Multiscale Fluid Dynamics with Molecules

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24/03/20

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Summary

- Introduction to Molecular Dynamics (MD)
- Insights from Molecular Dynamics (MD)
- Coupled Simulation

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Section 1

INTRODUCTION TO MOLECULAR DYNAMICS

Computational Fluid Dynamics

- Fields assumed to be continuous at every point in space
  - Mass Conservation

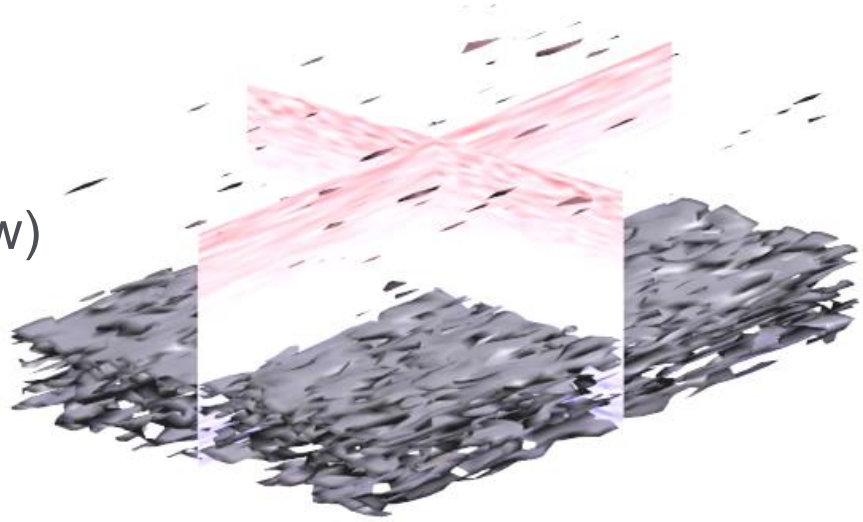
$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla} \cdot \rho \boldsymbol{u}$$

  - Momentum Balance (Newton's Law)

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

  - Energy Conservation

$$\frac{\partial}{\partial t} \rho \mathcal{E} dV = -\boldsymbol{\nabla} \cdot [\rho \mathcal{E} \boldsymbol{u} + \boldsymbol{\Pi} \cdot \boldsymbol{u} + \mathbf{q}]$$



Direct Numerical Simulation of Turbulent Couette Flow

Computational Fluid Dynamics

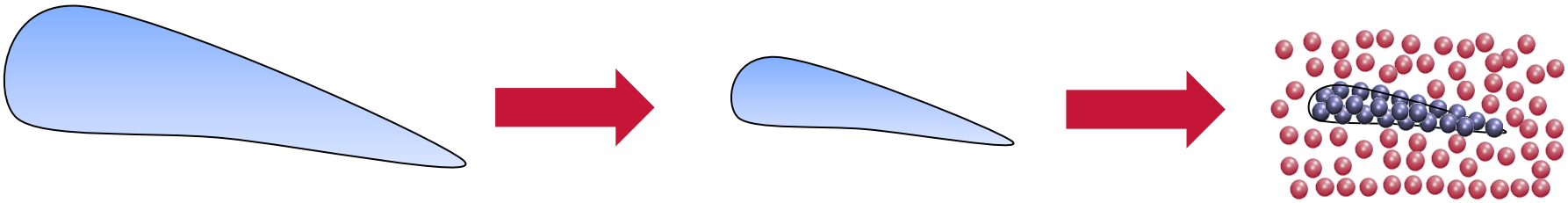
- The Incompressible Navier-Stokes Equation

$$\frac{\partial}{\partial t}\rho\boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} = -\boldsymbol{\nabla}P + \mu\nabla^2\boldsymbol{u} \qquad \boldsymbol{\nabla}\cdot\boldsymbol{u} = 0$$

- Non dimensional form

$$\frac{\partial}{\partial t}\boldsymbol{u} + \boldsymbol{u}\cdot\boldsymbol{\nabla}\boldsymbol{u} = -\boldsymbol{\nabla}P + \frac{1}{Re}\nabla^2\boldsymbol{u} \qquad Re = \frac{\rho U L}{\mu}$$

- Reynolds number
  - Ratio of convection to diffusion
  - Scaling argument applied to any scale -- is there a minimum?



Computational Fluid Dynamics

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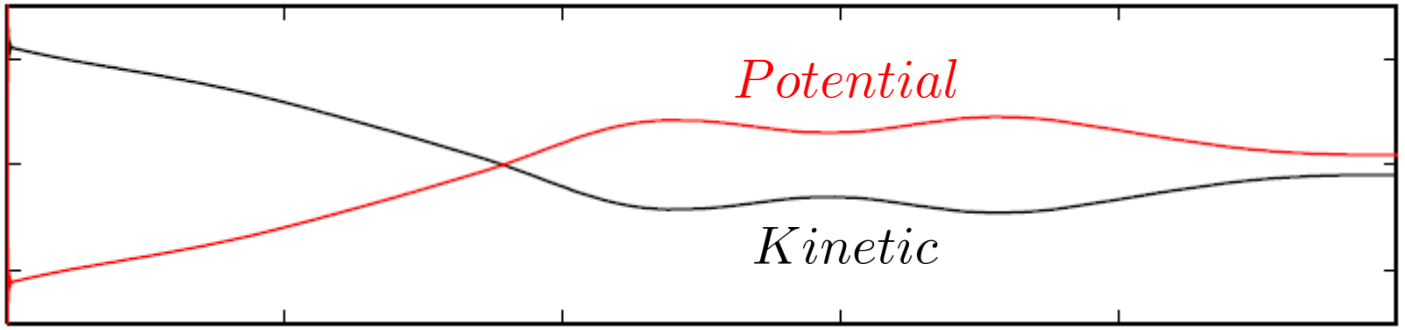
- Reynolds number
  - Scaling argument applied to any scale
- Is there a minimum?
  - Travis et al (1997) continuum valid in a nanometer channel
  - Most fluid dynamics appears to be identical for multi-phase flows
  - Molecular dynamics is a more fundamental model

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-liquid surface constructed with molecular roughness
  - Can model complex molecules, water, polymers, biomolecules

Molecular Dynamics

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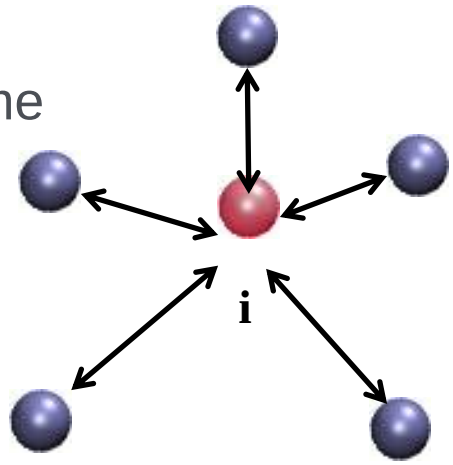
Discrete molecules in continuous space

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

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

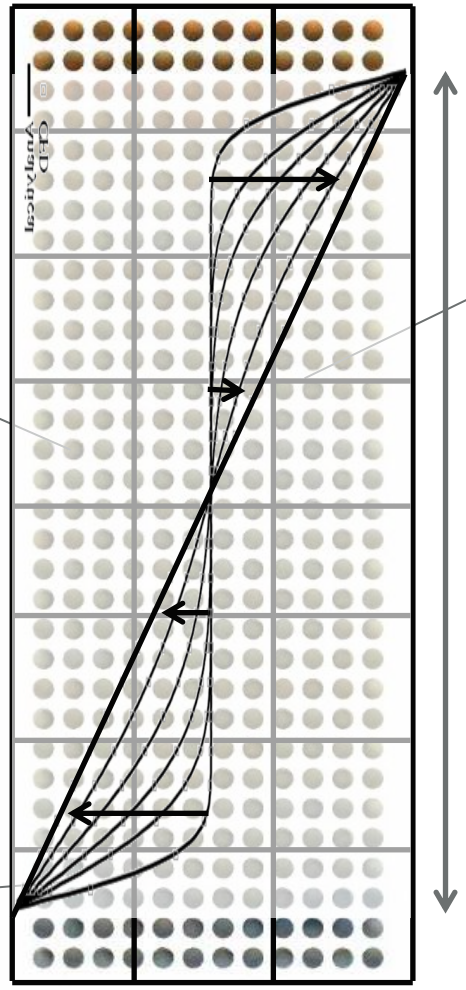


Acceleration obtained from forces

- Governed by Newton's law for an N-body system
- Point particles with pairwise interactions – electrostatics from quantum mechanics

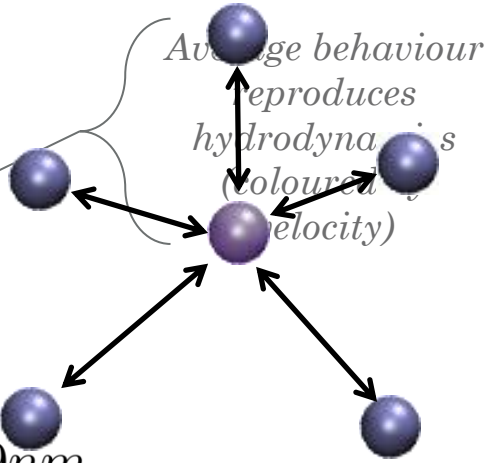
$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i = \sum_{i\neq j}^{N} \boldsymbol{f}_{ij} = \sum_{i\neq j}^{N} \boldsymbol{\nabla}\Phi_{ij} \qquad \Phi(r_{ij}) = 4\epsilon\left[\left(\frac{\ell}{r_{ij}}\right)^{12} - \left(\frac{\ell}{r_{ij}}\right)^{6}\right]$$

Molecular Dynamics



Liquid structure causes viscosity

Stick-slip near walls



Average behaviour reproduces hydrodynamics (coloured by velocity)

$H \approx 9nm$

Reynolds Number

$Re \approx 15$

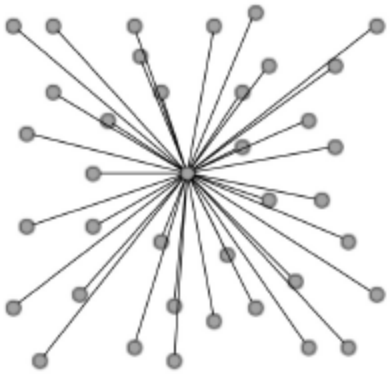
with

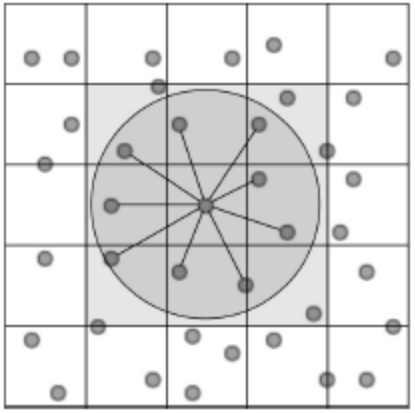
4096 molecules

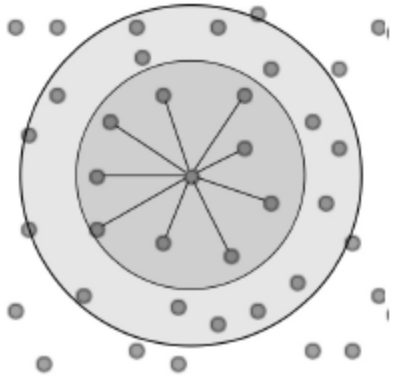
MD Computing

- 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)

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

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

MD Computing – Parallel optimisations

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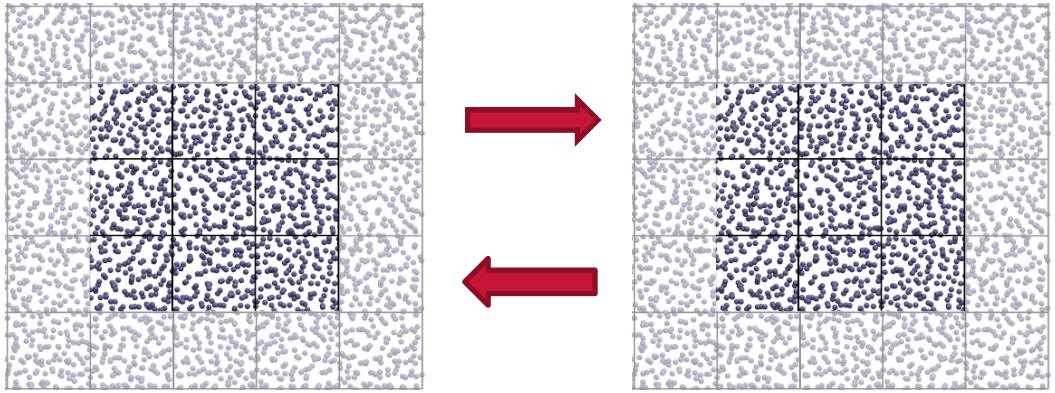
Localisations lends itself to parallel computing using MPI

- Spatial decomposition employed as in CFD
- Halo cells (ghost molecules) are used to link adjacent regions



Halo exchange of variable amounts of data

- MPI_Send
- MPI_Probe and MPI_Recv

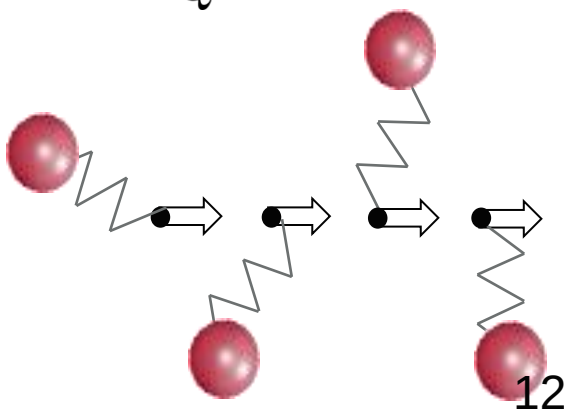
NEMD - Tethering and Thermostatting

- 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
    - (An)harmonic spring to tether site
  - With sliding
    - Slide site and (optionally) molecules

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

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

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



NEMD - Tethering and Thermostatting

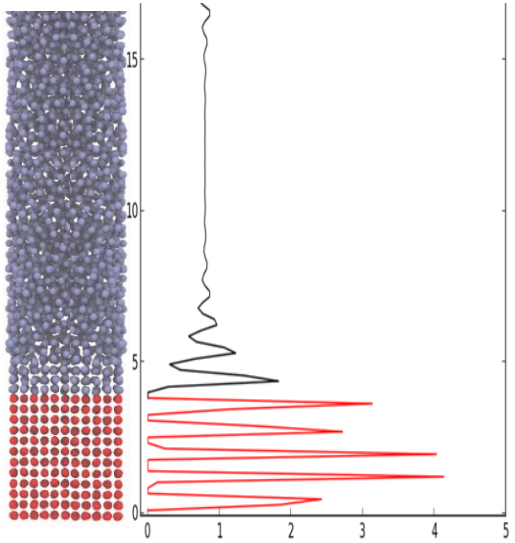
- Non Equilibrium Molecular Dynamics (NEMD) is the study of cases beyond thermodynamic equilibrium, with:
  - An MD system is completely described by position $\boldsymbol{r}_i$ and velocity $\boldsymbol{v}_i$ of all N molecules in the system
  - Theoretical underpinning in the form of the Liouville equation – a continuity equation in 6N degrees $f = f(\boldsymbol{r}_i, \boldsymbol{v}_i)$ which gives,

$$\frac{df}{dt} = \sum_{i=1}^{N} \left[\frac{\partial \boldsymbol{r}_i}{\partial t} \frac{\partial f}{\partial \boldsymbol{r}_i} + \frac{\partial \boldsymbol{v}_i}{\partial t} \frac{\partial f}{\partial \boldsymbol{v}_i} \right]$$

- Special interest group (SIG) in NEMD
  - Let me know if you want to join
  - Potential applications in a wide range of problems in fluid dynamics so need help identifying interesting challenges
  - The microscopic underpinnings of fluid dynamics

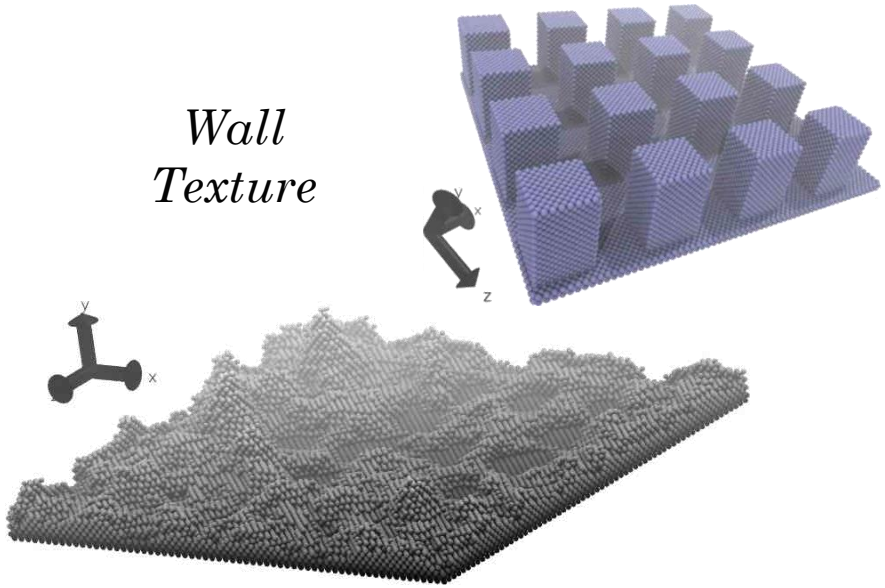
Molecular Dynamics – Complex Walls and Fluids

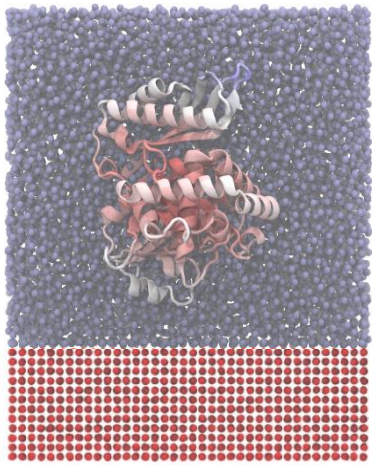
Liquid structure causes viscosity



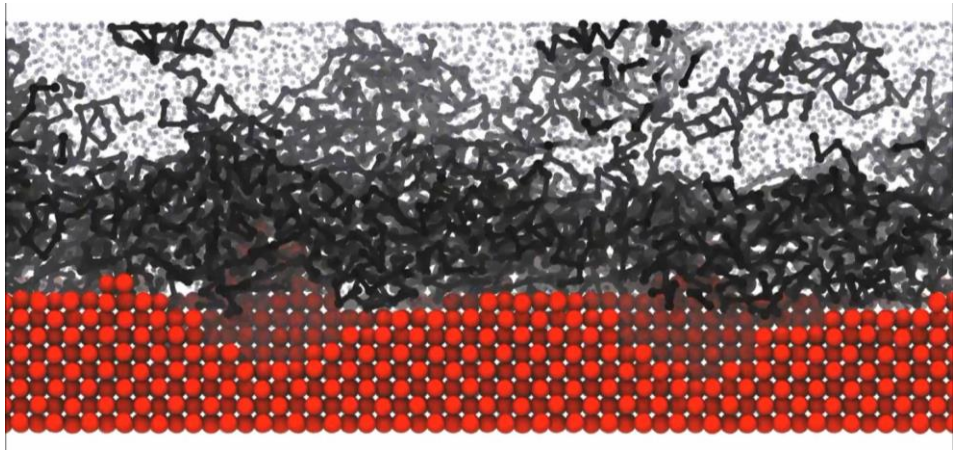
Stick-slip near walls

Wall Texture





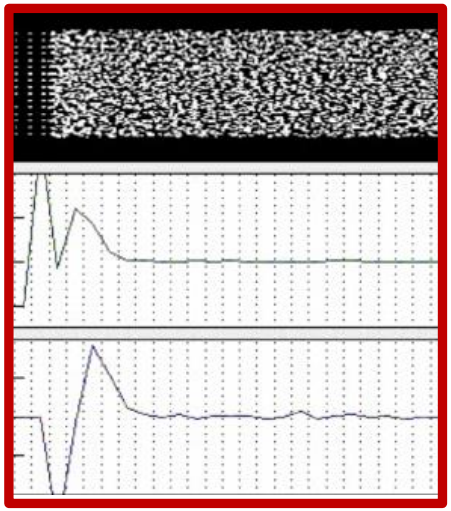
Molecules of arbitrary complexity



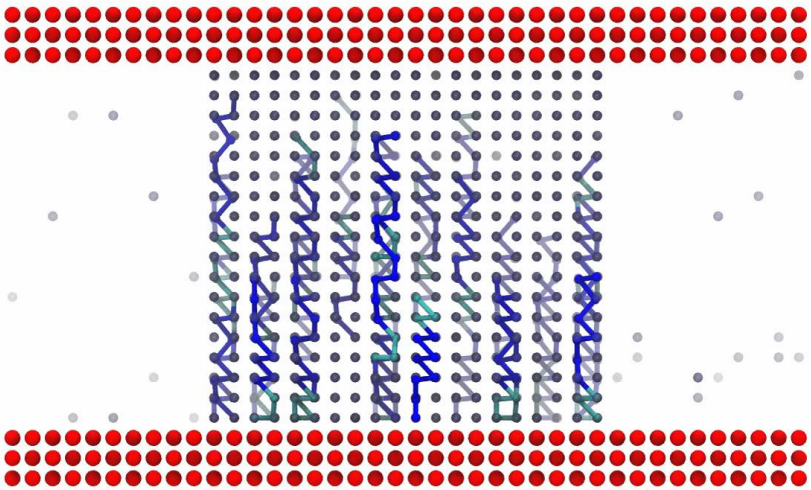
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

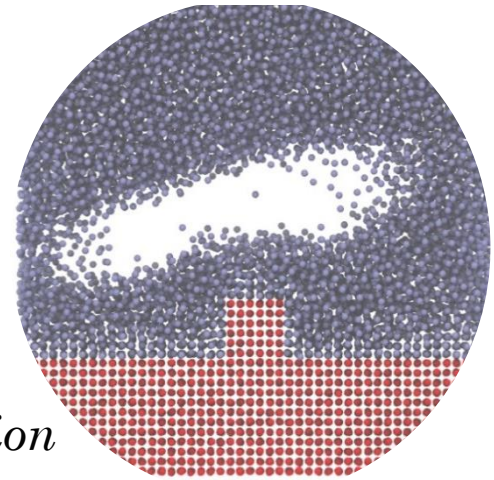
Shockwave



Droplet Formation

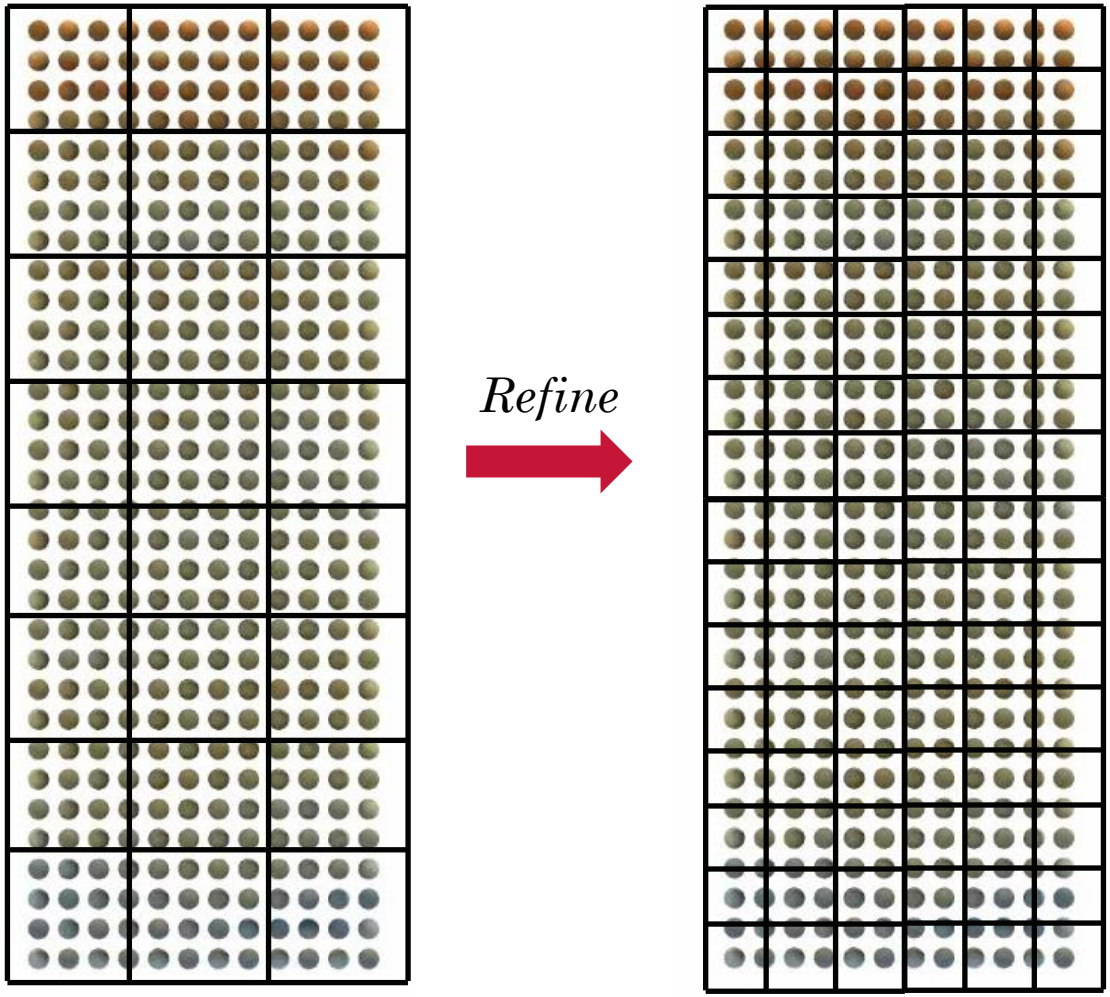


Nucleation



Contact line

Molecular Dynamics - Averaging



- Density in a cell

$$\rho = \frac{1}{V}\sum_{i=1}^{N}\langle m_i \rangle$$

- Momentum in a cell

$$\rho \boldsymbol{u} = \frac{1}{V}\sum_{i=1}^{N}\langle m_i \boldsymbol{v}_i \rangle$$

- Temperature in a cell

$$T = \frac{1}{3N}\sum_{i=1}^{N}\langle \boldsymbol{v}_i^2 \rangle$$

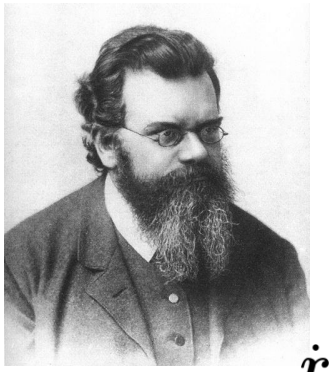
Pressure (stress) in an MD Simulation

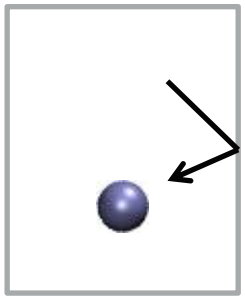
- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

$$\oint_S \Pi_{xy} \cdot dS_y = \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{yi} dS_{yi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \left\langle f_{xij} dS_{yij} \right\rangle}_{\text{Configurational}}$$

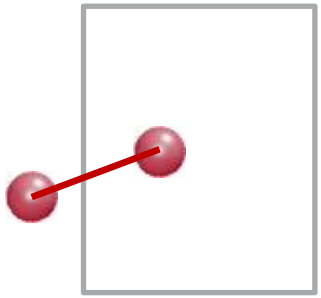
Kinetic theory part

Momentum due to average of molecules crossing a plane and returning





$$\dot{\boldsymbol{r}}_i = m_i \boldsymbol{v}_i + \boldsymbol{u}$$

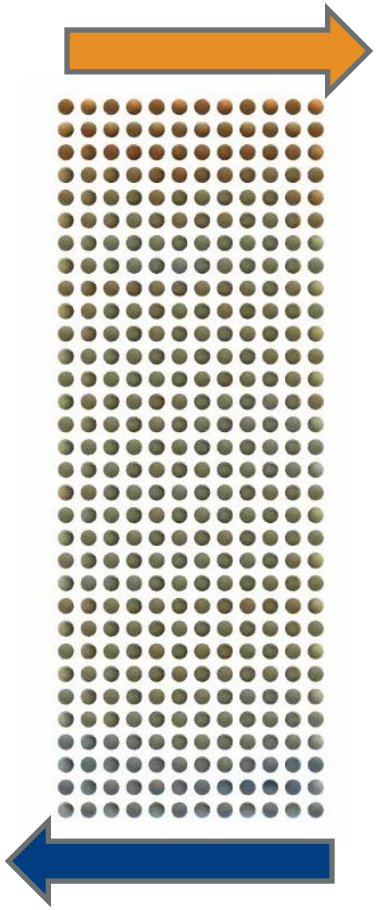


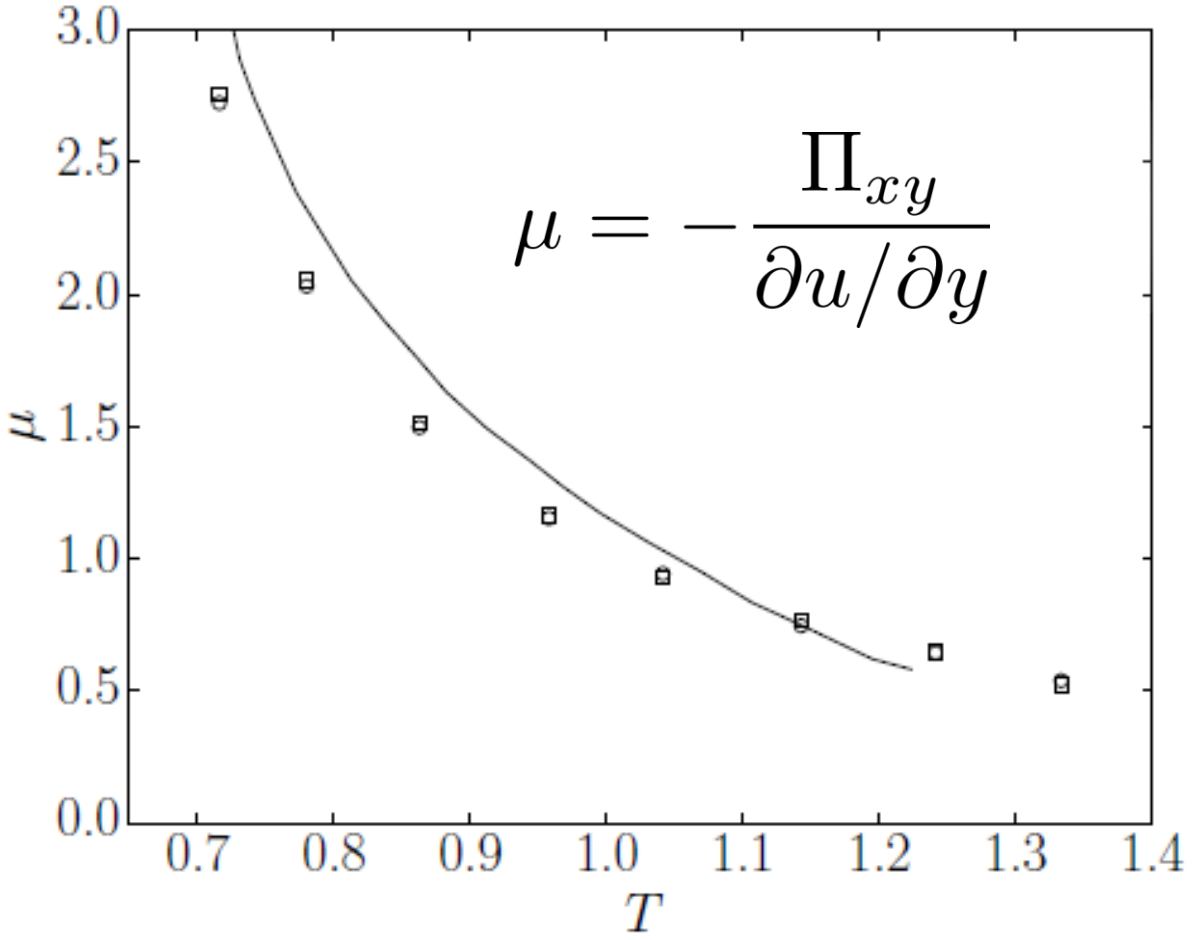
Configurational part

Inter-molecular bonds act like the stress in a stretched spring

Viscosity

- Good agreement with experiments





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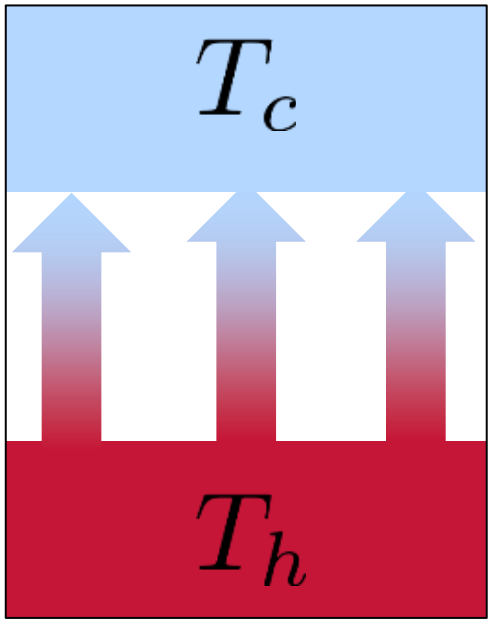
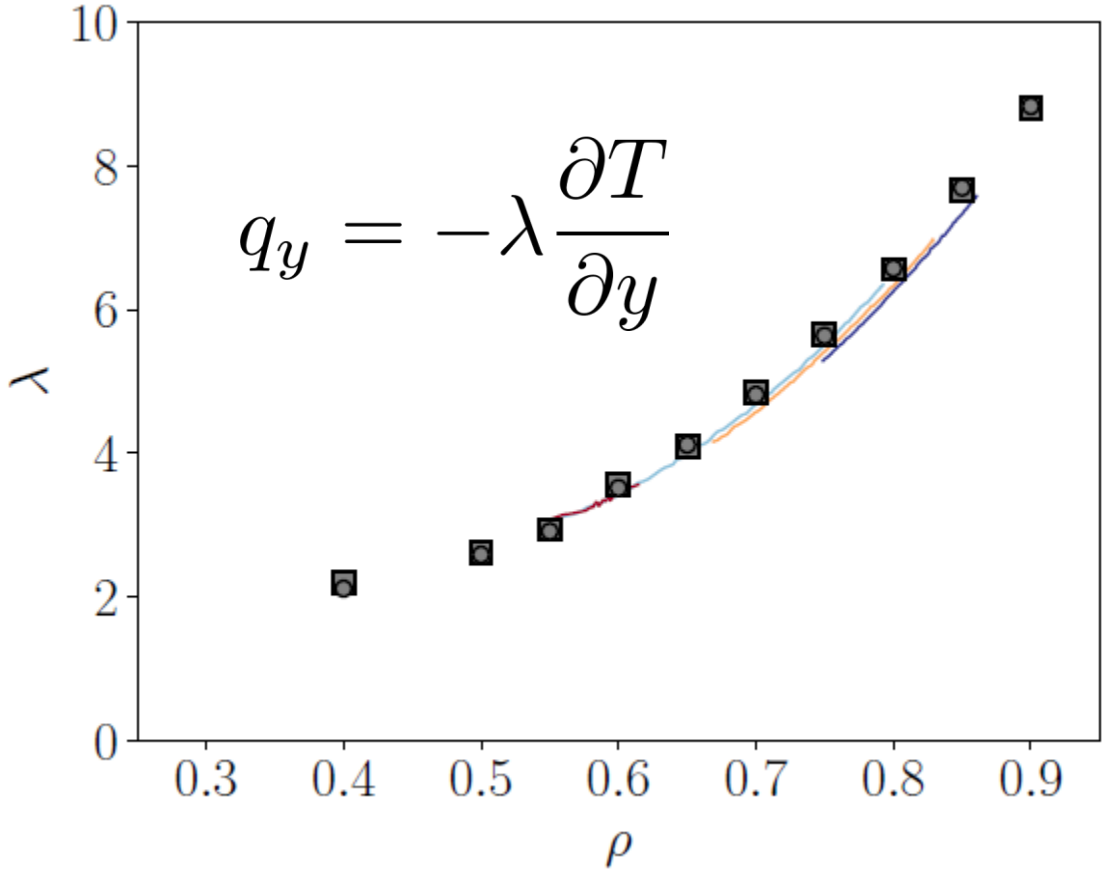
Fourier's law of heat conduction

- Good agreement with experiments



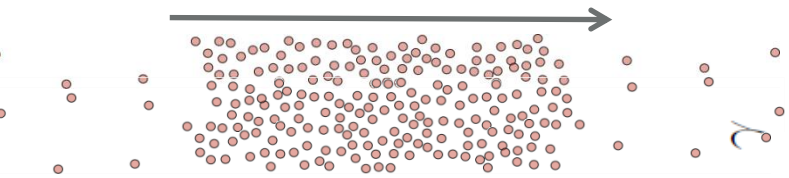
$$q_y = -\lambda \frac{\partial T}{\partial y}$$



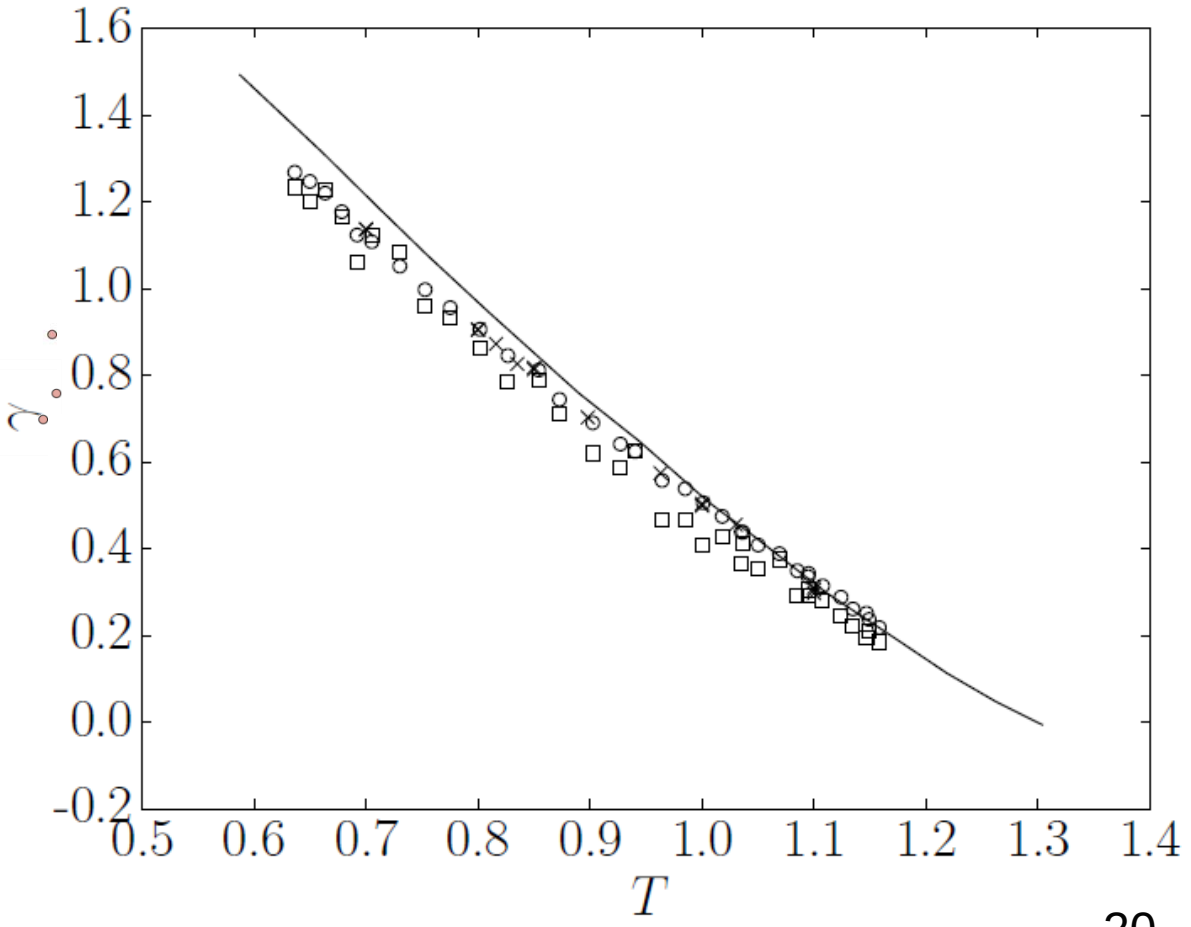
Results for Surface Tension

- Good agreement with experiments

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



Integrate over Liquid Vapour interface(s)



Section 2

INSIGHTS FROM MD

Insights From MD

- Turbulence
- Non-Newtonian fluids
- Multi-phase flow and nucleation

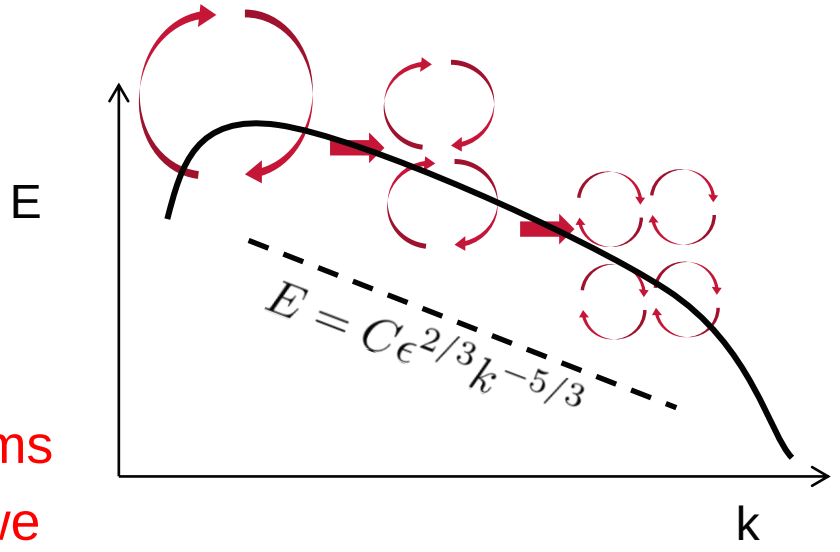
Section 2.1

INSIGHTS FROM MD

> Turbulence

Molecular Simulation of Turbulence

- Turbulent flow
  - Fluid flow which is spatially and temporally varying
  - Inertial effects dominate viscous
  - No clear order and not simply chaotic motions
- Some standard characteristics
  - Statistics are reproducible
  - The law of the wall
  - Range of scales
- Minimal Channel flow
  - Insight into fundamental mechanisms
  - For molecular dynamics this is all we can do with current computers



Molecular Simulation of Turbulence

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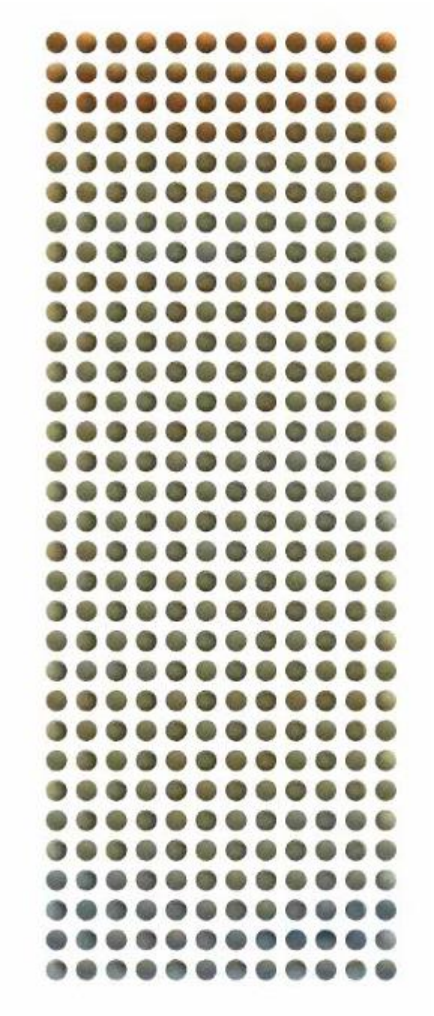
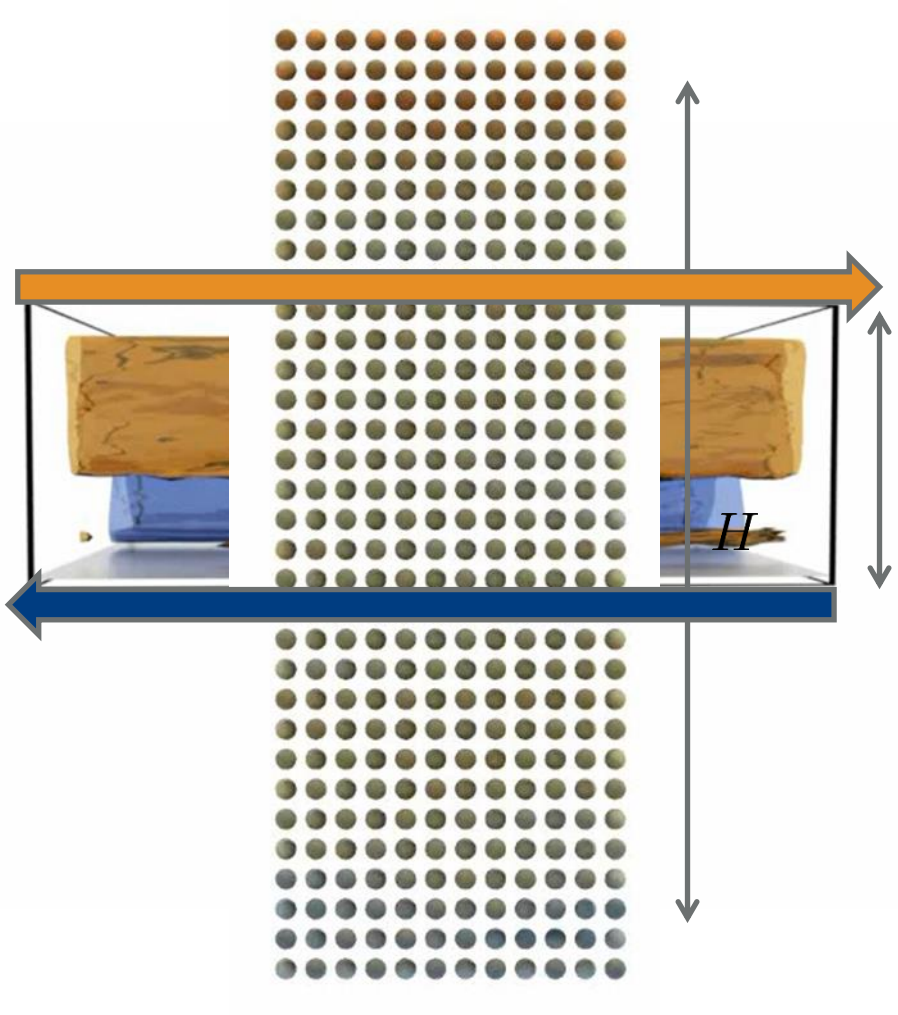


Molecular Simulation of Turbulence



Reynolds Number

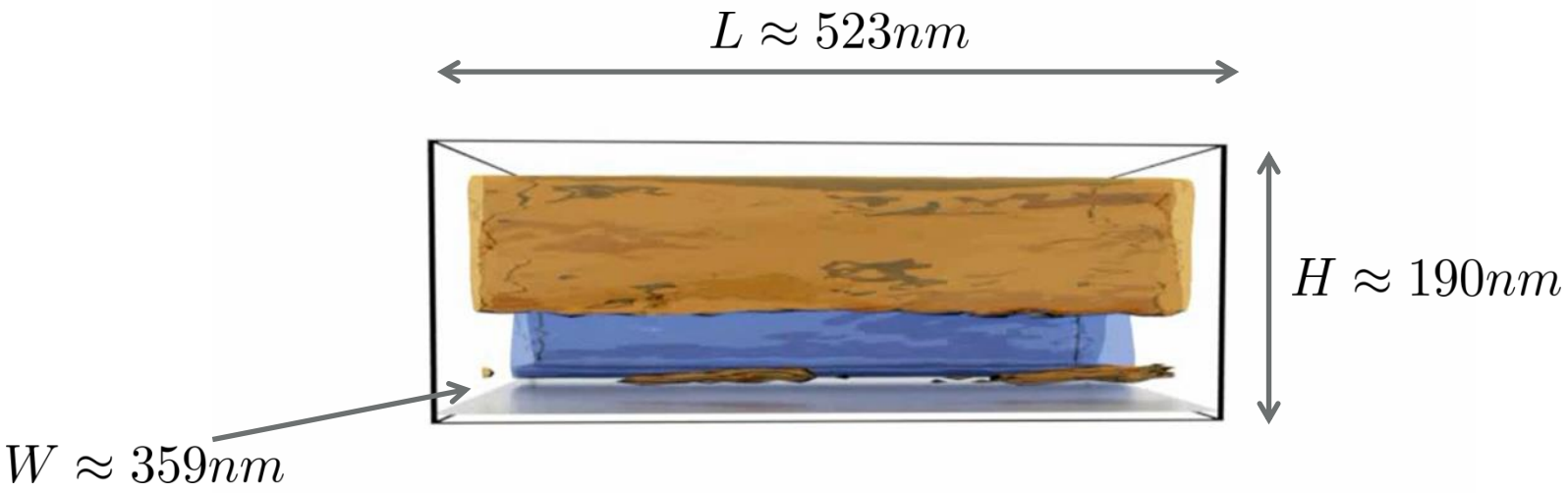
$Re \approx 400$

with

300 million molecules

Molecular Simulation of Turbulence

Minimal channel Couette flow



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Molecular Simulation of Turbulence

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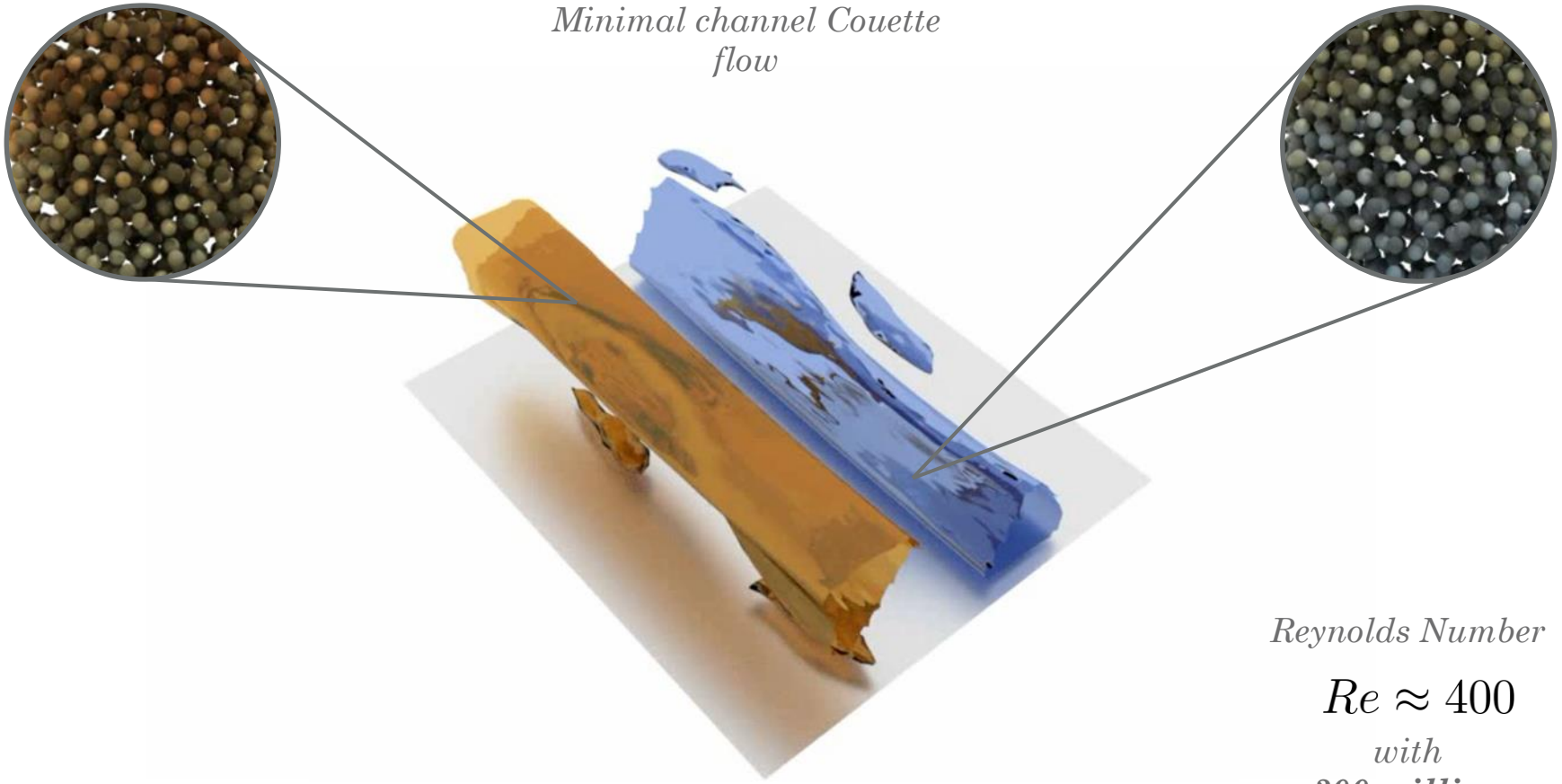

Isosurfaces of turbulent kinetic energy coloured by velocity

Reynolds Number

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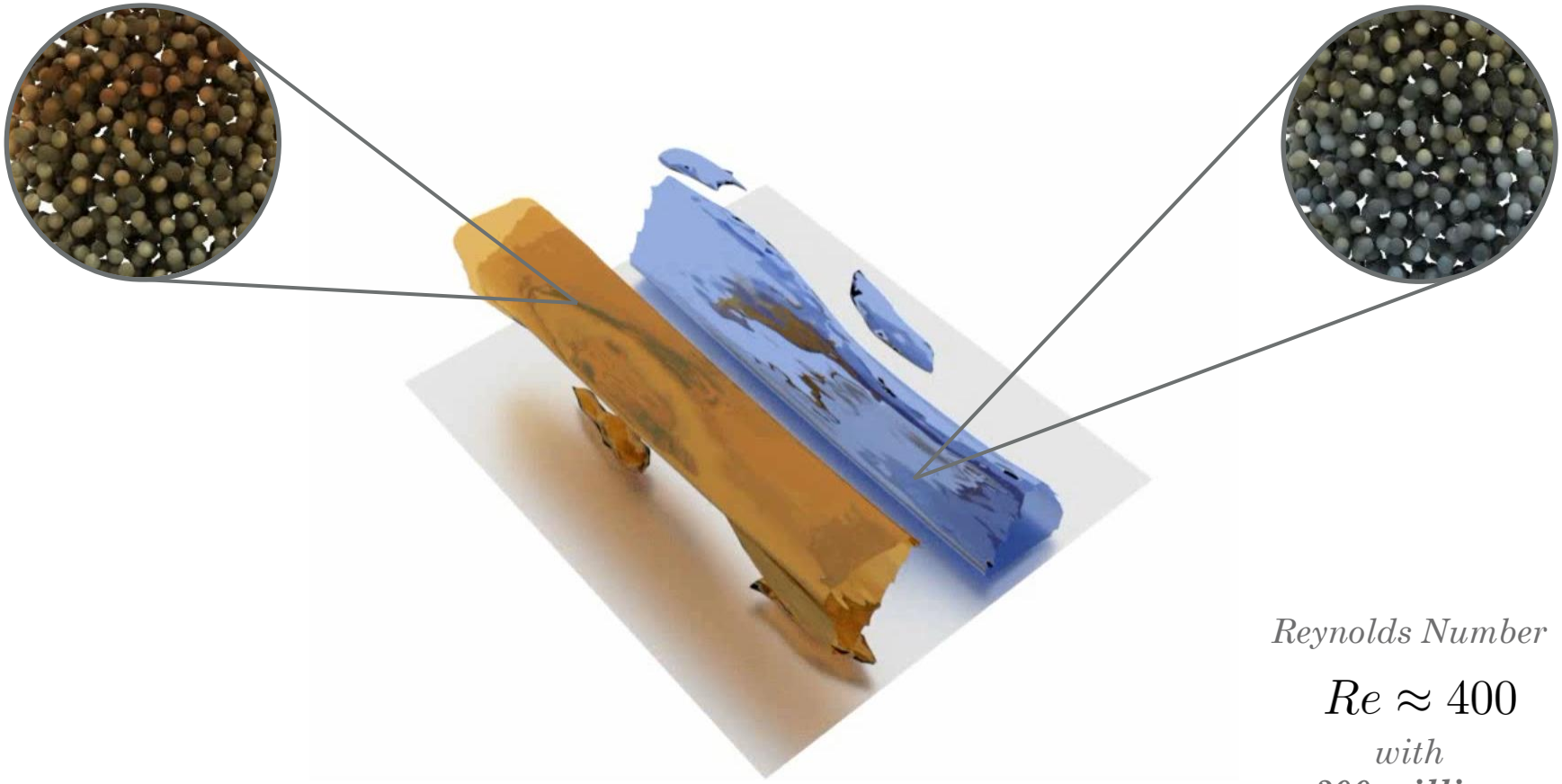
Molecular Simulation of Turbulence



Isosurfaces of turbulent kinetic energy coloured by velocity

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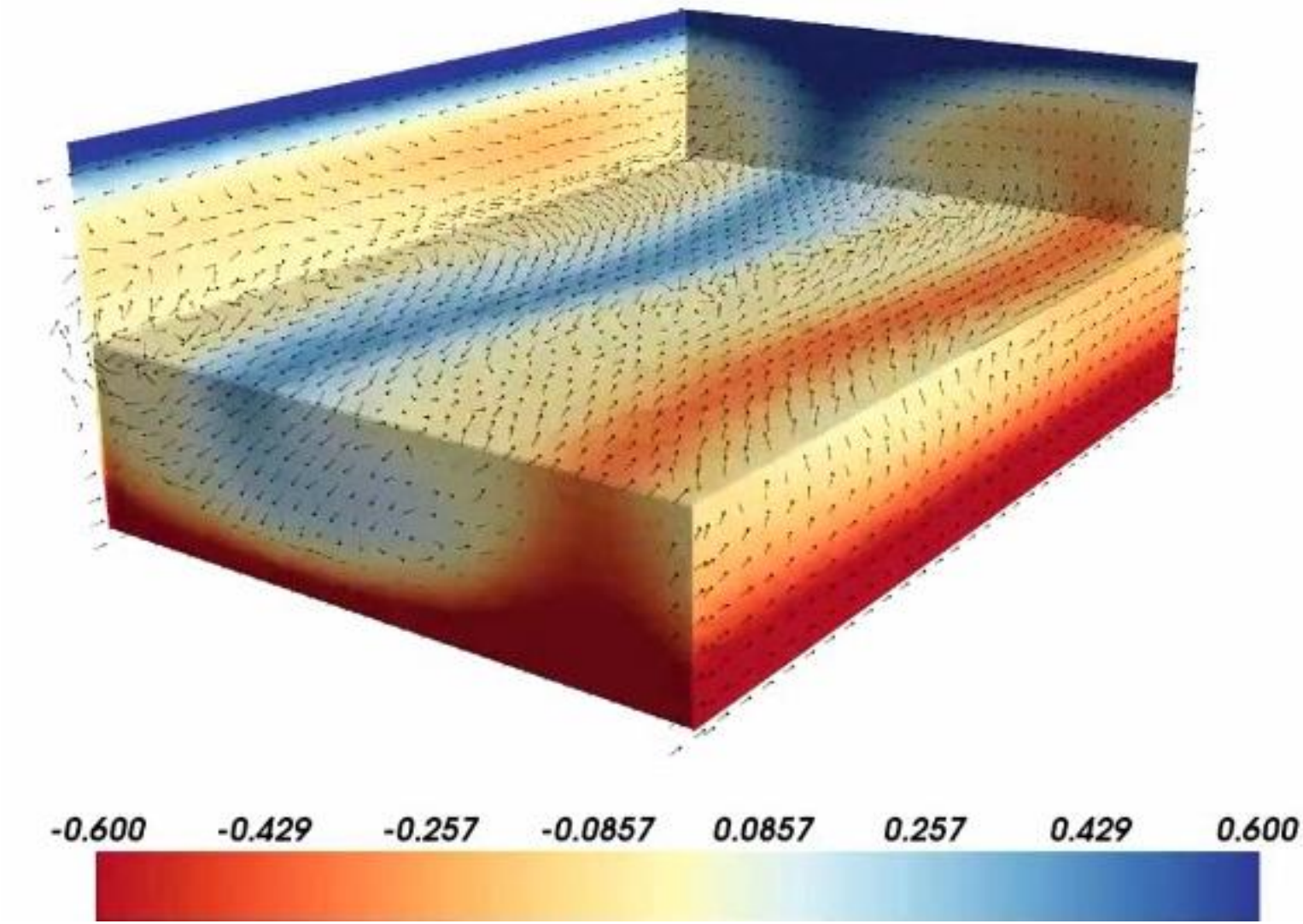
Molecular Turbulent Couette Flow



MD vs CFD

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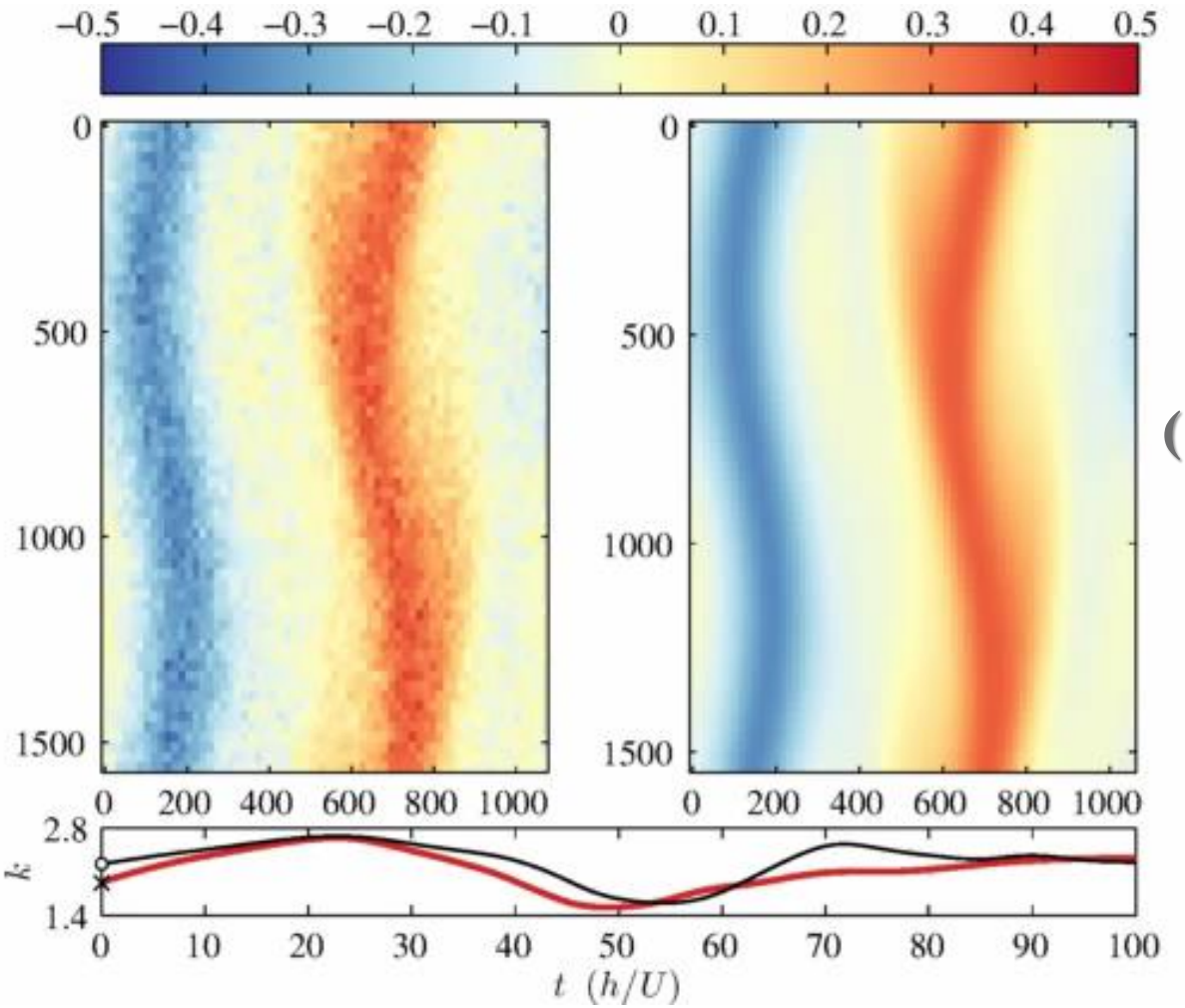
Centre slice velocity



MD

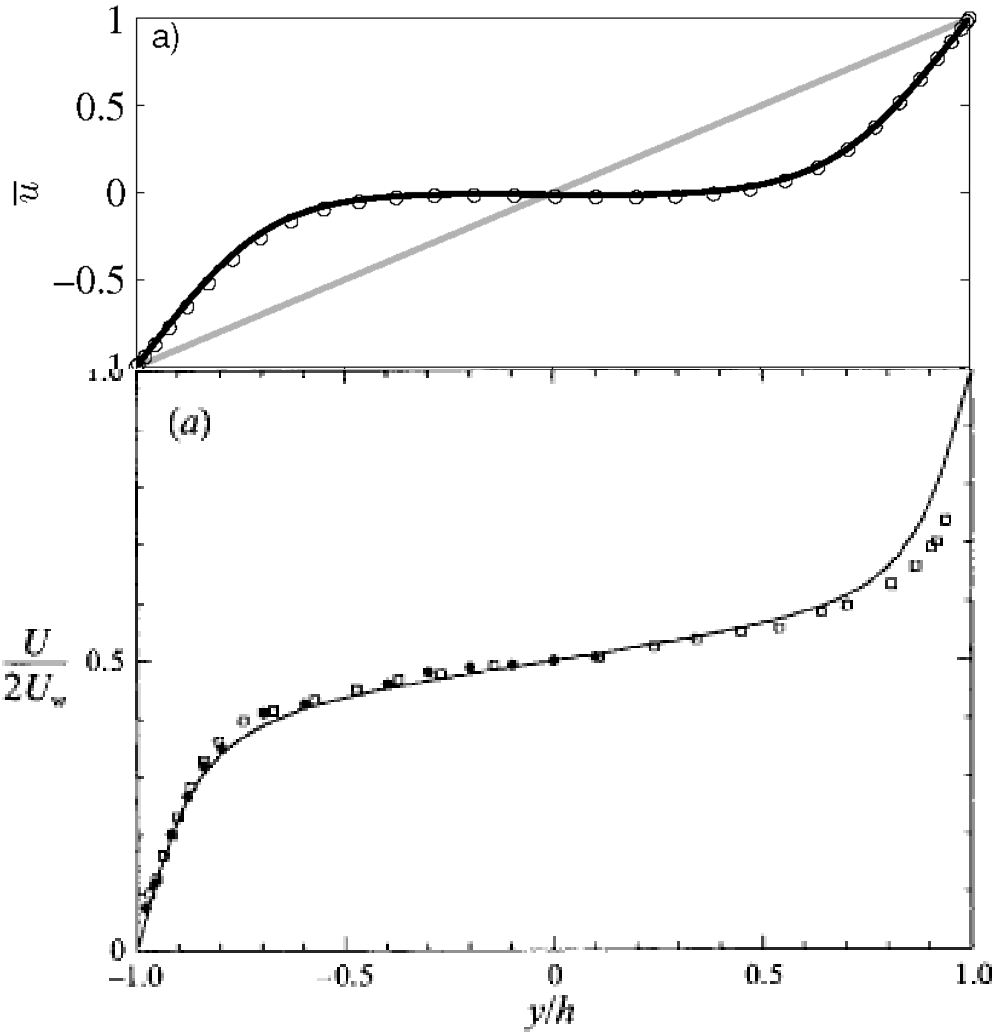
Own code written in Fortran and parallelised using MPI

CFD (Channelflow)

F. Gibson. Channelow: A spectral Navier-Stokes simulator in C++. Technical report, U. New Hampshire, 2012. Channelflow.org.

Statistical Results

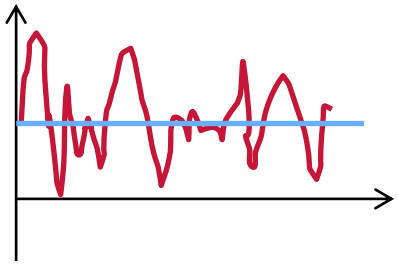
- Averaged velocity profile
- No longer Laminar profile across domain
- Good agreement with literature
  - Numerical continuum studies (points)
  - Experimental results from turbulent simulations (bottom graph)



By KNUT H. BECH[1], NILS TILLMARK[2], P. HENRIK ALFREDSSON[2] AND HELGE I. ANDERSSON[1]

Reynolds Decomposition

- Inspired by kinetic theory, Osborne Reynolds split fluid motion into average and fluctuating part



$$u = \overline{u} - u'$$

- Time average to get the Reynold Averaged Navier-Stokes equations
  - Reynolds stress tensor doesn't disappear
  - Approximated by eddy viscosity

$$\frac{\partial}{\partial t}\overline{\boldsymbol{u}} + \overline{\boldsymbol{u}} \cdot \boldsymbol{\nabla}\overline{\boldsymbol{u}} = -\boldsymbol{\nabla}\overline{P} + \frac{1}{Re}\nabla^2\overline{\boldsymbol{u}} + \boxed{\overline{\boldsymbol{u}'\boldsymbol{u}'}} \quad \Rightarrow \quad \overline{\boldsymbol{u}'\boldsymbol{u}'} \approx \mu_\tau \boldsymbol{\nabla}\boldsymbol{u}$$

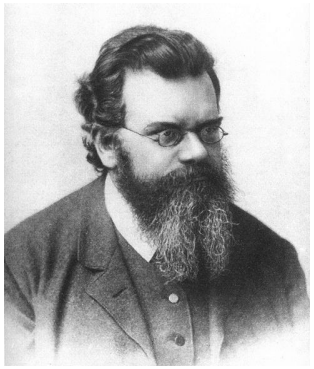
Pressure Tensor in an MD Simulation

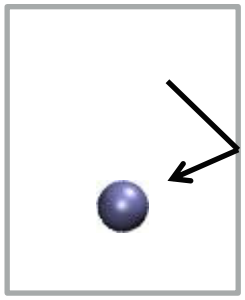
- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

$$\oint_S \Pi_{xy} \cdot dS_y = \underbrace{\sum_{i=1}^{N} \left\langle m_i v_{xi} v_{yi} dS_{yi} \right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} \left\langle f_{xij} dS_{yij} \right\rangle}_{\text{Configurational}}$$

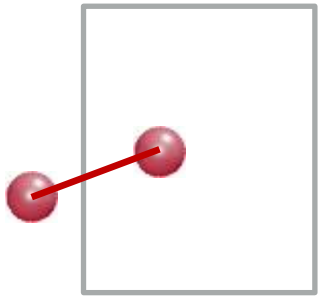
Kinetic theory part

Momentum due to average of molecules crossing a plane and returning





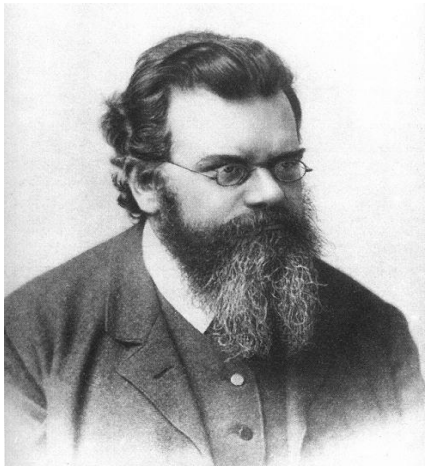
$$\dot{\boldsymbol{r}}_i = \boldsymbol{v}_i + \boldsymbol{u}$$



Configurational part

Inter-molecular bonds act like the stress in a stretched spring

Same Concept, Different Scales



Peculiar velocity

$$\dot{r}_i = v_i + u$$

Reynolds' Decomposition

$$u = u' + \bar{u}$$

- Kinetic part of the pressure tensor and Reynolds stress same mathematical quantity averaged over different length/time scales

$$\sum_{i=1}^{N} \overline{\langle \dot{\boldsymbol{r}}_i \dot{\boldsymbol{r}}_i \rangle} = \sum_{i=1}^{N} \overline{\langle \boldsymbol{v}_i \boldsymbol{v}_i \rangle} + \overline{\boldsymbol{u}'\boldsymbol{u}'} + \overline{\boldsymbol{u}\boldsymbol{u}}$$

Molecular average time $\langle \dots \rangle$ Continuum average time $\overline{\dots}$

Is Reynolds Stress just Kinetic Pressure?

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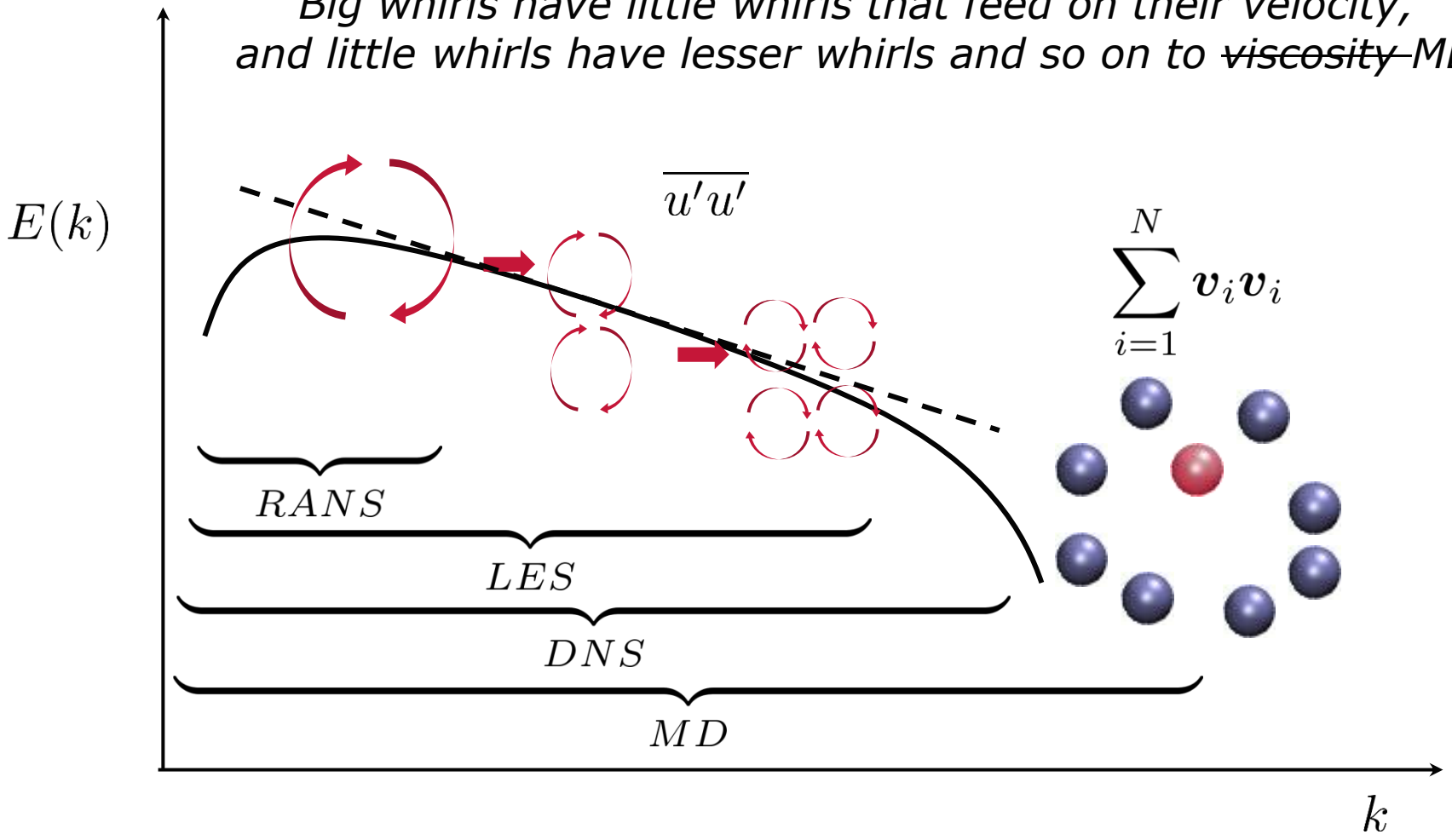
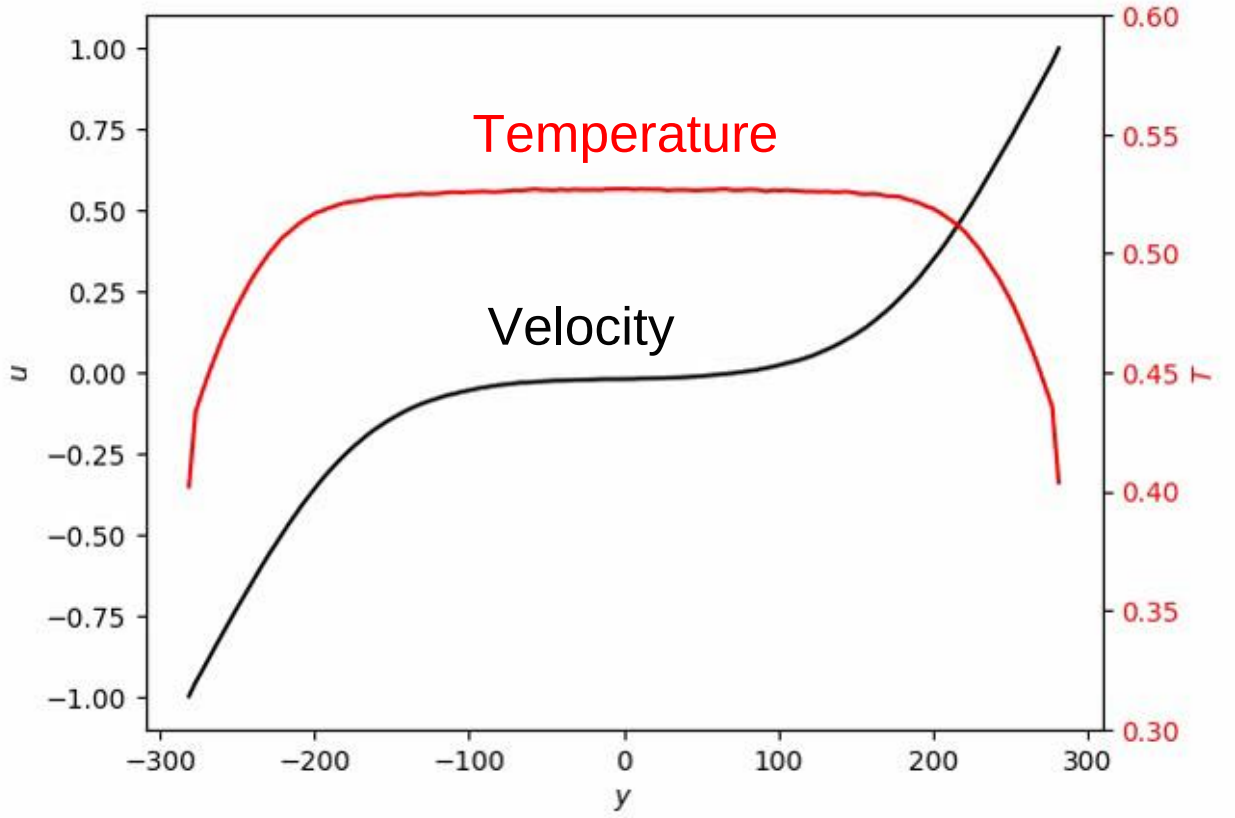
Big whirls have little whirls that feed on their velocity, and little whirls have lesser whirls and so on to ~~viscosity~~ MD



MD Conserves Energy

- Run over ~5 cycles or 500 flow through times
  - Temperature and Velocity are interconnected over a regeneration cycle



- Velocity in a cell

$$\boldsymbol{u} = \frac{1}{N}\sum_{i=1}^{N}\langle \boldsymbol{v}_i \rangle$$

- Temperature in a cell

$$T = \frac{1}{3N}\sum_{i=1}^{N}\langle \boldsymbol{v}_i^2 \rangle$$

MD Conserves Energy

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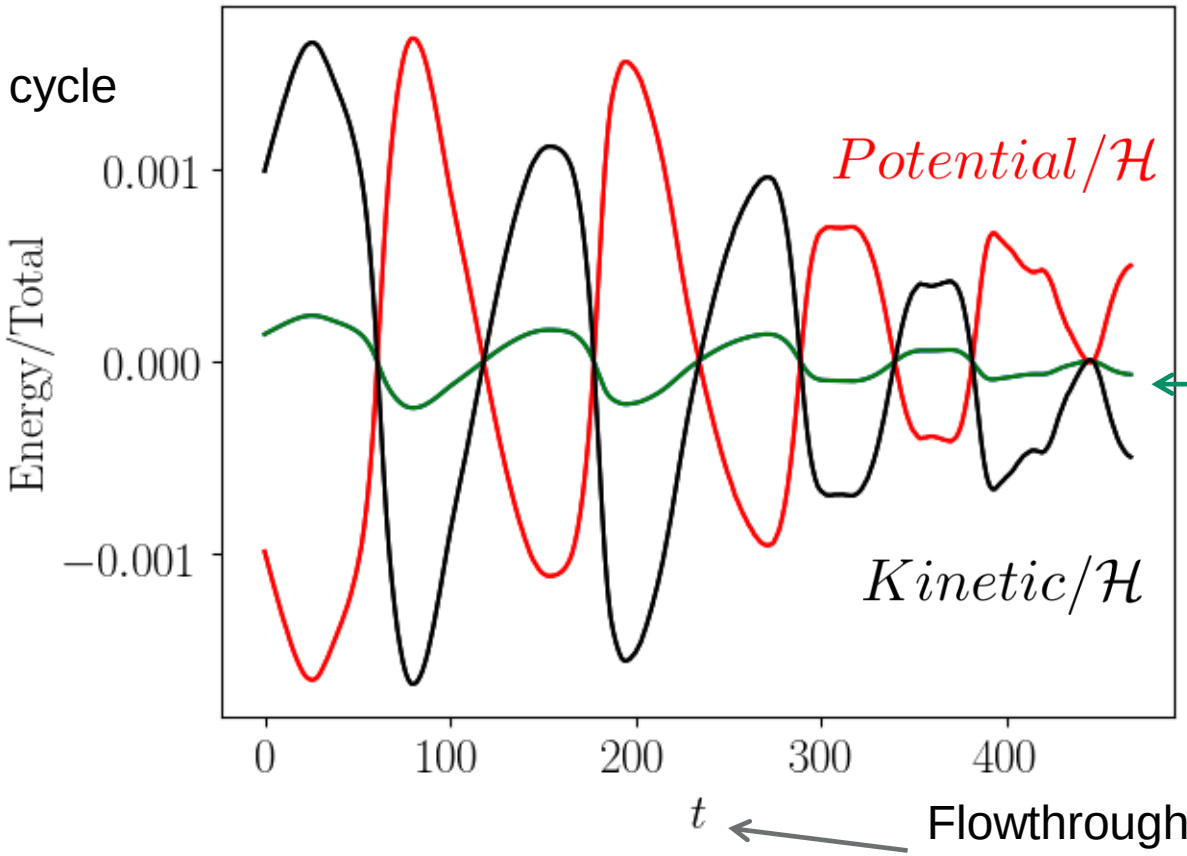
Interchange of kinetic, potential &TKE energy following the regeneration cycle

$$\frac{Kinetic}{\mathcal{H}} + \frac{Potential}{\mathcal{H}} = 1$$



Turbulent Kinetic Energy (TKE) a small part of kinetic, shown scaled up

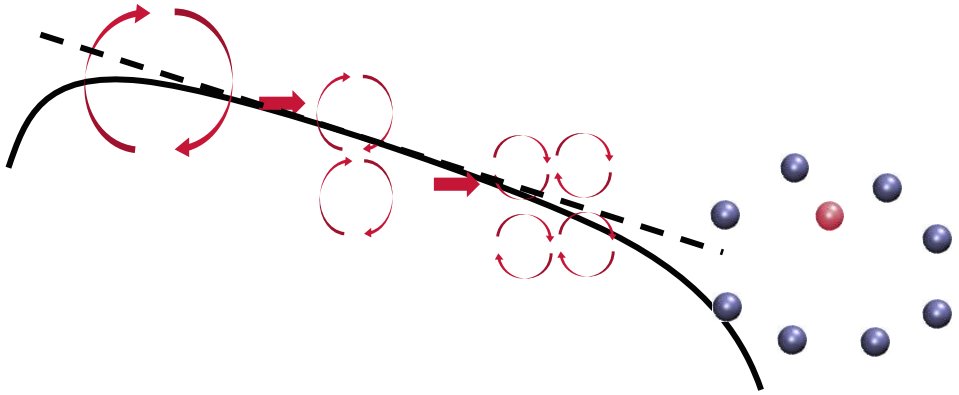
Flowthrough time (h/U)
A cycle is ~100

Section 2.2

INSIGHTS FROM MD

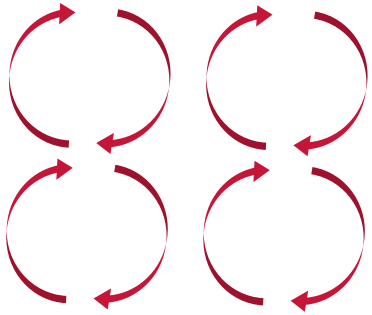
> Non-Newtonian Flows

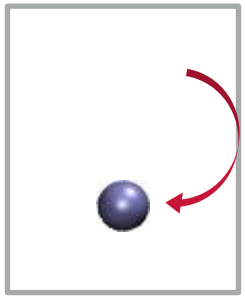
Back to the Hierarchy of Scales

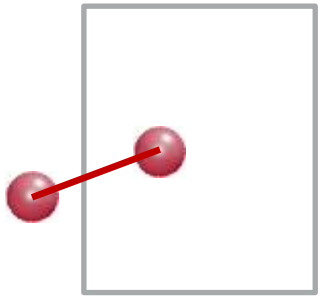


Can we gain insight from the liquid structure?

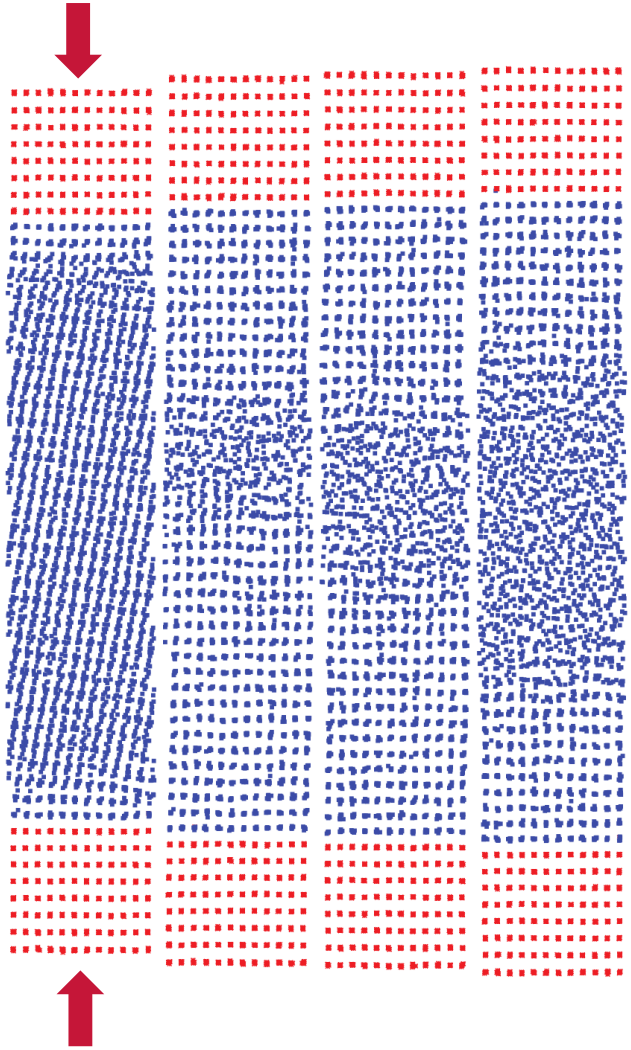
$$\underbrace{\rho\ \overline{u'\ v'}}_{\text{Reynold's Stress Tensor}} + \underbrace{\sum_{i=1}^{N}\left\langle m_i v_{xi} v_{yi} dS_{yi}\right\rangle}_{\text{Kinetic}} + \underbrace{\frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\left\langle f_{xij} dS_{yij}\right\rangle}_{\text{Configurational}}$$

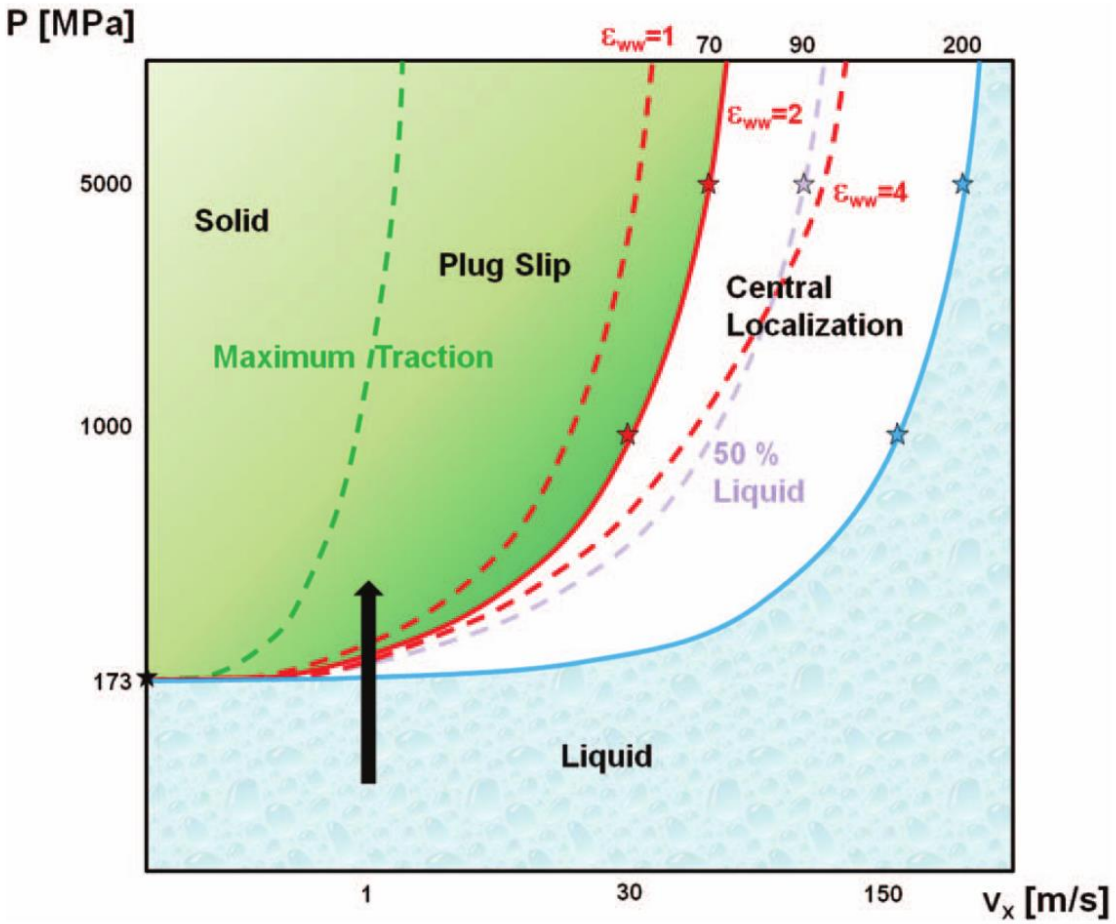






Different Tribological Regimes





From Stress to Viscosity

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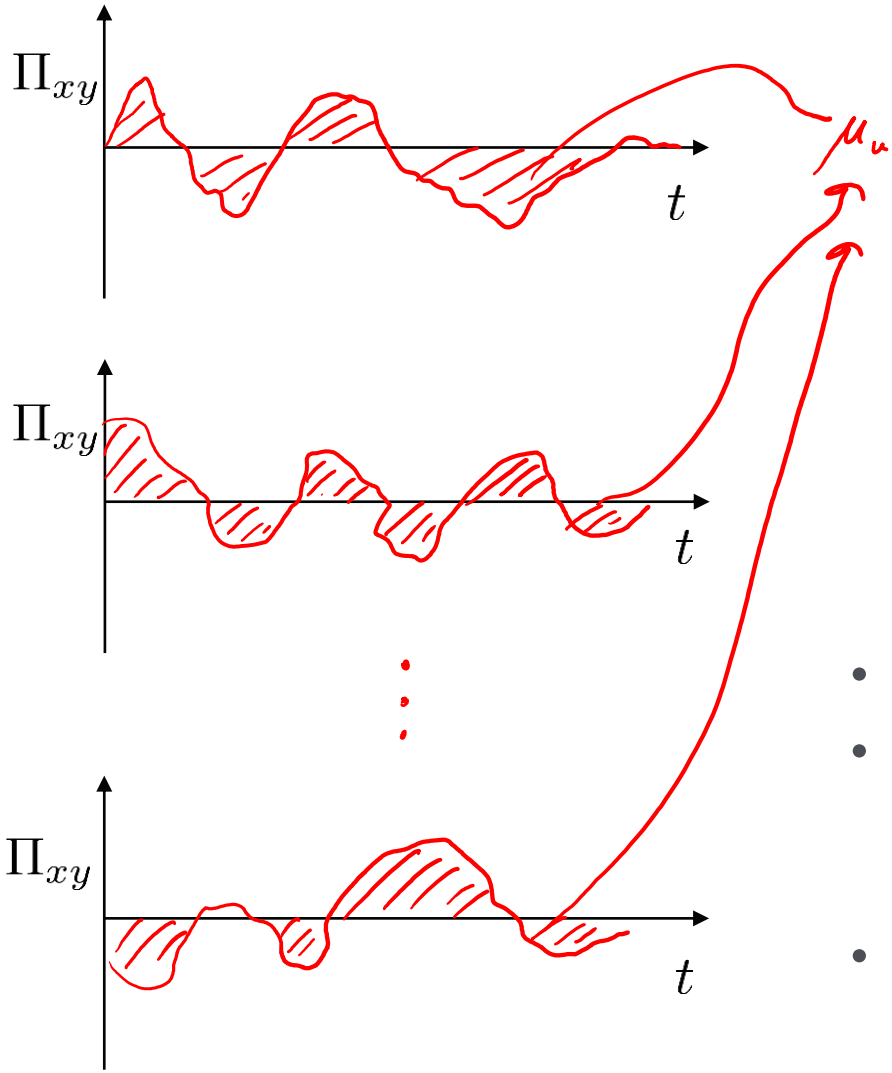
- Approximate stress in terms of viscosity

$$\frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla} \cdot \rho \boldsymbol{u}\boldsymbol{u} = -\boldsymbol{\nabla} \cdot \boldsymbol{\Pi} \approx -\boldsymbol{\nabla} P + \mu \nabla^2 \boldsymbol{u}$$

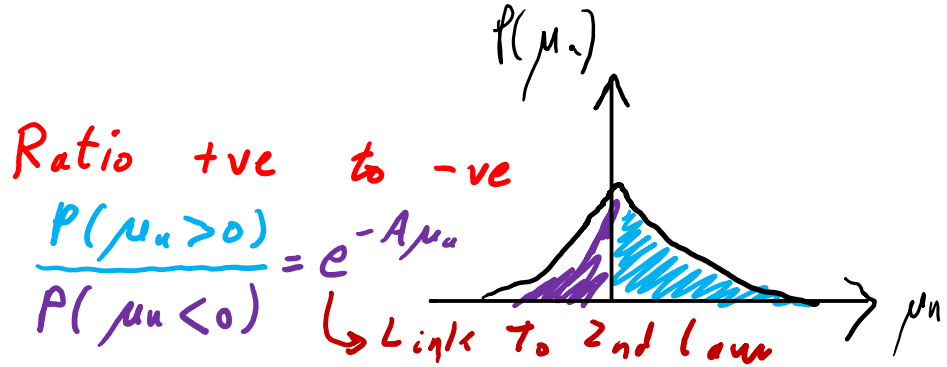
- Viscosity is the integral of the shear-stress correlation (Green Kubo) of **individual stress trajectories**

$$\mu = \frac{V}{k_B T} \int_0^t \left\langle \Pi_{xy}(\tau) \Pi_{xy}(0) \right\rangle d\tau$$

Viscosity



$$\mu_u = \frac{V}{k_B T} \int_0^t \Pi_{xy}(\tau)\Pi_{xy}(0)\ d\tau$$



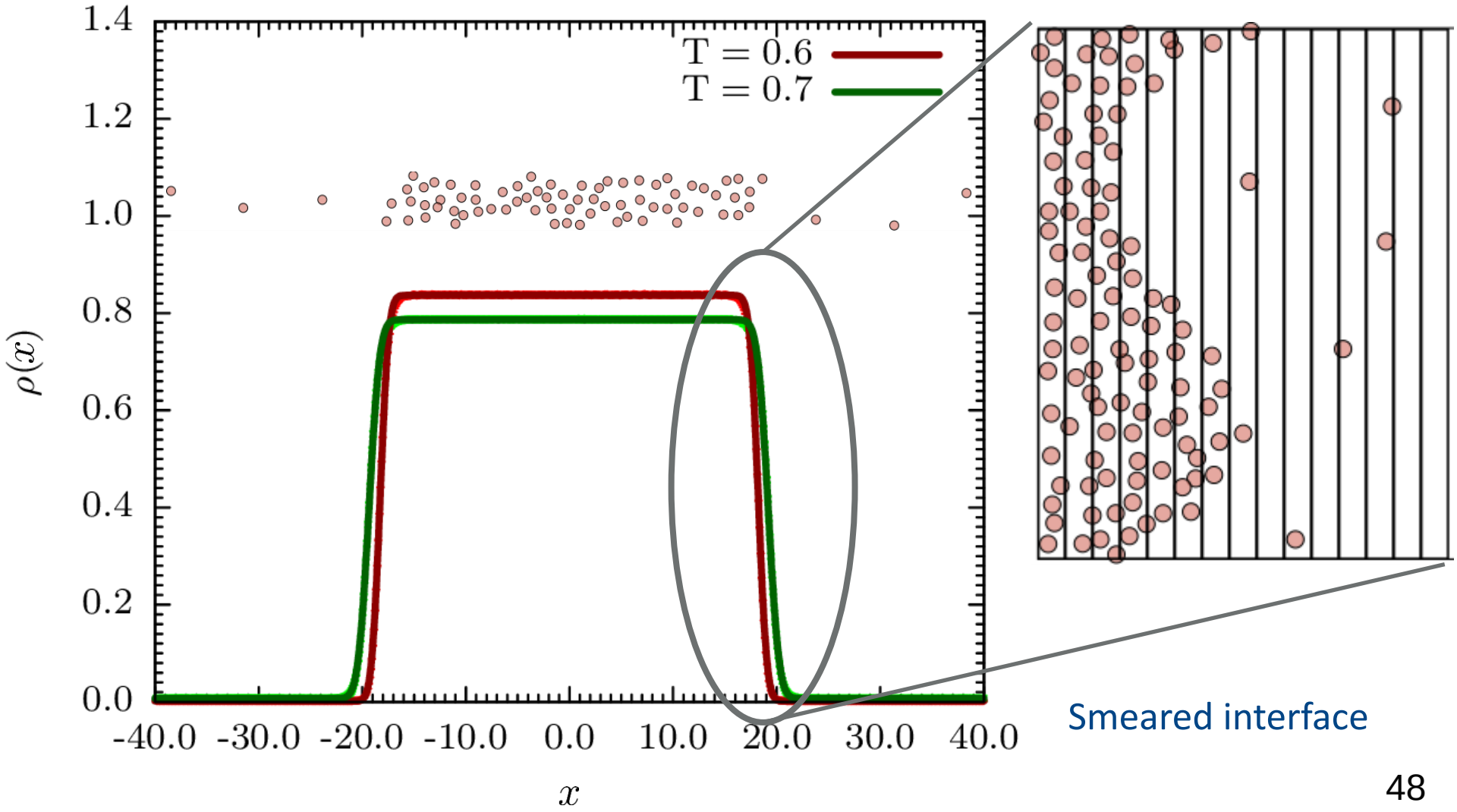
- Viscosity can be negative
- The second law of thermodynamics is not absolute, just exponentially more likely as system size increases
- Know as fluctuation theorem

Section 2.3

INSIGHTS FROM MD

> Multi-phase Flow

Multiphase Flows



Smeared interface

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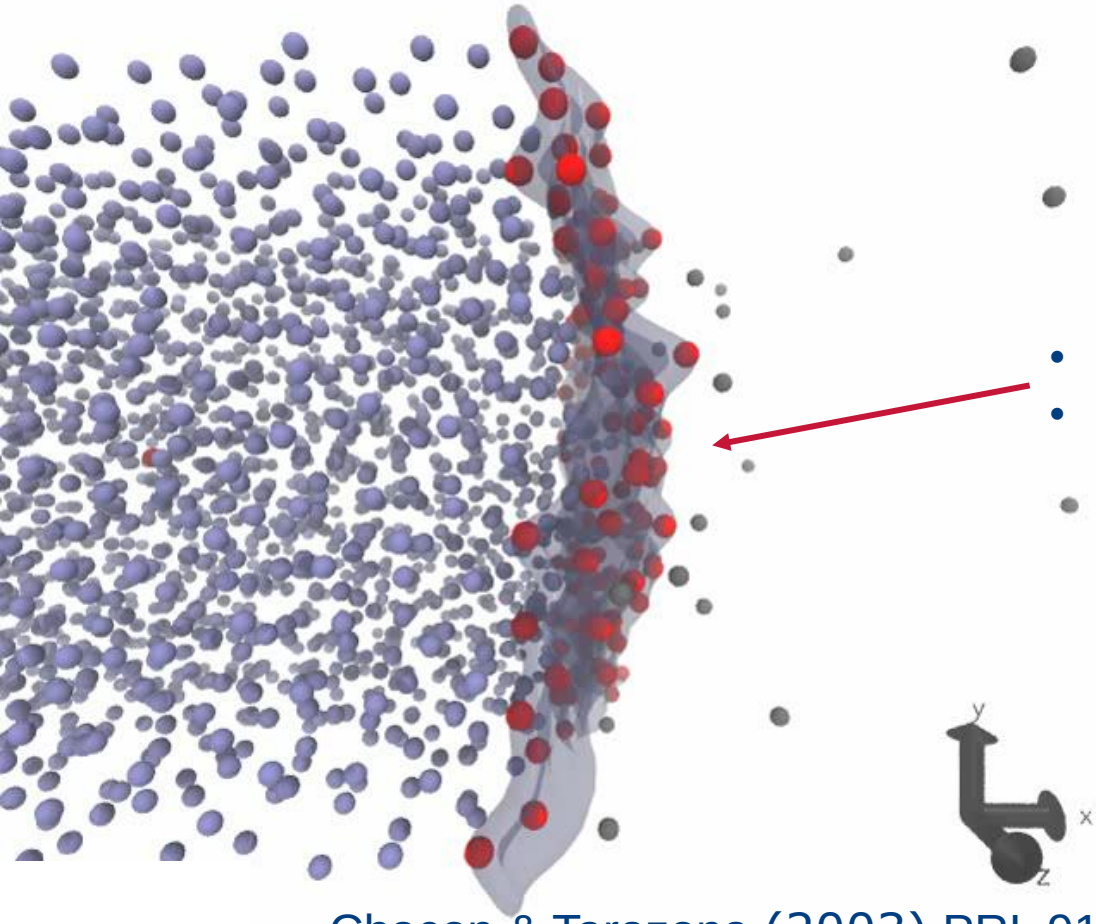
Intrinsic surface

- Molecular dynamics naturally forms a liquid vapour interface



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

Chacon & Tarazona (2003) PRL 91, 166103

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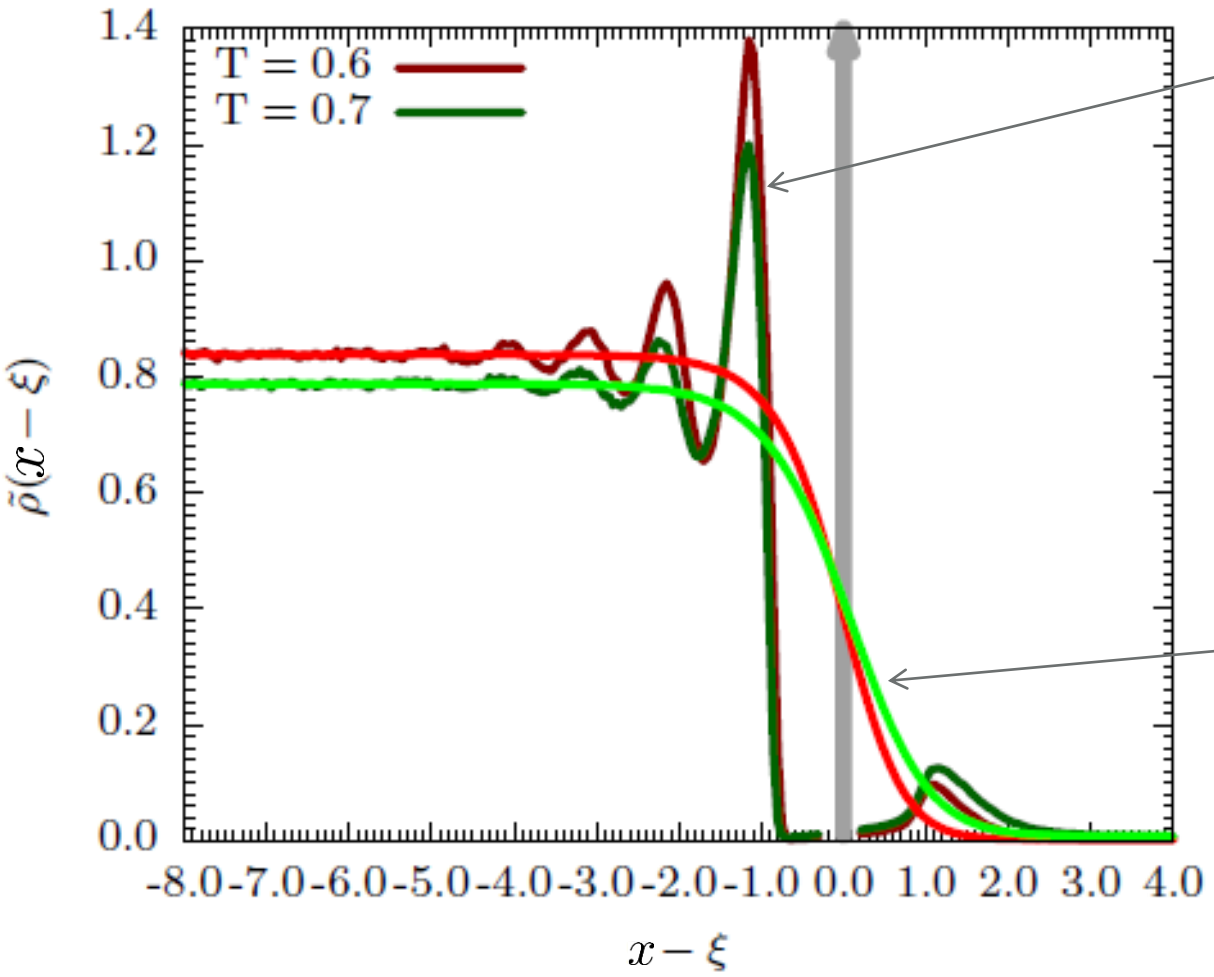
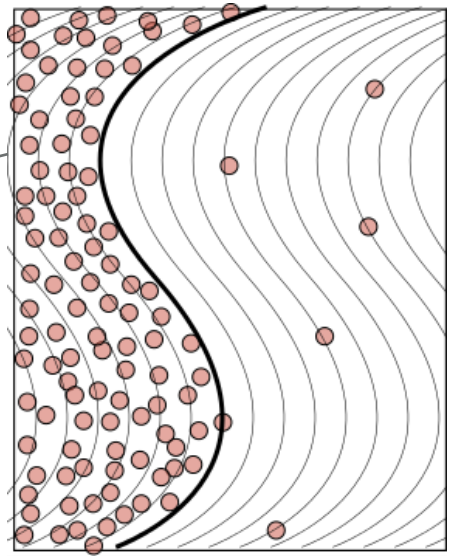
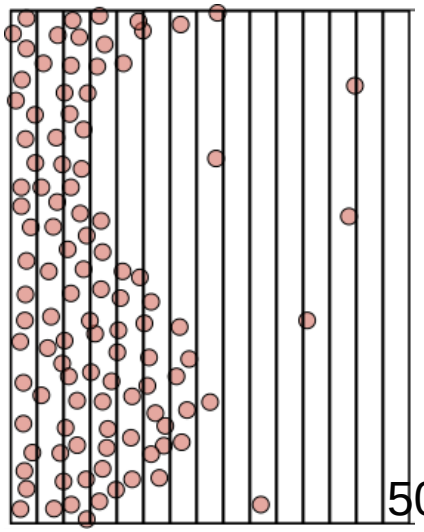
Results for Density

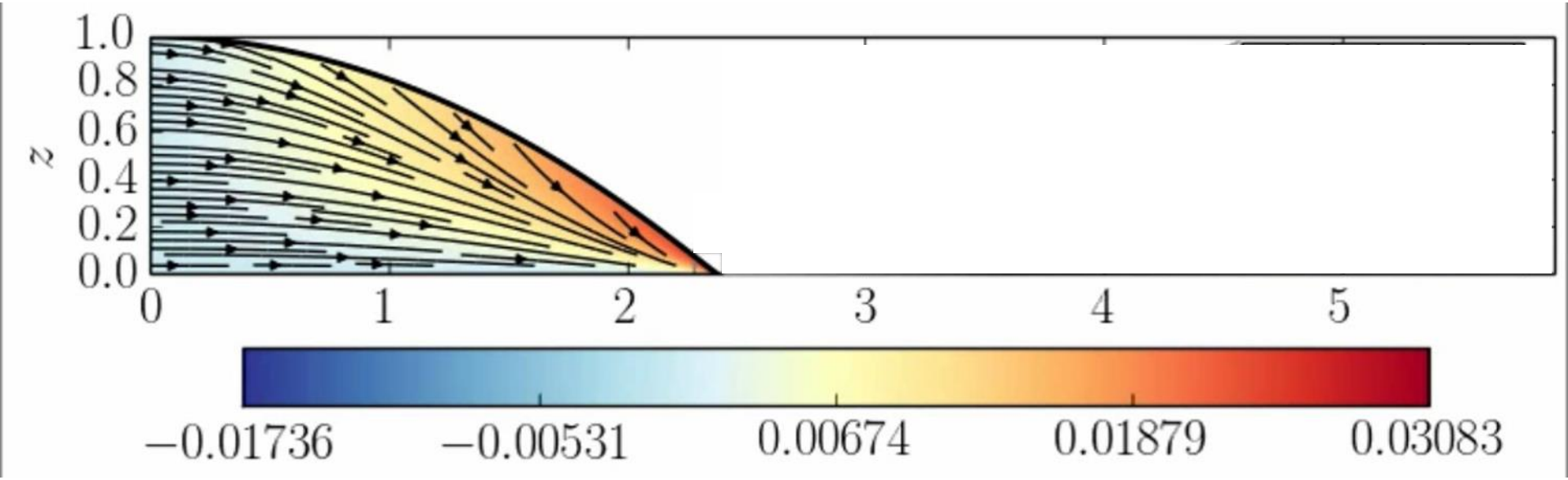






Dynamic Contact Line

1) Thompson and Robbins (1989)



Dynamic Contact Line

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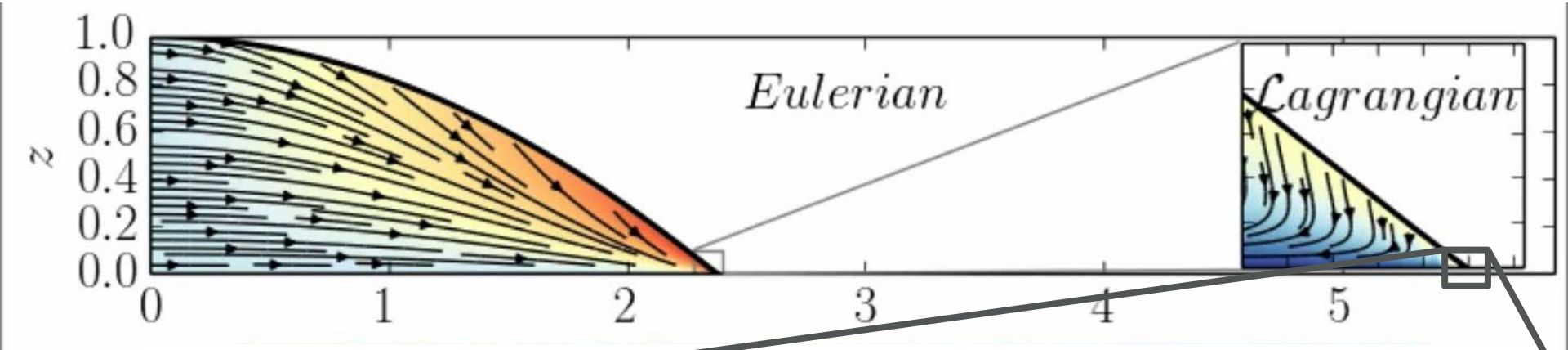
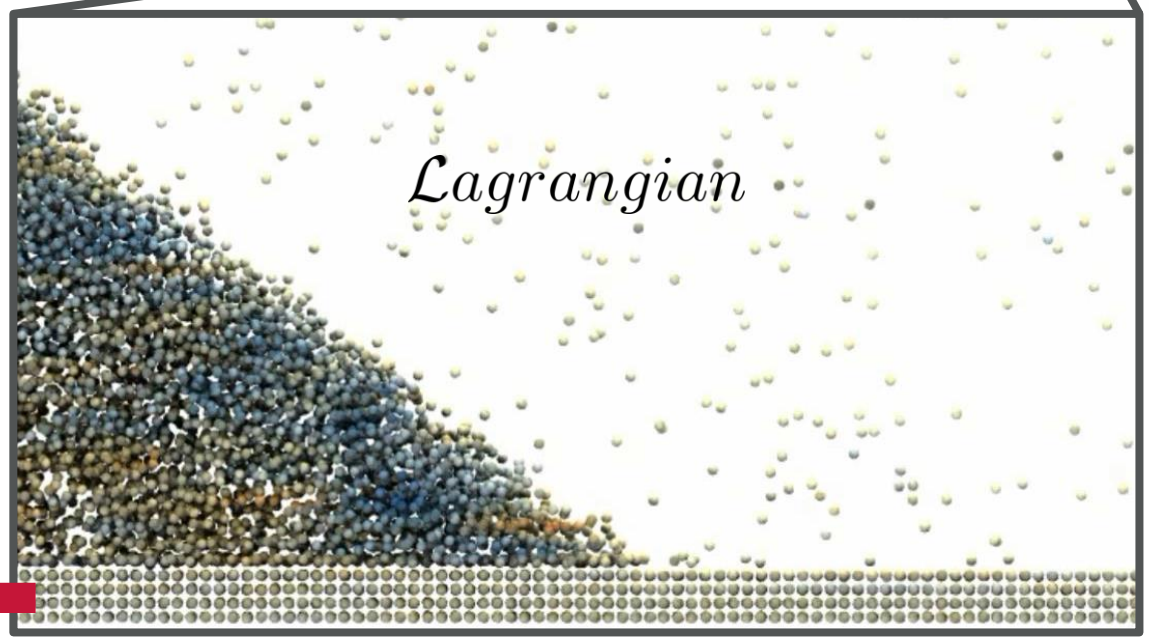


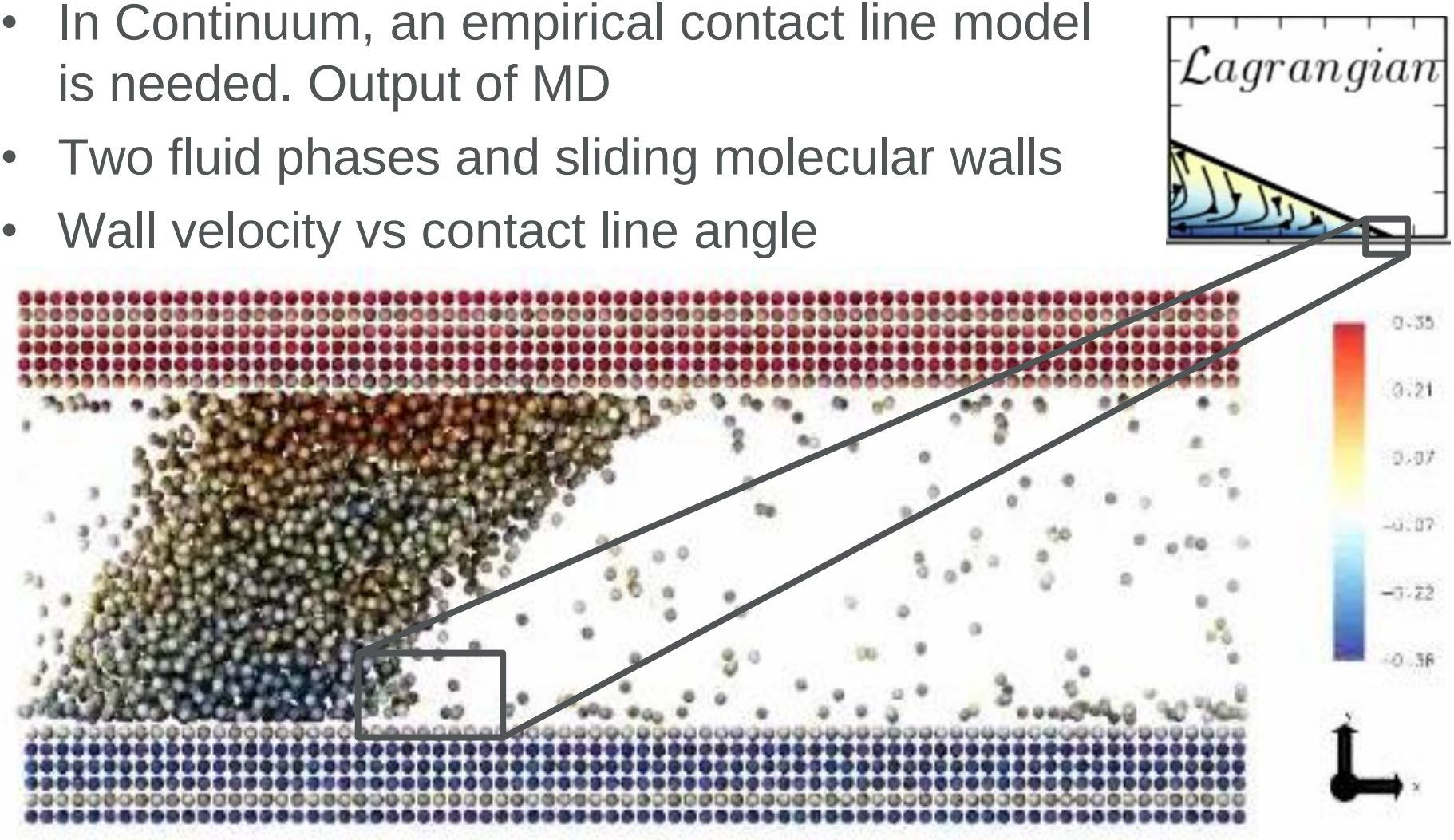
- Model the moving contact line with MD
- We want contact line speed as a function of continuum contact angle

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



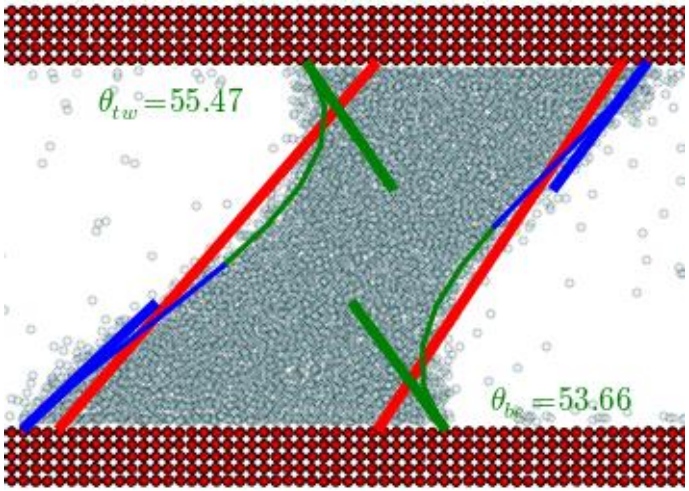
Dynamic Contact Line

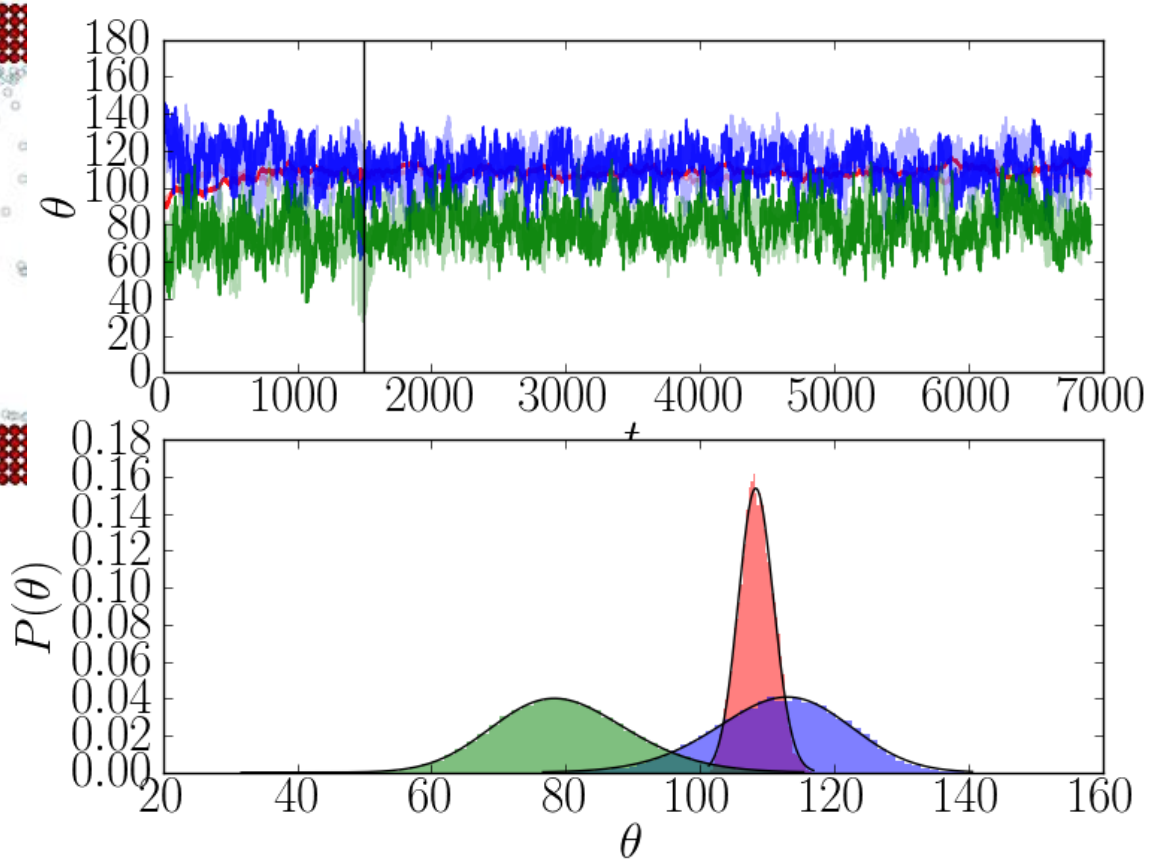
- In Continuum, an empirical contact line model is needed. Output of MD
- Two fluid phases and sliding molecular walls
- Wall velocity vs contact line angle



Time Evolution of Contact Angle

- Contact angles fluctuates as a function of time





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

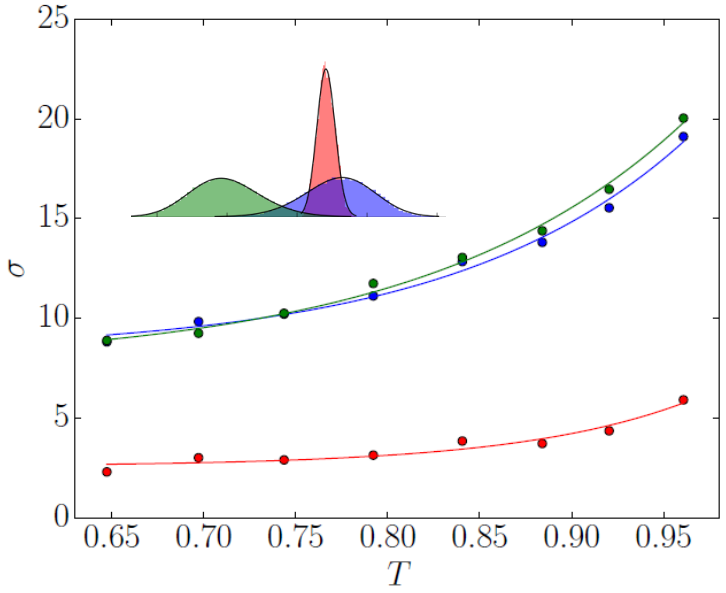
- *Linear*, *Advancing* and *Receding* angles

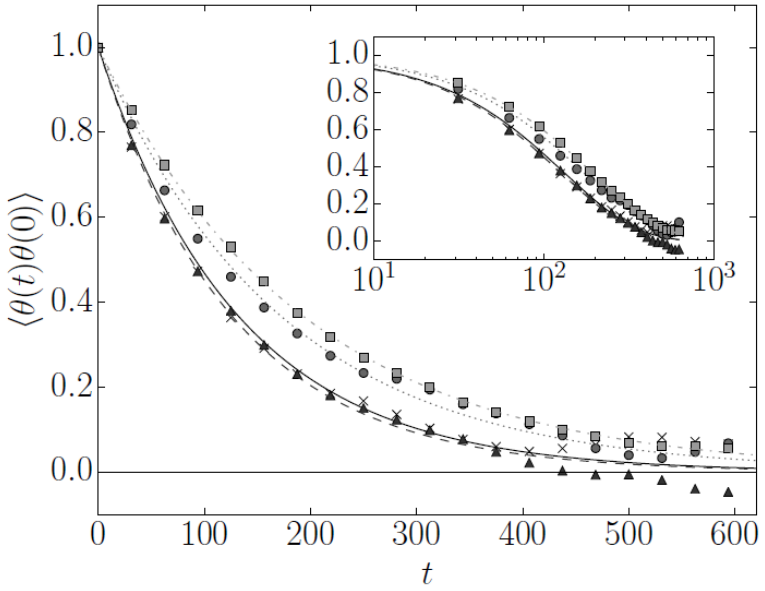
Building this into the Continuum Model

- 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.





Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

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Molecular Dynamics simulation of Nucleation

Wall w
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Work with Omar Matar & Tassos Karayiannis
EMBOSS EPSRC grant

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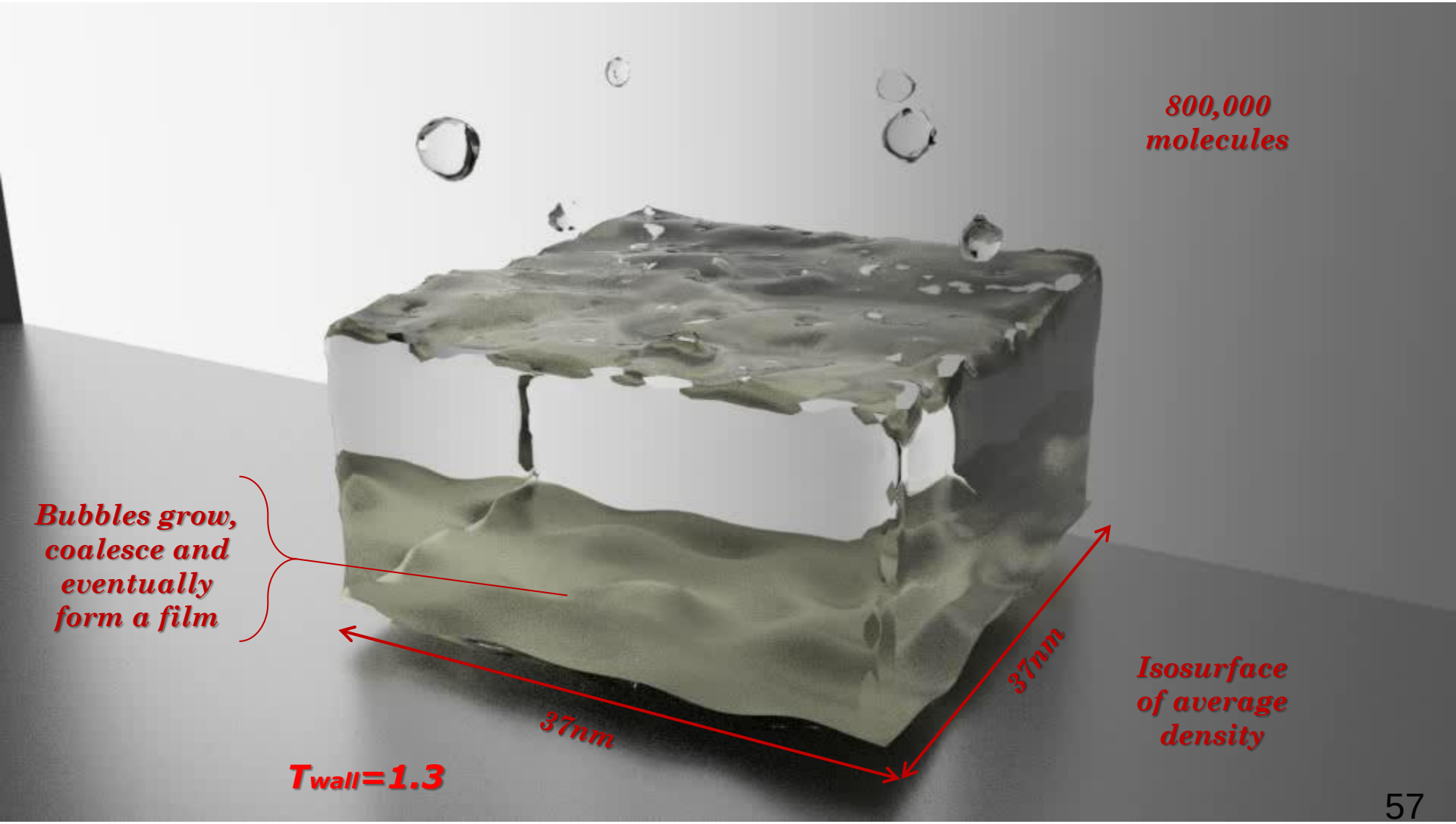
Isosurface of Density



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Section 2

COUPLED SIMULATION

Coupling – Using MD with CFD

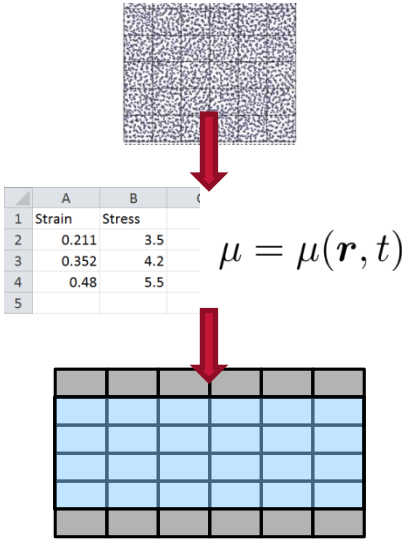
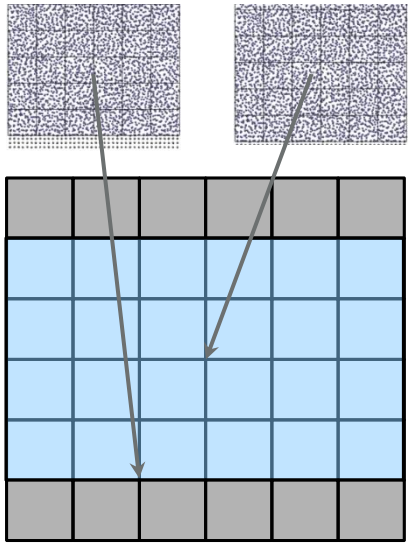


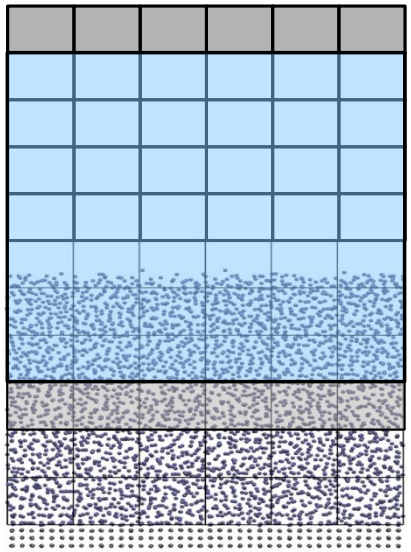
Table Lookup or Coefficients

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)

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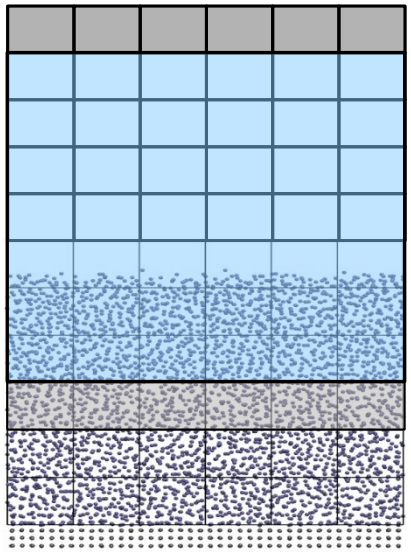

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Coupled CFD-MD Simulation

- Finite Volume Solver

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

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

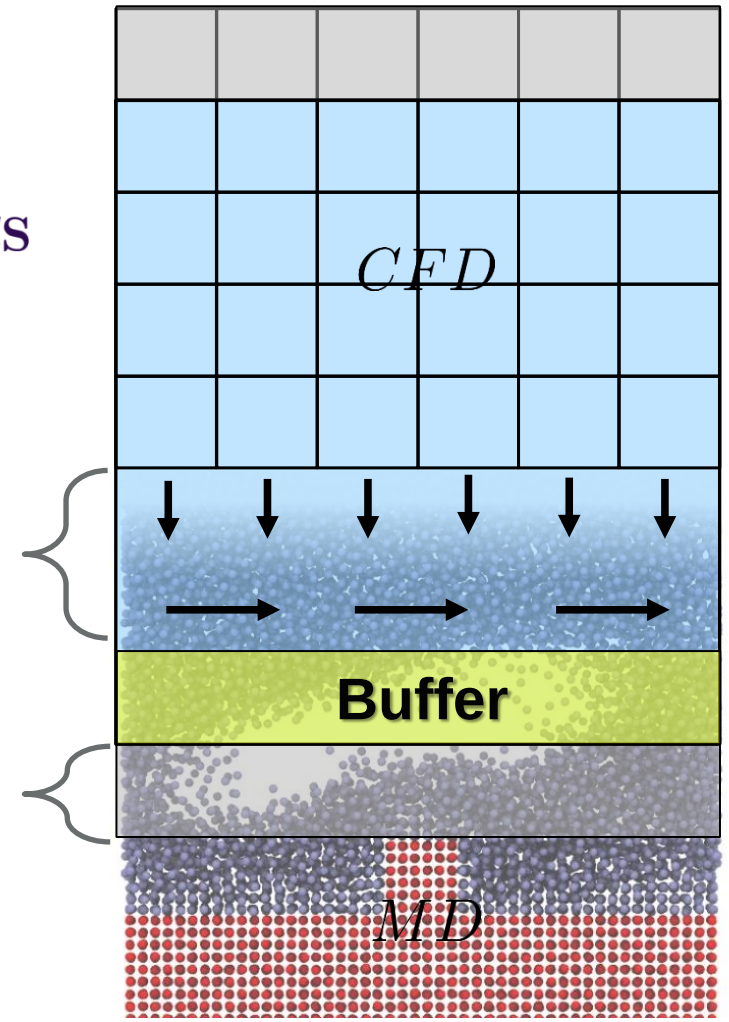
CFD→MD Boundary condition

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

MD→CFD Boundary condition

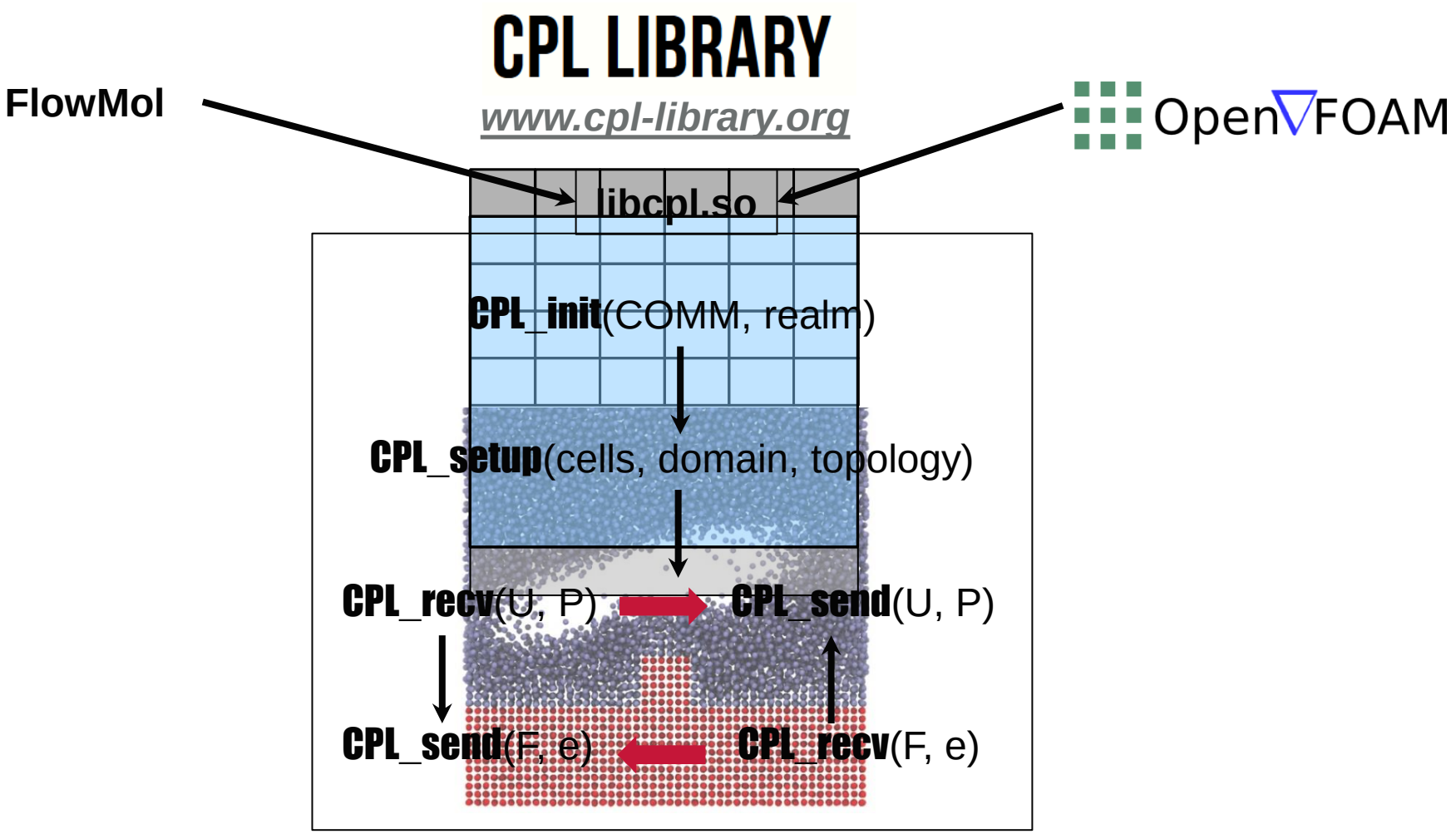
- Discrete molecules

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



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

Coupled Simulation Software



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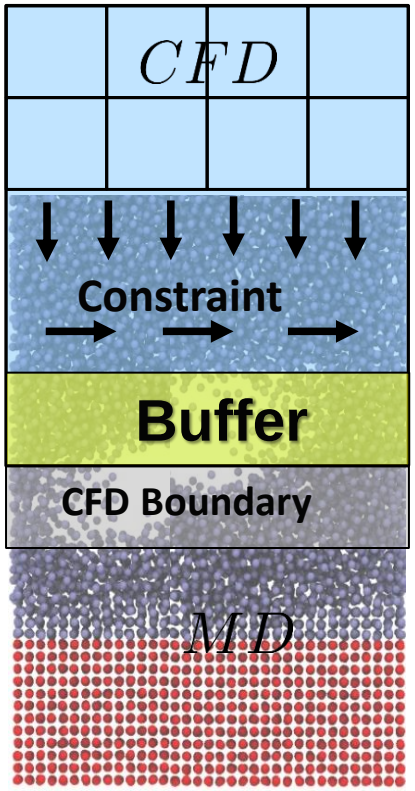
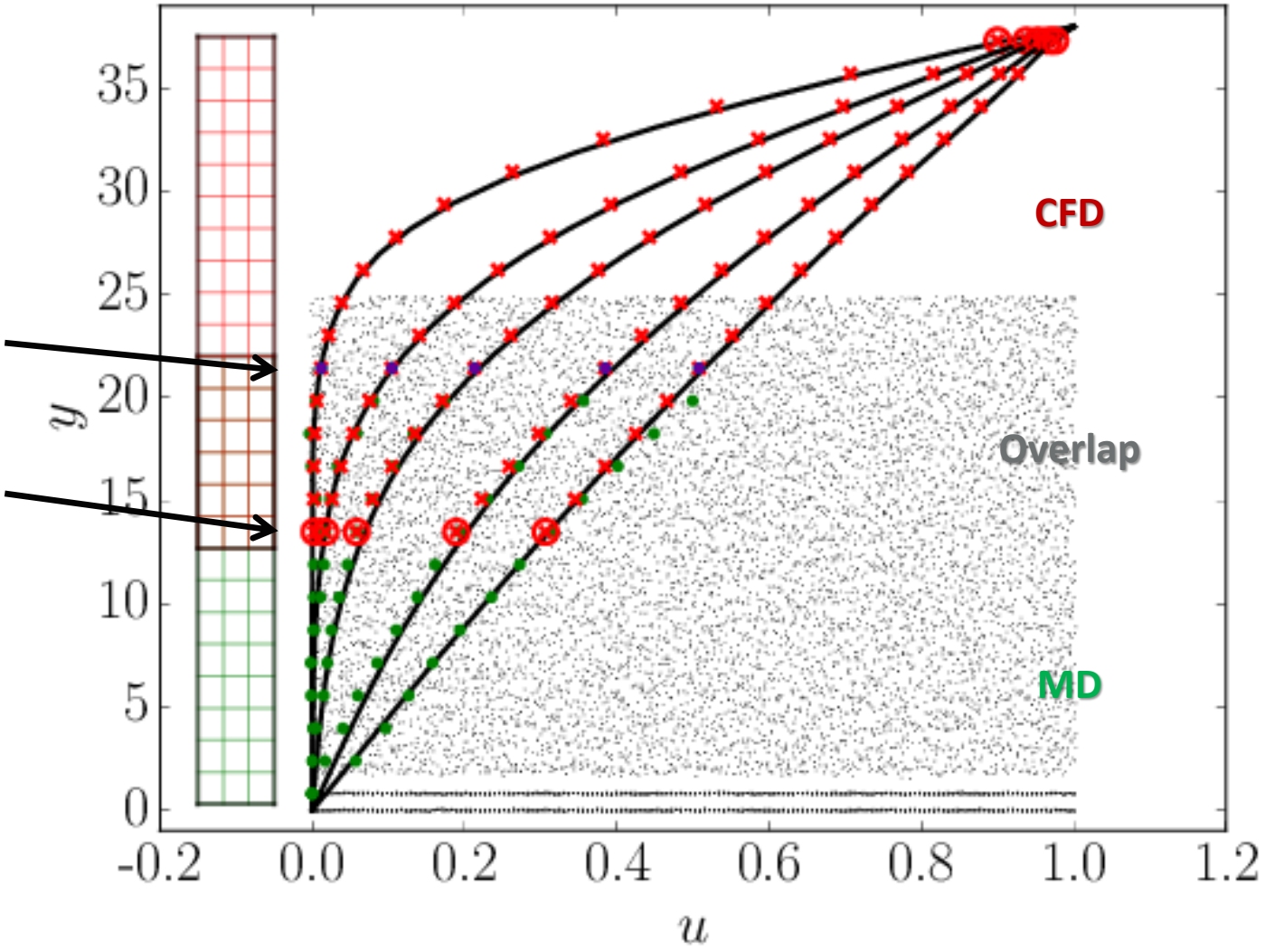
Coupling Results – Couette Flow





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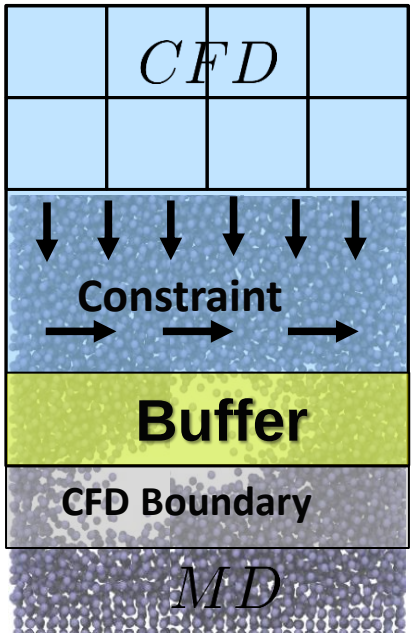
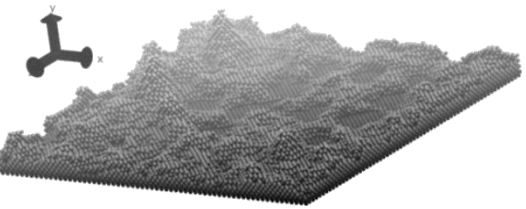
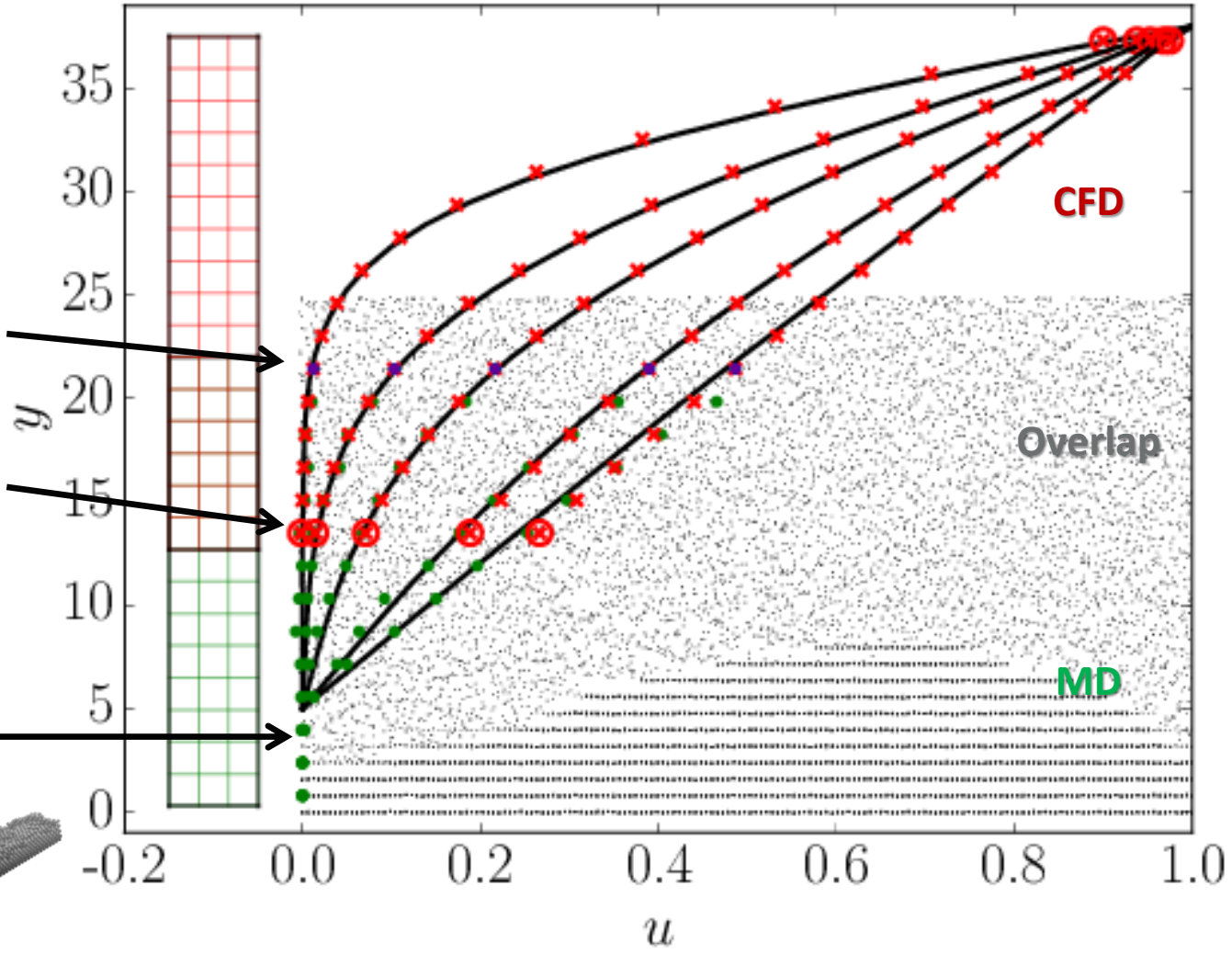
Coupling Results – Couette Flow



Rough wall shifts zero location





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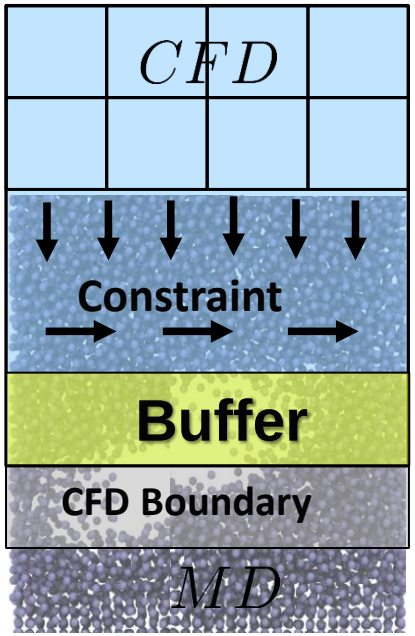
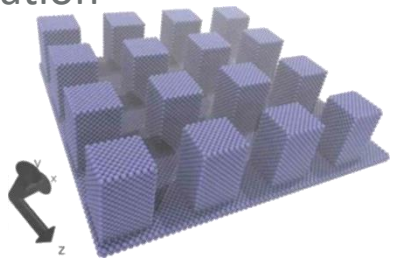
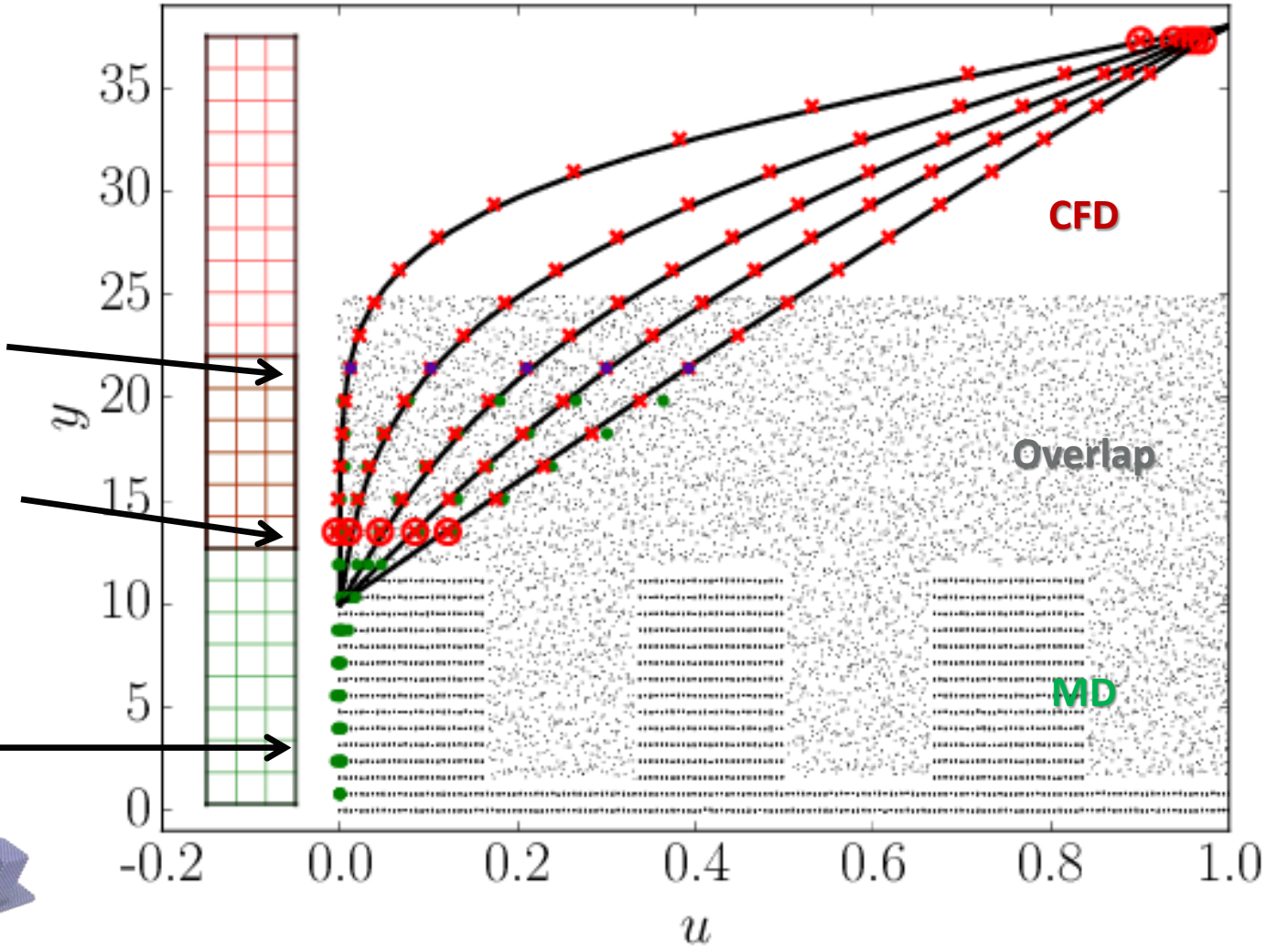
Coupling Results – Couette Flow



Posts shift zero location





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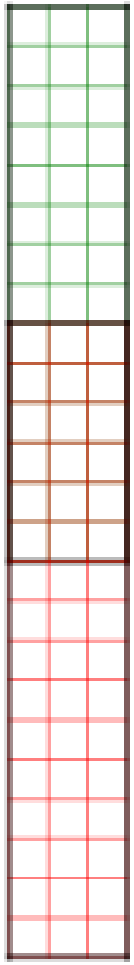
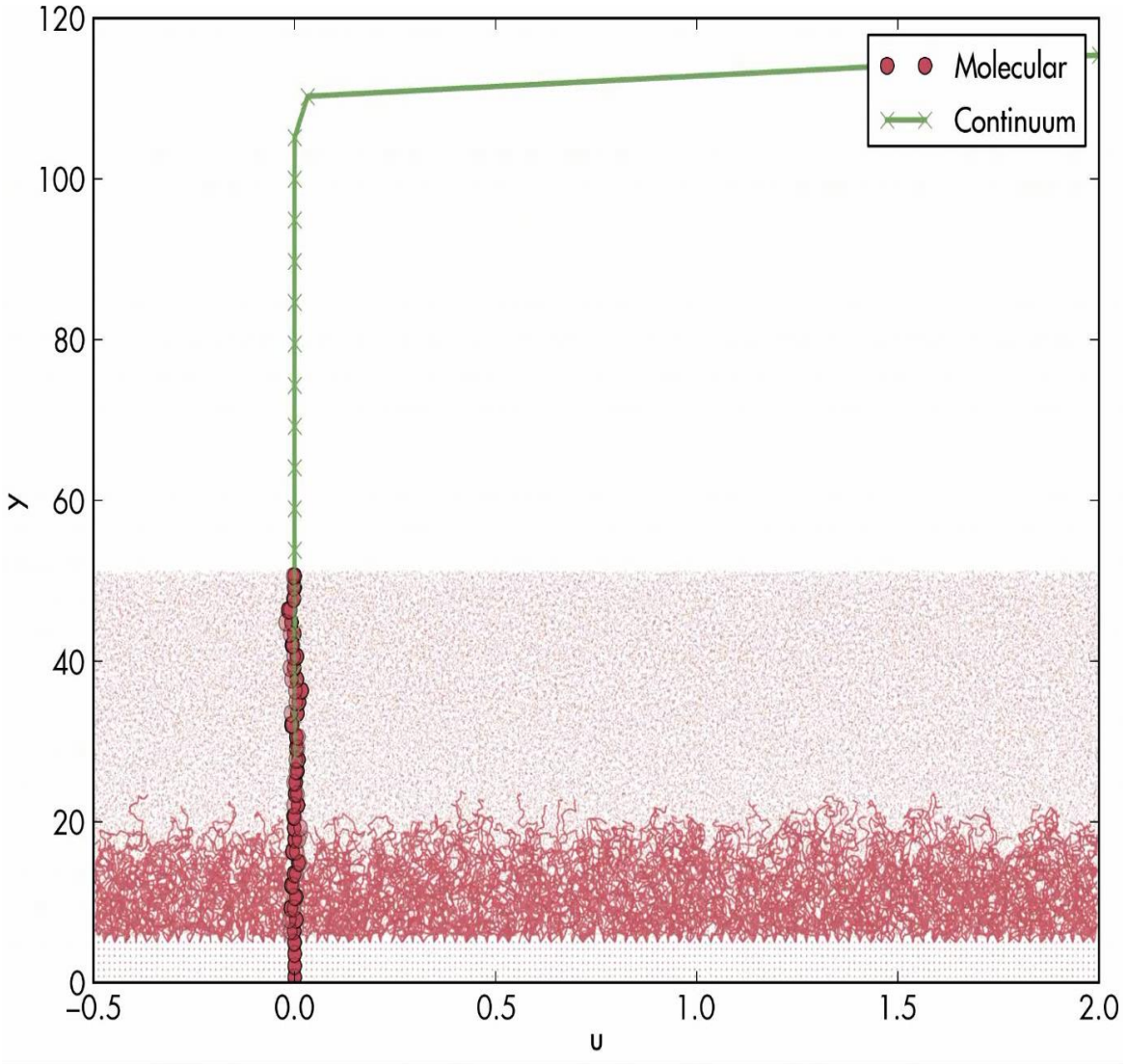
Coupling Results – Polymer Brushes



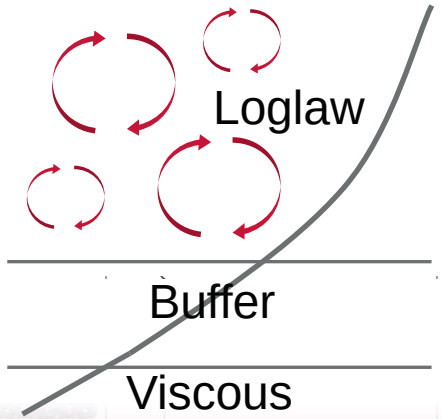
CFD Region

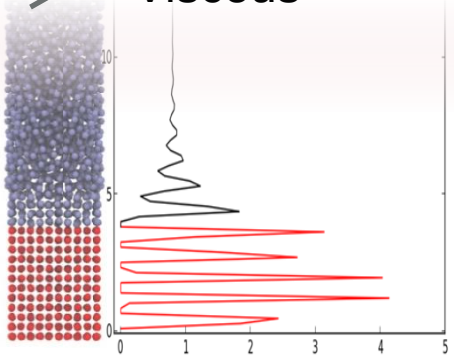
Overlap Region

MD Region

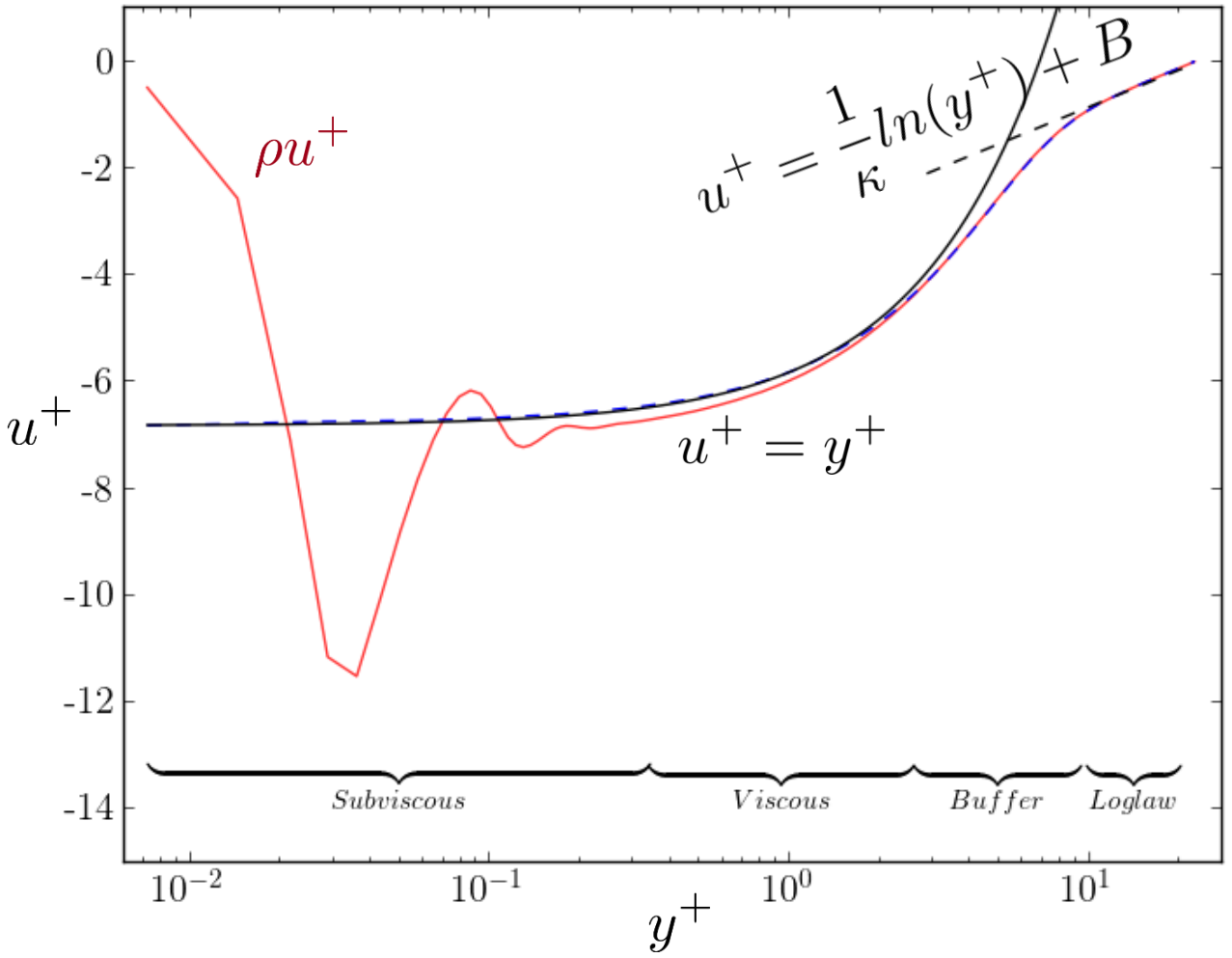


Coupling Results – Turbulent Couette

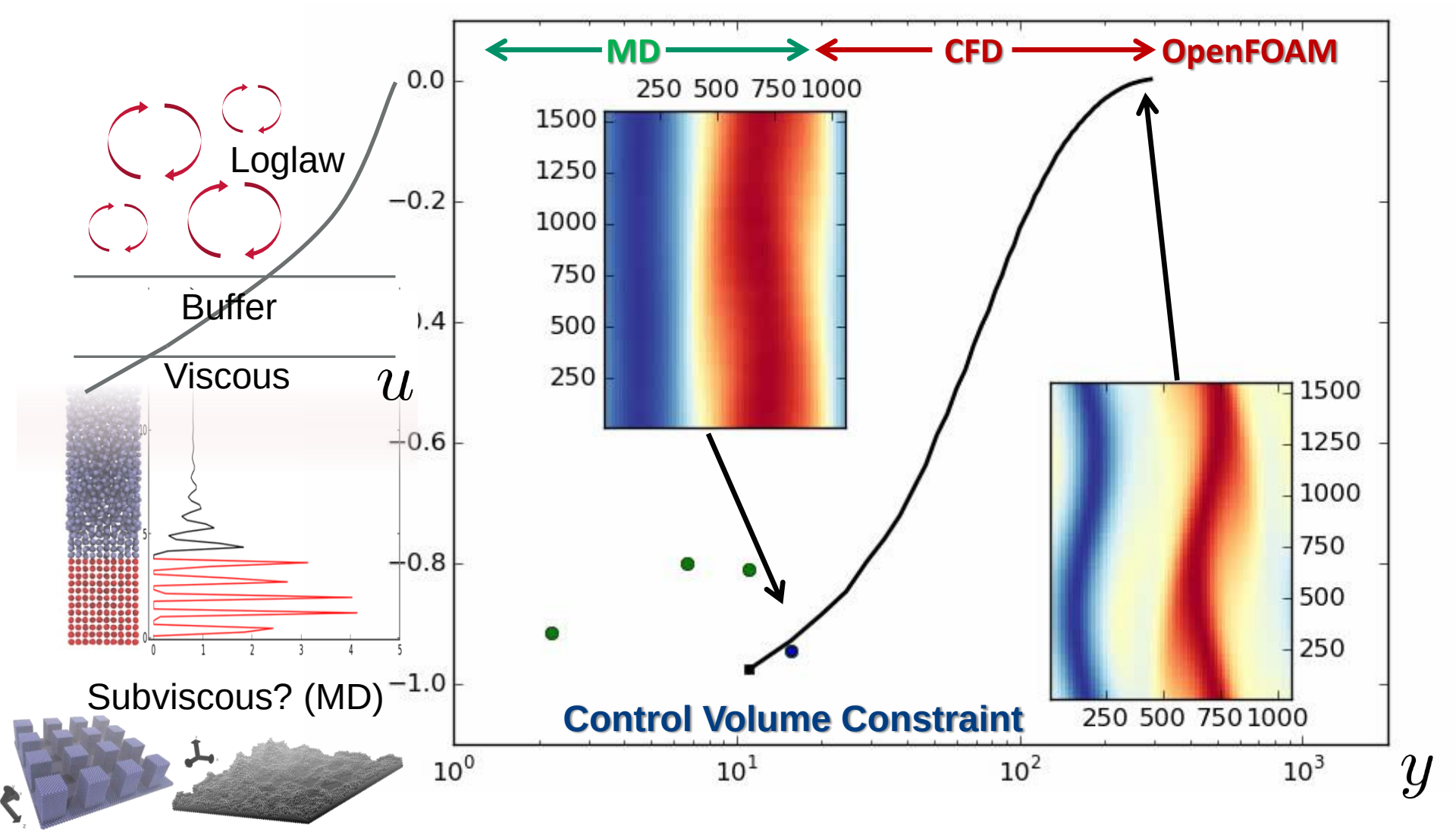




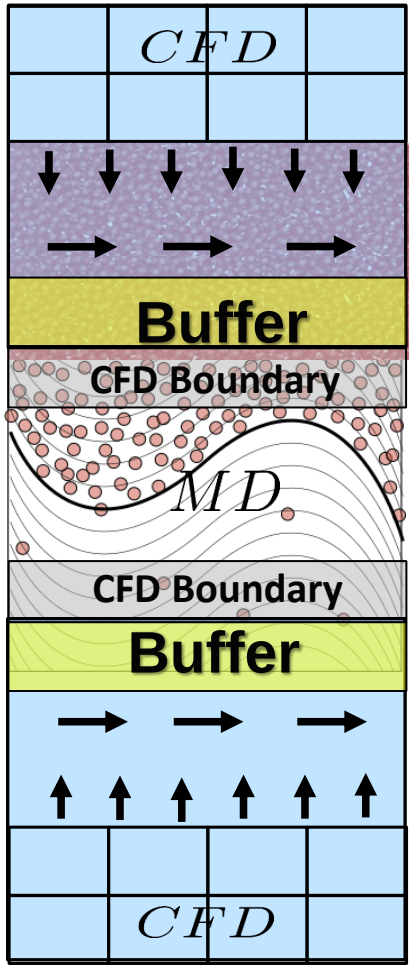
Subviscous? (MD)

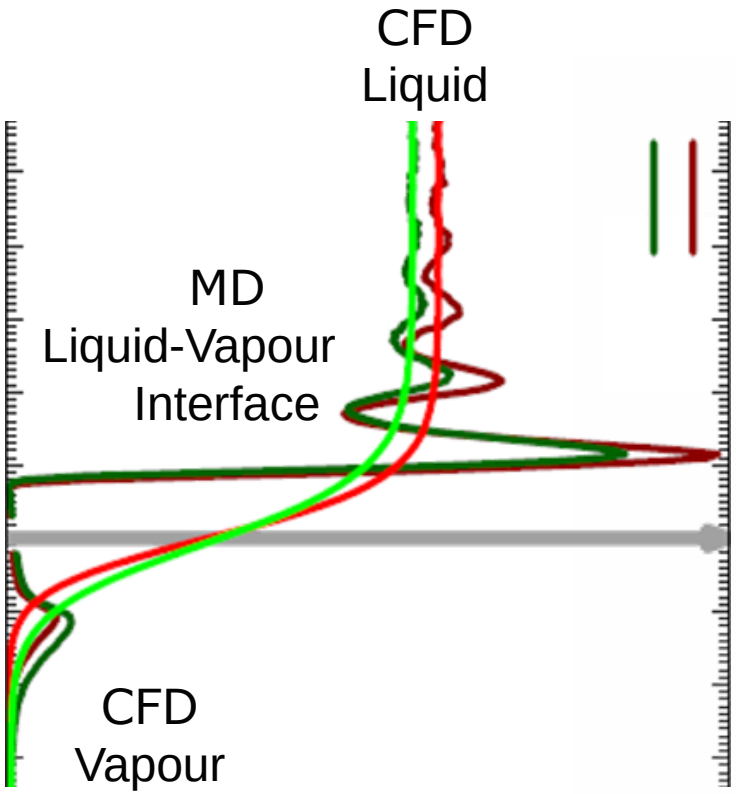


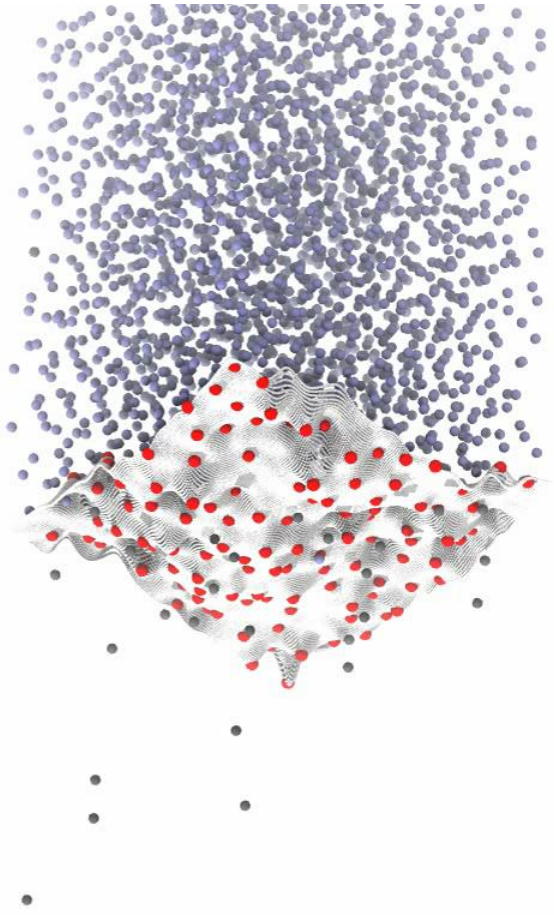
Coupling Results – Turbulent Couette



Coupled Simulation of An Interface

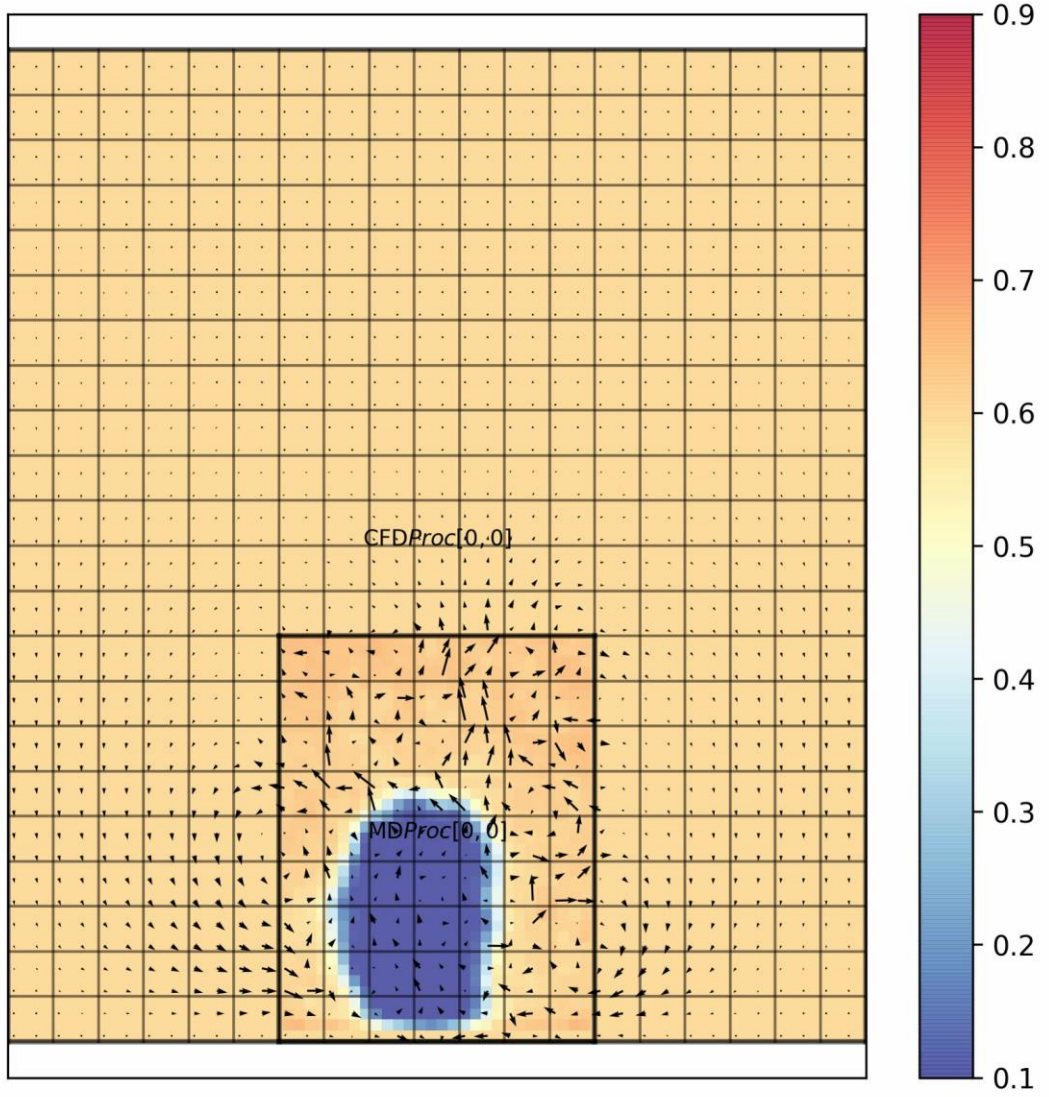






Coupled Simulation of Boiling

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



Summary

- Introduction to Molecular Dynamics (MD)
  - Solves Newton's law for individual molecules
  - Only empirical assumption is inter-molecular interaction (tuned by quantum mechanics detail)
  - Energy conserved and viscosity, surface tension, etc outputs
- Insights from Molecular Dynamics (MD)
  - Insights into minimal channel turbulent flow
  - Turbulent eddies are viscosity at inter-molecular scale, viscosity can be negative
  - Multi-phase flow, contact line and nucleation modelled
- Coupled Simulation
  - Use MD only where needed as part of a CFD simulation – including near wall, liquid vapour interfaces
  - Allows large simulations to be run cheaply