Videos here:
https://youtu.be/Afxr_gDoJB8

Brunel University London

Molecular Dynamics Modelling of Bubble Nucleation on Surfaces

Edward Smith

04/06/20

Surface Wettability Effects on Phase Change Phenomena

Summary

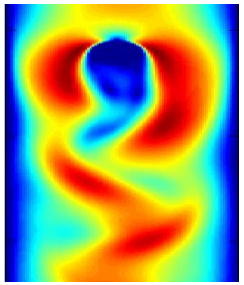
- Introduction – 5 mins
- Molecular Dynamics – 15 mins
  - Q&A session – 10 mins
- Coupled Simulation – 15 mins
  - Q&A Session – 10 mins

Introduction

www.edwardsmith.co.uk

Imperial College London

Master's → PhD Mechanical Engineering → EPSRC Fellowship

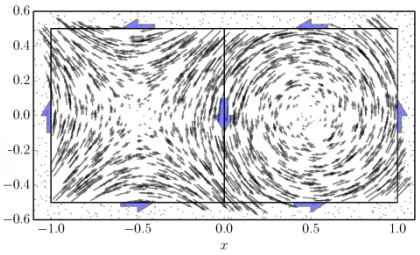


Lattice Boltzmann

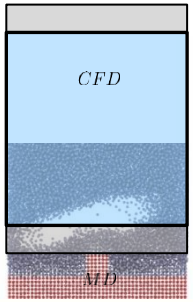
Coupled MD simulation

$$\vartheta_i \equiv \int_{x^-}^{x^+}\int_{y^-}^{y^+}\int_{z^-}^{z^+} \delta(x_i - x)\delta(y_i - y)\delta(z_i - z)dxdydz$$

Control Volume formulation

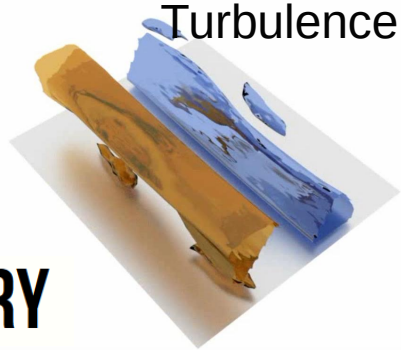


Constrained dynamics



CPL LIBRARY

Molecular Turbulence

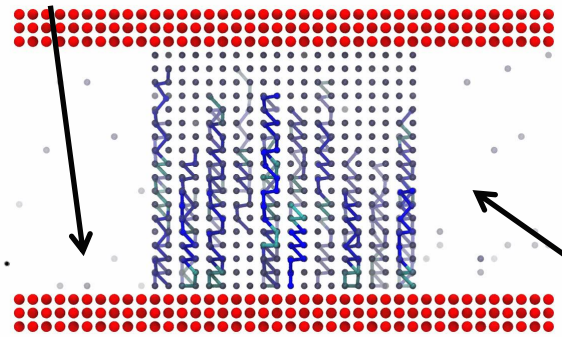


Swinburne → Chemical Eng. → Civil Eng. → Aerospace Eng.

Heat Flux

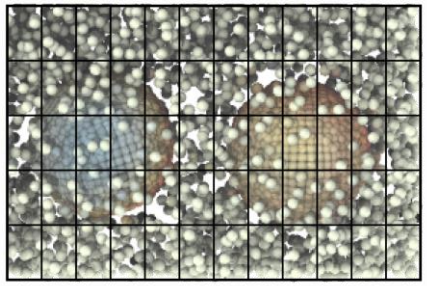
$$q = -\lambda\frac{\partial T}{\partial y} + \ldots$$

Moving Contact Line



Interface

Granular Mechanics



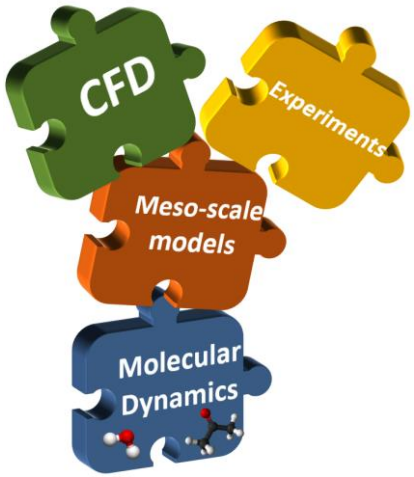
Brunel University London

Multiscale Fluid Dynamics

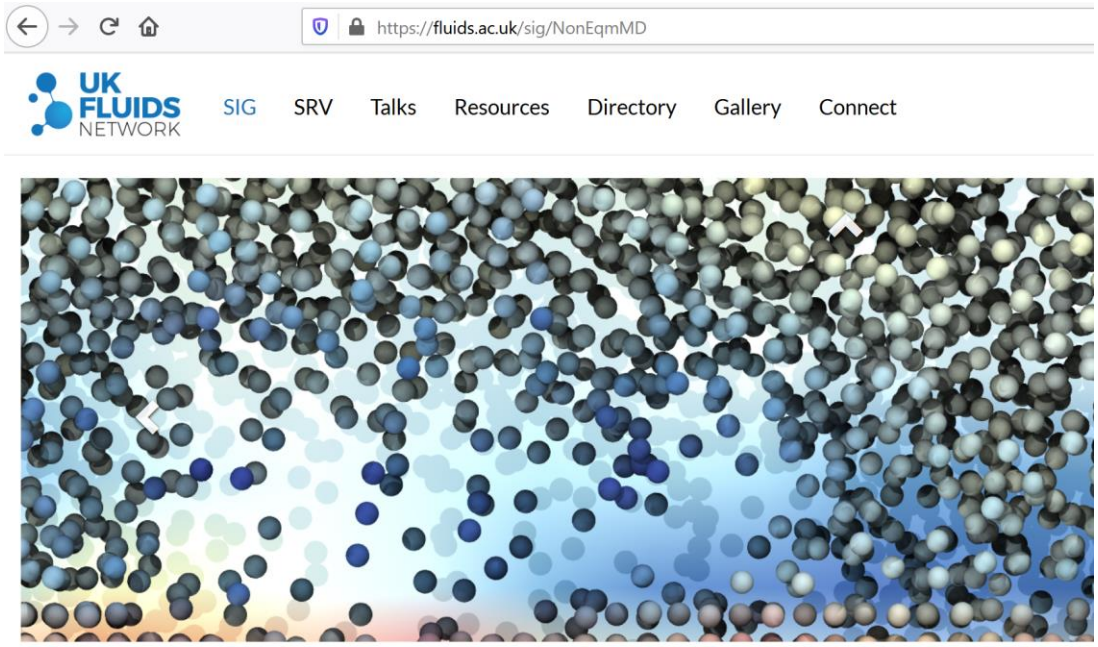
Introduction

Brunel University London

- **E**nhanced **M**ultiscale **Bo**iling **S**urface**s** (**EMBOSS**)



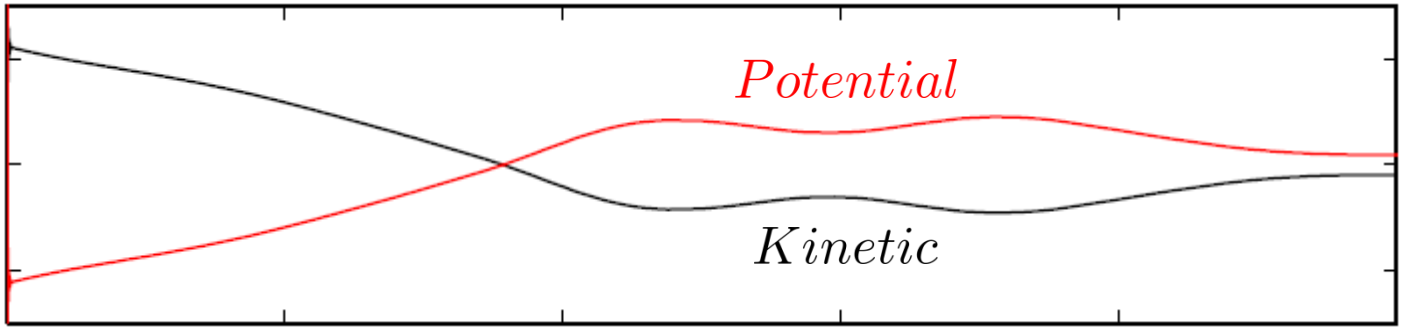
- UK Fluids Network Special Interest Group (SIG) in non equilibrium molecular dynamics



Molecular Dynamics

- Solving just Newton's law
  - Energy is automatically conserved → total = kinetic + potential

$\frac{dE}{dt}$



  - Pressure, viscosity, heat flux and surface tension do not need to be specified and, are in fact, all outputs of the simulation
  - Phase change (evaporation, condensation) occur with no additional models needed
  - Solid constructed with molecular roughness
  - Can model complex molecules, water, polymers, biomolecules

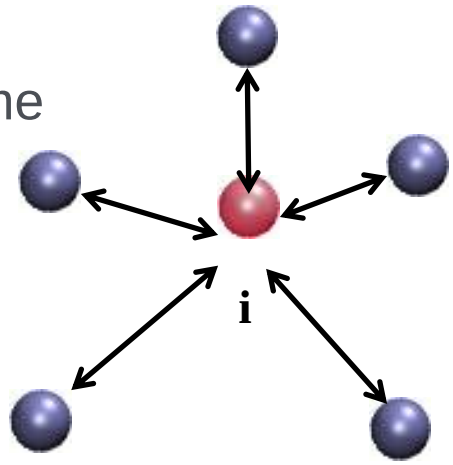
Molecular Dynamics

Brunel University London

Discrete molecules in continuous space

- Molecular position evolves continuously in time
- Acceleration→Velocity→Position

$$\ddot{\boldsymbol{r}}_i \rightarrow \dot{\boldsymbol{r}}_i \rightarrow \boldsymbol{r}_i(t)$$



Acceleration obtained from forces

- Governed by Newton's law for an N-body system
- Pairwise electrostatics interactions from quantum mechanics

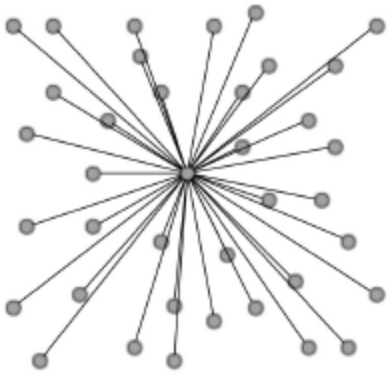
$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i \neq j}^{N} \boldsymbol{f}_{ij}$$

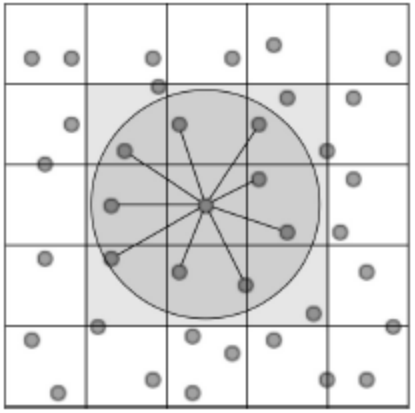
$$\Phi_{ij} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]$$

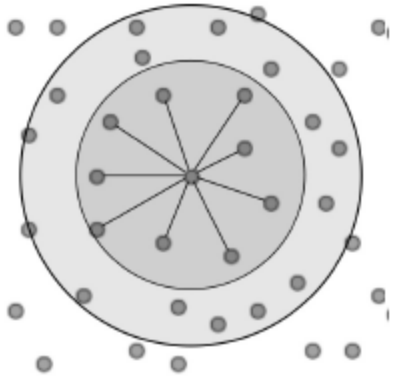
MD Computing

- Force Calculation
  - All pairs simulation uses local cell and neighbour lists to reduce the N^2 calculation to order N

$$F_i = \sum_{j \neq i}^{N} f_{ij}$$







- Move particles (leapfrog in time)

$$m_i \frac{dv_i}{dt} \approx m_i \frac{v_i(t + \Delta t/2) - v_i(t - \Delta t/2)}{\Delta t} = F_i$$

$$\frac{dr_i}{dt} \approx \frac{r_i(t + \Delta t) - r_i(t)}{\Delta t}$$

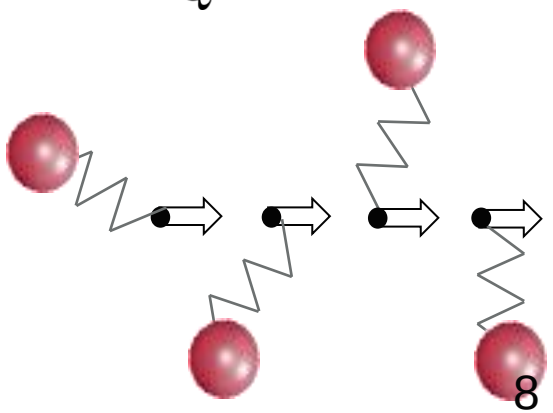
Non Equilibrium Molecular Dynamics

- Non Equilibrium Molecular Dynamics (NEMD) is the study of cases beyond thermodynamic equilibrium, with:
  - Temperature gradients
  - Flow of fluid (e.g. Couette or Poiseuille flow)
- We induce temperature gradients and flows
  - Thermostats (e.g. Nosé Hoover) remove heat from system
  - Tethered molecules with (an)harmonic spring to tether site
  - With sliding
    - Slide site and (optionally) molecules

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{teth} - \psi m_i \boldsymbol{c}_i$$

$$\dot{\psi} = \frac{1}{Q}\left[T - 3T_{target}\right]$$

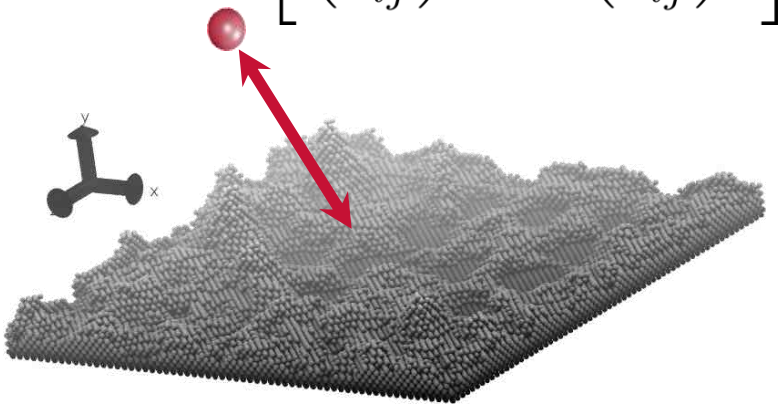
$$\boldsymbol{v}_i = \dot{\boldsymbol{r}}_i - \boldsymbol{u}$$

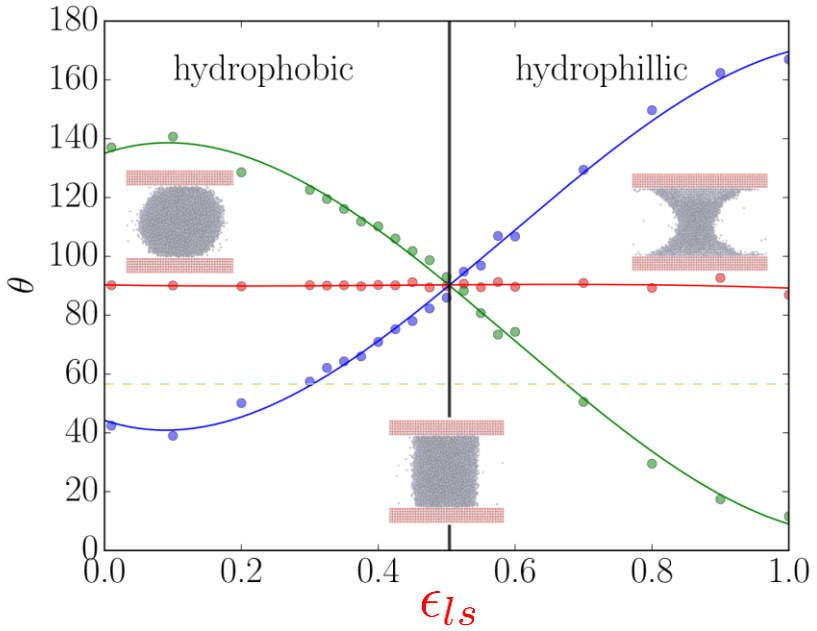


Surface Wettability

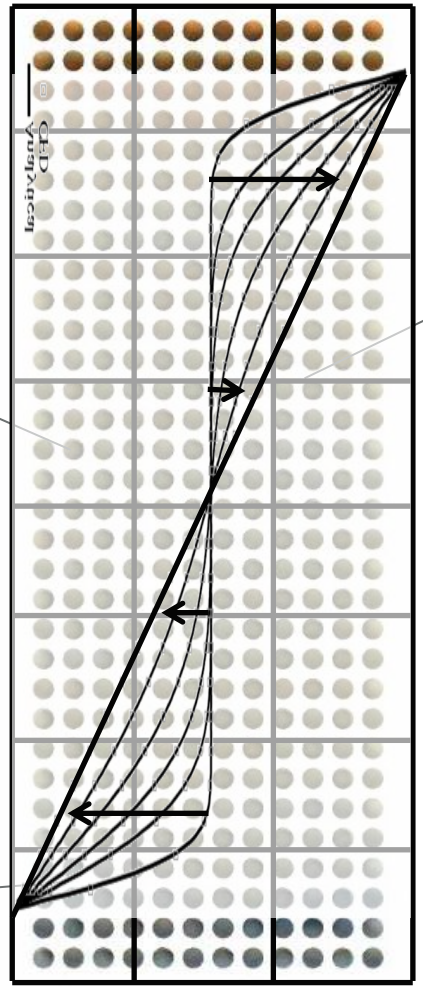
- Depends entirely on the “wetting” interaction between surface and fluid (MD’s dirty secret), tuned using:
  - Mixing rules, e.g. Lorentz-Berthelot $\epsilon_{ls} = \sqrt{\epsilon_l \epsilon_s}$
  - Bottom up simulation e.g. quantum mechanics
  - Top down e.g. to get desired contact angle

$$\phi(r_{ij}) = 4\epsilon_{ls}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$





Wall Bounded Flow



Liquid structure causes viscosity

Average behaviour reproduces hydrodynamics (coloured by velocity)

$H \approx 9nm$

Stick-slip near walls

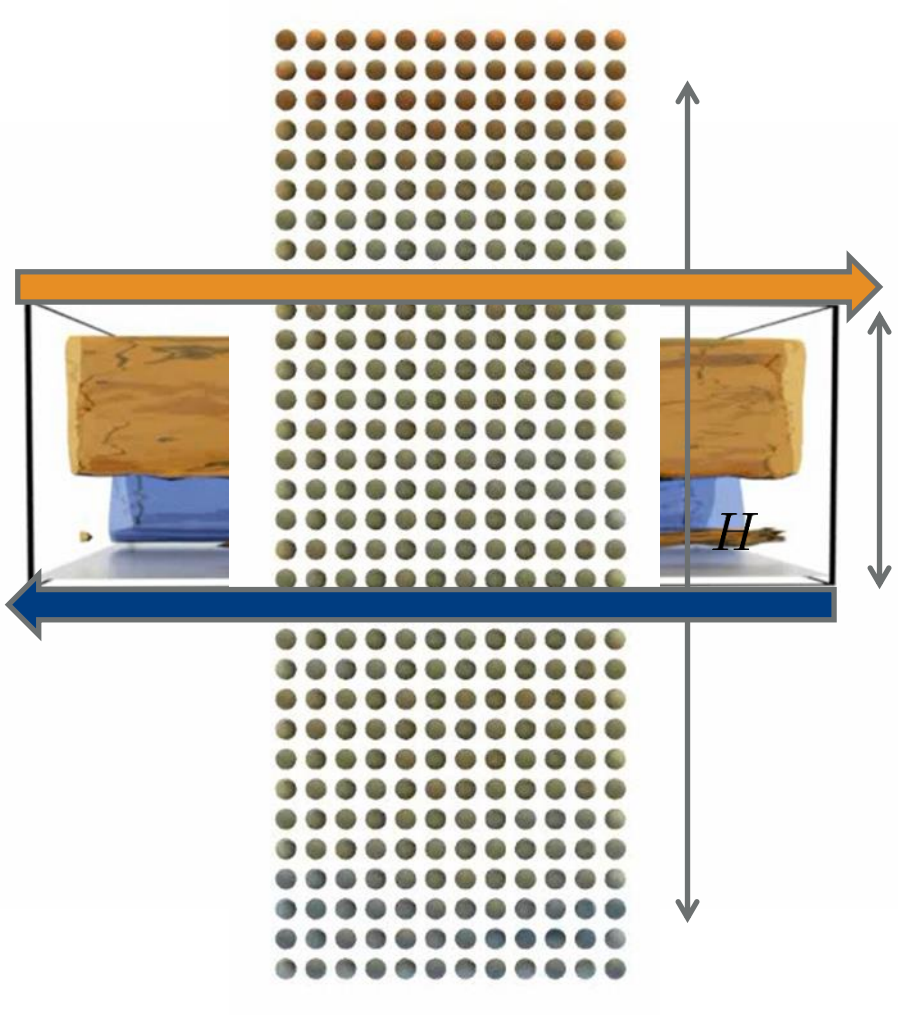
Reynolds Number

$Re \approx 15$

with

4096 molecules

Molecular Dynamics - Turbulence



Reynolds Number

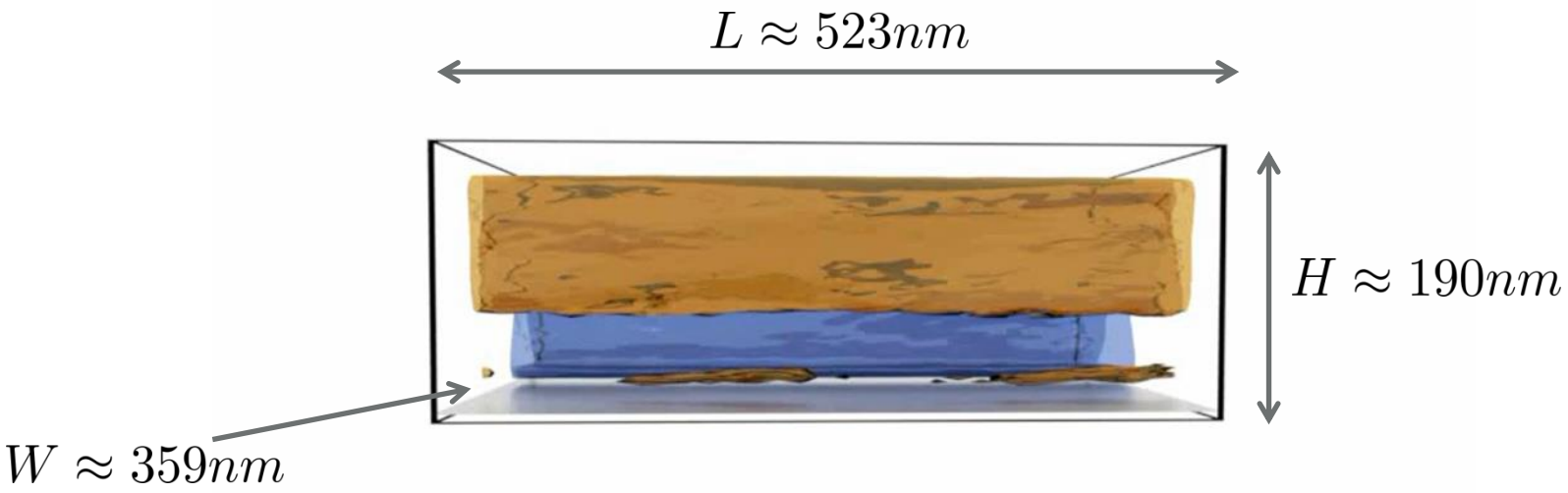
$Re \approx 400$

with

300 million molecules

Molecular Dynamics - Turbulence

Minimal channel Couette flow



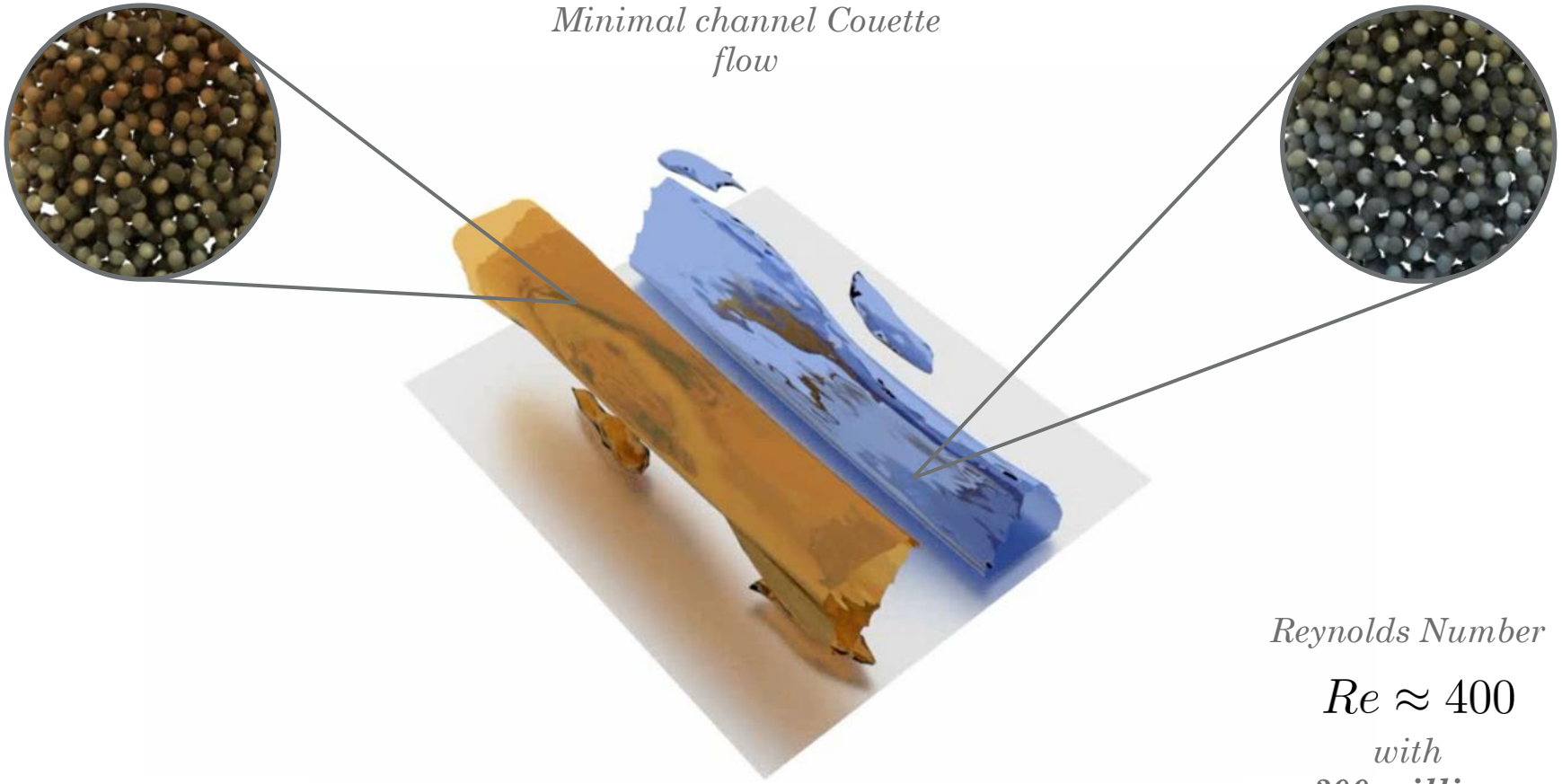
Reynolds Number

$Re \approx 400$

with
300 million molecules

Molecular Dynamics - Turbulence

Minimal channel Couette flow



Isosurfaces of turbulent kinetic energy coloured by velocity

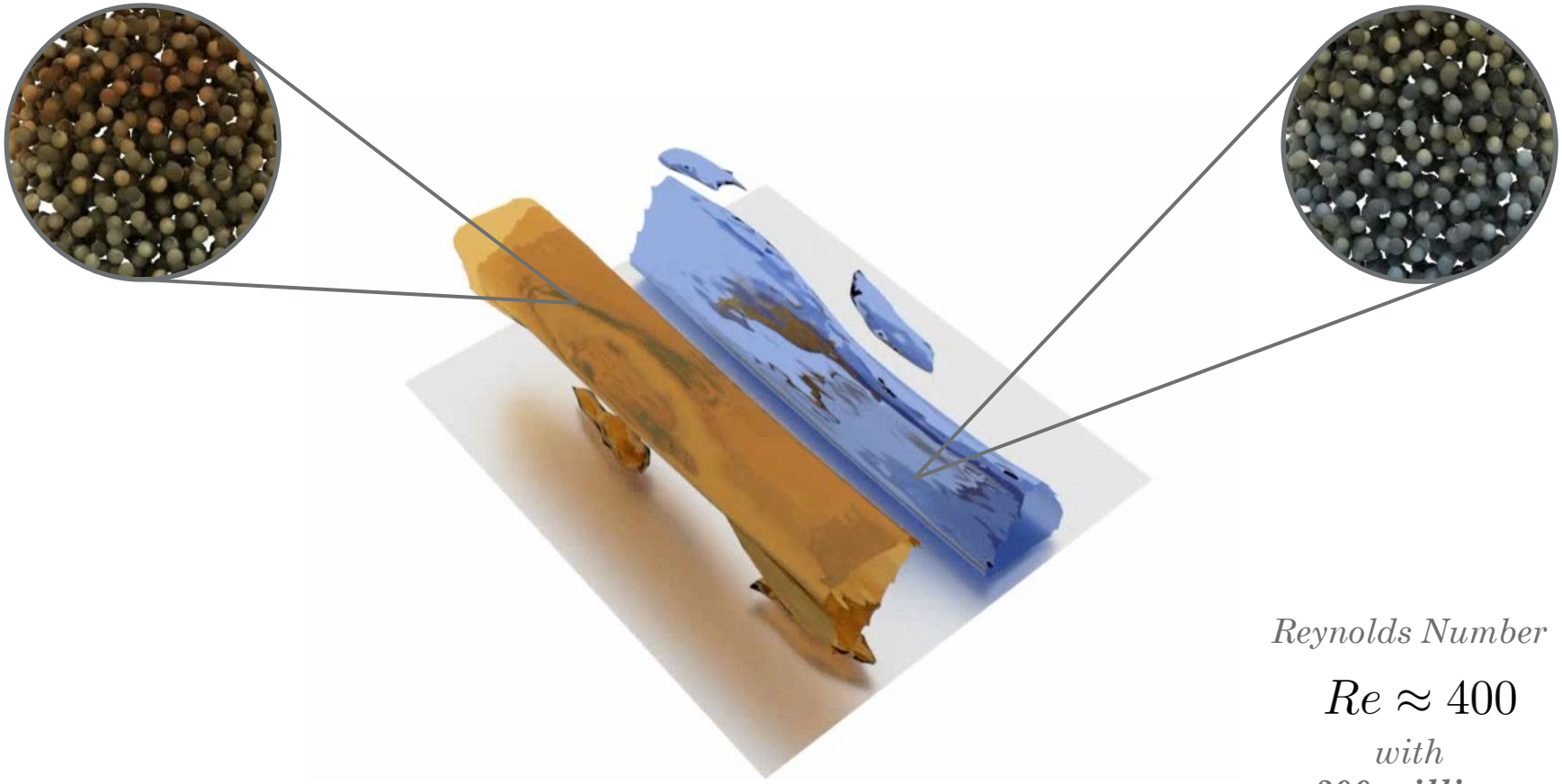
Reynolds Number

$Re \approx 400$

with

300 million molecules

Molecular Dynamics - Turbulence



Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

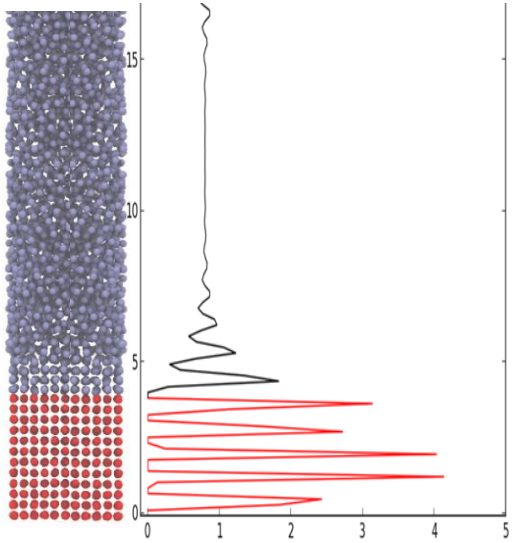
$Re \approx 400$

with

300 million molecules

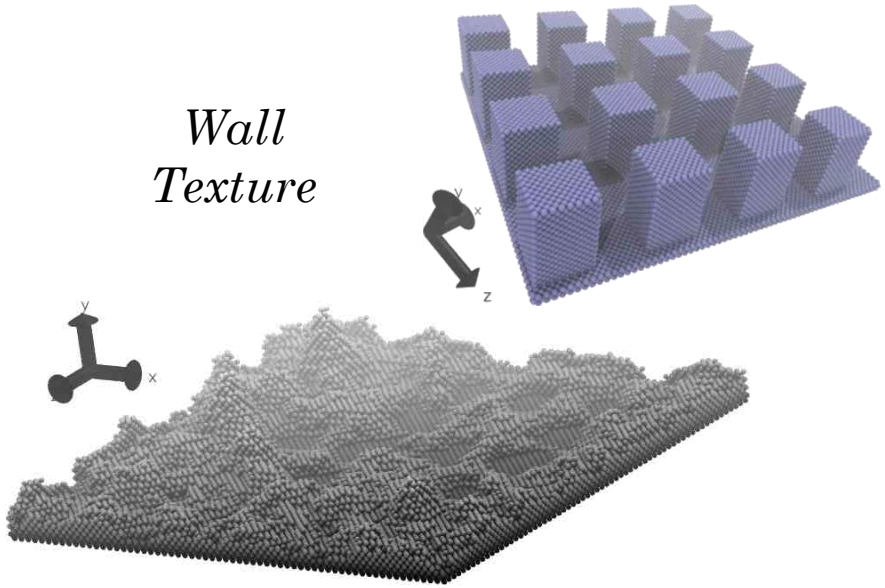
Molecular Dynamics – Complex Walls and Fluids

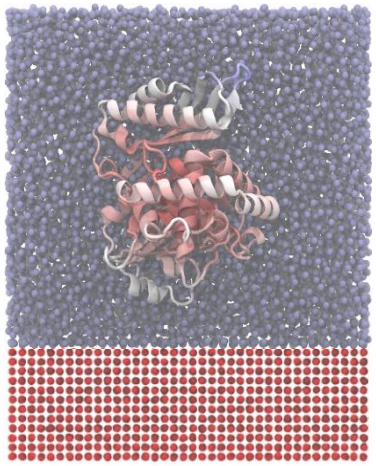
Liquid structure causes viscosity



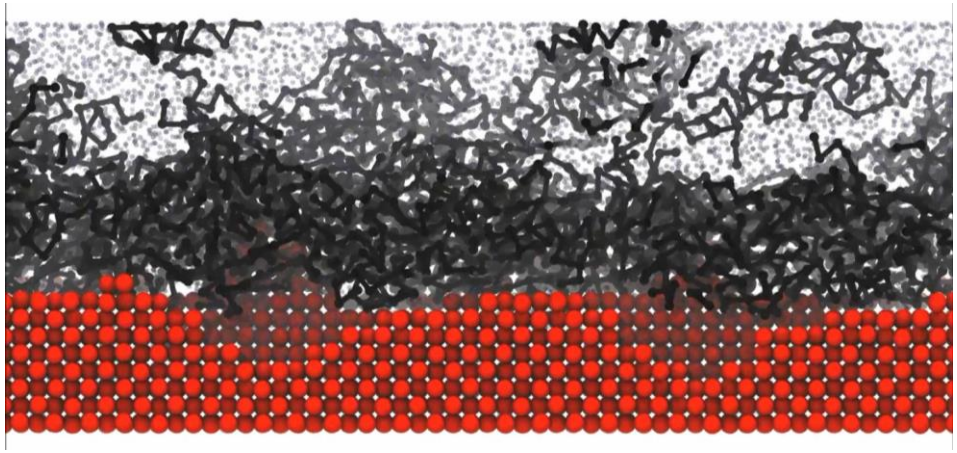
Stick-slip near walls

Wall Texture





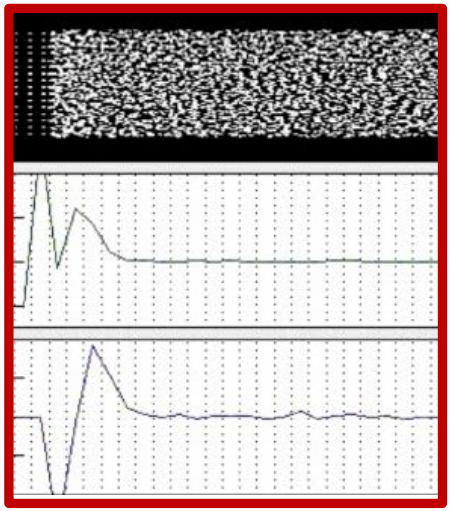
Molecules of arbitrary complexity



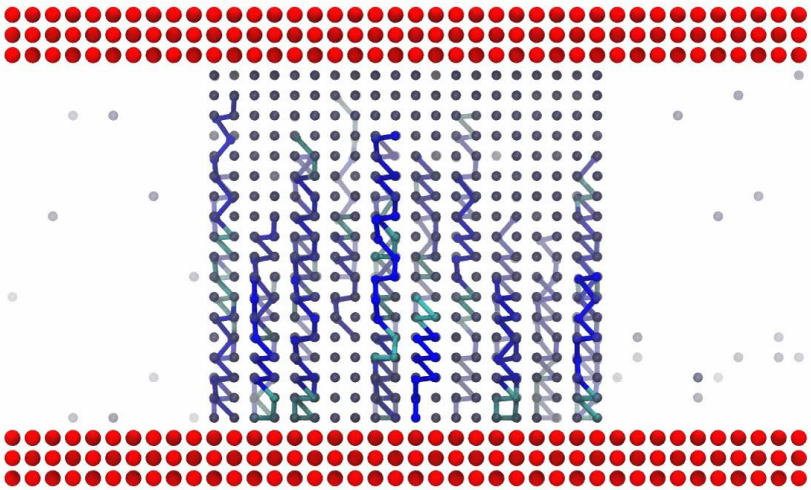
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

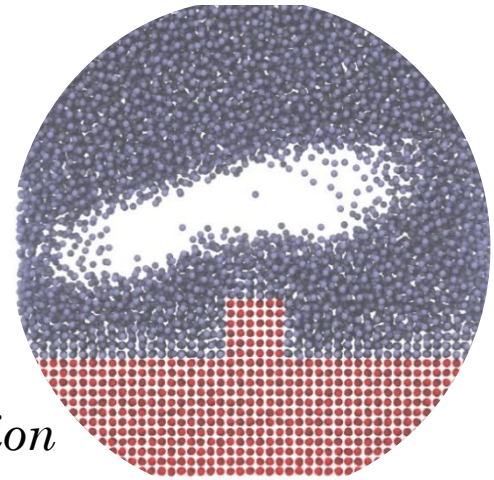
Shockwave



Droplet Formation

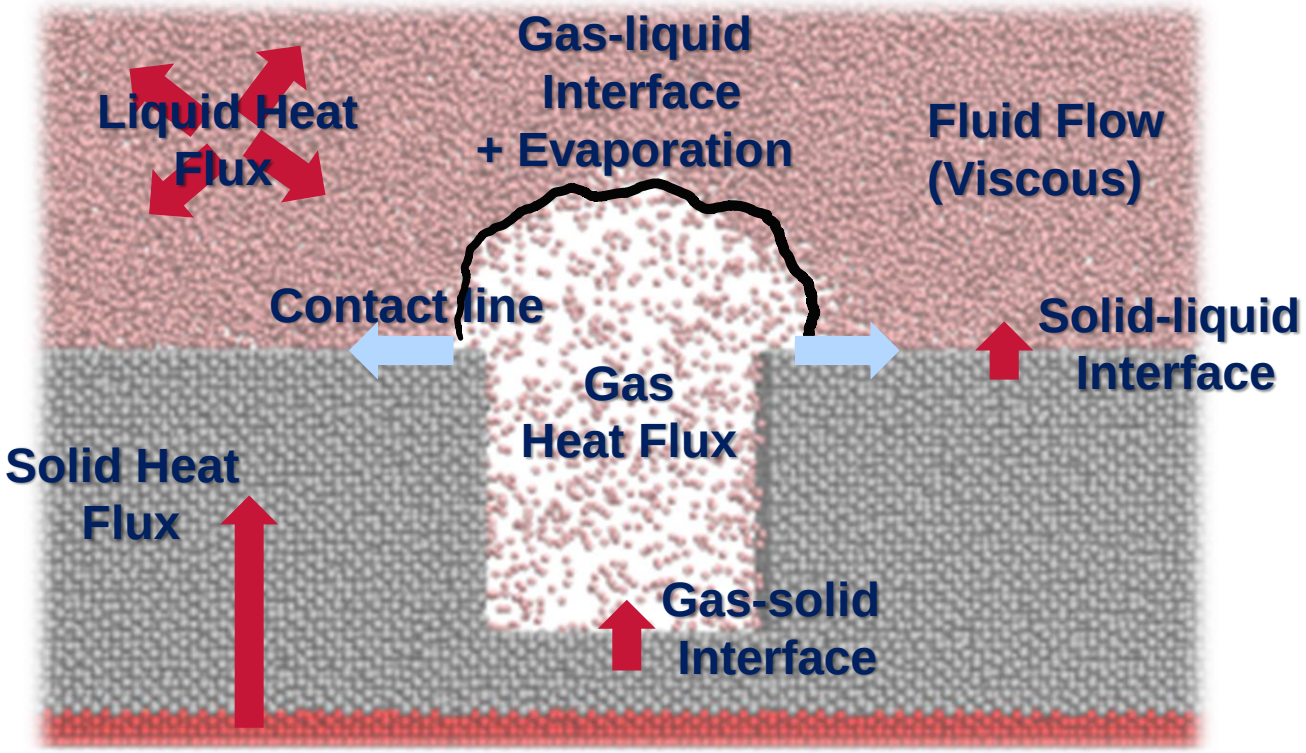


Nucleation



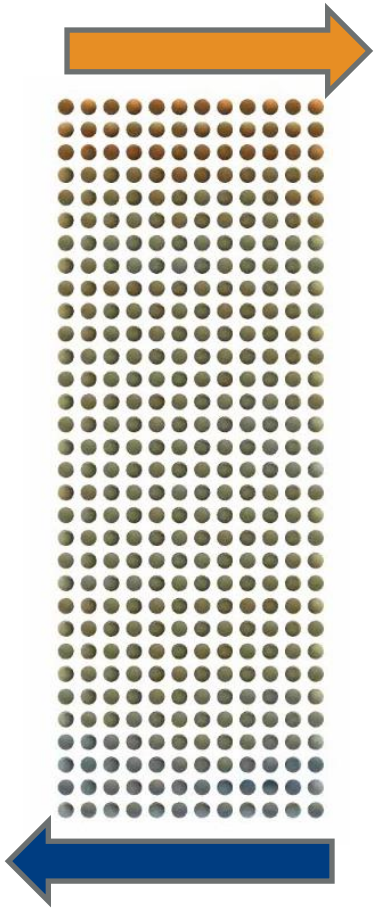
Contact line

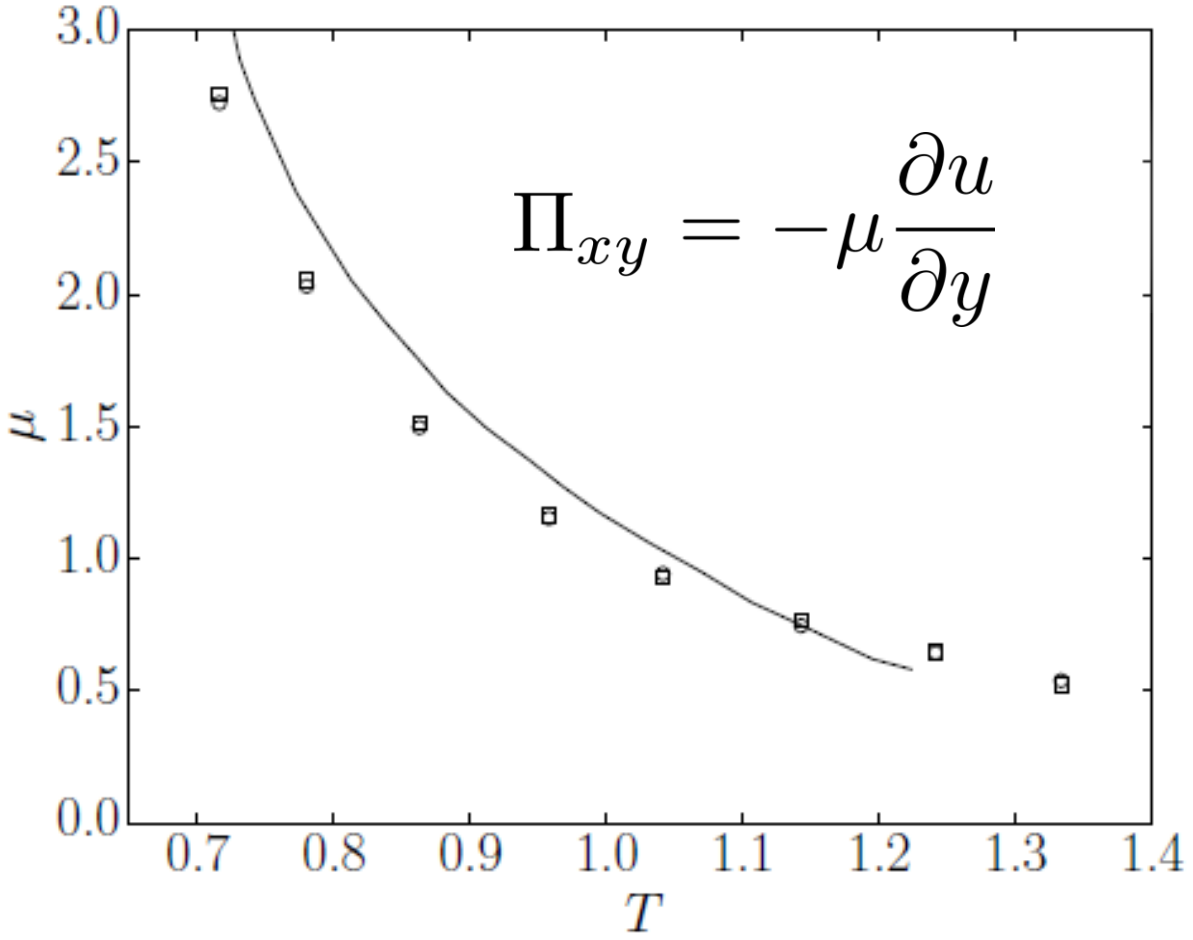
Factors in Bubble Nucleation



Viscosity

- Good agreement with experiments

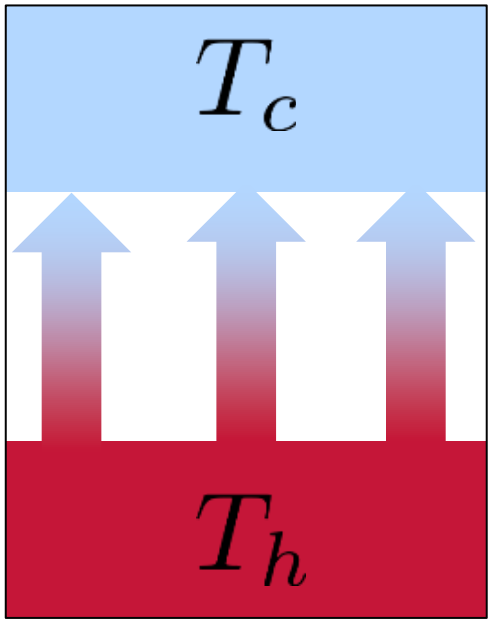


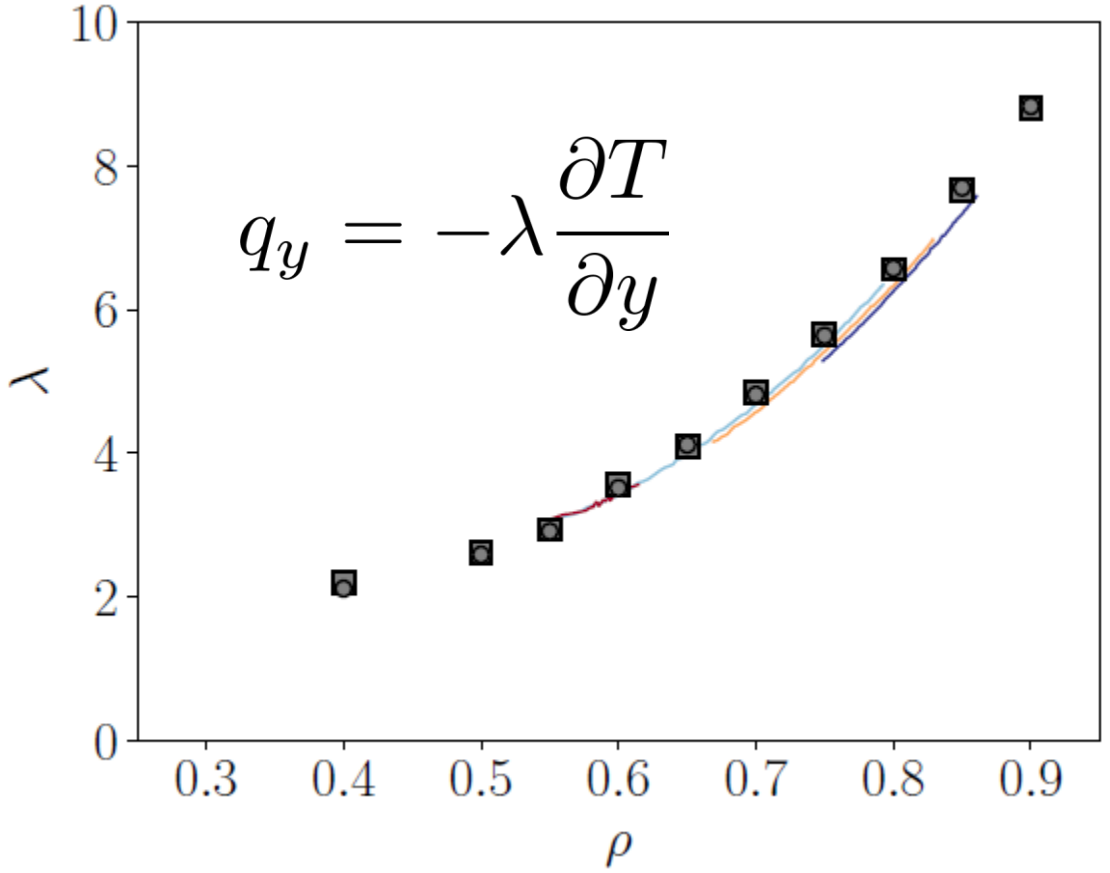


Brunel University London

Heat Conduction

- Good agreement with experiments

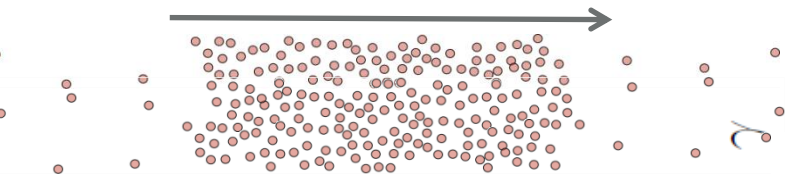




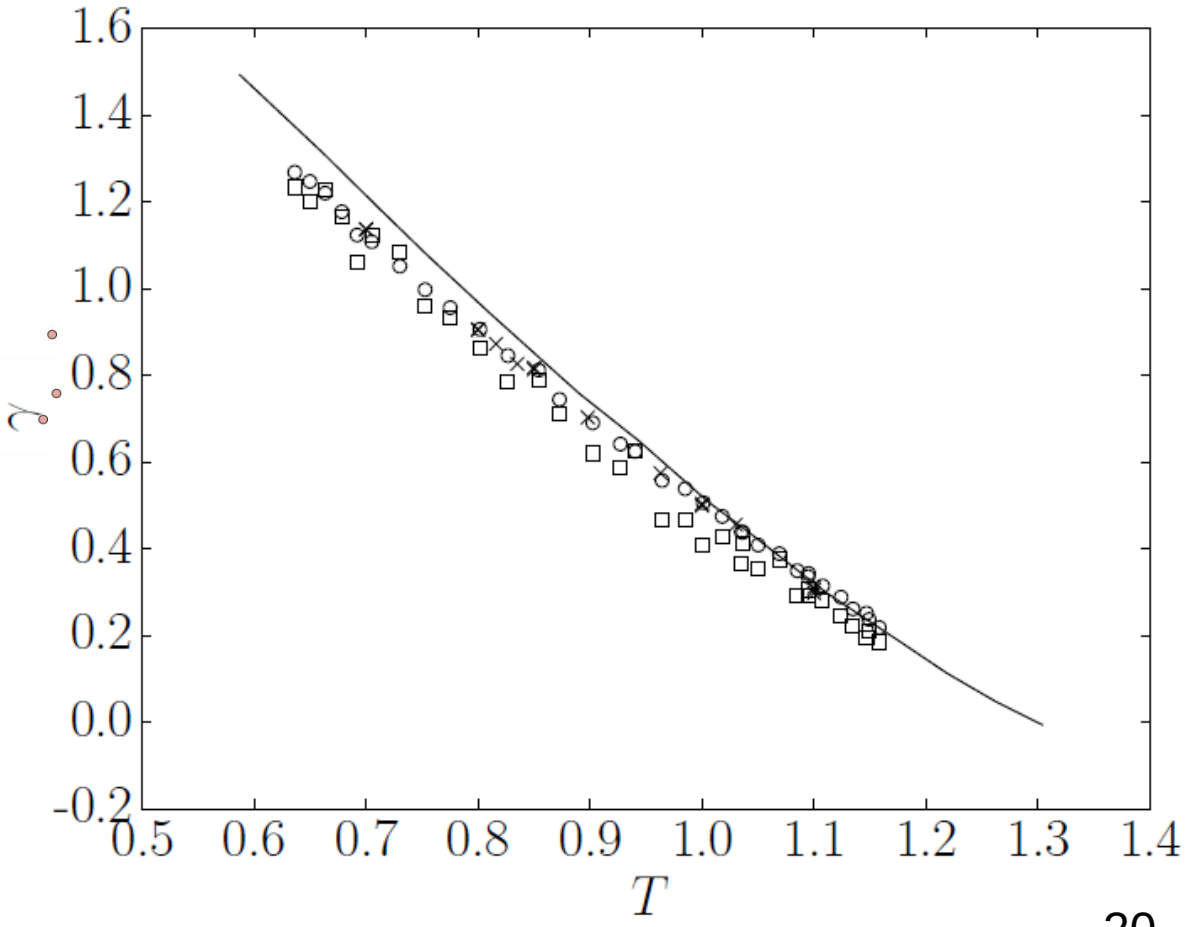
Surface Tension

- Good agreement with experiments

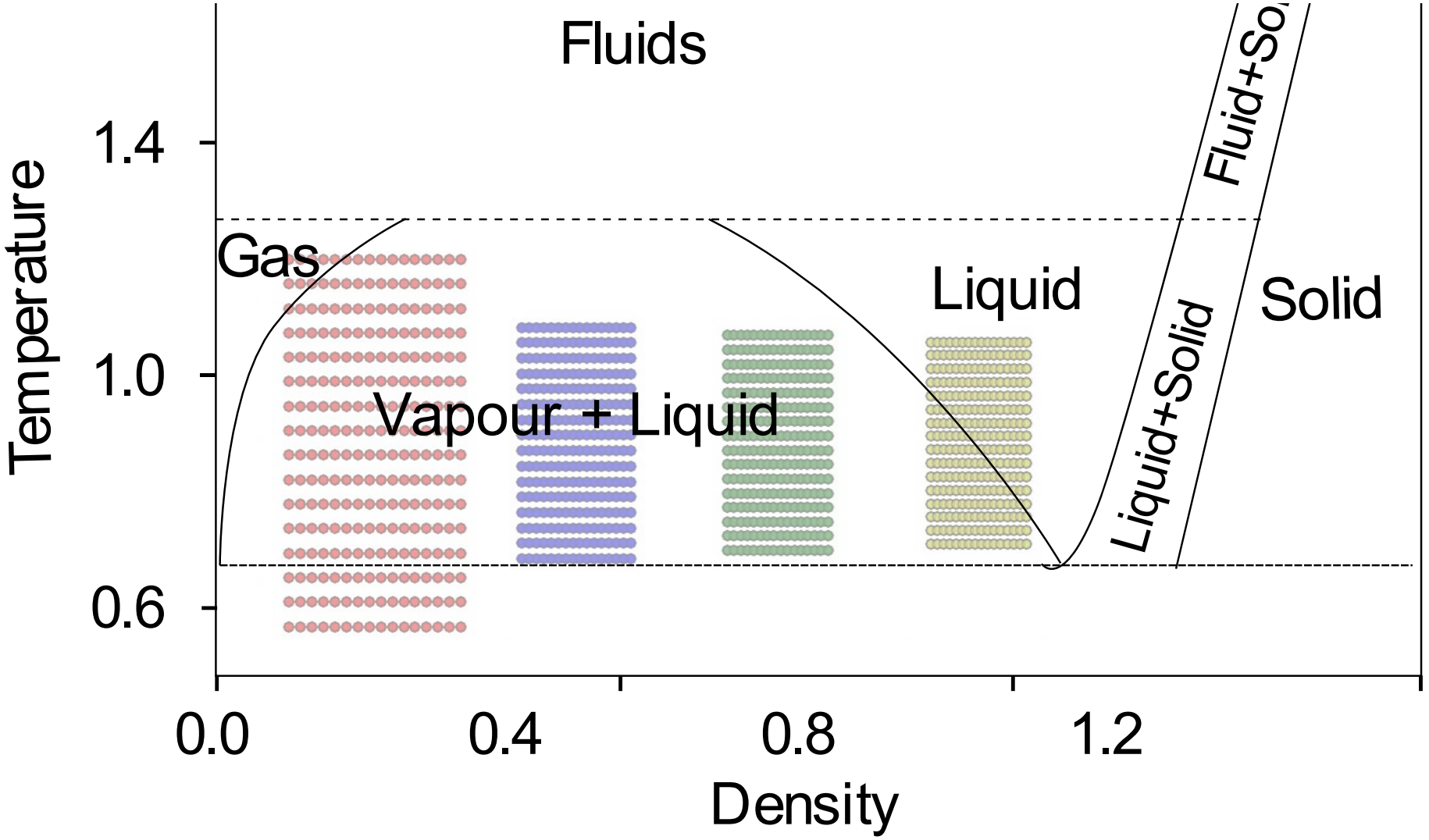
$$\gamma = \int_{-\infty}^{x} [\Pi_N - \Pi_T]\, dx$$



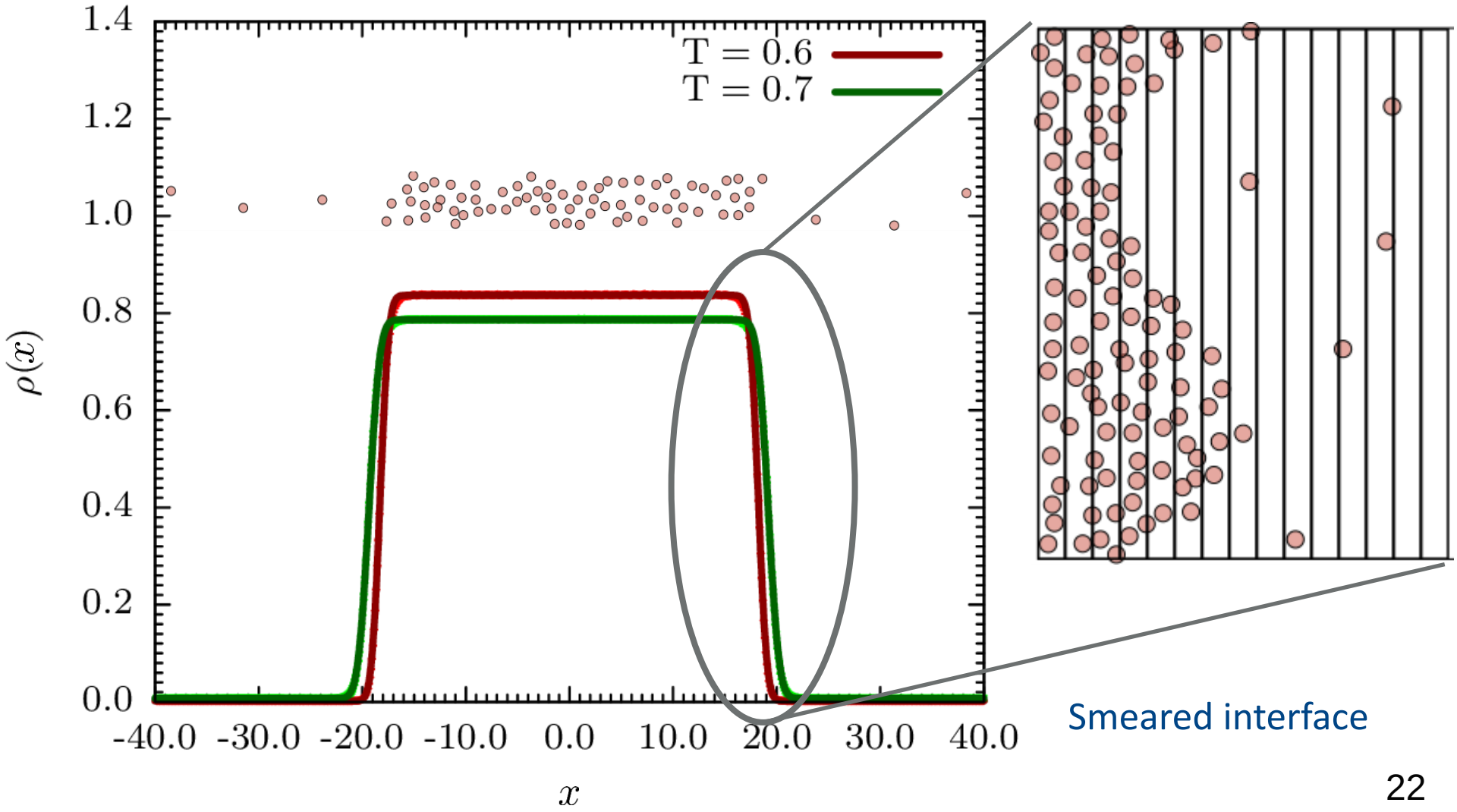
Integrate over Liquid Vapour interface(s)



Phase Change



Liquid-Vapour interface

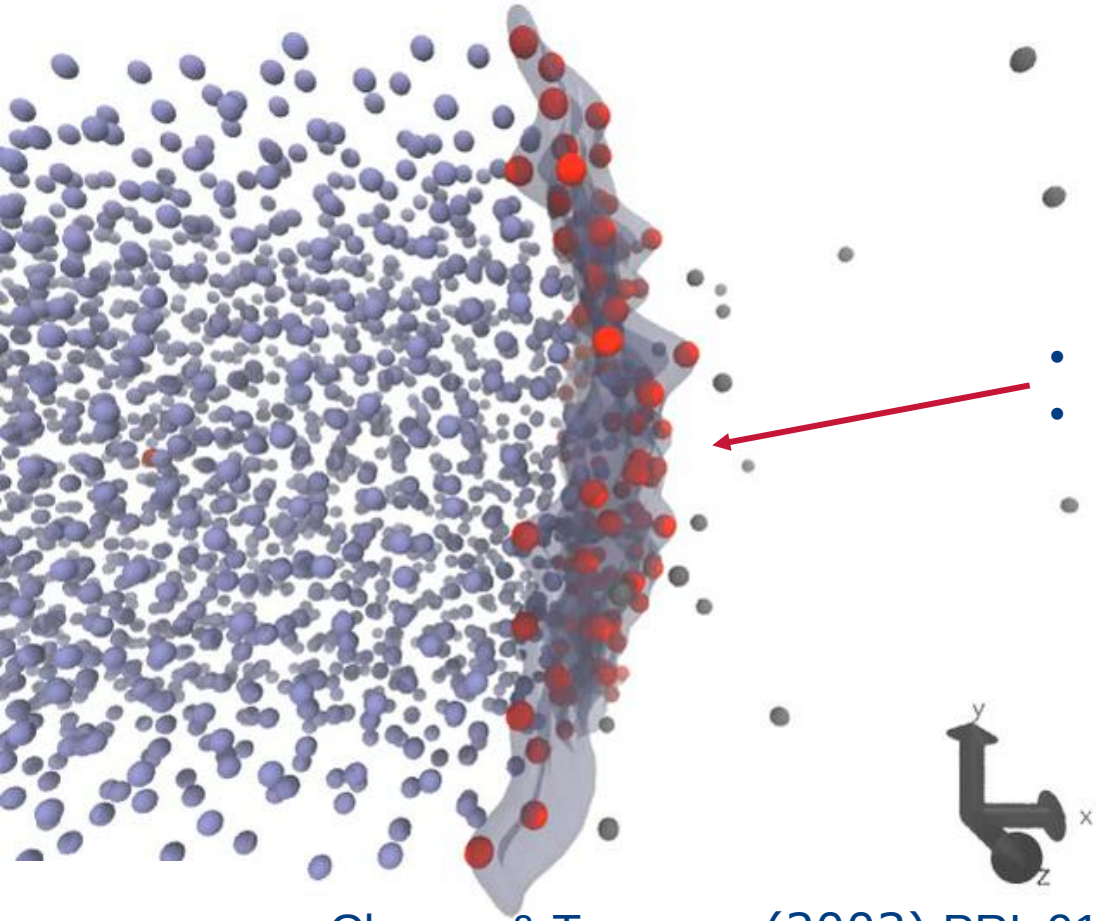


Smeared interface

Brunel University London

Liquid-Vapour interface

- Molecular dynamics naturally forms a liquid-vapour interface

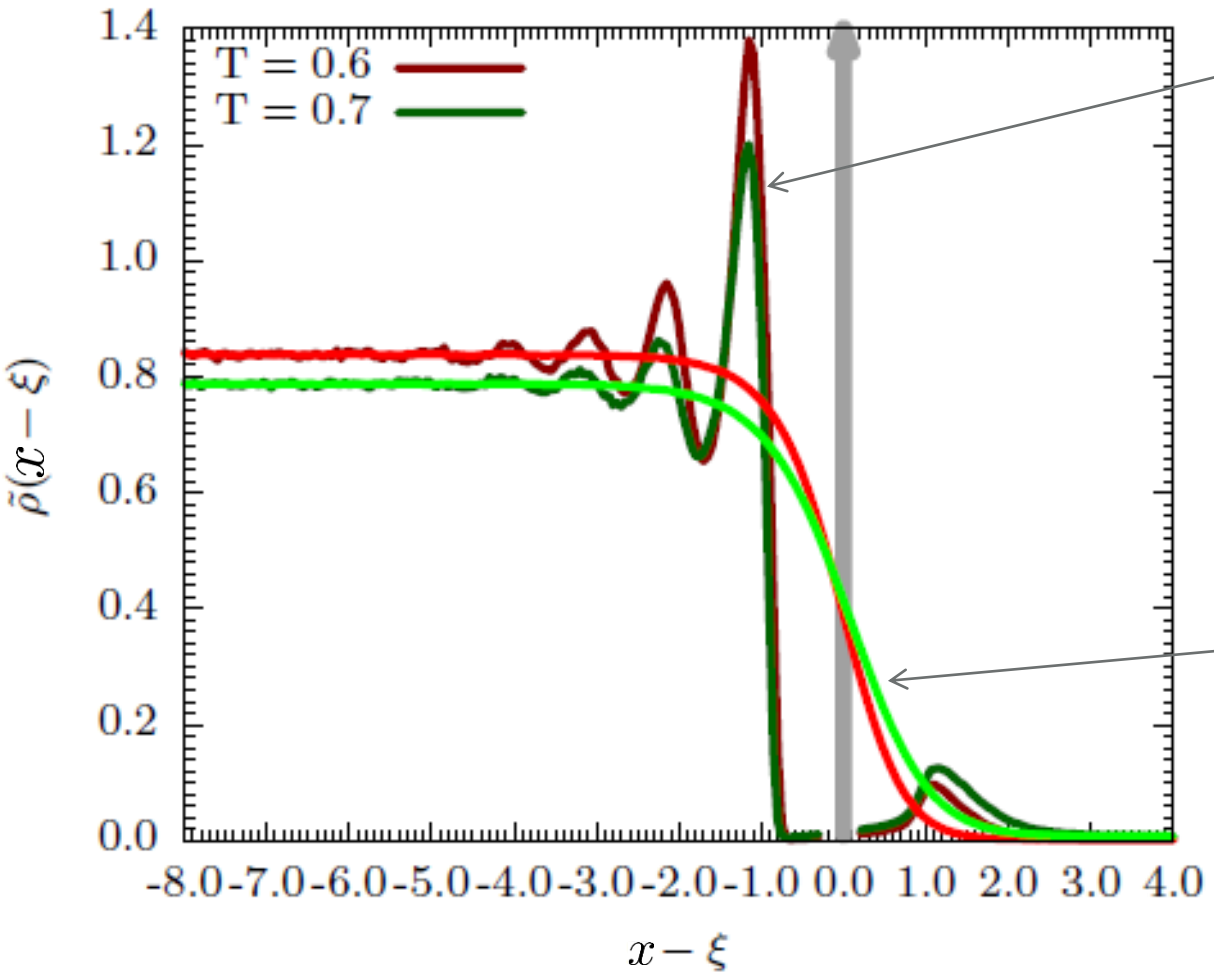


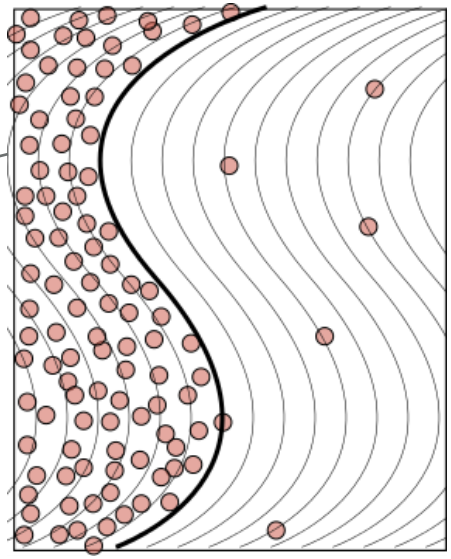
- Surface fitted by lest squares
- function of sines and cosines

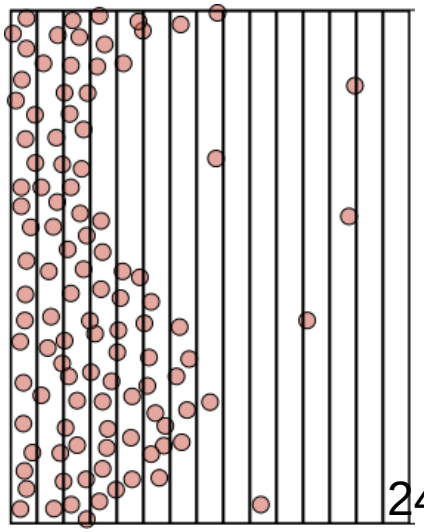
Chacon & Tarazona (2003) PRL 91, 166103

Brunel University London

Liquid-Vapour interface

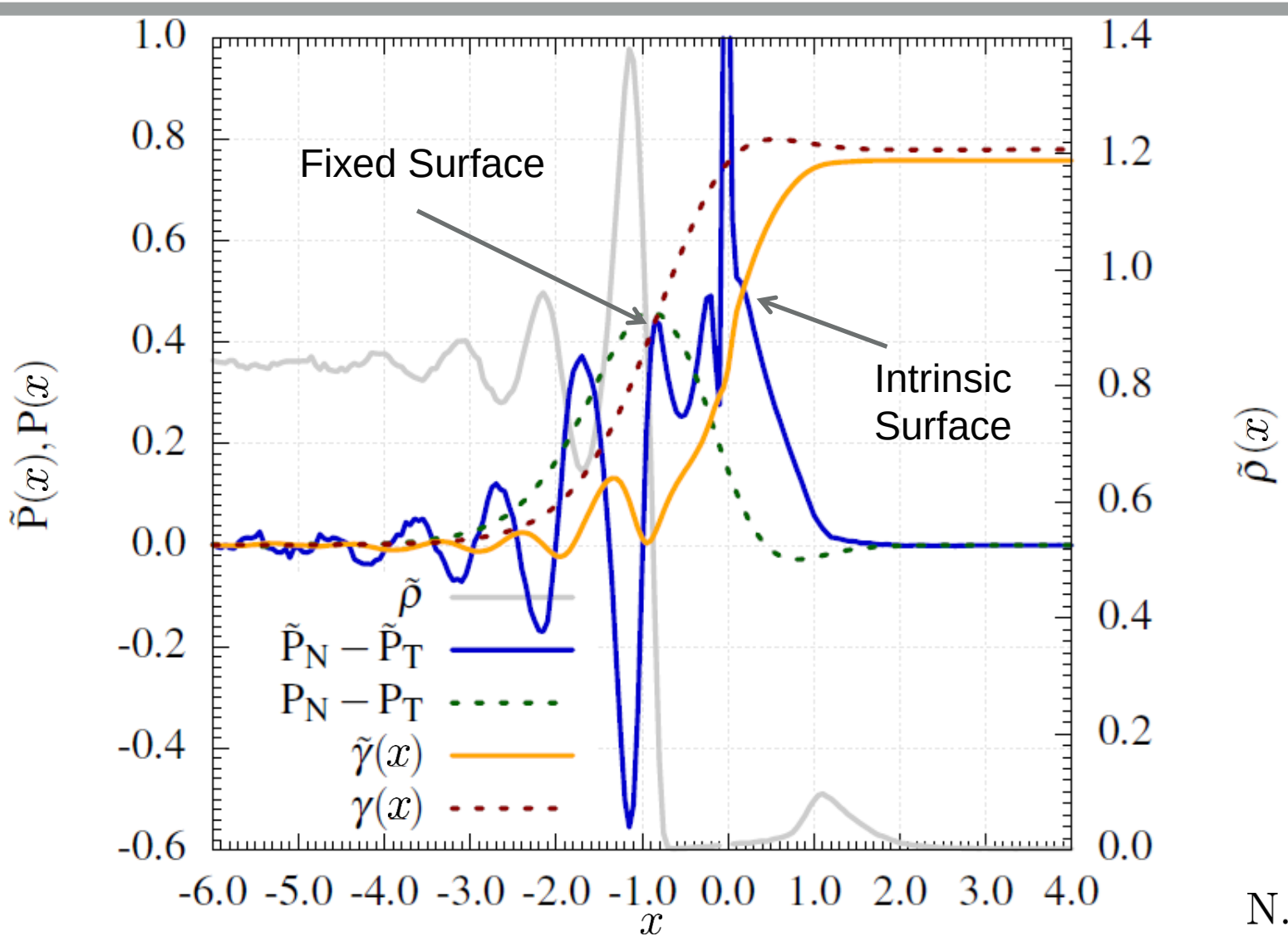






Brunel University London

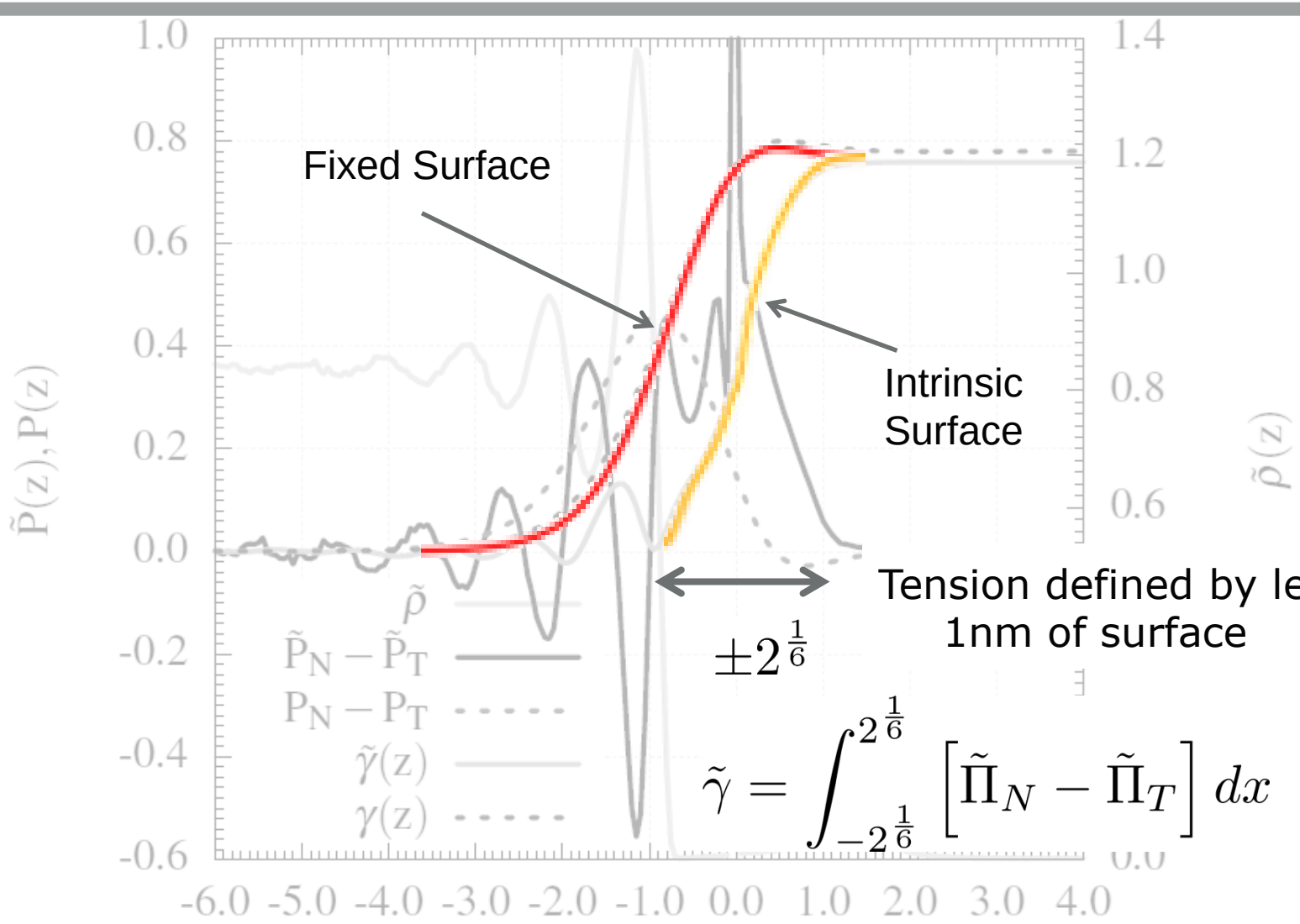
Results for Surface Tension



N.B. $\Pi \equiv P$

Brunel University London

Results for Surface Tension



Tension defined by less than 1nm of surface

$$\tilde{\gamma} = \int_{-2^{\frac{1}{6}}}^{2^{\frac{1}{6}}} \left[\tilde{\Pi}_N - \tilde{\Pi}_T \right] dx$$

Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Brunel University London

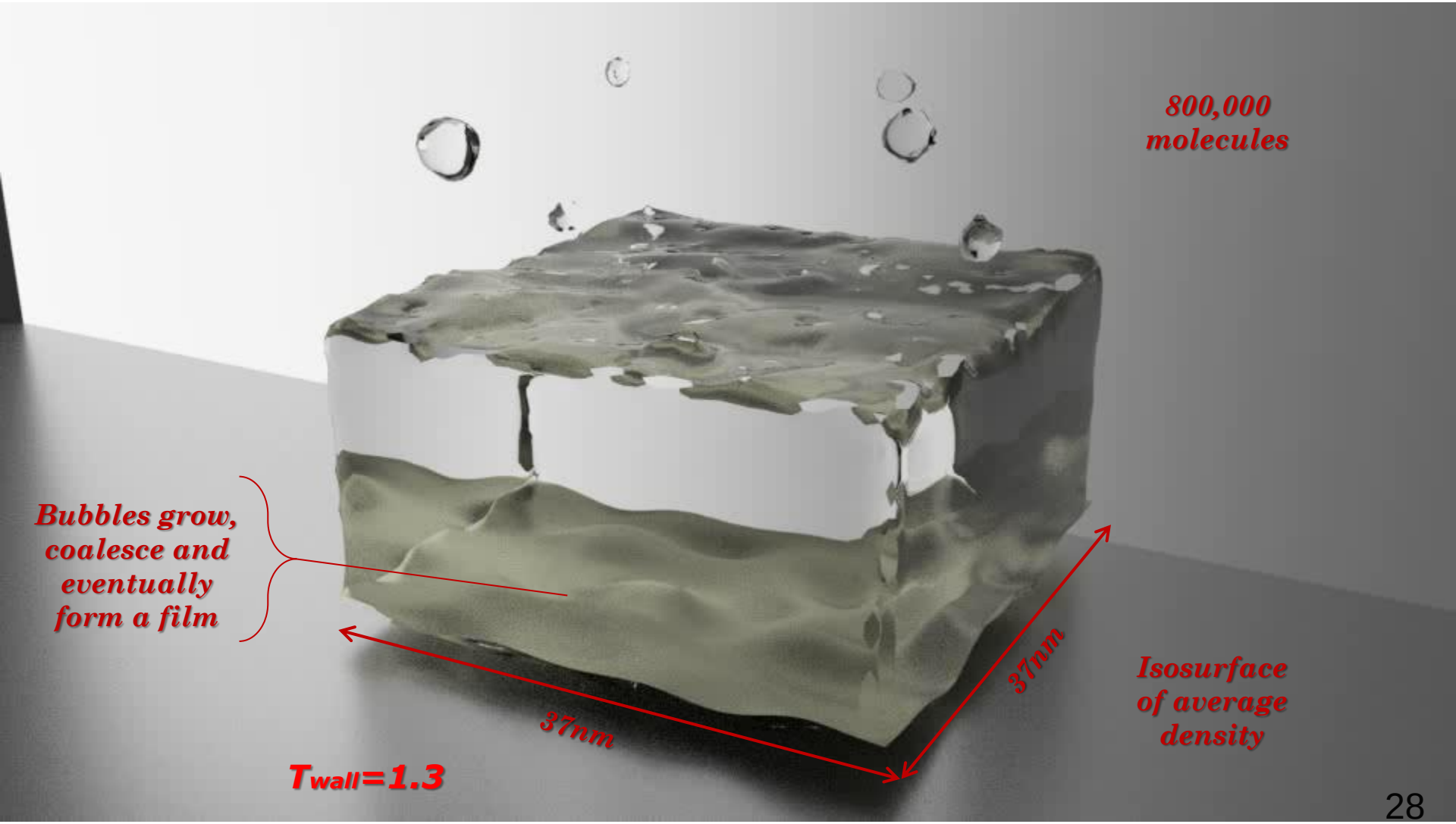
Molecular Dynamics - Nucleation

Wall w
mo
rou

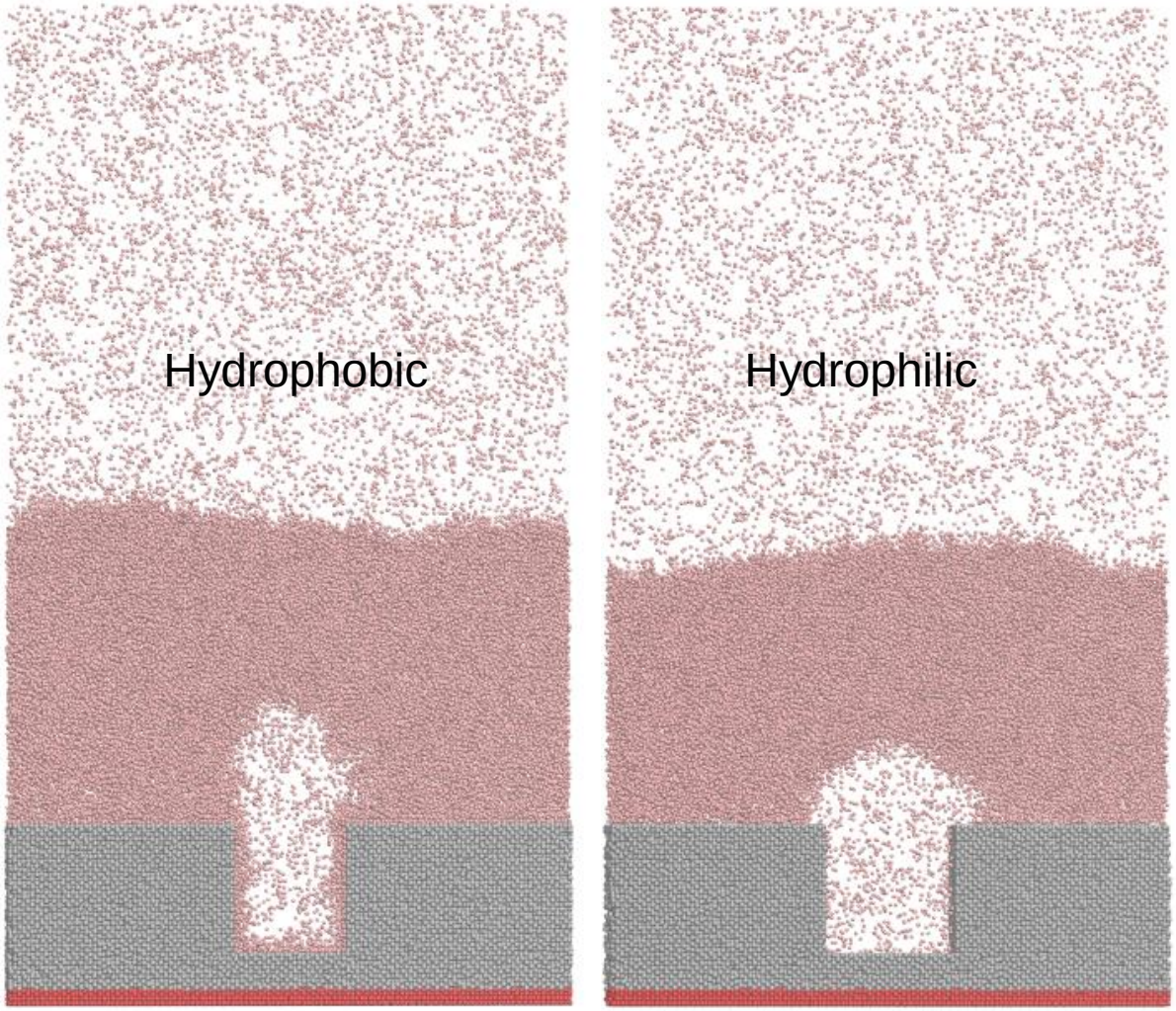
Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

Brunel University London

Isosurface of Density



Wetting and Nucleation

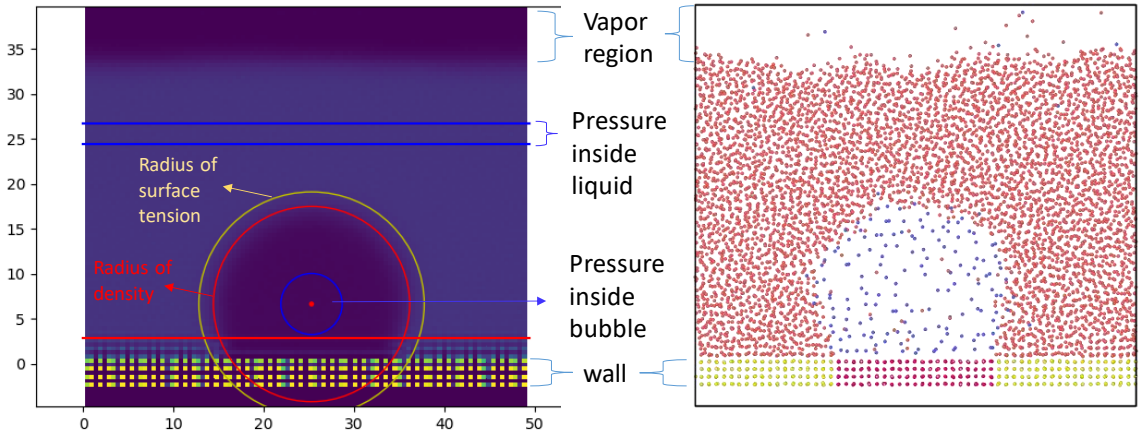


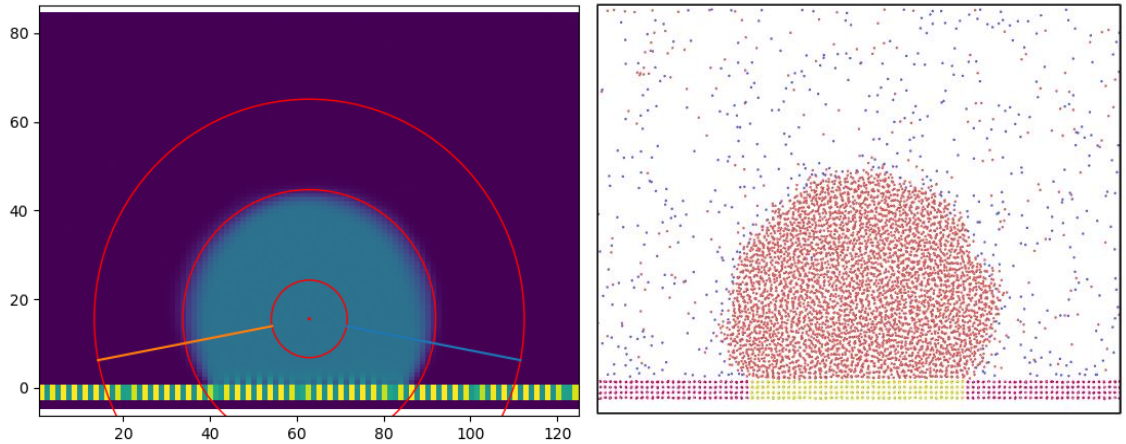
Work by

Alessio Lavino

at Imperial

Droplet vs. Bubbles



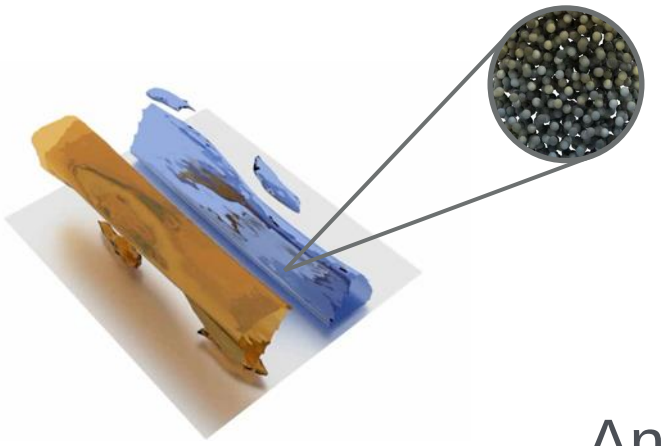


Work by

Wen Jun (Sonic)

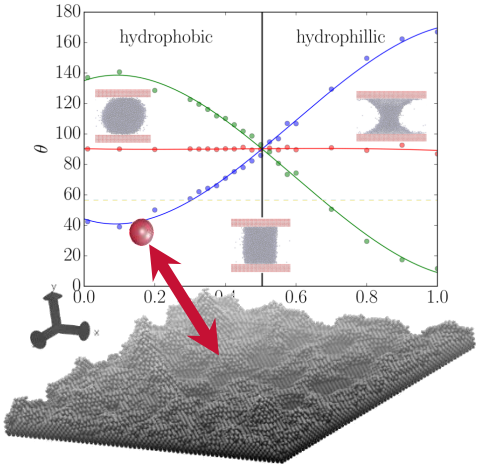
at Imperial

Questions

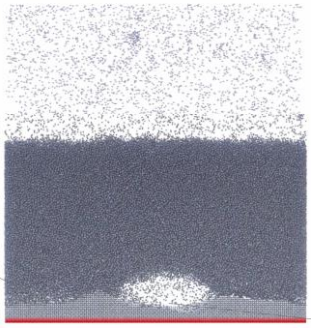


MD Turbulence

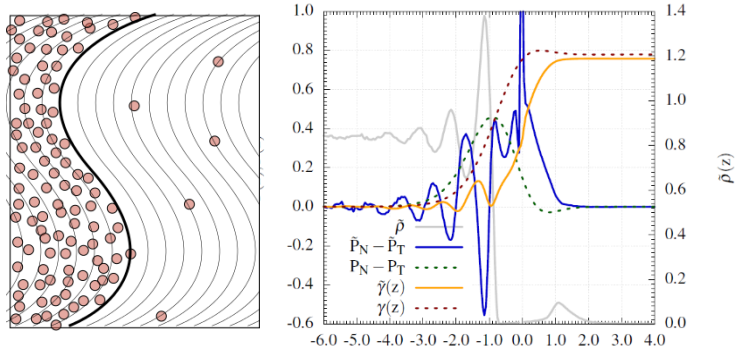
Any questions?



Surfaces and Wetting



Boiling



Intrinsic Interface

Brunel University London

Section 2

COUPLED SIMULATION

Coupling – Using MD with CFD

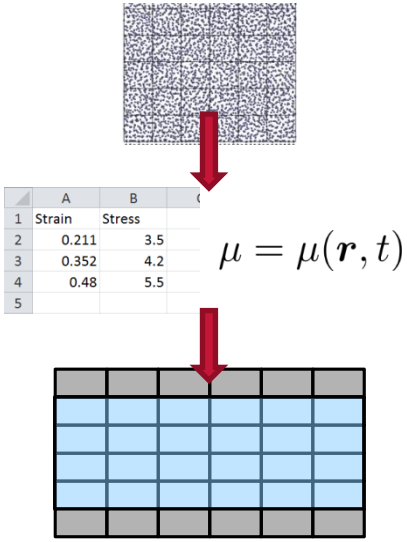
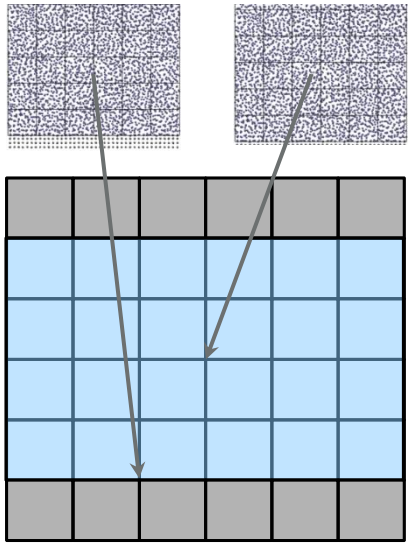


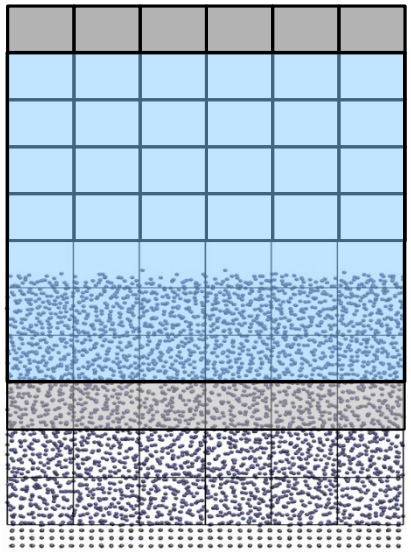
Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data



Embedded Models (HMM)

MD – embedded in a CFD simulation [1)]



Domain Decomposition

MD –CFD linked along an interface [2)]

1) Ren (2007), E et al (2003), Borg et al (2013) 2) O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni & Coveney, (2003), Mohamed & Mohamad, (2009)

Coupling – Using MD with CFD

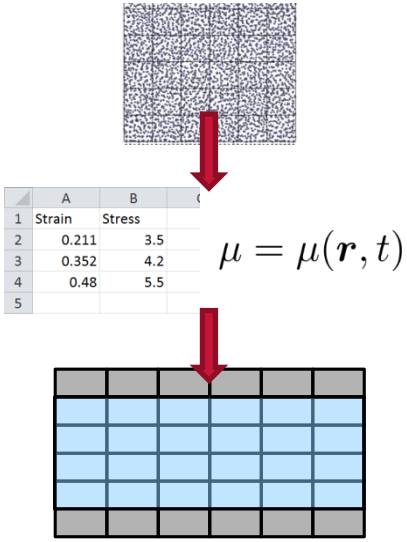


Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

Embedded Models (HMM)

MD – embedded in a CFD simulation [1)]

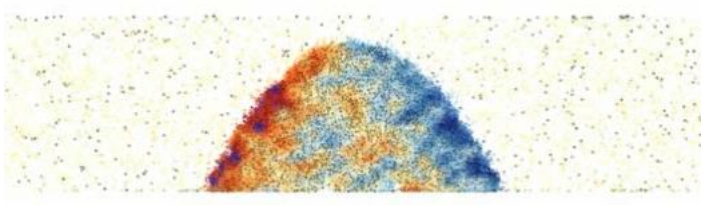
Domain Decomposition

MD –CFD linked along an interface [2)]

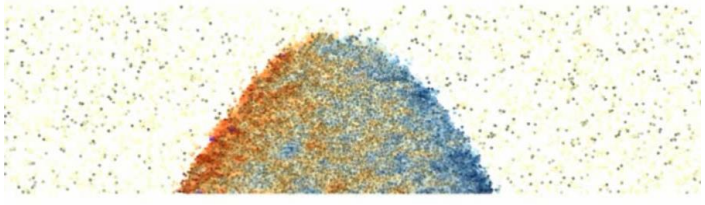
1) Ren (2007), E et al (2003), Borg et al (2013) 2) O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni & Coveney, (2003), Mohamed & Mohamad, (2009)

MD Simulation of Droplets

- Low Wettability



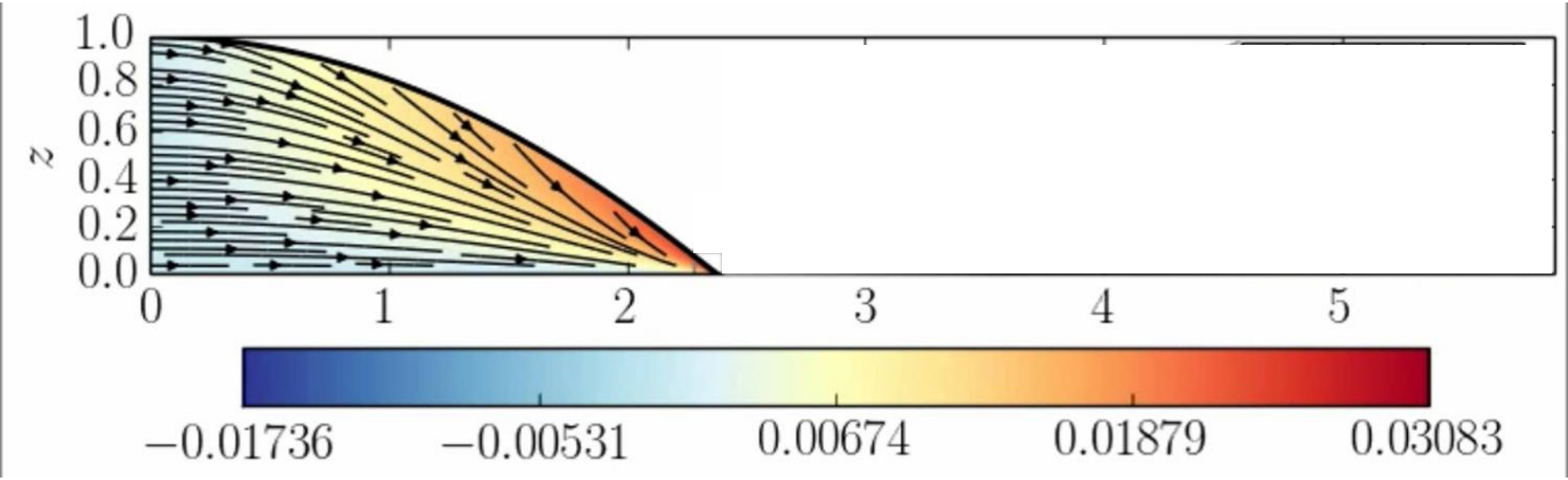
- Intermediate Wettability



- High Wettability

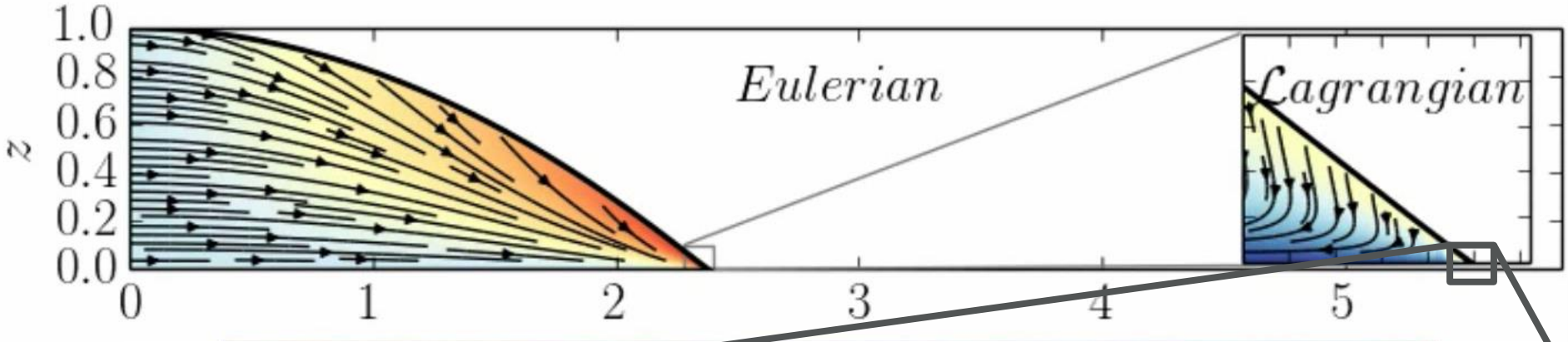
Brunel University London

Dynamic Contact Line

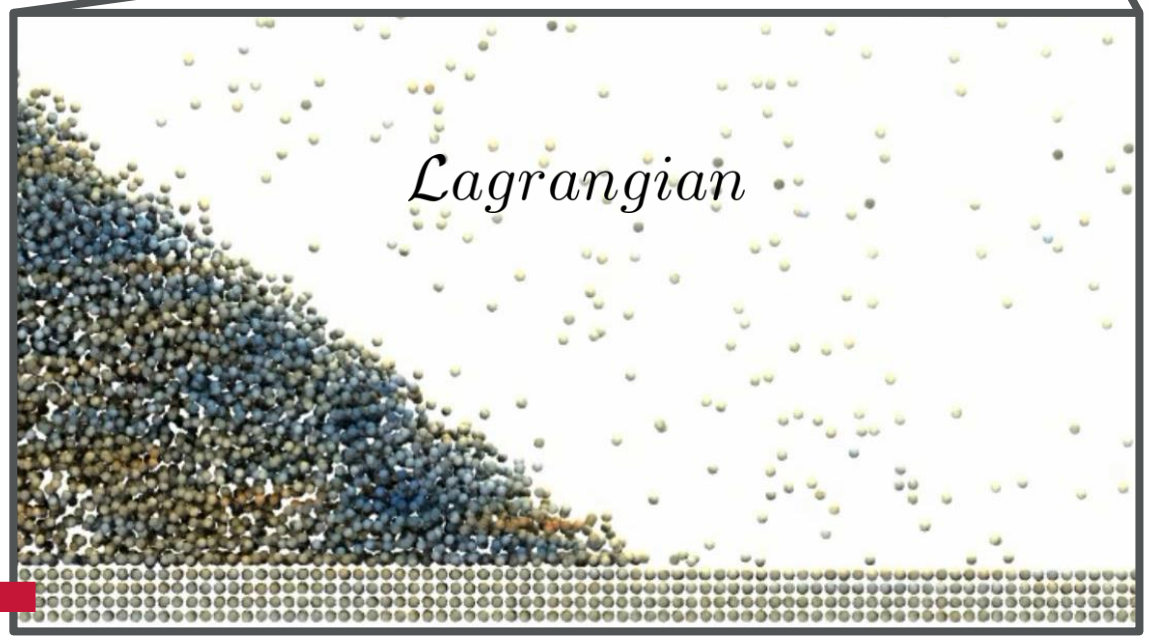


Brunel University London

Dynamic Contact Line



- Model the moving contact line with MD
- We want contact line speed as a function of continuum contact angle



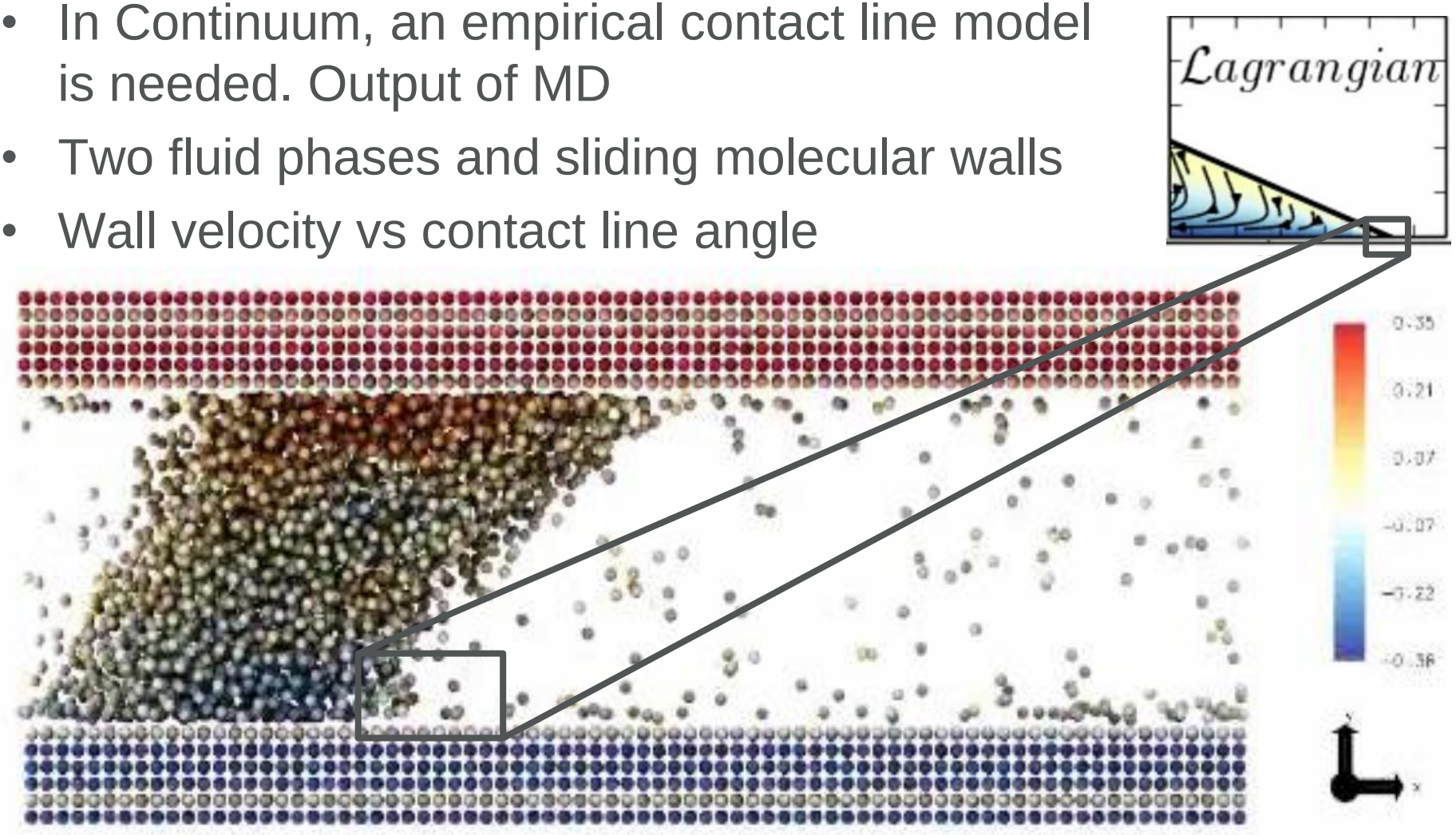
$$\frac{dx_c}{dt}$$

Work with Omar Matar, Erich Muller and Richard Craster

Brunel University London

Dynamic Contact Line

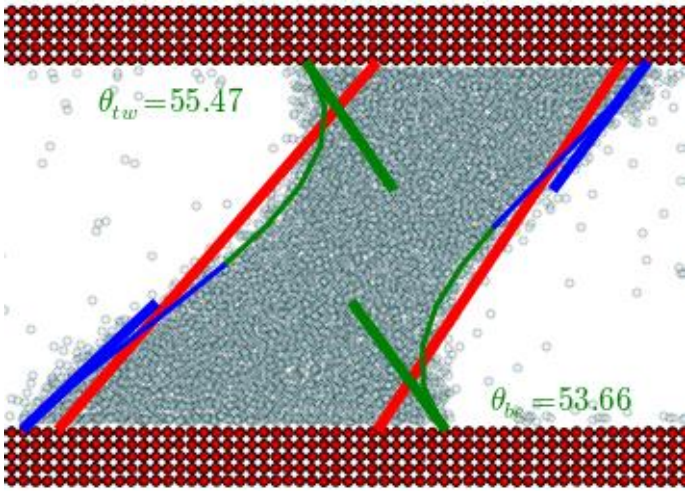
- In Continuum, an empirical contact line model is needed. Output of MD
- Two fluid phases and sliding molecular walls
- Wall velocity vs contact line angle

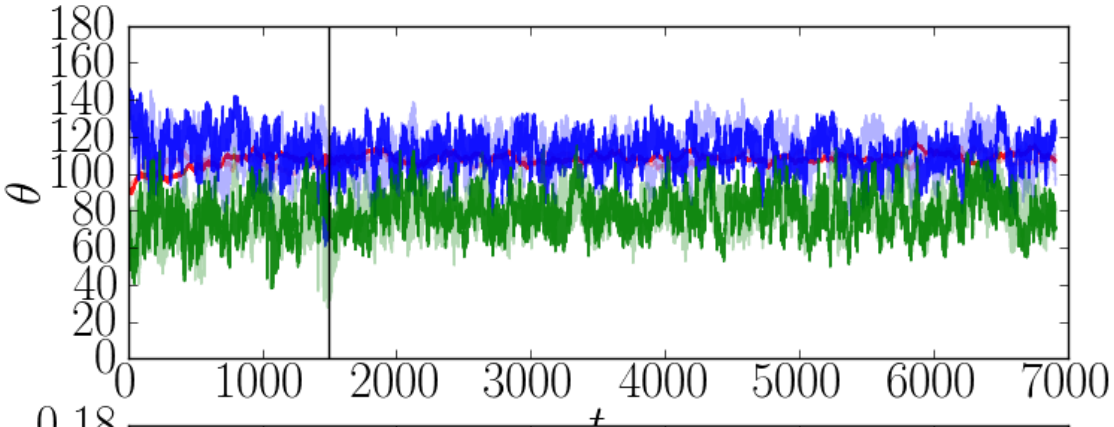


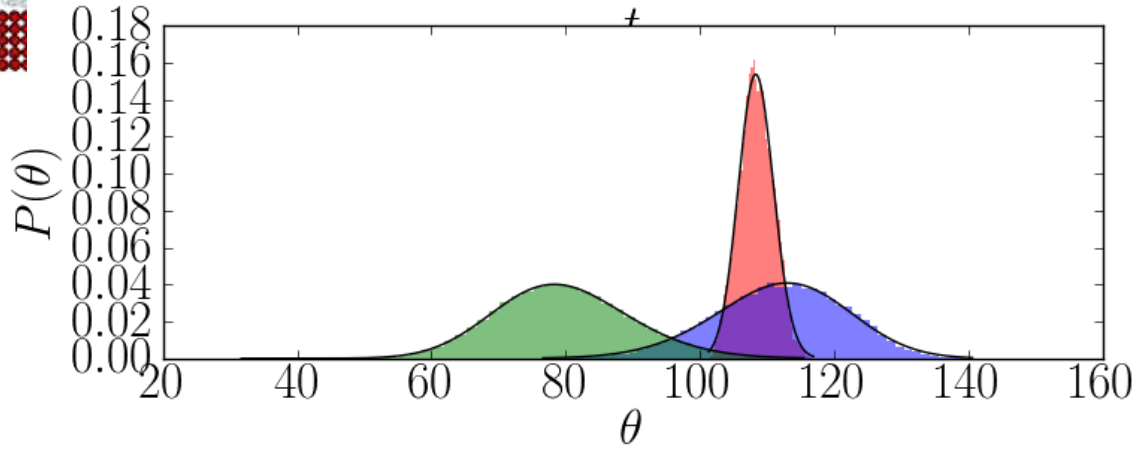
Brunel University London

Time Evolution of Contact Angle

- Contact angles fluctuates as a function of time







- Probability density function of angle shows range of micro-scale behaviour

- *Linear*, *Advancing* and *Receding* angles

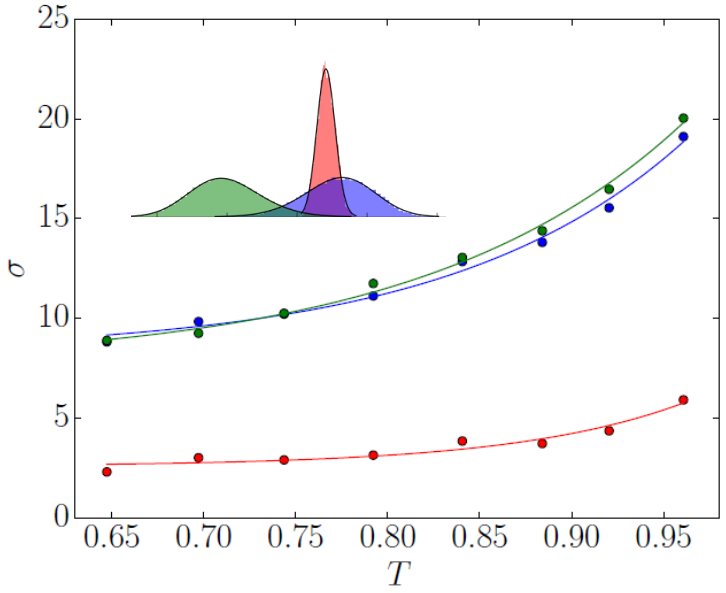
Brunel University London

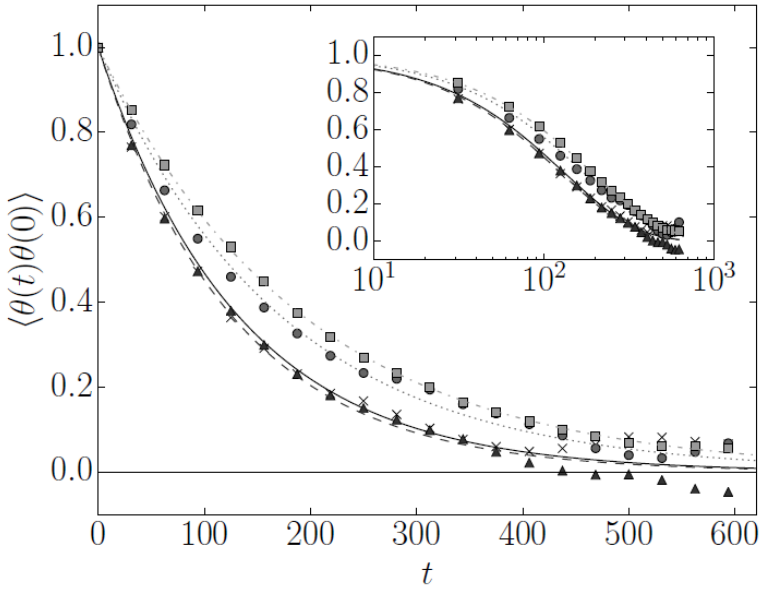
Building this into the Continuum Model

- A Langevin Equation uses random noise to model this

$$\dot{\theta} + \frac{k}{\Gamma}\left[\theta - \langle\theta\rangle\right] - \frac{1}{\Gamma}\xi(t) = 0 \text{ where } \langle\xi(t)\xi(t')\rangle = C\delta(t-t'),$$

- Coefficients parameterised using
  - Standard deviation – range of fluctuations
  - Autocorrelation – how quickly they decay.





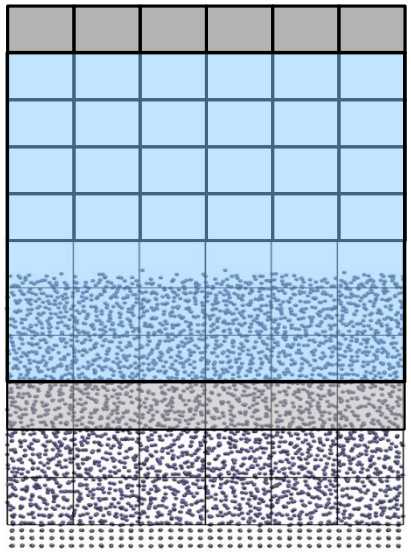
Coupling – Using MD with CFD

Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

Embedded Models (HMM)

MD – embedded in a CFD simulation [1)]



Domain Decomposition

MD –CFD linked along an interface [2)]

1) Ren (2007), E et al (2003), Borg et al (2013) 2) O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni & Coveney, (2003), Mohamed & Mohamad, (2009)

Coupled Simulation

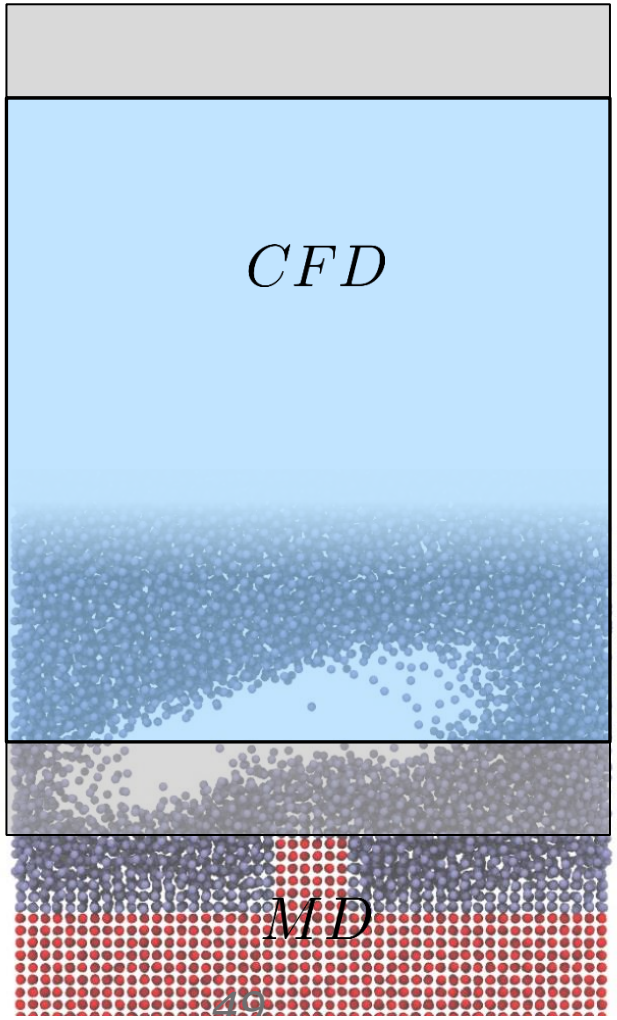
- Continuum Newton's law

$$\frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla} \cdot \rho \boldsymbol{u}\boldsymbol{u} = \boldsymbol{\nabla} \cdot \boldsymbol{\Pi}$$

Share the same **time** and **length** scales

- Discrete molecules

$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i \text{ for all i in N}$$



Brunel University London

Coupled Simulation

- Continuum Newton's law

$$\frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} = \boldsymbol{\nabla}\cdot\boldsymbol{\Pi}$$

$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i + \mathbf{F}_i^C \quad i \in \text{cell}$$

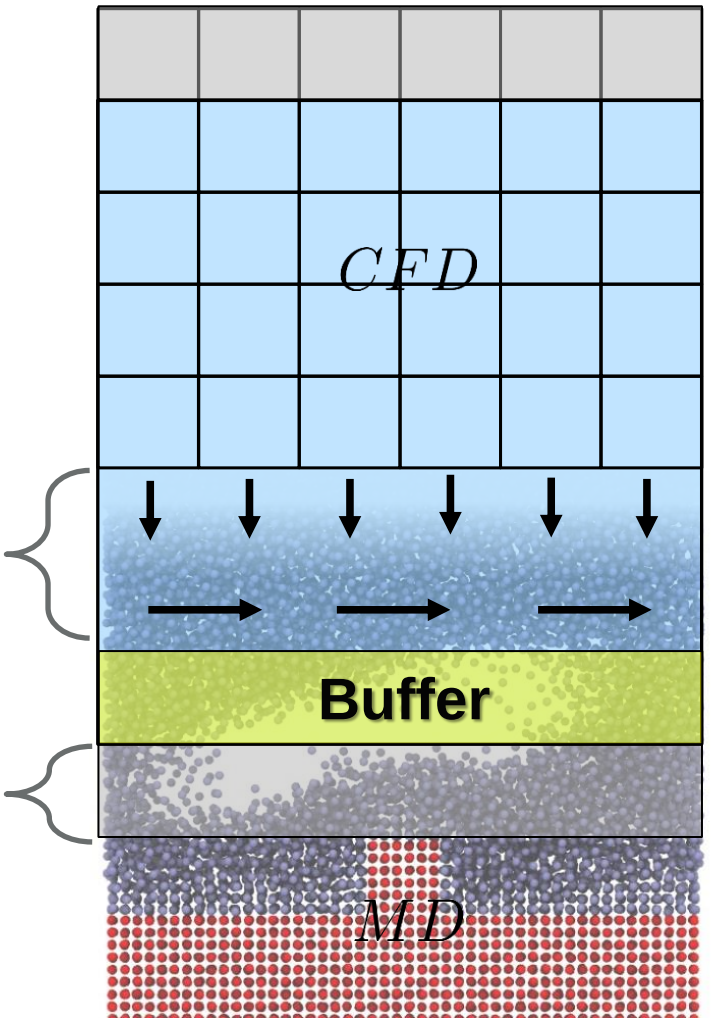
CFD→MD Boundary condition

$$\boldsymbol{u}^{BC} = \sum_{i\in\text{cell}} \boldsymbol{v}_i$$

MD→CFD Boundary condition

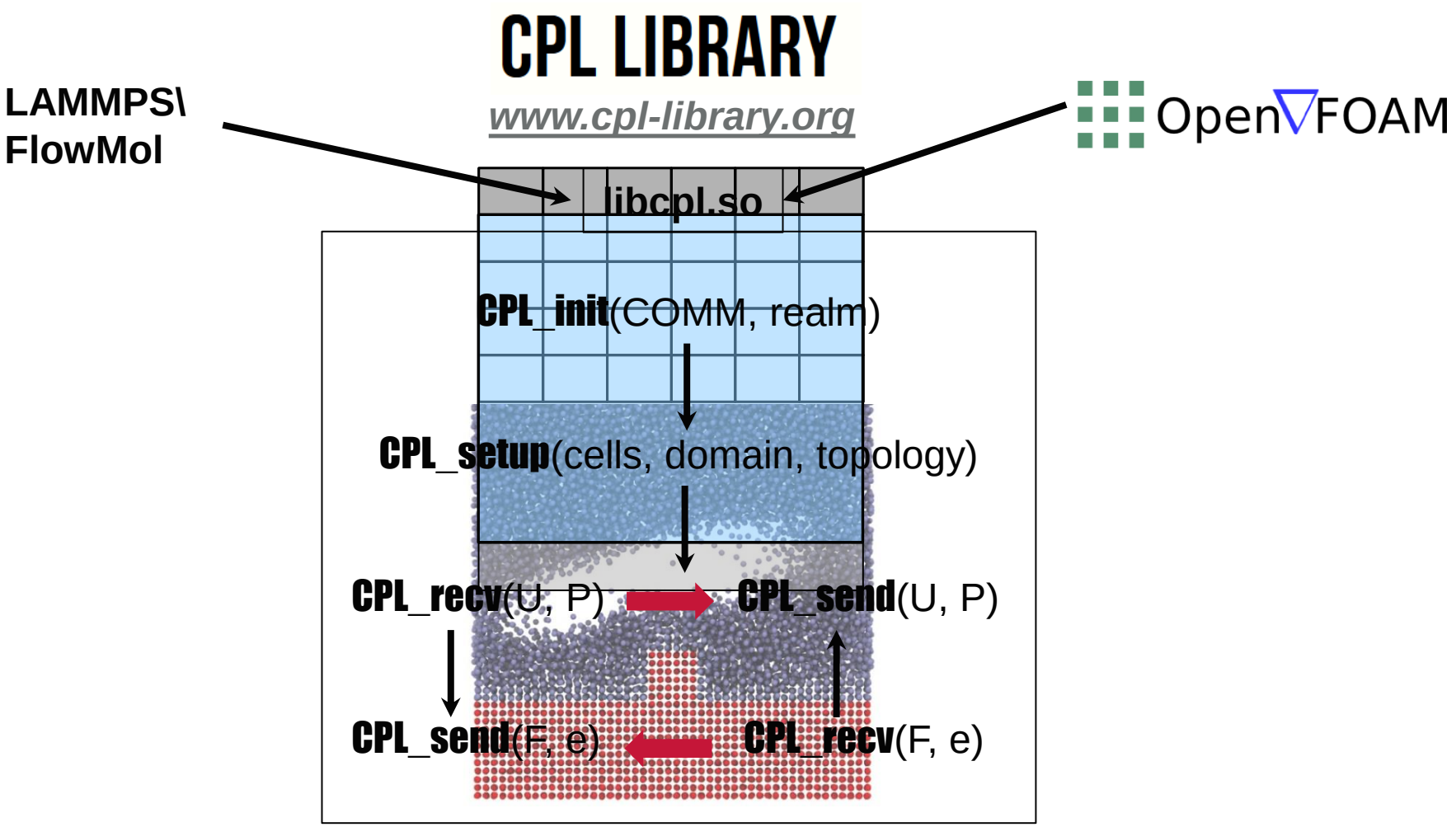
- Discrete molecules

$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i \text{ for all i in N}$$



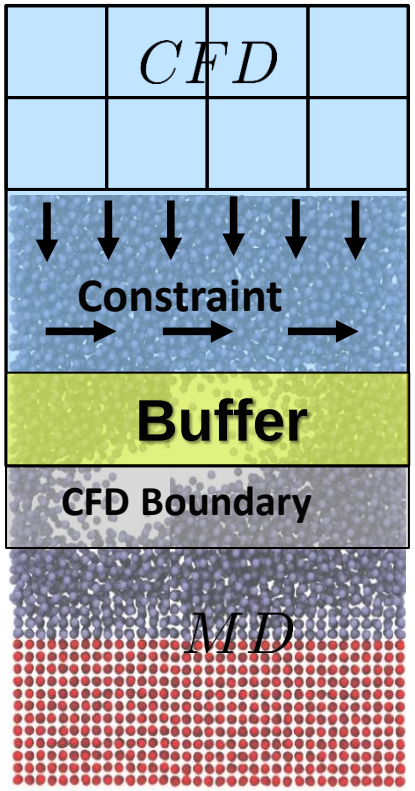
O'Connell Thompson (1995), Flekkoy (2000), Nie et al (2004), ***Smith et al (2012), Smith et al (2015)***

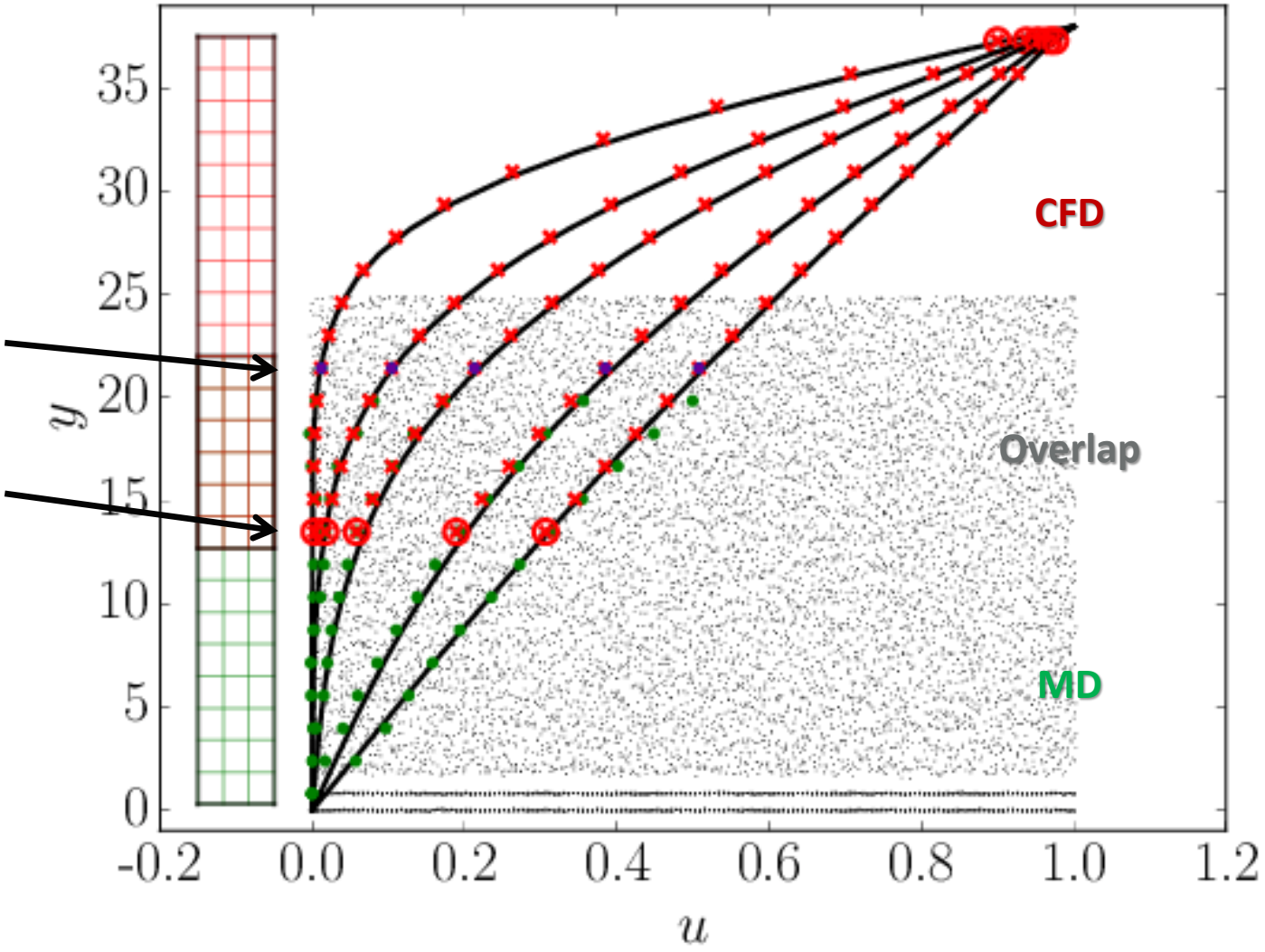
Coupled Simulation Software



Brunel University London

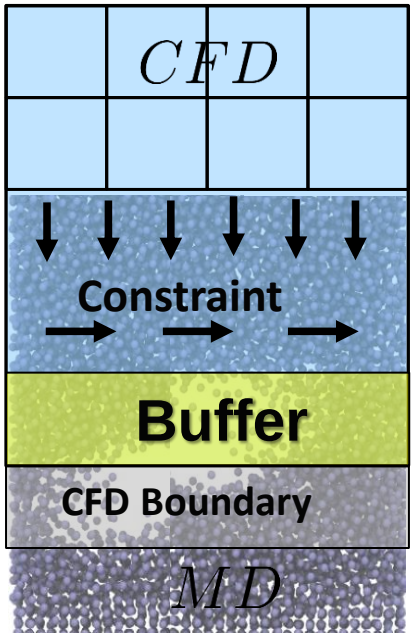
Coupling Results – Couette Flow



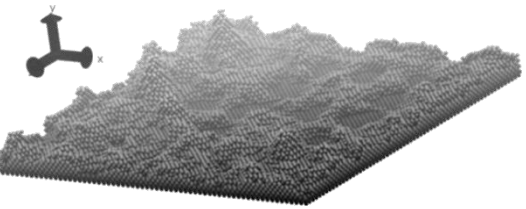


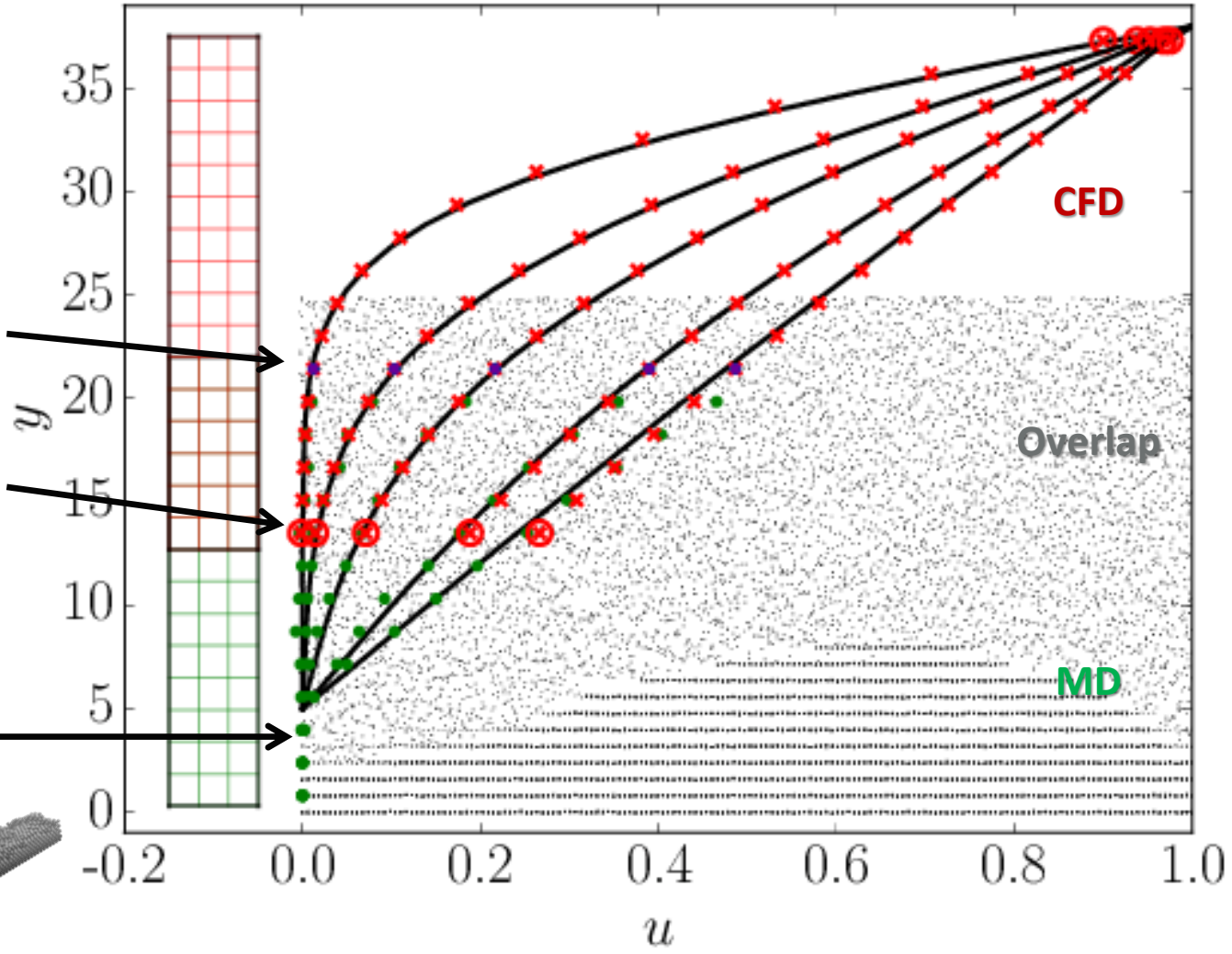
Brunel University London

Coupling Results – Couette Flow



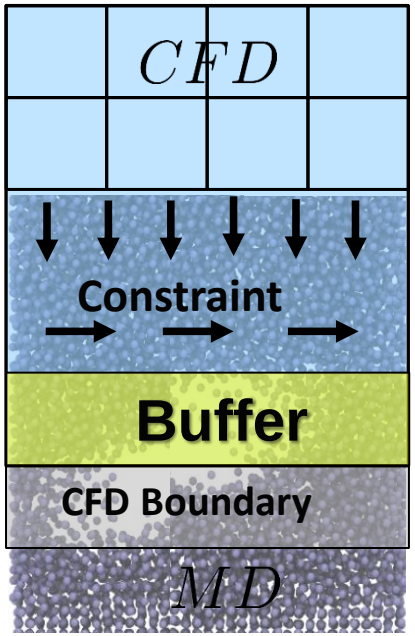
Rough wall shifts zero location



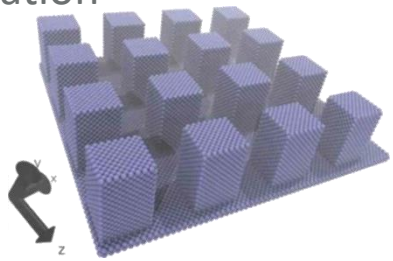


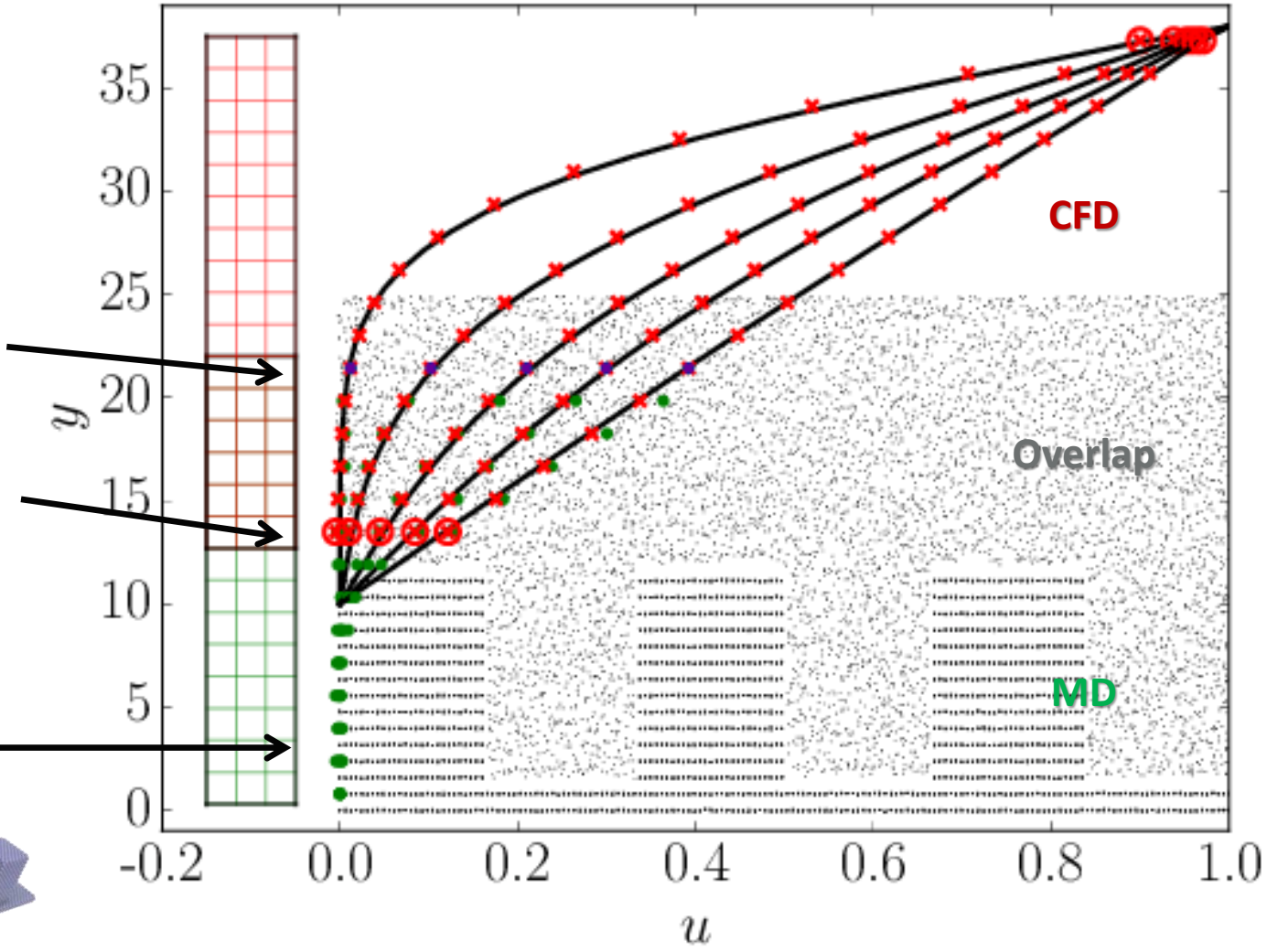
Brunel University London

Coupling Results – Couette Flow



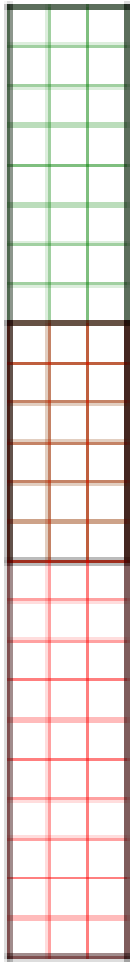
Posts shift zero location





Brunel University London

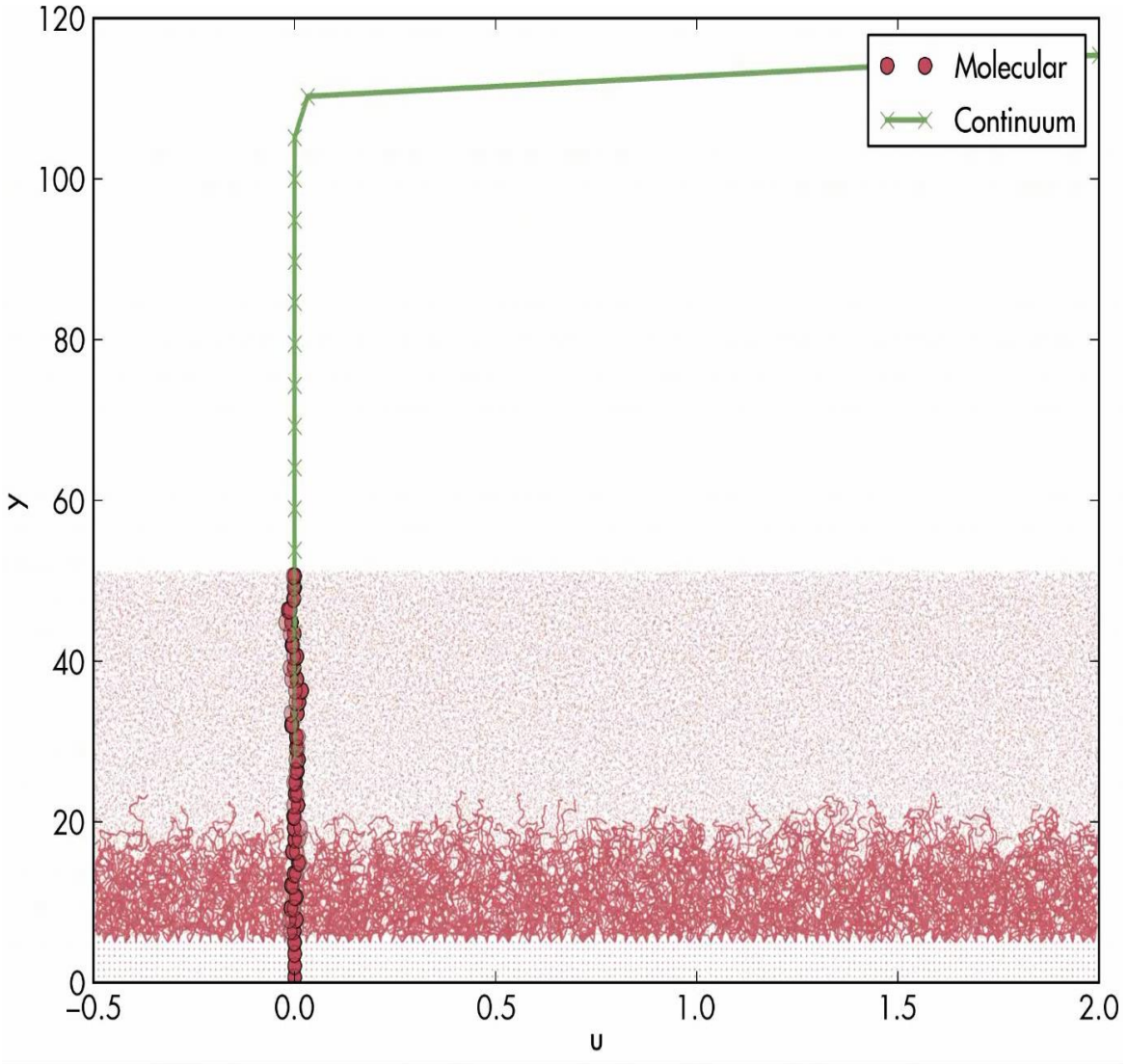
Coupling Results – Polymer Brushes



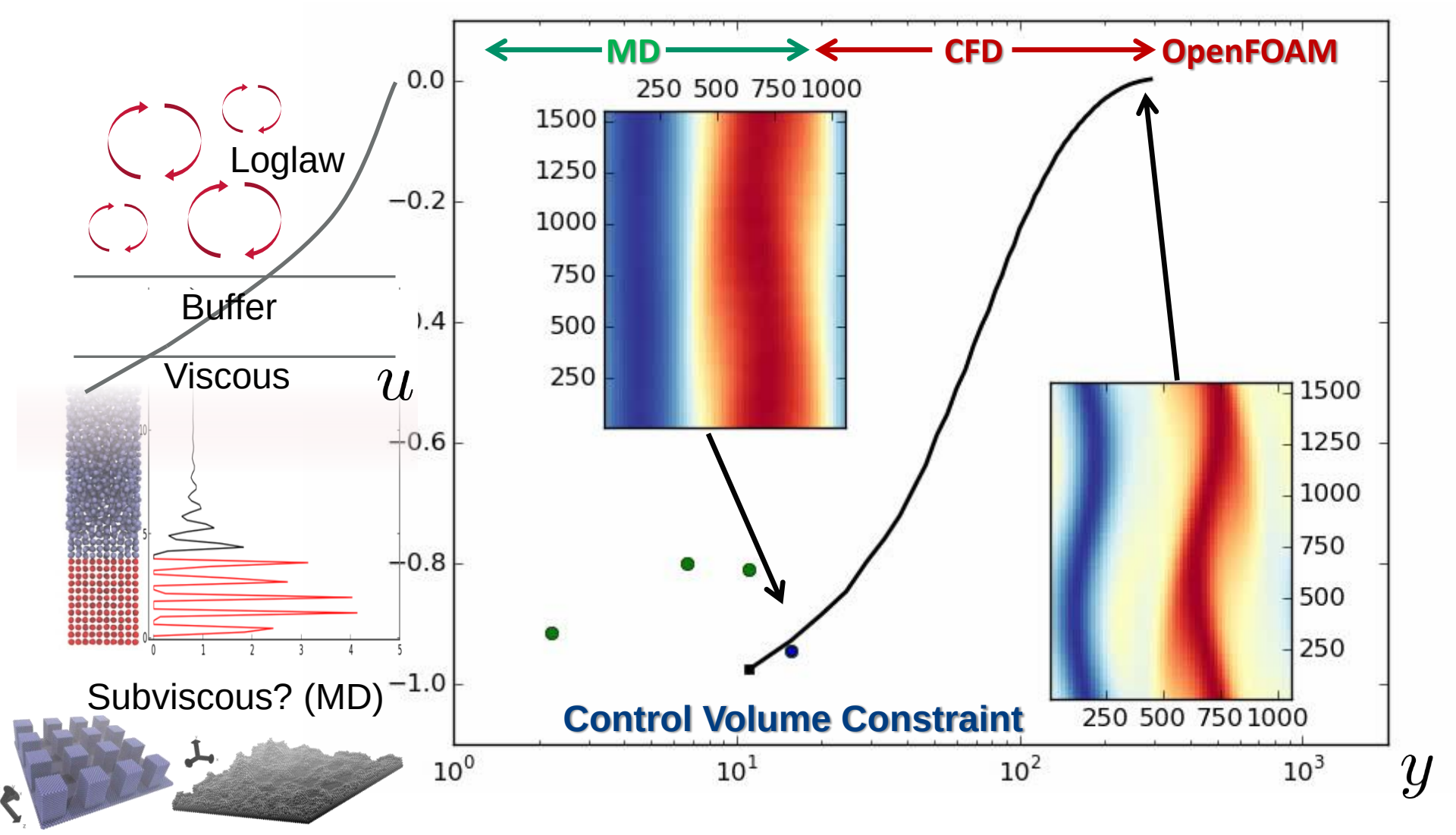
CFD Region

Overlap Region

MD Region

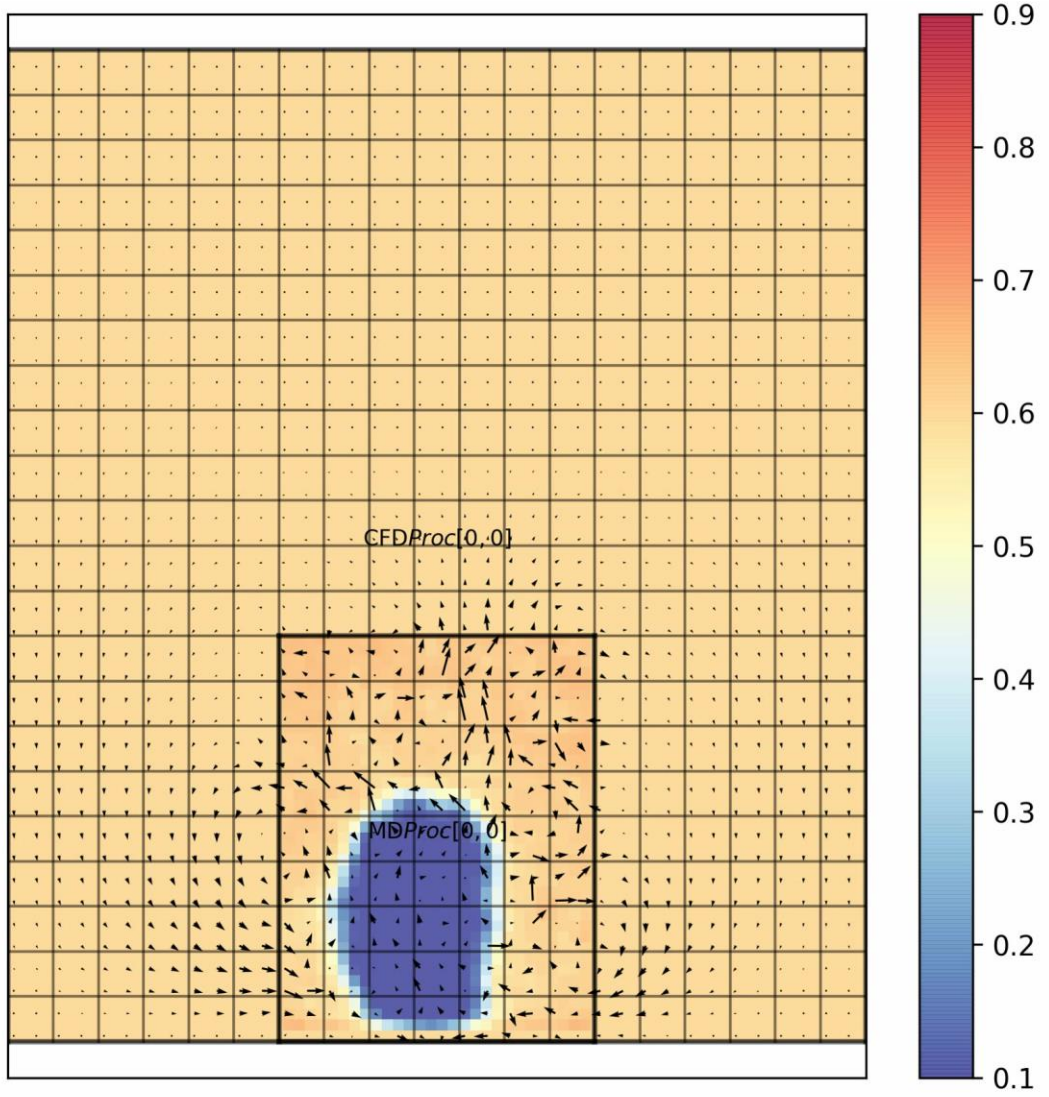


Coupling Results – Turbulent Couette



Coupled Simulation of Boiling

- Bubble nucleation occurs naturally in MD
- Density, velocity and temperature passed as boundary conditions



Summary

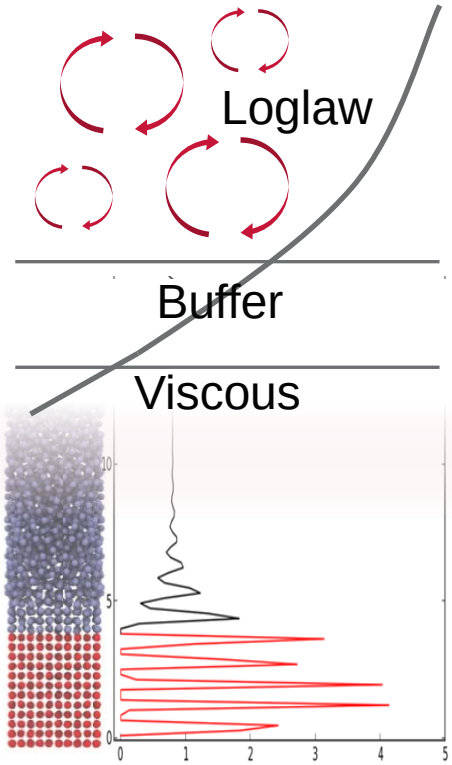
- Molecular Dynamics (MD)
  - Solves Newton's law for individual molecules - only assumption is inter-molecular potential from quantum mechanics
  - Viscosity, surface tension and heatflux predicted and match experimental results. Phase change occurs naturally
  - Walls can be designed with wetting tuned by interaction - boiling, nucleation and bubble growth occur naturally

- Coupled Simulation
  - Aims to make MD viable for engineering problems
  - Coarse-grained models from MD, e.g. moving contact line
  - MD only where needed as part of a CFD simulation – e.g. near walls, liquid-vapour interfaces, nucleation sites, etc

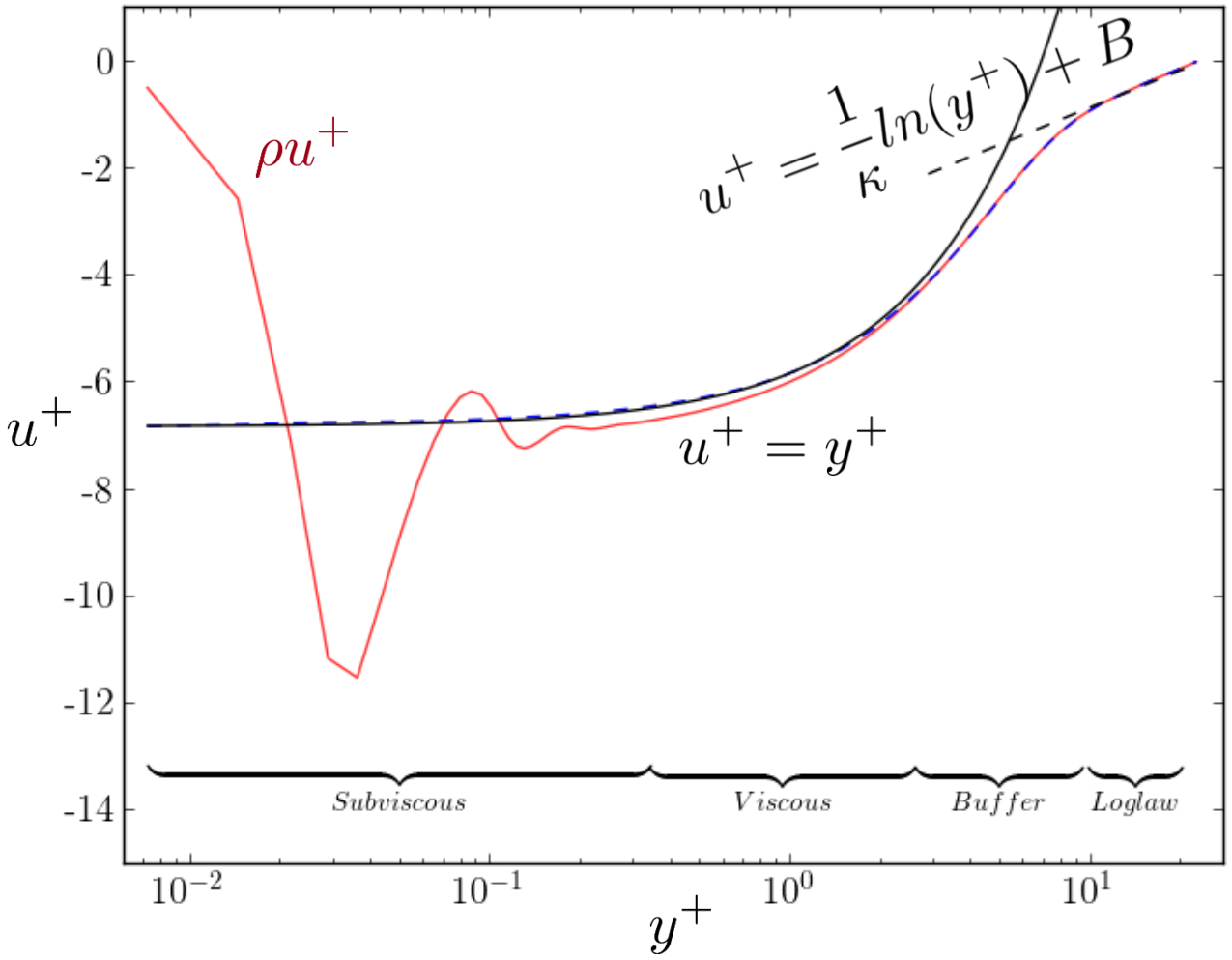
Questions

Thank you, any questions?

Coupling Results – Turbulent Couette



Subviscous? (MD)



Brunel University London

Coupled CFD-MD Simulation

- Finite Volume Solver

$$\frac{\partial}{\partial t}\int_V \rho \boldsymbol{u} dV = -\oint_S \rho \boldsymbol{u}\boldsymbol{u}\cdot d\mathbf{S} \quad -\oint_S \boldsymbol{\Pi}\cdot d\mathbf{S}$$

$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i + \mathbf{F}_i^C \quad i \in \text{cell}$$

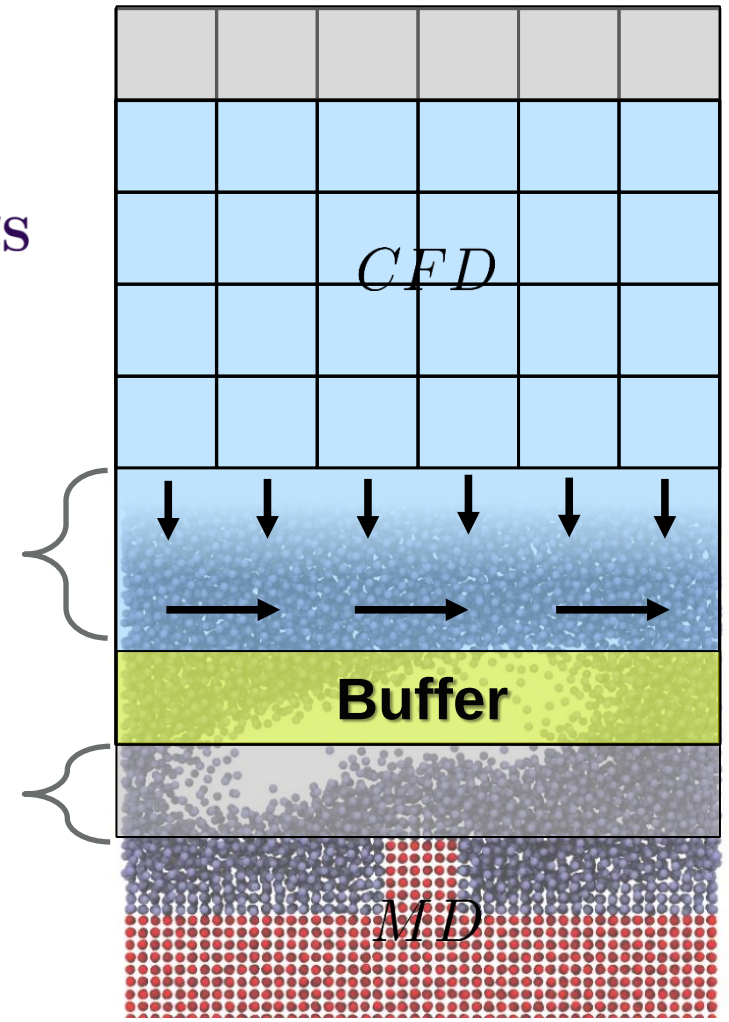
CFD→MD Boundary condition

$$\boldsymbol{u}^{BC} = \sum_{i\in\text{cell}} \boldsymbol{v}_i$$

MD→CFD Boundary condition

- Discrete molecules

$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i \text{ for all i in N}$$



O'Connell Thompson (1995), Flekkoy (2000), Nie et al (2004), ***Smith et al (2012), Smith et al (2015)***

The Control Volume Functional

- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

$$\vartheta_i \equiv \int_{x^-}^{x^+}\int_{y^-}^{y^+}\int_{z^-}^{z^+} \delta(x_i - x)\delta(y_i - y)\delta(z_i - z)dxdydz$$

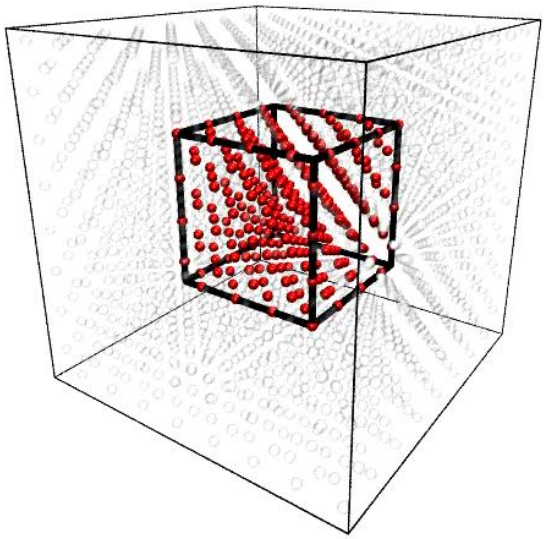
$$= \left[H(x^+ - x_i) - H(x^- - x_i)\right]$$

$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- In words

$$\vartheta \equiv \begin{cases} 1 & \text{if molecule is inside volume} \\ 0 & \text{if molecule is outside volume} \end{cases}$$



Derivative yields surface fluxes and stresses

- Taking the Derivative of the CV function

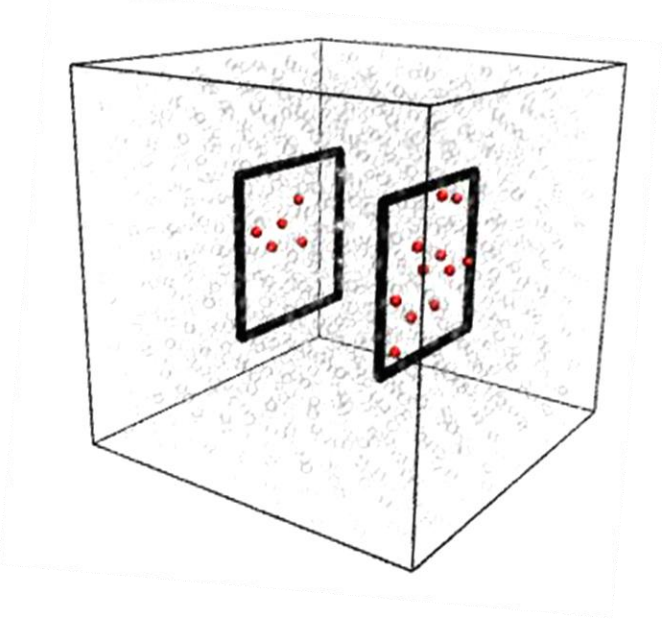
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

$$d\mathbf{S}_i = \boldsymbol{i} dS_{xi} + \boldsymbol{j} dS_{yi} + \boldsymbol{k} dS_{zi}$$

- Or in words

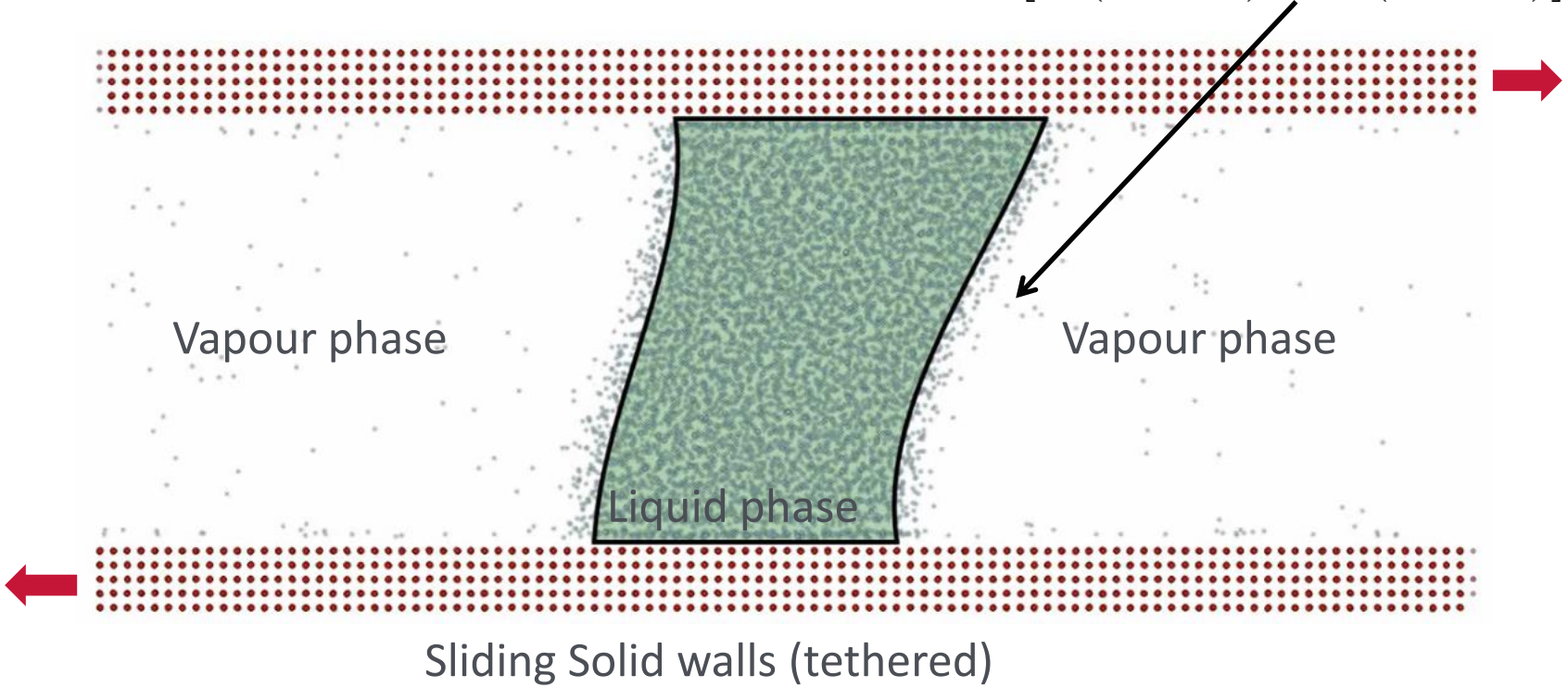
$$d\mathbf{S}_i \equiv \begin{cases} \infty & \text{if molecule on surface} \\ 0 & \text{otherwise} \end{cases}$$



Moving liquid-vapour interfaces

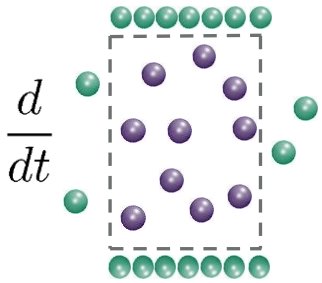
- Derivative now includes terms for moving surface, curvature, etc

$$dS_{xi}^{+} = \left[\dot{x} - \dot{x}_i + \dot{y}_i \frac{\partial \xi^{+}}{\partial y_i} + \dot{z}_i \frac{\partial \xi^{+}}{\partial z_i} + \frac{\partial \xi^{+}}{\partial t}\right] \delta\left(x^{+} + \xi^{+} - x_i\right) \times \left[H\left(y^{+} - y_i\right) - H\left(y^{-} - y_i\right)\right] \times \left[H\left(z^{+} - z_i\right) - H\left(z^{-} - z_i\right)\right]$$



Constrained Control Volume

- Apply force to ensure all forces and fluxes are controlled to agree with the continuum



$$\frac{d}{dt} = \frac{d}{dt}\int_V \rho \boldsymbol{u} dV$$