Imperial College London

Brunel University London

A Tutorial of Boiling Simulation using Coupled Molecular Dynamics and Computational Fluid Dynamics

Royal Society-DFID

Africa Capacity Building Initiative

19th July

Edward Smith

Molecular Dynamics

- Introductions to Computational Fluid Dynamics (CFD)
  - Assumptions and modelling paradigm
  - Introduction to numerical solutions
- Hands on 1
- Introductions to Molecular Dynamics (MD)
  - Assumptions and modelling paradigm
  - Introduction to numerical solutions
- Coupled Simulation
- Hands on 2

Slides and hands-on code at ***edwardsmith.co.uk/content/RS-DFID.zip***

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MOLECULAR DYNAMICS

Molecular Dynamics

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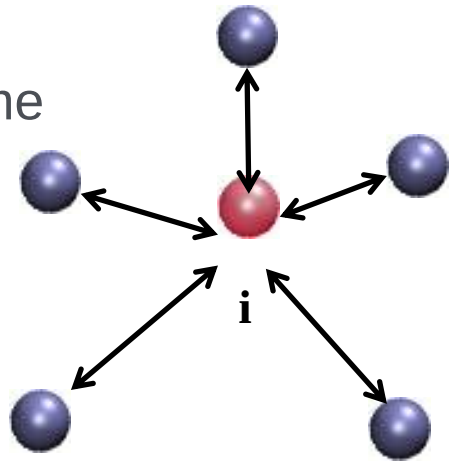
Discrete molecules in continuous space

- 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

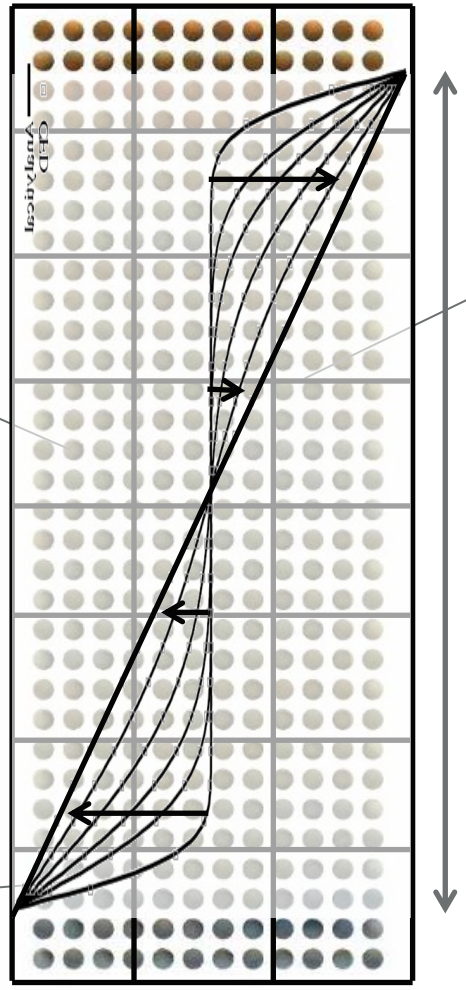
- Governed by Newton's law for an N-body system
- Point particles with pairwise interactions only

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

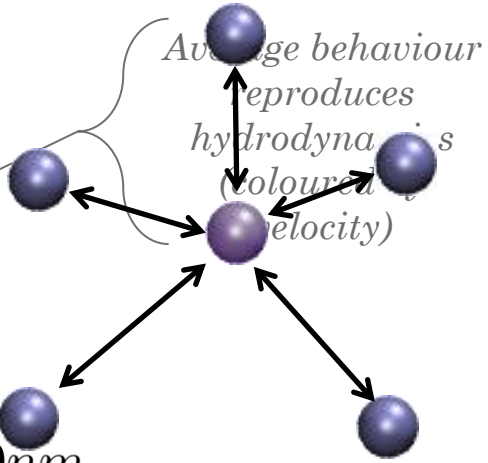
$$\Phi(r_{ij}) = 4\epsilon \left[\left(\frac{\ell}{r_{ij}} \right)^{12} - \left(\frac{\ell}{r_{ij}} \right)^{6} \right]$$

Molecular Dynamics

Liquid structure causes viscosity



Stick-slip near walls



$H \approx 9nm$

Reynolds Number

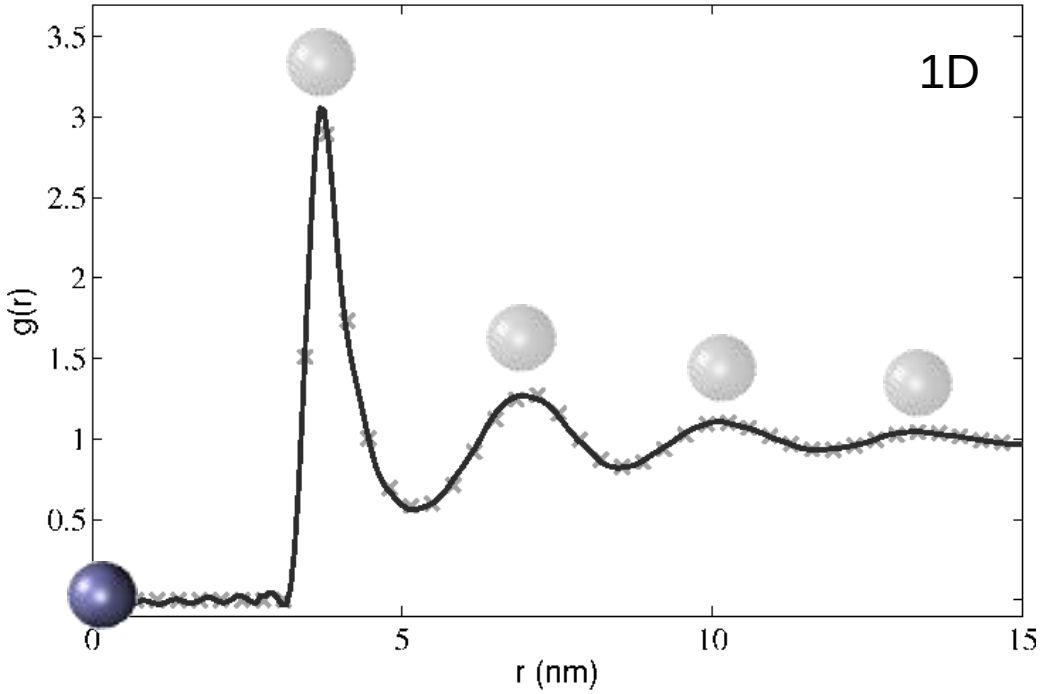
$Re \approx 15$

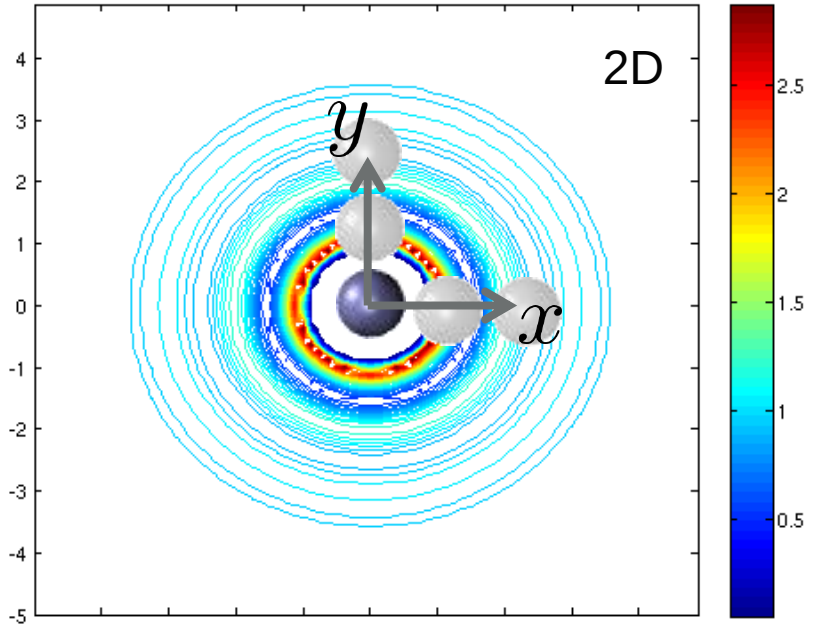
with

4096 molecules

Structure of Molecules

- The MD models the evolving structure of the molecular lattice



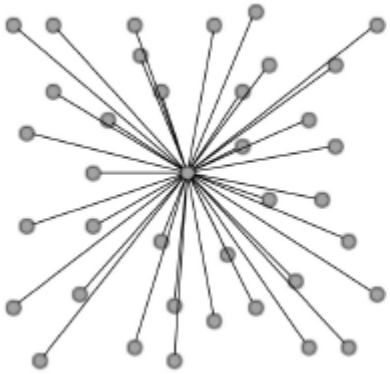


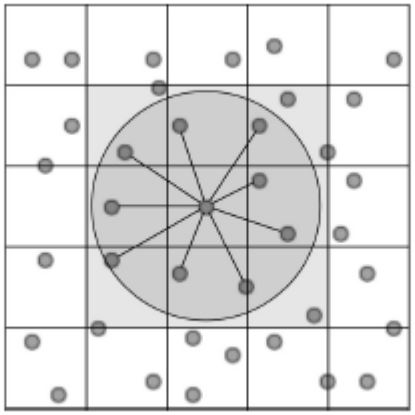
- Radial Distribution Function (RDF)

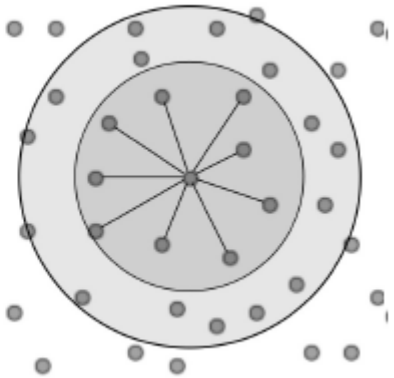
MD Computing

- 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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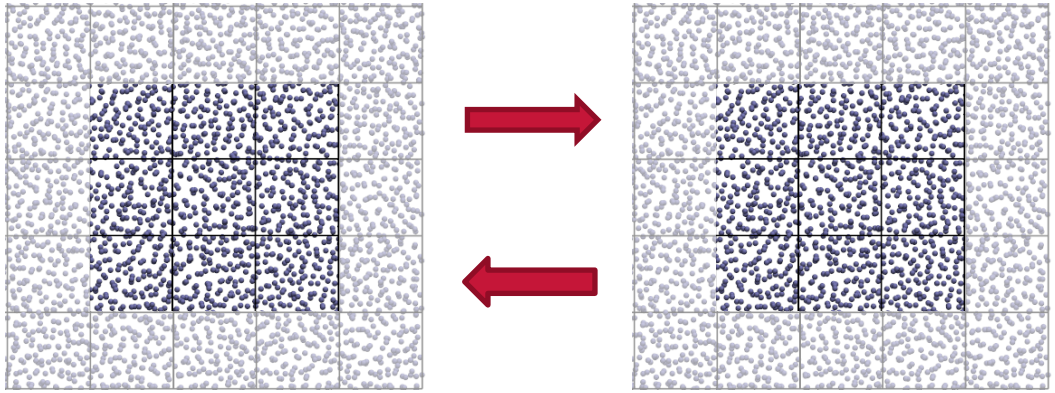
Localisations lends itself to parallel computing using MPI

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



Halo exchange of variable amounts of data

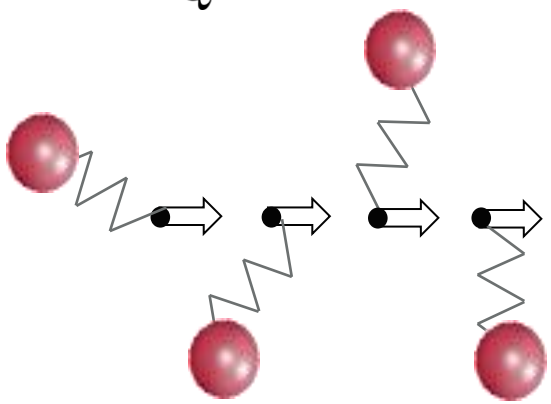
- MPI_Send
- MPI_Probe and MPI_Recv

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

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

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



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

Hand-On Session

- Minimal MD solver for two molecules

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

  - » Includes LJ force

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

  - » Time integrations

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

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

- MATLAB code

```
for n = 1:Nsteps
        %Calculate forces
        [a,U] = Force_calculation(ri,rj,rc);

        %Update molecular positions using leapfrog
        [ri,rj,vi,vj] = Leapfrog_int(ri,rj,vi,vj,a,delta_t);
end
```

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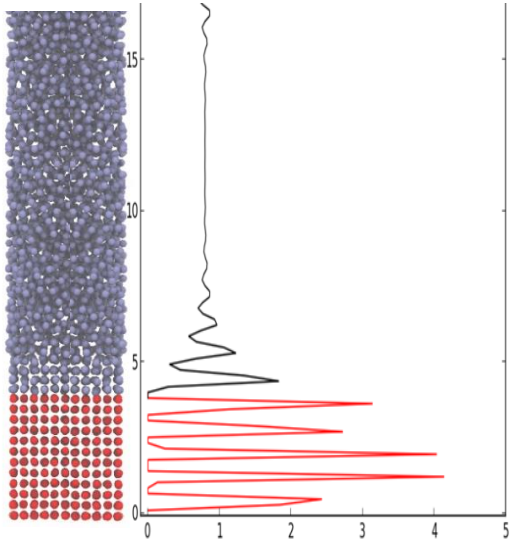
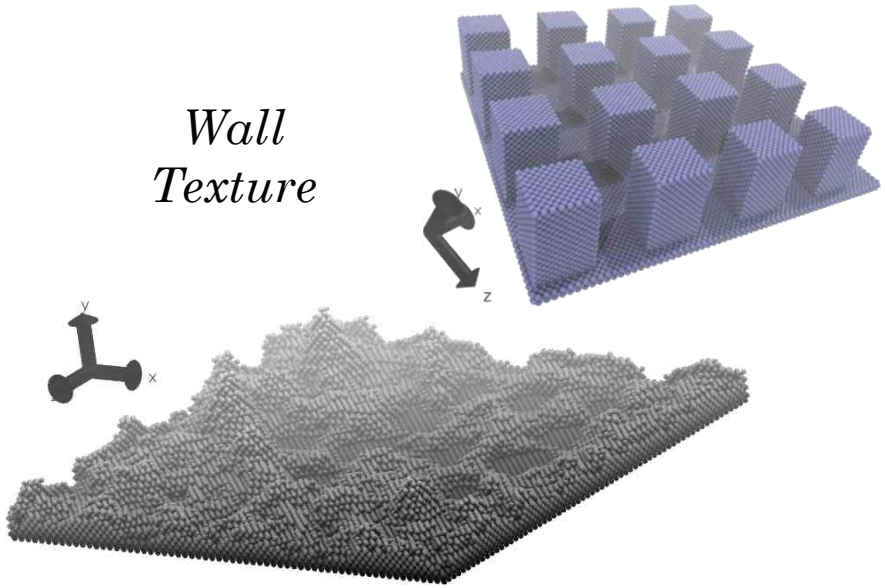
Molecular Dynamics – Complex Walls and Fluids

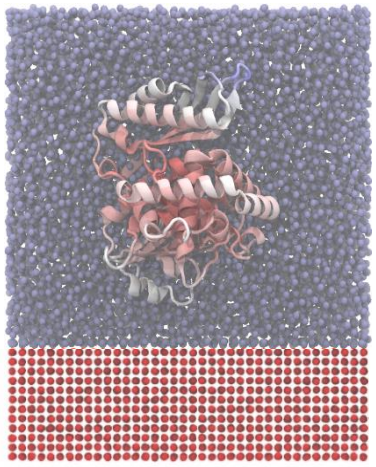
Liquid structure causes viscosity



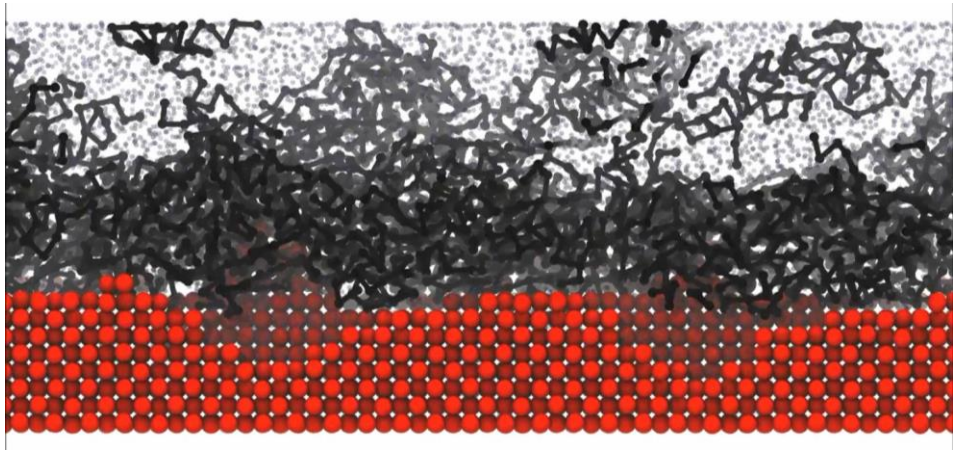
Stick-slip near walls

Wall Texture





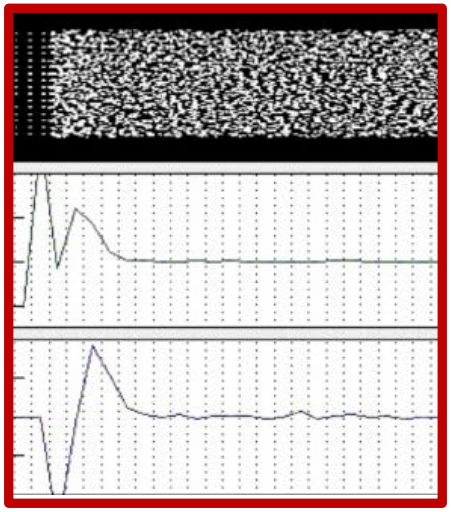
Molecules of arbitrary complexity



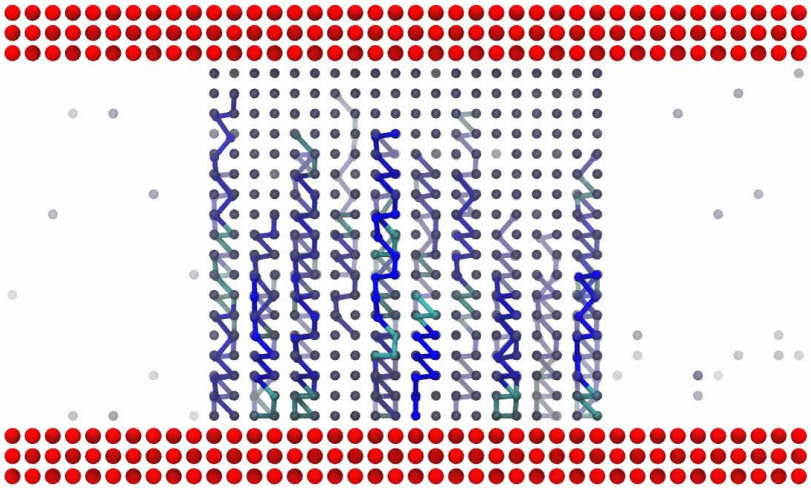
Oil, water and textured surface

Molecular Dynamics – Shocks and Multi-Phase

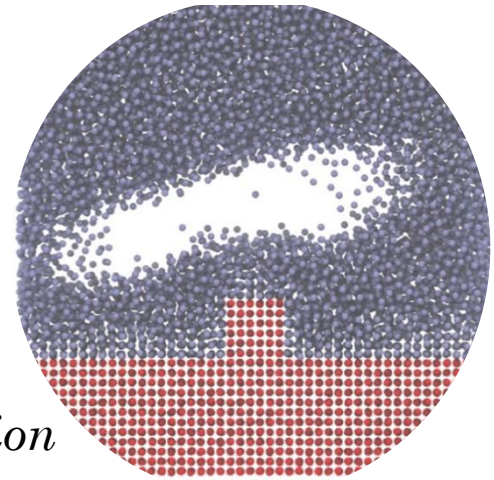
Shockwave



Droplet Formation

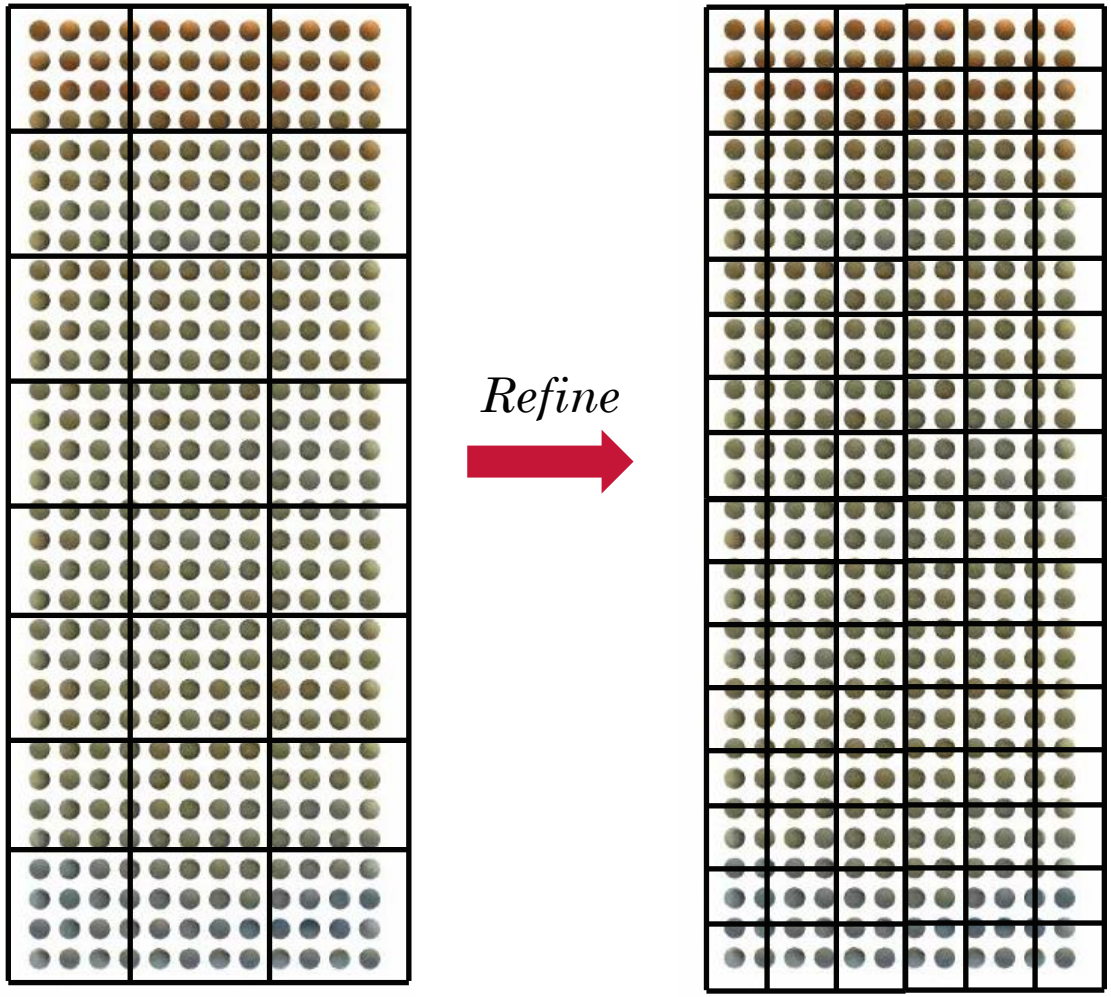


Contact line



Nucleation

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

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

Work with David Heyes,
Daniele Dini and Tamer Zaki

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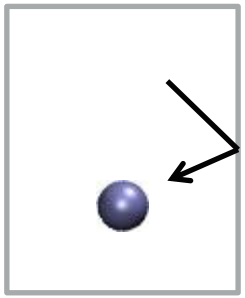
Pressure (stress) in an MD Simulation

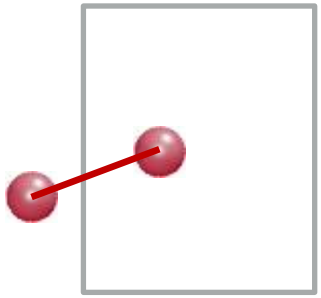
- Pressure definition in a dense molecular system
  - Kinetic part due to fluctuations
  - Configurational part due to liquid structure

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

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

Work with David Heyes and Daniele Dini

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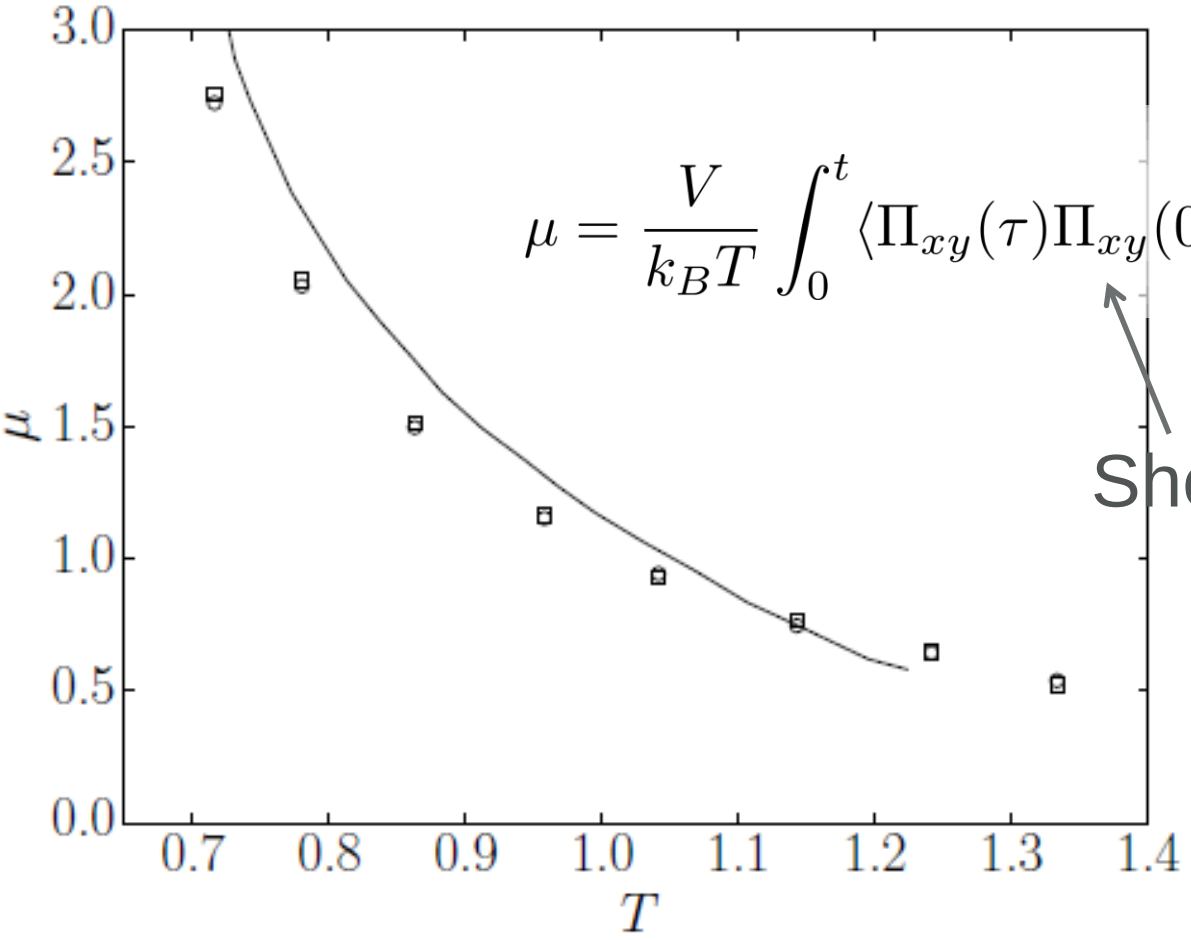
Viscosity

- Good agreement with experiments



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

Shear stress

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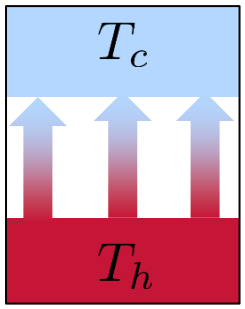
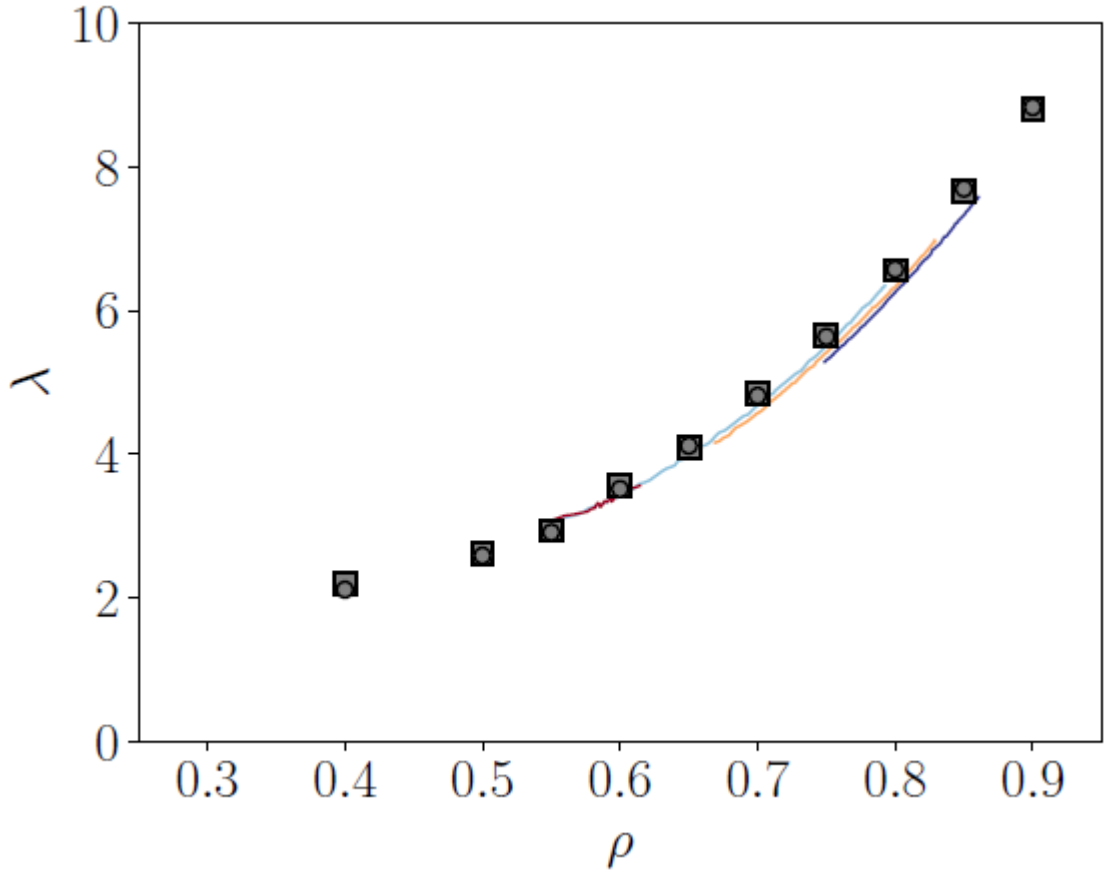
Fourier's law of heat conduction

- Good agreement with experiments

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





Work with Omar Matar, Richard Craster and Erich Muller

Results for Surface Tension

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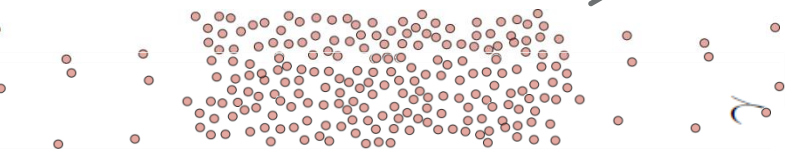
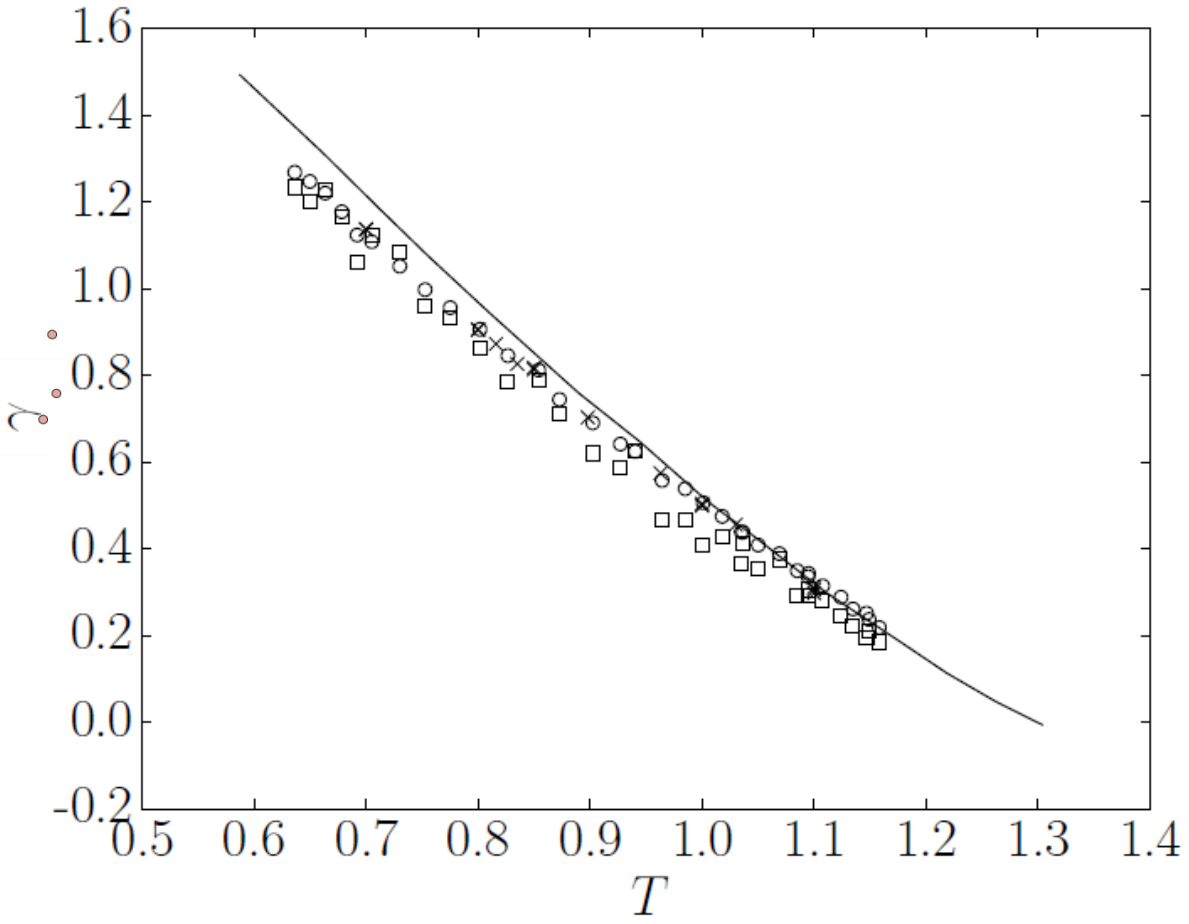
- Good agreement with experiments

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



Integrate over Liquid Vapour interface(s)



Work with Carlos Braga and Serrafim Kalliadasis

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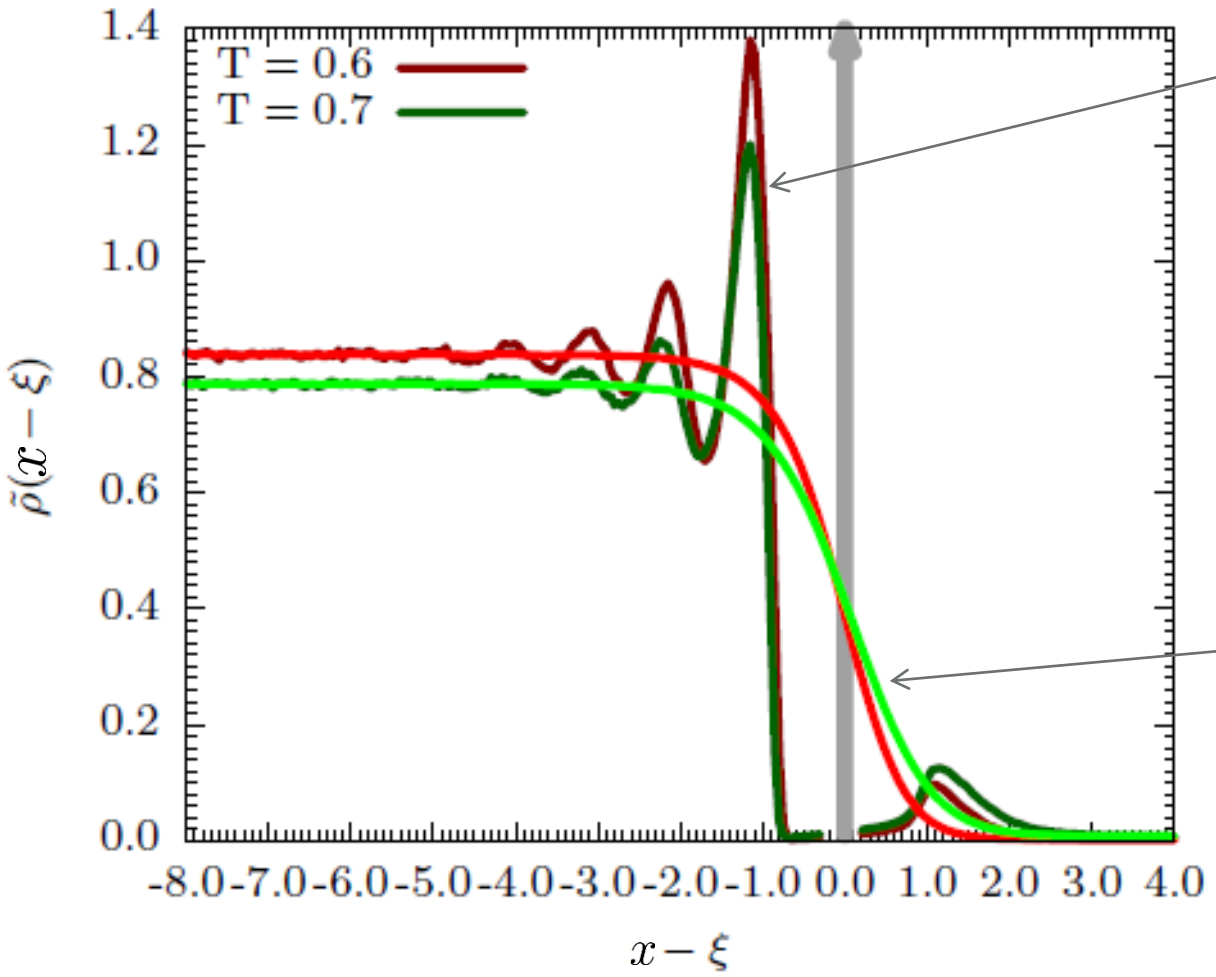
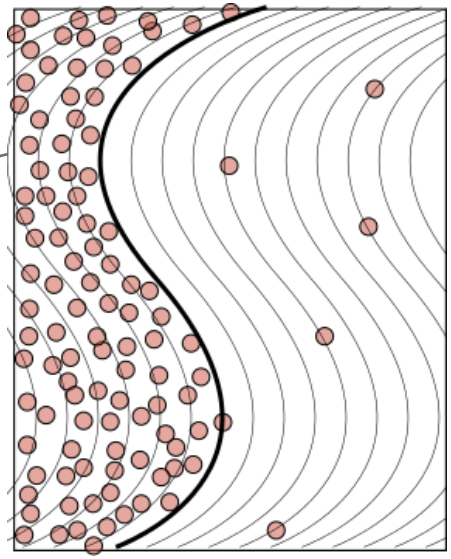
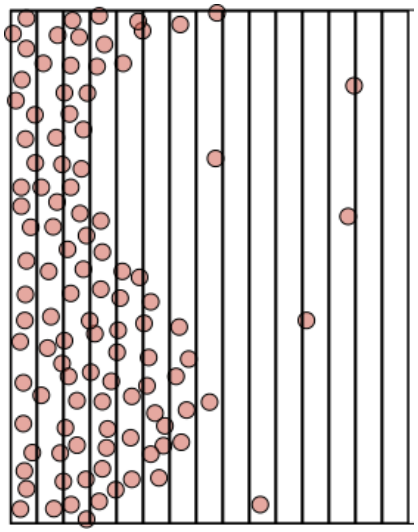
Results for Density



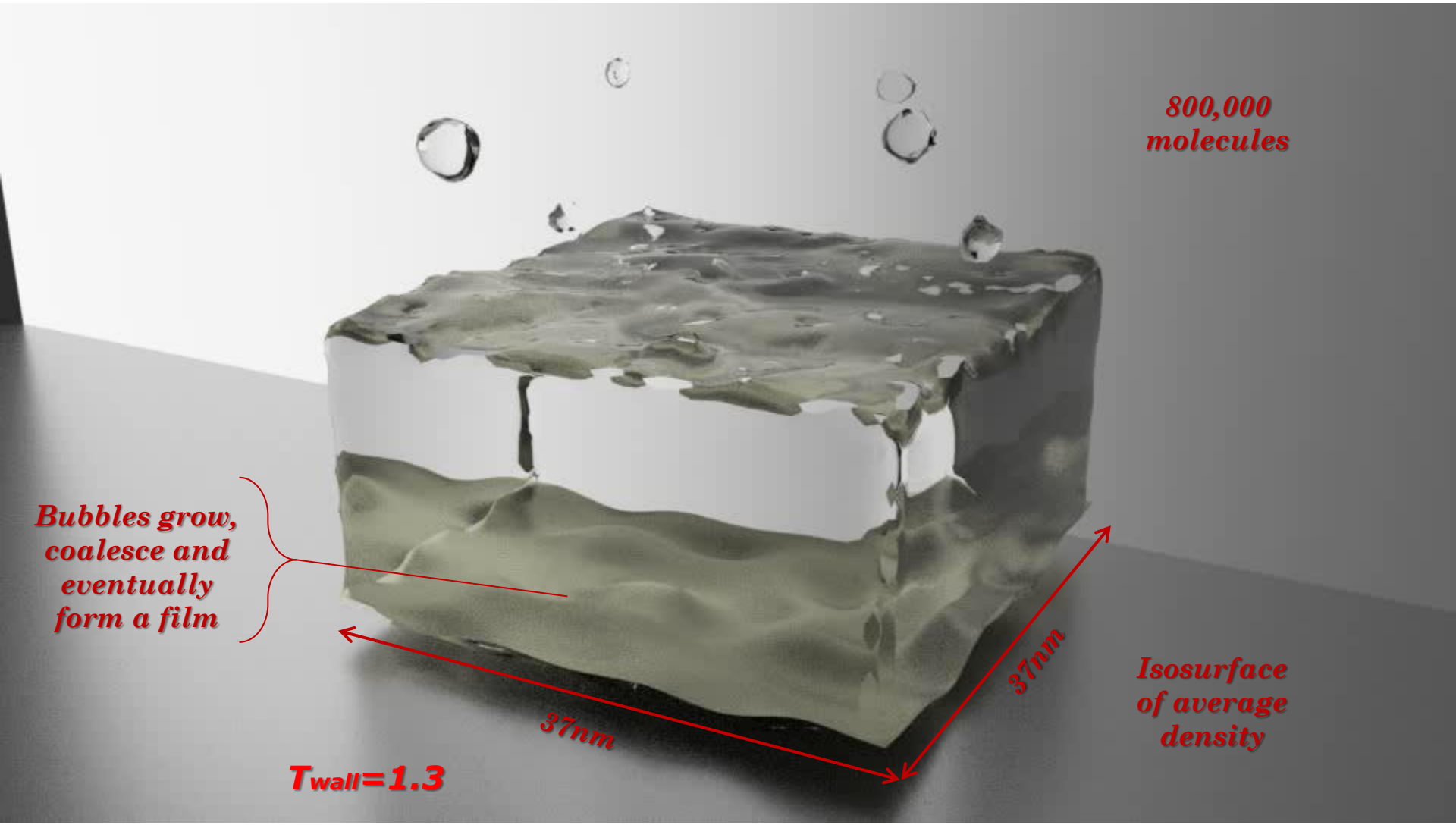




Nucleation

Wall w
mo
rou

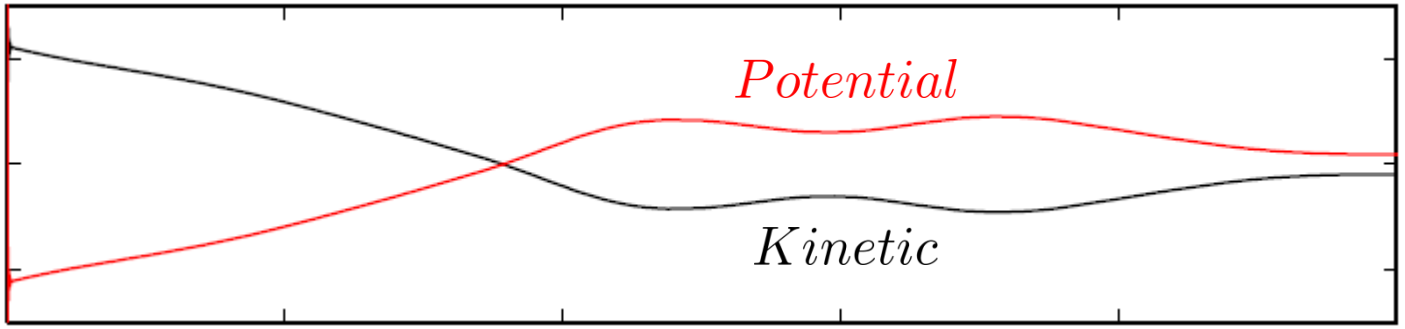
Isosurface of Density



Molecular Dynamics Summary

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

$$\frac{dE}{dt}$$



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

* www.nd.edu/~gtryggva/MultiphaseDNS/

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Hand-On Session

- Minimal MD solver for two molecules

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

  - » Includes LJ force

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- Atomify at **github.com/lammps/lammps-web**

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COUPLING

Coupling Overview

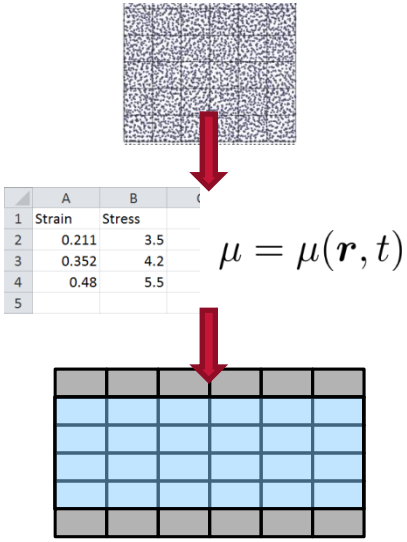
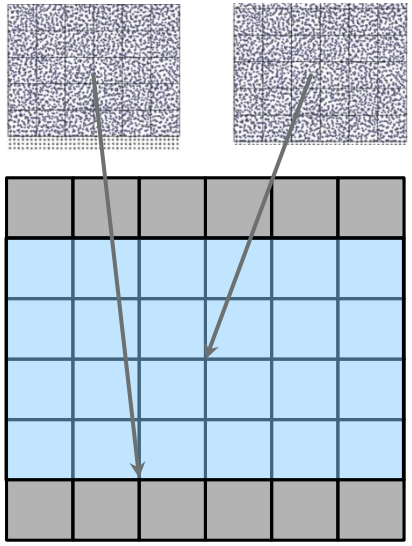


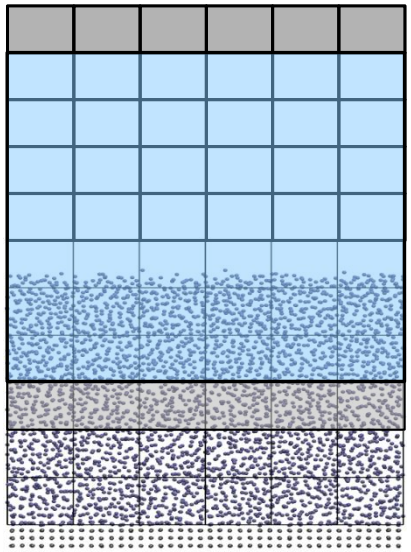
Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data



Embedded Models (HMM)

MD – embedded in a CFD simulation [1)]

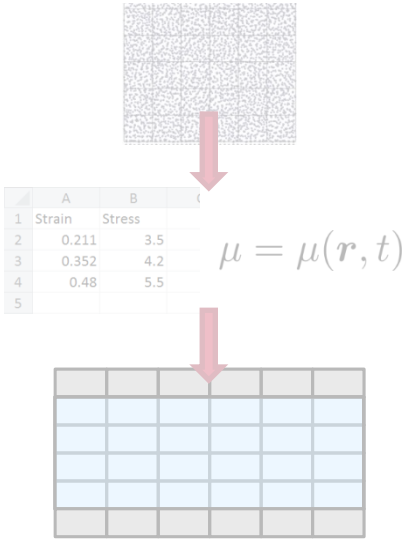


Domain Decomposition

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 Overview



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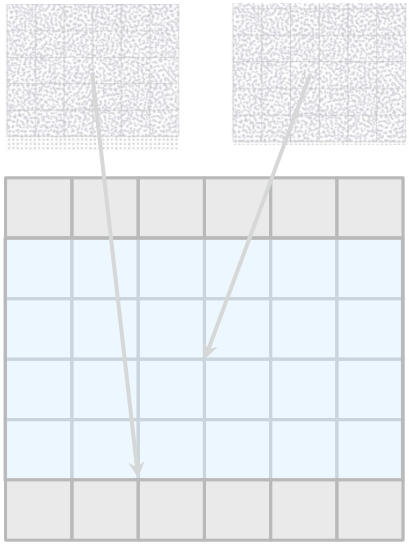

Embedded Models (HMM)

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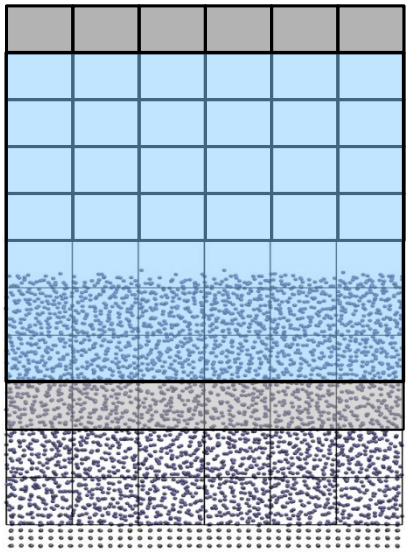

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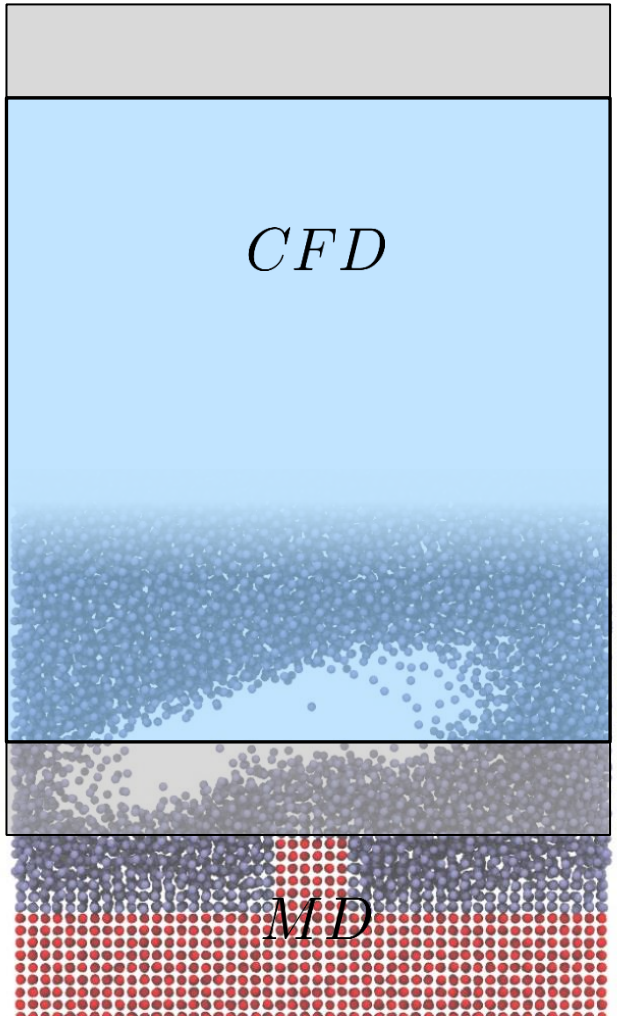
Coupled Simulation

- Assumes a continuous field

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

- Discrete molecules

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



Coupled Simulation

- Assumes a continuous field

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

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

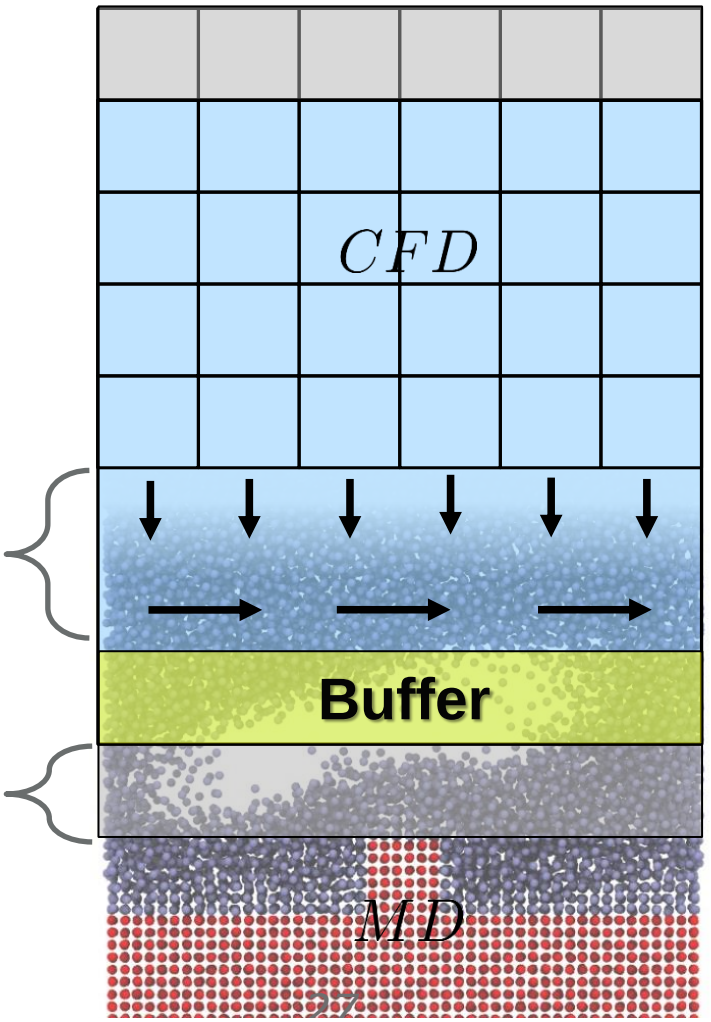
CFD→MD Boundary condition

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

MD→CFD Boundary condition

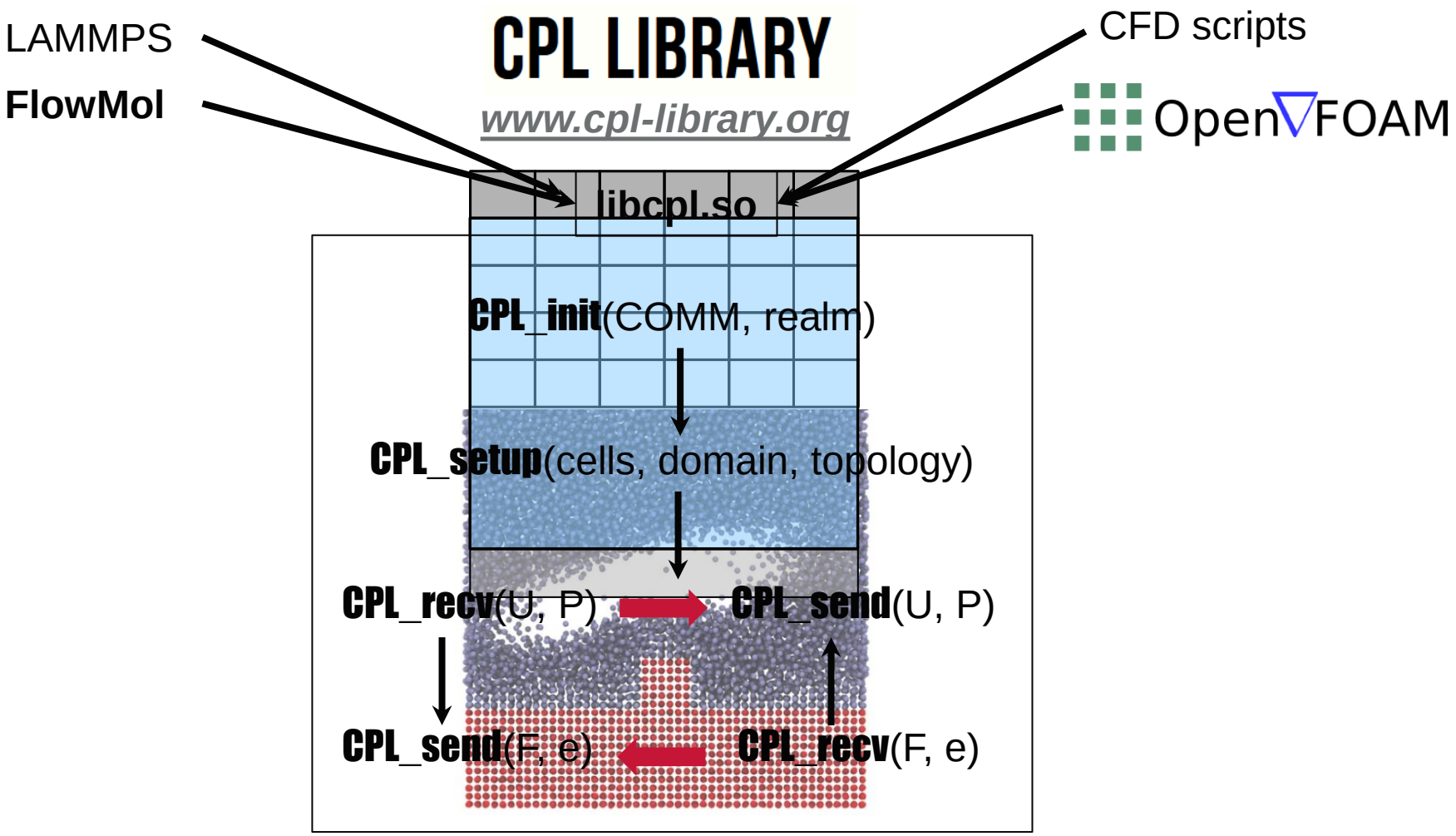
- Discrete molecules

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



O'Connell Thompson (1995), Hadjiconstantinou (1998), Flekkoy (2000), Nie et al (2004).

Coupled Simulation Software



Coupling Results – Couette Flow

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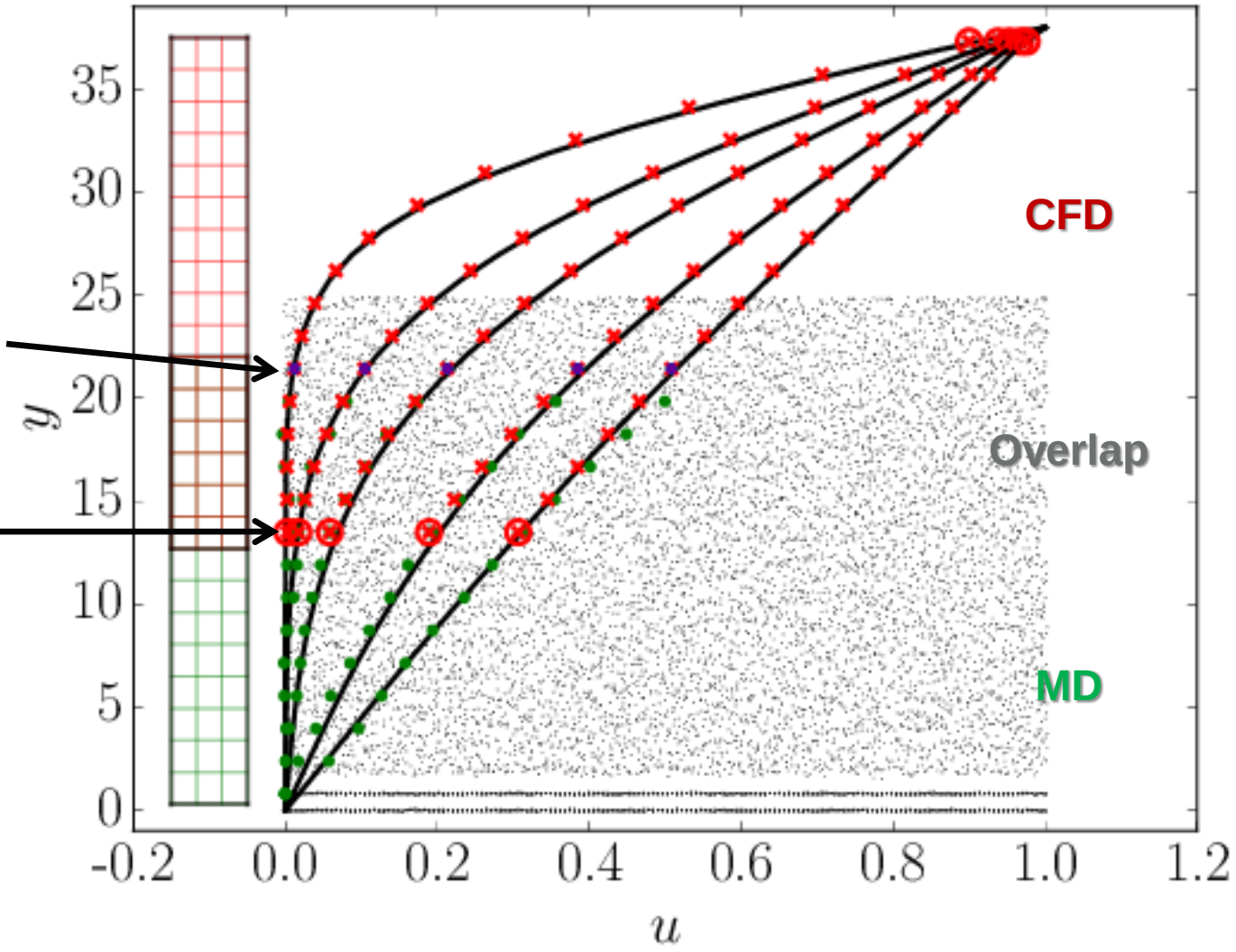
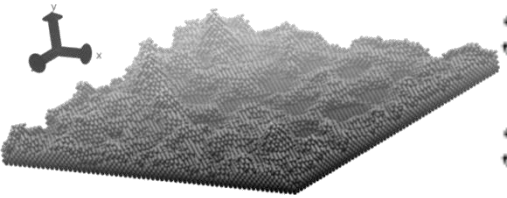
Constraint

CFD Boundary



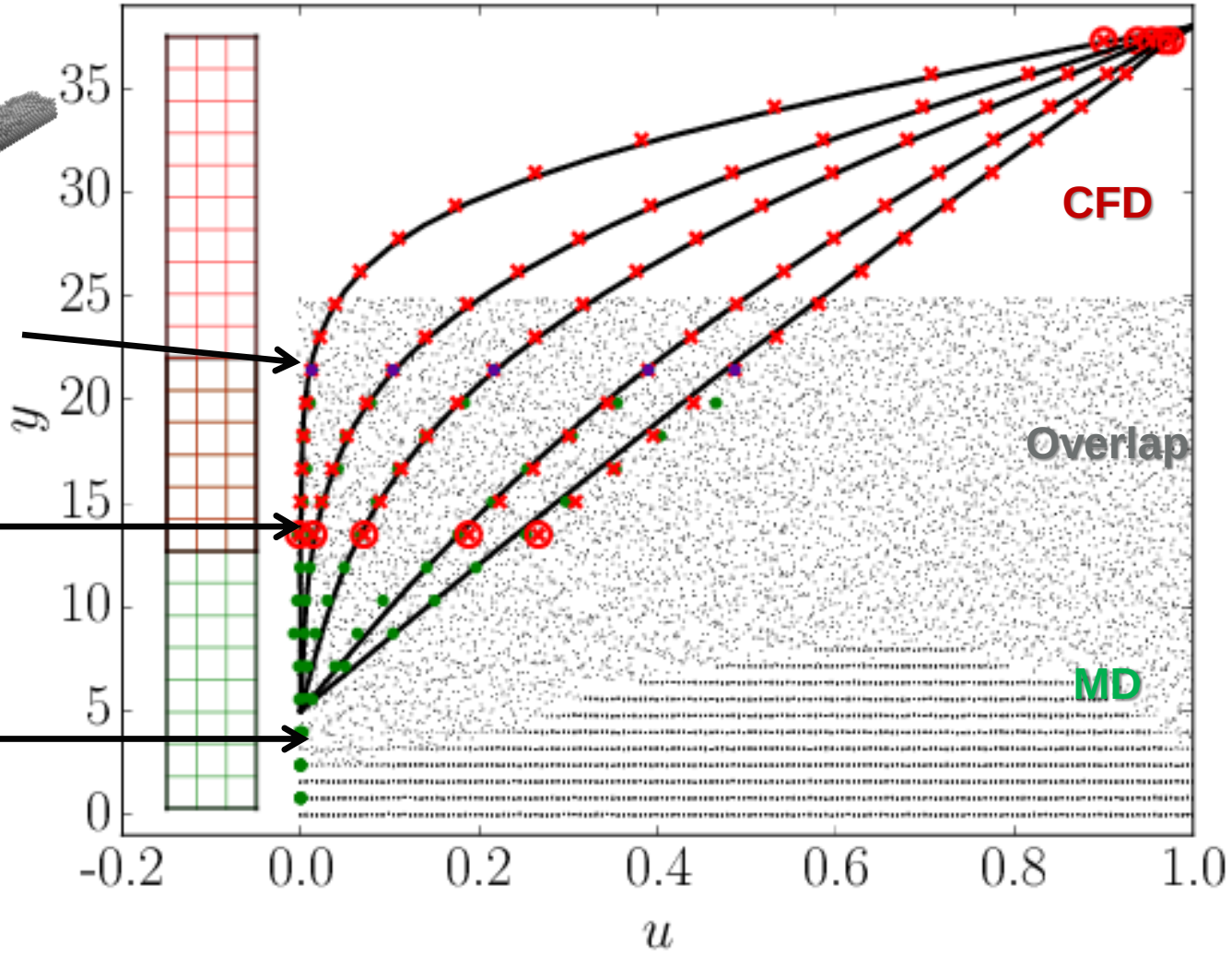
Coupling Results – Couette Flow



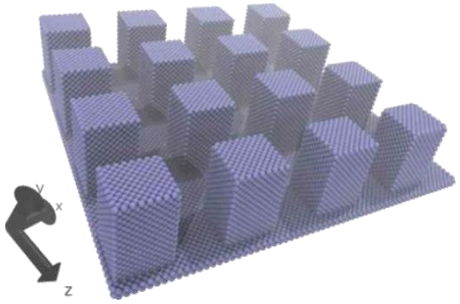
Constraint

CFD Boundary

Rough wall shifts zero velocity location



Coupling Results – Couette Flow



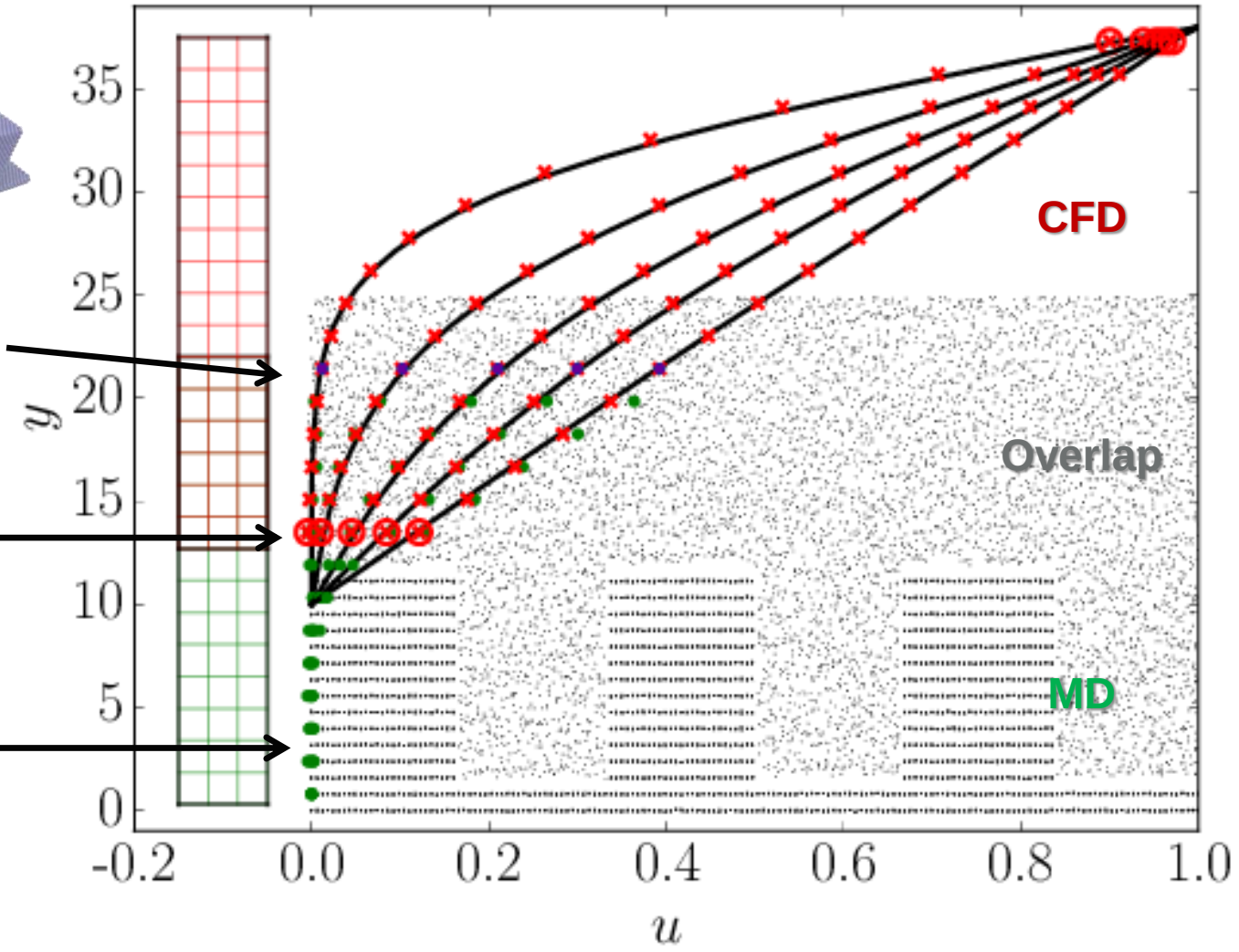
Constraint

CFD Boundary

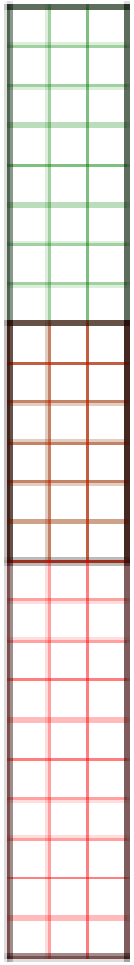
Posts shifts

zero velocity

location



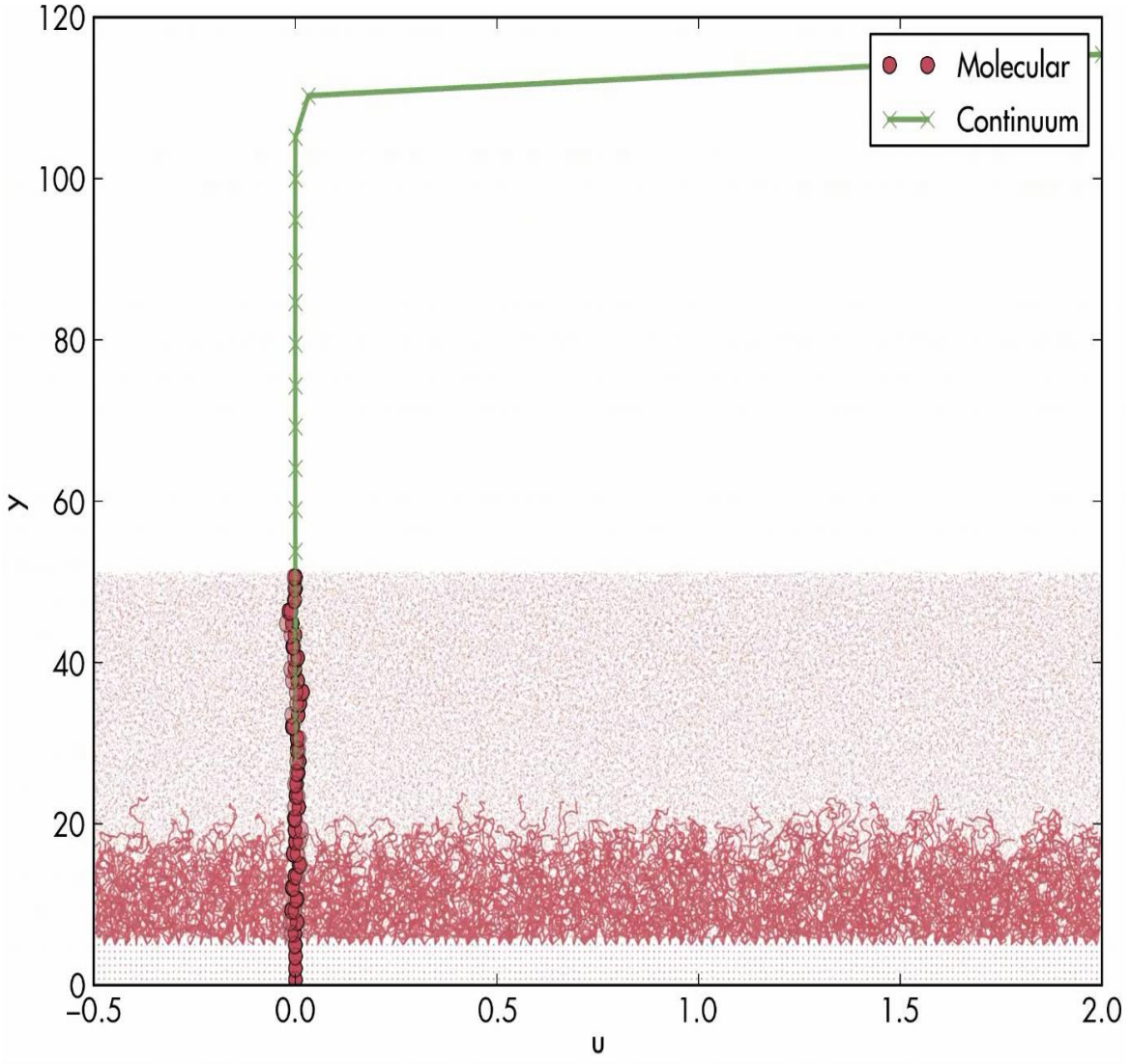
Coupling Results – Polymer Brushes



CFD Region

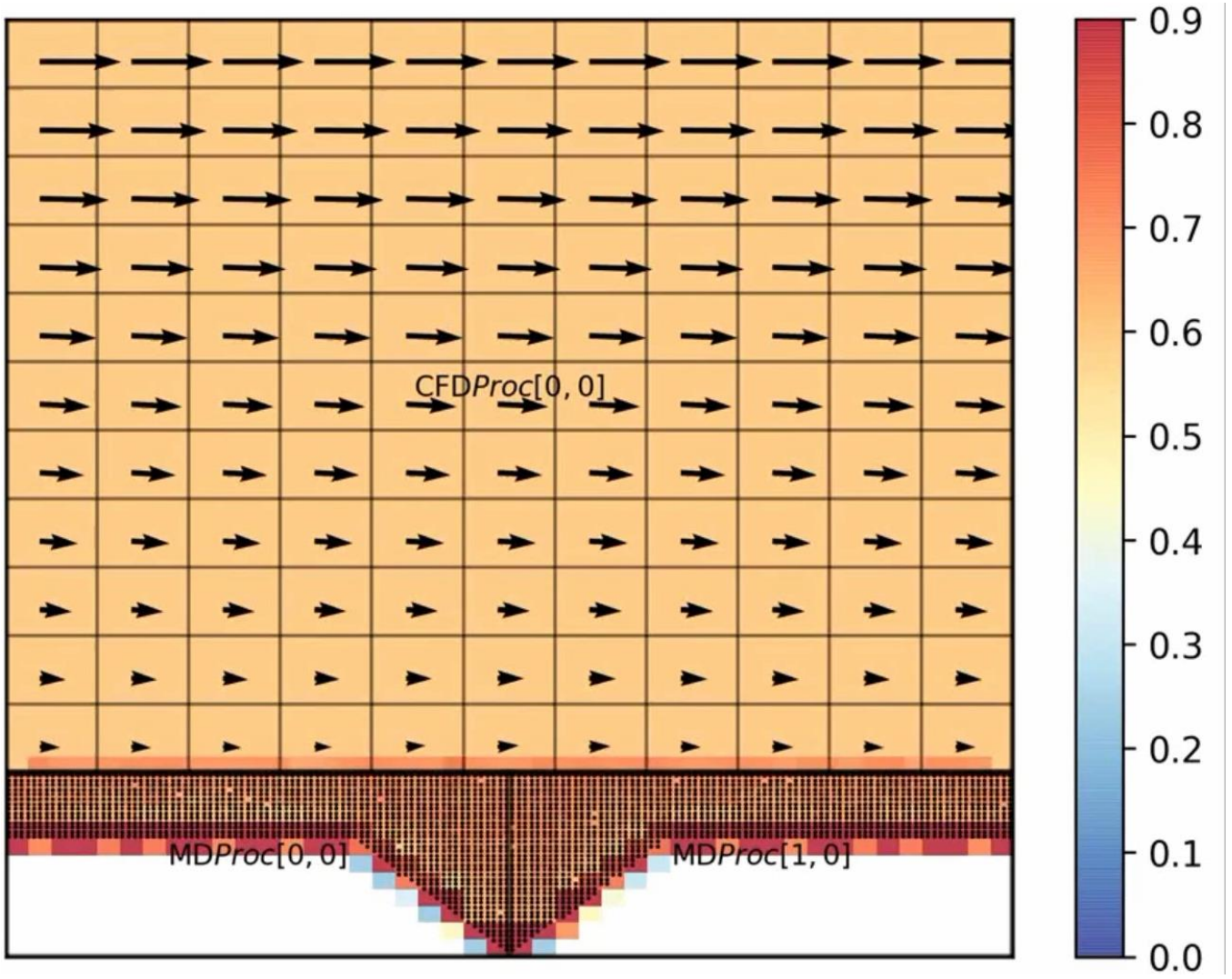
Overlap Region

MD Region

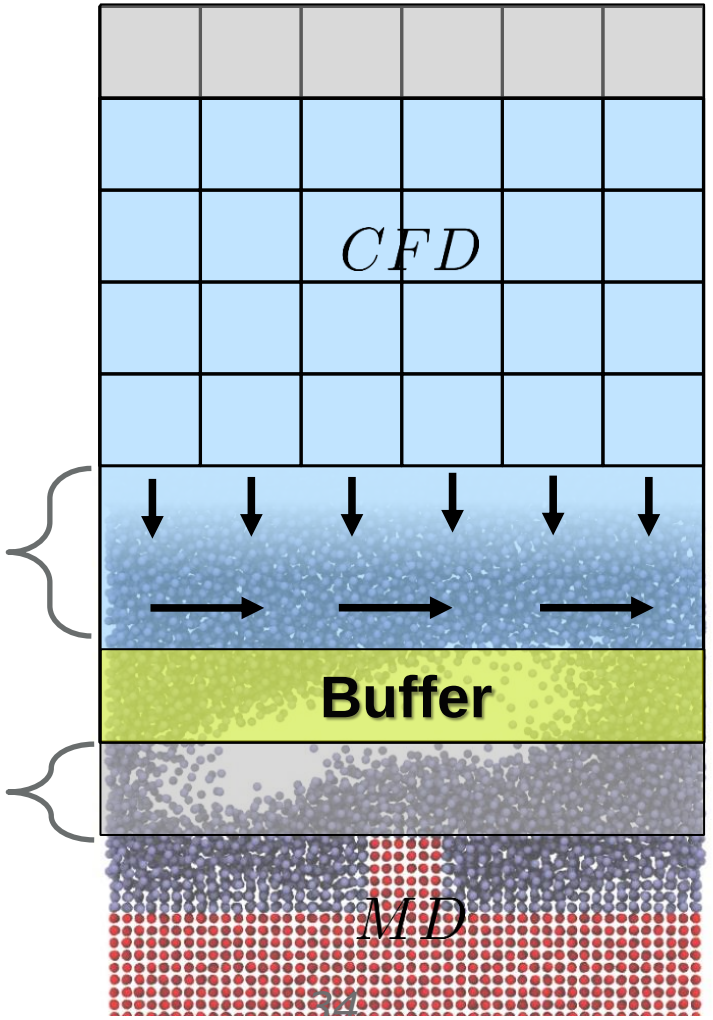


Coupled Simulation of Boiling

- Bubble nucleation occurs naturally in MD
- Density and velocity set CFD boundary conditions
- Flow in CFD carries bubble away



Hand-On Coupled Simulation



Hand-On Coupled Simulation

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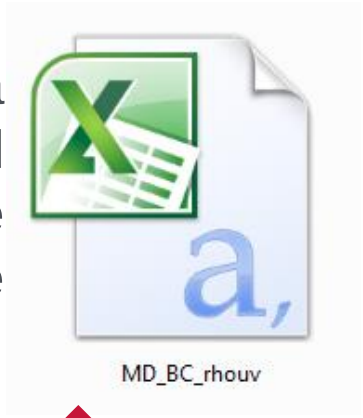
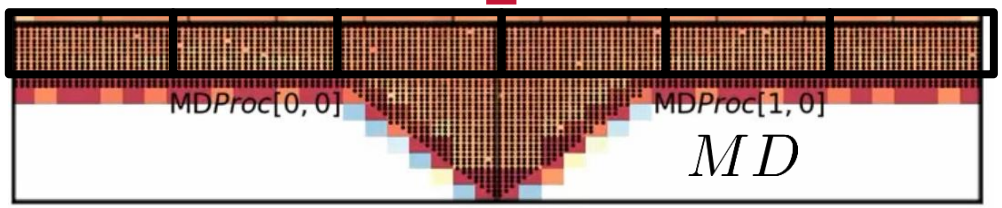
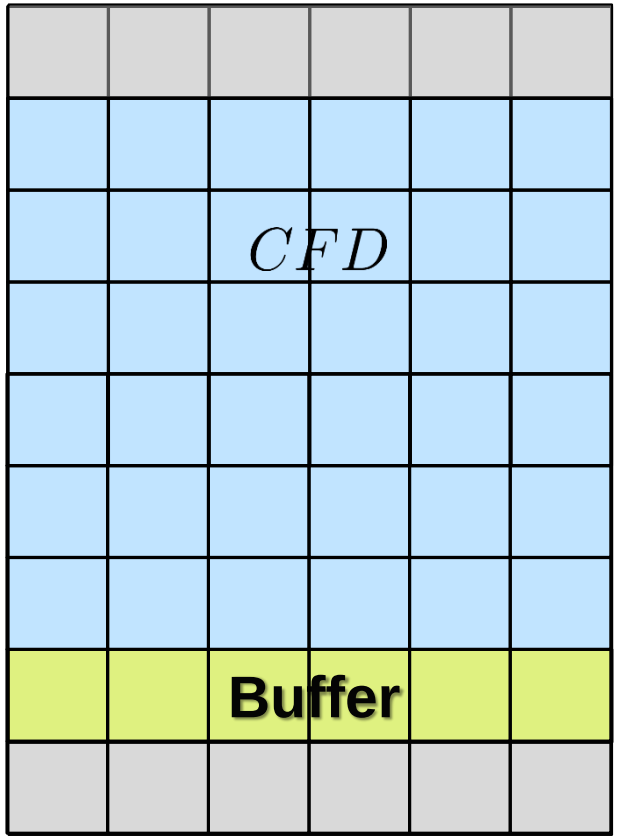
Comma separated variable (CSV) file



$$\rho = \frac{1}{V} \sum_{i \in cell}^{N} m_i$$

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





Hand-On Coupled Simulation

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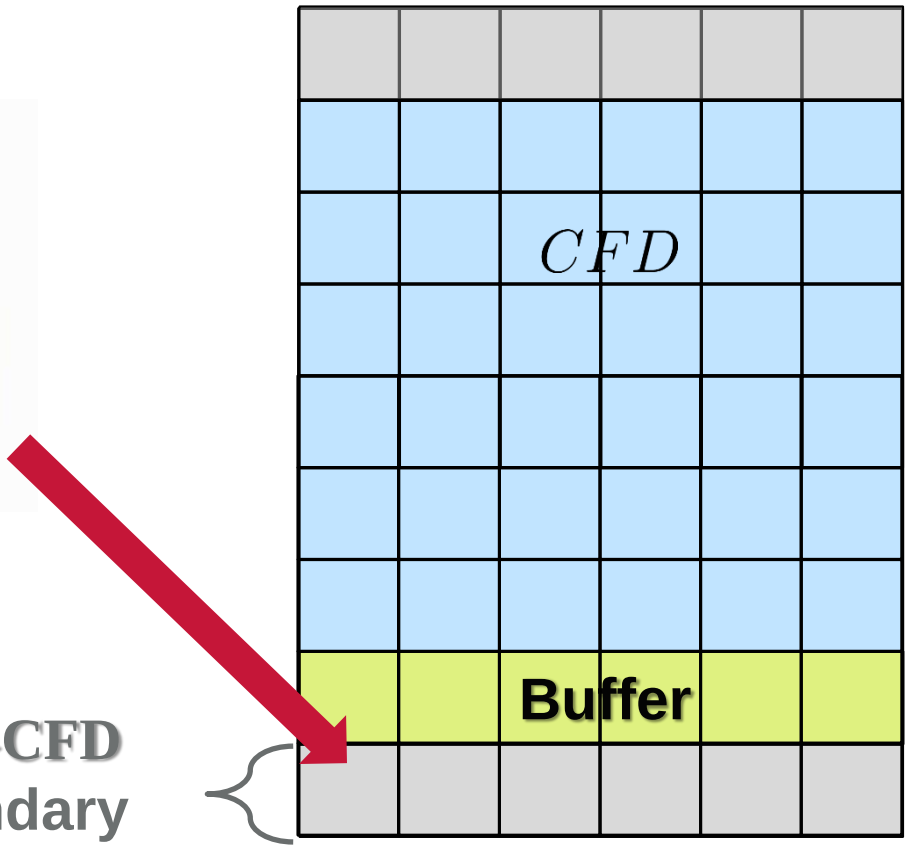
Comma separated variable (CSV) file



MD→CFD Boundary condition

* www.nd.edu/~gtryggva/MultiphaseDNS/

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Hand-On Session

- Minimal MD solver for two molecules

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

  - » Includes LJ force

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

  - » Time integrations

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

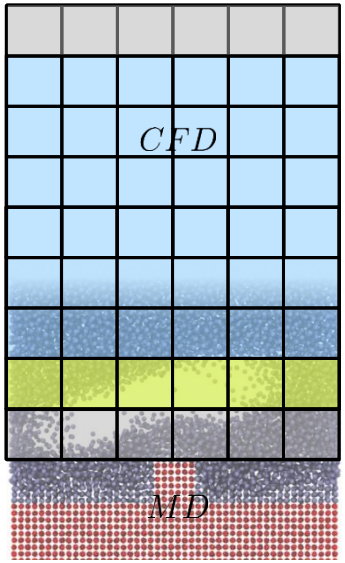
$$\frac{dr_i}{dt} \approx \frac{r_i(t+\Delta t) - r_i(t)}{\Delta t}$$

- Atomify at **github.com/lammps/lammps-web**
- MD simulation of nucleation saved as csv data to pass to **Tryggvason*** CFD
  - » Density

$$\rho = \frac{1}{V}\sum_{i\in cell}^{N} m_i$$

  - » Velocity

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



Slides and hands-on code at ***edwardsmith.co.uk/content/RS-DFID.zip***

Acknowledgements

- MINI with Victor Voulgaropoulos and Mirco Magnini funded by Dame Julia Higgins postdoctoral collaboration fund
- CPL library developed under a dCSE and eCSE computing grant and used for EPSRC grant EP/P010393/1
- A recent EPSRC grant EP/S019545/1 aims to apply this technique to smart surfaces for boiling

Slides and hands-on code at ***edwardsmith.co.uk/content/RS-DFID.zip***