Coupling Molecular Dynamics to Continuum Computational Fluid Dynamics

Edward Smith

Working with:
Prof D. M. Heyes, Dr D. Dini,
Dr T. A. Zaki & Mr David Trevelyan

Mechanical Engineering
Imperial College London

Imperial College London

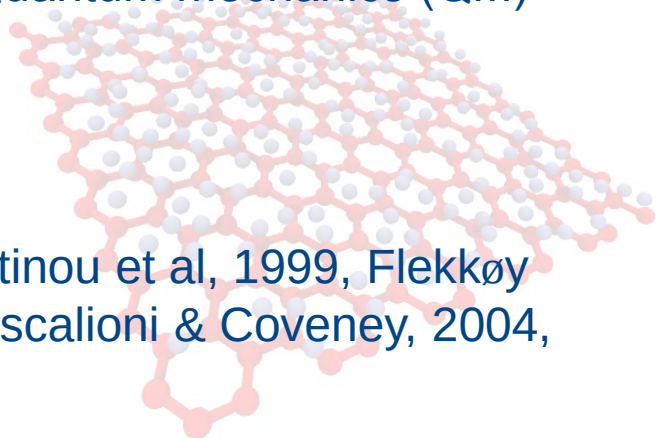
Outline

- **Introduction**
  - Motivation for coupling
  - Molecular dynamics (MD)
  - Computational fluid dynamics (CFD)
- **Coupling Theory**
  - Existing literature on coupling
  - Irving and Kirkwood (1950) and the control volume function
  - Coupling using constrained dynamics principles
- **Coupled Computational Development**
  - Computational development and the CPL_Library
  - Results from coupled simulations
  - Aims for the future

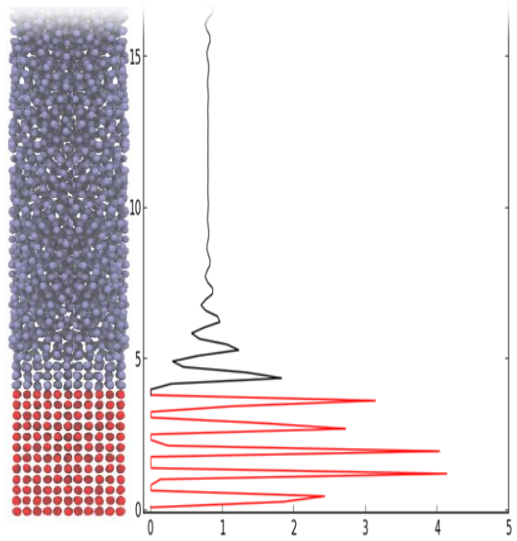
Introduction

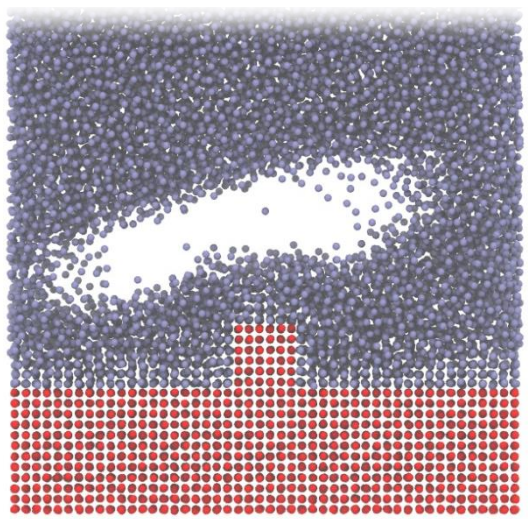
Motivation

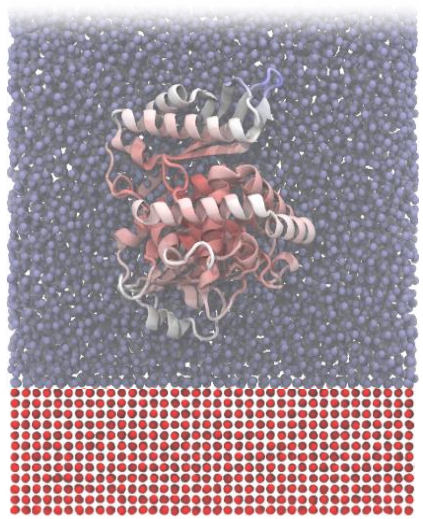
- **Modern engineering problems require sub-continuum models**
  - Molecular dynamics is still prohibitively expensive
  - Multi-scale coupling overcomes these limitations by linking to cheaper methods
  - Quantum mechanics ↔ Molecular dynamics (MD) (Karplus, Levitt and Warshel won the 2013 Nobel Prize for their work in the 1970)
- **Multi-scale coupling has been employed since the 1970's (Curtin & Miller 2003) in solid mechanics modelling**
  - Essential to fully capture both the complicated detail, *e.g.* for detail in the crack tip and the impact on the wider system
  - Continuum (FEA) ↔ Molecular mechanics (MM) ↔ Quantum mechanics (QM)
- **Classical coupling for fluids is less mature**
  - First work by O'Connell & Thompson in 1995
  - Developing area of research ever since (Hadjiconstantinou et al, 1999, Flekkøy et al 2000, Nie, Chen, E & Robbins 2004, Delgado-Buscalioni & Coveney, 2004, Borg et al, 2014)
  - Computational fluid dynamics (CFD) ↔ Molecular dynamics (MD)

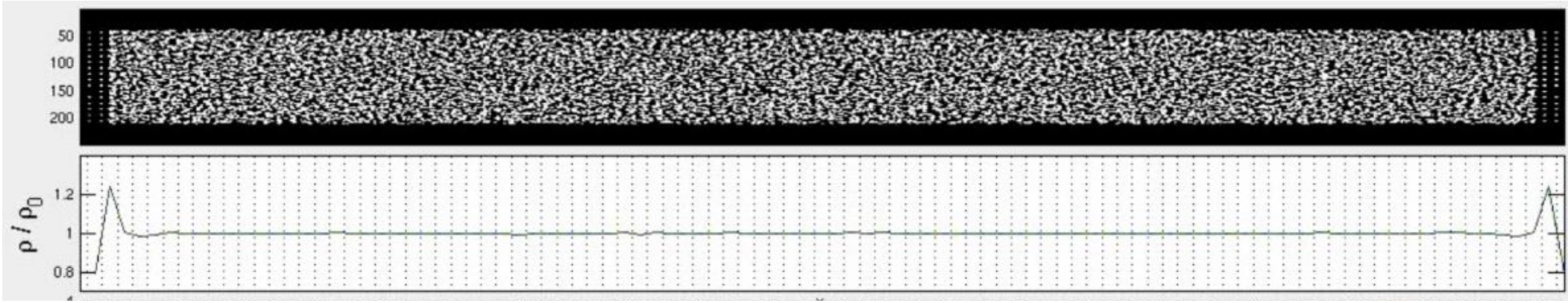


Why Use Molecular Dynamics?

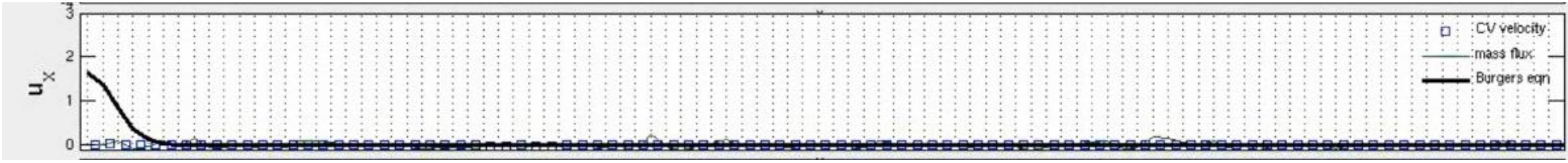








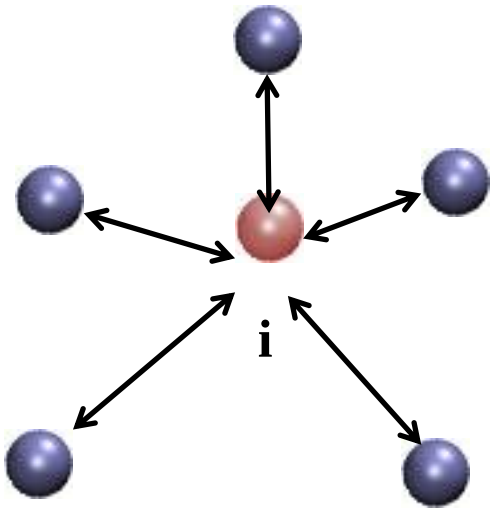
- **Paper by Root et al (2003) suggests micro-scale turbulence following the shock wave**



Molecular Dynamics

- **Discrete molecules in continuous space**
  - Molecular position evolves continuously in time
  - Position and velocity from acceleration

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

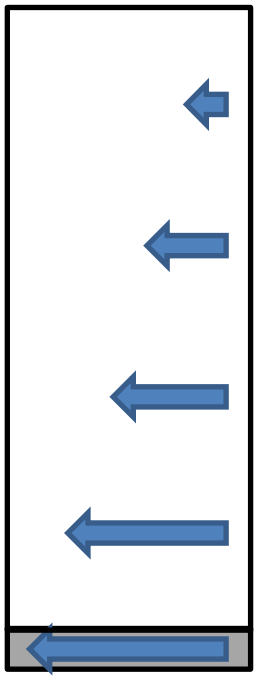


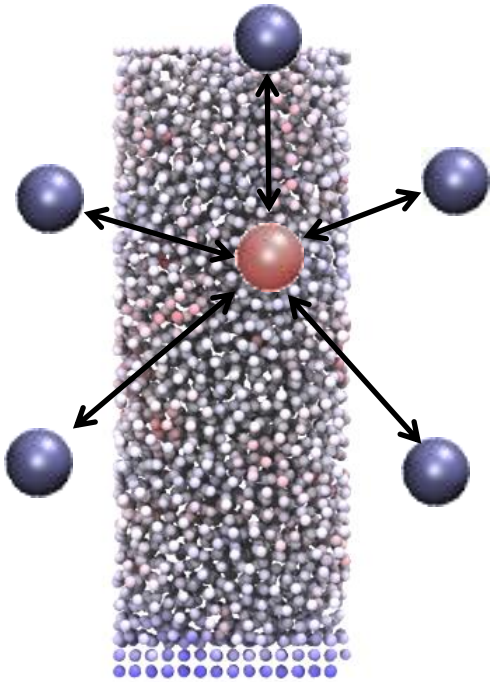
- **Acceleration obtained from forces**
  - Governed by Newton's law for an N-body system
  - Point particles with pairwise interactions only

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

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

Molecular Dynamics

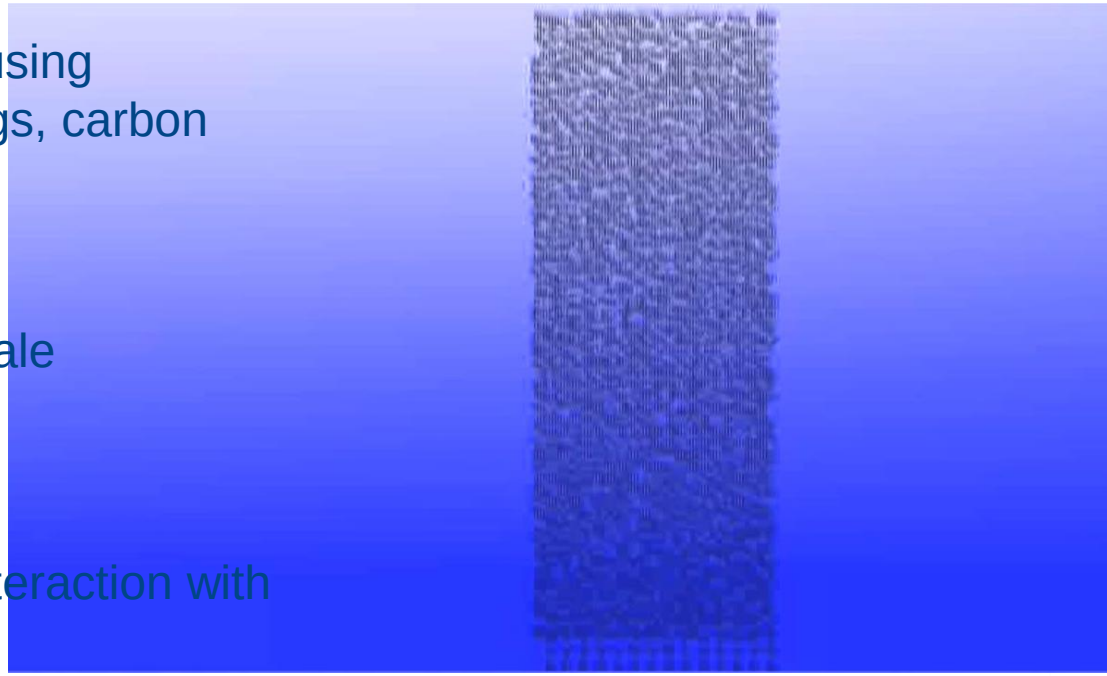




Molecular Dynamics Simulation of Couette Flow

Molecular Dynamics

- **Large scale MD is important in many cases**
  - Modelling flow drag reduction by using textured surfaces, polymer coatings, carbon allotropes, etc
  - Electronics and cooling of nanoscale transistors or NEMS/MEMS
  - Biological systems, e.g. protein interaction with surroundings
  - Nucleation of bubbles, chemical reactions and combustion



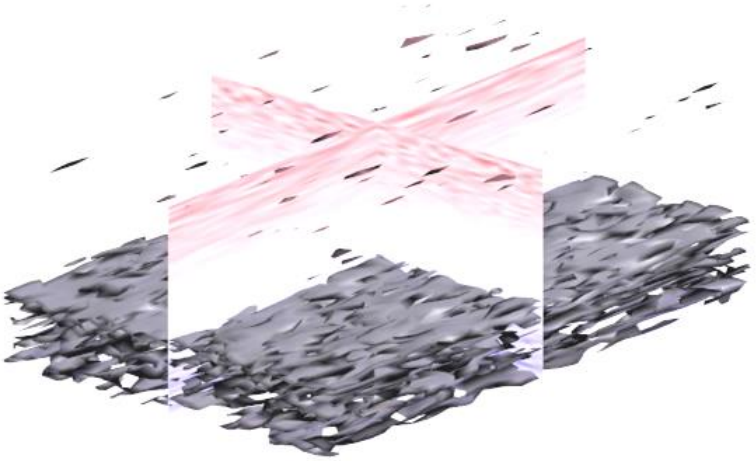
Continuum Field Equations

- **Assumed continuous at every point in space**
  - Mass Conservation

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

  - Momentum Balance (Newton's Law)

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



Direct Numerical Simulation of Turbulent Couette Flow

Solving the Continuum Equations

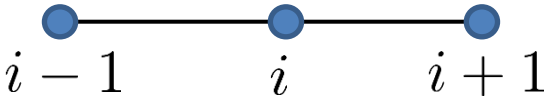
- **The Navier-Stokes Equation**

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

$$\boldsymbol{\Pi} = P\boldsymbol{I} - \mu\boldsymbol{\nabla}\boldsymbol{u}$$

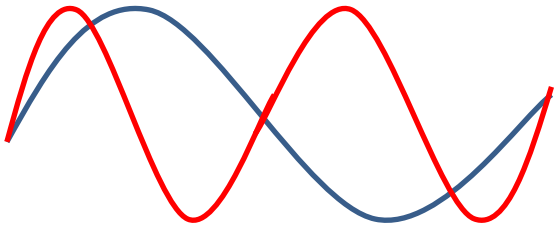
- **Finite Difference Method**

$$\frac{\partial u_i}{\partial x} \approx \frac{u_{i+1} - u_{i-1}}{\Delta x}$$



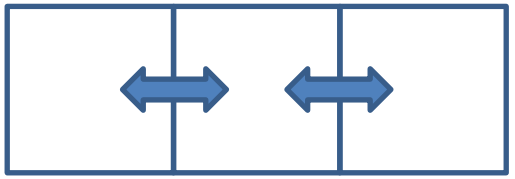
- **Spectral Methods**

$$u(x) = \sum_{n=1}^{X-1} \tilde{u}_n \overline{T}_n(y) e^{2\pi i(k_x x/L_x + k_z z/L_z)}$$



- **Finite Volume Method**

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



The Finite Volume Form

- **The integrated Navier-Stokes equation over a control volume**

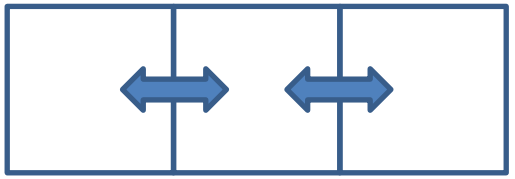
$$\int_V \frac{\partial}{\partial t}\rho \boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u}\ dV = \int_V -\boldsymbol{\nabla}\cdot\Pi\ dV \qquad \boldsymbol{\Pi} = P\boldsymbol{I} - \mu\boldsymbol{\nabla}\boldsymbol{u}$$

  - A reformulation of the equations of motion in terms of changes inside volumes and surface fluxes
  - Exactly conservative – what goes out comes in

- **Most commonly used CFD discretisation technique**
  - Splits the domain into a range of contiguous volumes and any shape of volume can be used
  - Better for discrete phenomena, e.g. shockwaves
  - Most importantly: Molecular Dynamics can be written in an equivalent form

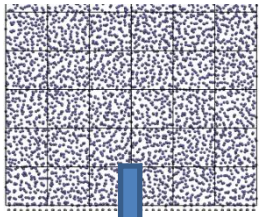
- **Finite Volume Method**

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



Coupling Methodology

Coupling Overview



	A	B
1	Strain	Stress
2	0.211	3.5
3	0.352	4.2
4	0.48	5.5
5		

$$\mu = \mu(\boldsymbol{r}, t)$$

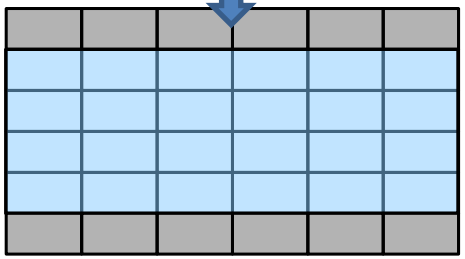


Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

Coupling Overview

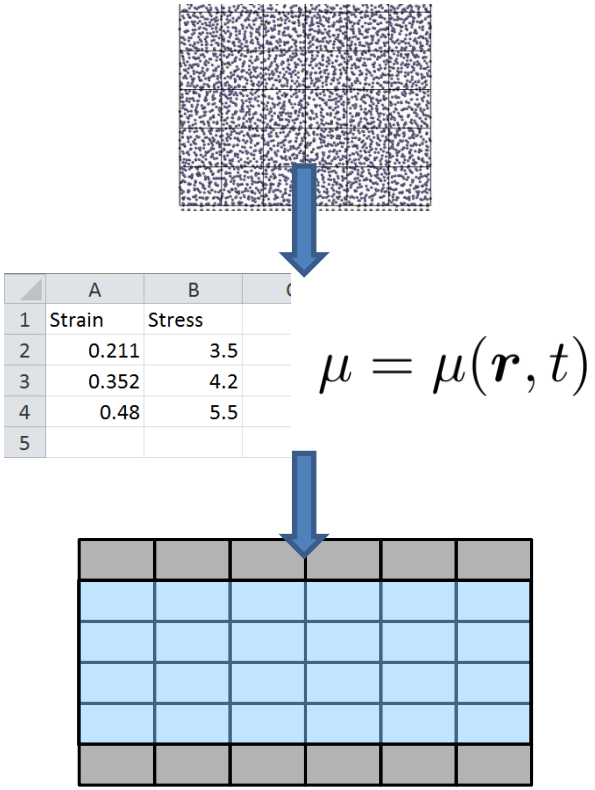
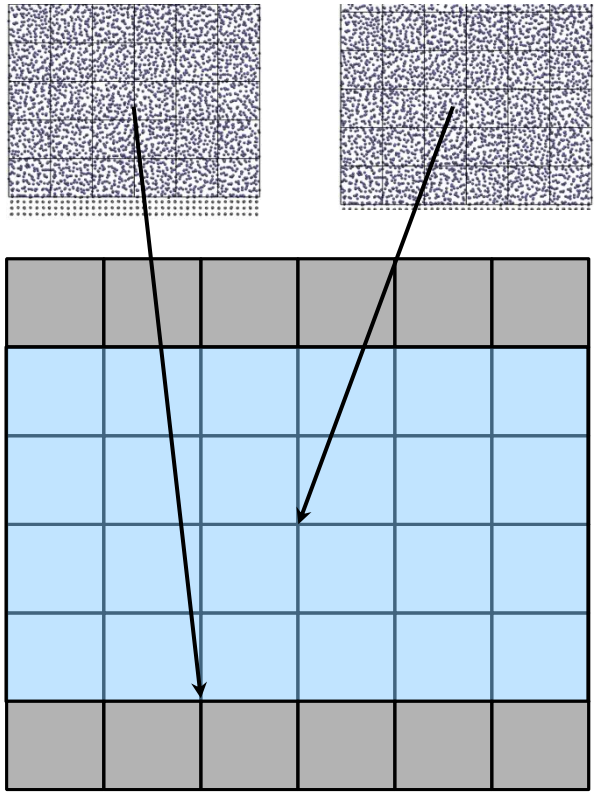


Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data



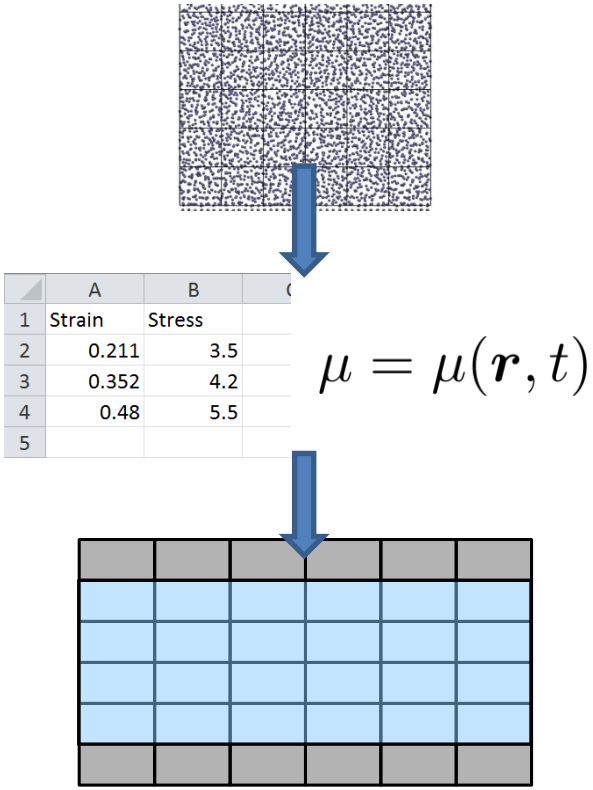
Embedded Models

MD – embedded in a CFD simulation

Used for Non-Newtonian effects

Ren (2007), E et al (2003), Borg et al (2013)

Coupling Overview

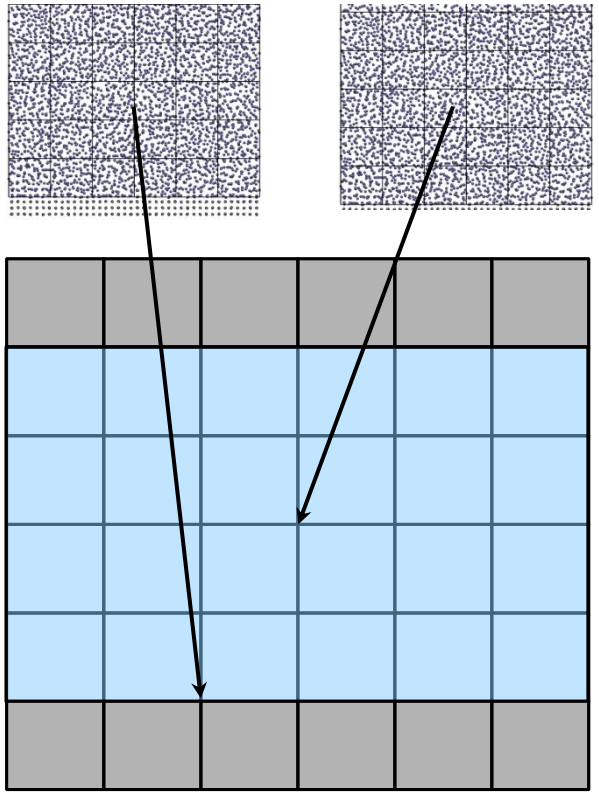


	A	B
1	Strain	Stress
2	0.211	3.5
3	0.352	4.2
4	0.48	5.5
5		

$$\mu = \mu(\boldsymbol{r}, t)$$

Table Lookup or Coefficients

MD parameter study stored in table and CFD uses data

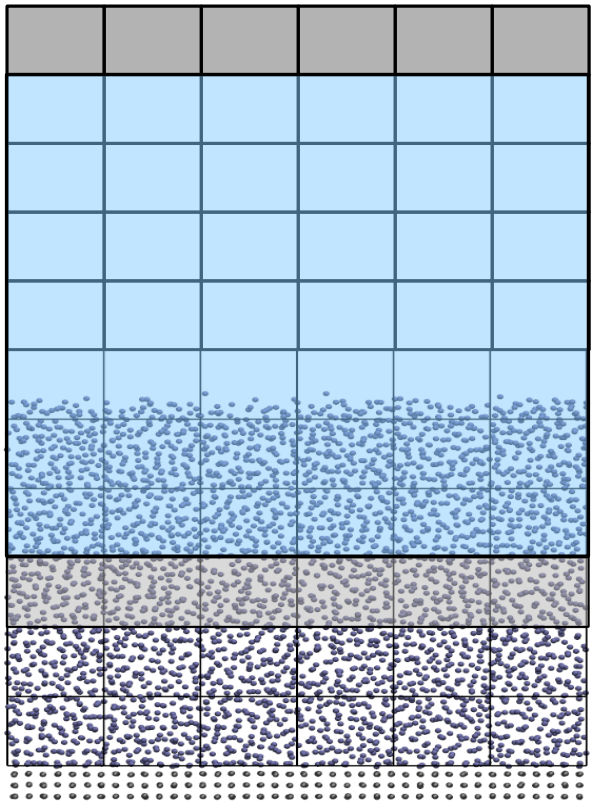


Embedded Models

MD – embedded in a CFD simulation

Used for Non-Newtonian effects

Ren (2007), E et al (2003), Borg et al (2013)



Domain Decomposition

MD –CFD linked along an interface with overlap

Used for wall textures and local features e.g. contact line

O'Connell and Thompson (1995), Flekkøy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni and Coveney, (2003)

Coupling Overview

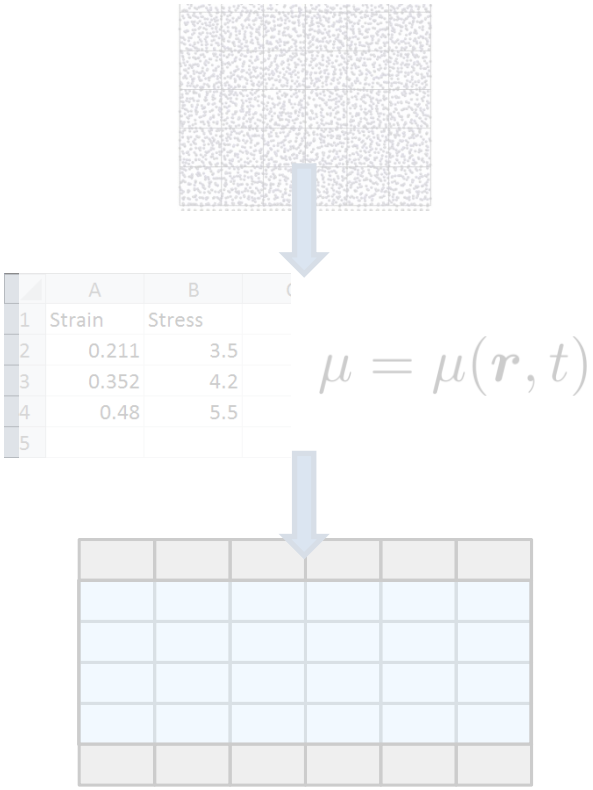


Table Lookup

MD parameter study stored in table and CFD uses data

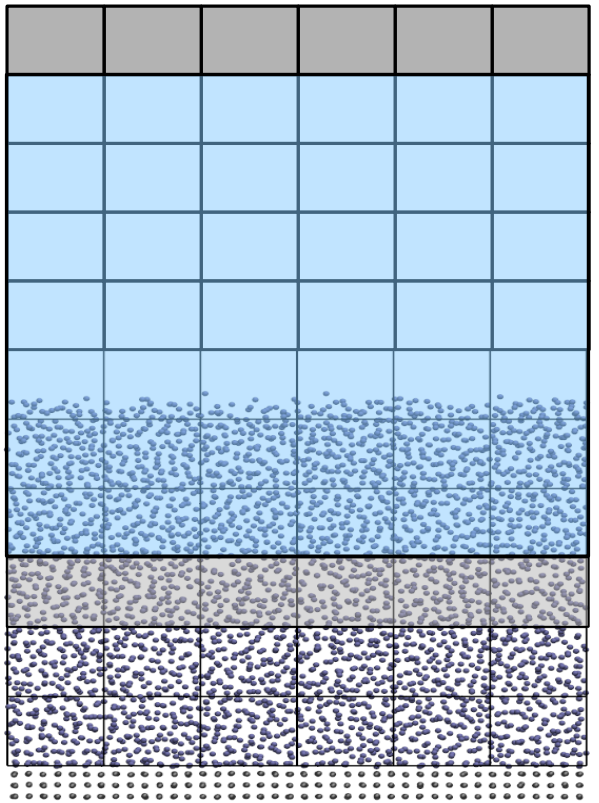
Simplest approach

Embedded Models

MD – embedded in a CFD simulation

Used for Non-Newtonian effects

E et al (2003), Borg et al (2013)



Domain Decomposition

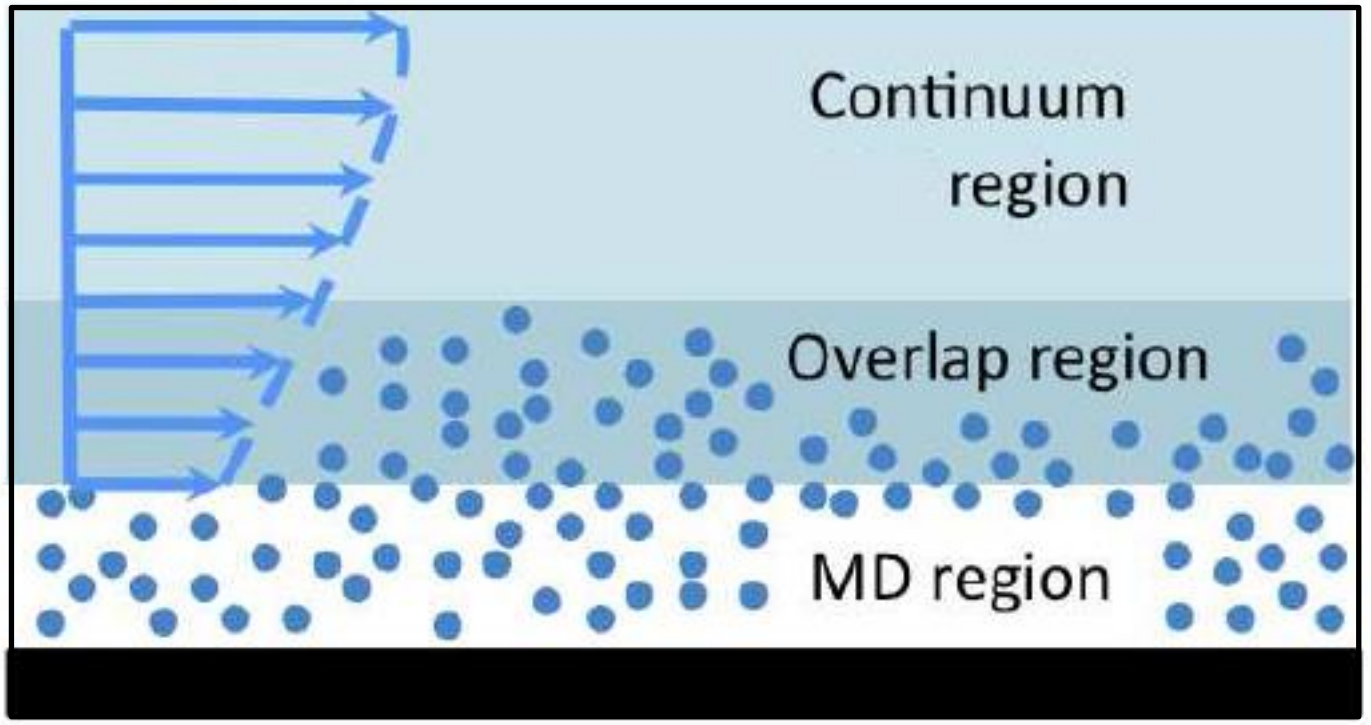
MD –CFD linked along an interface with overlap

Used for wall textures and local features e.g. contact line

O'Connell and Thompson (1995), Flekkoy at al (2000), Nie et al (2004), Hadjiconstantinou et al (1999), Delgado-Buscalioni and Coveney, (2003)

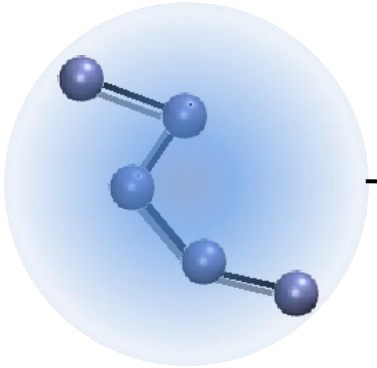
Domain Decomposition

- **Connect the two descriptions of matter**
  - Continuum only region – majority of the spatial domain
  - Overlap of arbitrary size – for purely numerical reasons
  - Molecular only region – required where molecular effects are important



Coupling Challenges

Boundary force and insertion of molecules

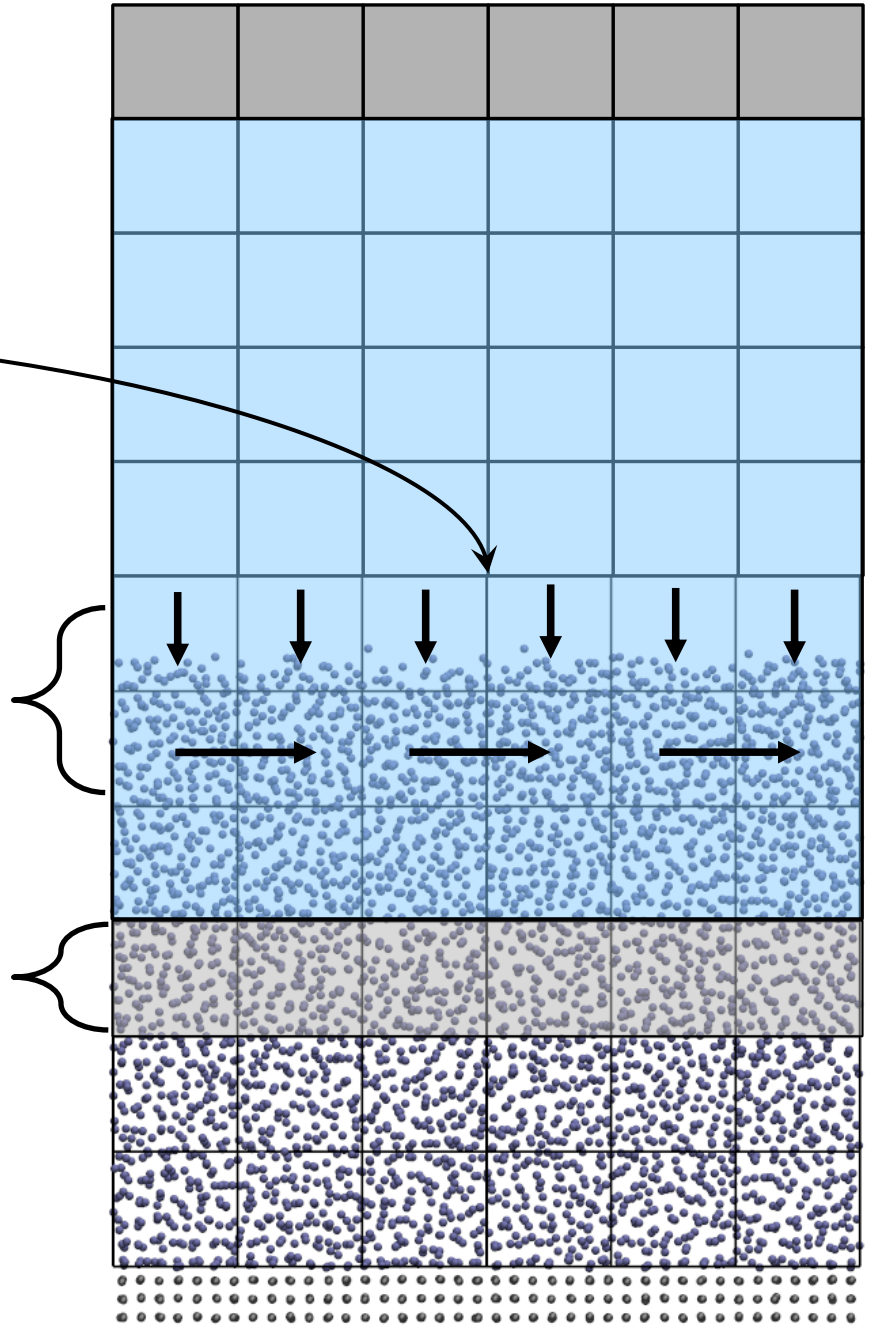


$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \boldsymbol{F}_i^{CFD}$$

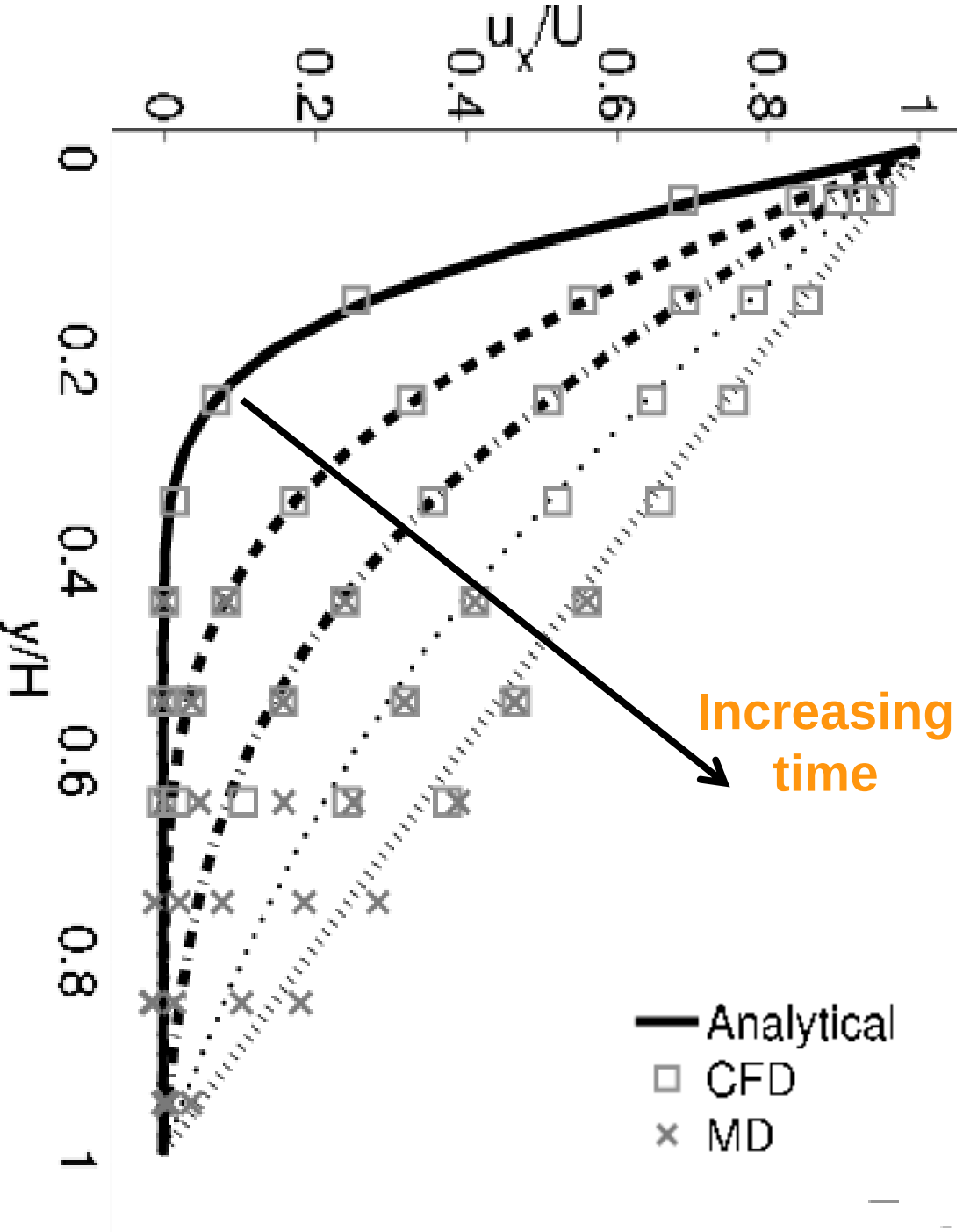
CFD→MD Boundary condition

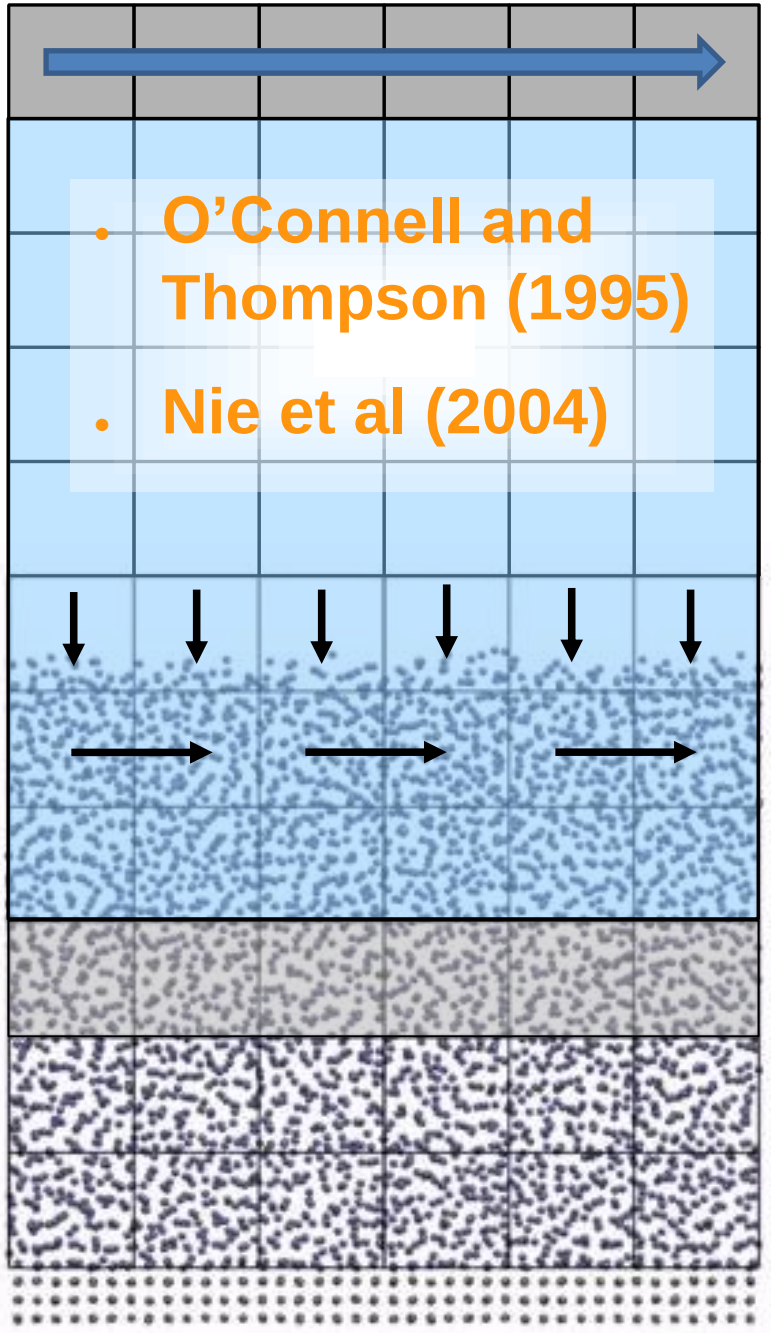
$$\boldsymbol{u}_{MD} = \frac{1}{N} \sum_{i=1}^{N_I} \boldsymbol{v}_i$$

MD→CFD Boundary condition

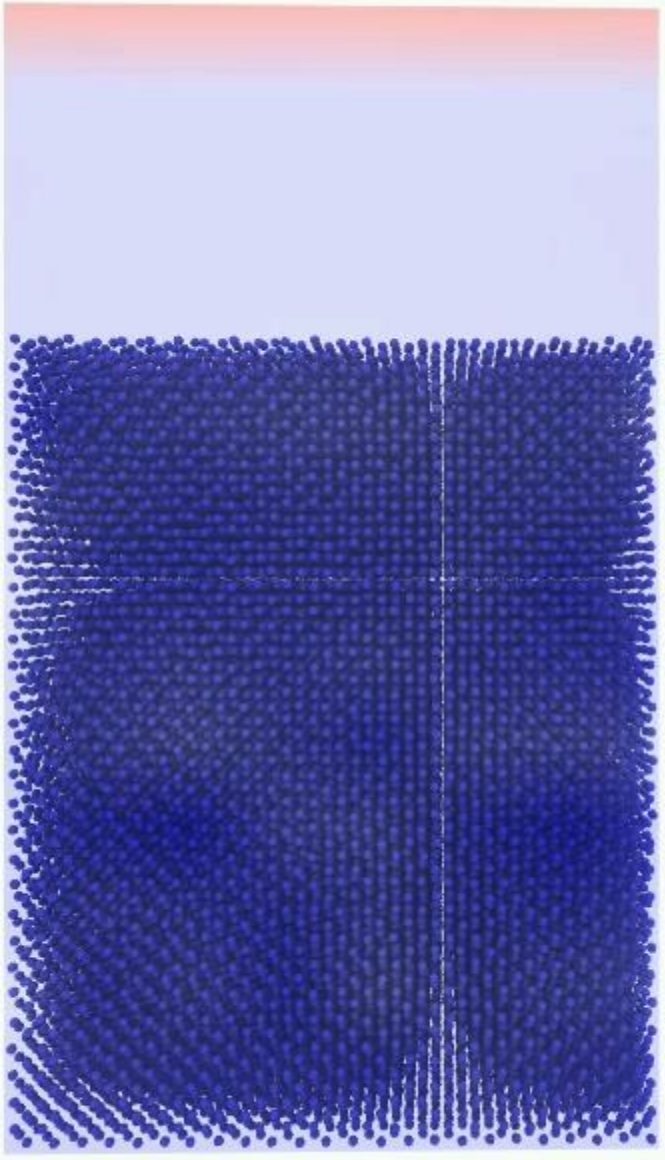


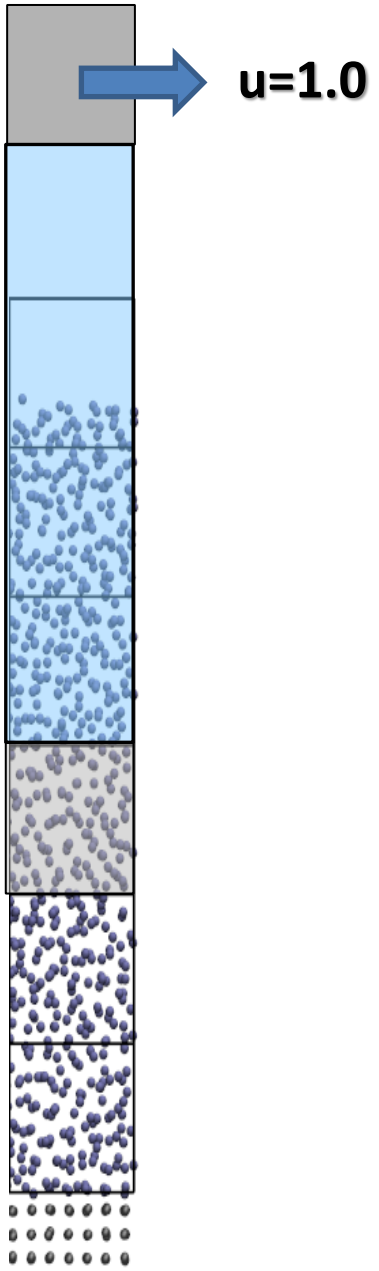
Coupling Results – Couette Flow





Coupling Results – Couette Flow





Notable Coupling Literature

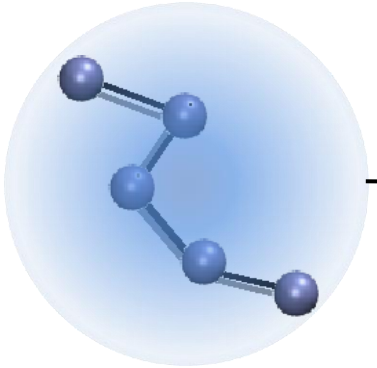
- **State or flux coupling? (Flekkøy at al, 2000)**

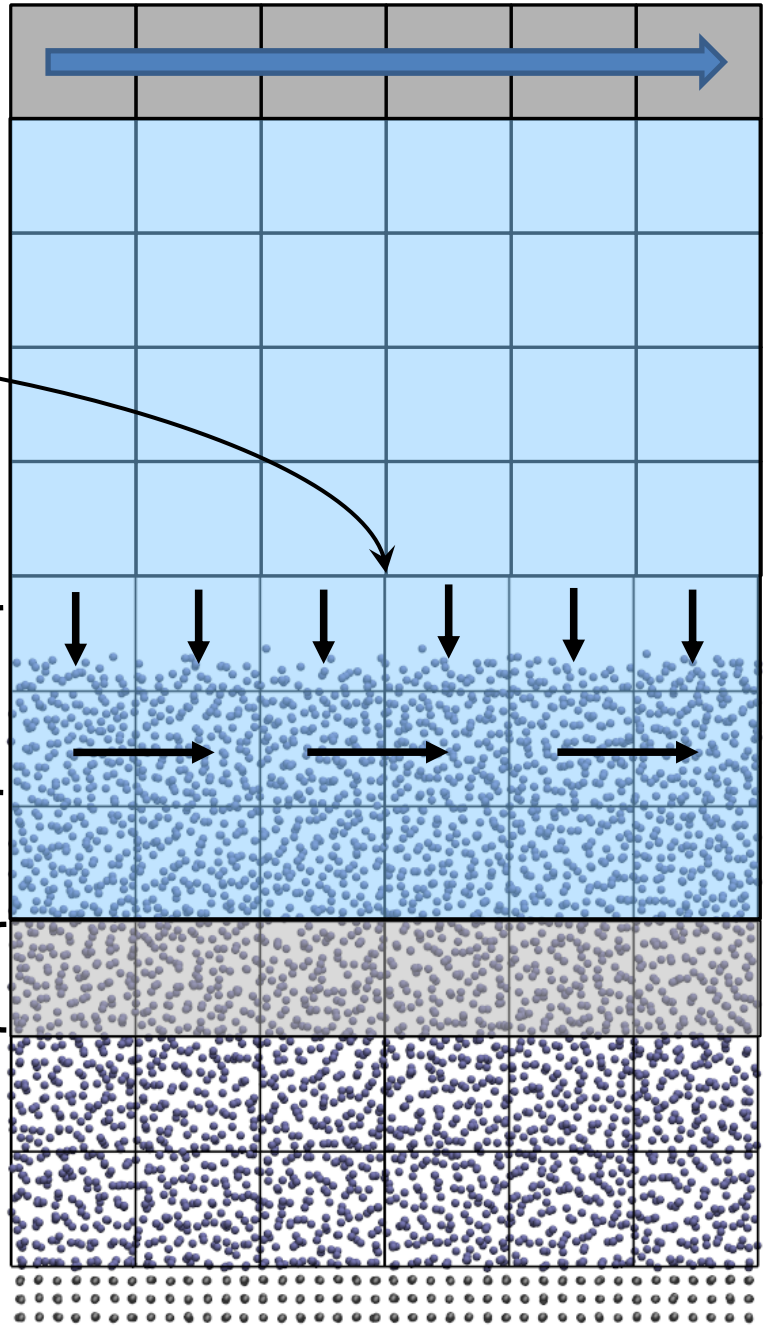
$$\boldsymbol{u}_{MD} = \boldsymbol{u}_{CFD} \quad or \quad \boldsymbol{\Pi}_{MD} = \boldsymbol{\Pi}_{CFD}$$

- **Moving contact line - steady state**
  - Hadjiconstantinou et al (1999) Schwartz domain decomposition
- **Flow past a carbon nanotube – steady state**
  - Werder et al (2005) – radial distribution function based forces
- **Oscillating wall and shock waves**
  - Delgado-Buscalioni and Coveney, (2003) flux coupling with energy
- **MD to Fluctuating hydrodynamics or Lattice Boltzmann**
  - Mohammed and Mohammad (2009) or Delgado-Buscalioni (2012)
- **Great progress, lots of methods and widely applied but are we sure the coupling methods are correct?**

Coupling Challenges

Boundary force and insertion of molecules





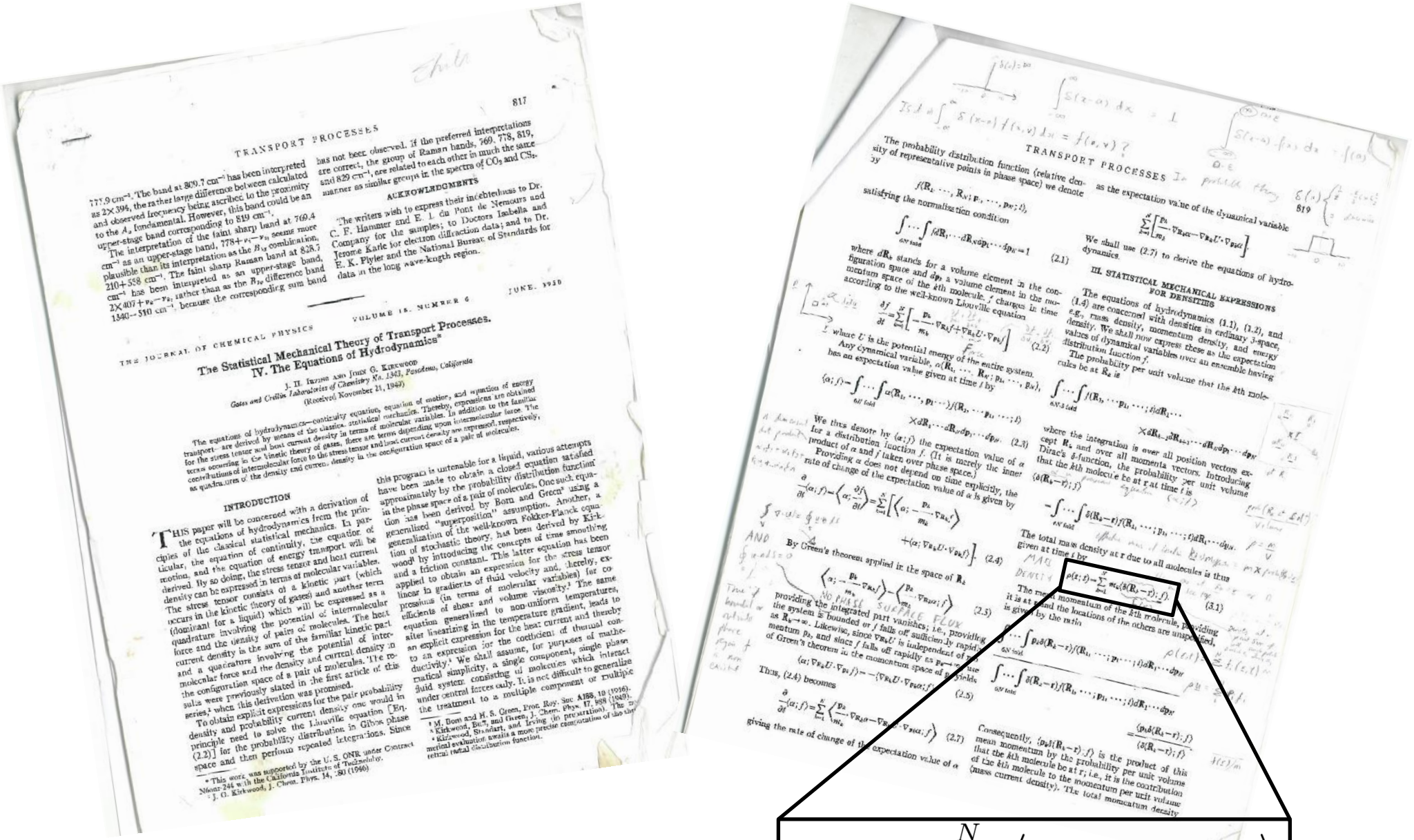
Consistent Framework

CFD→MD Boundary condition

MD→CFD Boundary condition

$$m_i\ddot{\boldsymbol{r}}_i = \mathbf{F}_i \overset{?}{\Longleftrightarrow} \frac{\partial}{\partial t}\rho\boldsymbol{u} + \boldsymbol{\nabla}\cdot\rho\boldsymbol{u}\boldsymbol{u} = \boldsymbol{\nabla}\cdot\boldsymbol{\Pi}$$

Irving and Kirkwood (1950)



THE JOURNAL OF CHEMICAL PHYSICS VOLUME 18, NUMBER 6 JUNE, 1950

The Statistical Mechanical Theory of Transport Processes. IV. The Equations of Hydrodynamics*

J. H. IRVING AND JOHN G. KIRKWOOD

Gates and Crellin Laboratories of Chemistry, No. 1343, Pasadena, California

(Received November 21, 1949)

The equations of hydrodynamics—continuity equation, equation of motion, and equation of energy transport—are derived by means of the classical statistical mechanics. Thereby, expressions are obtained for the stress tensor and heat current density in terms of molecular variables. In addition to the familiar terms occurring in the kinetic theory of gases, there are terms depending upon intermolecular force. The contributions of intermolecular force to the stress tensor and heat current density are expressed, respectively, as quadratures of the density and current density in the configuration space of a pair of molecules.

INTRODUCTION

THIS paper will be concerned with a derivation of the equations of hydrodynamics from the principles of the classical statistical mechanics. In particular, the equation of continuity, the equation of motion, and the equation of energy transport will be derived. By so doing, the stress tensor and heat current density can be expressed in terms of molecular variables. The stress tensor consists of a kinetic part (which occurs in the kinetic theory of gases) and another term (dominant for a liquid) which will be expressed as a quadrature involving the potential of intermolecular force and the density of pairs of molecules. The heat current density is the sum of the familiar kinetic part and a quadrature involving the potential of intermolecular force and the density and current density in the configuration space of a pair of molecules. The results were previously stated in the first article of this series,[1] when this derivation was promised.

To obtain explicit expressions for the pair probability density and probability current density one would in principle need to solve the Liouville equation [Eq. (2.2)] for the probability distribution in Gibbs phase space and then perform repeated integrations. Since this program is untenable for a liquid, various attempts have been made to obtain a closed equation satisfied approximately by the probability distribution function in the phase space of a pair of molecules. One such equation has been derived by Born and Green[2] using a generalized "superposition" assumption. Another, a generalization of the well-known Fokker-Planck equation of stochastic theory, has been derived by Kirkwood[3] by introducing the concepts of time smoothing and a friction constant. This latter equation has been applied to obtain an expression for the stress tensor linear in gradients of fluid velocity and, thereby, expressions (in terms of molecular variables) for coefficients of shear and volume viscosity.[3] The same equation generalized to non-uniform temperatures, after linearizing in the temperature gradient, leads to an explicit expression for the heat current and thereby to an expression for the coefficient of thermal conductivity.[4] We shall assume, for purposes of mathematical simplicity, a single component, single phase fluid system consisting of molecules which interact under central forces only. It is not difficult to generalize the treatment to a multiple component or multiple

* This work was supported by the U. S. ONR under Contract Nonr-744 with the California Institute of Technology.

[1] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946).

[2] M. Born and H. S. Green, Proc. Roy. Soc. A188, 10 (1946).

[3] Kirkwood, Buff, and Green, J. Chem. Phys. 17, 988 (1949).

[4] Kirkwood, Stahrfart, and Irving (in preparation). The numerical evaluation entails a more precise computation of the theoretical radial distribution function.

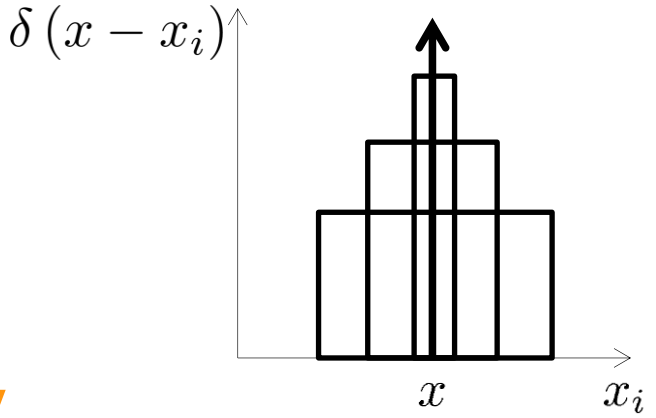
TRANSPORT PROCESSES 819

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

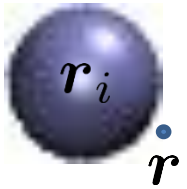
Selecting Functions

- **The Dirac delta selects molecules at a point**
  - Infinitely high, infinitely thin peak
  - Equivalent to the continuum differential formulation at a point

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

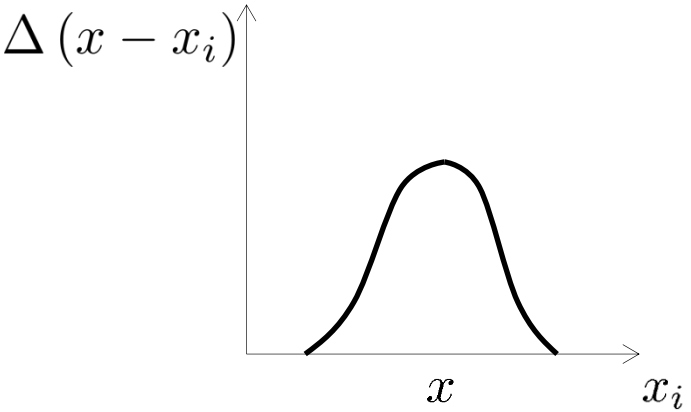


- **In a molecular simulation r is never exactly equal to r_i**
  - Other difficulties with the Dirac delta function



- **Relaxed weighting functions**
  - By Hardy(1981), Todd, Hansen and Daivis (2008), Hoover/Lucy (2009), Murdoch (2010)

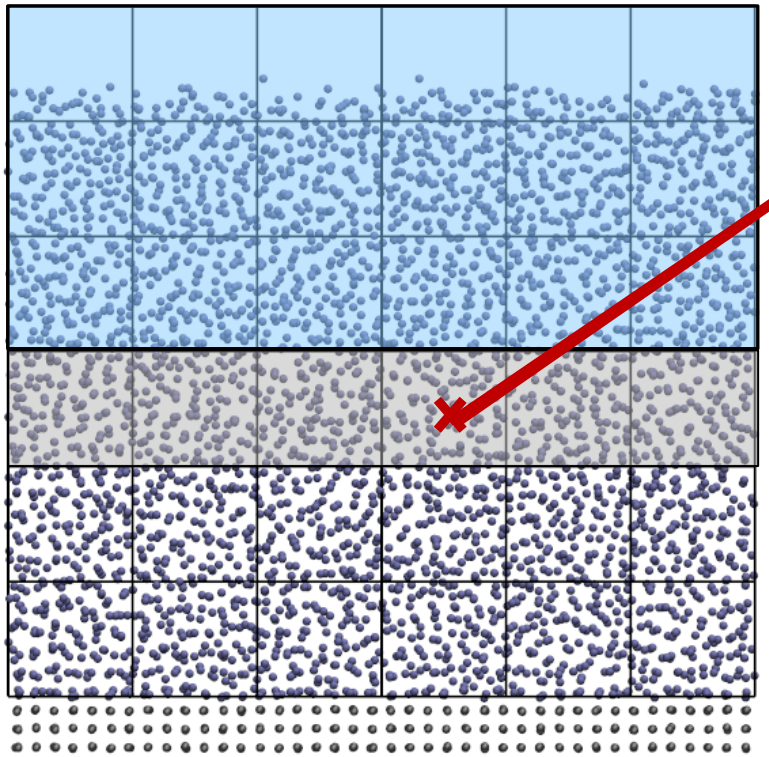
$$\rho(\boldsymbol{r},t) \approx \sum_{i=1}^{N} m_i \Delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right)$$

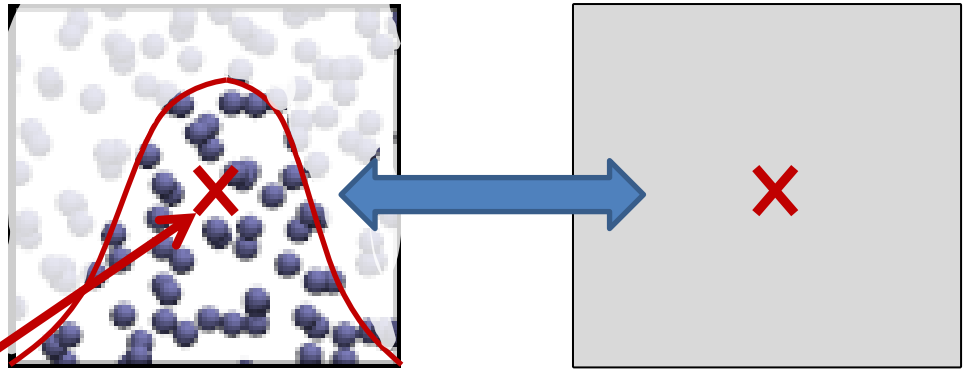


Imperial College London

An Equivalent Formulation

- **Both domains exist in the same physical space**





- Dirac Delta and continuum are formally equivalent at a point

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

- Average of an MD region gives an approximation at a point

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

- Instead, integrate both sides

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

The Control Volume (CV)

- **Writing the molecular system in terms of control volumes**
  - Mass

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

  - Momentum

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

  - Energy

$$\rho \mathcal{E} = \sum_{i=1}^{N} e_i \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) \qquad \int_V \rho \mathcal{E} dV = \sum_{i=1}^{N} e_i \int_V \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

Control Volume Function

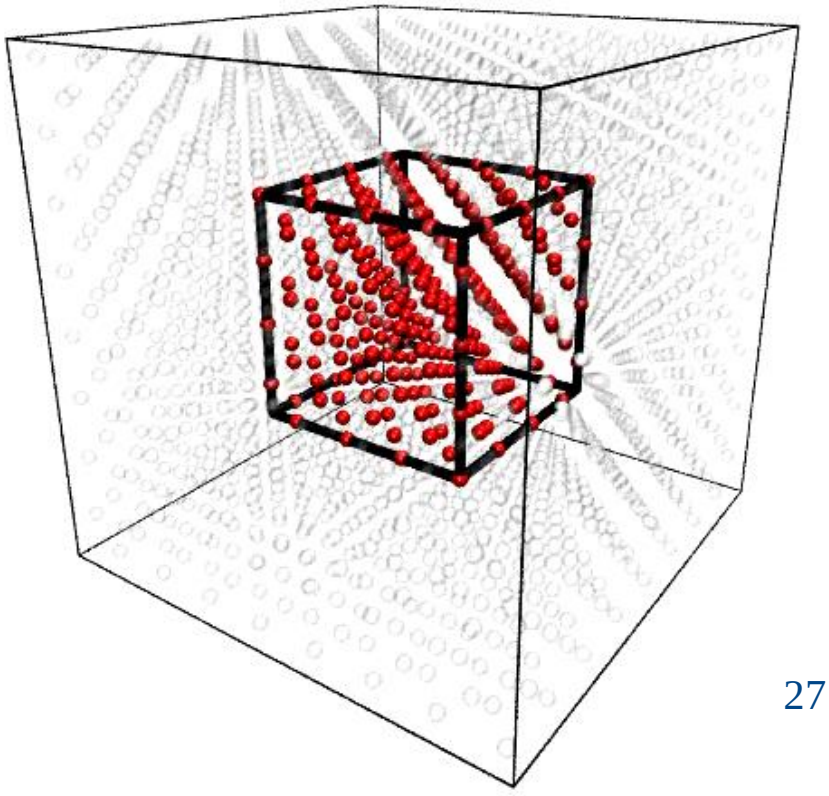
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

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

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

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

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



Derivatives yields the Surface Fluxes

- **Taking the Derivative of the CV function**

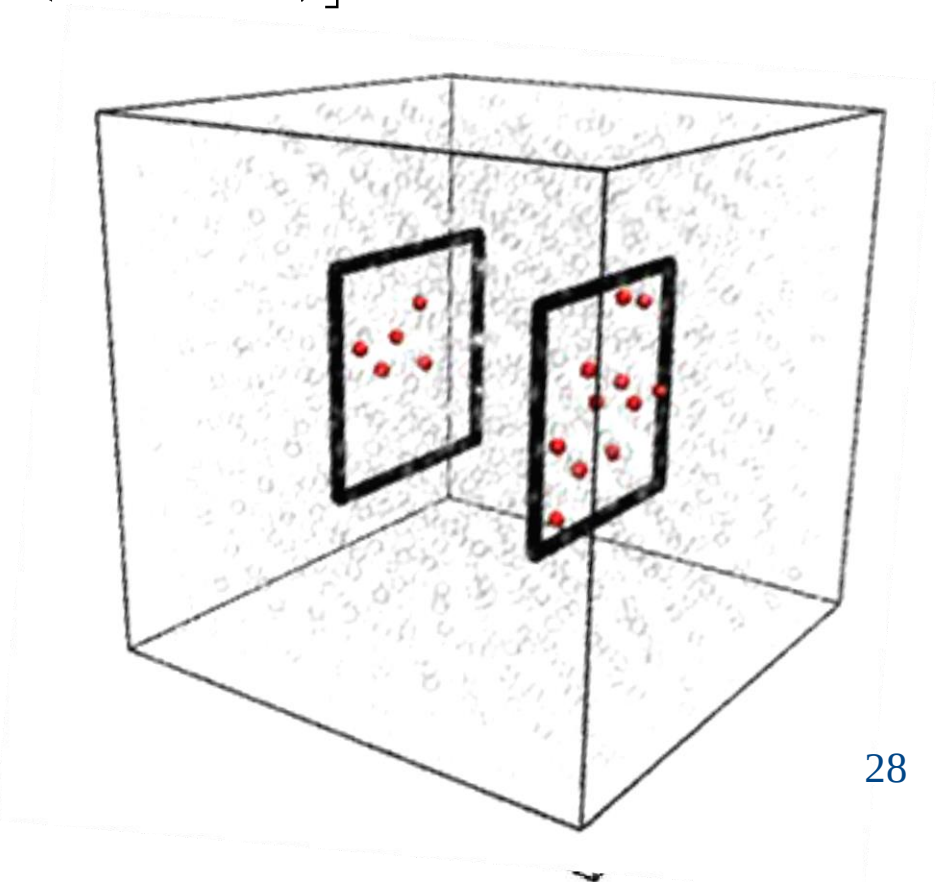
$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i} = \left[\delta(x^+ - x_i) - \delta(x^- - x_i)\right] \times \left[H(y^+ - y_i) - H(y^- - y_i)\right] \times \left[H(z^+ - z_i) - H(z^- - z_i)\right]$$

- **Surface fluxes over the top and bottom surface**

$$dS_{ix} = dS_{ix}^+ - dS_{ix}^-$$

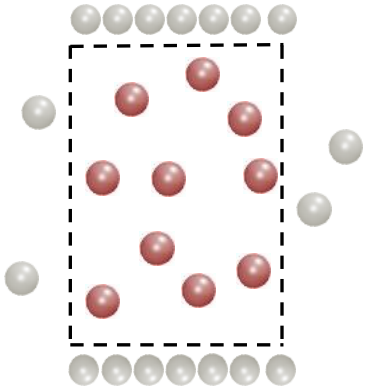
- **Vector form defines six surfaces**

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



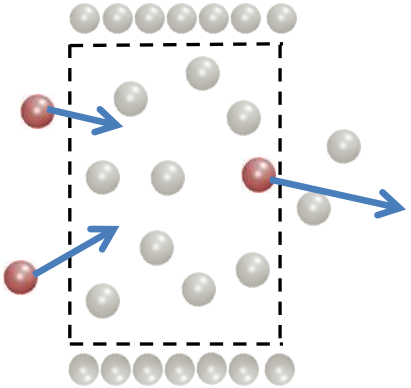
Control Volume Functional

- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**



$$\vartheta_i \equiv \int_V \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

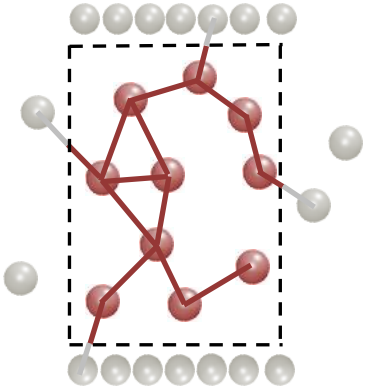
- **Its derivative gives the fluxes over the surface**



$$dS_{ix} \equiv -\frac{\partial \vartheta_i}{\partial x_i}$$

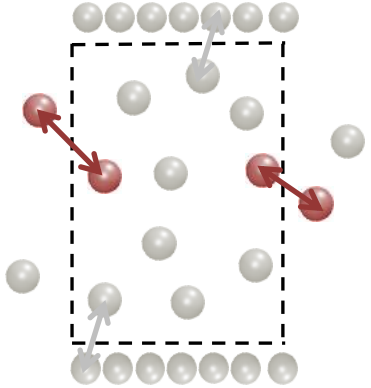
Control Volume Functional - Forces

- A CV based on the length of intermolecular interaction inside the volume (used in the volume average stress)



$$\vartheta_s \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij}) dV$$

- Its derivative gives the forces over the surface (as in the method of planes stress)



$$dS_{xij} \equiv \int_0^1 \frac{\partial \vartheta_s}{\partial x} ds$$

The Control Volume Equations

- **Using the CV functional, the following equations are derived**
  - Mass Conservation

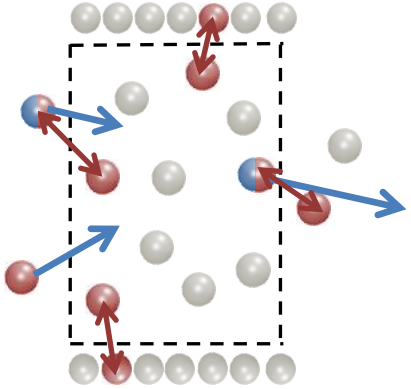
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i$$

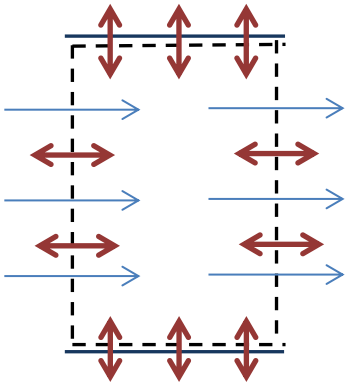
$$\frac{\partial}{\partial t}\int_V \rho dV = -\oint_S \rho \boldsymbol{u} \cdot d\mathbf{S}$$

  - Momentum Balance

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i + \frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij}\mathbf{n} \cdot d\mathbf{S}_{ij}$$

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

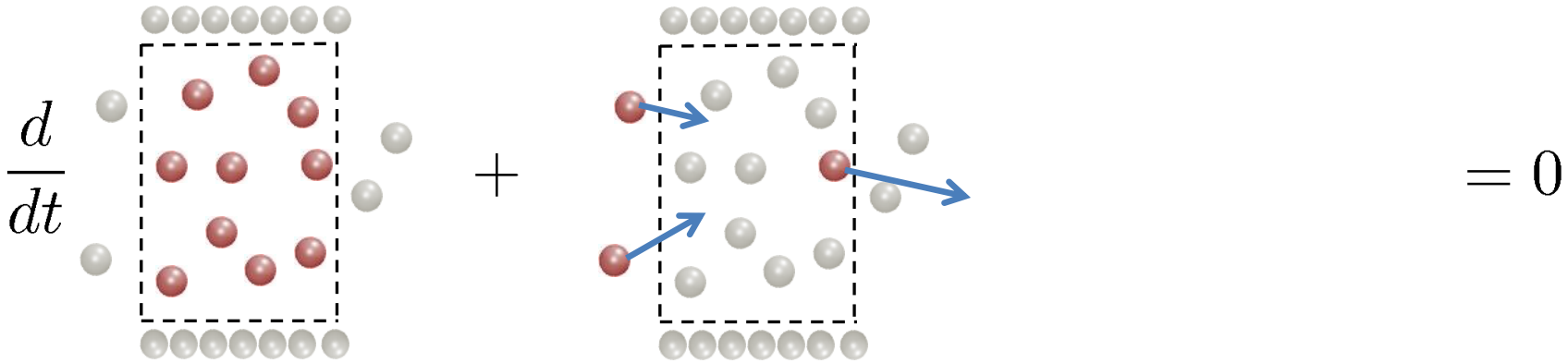




Exact Conservation

- **Mass Conservation**

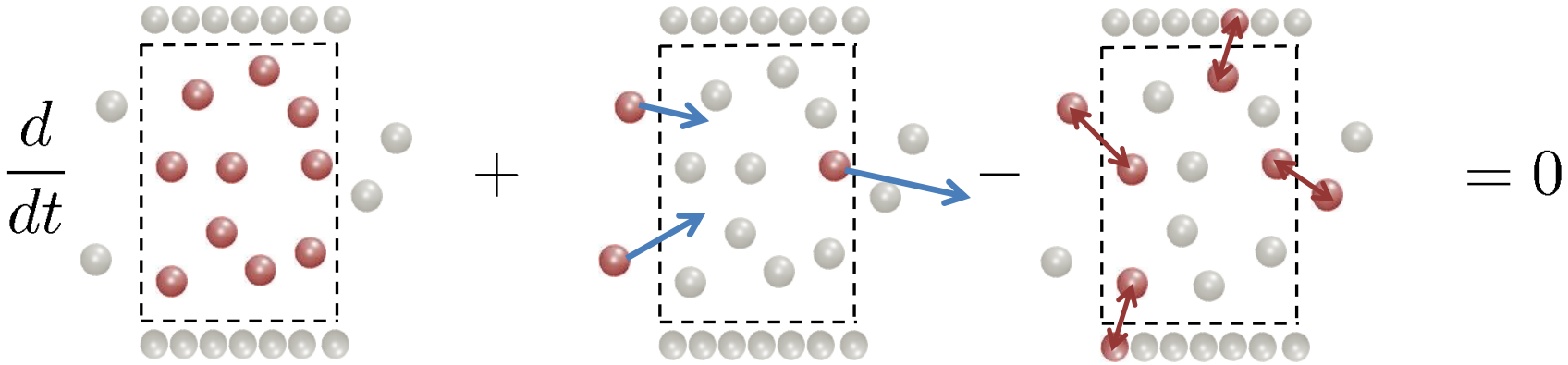
$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \vartheta_i}_{\text{Accumulation}} + \underbrace{\sum_{i=1}^{N} m_i \mathbf{v}_i \cdot d\boldsymbol{S}_i}_{\text{Advection}} = 0$$



Exact Conservation

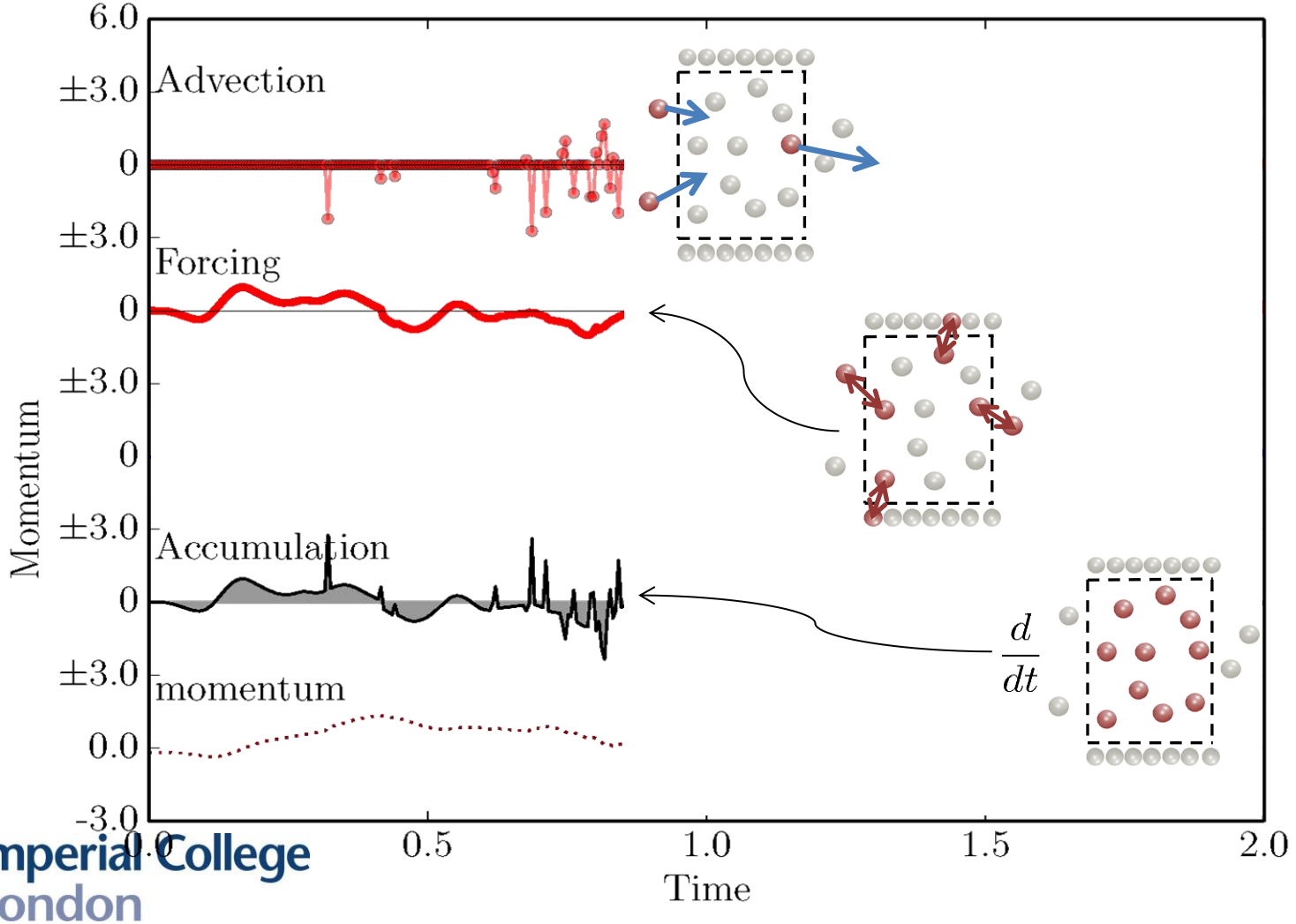
- **Momentum Balance**

$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\text{Accumulation}} + \underbrace{\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\text{Advection}} - \underbrace{\frac{1}{2}\sum_{i,j}^{N} \boldsymbol{f}_{ij} \mathbf{n} \cdot d\mathbf{S}_{ij}}_{\text{Forcing}} = 0$$



Exact Conservation

- **Results from any arbitrary volume**
  - Accumulation = Forcing + Advection
  - Momentum evolution is the integral of accumulation

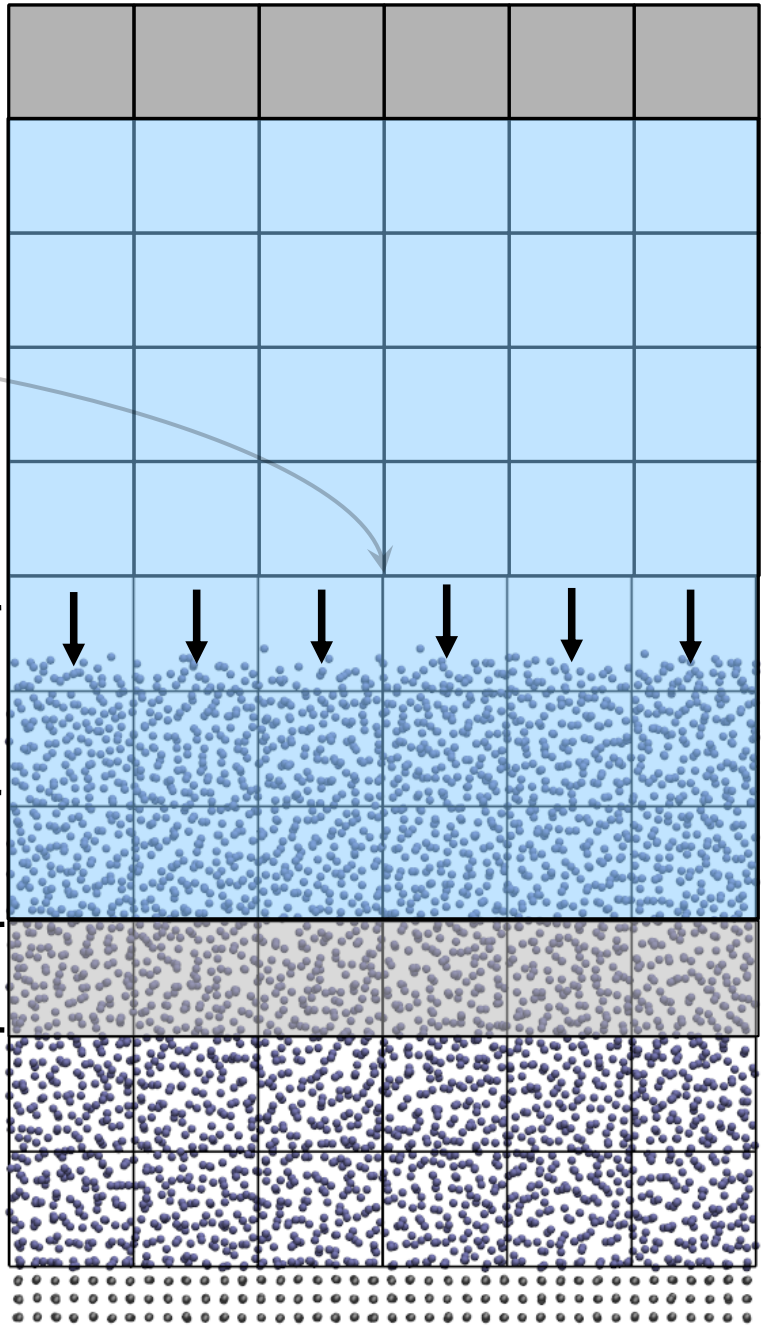


$$\underbrace{\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\mathbf{S}_i}_{\text{Advection}} \underbrace{- \frac{1}{2} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \mathbf{n} \cdot d\mathbf{S}_{ij}}_{\text{Forcing}} = \underbrace{\frac{d}{dt} \sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\text{Accumulation}}$$

Imperial College London

Coupling Using the Control Volume

Boundary force and
insertion of molecules



Consistent Framework ✓

CFD→MD Boundary condition

MD→CFD Boundary condition

Coupling Using the Control Volume

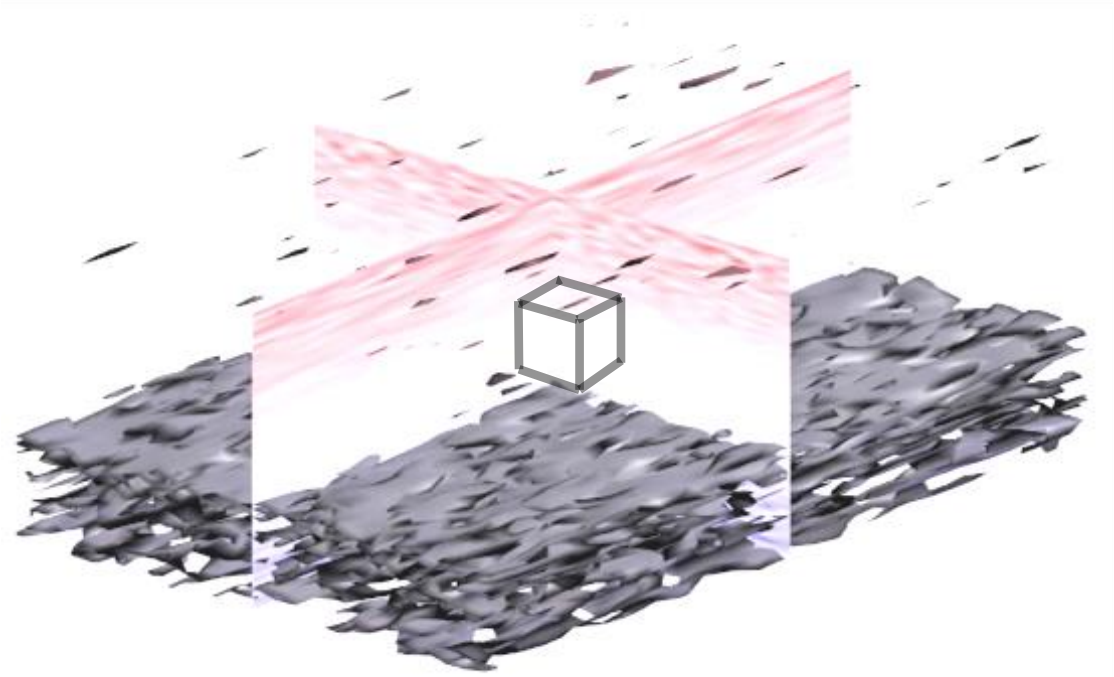
- **We now have an equivalent description in both regions**
  - Momentum or stresses inside an arbitrary control volume in both domains

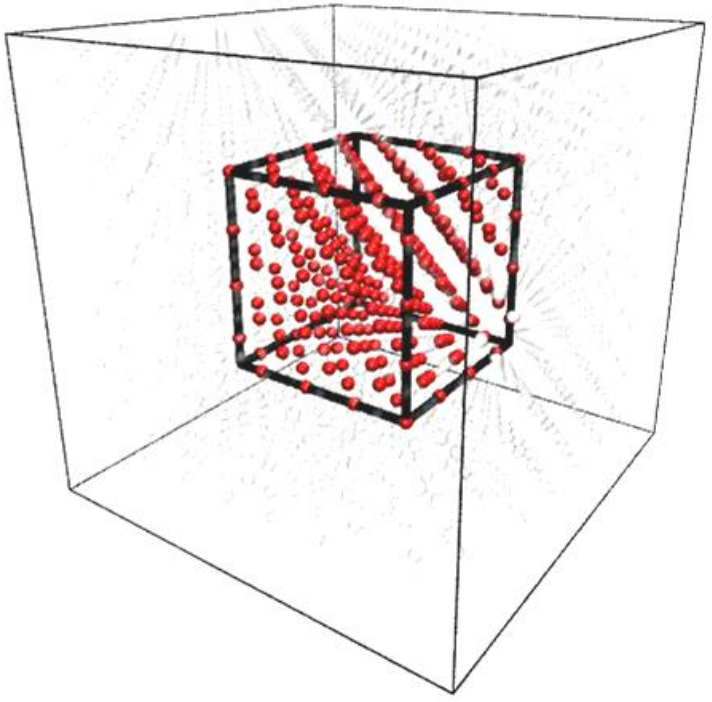
$$\int_V \rho u dV = \sum_{i=1}^{N} m_i \boldsymbol{v}_i \vartheta_i$$

State Coupling : O'Connell & Thompson (1995), Nie, Chen, E & Robbins (2004)

$$\oint_S \boldsymbol{\Pi} \cdot d\boldsymbol{S} = \sum_{i=1}^{N} m_i \boldsymbol{v_i} \boldsymbol{v_i} \cdot d\mathbf{S}_i + \frac{1}{4} \sum_{i,j}^{N} \boldsymbol{f}_{ij} \mathbf{n} \cdot d\mathbf{S}_{ij}$$

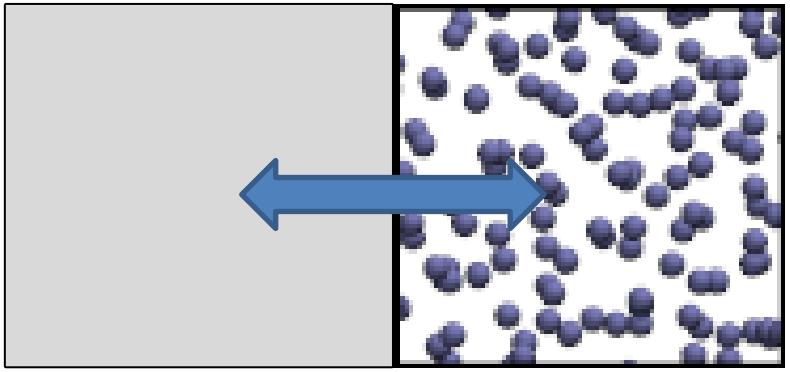
Flux Coupling: Flekkøy et al (2000), Delgado-Buscalioni & Coveney, (2004)





Consistent Formulation

- **We now have an equivalent description in both regions**
  - Flux out of one system can be supplied as a flux into the other – using method of planes stresses (Todd et al, 1995) in the MD and surfaces fluxes in the CFD
  - Potential to develop a coupled system which is exactly conservative

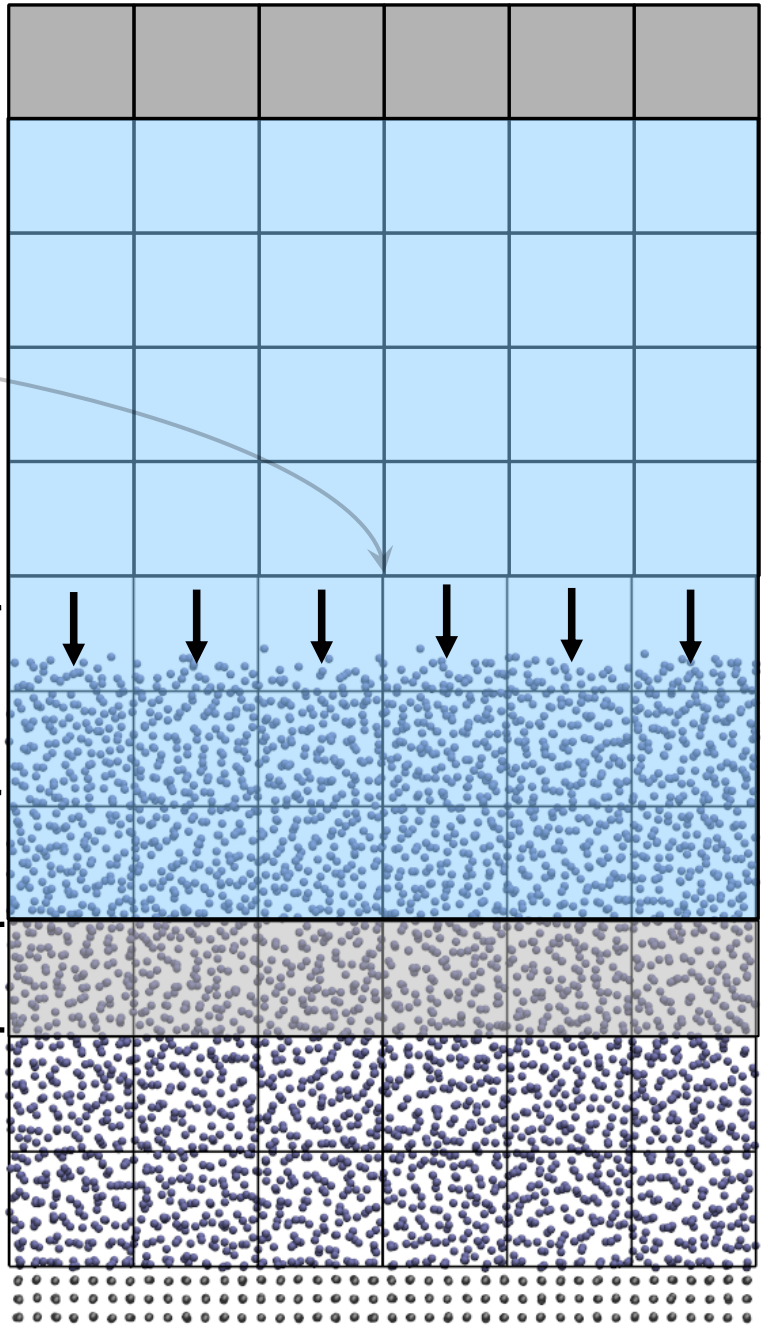


$$\int_{S_x^+} \mathbf{\Pi} \cdot dS_x^+ = \sum_{i=1}^{N} m_i \boldsymbol{v_i} v_{xi} dS_{xi}^- - \frac{1}{4} \sum_{i,j}^{N} \boldsymbol{f}_{ij} dS_{xij}^-$$

Imperial College London

Coupling Using the Control Volume

Boundary force and insertion of molecules



CFD→MD Boundary condition

MD→CFD Boundary condition ✓

Consistent Framework ✓

Constrained Control Volume

- **Non-unique solution**
  - Continuum field properties must specify N molecules
  - Hamilton's principle (subject to a constraint) used in the first fluids coupling scheme (O'Connell and Thompson 1995)
- **But now we want to apply a constraint localised using the control volume function**
  - CV function takes care of the localisation for us
  - Non-holonomic constraint

$$g(\boldsymbol{r}_i, \dot{\boldsymbol{r}}_i) = \sum_{i=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_i - \int_V \rho \boldsymbol{u} dV = 0$$

- **Gauss Principle of Least Constraint Applied**
  - Valid for any form of constraint

$$\frac{\partial}{\partial \boldsymbol{r}_{ij}} \sum_{i=1}^{N} \left[\boldsymbol{F}_i - \boldsymbol{r}_{ij}\right]^2 - \boldsymbol{\lambda} \cdot \boldsymbol{g} = 0$$

Constrained Control Volume

- **Gauss Principle of Least Constraint Applied**
  - Resulting constrained equations are differential e.g. the evolution of momentum is matched to the continuum

$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i \vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho \boldsymbol{u} dV - \frac{d}{dt}\sum_{n=1}^{N} m_i \dot{\boldsymbol{r}}_i \vartheta_i\right]$$

  - Surface fluxes and force ***exactly*** cancel the molecular terms and replace them with the coupled continuum values

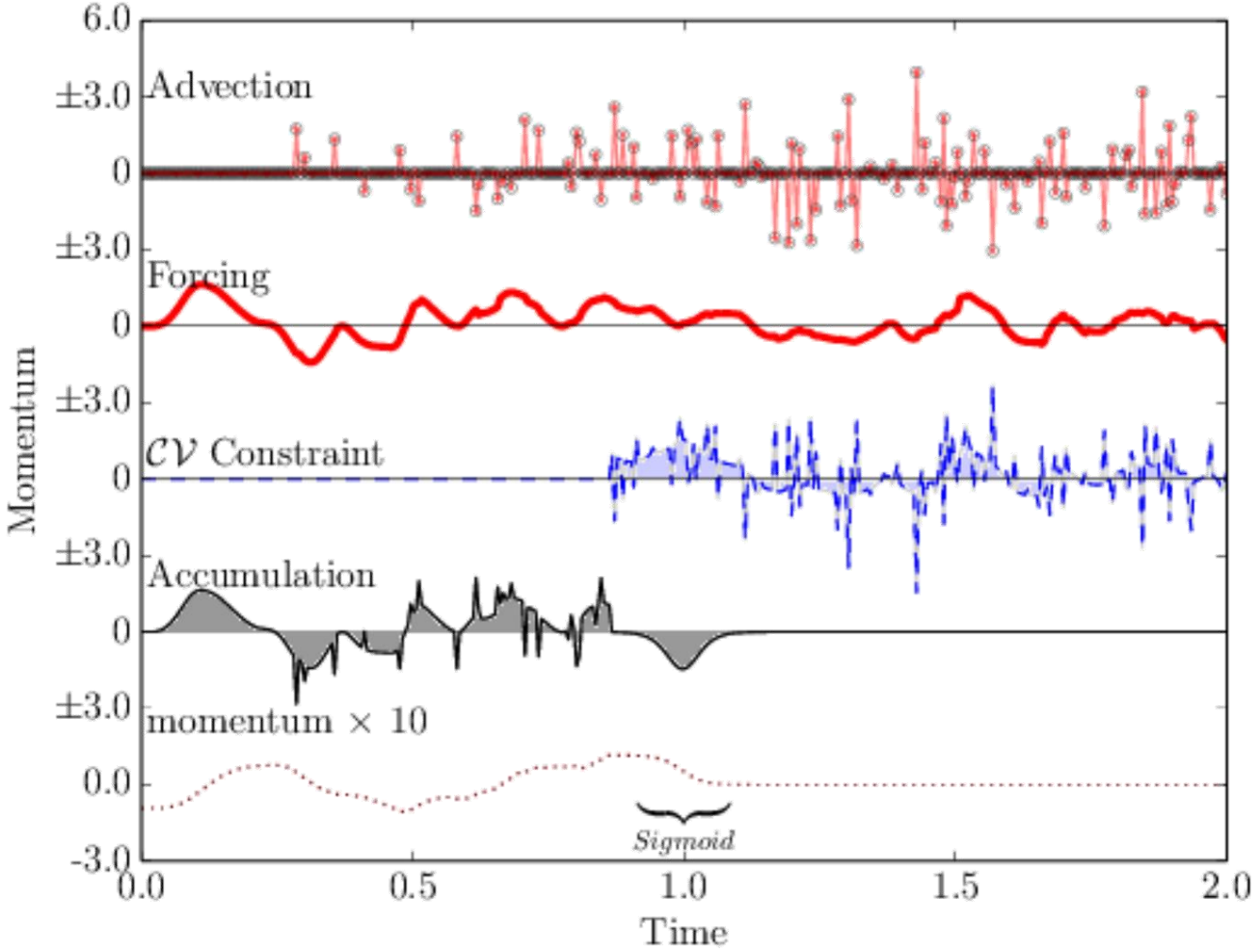
$$m_i \ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i \vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho \boldsymbol{u} dV + \overbrace{\sum_{n=1}^{N} m_i \dot{\boldsymbol{r}}_{\boldsymbol{n}} \dot{\boldsymbol{r}}_n \cdot d\mathbf{S}_n}^{\text{Advection}} - \overbrace{\sum_{n,m}^{N} \boldsymbol{f}_{nm}\mathbf{n} \cdot dS_{nm}}^{Forcing}\right]$$

- **An Iterative Implementation of the Constraint is Required**
  - Similar to SHAKE but iterating to cancel effects of momentum flux instead of bond length
  - Momentum control must be exact for a local differential constraint to be applied with no drift

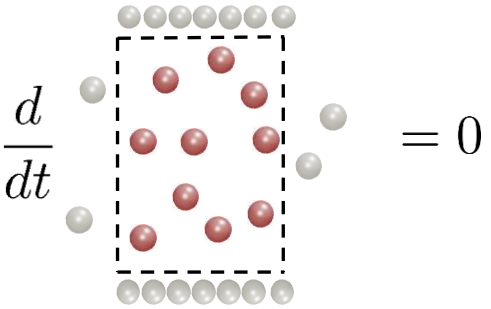
Constrained Control Volume

- **Provides a method of controlling a volume's velocity and stress**

$$m_i\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i\vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho\boldsymbol{u}dV + \overbrace{\sum_{n=1}^{N} m_i\dot{\boldsymbol{r}}_{\boldsymbol{n}}\dot{\boldsymbol{r}}_n\cdot d\mathbf{S}_n}^{\text{Advection}} - \overbrace{\sum_{n,m}^{N}\boldsymbol{f}_{nm}\mathbf{n}\cdot dS_{nm}}^{Forcing}\right]$$



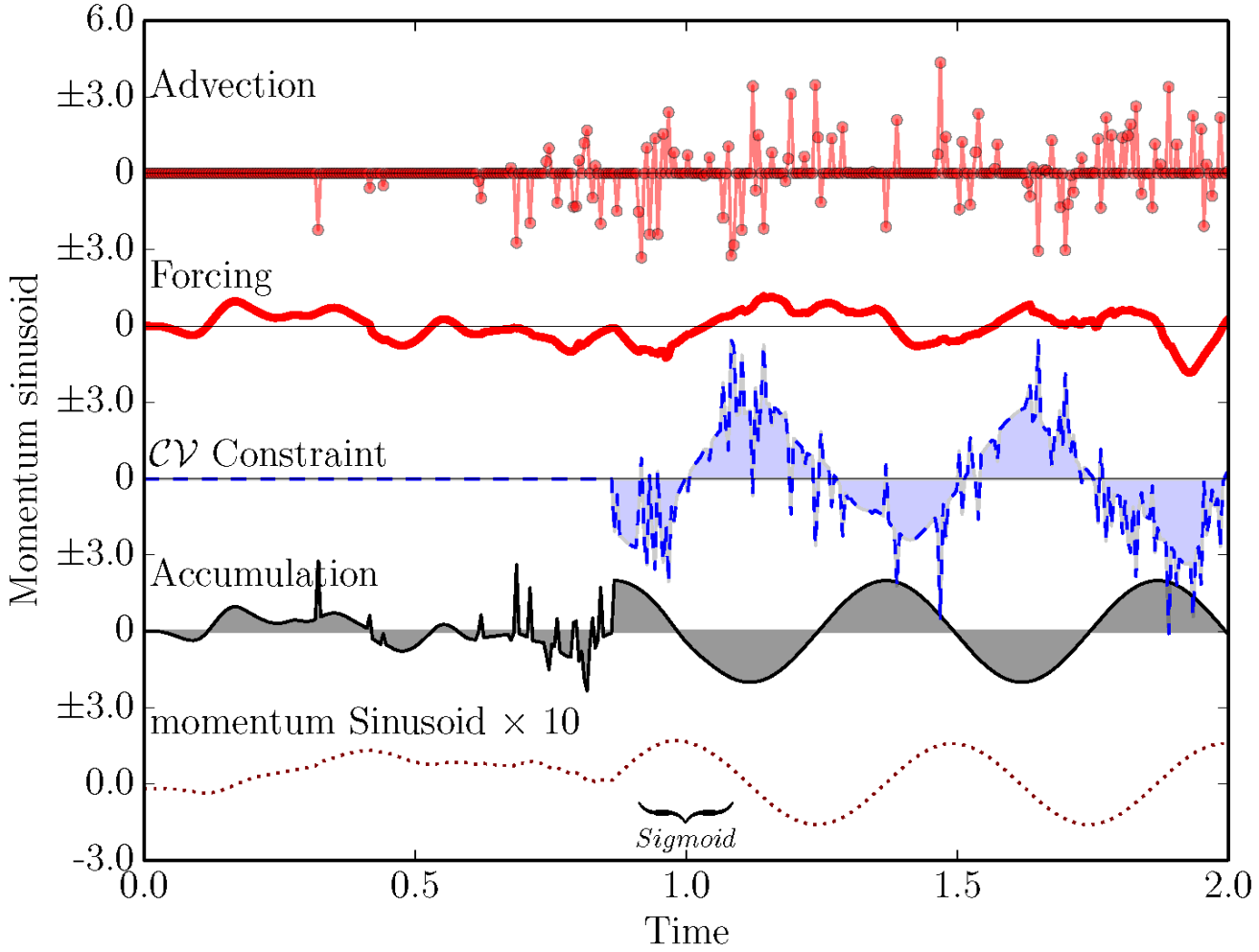
- Zero time evolution applied
- No velocity evolution results
- Exact control of momentum using iteration to cancel both Forcing and Advection



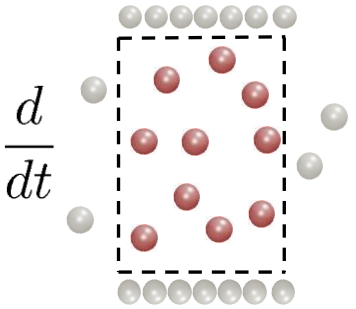
Constrained Control Volume

- **Provides a method of controlling a volume's velocity and stress**

$$m_i\ddot{\boldsymbol{r}}_i = \boldsymbol{F}_i + \frac{m_i\vartheta_i}{M_I}\left[\frac{d}{dt}\int_V \rho\boldsymbol{u}dV + \overbrace{\sum_{n=1}^{N} m_i\dot{\boldsymbol{r}}_{\boldsymbol{n}}\dot{\boldsymbol{r}}_n\cdot d\mathbf{S}_n}^{\text{Advection}} - \overbrace{\sum_{n,m}^{N}\boldsymbol{f}_{nm}\mathbf{n}\cdot dS_{nm}}^{Forcing}\right]$$



- Cosinusoidal time evolution applied
- Sinusoidal velocity evolution results
- Exact control of momentum using iteration to cancel both Forcing and Advection



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

Constrained Control Volume

- **Provides a method of controlling a volume's velocity and stress**

$$\sum_{n,m}^{N} \boldsymbol{f}_{nm} \mathbf{n} \cdot d\mathbf{S}_{nm} = \sum_{n,m}^{N} \left[\boldsymbol{f}_{nm} dS^{+}_{xnm} + \boldsymbol{f}_{nm} dS^{-}_{xnm} + \boldsymbol{f}_{nm} dS^{+}_{ynm} + \boldsymbol{f}_{nm} dS^{-}_{ynm} \right]$$

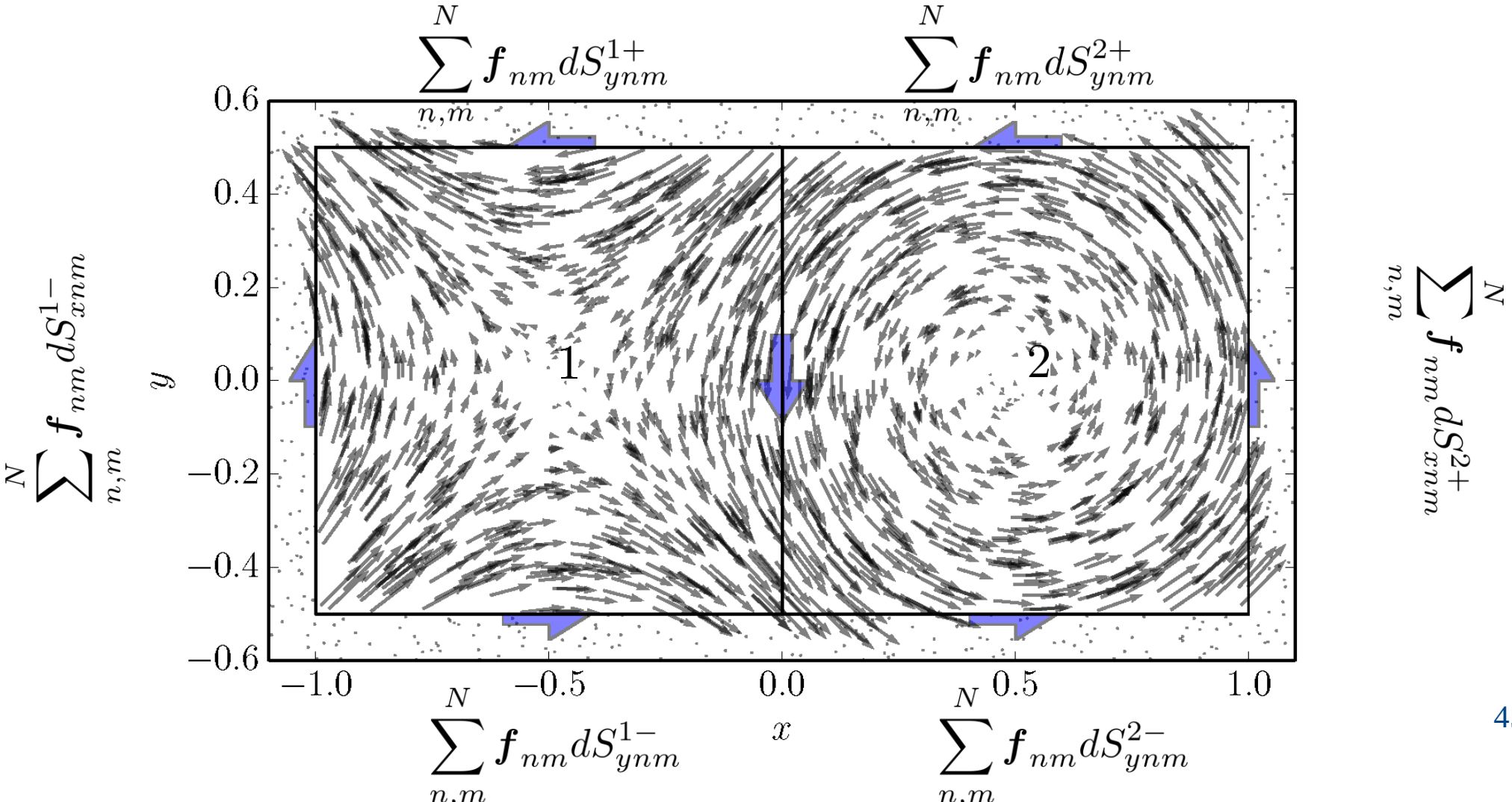
  - Forcing applies an arbitrary 18 component 3D stress field

Constrained Control Volume

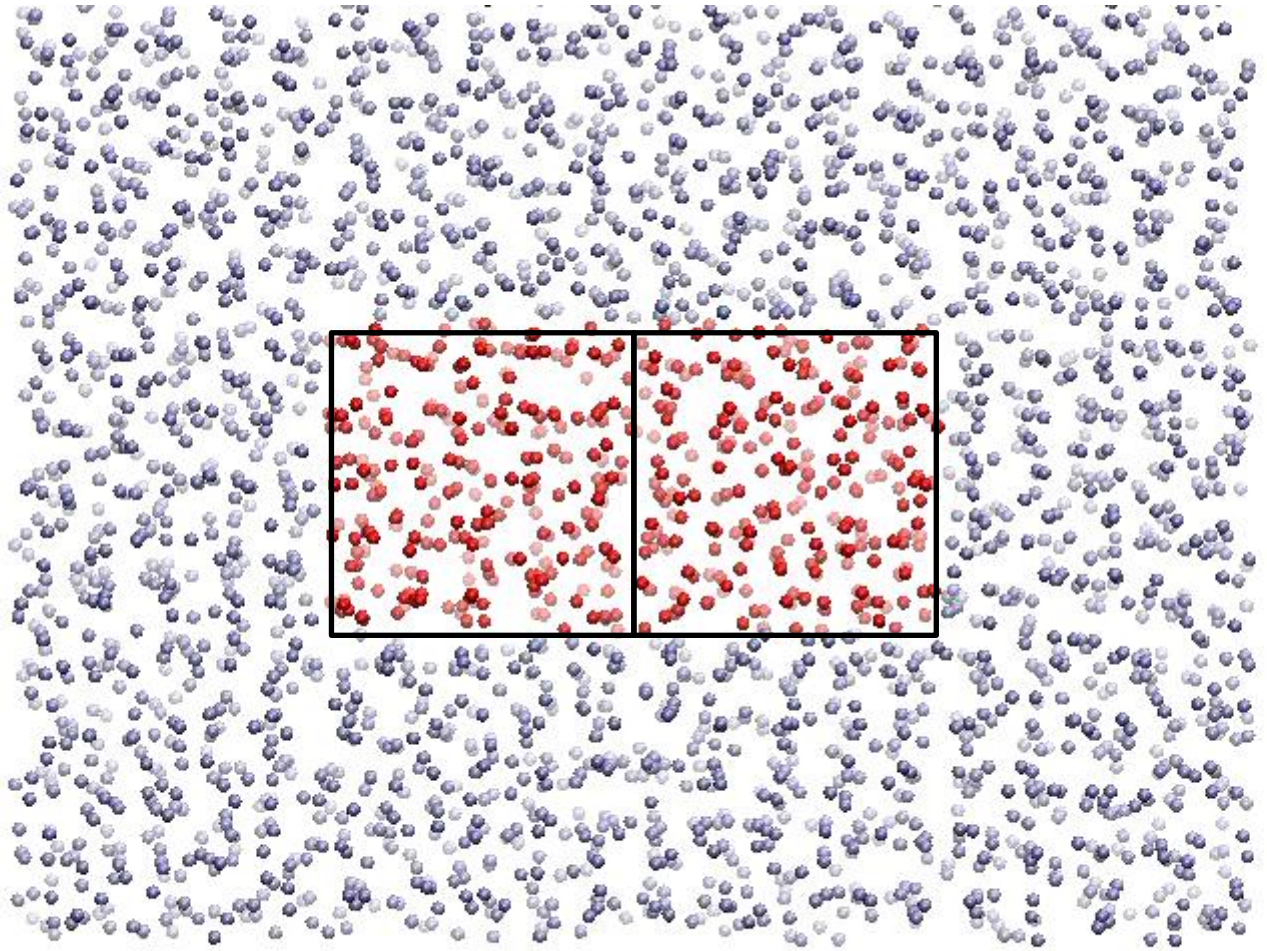
- **Provides a method of controlling a volume's velocity and stress**

$$\sum_{n,m}^{N} \boldsymbol{f}_{nm}\mathbf{n}\cdot d\mathbf{S}_{nm} = \sum_{n,m}^{N}\left[\boldsymbol{f}_{nm}dS^{+}_{xnm} + \boldsymbol{f}_{nm}dS^{-}_{xnm} + \boldsymbol{f}_{nm}dS^{+}_{ynm} + \boldsymbol{f}_{nm}dS^{-}_{ynm}\right]$$

  - Forcing applies an arbitrary 18 component 3D stress field

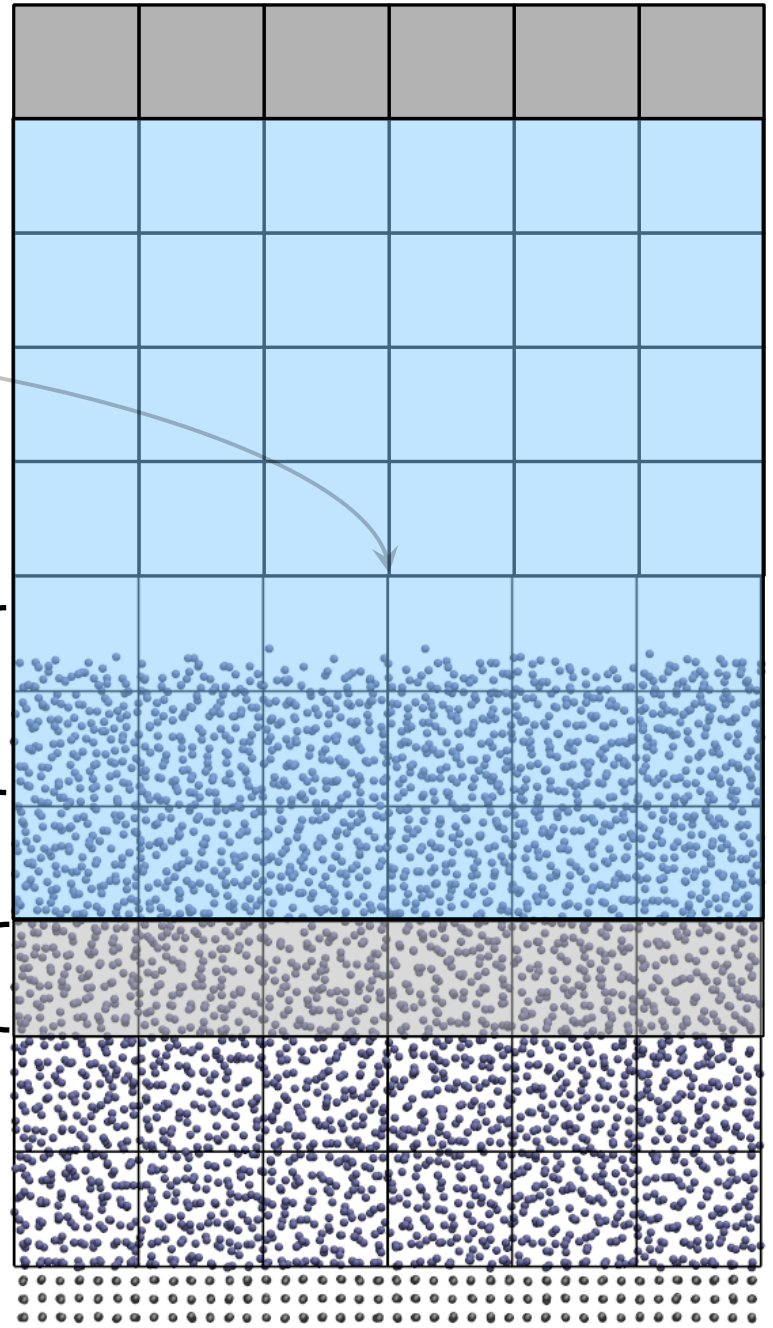


Constrained Control Volume



Coupling Using the Control Volume

Boundary force and
insertion of molecules



CFD→MD
Boundary
condition ✓

MD→CFD
Boundary
condition ✓

Consistent
Framework ✓

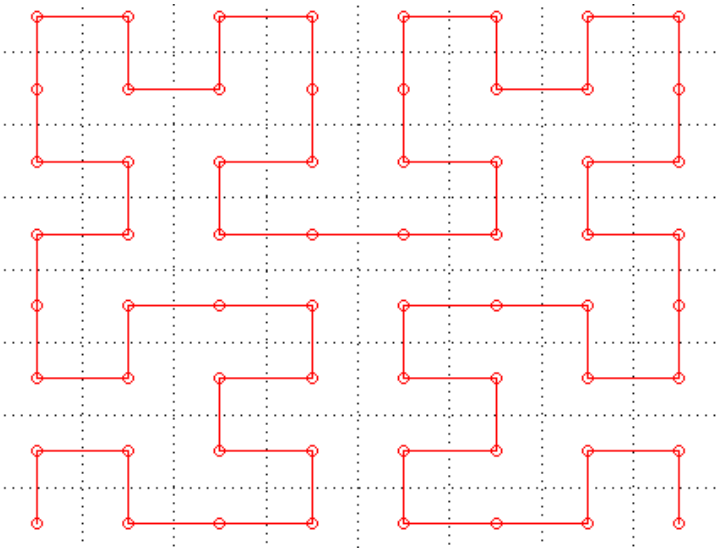
Consistent Framework

- **Both systems written in terms of the integrated volumes**
  - A common framework to develop a rigorous and consistent coupled system
  - What leaves one system goes into the other – conservation equations are exactly satisfied between descriptions
- **The control volume (CV) constraint**
  - Explicit localisation not considered previously
  - Applies both state and flux control simultaneously
  - Uses non-equilibrium MD techniques like Gauss principle
- **Long Term aim is to couple general (i.e. turbulent) simulation**
  - Very complicated flow fields must be applied
  - Loss of vorticity (in CFD cell rotation) may damage dynamics
  - CV constraint can apply all components as they are, transferring detailed flowfields
- **But first, some computational development**

Coupled Simulation

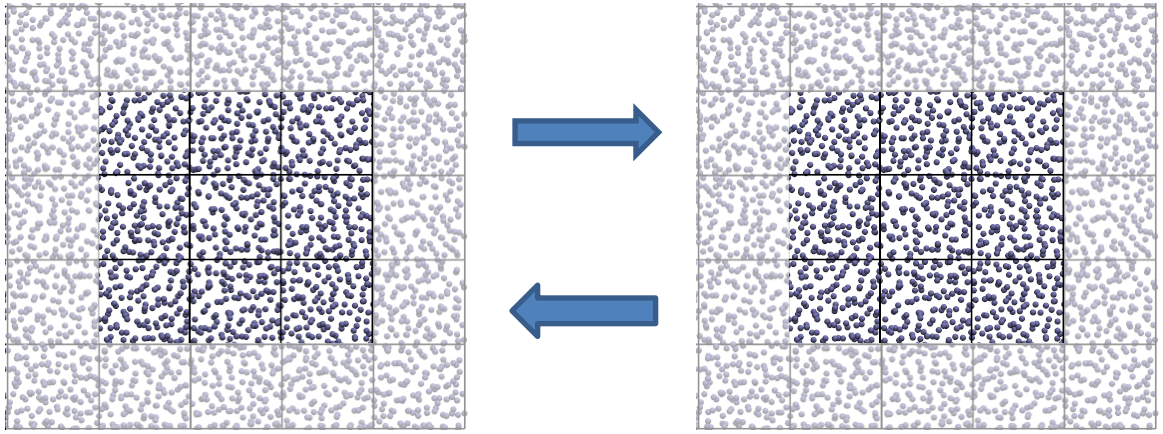
MD Computing – Serial optimisations

- **All pairs simulation uses local cell and neighbour lists**
  - N^2 calculation reduced to order N
  - Linked lists are used in order to manipulate data
  - Result in non-contiguous data access
- **Hilbert curve sorting improves cache efficiency of operations**
  - Improvement becomes greater on larger systems
  - Some tuning required
- **Heaviside function implemented in assembly language**
  - `cmplesd xmm1,xmm0 #Check input less than 0.0;`
  - `movsd xmm0,xmm2 #Save 1.0 into xmm0`
  - `andpd xmm0,xmm1 #AND 1.0 with all zeros/ones`



MD Computing – Parallel optimisations

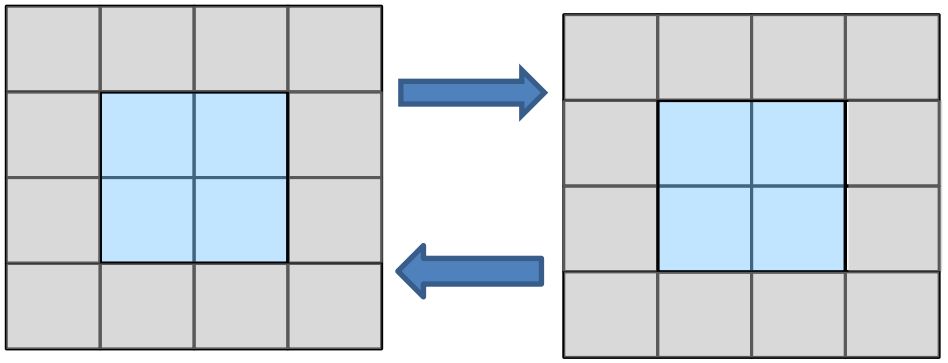
- **Localisations lends itself to parallel computing using MPI**
  - Spatial decomposition employed
  - Halo cells (ghost molecules) are used to link adjacent regions



- **Halo exchange of variable amounts of data**
  - MPI_Send, MPI_Probe and MPI_Recv employed

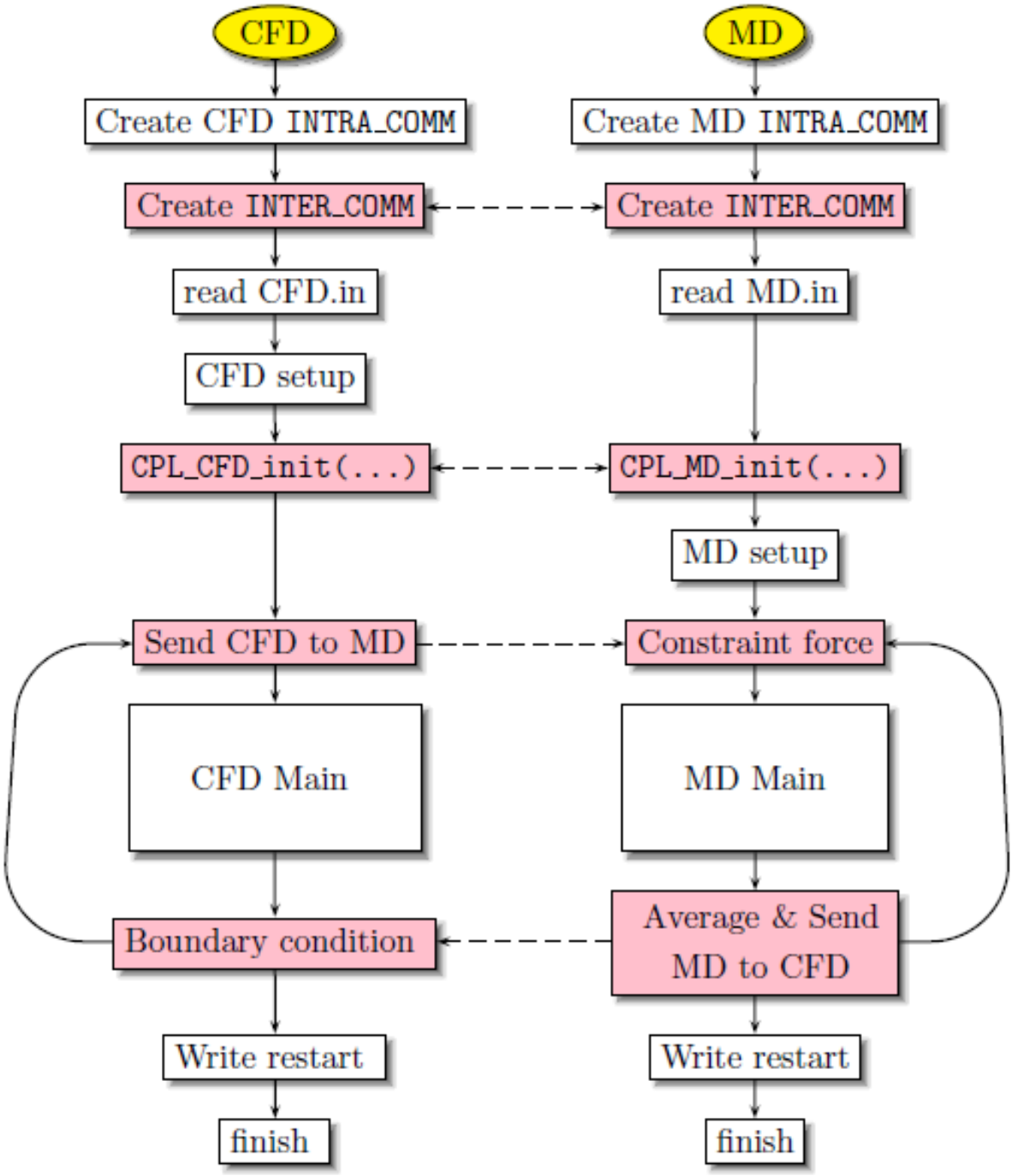
Computational Fluid Dynamics

- **Fortran finite volume (FV) Direct Numerical Simulation (DNS)**
  - Highly optimised algorithm used in simulation of turbulence
  - Fully parallelised using MPI (halo cells)
  - Extensively tested and verified (Zaki & Durbin, 2005, 2006)



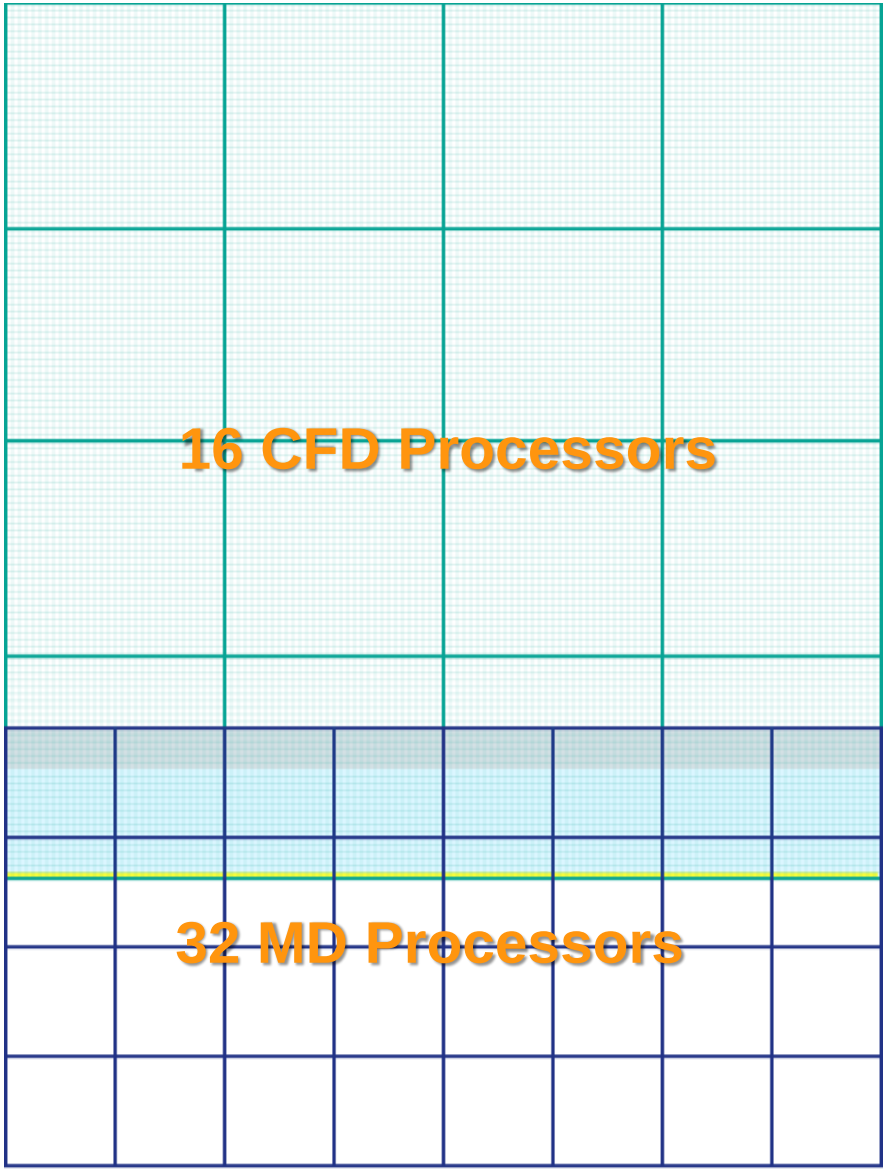
- **Other CFD codes used**
  - Simple 2D Finite Volume test code used during development
  - OpenFoam is also Finite Volume
  - Nektar++ and its FORTRAN predecessor Nek5000 both use Spectral Elements

CPL_LIBRARY Schematic



CPL_LIBRARY Overview

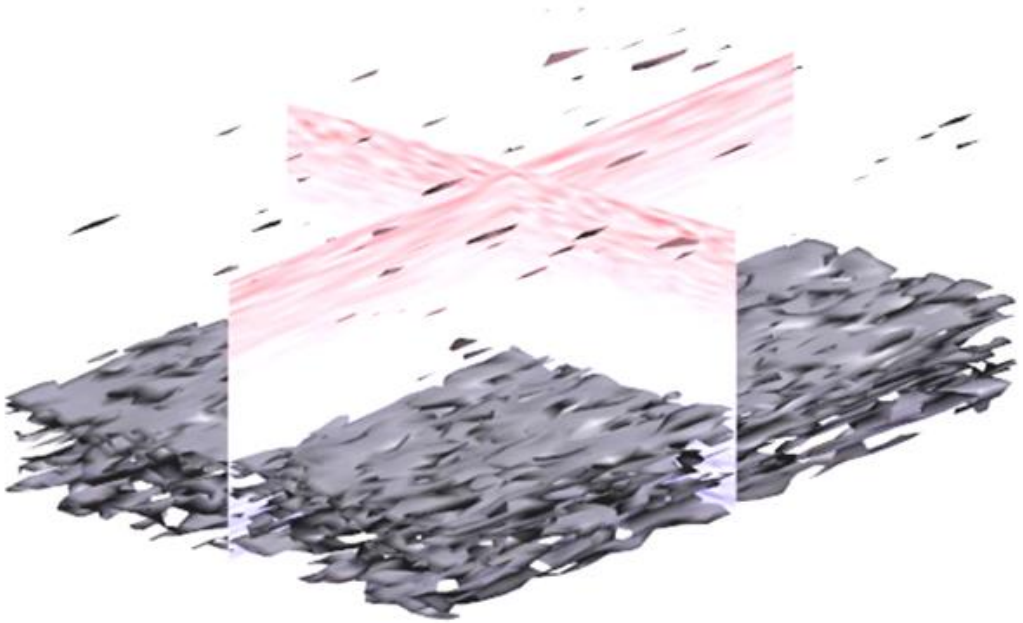
- **Based on the MPI module**
  - Designed in collaboration with Numerical Algorithms Group (NAG)
  - Lightweight and efficient library to preserve the scaling of the two codes
  - API using pure Fortran functions, unit tested and inclusive of error checking
- **Framework is general**
  - Exchange any arbitrary data arrays per continuum cell
  - Allows, in principle, the coupling of any continuum code to any molecular code
  - MPMD implementation enforces separate scope of the two solvers

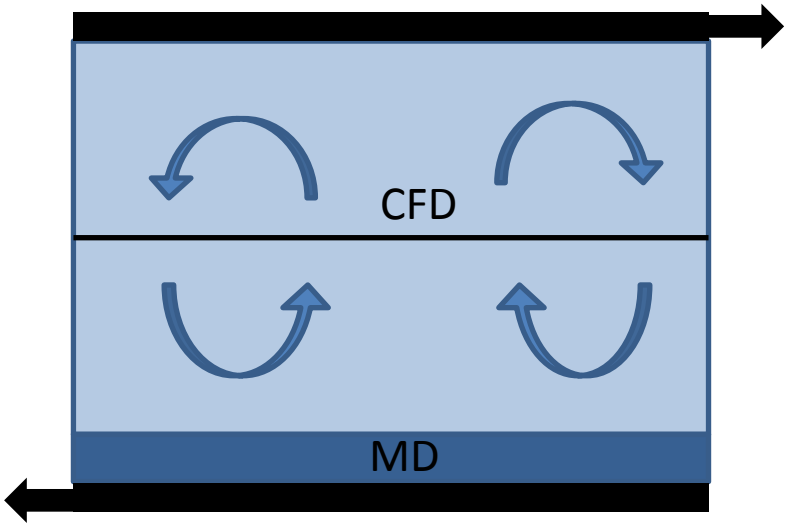


mpiexec –n 32./md.exe : -n 16 ./cfd.exe

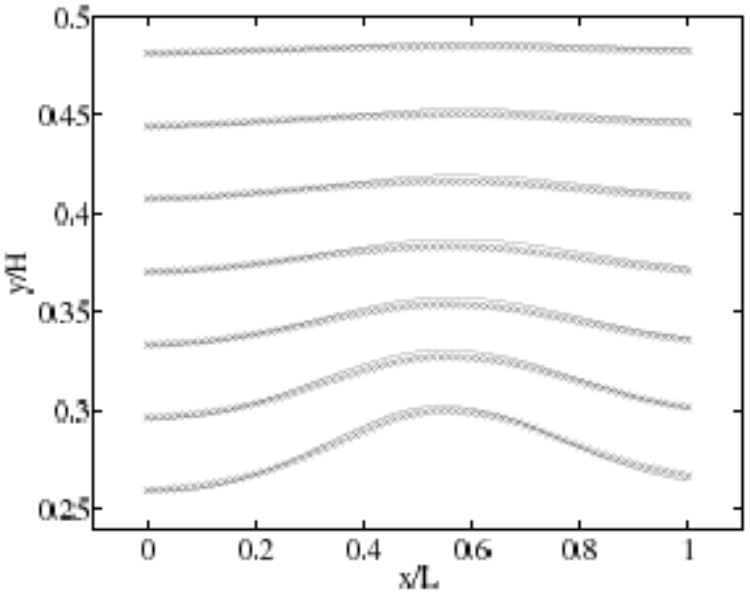
Turbulent Flow

- **Turbulent Flow in a channel**
  - CFD used for the majority of the domain
  - MD solves the near wall region which is known to have a major effect on the dynamics of the system

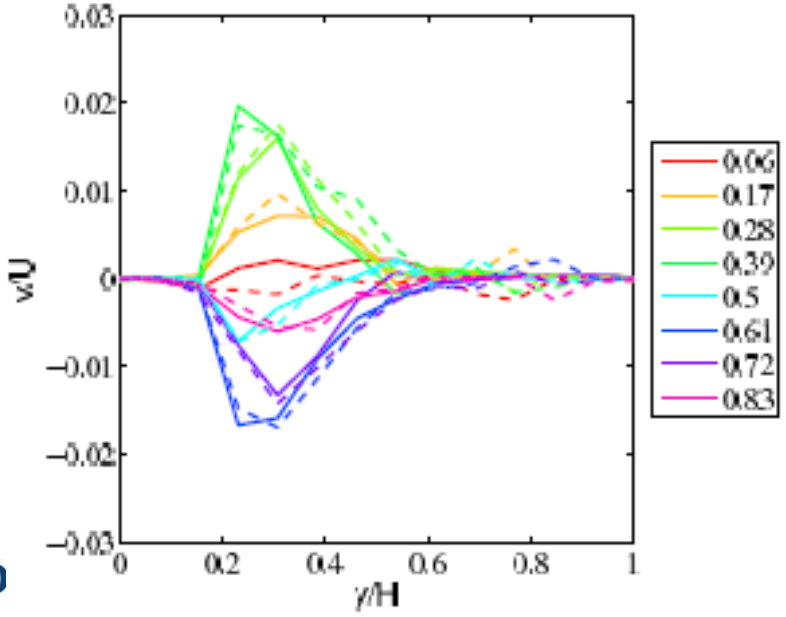




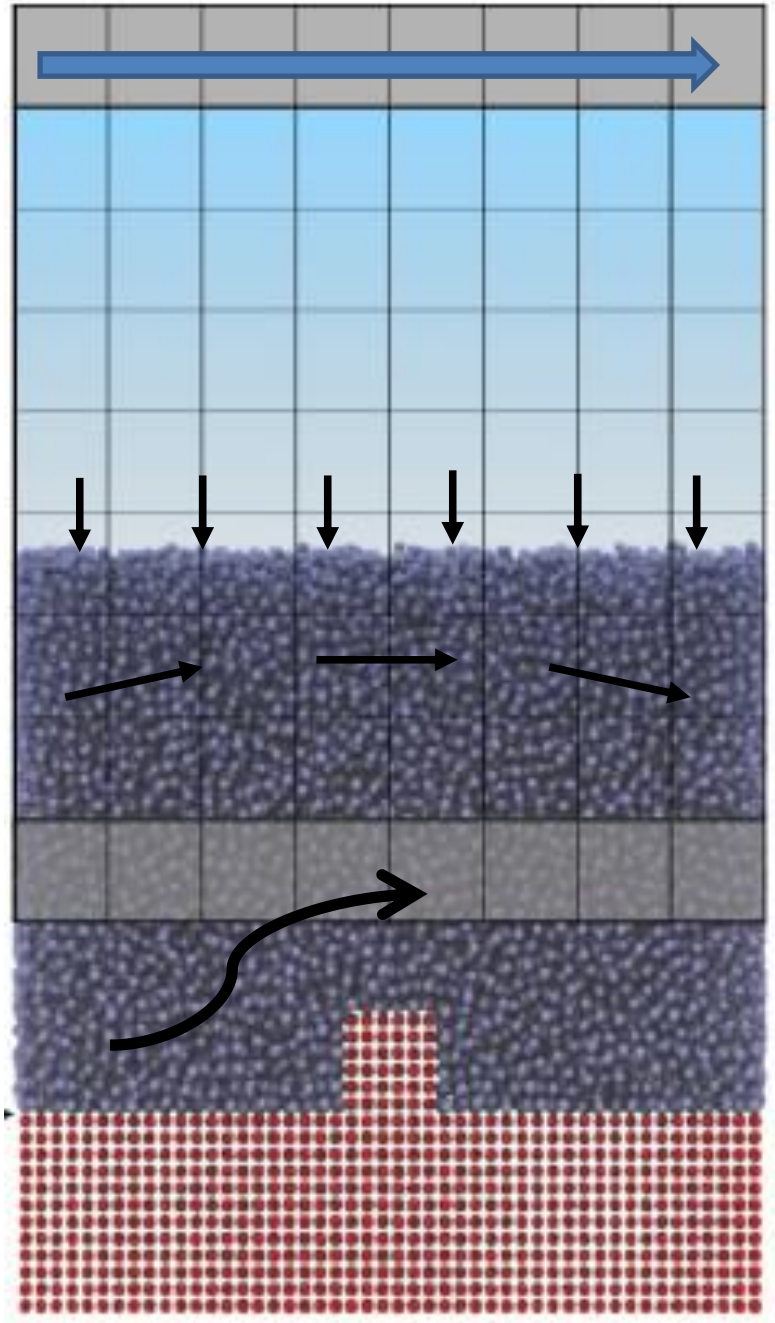
Couette Flow with Wall Roughness



(a) Streamlines: CPL (×) vs all MD (—)



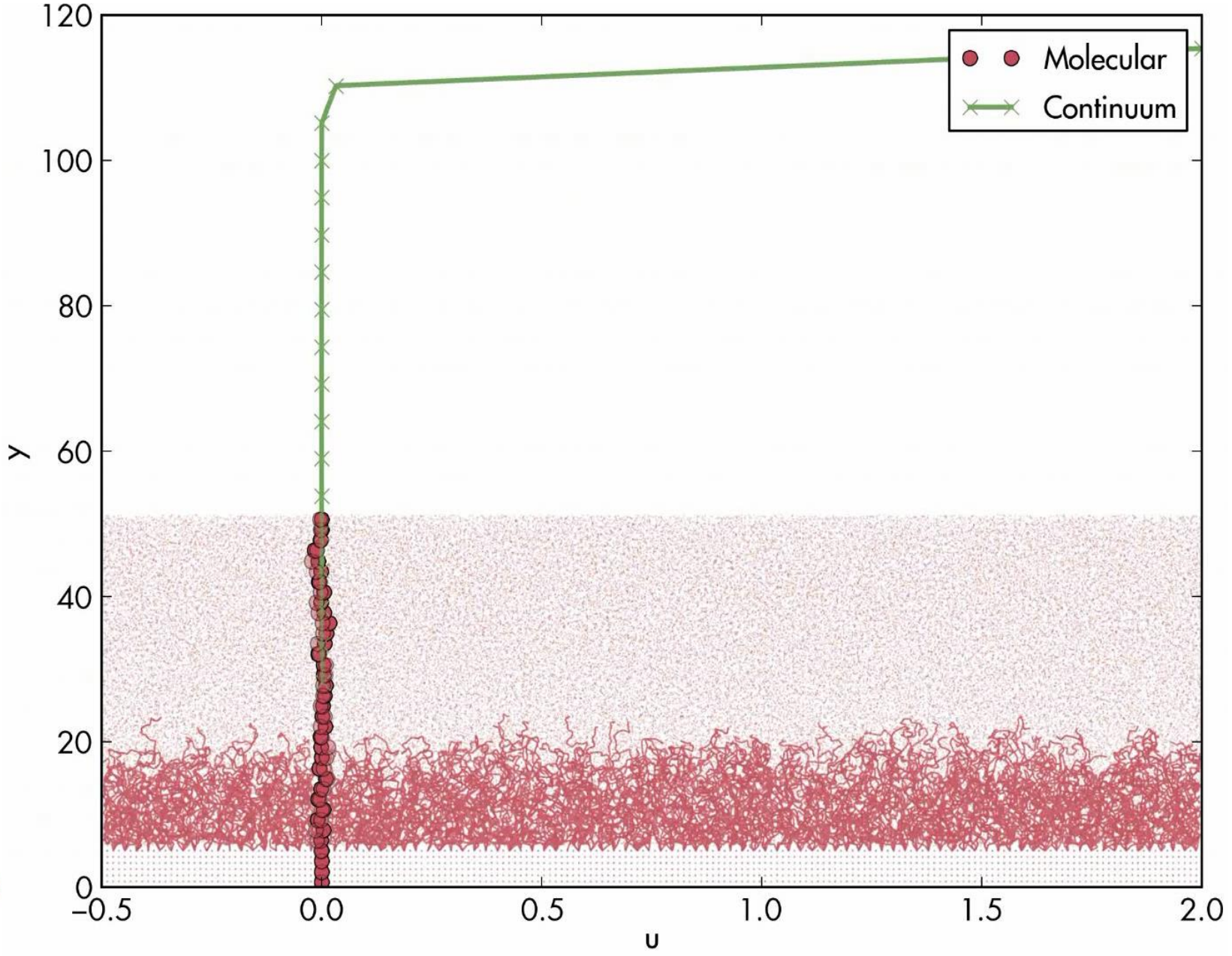
(b) Velocity v : CPL (—) vs all MD (- -)



Imperial Co
London

Polymer Brushes

- Simulation run by David Trevelyan



Imperial London

Conclusions

- **Multi-scale coupling is essential for modern engineering**
  - Useful to accelerate a molecular dynamics system where part of the domain matches the continuum solutions
  - Fluid coupling has developed over the last 15 years
- **Consistent framework for coupling fluid descriptions**
  - Control volume (CV) function expresses continuum and discrete systems in an equivalent formulation
  - Gauss principle, with the CV function, provides a constraint to control the state and flux in both domains
  - Links the literature and aims to provide a rigourous coupling framework
- **Computational developments**
  - CPL_library is an open source library to facilitates the exchange of data between two coupled codes (https://code.google.com/p/cpl-library/)
  - Large scale simulations with the aim to explore turbulent simulation and molecular wall textures

References

- **References**

J. H. Irving and J. G. Kirkwood, J. Chemical. Phys. 18(6), 817 (1950).
R.J. Hardy J. Chem. Phys. 76, 1 (1998)
P. Schofield and J. R. Henderson, Proc. R. Soc. London A 379, 231 (1982).
J. F. Lutsko, J. Appl. Phys 64(3), 1152 (1988)
S. T. O'Connell and P. A. Thompson, Phys. Rev. E 52, R5792 (1995).
B. D. Todd, D. J. Evans, and P. J. Daivis, Physical Review E 52(2), 1627 (1995).
J. Cormier, J. Rickman, and T. Delph, J. Appl. Phys 89-1, 99 (2001).
W.A. Curtin, R. E. Miller. *Mod Sim. Mater. Sci. Eng.* **11** R33 (2003)
M. Han and J. Lee, Phys. Rev. E 70, 061205 (2004).
R. Delgado-Buscalioni and P. V. Coveney,, Phil. Trans. R. Soc. London **362**, 1369 (2004)
A. Joshua A., C. D. Lorenz & A. Travesset. *J. Comp. Phys* 227.10 (2008)
Wm. G. Hoover, C. G. Hoover Phys. Rev. E 80 011128 (2009)
A. I. Murdoch, J. Elast. 100, 33 (2010).
D. M. Heyes, E. R. Smith, D. Dini, T. A. Zaki J. Chemical Phys. 135, 024512 (2011)

E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

- **Acknowledgements:**

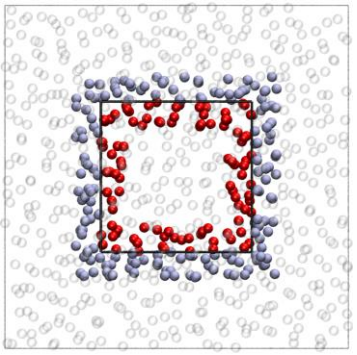
- Professor David Heyes
- Dr Daniele Dini
- Dr Tamer Zaki
- Mr David Trevelyan
- Dr Lucian Anton (NAG)

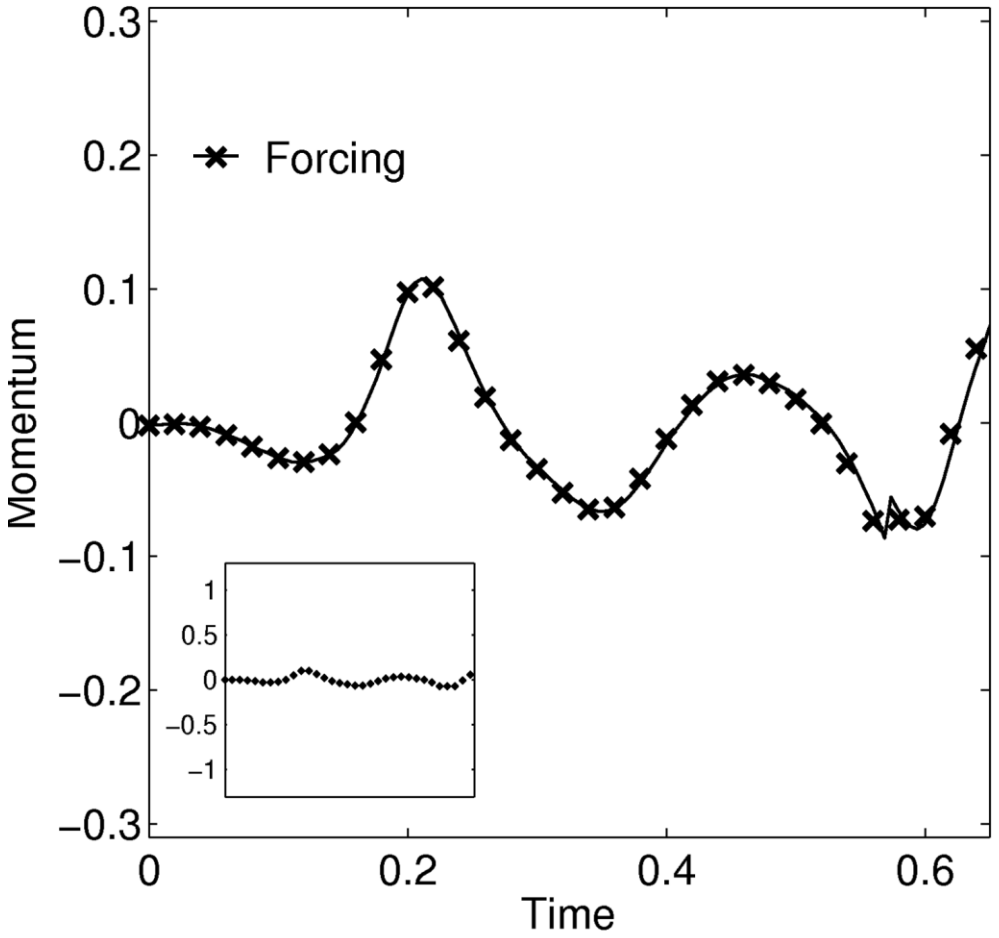
Extra Material

Testing Momentum Balance

- **Momentum Balance**

$$\underbrace{\sum_{i=1}^{N}\sum_{j\neq i}^{N}\mathbf{f}_{ij}\vartheta_{ij}}_{\textit{Forcing}}$$



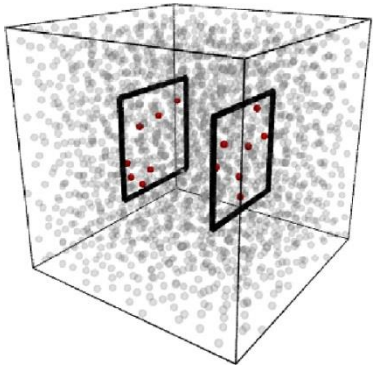


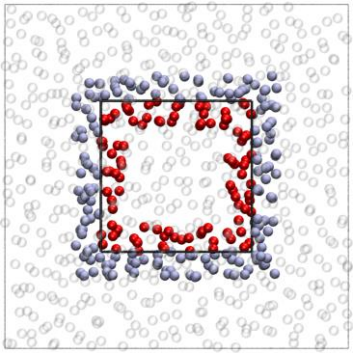
Imperial College London

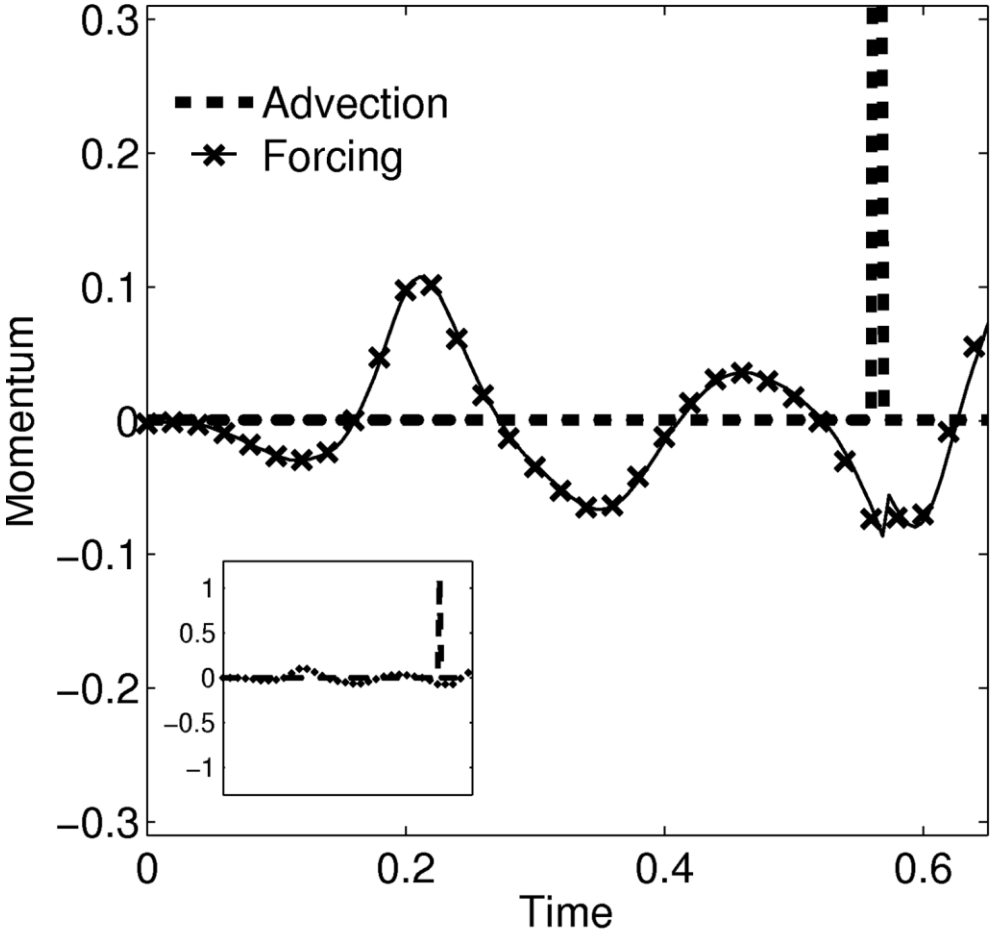
Testing Momentum Balance

- **Momentum Balance**

$$\underbrace{-\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\boldsymbol{S}_i}_{\textit{Advection}} + \underbrace{\sum_{i=1}^{N}\sum_{j\neq i}^{N} \mathbf{f}_{ij}\vartheta_{ij}}_{\textit{Forcing}}$$





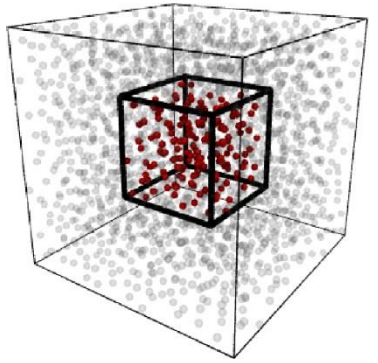


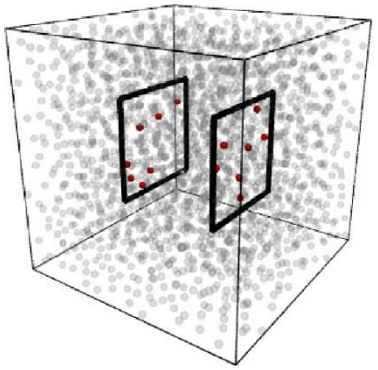
Testing Momentum Balance

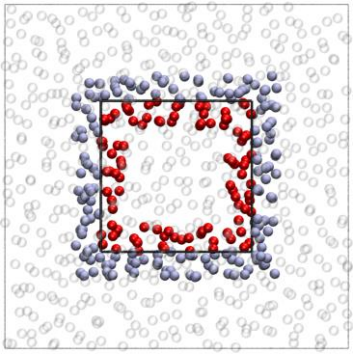
- **Momentum Balance**

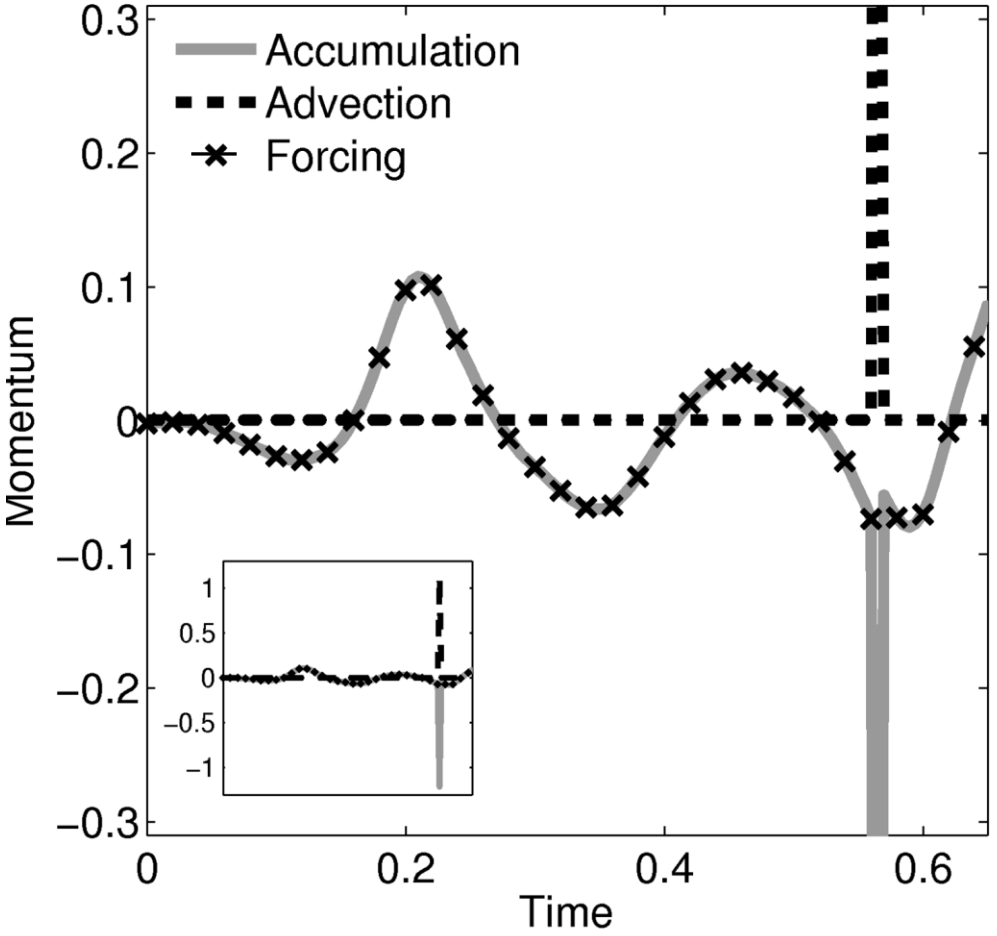
$$\underbrace{\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i}_{\text{Accumulation}} = \underbrace{-\sum_{i=1}^{N} m_i \mathbf{v}_i \mathbf{v}_i \cdot d\boldsymbol{S}_i}_{\text{Advection}} + \underbrace{\sum_{i=1}^{N}\sum_{j\neq i}^{N} \mathbf{f}_{ij}\vartheta_{ij}}_{\text{Forcing}}$$

$\frac{d}{dt}$









Imperial College London

Control Volume Function (revisited)

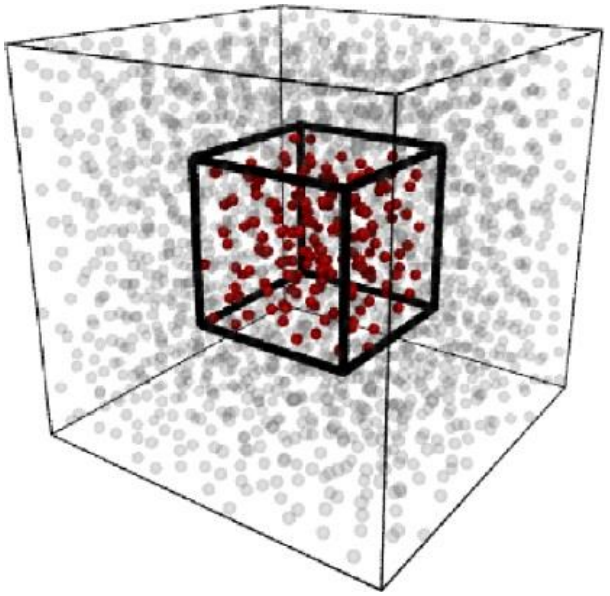
- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

$$\vartheta_i \equiv \int_V \delta\left(\boldsymbol{r} - \boldsymbol{r}_i\right) dV$$

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

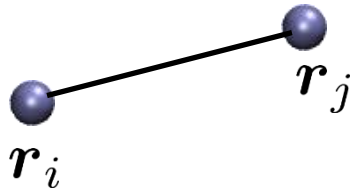
$$\times \left[H(y^+ - y_i) - H(y^- - y_i)\right]$$

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



- **Replace molecular position with equation for a line**

$$\boldsymbol{r}_i \rightarrow \boldsymbol{r}_i - s\boldsymbol{r}_{ij}$$



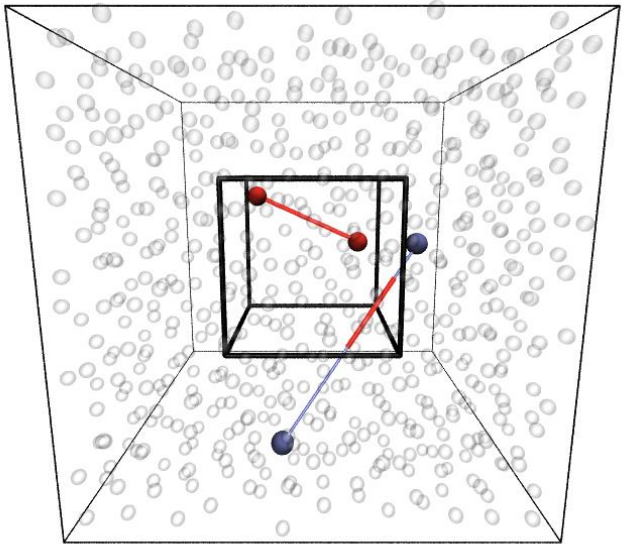
Imperial College London

For full details, please see
E.R. Smith, D.M. Heyes, D. Dini, T.A. Zaki, Phys. Rev. E 85. 056705 (2012)

Control Volume Function (revisited)

- **The Control volume function is the integral of the Dirac delta function in 3 dimensions**

$$\vartheta_s \equiv \int_V \delta(\mathbf{r} - \mathbf{r}_i + s\mathbf{r}_{ij})dV =$$
$$\left[H(x^+ - x_i + sx_{ij}) - H(x^- - x_i + sx_{ij})\right]$$
$$\times \left[H(y^+ - y_i + sy_{ij}) - H(y^- - y_i + sy_{ij})\right]$$
$$\times \left[H(z^+ - z_i + sz_{ij}) - H(z^- - z_i + sz_{ij})\right]$$



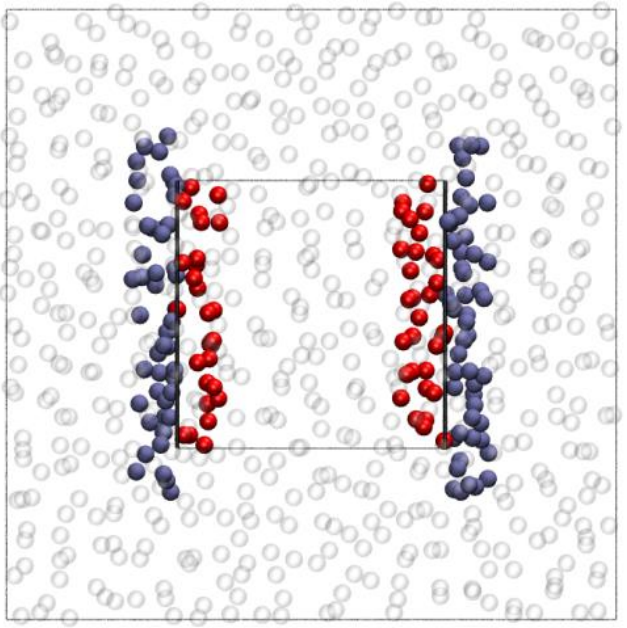
- **Length of interaction inside the CV**

$$\ell_{ij} = \int_0^1 \vartheta_s ds$$

Derivatives Yield the Surface Forces

- **Taking the Derivative of the CV function**

$$\frac{\partial \vartheta_s}{\partial x} \equiv \left[\, \delta(x^+ - x_i + s x_{ij}) \;-\; \delta(x^- - x_i + s x_{ij})\right]$$
$$\times \boxed{\left[H(y^+ - y_i + s y_{ij}) \;-\; H(y^- - y_i + s y_{ij})\right]}$$
$$\times \boxed{\left[H(z^+ - z_i + s z_{ij}) \;-\; H(z^- - z_i + s z_{ij})\right]}$$



- **Surface fluxes over the top and bottom surface**

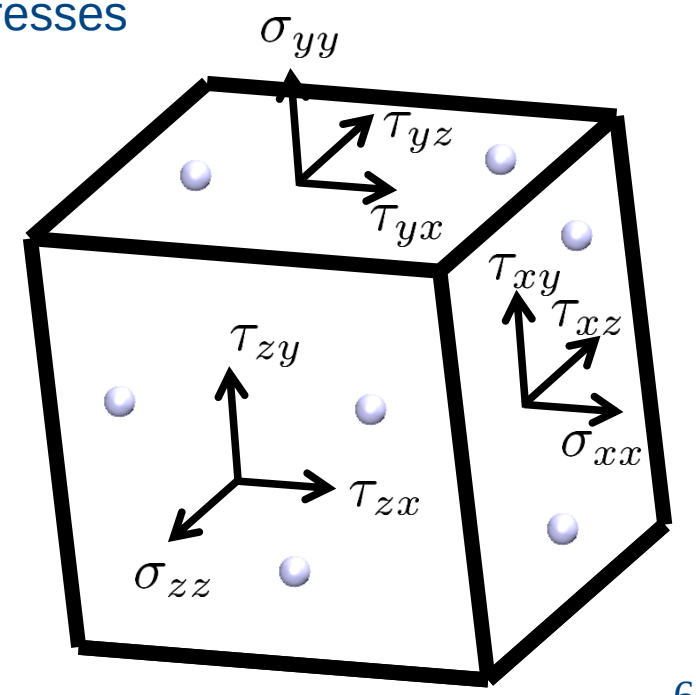
$$dS_{xij} \equiv \int_0^1 \frac{\partial \vartheta_s}{\partial x} ds = dS^+_{xij} - dS^-_{xij}$$

$$dS^+_{xij} = \frac{1}{2} \underbrace{\left[sgn(x^+ - x_i) - sgn(x^+ - x_j)\right]}_{MOP} \boxed{S_{xij}}$$

Imperial College London

More on the Pressure Tensor

- **Extensive literature on the form of the molecular stress tensor**
  - No unique solution Schofield, Henderson (1988)
  - Two key forms in common use – Volume Average (Lutsko, 1988) and Method of Planes (Todd et al 1995)
- **Link provided between these descriptions**
  - Through formal manipulation of the functions
  - Exposes the relationship between the molecular stresses and the evolution of momentum
- **In the limit the Dirac delta form of Irving and Kirkwood (1950) is obtained**
  - This suggests the same limit is not possible in the molecular system
  - Arbitrary stress based on the volume of interest



Moving reference frame

- **Why the continuum form of Reynolds' transport theorem has a partial derivative but the discrete is a full derivative**
  - Eulerian mass conservation

$$\vartheta_i = \vartheta_i(\boldsymbol{r}_i(t), \boldsymbol{r})$$

$$\frac{d}{dt}\sum_{i=1}^{N} m_i\vartheta_i = -\sum_{i=1}^{N} m_i\mathbf{v}_i \cdot d\boldsymbol{S}_i$$

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

  - Lagrangian mass conservation

$$\vartheta_i = \vartheta_i(\boldsymbol{r}_i(t), \boldsymbol{r}(t))$$

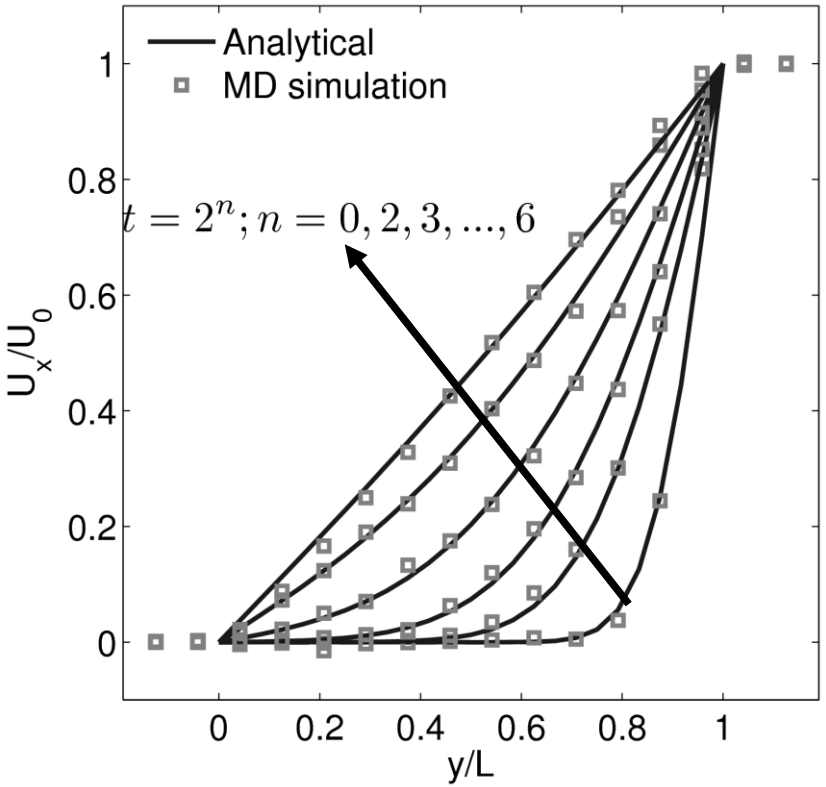
$$\frac{d}{dt}\sum_{i=1}^{N} m_i\vartheta_i = -\sum_{i=1}^{N} m_i\left(\mathbf{v}_i + \overline{\boldsymbol{u}}\right)\cdot d\boldsymbol{S}_i$$

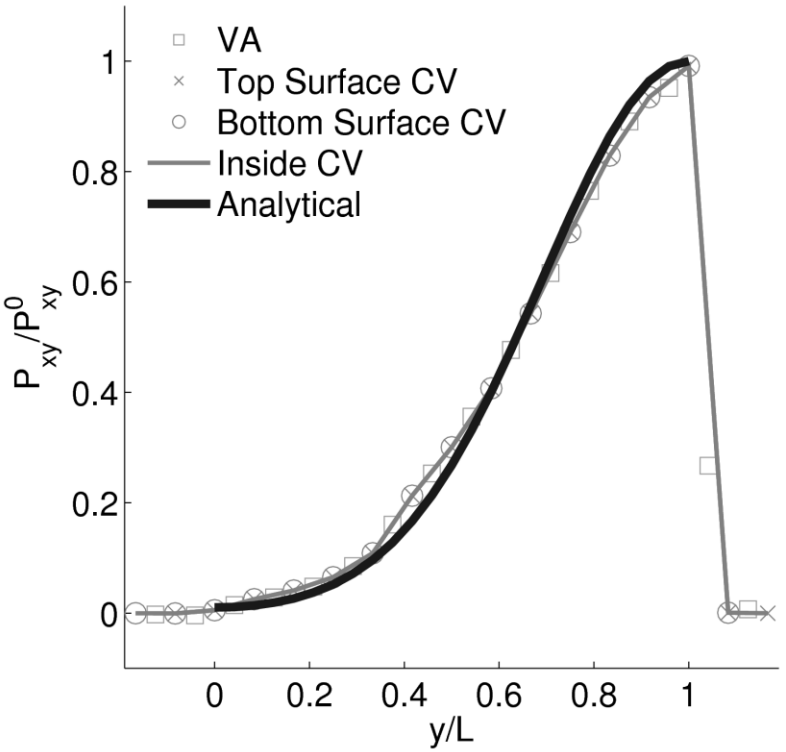
$$\frac{d}{dt}\int_V \rho dV = \oint_S \rho\left(\boldsymbol{u} - \overline{\boldsymbol{u}}\right)\cdot d\boldsymbol{S}$$

$$\overline{\boldsymbol{u}}\cdot d\boldsymbol{S}_i = \frac{d\boldsymbol{r}}{dt}\cdot\frac{d\vartheta_i}{d\boldsymbol{r}}$$

$$\oint_S \rho\boldsymbol{u}\cdot d\boldsymbol{S} - \oint_S \rho\overline{\boldsymbol{u}}\cdot d\boldsymbol{S} = 0$$

Continuum Analytical Couette Flow





$$u_x(y,t) = \begin{cases} U_0 & y = L \\ \sum_{n=1}^{\infty} u_n(t) sin\left(\frac{n\pi y}{L}\right) & 0 < y < L \\ 0 & y = 0 \end{cases}$$

$$\Pi_{xy}(y,t) = \frac{\mu U_0}{L}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n e^{-\frac{\lambda_n \mu t}{\rho}} cos\left(\frac{n\pi y}{L}\right)\right]$$

$$\text{Where, } \lambda_n = \left(\frac{n\pi}{L}\right)^2 \text{ and } u_n(t) = \frac{2U_0(-1)^n}{n\pi}\left(e^{-\frac{\lambda_n \mu t}{\rho}} - 1\right)$$

Unsteady Couette Flow

- **Continuum Analytical**
  - Simplify the momentum balance (Navier-Stokes) equation

$$\frac{\partial}{\partial t}\boldsymbol{u} + \boldsymbol{\nabla}\cdot\boldsymbol{u}\boldsymbol{u} = \frac{1}{\rho}\boldsymbol{\nabla}\mathrm{P} + \frac{\mu}{\rho}\boldsymbol{\nabla}^2\boldsymbol{u}$$

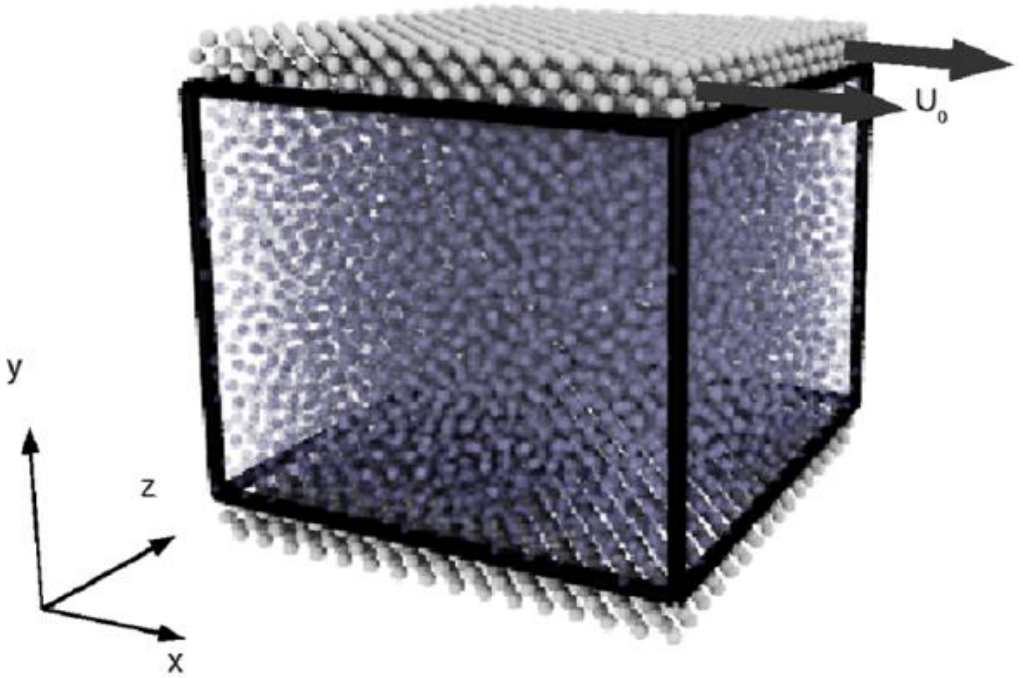
  - Solve the 1D unsteady diffusion equation.

$$\frac{\partial u_x}{\partial t} = \frac{\mu}{\rho}\frac{\partial^2 u_x}{\partial y^2}$$

  - With Boundary Conditions

$$u_x(0,t) = 0$$
$$u_x(L,t) = U_0$$
$$u_x(y,0) = 0$$

- **Molecular Dynamics**
  - Fixed bottom wall, sliding top wall with both thermostatted



Unsteady Couette Flow

- **Continuum Analytical**
  - Simplify the control volume momentum balance equation

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

  - Simplifies for a single control volume

$$\frac{\partial}{\partial t}\int_V \rho u_x dV = \int_{S_y^+} \sigma_{xy} dS_f^+ - \int_{S_f^-} \sigma_{xy} dS_y^-$$

  - With Boundary Conditions

$$u_x(0,t) = 0$$
$$u_x(L,t) = U_0$$
$$u_x(y,0) = 0$$

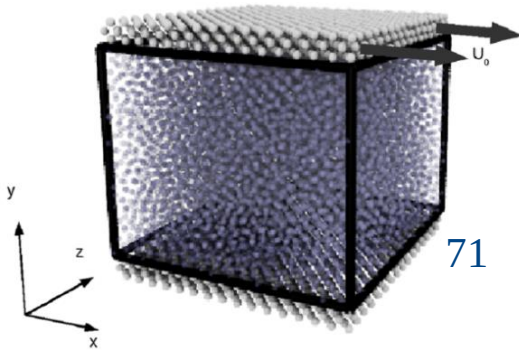
- **Molecular Dynamics**
  - Discrete form of the Momentum balance equation

$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = -\oint_S \rho \boldsymbol{u}\boldsymbol{u}\cdot d\boldsymbol{S} - \sum_{i=1}^{N}(\boldsymbol{v}_i - \boldsymbol{u})(\boldsymbol{v}_i - \boldsymbol{u})\cdot d\boldsymbol{S}_i - \sum_{i=1}^{N}\sum_{j\neq i}^{N} \varsigma_{ij}\cdot d\boldsymbol{S}_{ij}$$

  - Simplifies for a single control volume

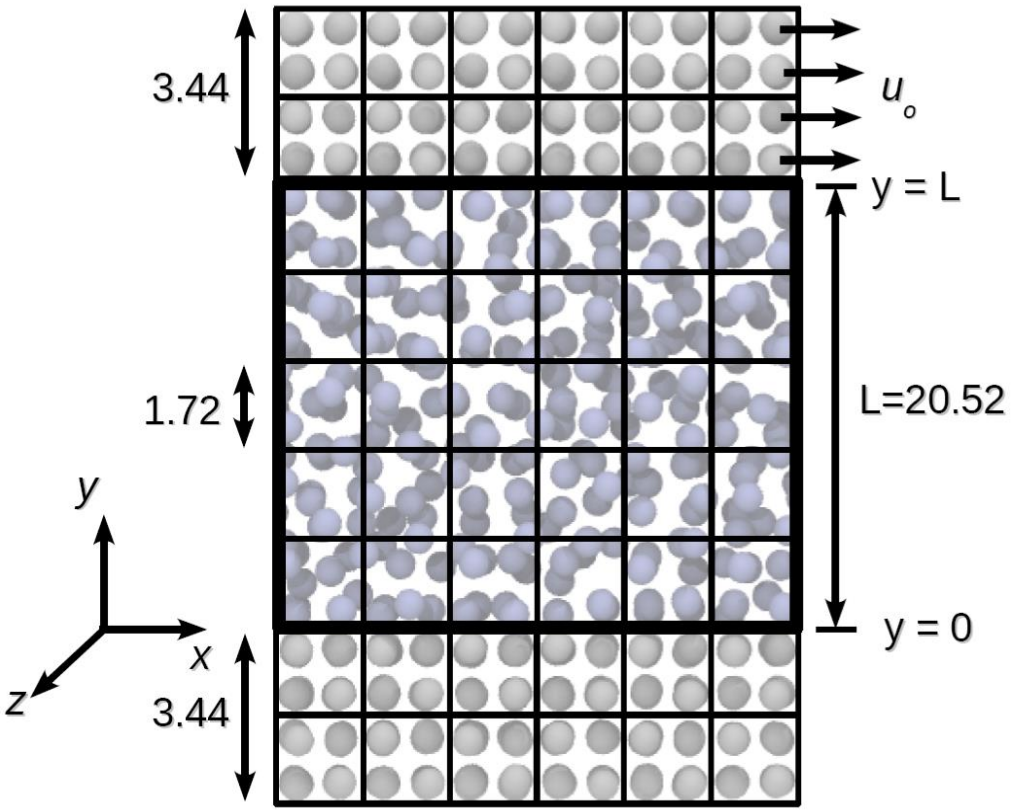
$$\frac{d}{dt}\sum_{i=1}^{N} m_i \mathbf{v}_i \vartheta_i = \sum_{i,j}^{N} f_{xij} dS_{yij}^+ - \sum_{i,j}^{N} f_{xij} dS_{yij}^-$$

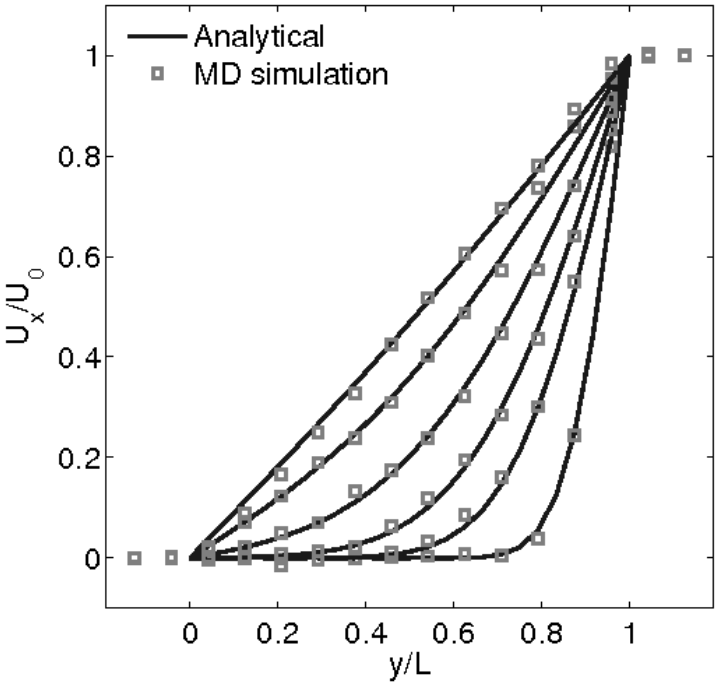
  - Fixed bottom wall, sliding top wall with both thermostatted

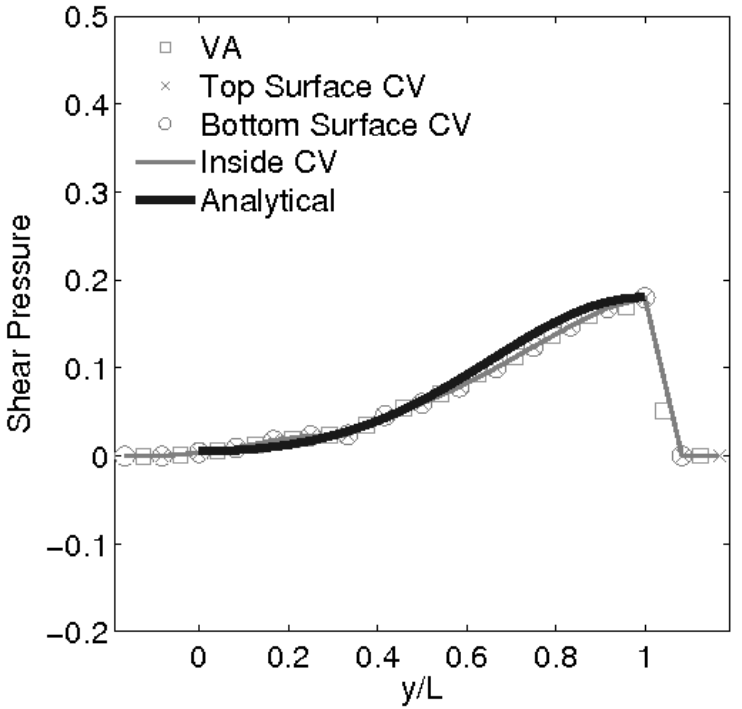


Unsteady Couette Flow

- **Simulation setup**
  - Starting Couette flow
  - Wall thermostat: Nosé-Hoover
  - Averages are computed over 1000 time steps and 8 realizations

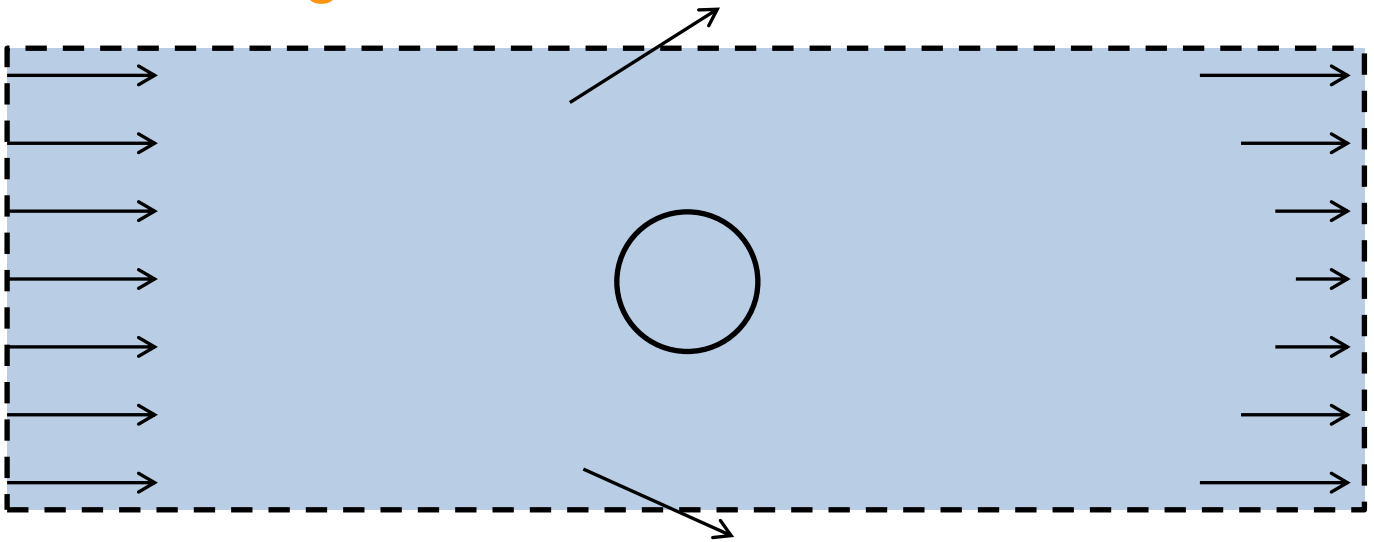






Flow past a cylinder

- Use of the momentum conservation of the control volume to determine the drag coefficient



- Drag over a Carbon Nano-tube can be determined