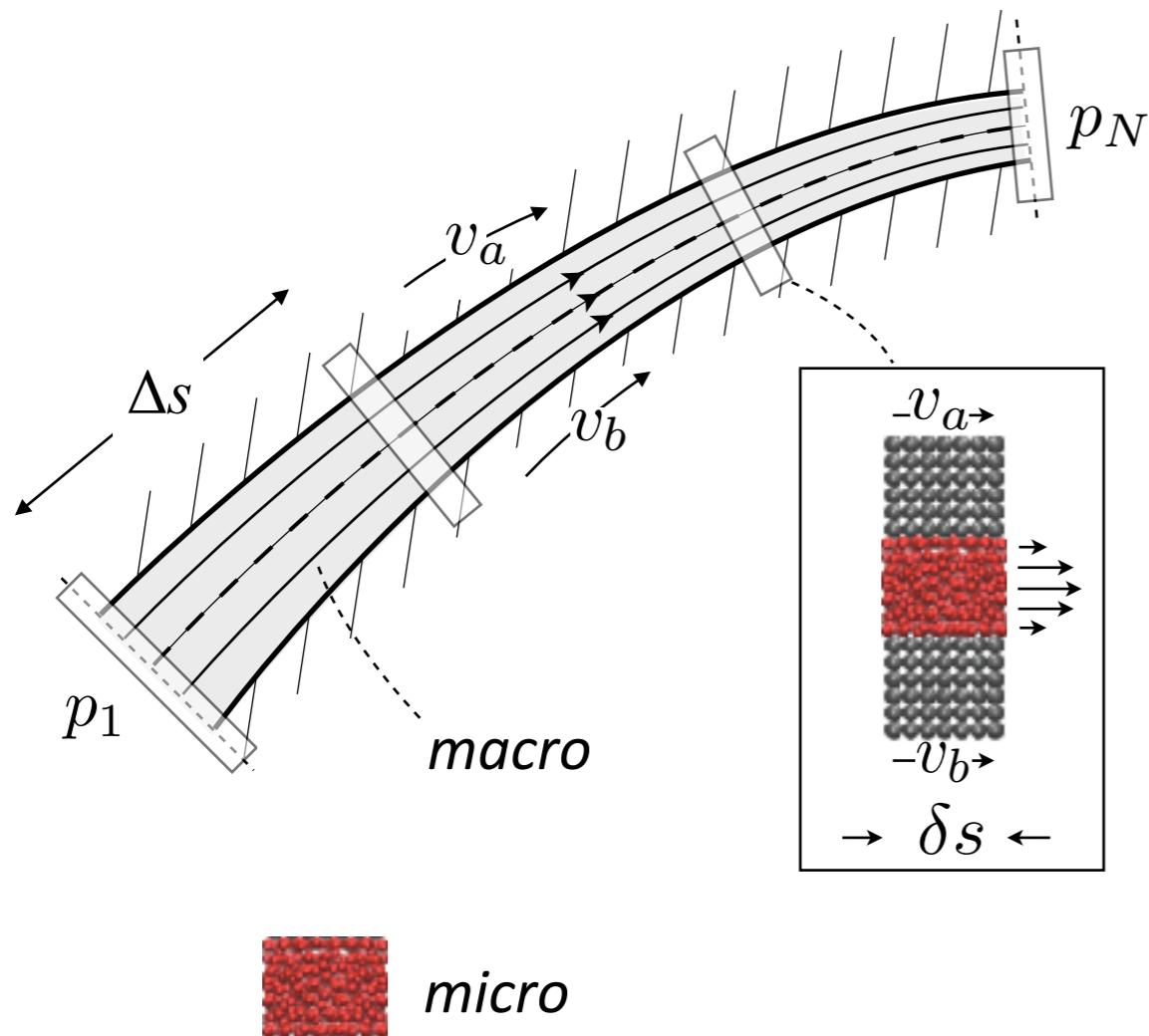
molecular pre-simulations



CFD simulations

Type B. Sequential
(molecular-then-continuum)

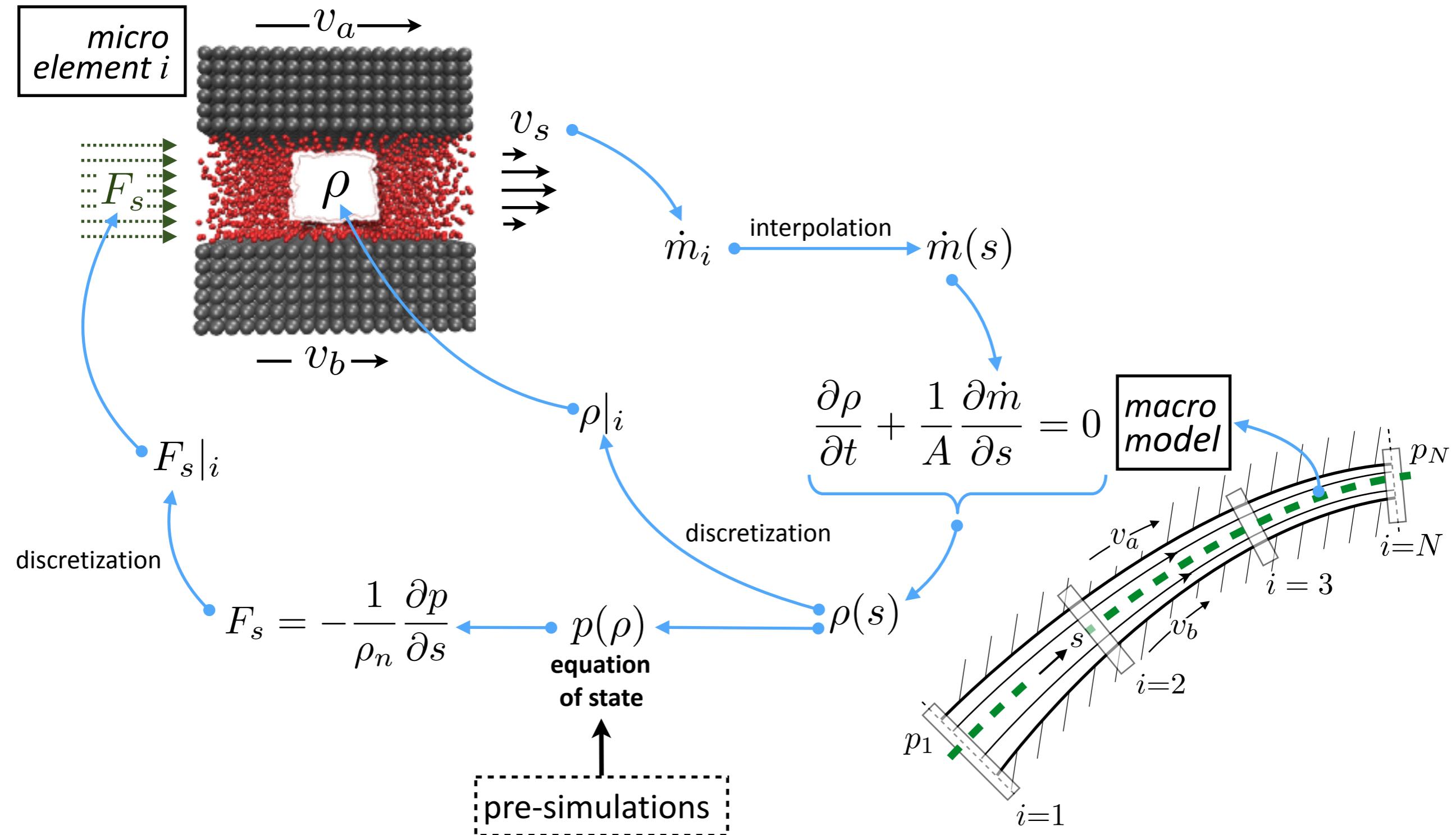
Concurrent modelling



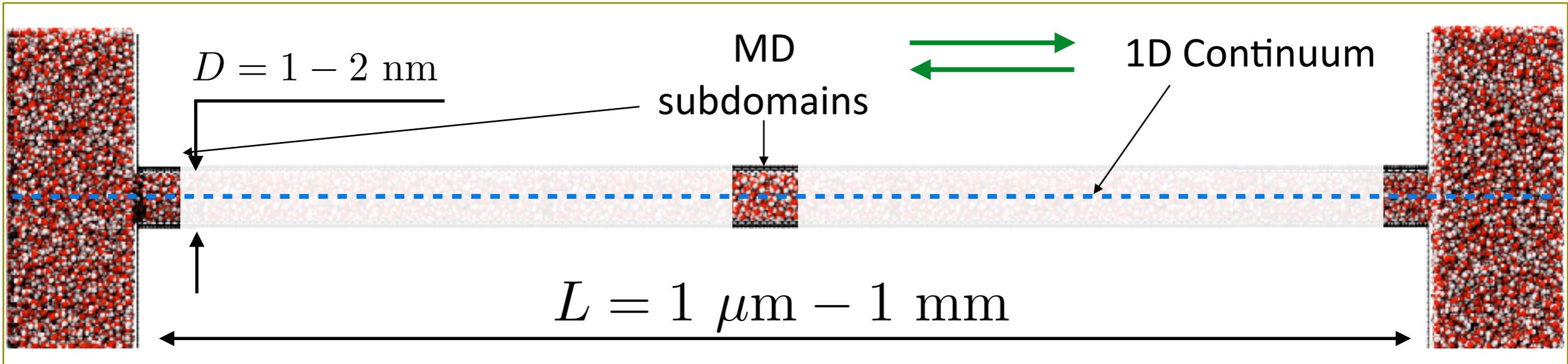
internal-flow multiscale method (IMM)

- ▶ nanofluidic geometries typically long in the flow direction
- ▶ length scale separation enables *local parallel flow* assumption
- ▶ macro model is continuum fluid dynamics
- ▶ micro model is molecular dynamics in periodic sub-domains with forcing
- ▶ computational savings due to spatial scale separation $\sim g_L = \Delta s / \delta s$
- ▶ how do we couple micro to macro?

Concurrent modelling

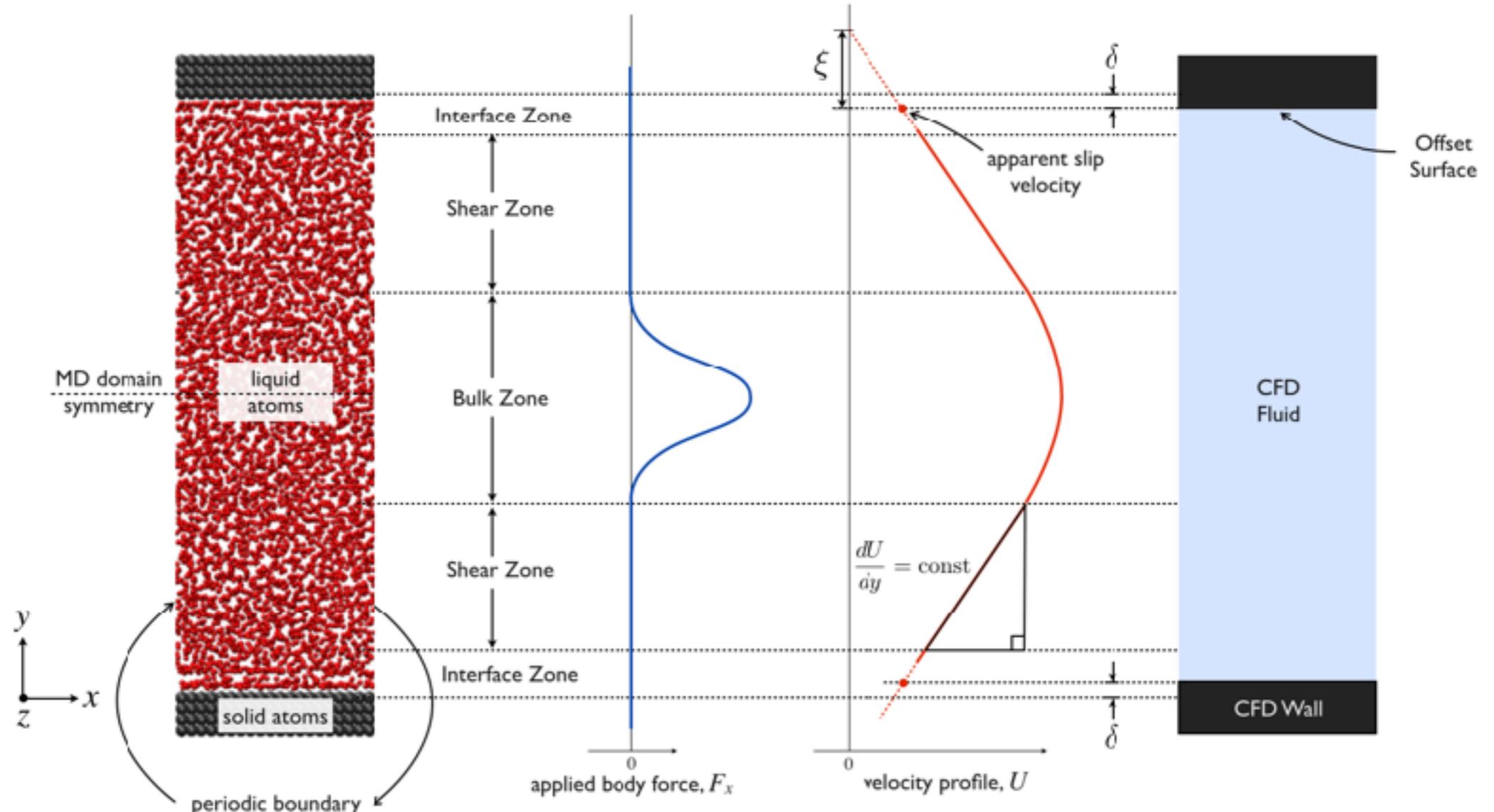


IMM simulations of the flow in long CNTs



- ▶ the flow is highly scale separated in the streamwise direction (and is steady)
- ▶ decompose the channel system into smaller MD subdomains...
- ▶ ... which we “stitch back together” by using a 1D linear flow response between applied pressure drop (continuum) and measured mass flow rate (MD)
- ▶ linear interpolation of pressure through the gaps
- ▶ apply coupling between the continuum model and the MD subdomains
- ▶ computational savings come from having fewer molecules in the MD realisations

Sequential modelling

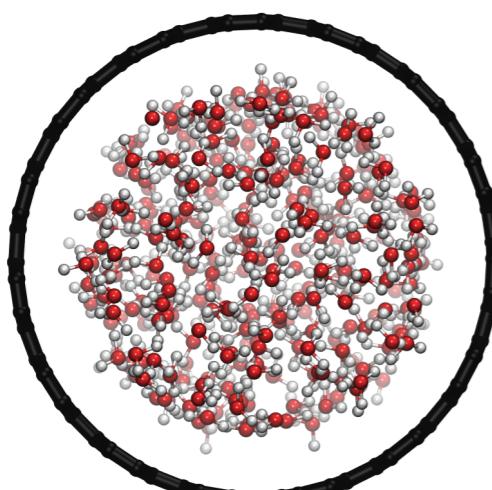


- ▶ bulk zone: measure state properties, $p = p(\rho)$
- ▶ artificial force in bulk zone creates a velocity profile
 - ▶ shear zone: measure constitutive properties, $\mu = \mu(\rho)$
 - ▶ interface zone: measure slip boundary properties $\xi = \xi(\rho, \gamma)$, depletion layer

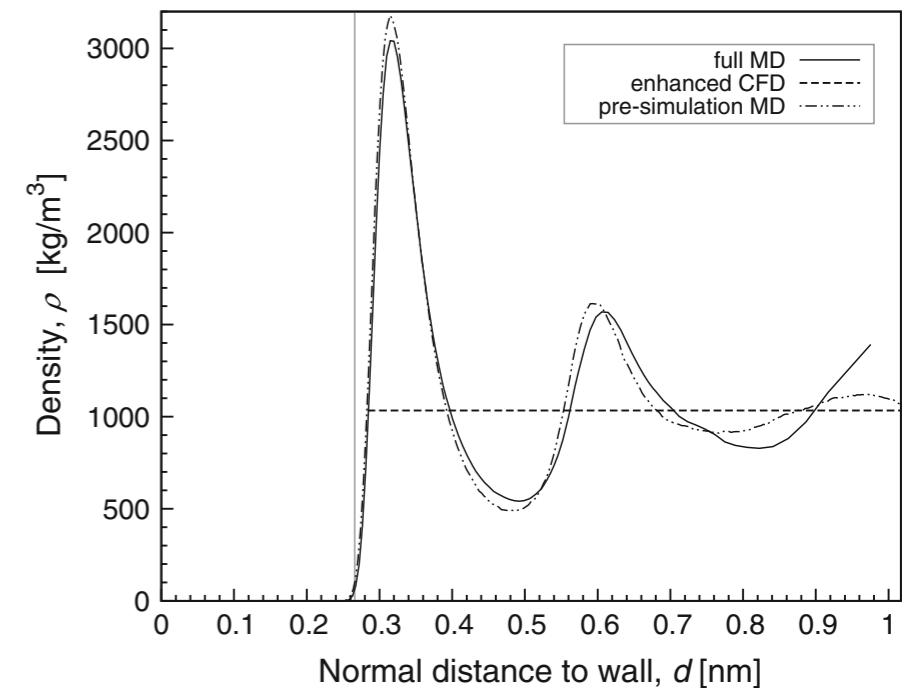
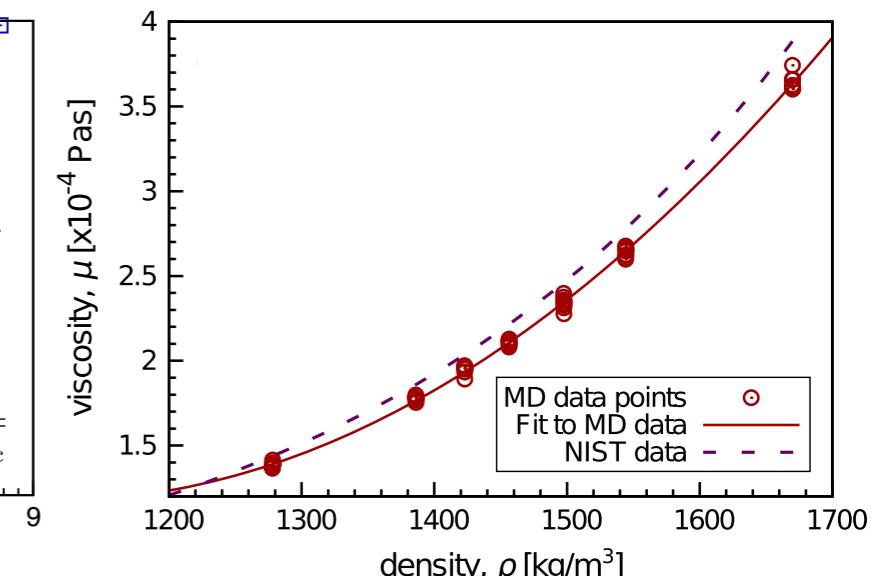
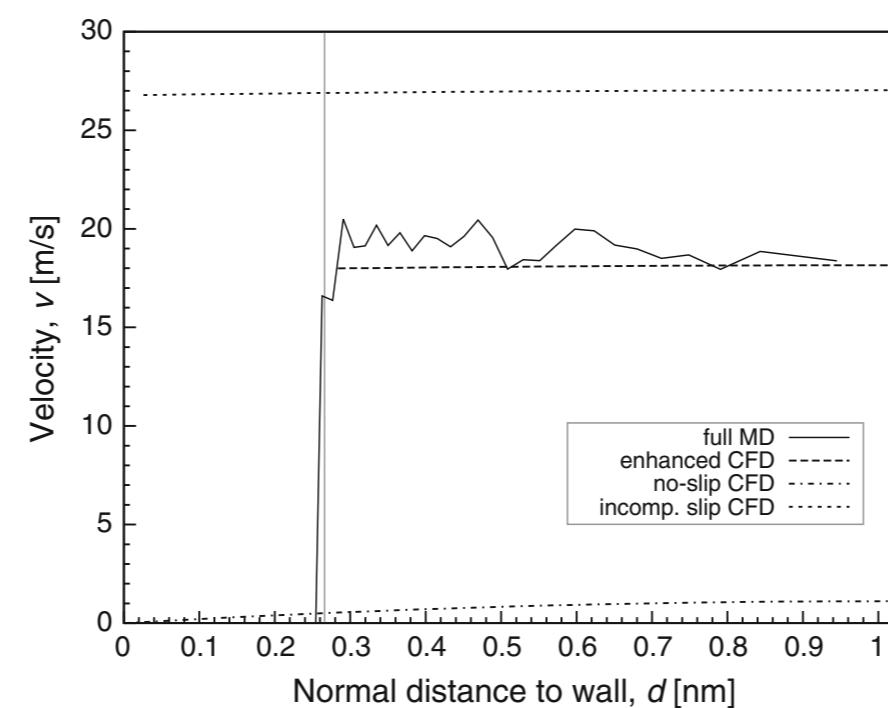
What is ‘non-continuum’ fluid dynamics?

2. Fluid dynamic models can be modified to include *some* features of non-continuum flow behaviour — but to what extent is this possible and helpful?

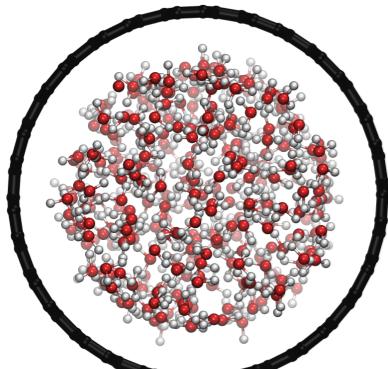
- e.g. flow in nanotubes
- molecular pre-simulations providing constitutive and boundary data
- some non-continuum features are captured well – some are not!



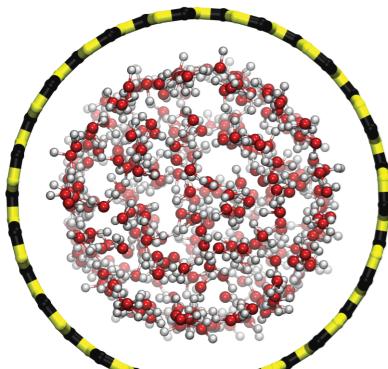
flow in a CNT showing layering



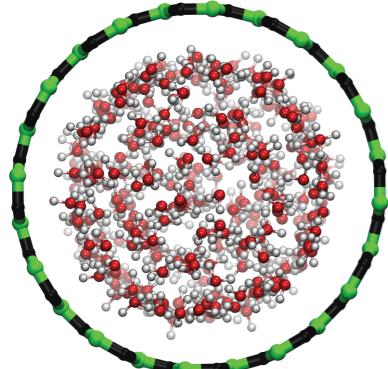
Different nanotube materials



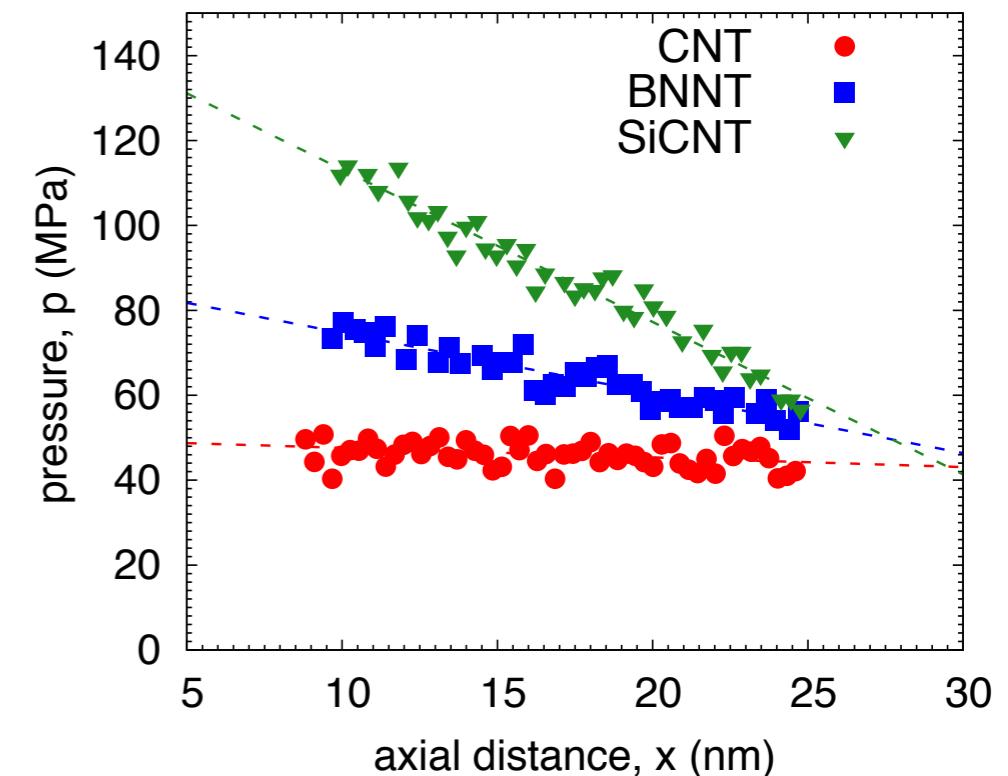
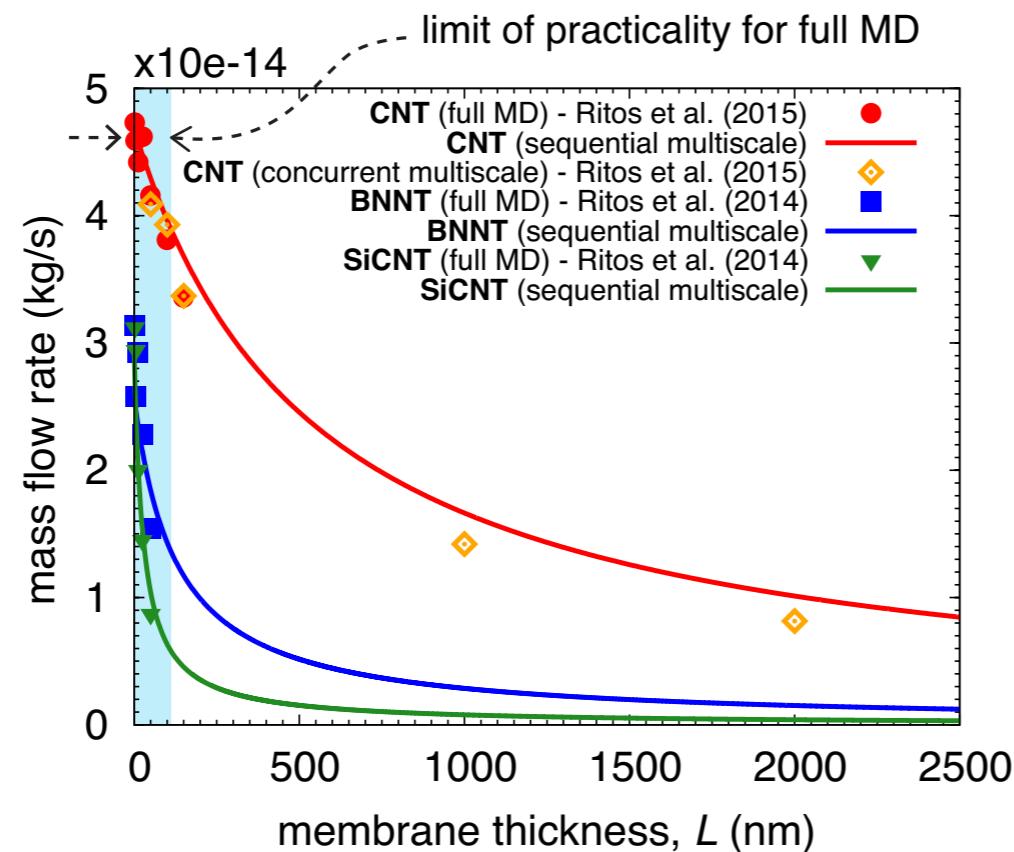
CNT



BNNT

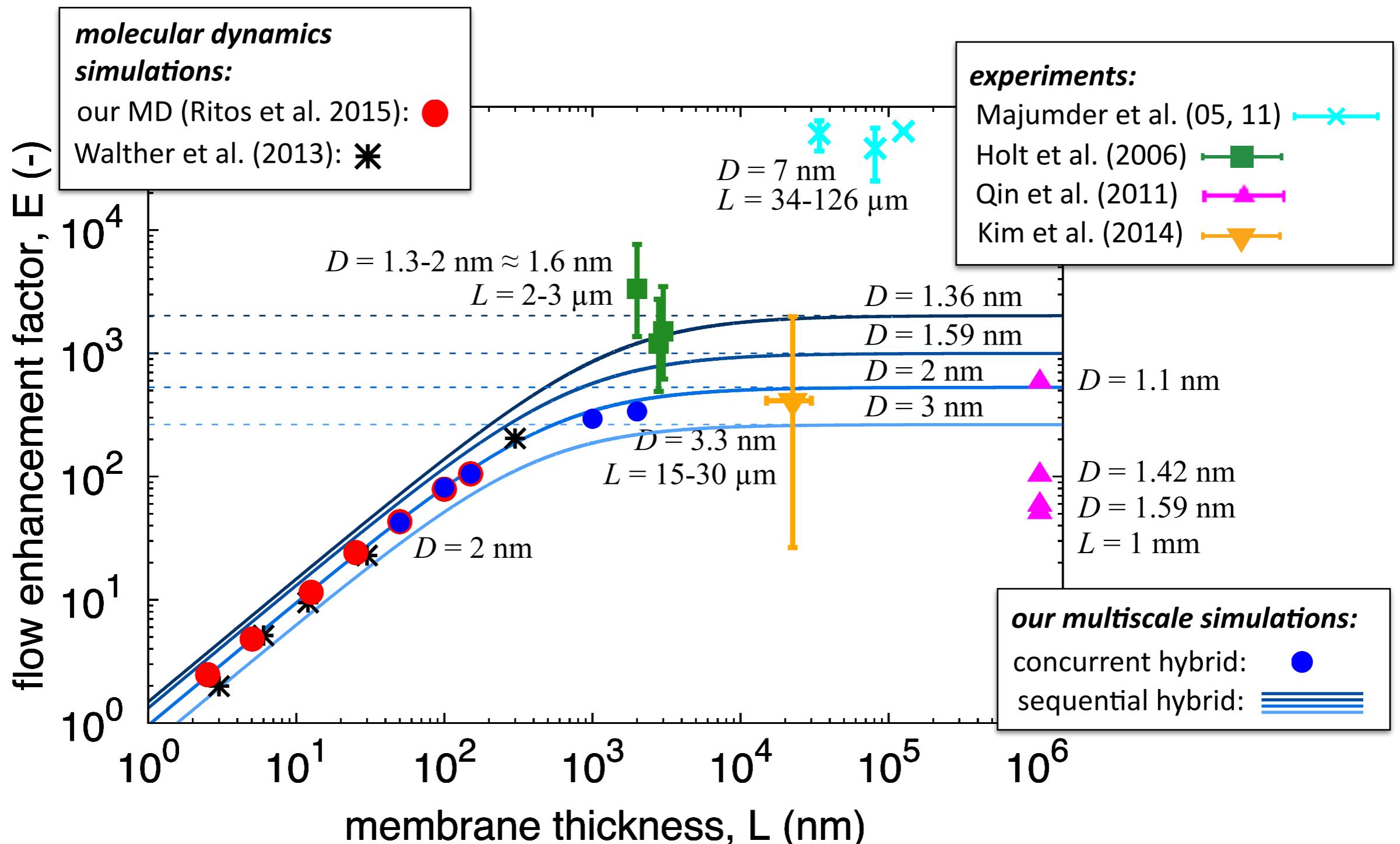


SiCNT



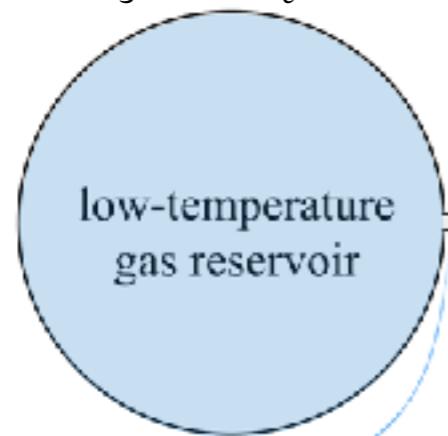
- ▶ different tube materials, but very similar diameters ($\sim 2.05 \text{ nm}$)
- ▶ great difference in the mass flow rates means that the tube material affects the flow behaviour
- ▶ CNTs seem to exhibit the lowest internal surface/water friction
- ▶ BNNTs and SiCNTs have higher surface/water friction

Flow in CNTs: comparison with experiments

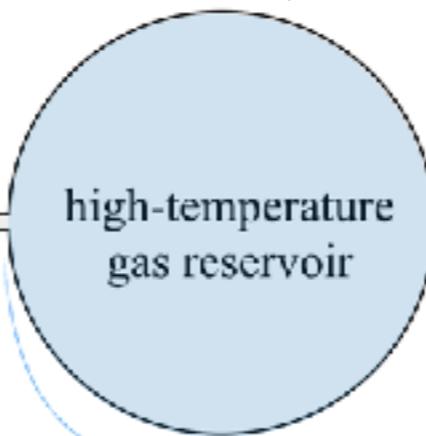


Multiscale analysis of the Knudsen pump

$$\frac{dp_c}{dt_3} = -\frac{\mathcal{R}\theta_c}{V_c} \dot{m}_{(z=0)},$$



$$\frac{dp_h}{dt_3} = -\frac{\theta_h}{\theta_c} \frac{V_c}{V_h} \frac{dp_c}{dt_3}$$



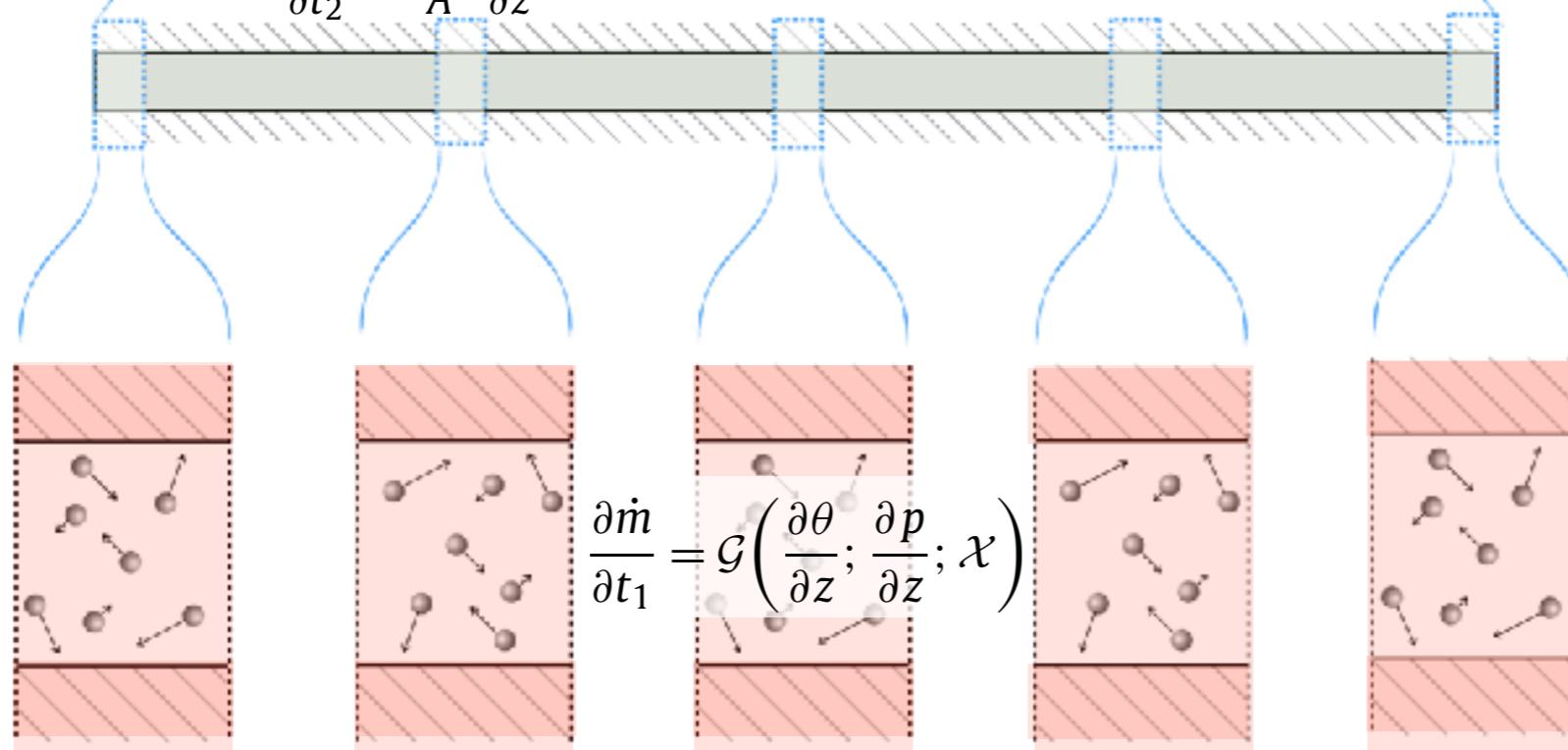
capillary

mass conservation

$$T_{\text{macro}}=100 \text{ s}$$

$$\frac{\partial p}{\partial t_2} + \frac{\mathcal{R}\theta}{A} \frac{\partial \dot{m}}{\partial z} = 0$$

$$\theta = \theta_c + (\theta_h - \theta_c)(e^{\alpha z} - 1)/(e^{\alpha \ell} - 1)$$



continuity equation

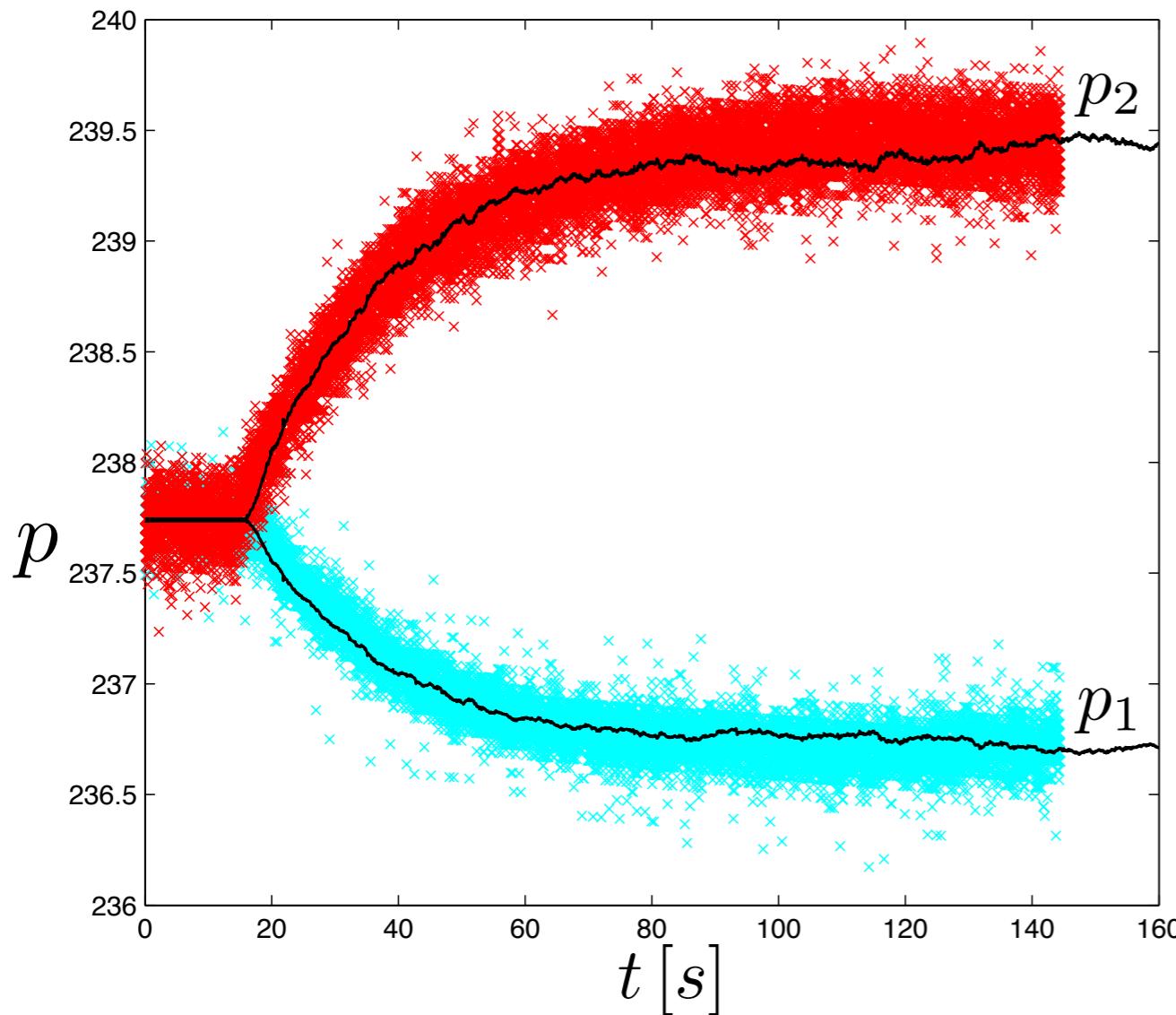
$$T_{\text{meso}}=5 \text{ ms}$$

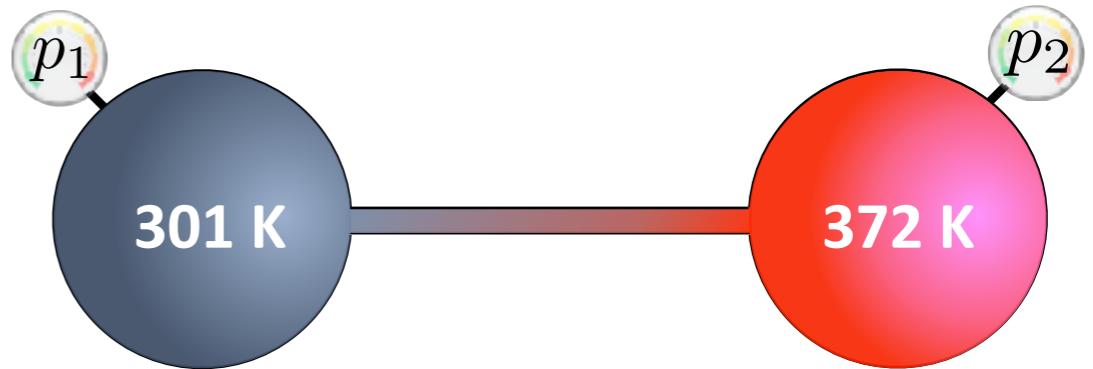
particle method (DSMC)

$$T_{\text{micro}}=10 \mu\text{s}$$

The Knudsen pump: results

M. Rojas-Cárdenas, I. Graur, P. Perrier, J. G. Méolans, Time-dependent experimental analysis of a thermal transpiration rarefied gas flow, Physics of Fluids 25 (2013).



- ▶ argon gas, initial pressure: 238 Pa
 - ▶ channel length: 52.7 mm
 - ▶ channel radius: 0.242 mm
- 

301 K **372 K**

19.81 cm³ **14.85 cm³**

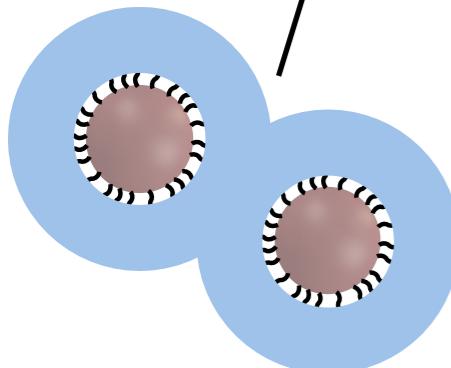
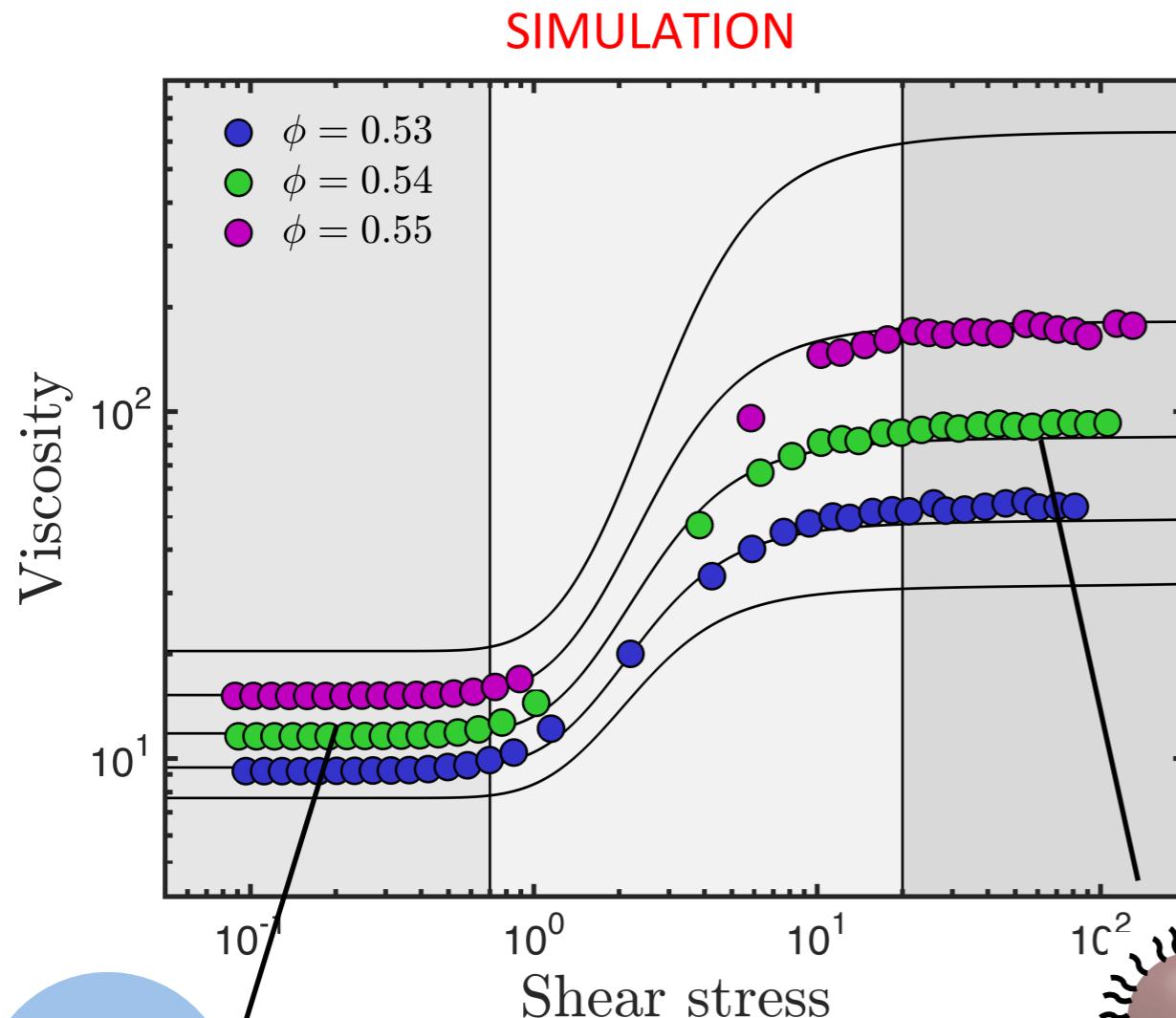
 - ▶ multi-scale analysis: 300× fewer particles
 - ▶ asynchronous coupling: 40,000× fewer timesteps
 - ▶ **10M×** faster than a full particle simulation

Granular simulations

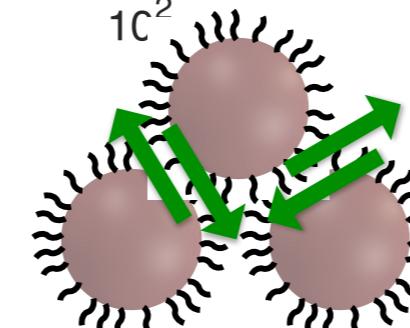
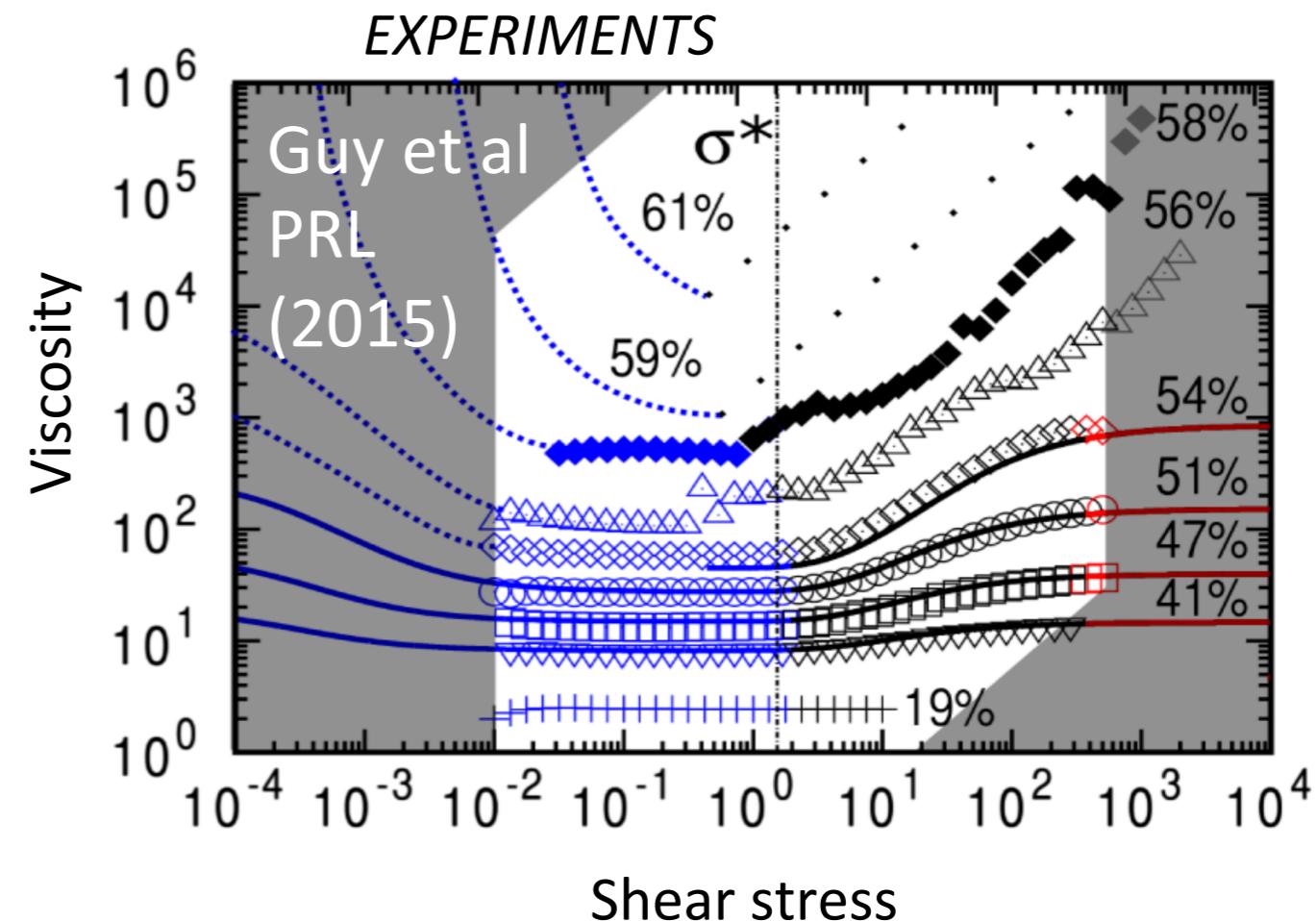
Jin Sun j.sun@ed.ac.uk

Frictional shear thickening

Jin Sun j.sun@ed.ac.uk



particle simulation taking into account lubrication and contact forces



'Frictional' shear thickening

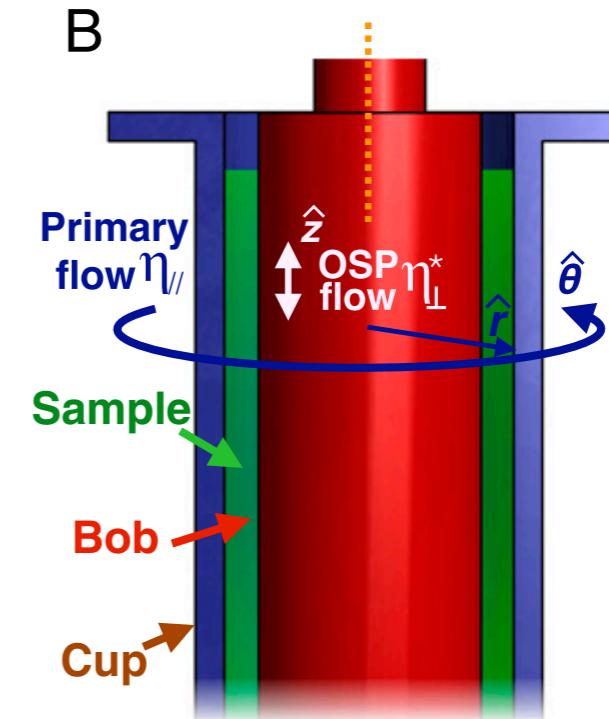
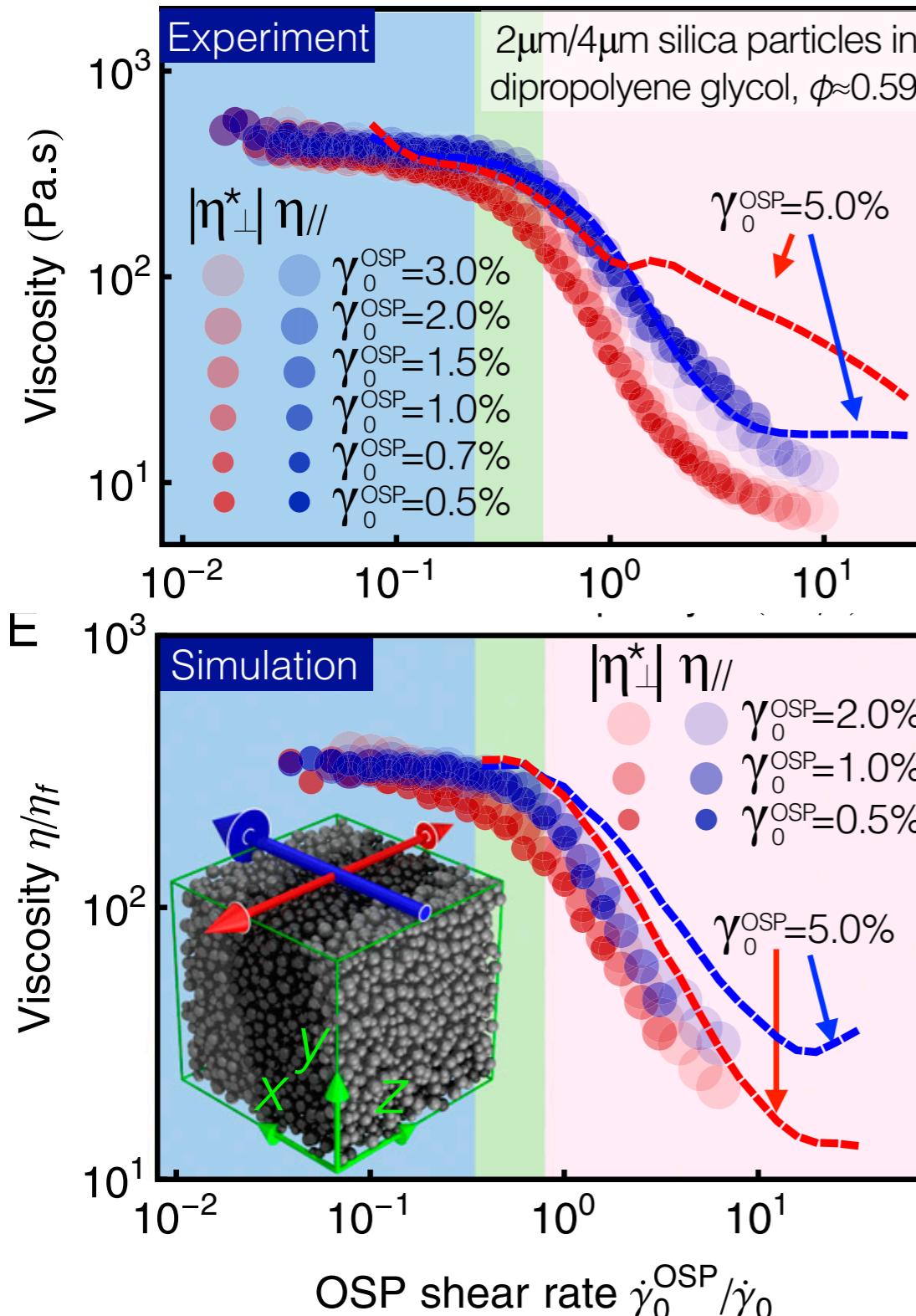
Lubricated contacts
(like a colloid)

to

Frictional contacts
(like large grains)

Tune the suspension viscosity

Jin Sun j.sun@ed.ac.uk



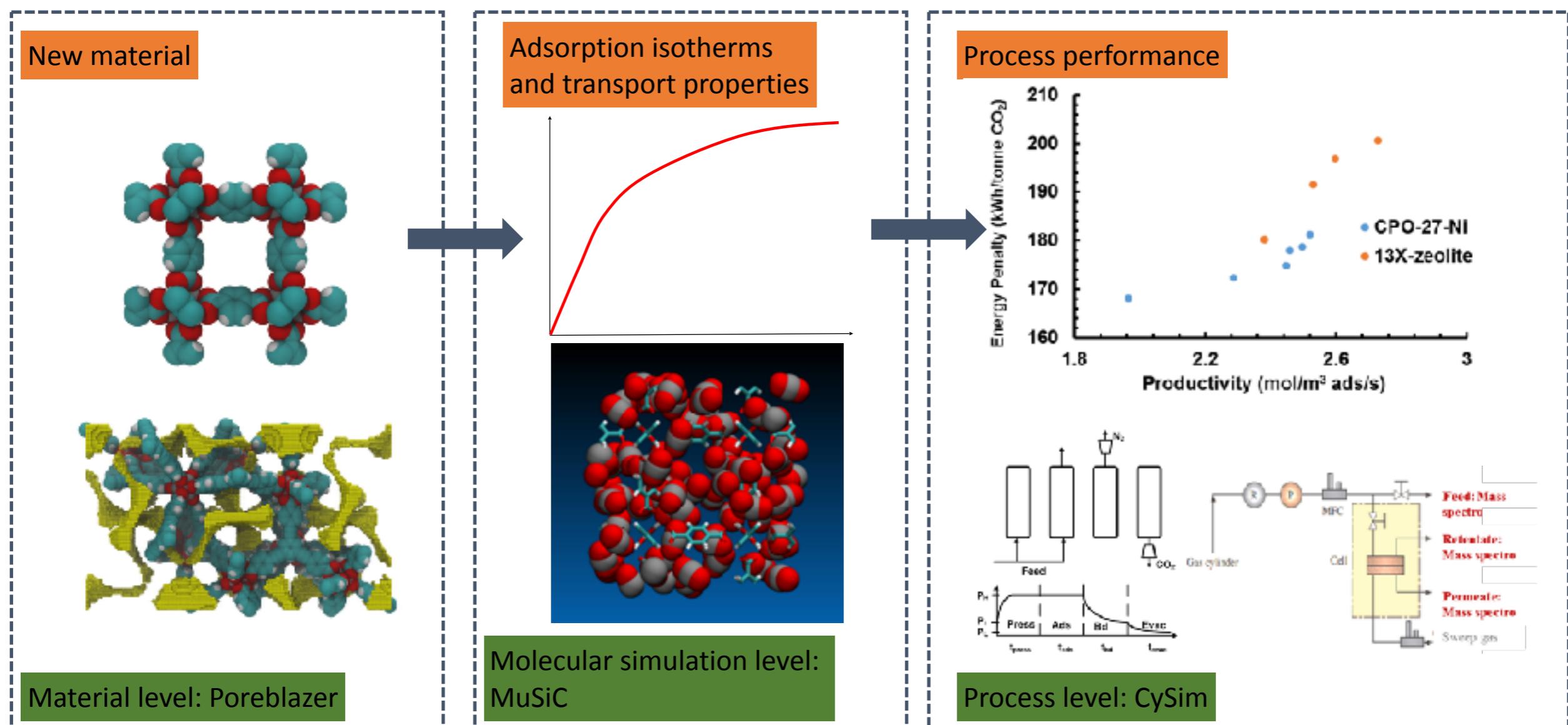
- ▶ Apply orthogonal superimposed perturbation to primary flow
- ▶ Shear thickened viscosity can be reduced by orders of magnitude
- ▶ Blue dots: primary viscosity; red dots: orthogonal complex viscosity

Materials investigations

Lev Sarkisov lev.sarkisov@ed.ac.uk

Multiscale optimization of porous materials

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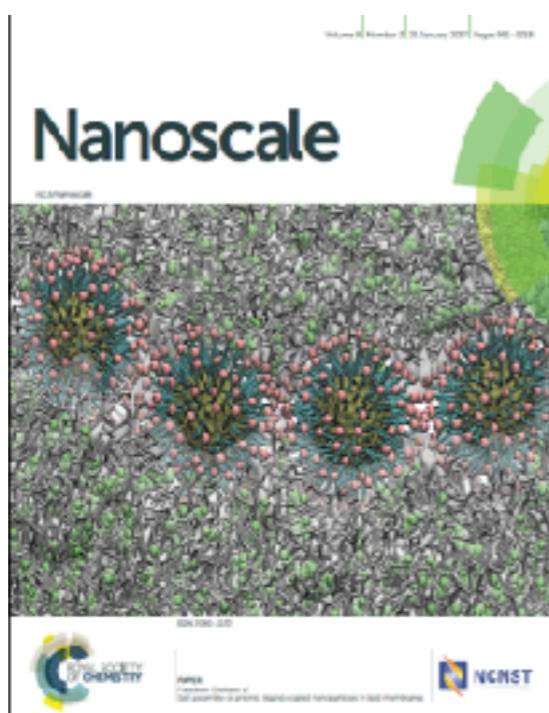
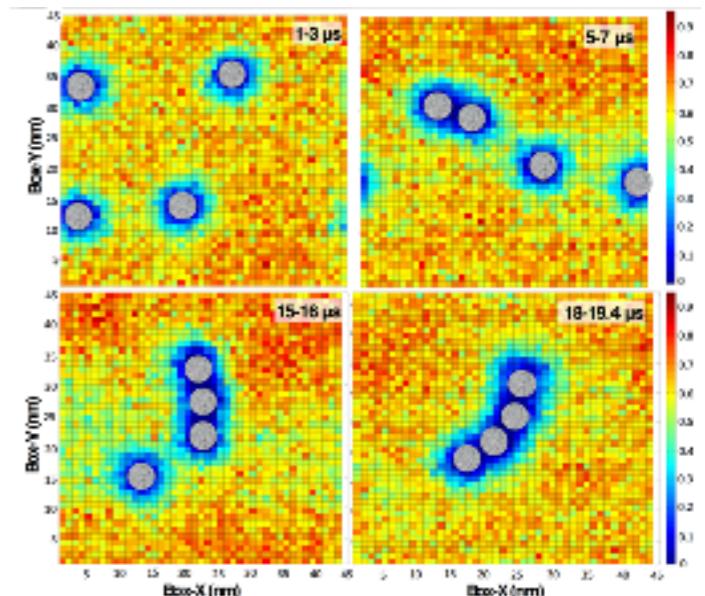
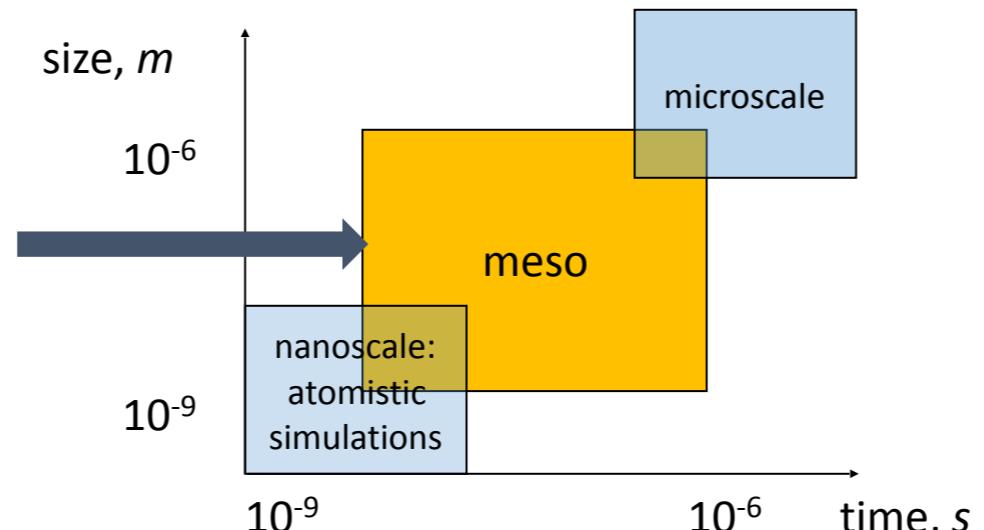
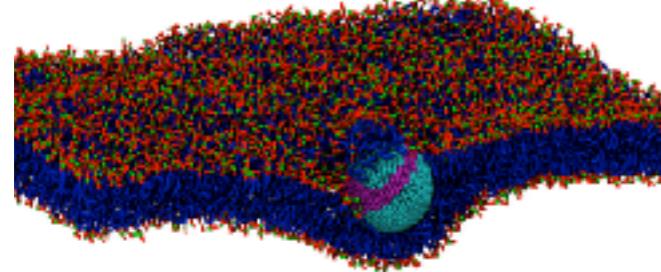


Simulations of bio/nano interfaces

Lev Sarkisov lev.sarkisov@ed.ac.uk

Bio/nano interfaces

- μs time scale
- 10s of nm length scale
- 10^6 interaction sites



Angelikopoulos, Sarkisov, Cournia, Gkeka (2017) *Nanoscale* 9:1040-1048

Gkeka, Angelikopoulos, Sarkisov, Cournia (2015) *PLOS Comput. Biol.* 10:e1003917

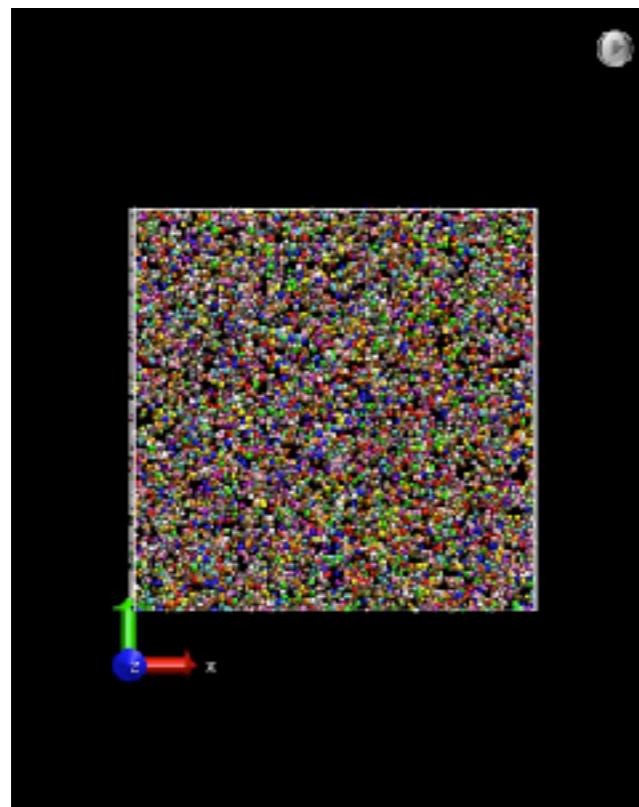
Nucleation in fluids

Martin Sweatman martin.sweatman@ed.ac.uk

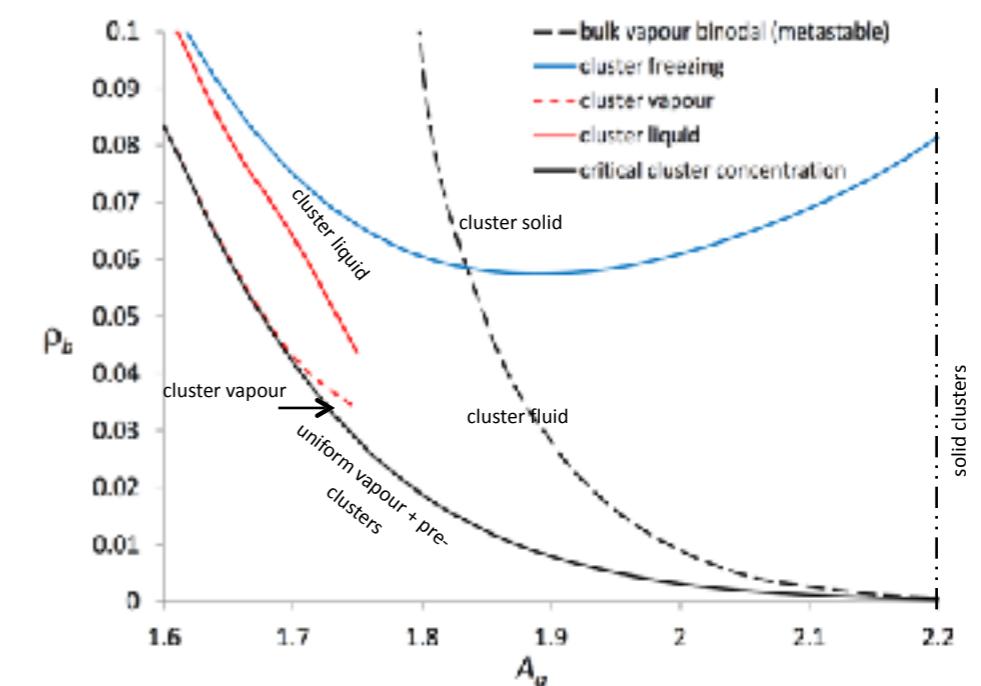
Statistical mechanics of fluids

Martin Sweatman martin.sweatman@ed.ac.uk

- ▶ clustering and non-classical nucleation are increasingly recognised as crucial in many diverse areas of science and engineering, from bio-mineralisation to pharmaceutical crystallisation and the structure of molecular mixtures
- ▶ by developing a new thermodynamic model of clustering we have achieved a deeper understanding of this phenomenon for SALR fluids – e.g. aqueous solutions where the solute has competing short-range attractive and long-range repulsive interactions
- ▶ many soft matter systems have these kinds of interactions including biological, polymer, nanoparticle and colloidal dispersions



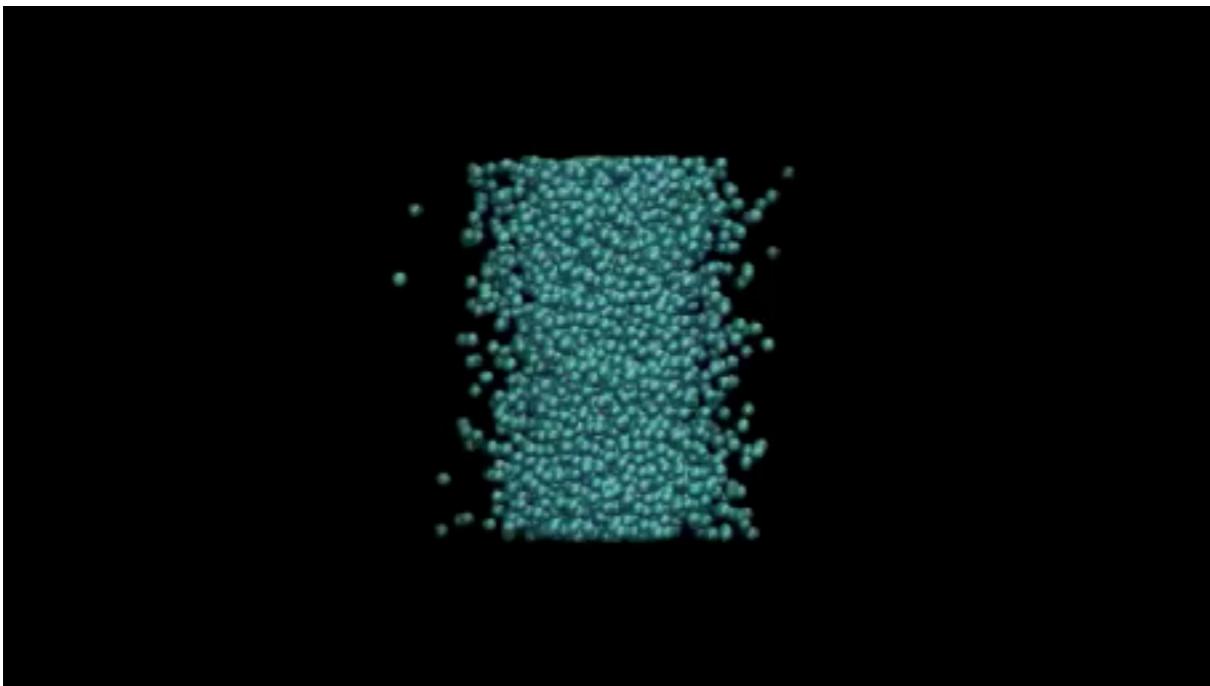
Monte-Carlo simulation of the cluster fluid phase of fluids with SALR interactions



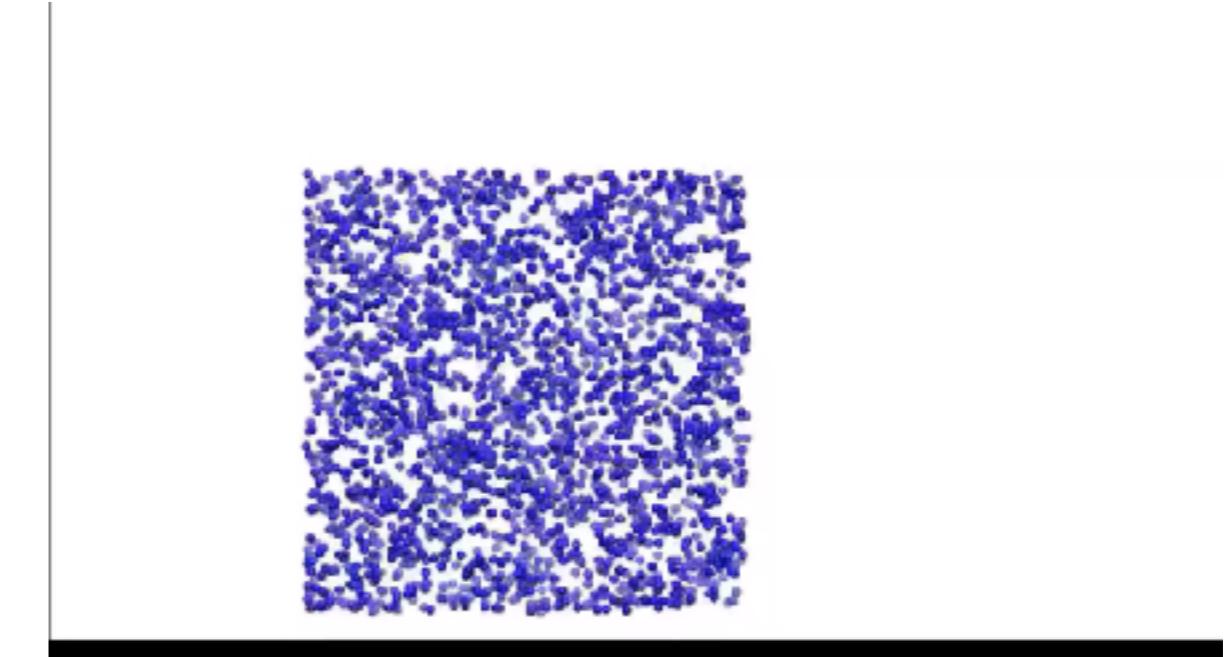
Phase diagram generated by a thermodynamic model for SALR fluids

Statistical mechanics of fluids

Martin Sweatman martin.sweatman@ed.ac.uk



we have since confirmed the existence of a cluster vapour to condensed cluster phase transition predicted by our thermodynamic model



work just submitted shows how these giant clusters can ‘reproduce’, thereby potentially enabling ‘cluster evolution’ in reacting systems

- ▶ We are using classical MD to obtain the effective inter-molecular interactions for some biologically relevant small molecules (amino acids and nucleobases), to see if they have SALR interactions in water



Conclusions

Summary

- ▶ multiscalarity due to the molecular nature of materials is a substantial challenge
- ▶ non-intuitive fluid dynamics can be exploited for engineering applications
- ▶ molecular dynamics and hybrid molecular/continuum methods are sophisticated tools for modelling the performance of some emerging flow technologies
- ▶ for time-dependent problems, hybridisation in time *and* space can create substantial computational savings with little loss of accuracy
- ▶ need to balance simulation accuracy with computability: choice of model depends on the flow system, modelling needs, and computational resources

Our capabilities in Engineering

- ▶ kinetic theory-based models; Molecular Dynamics; DSMC simulations; statistical mechanics; discrete element methods
- ▶ hybrid methods for scale-separated and non-scale-separated flows
 - ➡ greater than 10× more efficient than purely particle methods
- ▶ software for parallel machines released open source to sit alongside OpenFOAM



With thanks to ...



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Srinivasa Ramisetti, Konstantinos Ritos, Lei Wu,
Jun Zhang, Wenjing Zhou

Staff and Collaborators

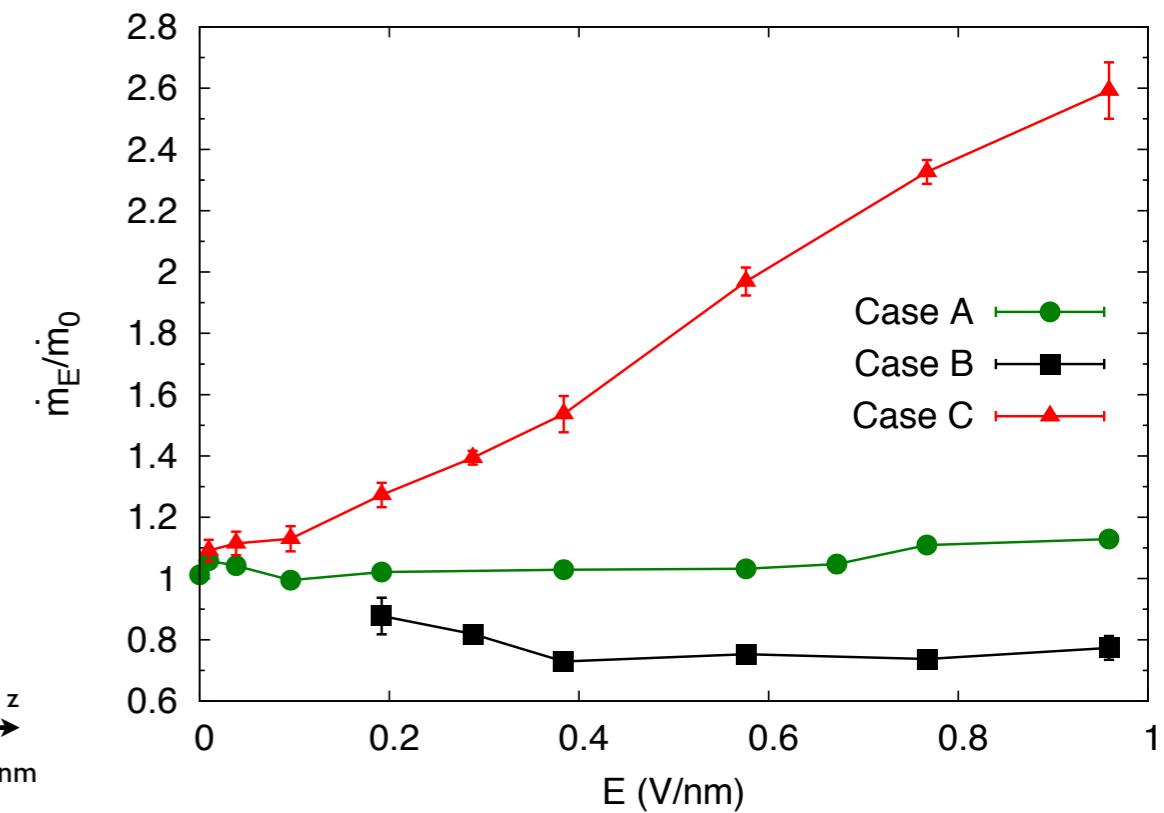
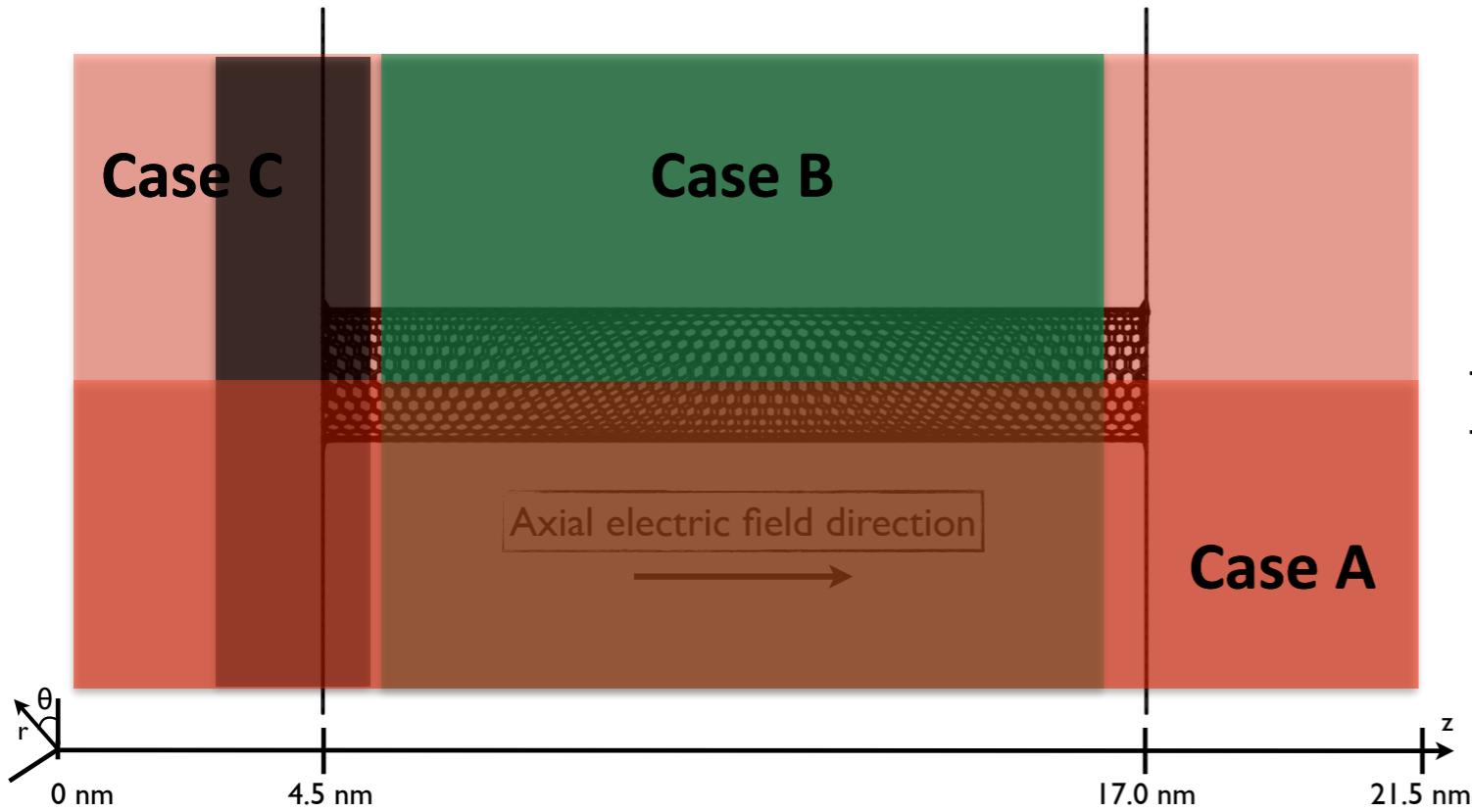
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Yonghao Zhang (Strathclyde University)
David Emerson (Daresbury Lab)
Duncan Lockerby, James Sprittles (Warwick University)
Davide Mattia (Bath University)

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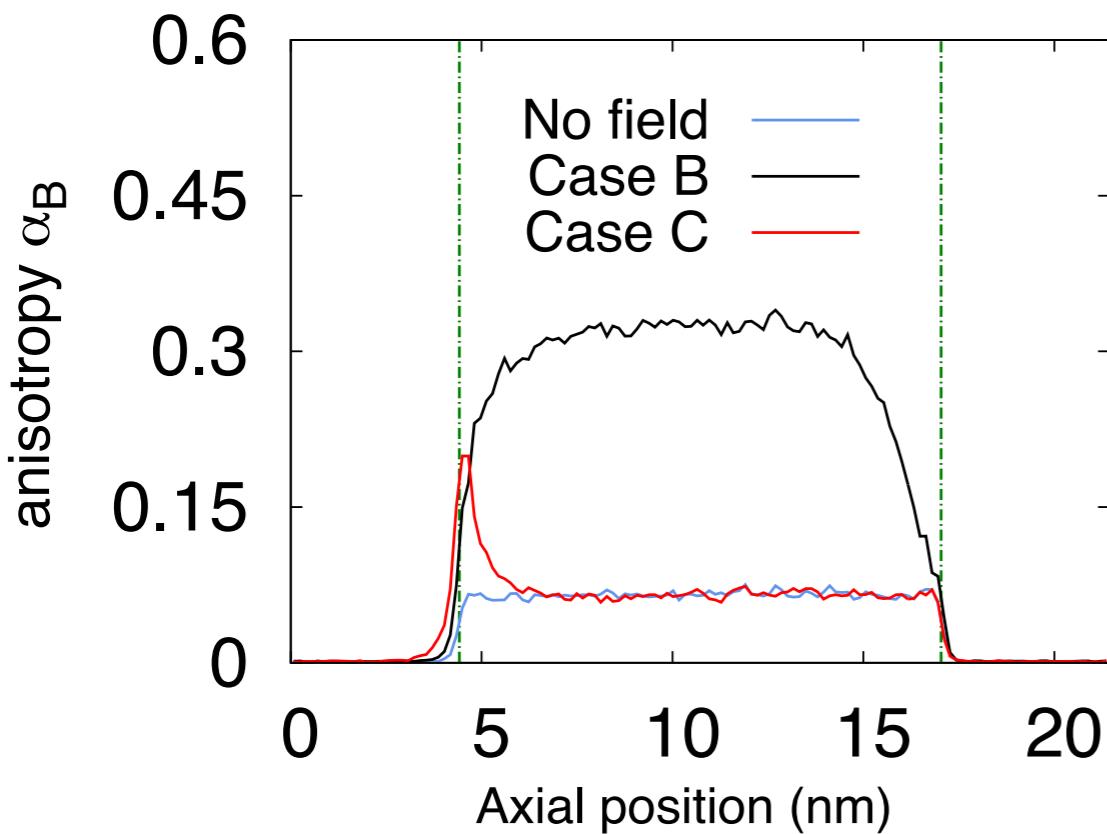
jason.reese@ed.ac.uk

Non-continuum behaviour in wider CNTs?



- ▶ (15,14) CNT, diameter 2 nm, length 12.5 nm, supported by graphene sheets between two water reservoirs
- ▶ 100 MPa pressure difference
- ▶ TIP4P/2005 water model; electrostatic and Lennard-Jones; 33,000 molecules
- ▶ ‘relaxed’ for 4 ns, production runs for 4 ns
- ▶ localised electric fields 0.01–1.0 V/nm along CNT axis; $\mathbf{F}_i = q_i \cdot \mathbf{E}$ in the MD
- ▶ when field is over:
 - ▶ whole system, does not change mass flow rate
 - ▶ CNT only, decreases flow
 - ▶ CNT inlet only, increases flow

Non-continuum behaviour in wider CNTs?



- ▶ biaxial water molecules encourage analysis techniques similar to liquid crystals
- ▶ an electric field at the inlet causes molecular ‘pre-ordering’ (before entering the CNT)
 - ➡ seems to reduce losses during change from bulk isotropy to confined anisotropy
- ▶ higher flow rates can be obtained

