Imperial College London

Brunel University London

Molecular Structure at an Interface

By Edward Smith

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Brunel University London

Brunel Centre for Advanced Solidification Technology

Experimental Techniques Centre

A Research-Focused Engineering University

Continuum Methods

Classical Molecular

Quantum

MATERIALS AND MOLECULAR MODELLING HUB

Overview

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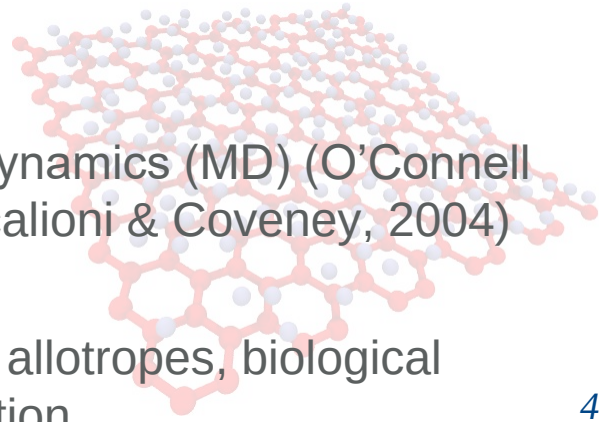
- Molecular Structure at the Interface
  - A local region containing molecular detail
  - Coupling to a (cheaper) model for the remaining domain
- A Coupling Framework
  - Eulerian control volumes and molecular stress
  - Extension to general interfaces
- Some Examples of Coupled Interfaces
  - Using molecular detail at the interface
  - Limits of the classical picture

Motivation

- Modern engineering problems require sub-continuum models
  - Quantum mechanics is limited to very small systems
  - Even molecular dynamics is prohibitively expensive
  - Multi-scale coupling overcomes these limitations by linking to cheaper methods

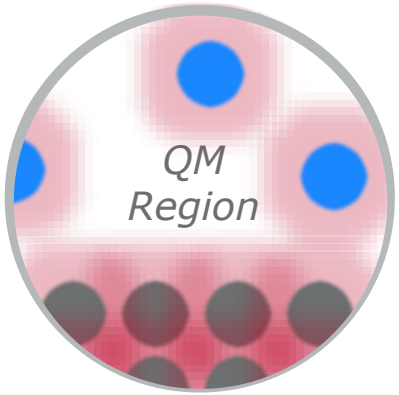
- Multi-scale coupling has been employed since the 1970's (Curtin & Miller 2003) in solid mechanics modelling (*e.g.* for crack tips)
  - Essential to capture detail in the crack itself and the impact on the wider system
  - Continuum ←→ Molecular mechanics (MM) ←→ Quantum mechanics (QM)

- Classical coupling for fluids is less mature
  - Computational fluid dynamics (CFD) ←→ Molecular dynamics (MD) (O'Connell & Thompson 1995, Flekkøy et al 2000, Delgado-Buscalioni & Coveney, 2004)
  - Linking CFD ←→ MD ←→ QM is a natural next step
  - Important for *e.g.* nucleation events, flow over carbon allotropes, biological systems, electronics, chemical reactions and combustion



Motivation

- Long term goal is to seamlessly link various scales of modelling
  - Fine/coarse graining as required based on the problem of interest
  - Dynamic resource allocation and load balancing on multi-core architectures



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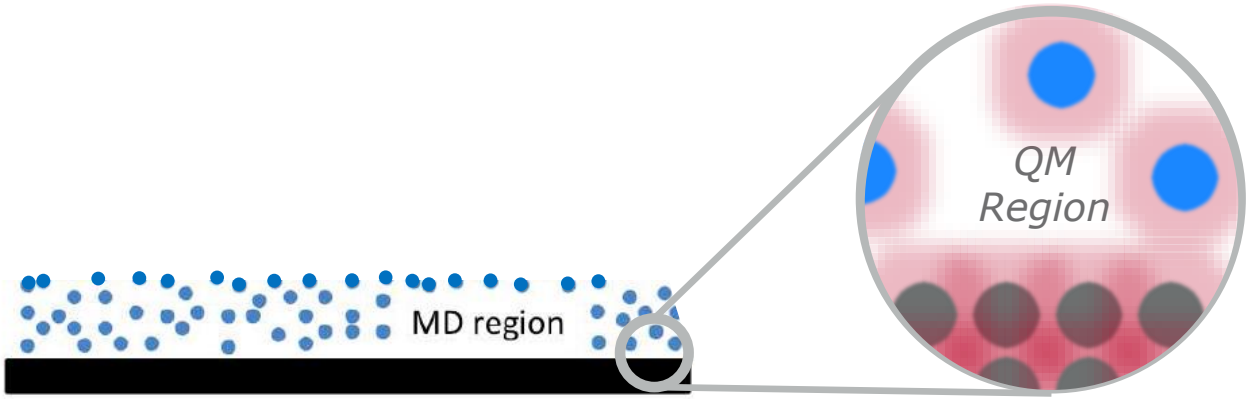

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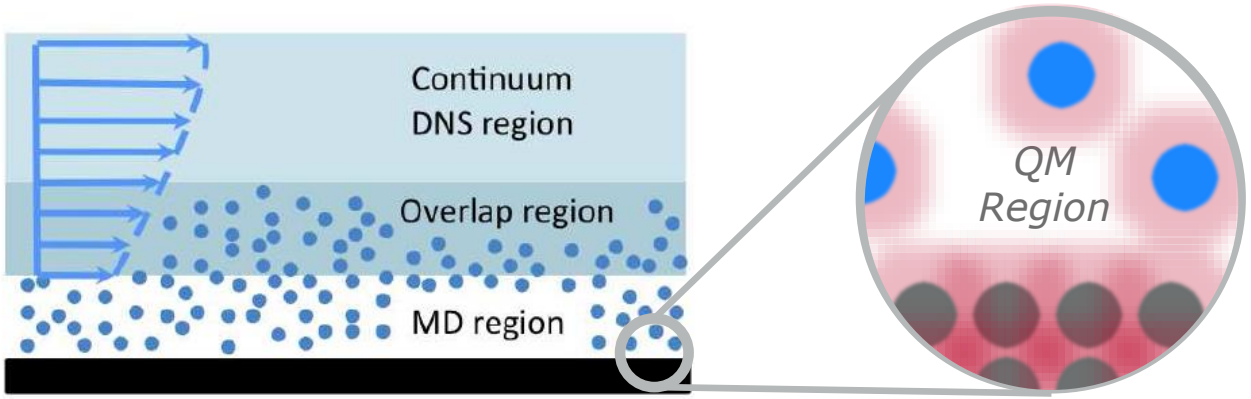

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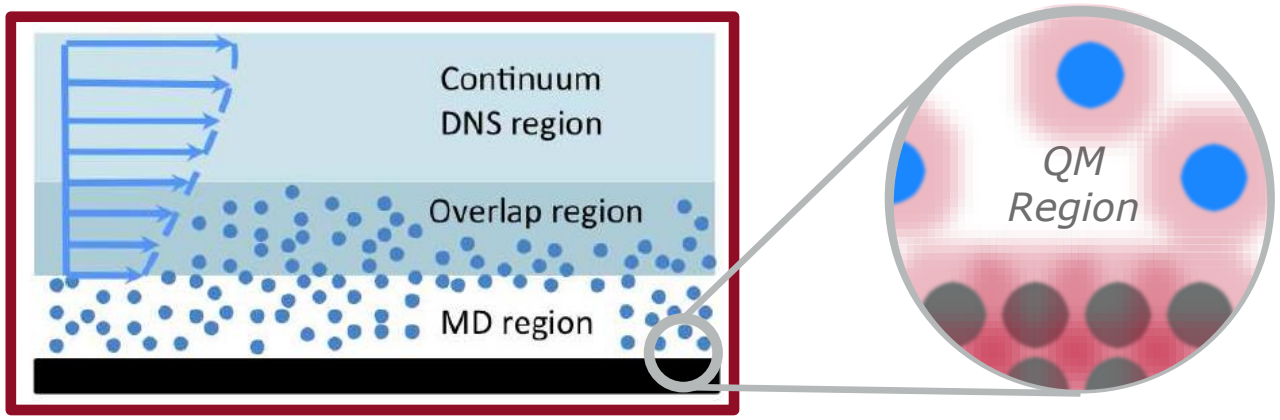
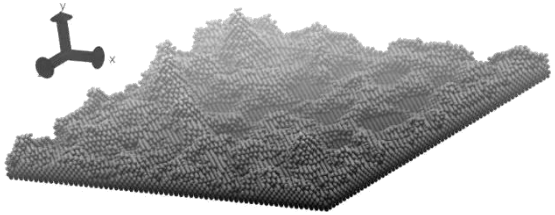


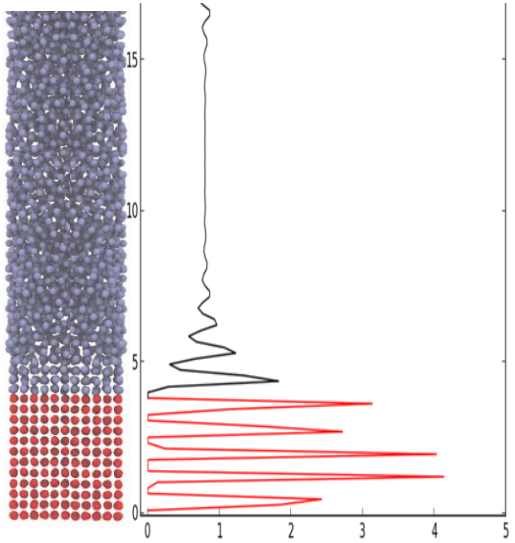
- Reduce the problem to one of modelling the interface with molecules
  - The material surface covered in liquid OR a liquid-vapour interface



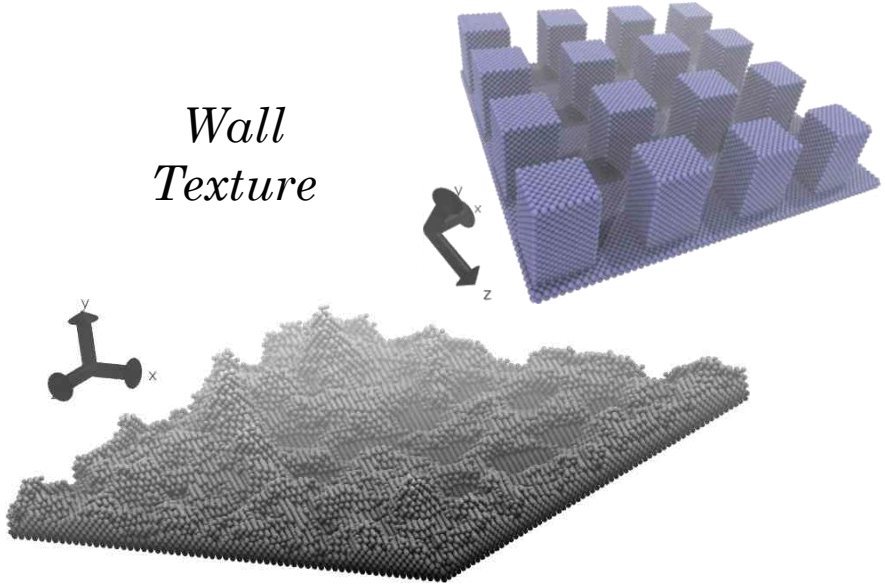
Solid-Liquid Interfaces

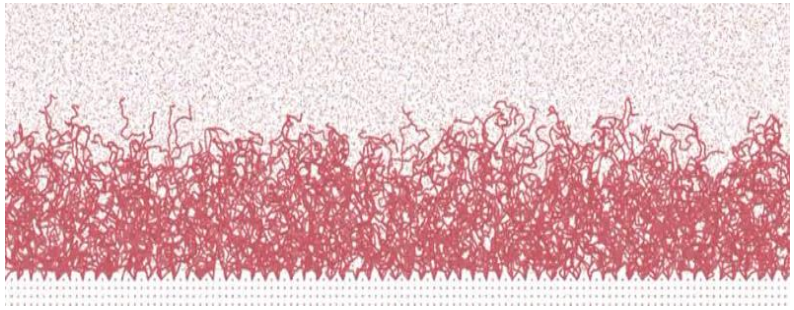
Liquid structure causes viscosity

Stick-slip near walls

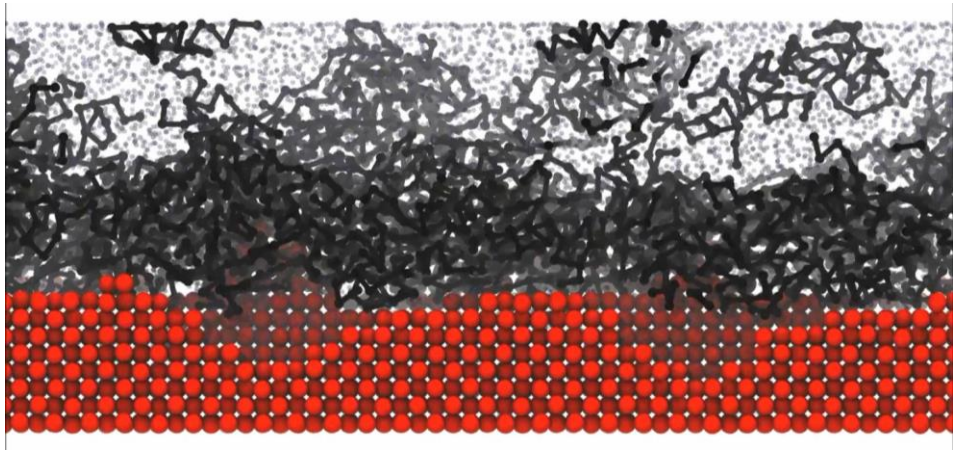


Wall Texture





Polymer Brushes/Coating



Oil, water and textured surface

Classical Molecular Dynamics

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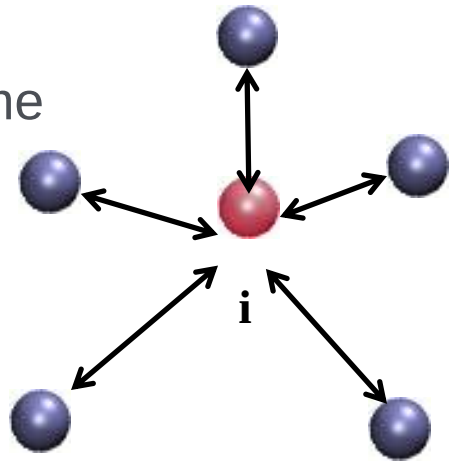
Discrete molecules in continuous space

- Molecular position evolves continuously in time
- Position and velocity from acceleration

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

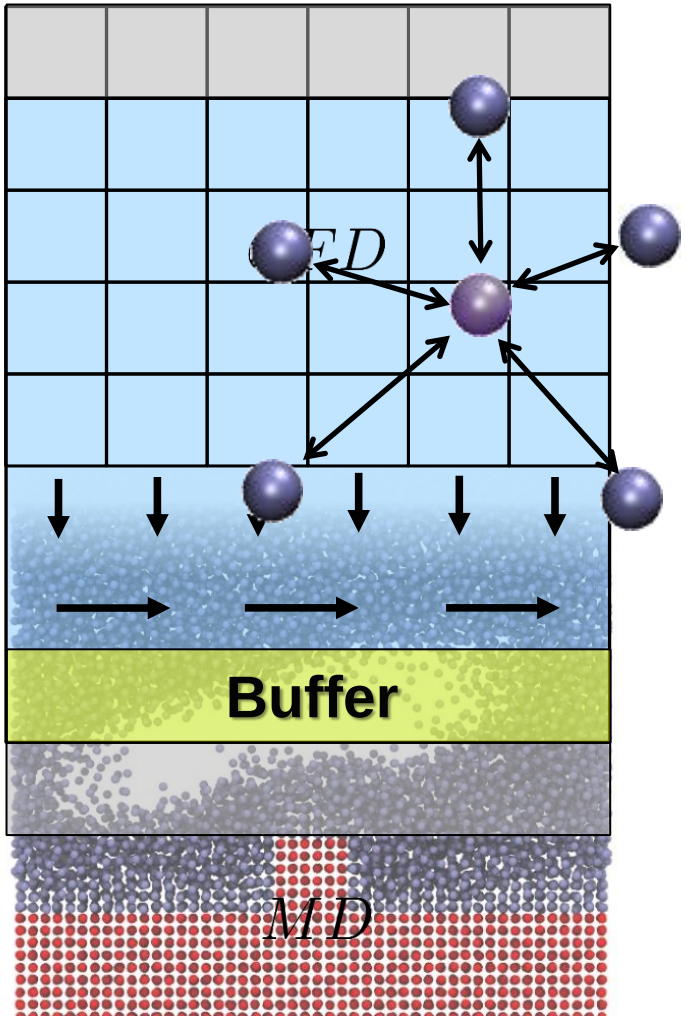


Acceleration obtained from classical forces

- Newton's law for an N-body system in own solver called "Flowmol"
- Point particles Lennard-Jones interactions (SAFT γ Mie extension)

$$m_i\ddot{\mathbf{r}}_i = \mathbf{F}_i = \sum_{i\neq j}^{N} \boldsymbol{f}_{ij} = \sum_{i\neq j}^{N} \boldsymbol{\nabla}\Phi_{ij} \qquad \Phi(r_{ij}) = 4\epsilon\left[\left(\frac{\ell}{r_{ij}}\right)^{12} - \left(\frac{\ell}{r_{ij}}\right)^{6}\right]$$

Coupled To Continuum Equations



Coupled To Continuum Equations

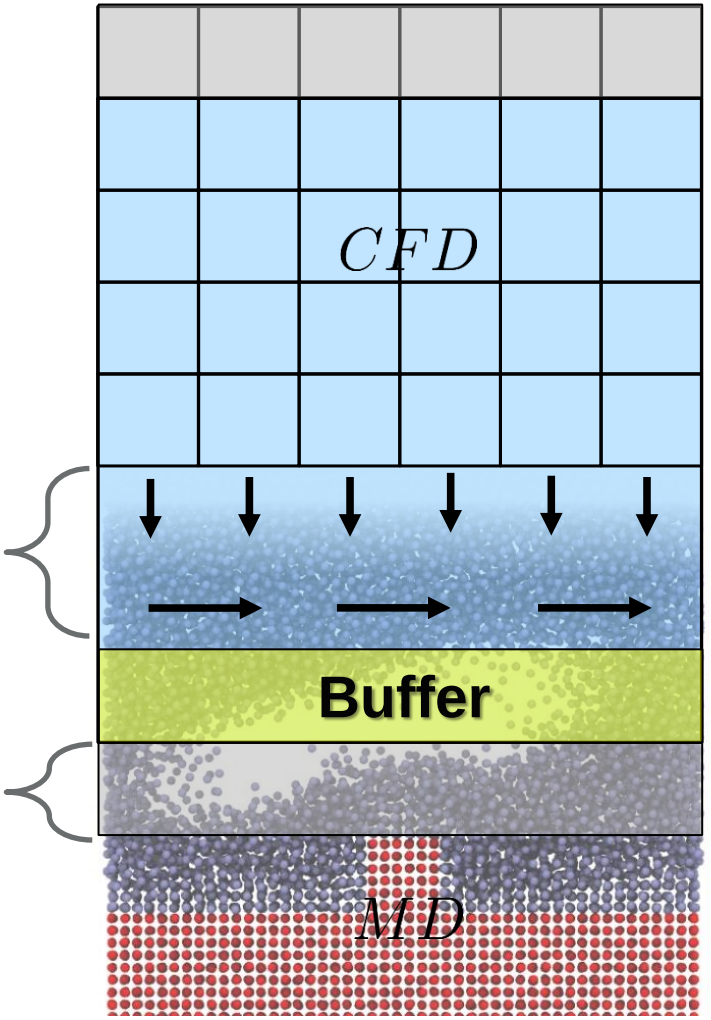
- Computational Fluid Dynamics

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

- No Hamiltonian, use Newton's law

CFD→MD Boundary condition

MD→CFD Boundary condition



A Coupling Framework

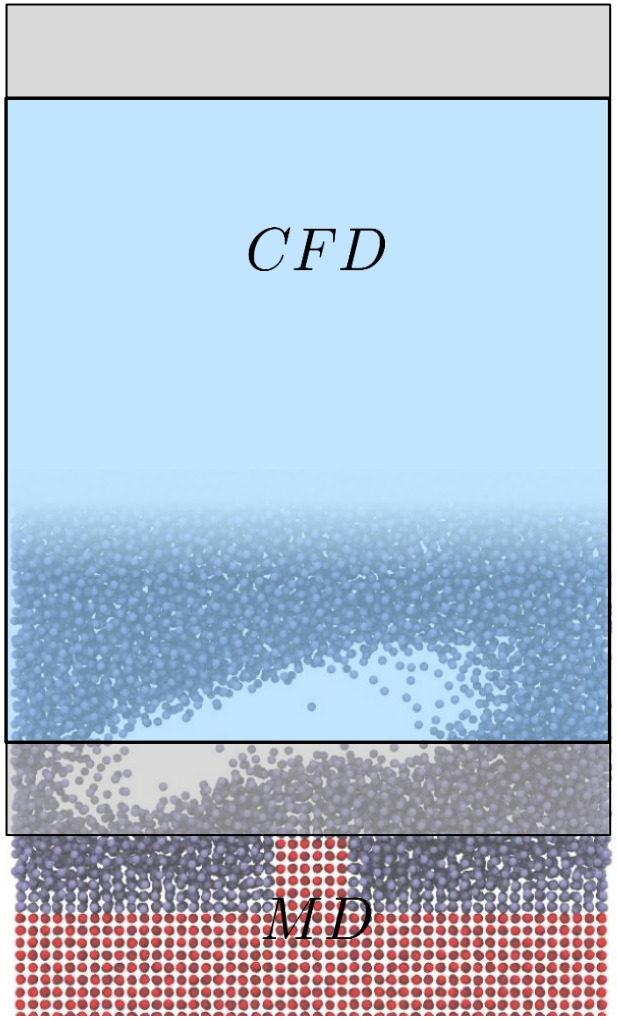
- Continuum Region, density at a point

$$\rho(\boldsymbol{r}, t)$$

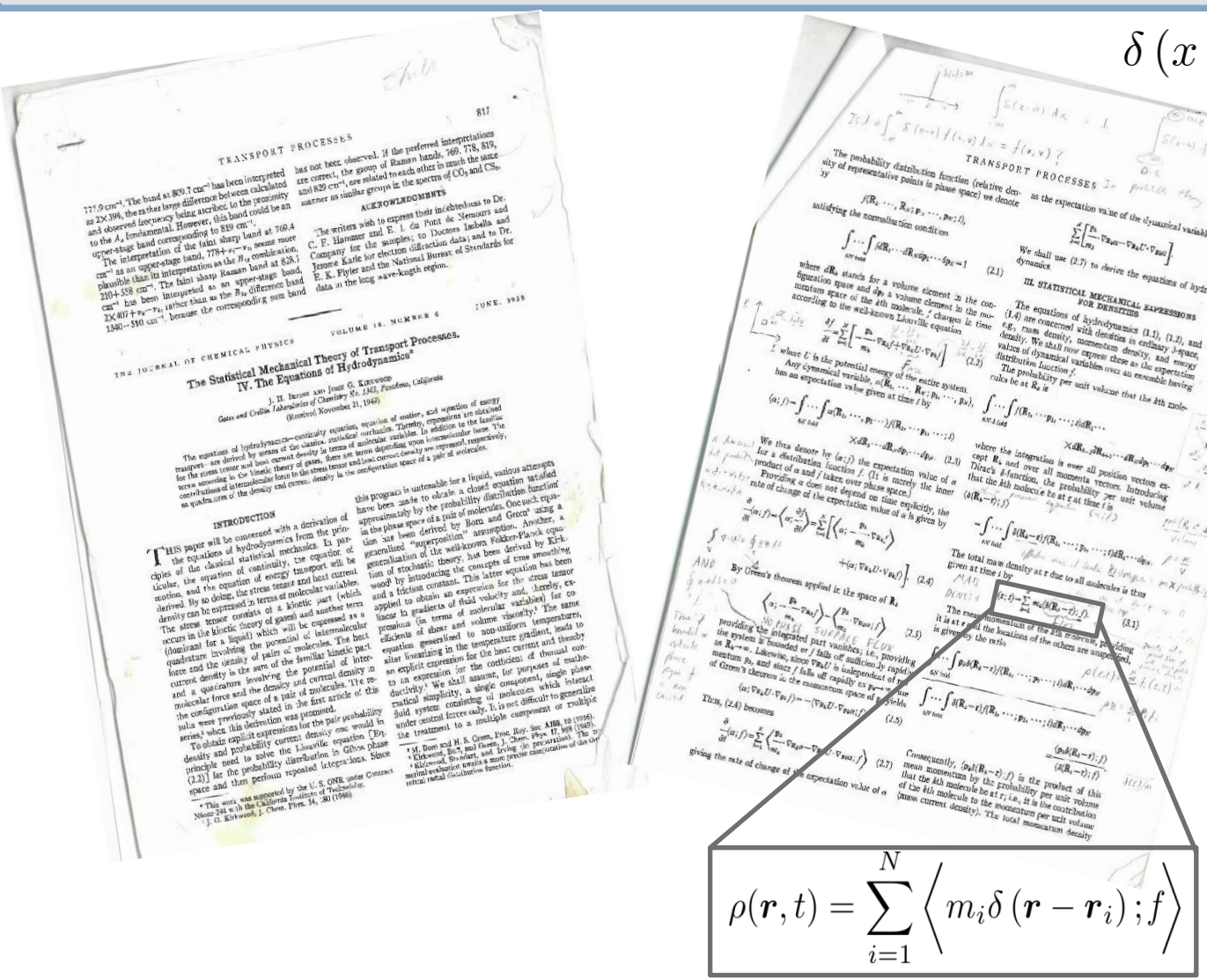
Share the same **time** and **length** scales

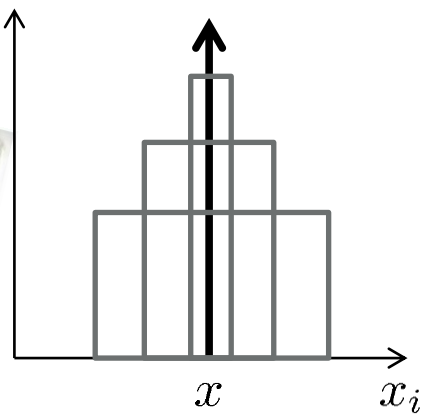
- Discrete molecules

$$m_i \text{ for all i in N}$$



Irving and Kirkwood (1950)





The Dirac delta infinitely high, infinitely thin peak formally equivalent to the continuum differential formulation

$$\rho(\boldsymbol{r},t) = \sum_{i=1}^{N} \left\langle m_i \delta(\boldsymbol{r} - \boldsymbol{r}_i); f \right\rangle$$

The Control Volume (Weak) Form

- The “weak formulation” expresses the equations in integrated form

$$\int_V \rho(\boldsymbol{r},t)dV = \sum_{i=1}^{N} m_i \int_V \delta\left(\boldsymbol{r}-\boldsymbol{r}_i\right) dV$$

- Integrating the Dirac delta function exactly provides a combination of Heaviside functions

- This turns out to have some nice properties

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)

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

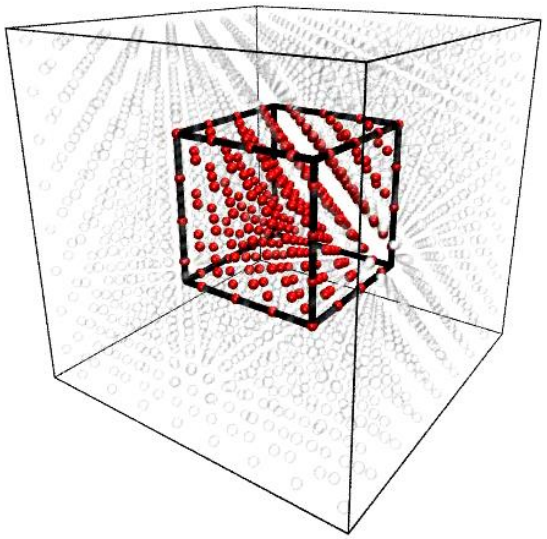
$$= \left[H(x^+ - x_i) - H(x^- - x_i)\right]$$

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

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

- In words

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



Derivative is surface fluxes and stresses

- Taking the Derivative of the CV function

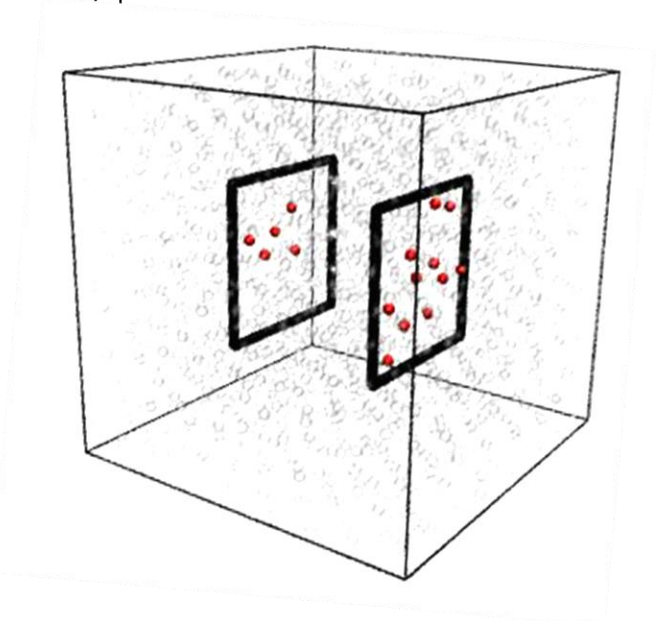
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- Vector form defines six surfaces

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

- Or in words

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



Pressure (Stress)

- Pressure is the key molecular quantity to couple to larger scales
- Pressure is simply the negative of stress (in fluids we typically have a larger thermal component and subtract fluids flow)

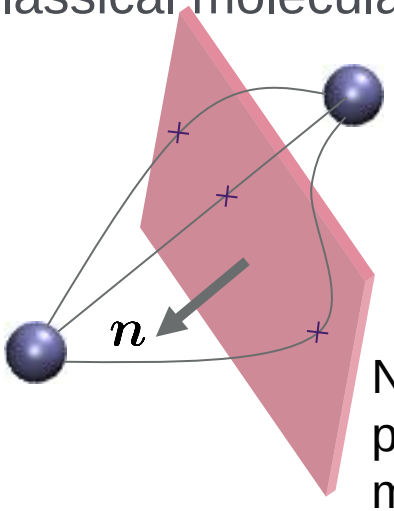
$$\boldsymbol{P} = -\boldsymbol{\sigma}$$

- The stress is known to be non-unique in classical molecular systems

Statistical mechanics of inhomogeneous fluids

By P. Schofield† and J. R. Henderson‡

$$\sigma_C^{\alpha\beta}(\boldsymbol{R},t) = \sum_i [\nabla_i^\alpha \Phi(\{\boldsymbol{r}_i\})] \oint_{C_{0l}} \mathrm{d}l^\beta \, \delta(\boldsymbol{R}-\boldsymbol{l}).$$



No unique interaction path

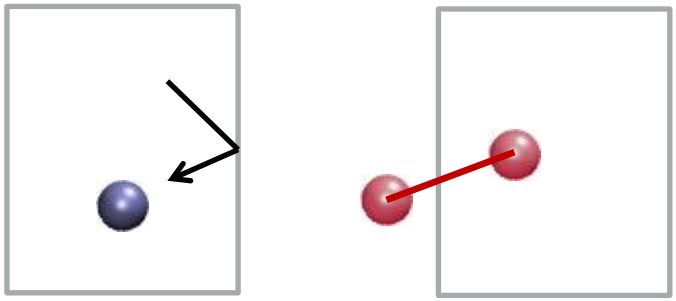
No unique plane of measurement

Pressure (Stress)

- This integrated volume gives a surface definition of stress
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

$$P_{xy} = \underbrace{\sum_{i=1}^{N} \left\langle m_i \dot{y}_i dS_{ix} \right.}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{j \neq i}^{N} \left. f_{ijy} dS_{ijx} \right\rangle}_{\text{Configurational}}$$

Kinetic theory part
Momentum due to molecules crossing a surface and returning



Closed volume – any contour must cross a surface

Configurational part
Inter-molecular bonds over the surface of the box

Coupled Simulation

- Control (Finite) Volume form

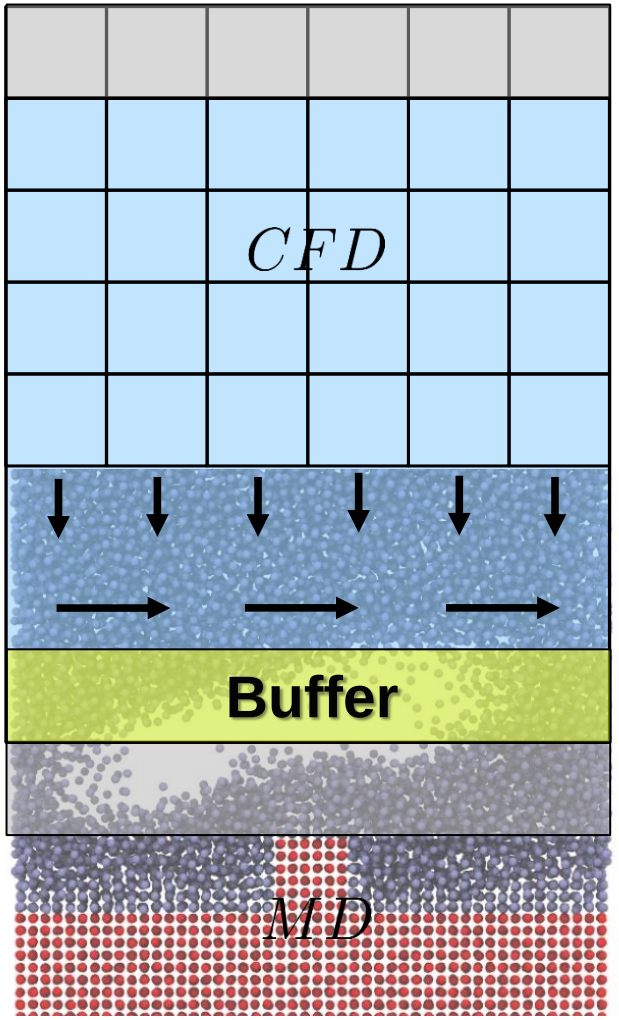
$$\frac{\partial}{\partial t}\int_V \rho \boldsymbol{u} dV = -\oint_S \rho \boldsymbol{u}\boldsymbol{u}\cdot d\mathbf{S} - \oint_S \boldsymbol{P}\cdot d\boldsymbol{S}$$

$$m_i \ddot{\boldsymbol{r}}_i = \mathbf{F}_i + \mathbf{F}_i^C \vartheta_i$$

CFD→MD Boundary condition

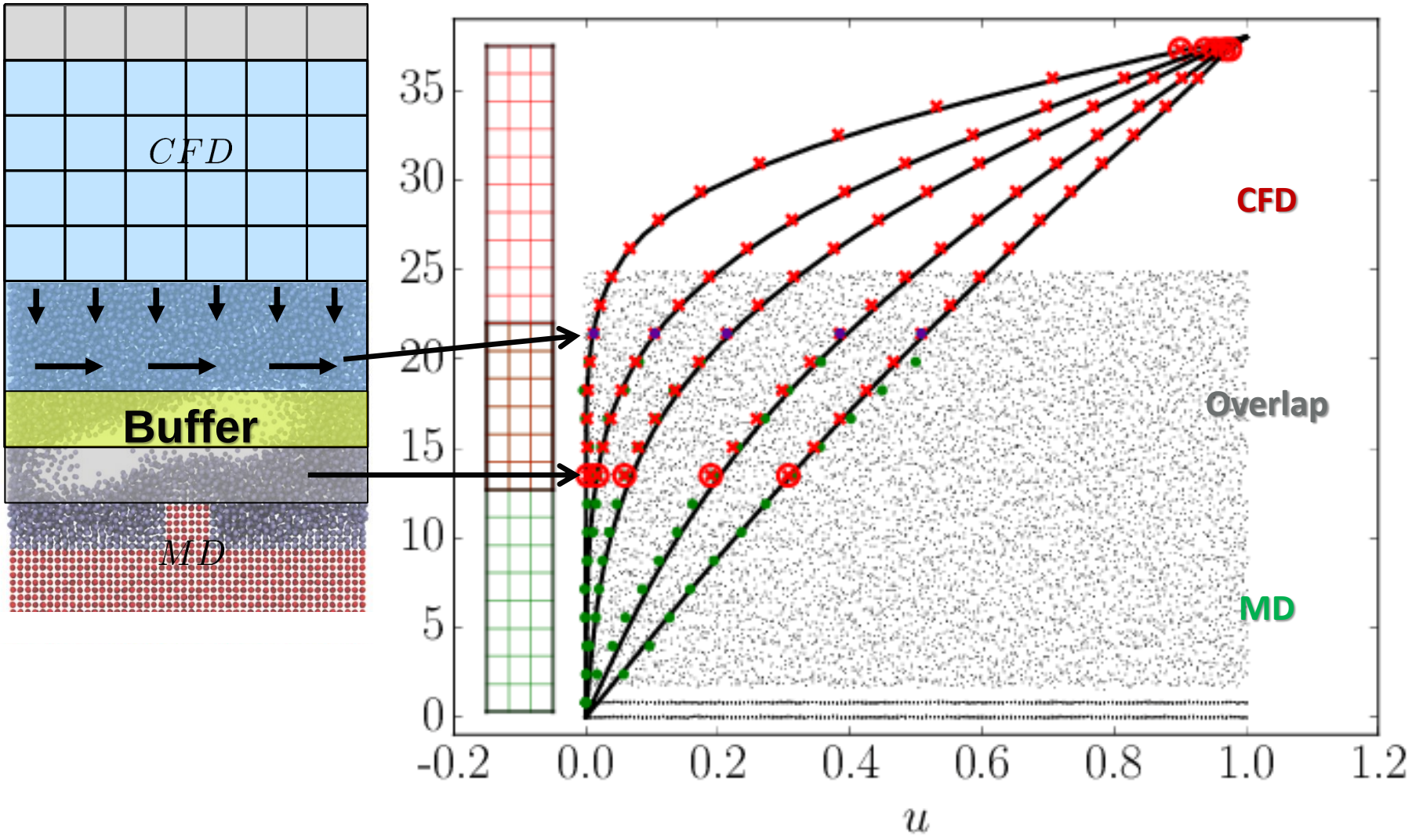
$$\int_V \boldsymbol{u}^{BC} dV = \sum_{i=1}^{N} \boldsymbol{v}_i \vartheta_i$$

MD→CFD Boundary condition

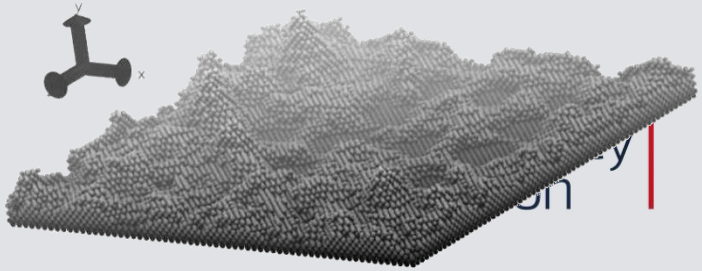


- Both in same Eulerian (fixed) reference

Coupling Results – Sheared (Couette) Flow



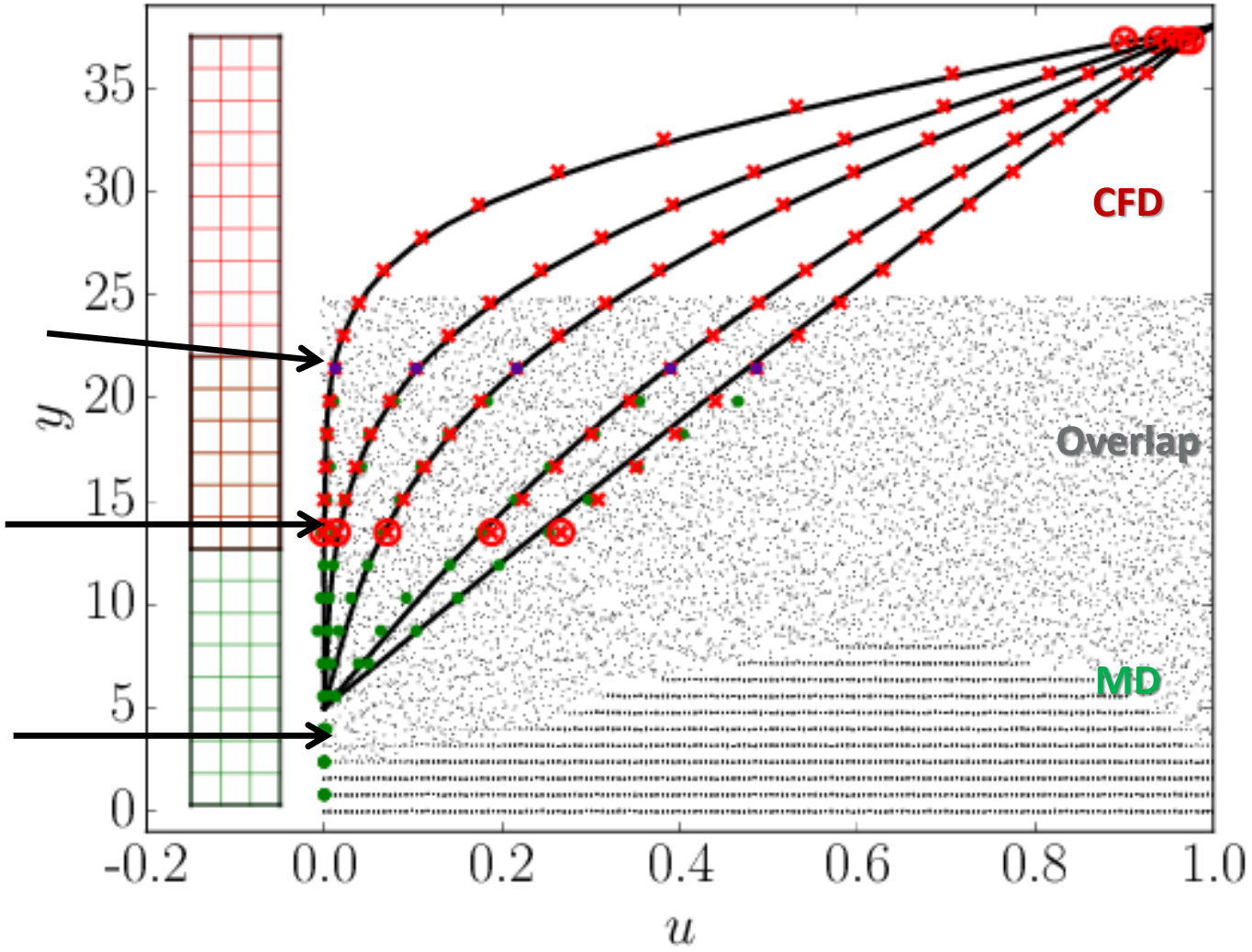
Coupling Results – Couette Flow



Constraint

CFD Boundary

Rough wall shifts zero velocity location



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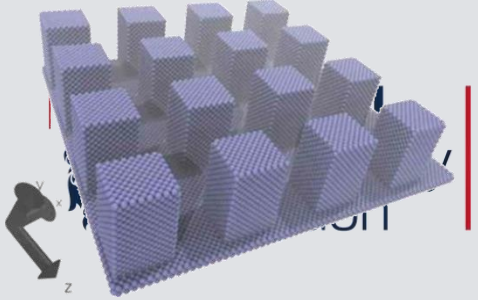


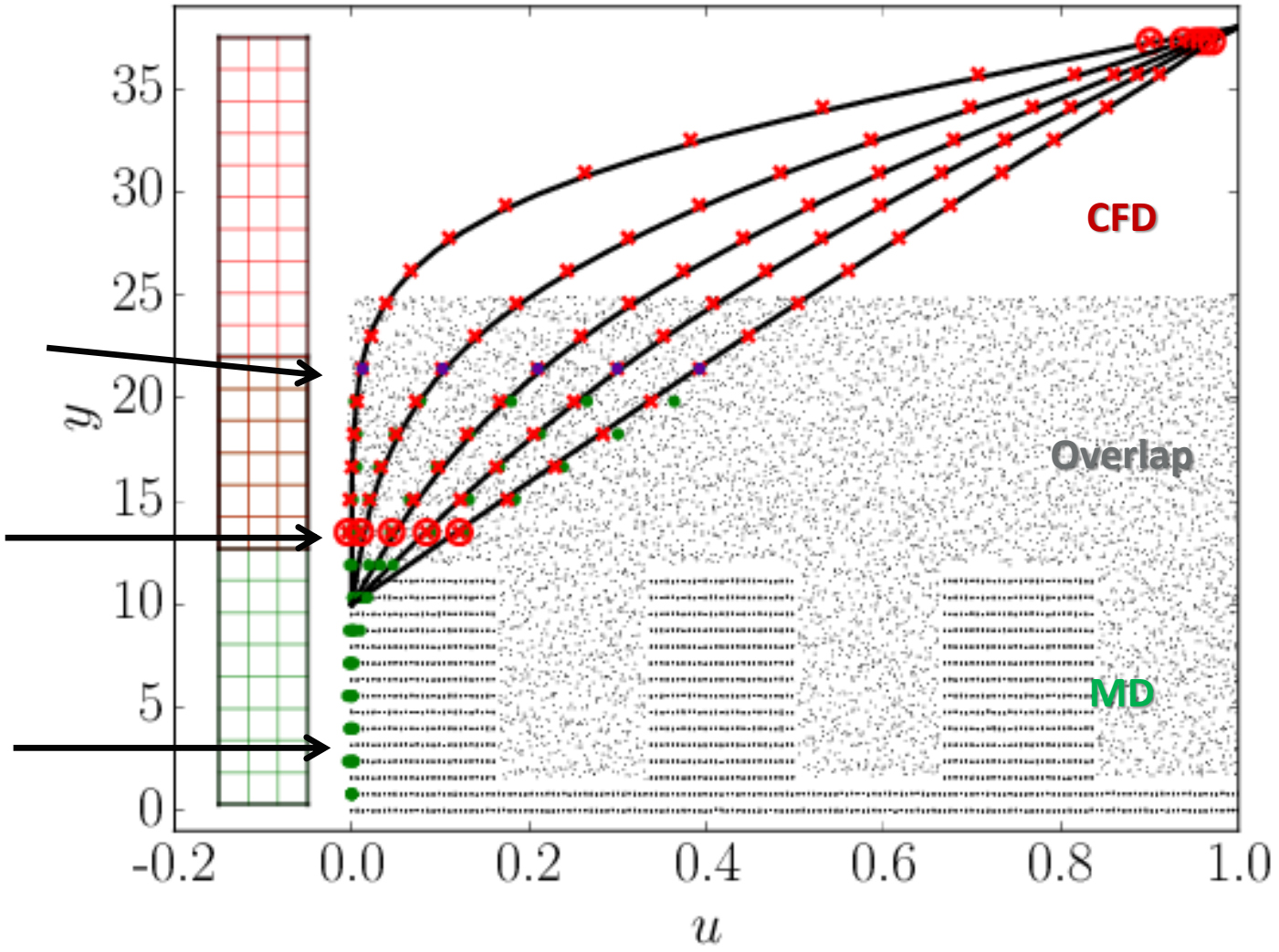
Constraint

CFD Boundary

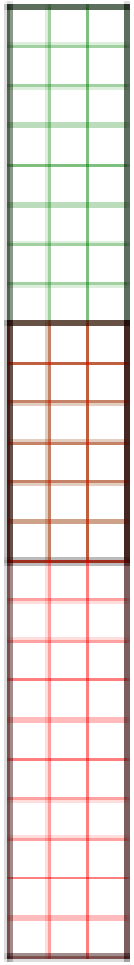
Posts shifts

zero velocity

location



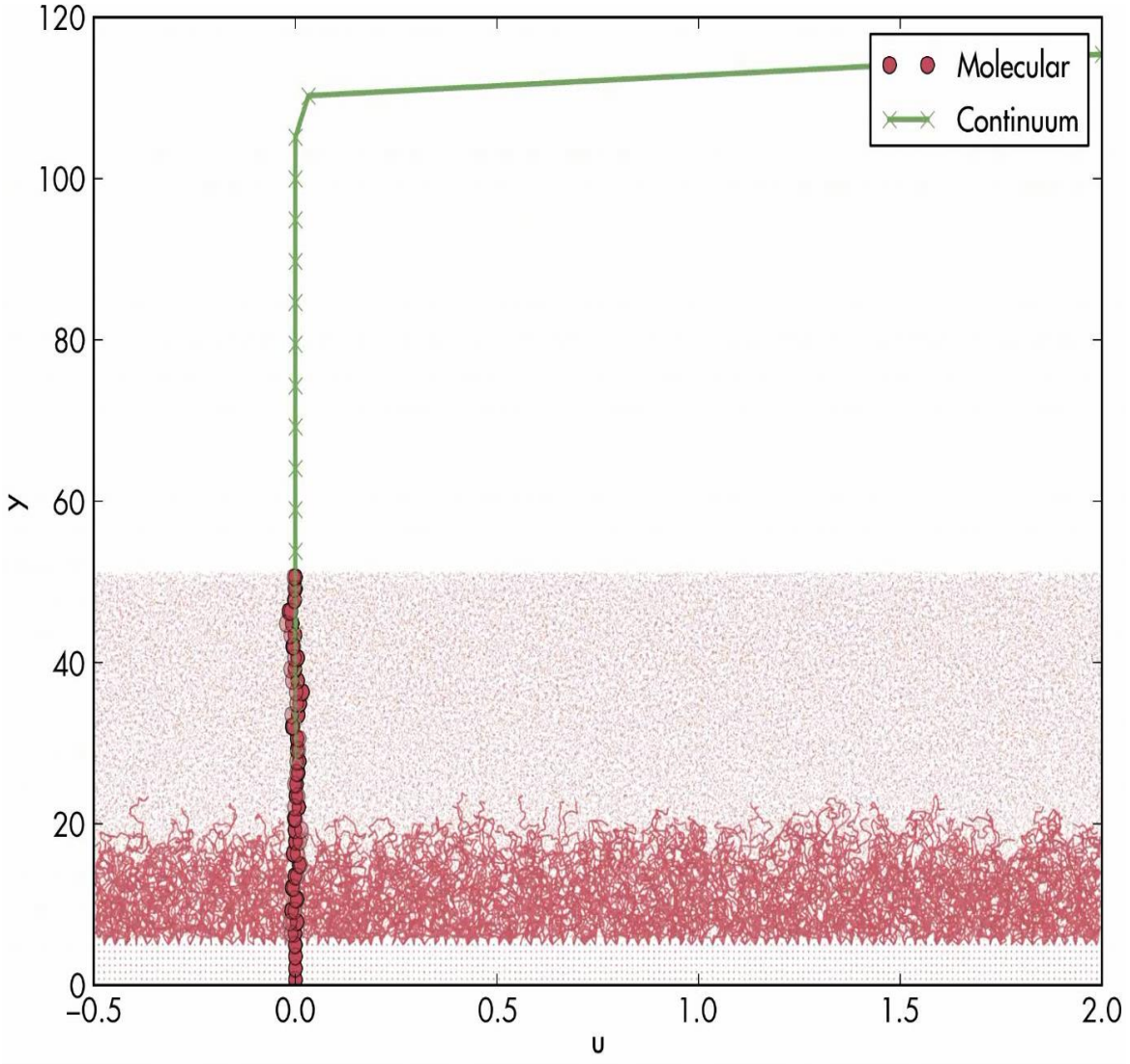
Coupling Results – Polymer Brushes



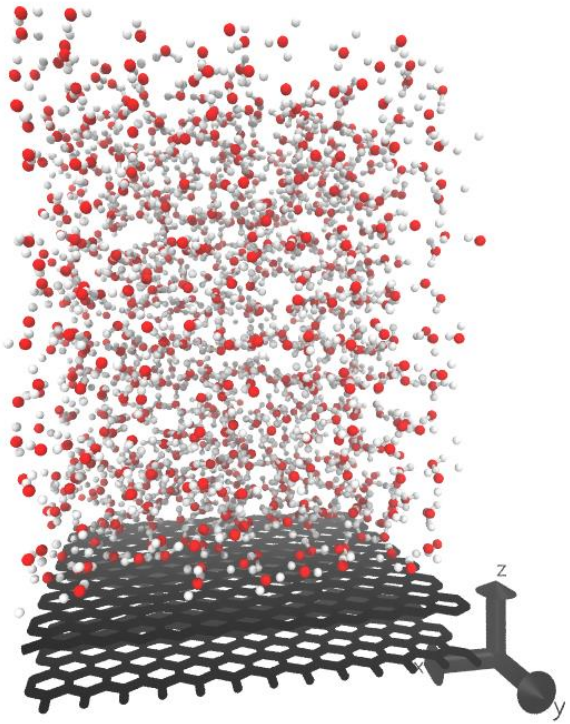
CFD Region

Overlap Region

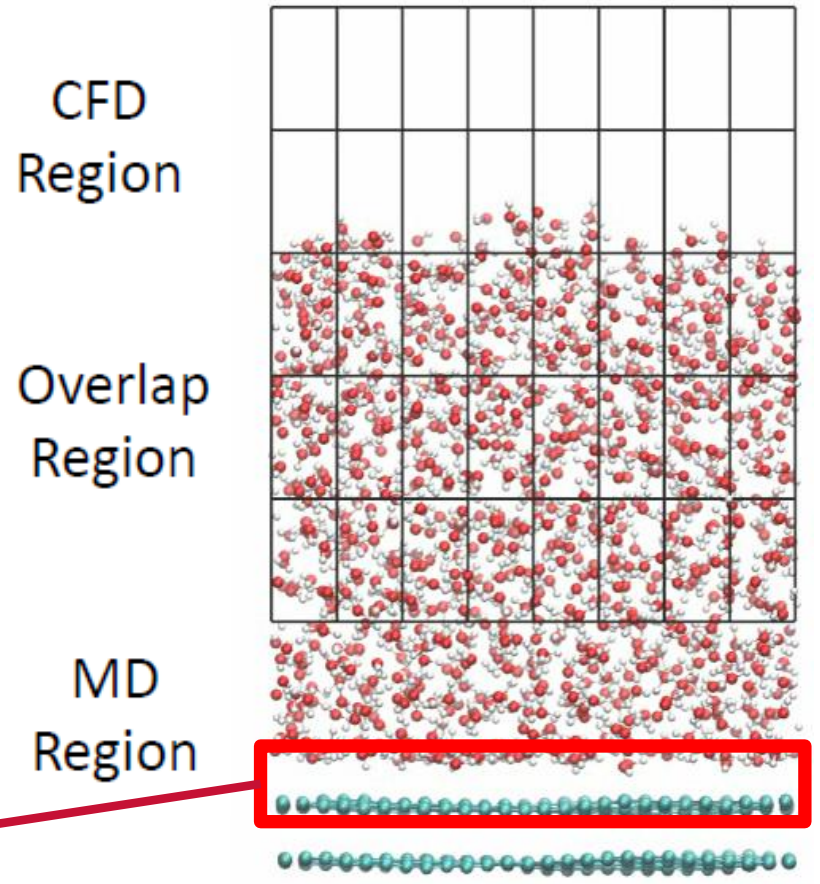
MD Region



Coupling Flow Over Graphene



QM by Maria Clelia Righi and Mauro Ferrario at University of Moderna



- Classical potentials result in slip-length prediction on graphene which vary by orders of magnitudes

Molecular Simulation of Turbulence

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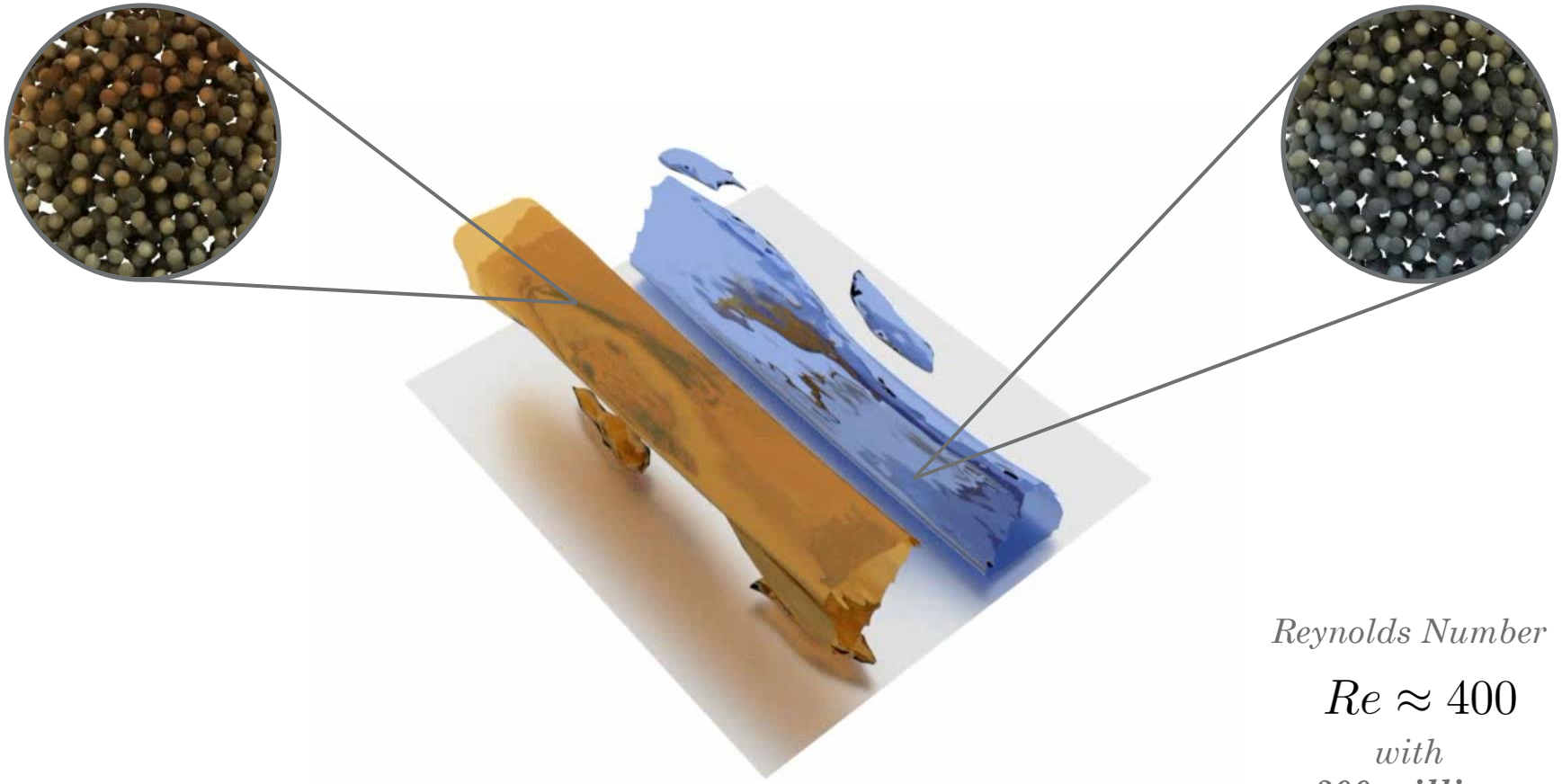


Isosurfaces of turbulent kinetic energy coloured by velocity

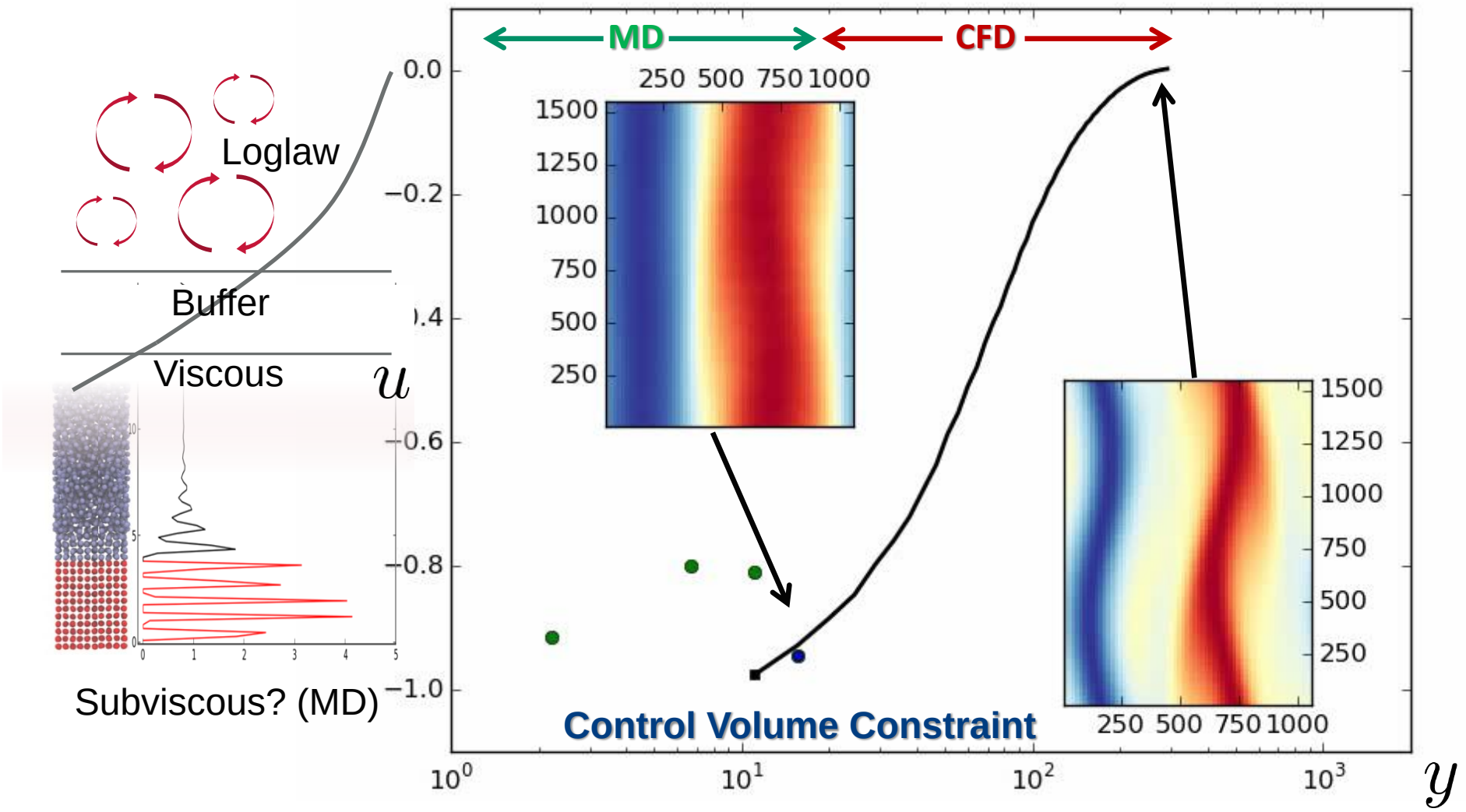
Reynolds Number

$Re \approx 400$

with

300 million molecules

Coupling Results – Turbulent Couette



Liquid-Vapour Interface

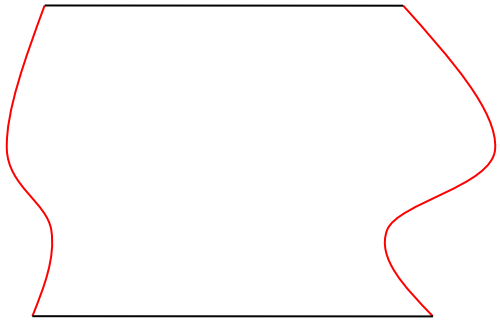
- The Control volume functional is the formal integral of the Dirac delta functional in 3 dimensions (3D top hat or box car function)

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

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

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

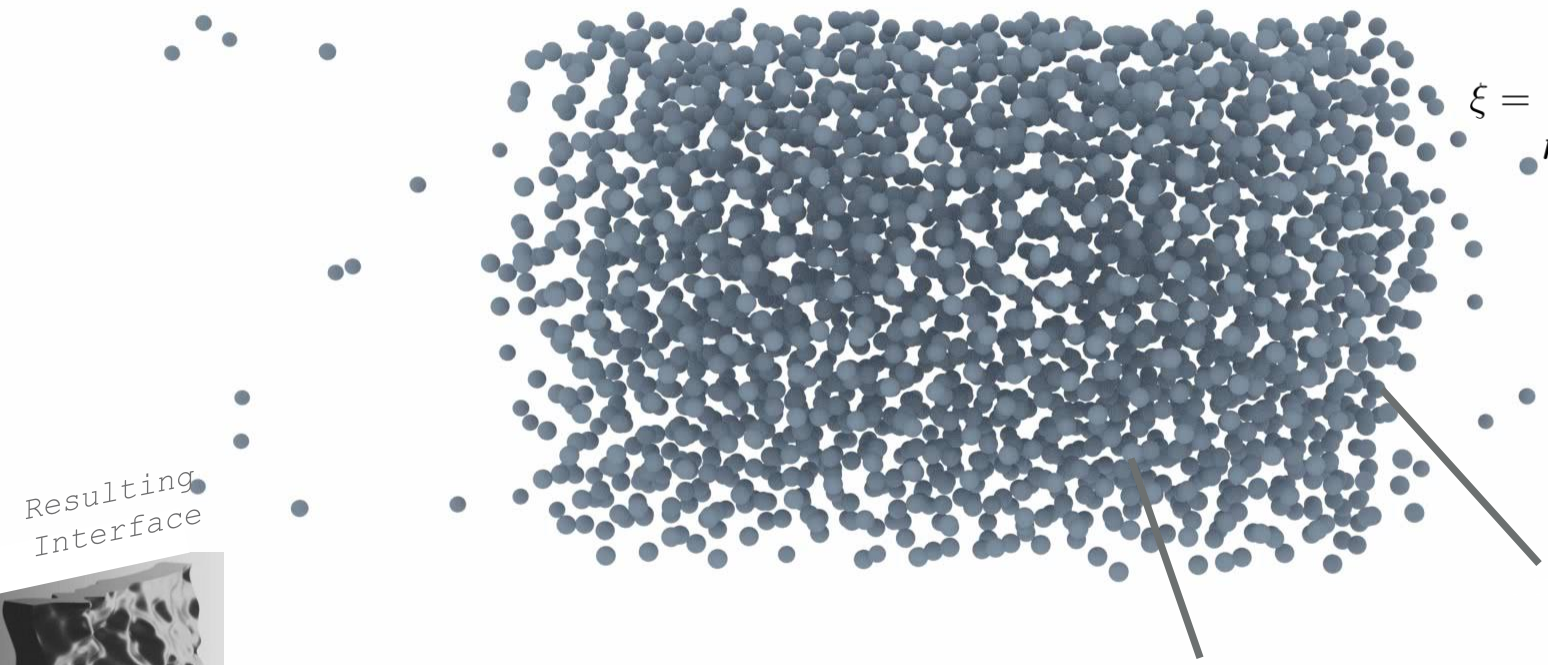
$$\times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$



- In words

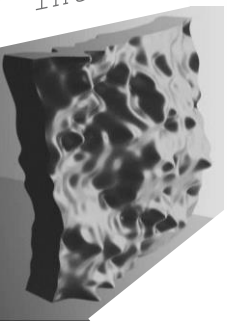
$$\vartheta \equiv \begin{cases} 1 & \text{if molecule is inside volume} \\ 0 & \text{if molecule is outside volume} \end{cases}$$

Liquid-Vapour Interface



$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$

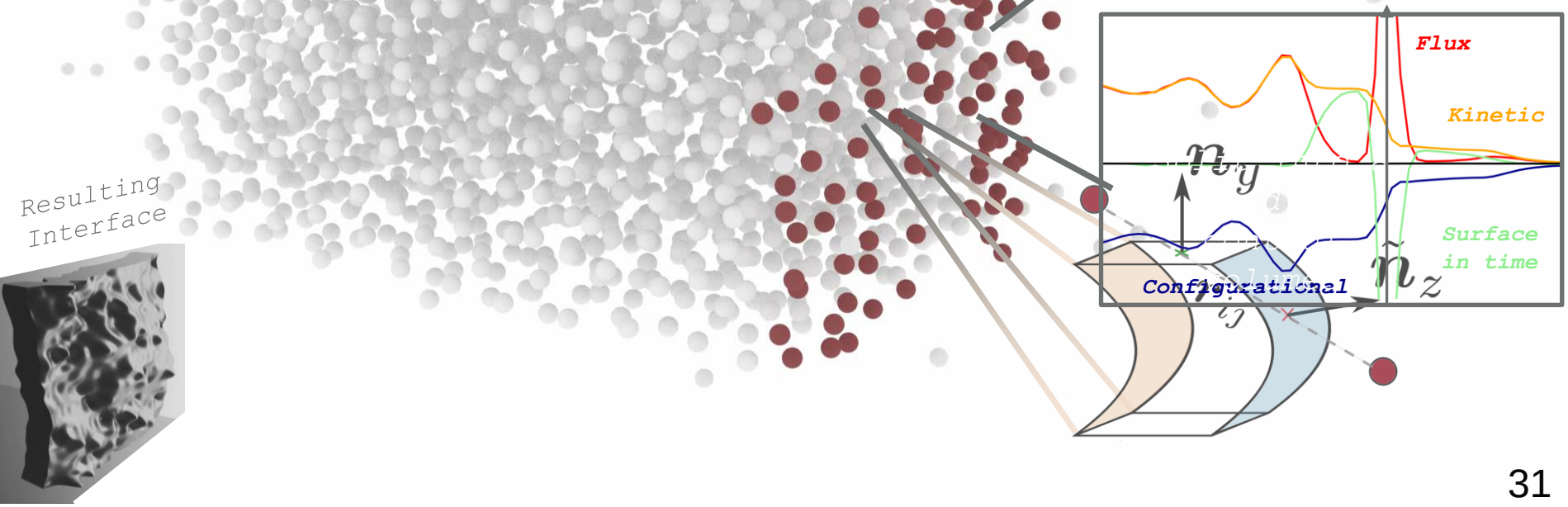
Resulting Interface



Liquid-Vapour Interface

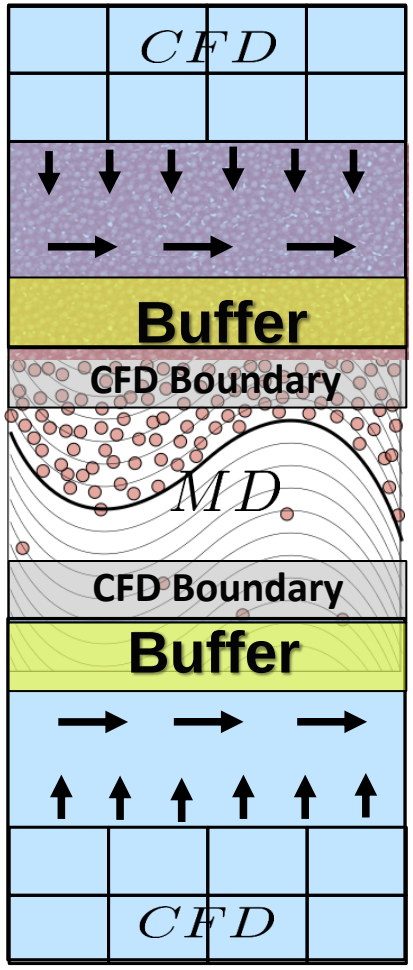
Time evolving Fourier surface fitted

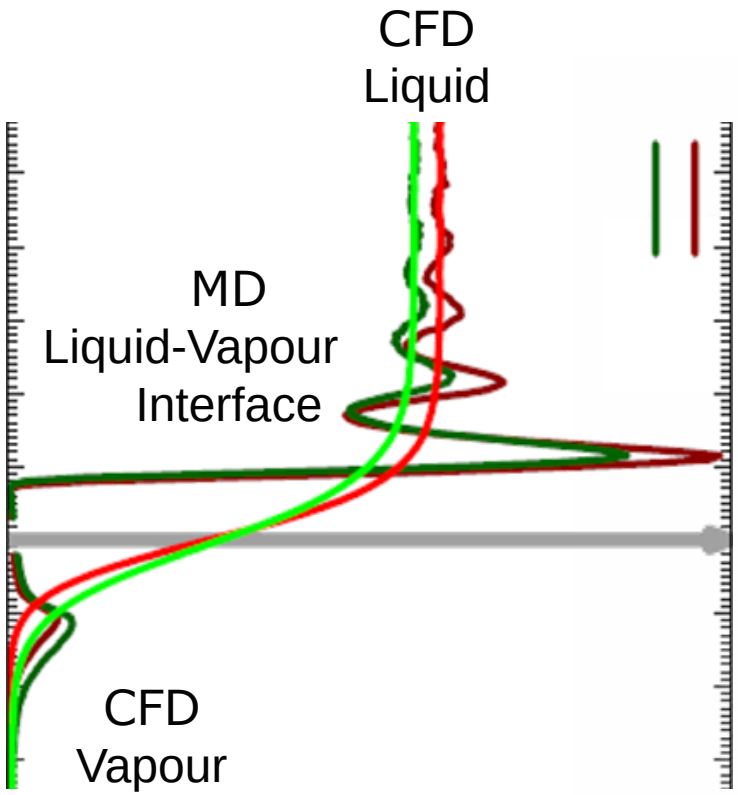
$$\xi = \sum_{\boldsymbol{k}<k_u} \hat{\xi}_{\boldsymbol{k}}(t) e^{2\pi i \boldsymbol{k}\cdot\boldsymbol{r}},$$

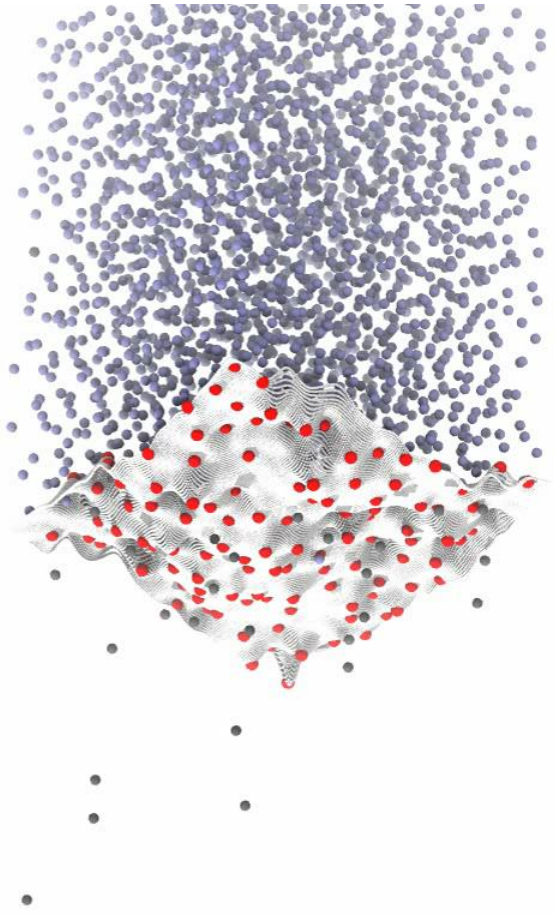


Resulting Interface

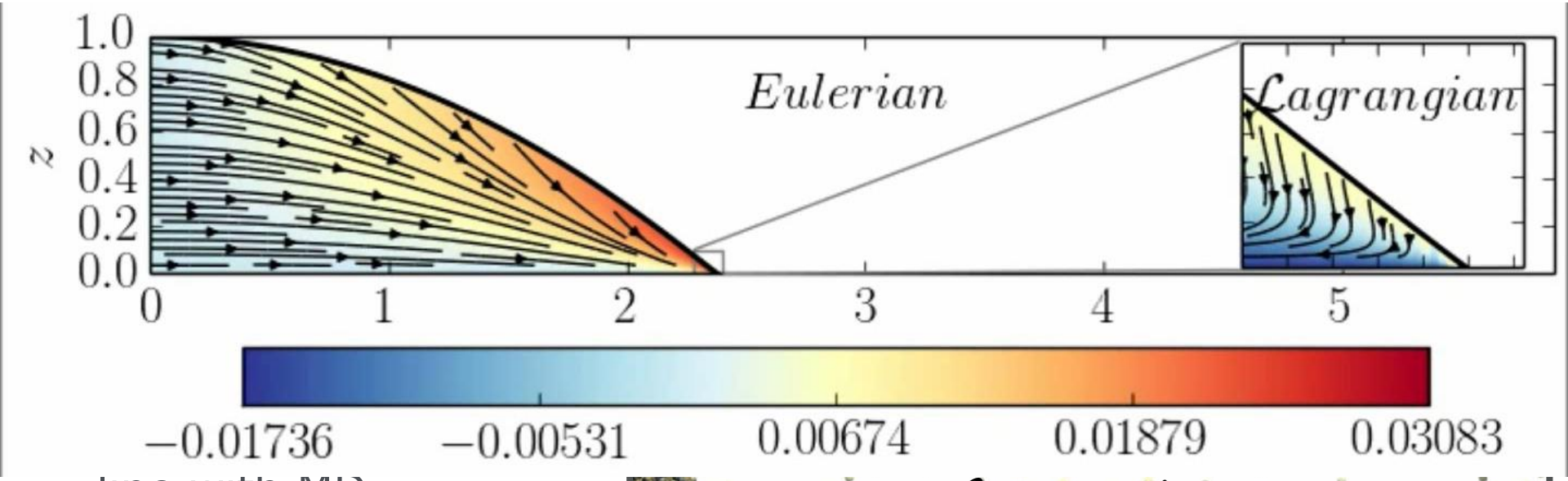
Coupled Simulation of an Interface



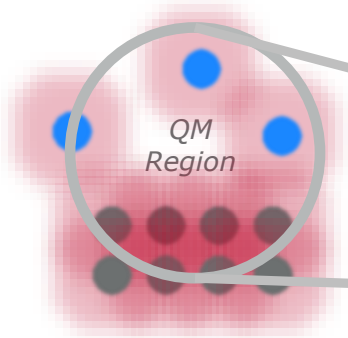


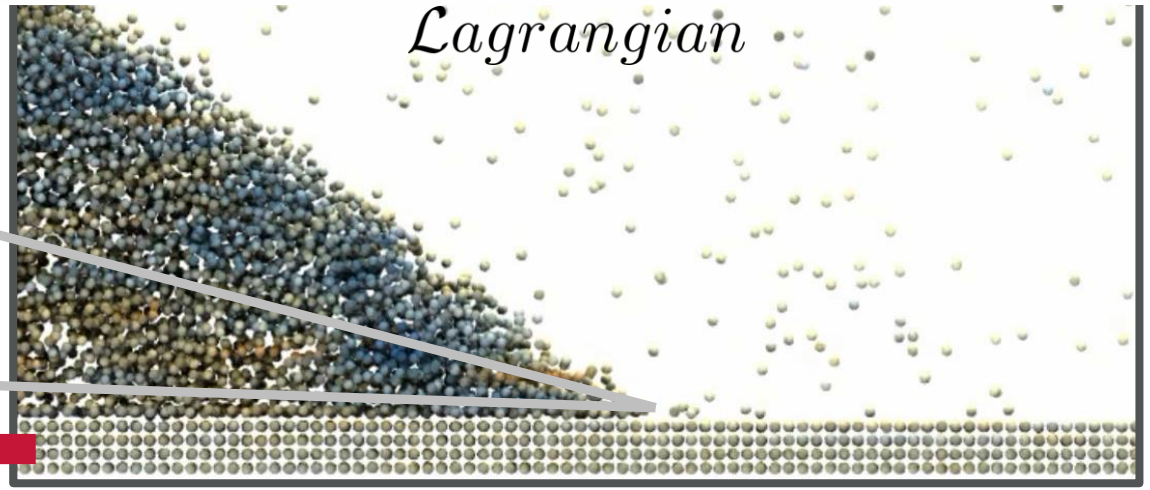


Moving Contact Line



line with MD





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

Molecular simulation of Nucleation

Wall w
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Molecular simulation of Nucleation

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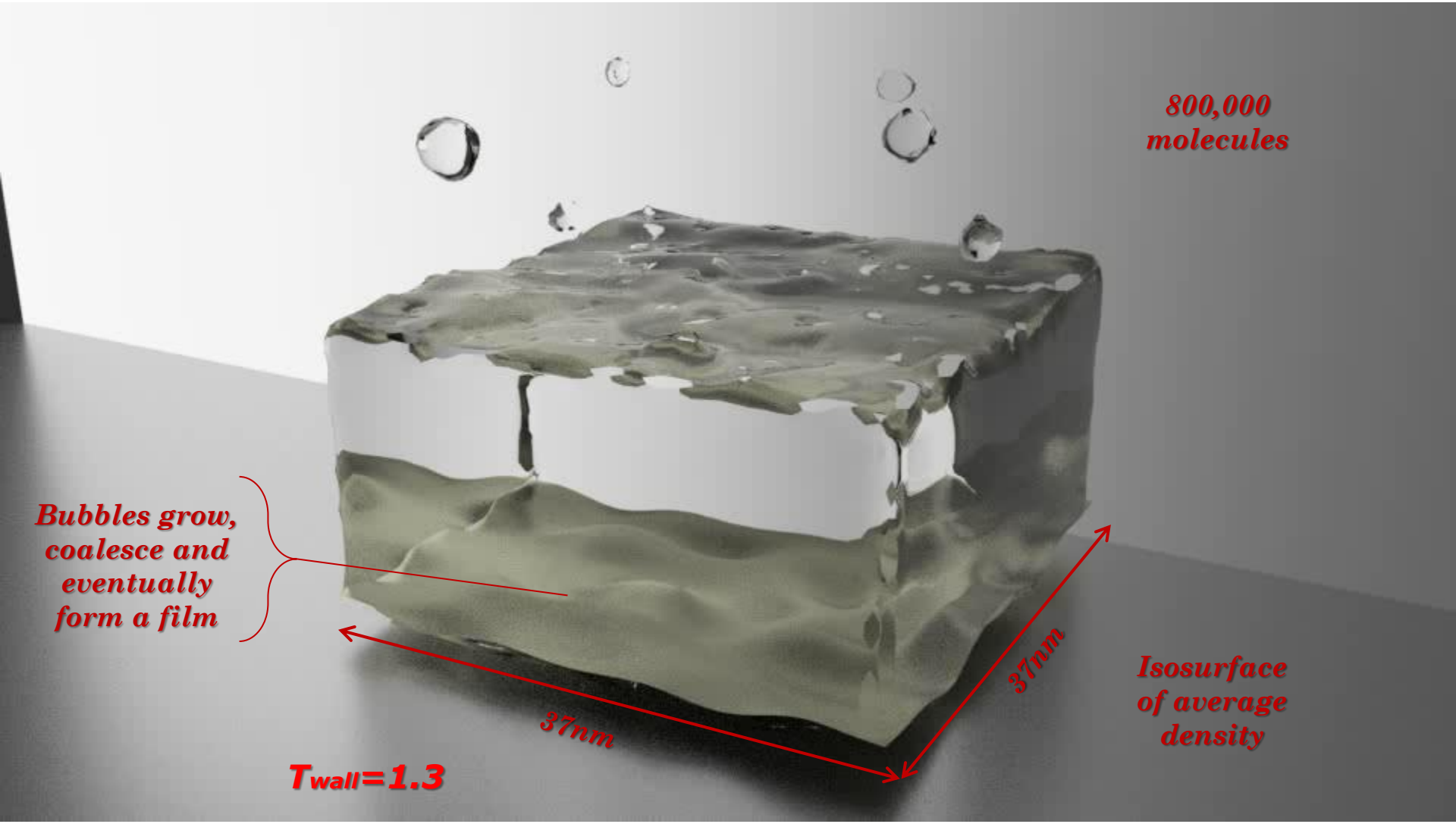
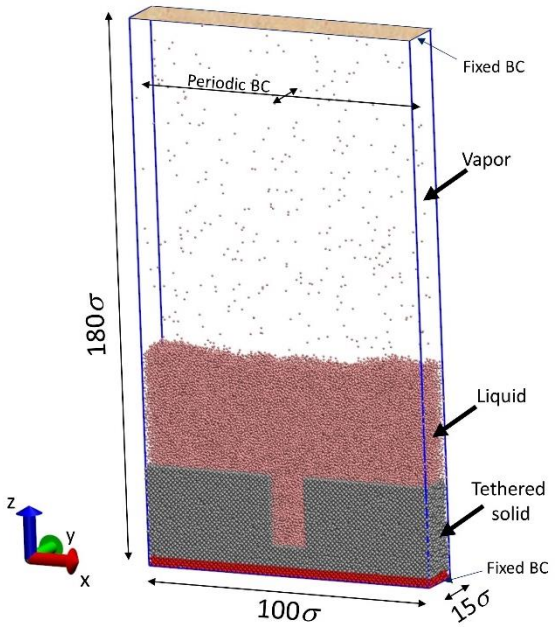
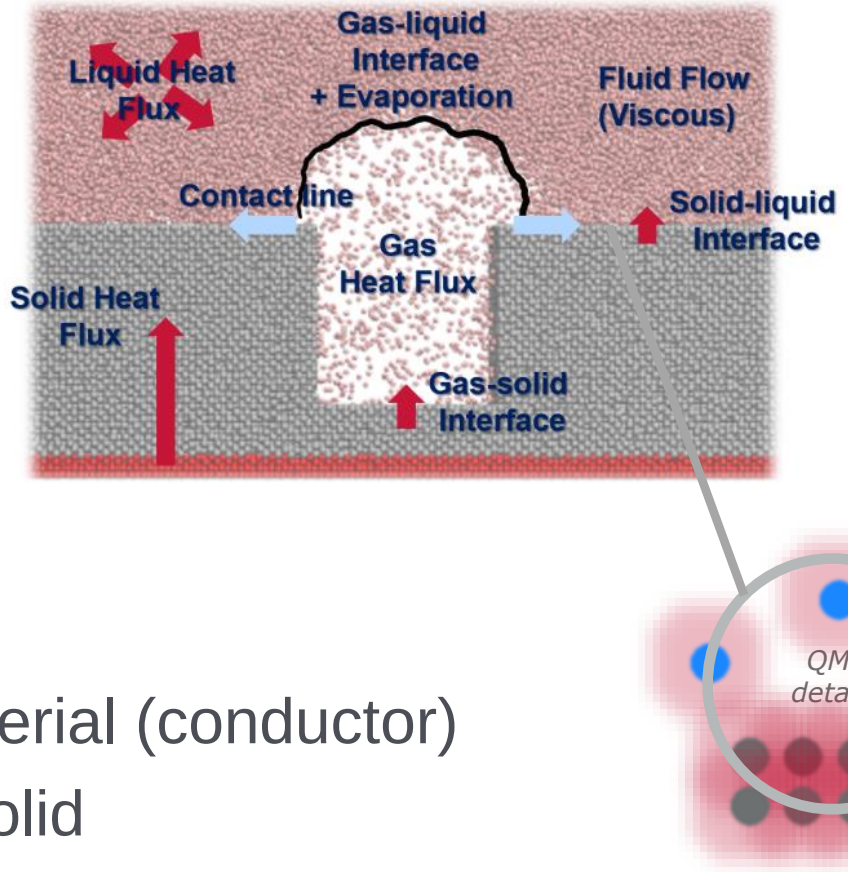


Molecular simulation of Nucleation



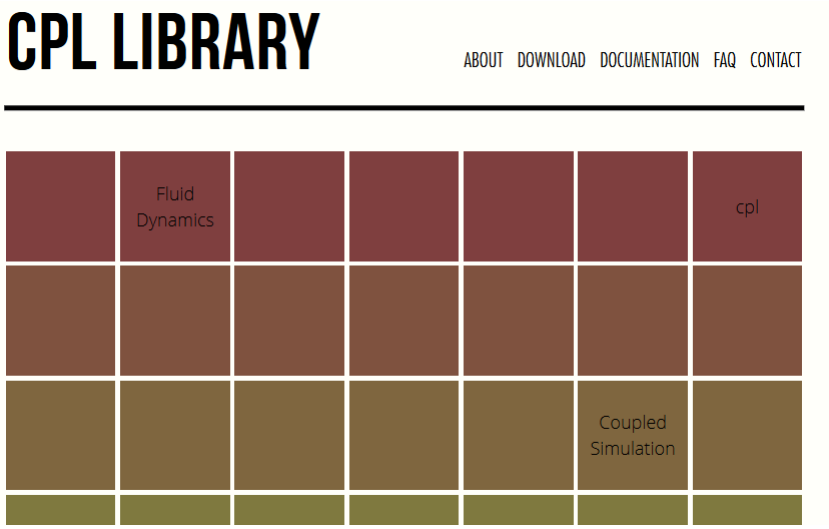


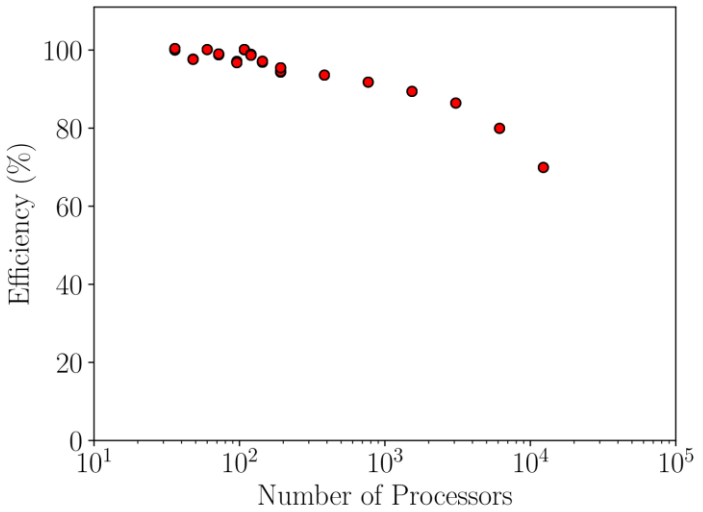
Quantum detail needed for

- Heat transfer in wall material (conductor)
- Interaction of fluid and solid
- Detail of structure if material is connected to a fluid

Software for Coupling

- Open Source (www.cpl-library.org) Fortran, C, C++ and Python bindings
- Designed to facilitate the linking of massively parallel codes with minimal impact on performance of each code (based on MPI)
- Shared library with no external dependencies beyond standard packages
- Minimal set of functions and examples with Python and google tests with key functionality (and examples) subject to continuous integration testing
- Aims to allow coupling and topology linking of programs





Summary

- Molecular Structure at the Interface
  - A local region containing molecular detail
  - Coupling to a (cheaper) model for the remaining domain
- A Coupling Framework
  - Eulerian control volumes and molecular stress
  - Extension to general interfaces
- Some Examples of Coupled Interfaces
  - Using molecular detail at the interface
  - Limits of the classical picture

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Thank you

Any Questions?

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